Effects of multi-photon interferences from internally generated fields in strongly resonant systems

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Abstract

In studies of various nonlinear optical phenomena, strong resonant features in the atomic or molecular response to multi-photon driven processes have been used to greatly enhance the visibility of otherwise weak higher-order processes. However, there are well defined circumstances where a multi-photon-resonant response of a target system leads to the generation of one or more new electromagnetic fields that can drastically change the overall system response from what would be expected from the imposed laser fields alone. New effects can occur and dominate some aspects of the nonlinear optical response because of the constructive or destructive interference between transition amplitudes along multiple excitation pathways between a given set of optically coupled states, where one of the pathways involve internally generated field(s). Under destructive interference some resonant enhancements can become completely canceled (suppressed).

This review focuses on the class of optical interference effects associated with internally generated fields, that have been found to be capable of influencing a very significant number of basic physical phenomena in gas or vapor phase systems. It provides a historical overview of experimental and theoretical developments and a modern understanding of the underlying physics and its various manifestations that include: suppression of multi-photon excitation processes, suppression of stimulated emissions (Raman, hyper-Raman, and optically pumped stimulated emissions), saturation of parametric wave-mixing, pressure and beam-geometry dependent shifting of multi-photon-resonant absorption lines, and the suppression of Autler–Townes splitting and ac-stark shifts. Additionally, optical interference effects in some modern contexts, such as achieving multi-photon induced transparency, establishing single-photon self-interference based induced transparency, and generating entangled single photon states, are reviewed.

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### Nomenclature

- \( \tau, \omega \) effective pulse duration and Fourier transform variable
- \( \rho_{nm} = \langle n | \hat{\mu} | m \rangle \) dipole matrix element between states |\( m \rangle \) and |\( n \rangle \)
- \( d_j = \delta_j \tau + A \tau + i \gamma_{mn} \tau / 2 \) dimensionless complex detuning with laser detuning \( \delta_j \)
- \( \gamma_{mn} \) decoherence rate between states |\( m \rangle \) and |\( n \rangle \)
- \( \gamma_l \) ionization line width of a given state
- \( \gamma_A \) additional frequency shift due to collisional effects
- \( D_j = d_j + \eta \) \( \eta = \omega t \) is dimensionless Fourier transform variable
- \( \kappa_{nm} = 2 \pi N_0 \omega_{mn} | \mu_{mn} |^2 / (\hbar c) \) concentration of the resonant medium
- \( \rho_{mn} \) is slowly varying density matrix element between states |\( m \rangle \) and |\( n \rangle \)
- \( \rho_{mn}^{(1)} = \Omega_{mn} = \mu_{mn} E_L / (2 \hbar) \) one-half Rabi frequency for the |\( m \rangle \) - |\( n \rangle \) one-photon transition coupled by the laser field \( E_L \)
- \( \rho_{mn}^{(N)} \) one-half Rabi frequency for the |\( m \rangle \) - |\( n \rangle \) \( N \)-photon transition coupled by a laser field
- \( A_{mn}(z, \eta), A_{mn}^{(N)}(z, \eta) \) Fourier time transform of \( \rho_{mn}, \rho_{mn}^{(N)} \)
- \( A_j(z, t), C_j(z, t) \) wave function amplitudes of the state |\( j \rangle \)
- \( t_r = t - z / c \) retarded time in the frame moving with the light field that travels with group velocity \( c \)
- \( t_{r0} = t - n_0(\omega) \) retarded time in the frame moving with the light, \( n_0(\omega) \) is the non-resonant part of the refractive index
- \( T_r = t_{r0} / \tau \) dimensionless retarded time in the frame moving with the light field
- \( \Delta k \) phase mismatch between the generated wave and laser wave vectors with the resonant contribution from the generated field included
- \( \Delta K \) phase mismatch between the generated wave and laser wave vectors with the resonant contribution from the generated field excluded

### Abbreviations

- ASE amplified spontaneous emission
- CIRC circularly polarized light
- CPCP counter-propagating circularly polarized light
- CPT coherent population transfer
- EIT electromagnetically induced transparency
- FWHM full width at half maximum
- FWM four wave mixing
- HR hyper-Raman
- IR infra-red
- ITWM/IFWM inelastic two-wave mixing/inelastic four-wave mixing
- LHS left-hand side
- LIN linearly polarized light
- MPI multi-photon ionization
- OPSE optically pumped stimulated emission
- PFWM/PSWM parametric four-wave mixing/parametric six-wave mixing
- RHS right-hand side
- RWA rotating wave approximation
- SEHRS/SHR stimulated electronic hyper-Raman emission/scattering
- SVA slowly varying amplitude
- TH third harmonic
- TWM two-wave mixing
- UV ultra-violet
- VUV vacuum ultra-violet
**Convention used in figures**

1. In all energy-level diagrams solid arrows represent external laser fields whereas dashed arrows represent internally generated fields.
2. In all energy-level diagrams solid lines represent real energy levels where dashed lines represent virtual energy levels produced by laser excitations.

1. **Introduction: Historical development and rationale for this review**

   It is now widely appreciated that internally generated fields can exert very strong influences on a wide variety of multi-photon mediated processes in resonant media. However, this understanding was not revealed through systematic experimental or theoretical studies that sprang from an appreciation of the broad consequences of the phenomenon. On the contrary, the subjects of this review were discovered and then rediscovered in new contexts. In a number of instances experiments revealed new behavior that was successfully explained theoretically. But in many other cases, theoretically predicted behavior was subsequently observed experimentally. Theoretical formalism adopted by different investigators differed greatly. Thus, to establish a reasonable perspective on the subjects of this review, an approximate chronological trace of the developments is presented and a rationale for a systematic review of the field is offered.

   Historically, mid-1970s to the mid-1980s represents a milestone period in the field of spectroscopy when relatively high powered tunable pulsed dye lasers become widely available. The rapid development of this laser technology led to an intense interest in studies of various nonlinear optical processes involving multi-photon-resonant atomic and molecular transitions in strongly resonant (gaseous phase) media. Resonantly enhanced multi-photon ionization (MPI) of atomic and molecular gases and vapors were popular subjects for a variety of novel spectroscopic studies [1–5]. MPI spectroscopic methodologies offered obvious extensions beyond classic absorption/emission methods. States of relatively high energy could be reached with absorption of two or more visible photons and transitions normally forbidden under parity or angular momentum selection rules could often be accessed through multi-photon schemes.

   With the large resonant enhancements realizable in gases and vapors, early tunable pulsed dye lasers were quite capable of driving observable multi-photon-resonant transitions through second, third and fourth order, even in a molecular beam experiment [1–6]. Combined energy and symmetry considerations usually provided identification of observed spectral features in conformance with theoretical expectations. However, as the subject matured, a puzzling anomaly was noted in MPI studies of Xe by Aron and Johnson [5]. With a tightly focused pulsed beam in an ionization cell, several three- and four-photon-resonant transitions were observed in Xe ionization signals at pressures of 1–100 Torr. However, they failed to observe the anticipated multi-photon resonant-enhanced ionization signals at frequencies corresponding to three-photon excitation of the strongly allowed transitions from the ground state to 6s and 6s' levels in Xe (Fig. 1). This was the first observation of what turned out to be a very general phenomenon. It was later to be found that all \( \Delta J = 1 \) odd-parity, multi-photon resonant transitions are strongly suppressed at pressures as low as \( 10^{-4} \) Torr (with narrow bandwidth excitation) whereas two- and four-photon resonance enhancements behave normally, as do three-photon enhancements with \( \Delta J = 3 \).

   Later, in an attempt to understand the data observed by Johnson [5], Compton et al. [6] studied photoelectron spectra of Xe in a low pressure atomic beam apparatus and in a gas cell experiment (Fig. 2). They found that the three-photon-resonant \( (6s[3/2](J = 1)) \) transition was the strongest of all the observed MPI resonance signals at very low concentrations (i.e., in the atomic beam experiments). In a gas cell experiment, Miller et al. [7] found that an asymmetrical photoionization line shape, very much like the phase matching curve for third-harmonic (TH) light generated by a focused Gaussian-type laser beam, could be easily observed. However, no signal that was clearly attributable to three-photon excitation followed by laser ionization could ever be seen in the gas cell experiments, even though the ionization due to MPI by TH light plus laser photons was clearly seen at pressures exceeding tenths of one-Torr [7]. MPI calculations indicated that the absorption of three laser photons followed by laser ionization should yield a sharp peak when tuning through three-photon resonance, with a much larger amplitude than that expected from simultaneous off-resonance absorption of the weak TH/four-wave mixing (FWM) field and laser photons to ionize. The fact that the gas cell experiment showed no sharp resonant peak, but did show ample signal due to simultaneous absorption of an off-resonance TH photon plus laser photons made the experimental results very puzzling.

   Subsequently, Miller et al. [7] and Payne et al. [8] showed that, at pressures above a small fraction of 1 Torr, the three photon 6s transition in Xe was accompanied by TH production. Moreover, when the three-photon excitation
Fig. 1. MPI spectrum in the 430–442 nm region that encompasses the wavelength at one-third the photon energy of the 146.9 nm atomic excitation $^1S_0 \rightarrow 5p^3(^2P_{3/2})6s$. No peak was seen in the spectrum at 440.9 nm corresponding to three-photon resonance with the $5p^3(^2P_{3/2})6s(J = 1)$ atomic level, though for three photons this $\Delta J = 1$ transition is allowed. The peak shown near 440 nm represents four-photon resonance with atomic $4f(^9/2)(J = 4)$ level. Reproduced from [5] with permission.

Fig. 2. MPI spectrum showing Xe $6s$ and $4f$ resonances in the pressure region where the $6s$ ion signal disappear. Trace (a) was taken with an atomic beam apparatus. Traces (b)–(e) were taken with a gas cell apparatus. Reproduced from [7] with permission.

problem was formulated to include TH production simultaneous with three-photon-resonant excitation, it was shown that the TH field had a dramatic influence on the excitation–ionization signals [8]. The theory showed that internal generation of a TH field could suppress or “cancel” the direct three photon pumping of a one-photon allowed transition, independent of pump-laser intensity. A more detailed treatment by Payne and Garrett [9] of the same physical model [8] established the influence of TH generation on three-photon excitation in a finite medium including details of propagation behavior, pressure dependent line-shapes, laser bandwidth and oscillator strength dependence of the cancellation effect, laser-intensity independence, and robustness of the effect under broad-band excitation and high concentration.
Miller and Compton [10] extended the experiments to include other noble gases, Kr and Ar, and confirmed the predicted [8,9,14] behavior for three-photon excitation of the lowest optically allowed transitions in all cases (the transitions for all of these early experiments are depicted in Fig. 3). Indeed, with beams focused with \( f = 38 \text{ mm} \) focal length, measurements of multi-photon ionization and TH production profiles for regions near three-photon resonances were very similar in character: Xe \( 6s(3/2)J = 1, \) \( 6s'(1/2)J = 1 \); Kr \( 5s(3/2)J = 1 \); and Ar \( 4s(3/2)J = 1 \) all showed MPI and TH generation profiles that appeared quite similar in wavelength dependence (see the results for Xe \( 6s' y(1/2)J = 1 \) in Fig. 4). Only at the very lowest pressures (\( \leq 0.5 \text{ Torr} \)) did the MPI signal appear to occur at the resonance position. Otherwise, the ionization tracked TH output on the blue (higher energy) side of resonance and was due entirely to TH generation and re-absorption on the wing of the resonance line.

Very insightful and strong evidence for the theoretical picture [8,9,14] was provided by a new experiment by Glownia and Sander [11] who designed a scheme whereby three-photon excitation of the \( 6s \) state in Xe could be probed with linearly polarized, circularly polarized or with counter-propagating circularly polarized (CPCP) beams. The CPCP beams were both right-hand-circularly or left-hand-circularly polarized so that they had opposite senses of rotation in the atom-rest reference frame. This third configuration allowed for production of a \( J = 0 \) to \( J = 1 \) (optically allowed) transition with \( \Delta M = \pm 1 \), but with no TH production. Their results taken at 5 and 50 Torr of Xe are shown in Fig. 5. They found that with circularly or linearly polarized light no \( 6s \) resonance was observed at any Xe pressure in their MPI cell, though nearby four-photon transitions to \( 4f \) levels gave strong signals. However, with the CPCP beams, signals corresponding to three-photon transitions to \( 6s \) were not only present, but stronger than any of the other resonant signals.

An experiment by D.J. Jackson and J.J. Wynne in 1982 [12] added a new element to the picture of this phenomenon. The key in this experimental study was the evidence that the strongly resonant three-photon excitation–ionization of the \( 6s \) state in Xe could be restored by retro-reflecting a linearly polarized beam. Using a simpler nonlinear-susceptibility picture and again including both three-photon excitation and TH generation in treating the atomic response, they showed that the cancellation of the excitation could be exposed as an interference between two pathways connecting the ground and excited states. With counter-propagating beams the interference was incomplete and three-photon excitation was
Fig. 4. MPI spectra and third-harmonic-generation line shapes near the 6$s'$ resonance in Xe recorded at various pressures from 0.5 to 25 Torr. The upper wavelength scale corresponds to the laser and the lower scale to the third-harmonic generation. Reproduced from [10] with permission.

Fig. 5. MPI spectrum showing Xe 6$s$ and 4$f$ resonances taken with linearly polarized light (LIN), circularly polarized light (CIRC), and counter-propagating circular polarized light (CPCP) as a function of Xe pressure. The laser energy is 0.7 mJ for the CPCP case, and 1.4 mJ for both LIN and CIRC cases. Reproduced from [11] with permission.

thereby restored (Fig. 6). That is, excitation was absent with traveling-wave beam geometry, but present at the proper resonant frequency with standing-wave beam geometry. More extensive data showing simultaneous TH and MPI spectra were reported subsequently by Jackson et al. [13]. Through pressure and confocal parameter dependent measurements of TH and MPI profiles, the authors showed that no signal appeared exactly at three-photon resonance and that instead, the ionization was all due to TH production. Peaks and widths of the profiles were consistent with phase matching.
Fig. 6. MPI spectrum showing Xe 6s and 4f ionization signals vs laser wave number when traveling-wave and standing-wave excitations are applied. The incoming power (77 kW in both scans) is retro-reflected to produce the standing wave. The pressure is 1.5 Torr and the beam area at the focus is $1.8 \times 10^{-7}$ cm$^2$. The unperturbed 6s and 4f resonance positions are indicated by tick marks below. Reproduced from [12] with permission.

considerations for beams focused by lenses of 11, 19, 28, and 80 mm focal lengths (Fig. 7). Jackson et al. introduced the terminology of “destructive interference” (rather than “suppression” as in [9]) to describing the effect of the competing excitation pathways for the transition. Additional confirmation of the picture was provided in a full treatment for focused beams by Payne and Garrett [14] with details of pressure dependent line shapes for excitation and ionization, onset criteria, retro-reflection, and demonstration of the robustness of the phenomenon in focused beam geometries. An experimental study in Hg vapor [15] in 1983 and a completely quantum treatment of the effect by Agarwal and Tewari [16] in 1984 again showed the expected interference effects.

Shortly after the works of Jackson et al., Payne et al. [17] predicted theoretically and demonstrated experimentally that if unfocused counter-propagating laser beams are used in the presence of high concentrations of a positively dispersive buffer gas, the MPI signal from a three-photon resonant medium at low concentrations has two components of similar amplitude and identical line shapes. One component is near the unperturbed three-photon resonance, and is due to absorbing two-photons propagating in one direction and one-photon propagating in the other direction. The other component is present without the counter-propagating beam and is due to the absorption of a TH photon and laser photons. The location of the second peak is the point where phase matching occurs and it is shifted to the blue (high frequency side) of the three-photon resonance by an amount proportional to the concentration of the resonant medium.

Over the following three years the unfocused beam configuration by Payne et al. [17] was used to: (1) determine oscillator strengths of ground state to several resonant states in inert gases [18]; (2) to measure absorption coefficients of vacuum ultra violet (VUV) light in the region near inert gas resonances; and (3) to determine pressure broadening of resonance levels in inert gases at pressures where the mean free path of resonance photons is barely larger than the VUV wavelength for the transition [19]. In case (3) it was discovered that the pressure broadened widths measured with counter-propagating beams agreed well with line broadening theory, but there was an unexplained pressure dependent line shift to higher frequency (blue) that was about 50% of the full width at half maximum (FWHM) of the pressure broadened line for all of the five different resonance states studied in Kr and Xe. In 1989 the mechanism of the pressure dependent shifts present in these studies was finally explained by Friedburg et al. [20,21] as being due to dispersion forces related to the presence of the polarization of the medium. It should be noted that these shifts observed with counter propagating beams were not the MPI profile “shifts” observed in early experiments with unidirectional focused
beams, where ionization profiles were observed to shift in step with phase-matched TH production profiles and to eventually disappear with gas pressure [17–19].

In the early 1990, Chen and Elliot [22,23] took a novel approach in measuring destructive-constructive interference between a three-photon and a one-photon pathways. A double-chamber apparatus with a TH delay segment was constructed so that both the amplitude and phase of the laser and the TH field could be varied in a controllable fashion. The laser and delayed TH fields were injected into the second chamber filled with low concentration atomic mercury vapor, and the photoelectrons were collected as the relative phase between the laser and the TH fields was varied. Their observation showed clear and convincing destructive-constructive modulation in the counting of the photoelectrons.

The early experimental [6,7,10–13,15,17–19,22–26] and theoretical investigations [8,9,12–14,16,17,27] of wave-mixing interferences were directed toward excitation of a level that is simultaneously driven by three-photon and one-photon transition amplitudes. But a different type of quantum interference involving coupling of an even photon transition by two simultaneous two-photon pathways was presented by Malcuit et al. [28] and by Krasnikov et al. [29]. Malcuit et al. [28] studied emissions associated with two-photon excitation of $3s \rightarrow 3d$ in Na vapor. They observed a changing ratio of forward to backward intensity which was attributed [30] to competition with ASE from parametric four-wave mixing due to two-photon destructive interference.

Krasnikov et al. [29] also studied two-photon excitation in Na, in this case $3s \rightarrow 4s$ transitions. They showed that the generation of four-wave-sum-frequency mixing in the vapor could suppress two-photon absorption by two orders of magnitude through destructive interference (which was designated as “parametric brightening”).

Fig. 7. Confocal parameter dependence of TH field (upper curve) and ionization signal (lower curve) vs laser energy in cm$^{-1}$. The tick marks below indicate the position of the unperturbed $6s'$ and $4f$ resonances. Reproduced from [13] with permission.
Additionally, similar interference-based suppression of an effected set of co-propagating optically pumped stimulated emissions was subsequently demonstrated by Garrett [45].

This destructive interference phenomenon involving internally generated wave-mixing fields was rediscovered and broadened in the context of multi-photon ionization in gases, and its manifestations were variously referred to as “collective emission” [8], “cooperative effect” [9], “destructive interference” [12,13], “parametric brightening” [29], “parametric bleaching” [33], “wave-mixing competition” [16,28,30,34], “cancellation effect” [14,16,35,36], and “optical balance” [37]. In the broadest sense, the theoretical treatments may appear very dissimilar, but nevertheless contain very similar physical pictures.

In the same period, detailed studies on nonlinear processes near S–D resonances in alkali metals were carried out at ORNL. In these studies unanticipated and complicated behavior was found to occur in emissions associated with tuning a relatively strong unfocused laser beam near the 3s–3d and 3s–4d two-photon resonances in Na. Strong forward conical emissions were produced by angle-phase-matched PFWM in both cases. Axial emissions (easily selected with pin-hole arrangements) showed asymmetric forward–backward emission profiles with backward stronger than forward intensities. Also, forward axial beams [31,38] showed four parametric four-wave mixing (PFWM) emissions present near 330 nm and 2.33 µm in addition to the laser. Backward beams contained two stimulated hyper-Raman (SHR) emissions terminating on different fine structure levels of the 4p state and two emissions associated with excitation of the 3p[3/2] and 3p[1/2] states. Again, a forward–backward asymmetry was observed that increased with larger detuning from two-photon resonance. Upon careful analysis it was deduced that the forward SHR should be suppressed by the three-photon interference effect observed earlier in MPI studies in noble gases. Indeed with further detuning from two-photon resonance (pure SHR emission) the forward SHR emission became completely suppressed while backward emissions remained normal [31]. The basis for the effect is easy to see. In SHR production two-laser photons are absorbed simultaneously, accompanied by a stimulated coherent emission and an excitation from the ground state to the final p state. However, because the P states have allowed transitions to the ground state, the combined laser fields and forward propagating coherent Raman field together produce a four-wave-difference frequency-mixing field at the S → P transition frequency. The generated difference frequency wave-mixing field can lead to, under suitable conditions, a destructive interference between one- and three-photon excitation which prohibits production of population in the P states. Consequently, one finds that there is no HR gain in the forward direction. With suitable laser pulse duration, however, the gain is present and large for backward HR emission [31,38–40]. The effect was independently predicted by Malakyan [39] and the shown to occur by Garrett et al. in Xe [41] and by Lu and Liu [42] in Li vapor. Additionally, similar interference-based suppression of an effected set of co-propagating optically pumped stimulated emissions was subsequently demonstrated by Garrett [45].

The axially phase-matched PFWM [38] in Na vapor provided a new method of demonstrating the effect of the two-photon interference effect on PFWM. Wunderlich et al. [40] made absolute measurements on the intensity of both sets of parametric waves as a function of Na vapor concentration. Payne modified the Manykin and Afanas’ev theory and was able to predict the concentration at which two-photon cancellation should occur and the corresponding intensity of the parametric waves under conditions of destructive interference. It was predicted that the parametric wave intensity would cease to increase as a function of concentration or path length in the vapor when the generated intensities grew to a predicted interfering magnitude. The saturation was observed experimentally, and the estimates of the concentration for the destructive interference to occur agreed well with the concentration where the parametric intensity became pressure independent [40,46]. In addition, absolute measurements of the two parametric waves showed that the intensities were quite close to what were required for the two-photon Rabi frequency due to the two parametric waves to balance that due to the pump laser, a clear signature of two-photon interference effect in PFWM.

In the case of the PFWM generation in Na 3s–3d excitations, as reported by Malcuit et al. [28] and several similar situations, strong angle phase matched PFWM is produced. However, the ORNL group was unable to give conclusive experimental demonstration of two-photon destructive interference in any of these cases.
In the course of the SHR studies, Payne showed that the pressure dependent shift that had been observed in MPI studies in Xe [19] could be shown to be a further consequence of FWM destructive-constructive interference [47,48], and that it should appear in the backward HR emissions involving terminal states that are dipole coupled back to the ground state (unobservable in Na because of concentration limitations in a heat pipe.) Further analysis [47] led to the realization that the frequency shifts seen in three-photon excitations with counter propagating beams could be made very large indeed with special laser beam geometries [47,48]. To test this prediction additional MPI studies were made in Xe of three-photon pumping of the familiar 6s state with two laser beams crossed at various crossing angles. The shift of the 6s resonance was predicted to be linear in pressure and strongly dependent on crossing angle [47]. The experiments produced the predicted shifts in very good agreement with predicted values [48,49].

Subsequently, attention was redirected to measurements of interference-based shifts predicted to occur in backward SHR emissions. New experiments by Garrett et al. [41] in high pressure Xe revealed the expected SHR shifts to shorter wavelength, linear in Xe concentration, again in good agreement with theory. These studies were later extended to demonstrate the same interference-based shift in optically pumped stimulated emissions (OPSE), again in Xe [50,51].

Further important consequences of the wave mixing interference effects were revealed in the late 1980s and early 1990s when several observations of the effects of a near three-photon intermediate resonance on four-photon resonance enhancements to MPI were reported [52–55]. These experiments, involving four-photon-resonant enhancements in two-color-induced MPI of spectra of Xe, revealed that a four-photon excitation could be suppressed if the excitation occurred near a three-photon intermediate resonance that supported the three-photon interference effect. With counter propagating beams the resonant enhancement was restored [54,55]. Additionally, the TH yield profiles (focused beams) could show a peak or a dip at the position of a four-photon resonance [53], depending on pressure and laser intensity parameters. The four-photon cancellation effect was well described theoretically [35,36,56], where the role of interference near a three-photon intermediate state was established. Of great significance in these studies was the demonstration that the three-photon interference effect could, at high pressures, extend far away from the line-center of a three-photon resonance. Detailed treatments of Payne et al. [35] and of Tewari [56] revealed how four-photon-resonant peaks in MPI and TH profiles could be converted to dips through choices in concentration and laser intensity parameters. Some of the theoretically predicted effects were tested in detail for studies with focused and unfocused laser beams by Hart et al. [54]. The four-photon cancellation effects clearly demonstrated how three-photon destructive interference evolves at large phase mismatch for the wave-mixing field.

In 1993, Payne et al. predicted [57] another dramatic manifestation of multi-photon destructive interferences on a familiar optical phenomenon. They showed that for properly chosen transitions in a classic two-color Stark shift measurement a destructive interference could completely suppress the a.c. Stark shift when the experiment was carried out with co-propagating laser beams, yet with counter-propagating beams the shifts were pressure independent. The first experiment demonstration by Deng et al. [59,60] showed that not only do a.c. Stark shifts disappear at high concentration when co-propagating laser beams are used, but also the same suppression happens with Autler–Townes splittings [61–63]. The theory was subsequently revised to incorporate Autler–Townes splitting, and was applied in the analysis of a subsequent experimental studies of the suppression of Autler–Townes splittings in Rb by Deng et al. [61–63]. In these studies an even parity transition from ground state to a chosen excited state would be mediated by tuning one laser beam through a two-(four-) photon resonance. A second high intensity beam dipole couples this chosen exited state to another excited state of the system, which is dipole coupled back to the ground state. With counter propagating laser beams the ionization enhancement due to the two-photon resonance will show a very large a.c. Stark shift if the second laser is kept tuned very close to the one-photon resonance between the two excited states. At elevated concentrations with co-propagating beams a result of destructive interference between three-photon excitation by the lasers and one-photon excitation by the FWM field generated. This destructive interference lead to zero polarization of the medium at the FWM frequency, and there is no longer any coupling via the second laser between the two excited states. Thus, with co-propagating laser beams, the a.c. Stark shift must vanish from the two-photon resonantly enhanced photoionization profile, which looks as it would in the absence of the second laser field. If one of the lasers counter-propagates relative to the other, however, the excitations to the FWM generating state by the two different pathways is not balanced and the interference effect in incomplete. Consequently, the a.c. Stark shifts will be present at all reasonable pressures.

It should be pointed out that early experiments on three-photon destructive interference, that showed the suppression of resonance photoionization by a factor of several hundred, also implied that the absorption of the TH or FWM was suppressed by a similar factor. Thus, the early experimental observations (prior to 1983 or so) of the disappearance of
MPI signals [3–7,10–13] and the characteristic growth changes in two-photon absorption [32,33] could be considered as the first experimental indicators of multiphoton induced transparency. The first actual measurements verifying, under conditions of destructive interference, the FWM becomes pressure independent, however, was given by Deng and Payne et al. [59–63] in a series of studies on suppression of Autler–Townes splitting, matched pulse propagations in highly resonant media, and suppression of multi-wave mixing production. It was in these studies that Deng et al. first introduced the terminology of “multi-photon induced transparency”. In a subsequent series of experiments by Deng et al. [59–63] all dramatic predictions described by Payne et al. [57] and Deng et al. [58] were observed in good agreement with the theory.

It is very clear experimentally and theoretically that internally generated fields can significantly alter various resonant and near-resonant nonlinear processes in atomic gases and vapors and in some molecular gases [64–66]. To properly treat various resonant nonlinear processes in gaseous or vaporeous media, it is often necessary to include in the analysis not only the externally injected photon sources, but also the generation of new fields that evolve internally from the nonlinear polarizations created by the imposed fields. The overall dynamic response of particular systems can show dramatic effects resulting from interference between transition amplitudes due to the externally applied and those due to the internally generated fields. This review will attempt to provide an overview of the underlying physics of wave-mixing interference effects and the various manifestations that can, under proper circumstances, ensue. These manifestations include those mentioned in the approximate chronological sketch presented above, plus some recent progresses involving highly efficient FWM in the presence of induced transparencies [67], multi-photon induced transparency [68] and FWM in the presence of multiple multiphoton induced transparencies [67–69], inelastic two- and four-wave mixing (ITWM, IFWM) [69,70], inhibition of three-photon destructive interference [68], FWM channel opening techniques [71], and multi-mixing wave generation with coherently prepared states [69,70].

All of the effects mentioned here (except ITWM/IFWM and destructive interference effects manifested there) have involved atomic transitions wherein the ground state remained undepleted. Thus, the theories have all been linear in the multiphoton Rabi frequency which connects the ground state to the lowest multiphoton resonance.

One of the most noticeable features that comes from these theories is the prediction and subsequent experimental verification of zero polarization at the FWM field frequency. That is, the medium becomes highly transparent to the FWM field once the destructive interference is established even though the FWM field is tuned near or onto a strong one-photon resonance. We emphasize, however, that this transparency is fundamentally different from the transparency induced by externally provided lasers in the conventional electromagnetically induced transparency (EIT) [72–74] process widely known with a three-state A scheme. In the latter case at least one of these lasers must be intense to drive the system transparent and the process is independent to any propagation effect.

At this juncture it is imperative for the authors to note that this review is limited to a subset of the totality of quantum interferences in optical phenomena. In particular, it does not include the extensive literature and discussion on the more recent subject of EIT and closely related topics. Broadly speaking, similar interference phenomena are the subjects of this related field. However in the conventional EIT problems the photon sources are typically introduced from outside the medium, whether or not the medium is of high or low number density. The subjects under review are inclusive of the somewhat more complicated circumstances where a new field, or multiple fields, are generated within a resonant, higher density medium, and the evolution of the amplitudes and phases of these and the input field together determine the overall response of the system. However, this separation of subject matter is not completely clean. Some recent studies, included here, detail how internally generated fields can provide additional transparency to conventional EIT, and that the two phenomena can become closely related and evolve to satisfy identical interfering relationships [67,69,70].

In spite of the “maturity” of these fields, many new manifestations of the interference effects are still under current investigation. Moreover, though hundreds of papers describing many different destructive interference effects have been published since the first observation of the effect in Xe, no comprehensive review of these subjects has yet been published. Furthermore, the theoretical studies in this field have been conducted by researchers coming from widely different backgrounds, using very different techniques, including a susceptibility treatment, time dependent Schrödinger equation, and density matrix formulations. In addition, there has been no uniformity in the type of approximations used in implementing Maxwell’s equations. We also point out that many of the most dramatic effects of this kind come about because of the very narrow resonances. For this reason related phenomena are beginning to be discovered when nonlinear studies are carried out in very cold atomic vapors where Doppler effects are not present. This is currently an area of intense research activity. Thus it is hoped that the field will benefit from a comprehensive review that treats all of the major effects from a uniform and modern theoretical point of view.
The scope of the present review encompasses theoretical and experimental studies involving the interference phenomena described above. The problems will be formulated in a uniform notation, with the atomic behavior being treated from the point of view of the density matrix, and with Maxwell’s equations being applied within the slowly varying amplitude (SVA) approximation. The plan and contents of the paper are provided by the table of contents.

2. Preamble on the basic mathematics used in this review

The main purpose of this section is to provide a clear and concise description of the basic mathematics, notations, and conventions that will be used throughout this review. For those readers already familiar with the present subject matter, this section can be passed over except for a few specific definitions of relevant terms. This section is organized into three subsections that cover the basic physics principles involved in a semi-classical treatment of the quantum destructive interferences that often occur when sufficiently strong lasers are tuned near multi-photon resonances. Such interferences can occur in extended media where the initial and final states are coupled by two alternative pathways. In the context of this review, one path is provided by input laser fields, whereas a second path is created internally within the extended system by wave-mixing processes. In one class of interest, an initial state is coupled to a final state via odd-number multi-photon processes. The final state is also coupled by a one-photon transition back to the initial state. In this class, an odd-photon destructive interference can occur between the odd-photon laser induced coupling and the one-photon coupling due to an internally generated field, both occurring between the same two upper and lower states. In a second class where the initial and final states are coupled by a laser induced even-numbered multi-photon processes, an even-photon destructive interference can occur between the even-photon coupling by the laser fields and the multiple parametric wave-mixing fields generated internally. These striking phenomena will be discussed in detail in the next section using the mathematics described in this section.

The topics in this section are divided into three subsections:

a. In the first subsection the definitions of field, propagation, half Rabi frequency and index of refraction of the medium are introduced first, followed by the equations of time-dependent perturbation theory and the application of the perturbation theory to the derivation of expressions for a.c. Stark shifts, multi-photon half Rabi frequencies, and equations of motion for the probability amplitudes of effective two-state and three-state models of multiphoton near-resonance excitation.

b. In the second subsection the necessity of making use of the density matrix for treating Doppler broadened or pressure broadened media is first explained, followed by the derivation of the equations of motion for the elements of the density matrix for the same effective two-state and three-state models of multiphoton near-resonance excitation.

c. In the third subsection Maxwell’s equations are discussed along with related topics such as indices of refraction. Explanations are given on properly accounting for the effect of buffer gases and for the resonant contribution to the propagation problem in formulating a few-state model. A major component of this subsection is the derivation of Maxwell’s equation using the SVA approximation. It will be shown that this approximation is valid when (1) the pulse length of the laser field involved is not too short, and (2) the optical properties of the medium do not change appreciably over distances on the order of the wavelength of the light fields.

Through this preamble we hope to establish the approximations, the formalism and the terminology used throughout this review.

2.1. Few-state systems coupled by multiphoton processes

In order to demonstrate the relevant mathematics for the succeeding subjects, we choose to first describe an effective two-state system [75] with near resonant one- and three-photon coupling between the two atomic states (Fig. 8a–c). The systematic treatment of this problem begins with the familiar formalism used in time dependent perturbation theory [76]. The time dependent Schrödinger equation in configuration space \( \vec{r}, t \) is given by

\[
\frac{i\hbar}{\partial t} \langle \Psi(t) \rangle = (\hat{H}_0 + \hat{V})\langle \Psi(t) \rangle,
\]  
(2.1)
where $\hat{H}_0$ is the Hamiltonian of an isolated atom in the gas that makes up the medium and $|\Psi(t)\rangle$ is a state vector. The operator $\hat{V} = -\hat{\mu} \cdot \vec{E}$ represents the interaction between the atom and one or multiple laser fields $\vec{E}_{Lj}(\vec{r}, t)$ (where $j$ enumerates the number of laser fields). All laser fields are assumed to be of single frequency with transform limited bandwidth. In addition, $\hat{\mu} = e\vec{r}$ is the electric dipole operator for a given transition, $e$ is the electron charge and $\vec{r}$ is the vector position operator. This form of the interaction follows from the assumption that the wavelengths of lasers are much larger than the size of an atom. A similarity transformation has been applied to the Hamiltonian which contains $\hat{\mu} \cdot \vec{E}$ and the amplitude of the light field divided by $\lambda$. Thus, this simple form of the interaction can be used correctly to all orders.

2.1.1. Definitions of the field, propagation, half Rabi frequency, and index of refraction of the medium

Throughout this and subsequent sections of this review a laser field is described by an electric field of the form

$$\vec{E}_{Lj}(\vec{r}, t) = \vec{E}_{L0j}(\vec{r}, t) \cos(\omega_{Lj}t - \vec{k}_{Lj} \cdot \vec{r}),$$

where $\omega_{Lj}$ and $\vec{k}_{Lj}$ are the frequency and wave vector of the laser field, respectively. $\vec{E}_{L0j}(\vec{r}, t)$ is the slowly varying amplitude of the laser field. It is assumed that $\vec{E}_{L0j}$ depends only on $t - z/c$, and that it has a pulsed nature so that the field is non-zero only for values of $t - z/c \simeq 0$. That is, this field, with the maximum amplitude occurring at $z = 0$ for $t = 0$, is close to zero for $|t - z/c|/\tau \gg 1$ where $\tau$ is a measure of the laser pulse duration.

The propagation direction of the linearly polarized laser field is chosen to be along the positive $z$-axis. Accordingly, it is convenient to assume that the plane of polarization is parallel to the $y$-axis, and the above expression becomes

$$\vec{E}_{Lj}(z, t) = \vec{E}_{L0j}(z, t) \cos(\omega_{Lj}t - \vec{k}_{Lj}z) = \frac{\vec{E}_{L0j}(z, t)}{2} e^{-i(\omega_{Lj}t - \vec{k}_{Lj}z)} + c.c.,$$

where $\vec{k}_{Lj} = \hat{z}k_{Lj}$, with $\hat{z}$ being the unit vector along the $+z$ axis. In the case of circularly polarized light, the $\vec{E}$ vector rotates in the $x-y$ plane while the field propagates along the positive $z$-axis.

The Rabi frequency for a transition driven by a laser field between levels $n$ and $m$ is defined as the product of the dipole matrix element $\mu_{mn}$ and the amplitude of the light field divided by $\hbar$, where the amplitude multiplies the complex exponential of propagation. The choice of the cosine functional form given in the above expression for the laser field yields this product as $\Omega_{mn}^{(1)} = \mu_{mn} E_{L0j}/(2\hbar)$. This is the half of the usual one-photon Rabi frequency definition, as designated by the superscript (1). Thus, throughout this review, $2\Omega_{mn}^{(1)} = \mu_{mn} E_{L0j}/\hbar$ is the usual one-photon Rabi frequency. In this review the superscript (1) denoting one-photon process is often suppressed, therefore $\Omega_{mn} \equiv \Omega_{mn}^{(1)}$. In the case of $N$-photon Rabi frequency, however, the superscript $(N)$ denoting the $N$-photon process is always kept.
The time evolution operator allows one to derive the fundamental equation of time-dependent perturbation theory by motion of the time evolution operator, used in the time dependent Schrödinger equation. Substitution of this expression into Eq. (2.1) gives the equation of 

\[ \hat{T}(t) \]

2.1.2. Time-dependent perturbation formalism

Time dependent perturbation theory is adopted here wherein one defines the time evolution operator, \( \hat{T}(t) \), so that \( \hat{T}(t)|\Psi(\infty)\rangle = |\Psi(t)\rangle \), where \( |\Psi(t = \infty)\rangle \) is an arbitrary initial state of the atom. The time evolution operator maps the arbitrary initial state into \( |\Psi(t)\rangle \). It therefore contains all of the time dependence when \( \hat{T}(t)|\Psi(\infty)\rangle = |\Psi(t)\rangle \) is used in the time dependent Schrödinger equation. Substitution of this expression into Eq. (2.1) gives the equation of motion of the time evolution operator,

\[
\frac{i\hbar}{\partial t} \hat{T}(t) = (\hat{H}_0 + \hat{V})\hat{T}(t).
\] (2.2)

The time evolution operator allows one to derive the fundamental equation of time-dependent perturbation theory by defining an operator \( \hat{S}(t) = e^{i\hat{H}_0 t/\hbar} \hat{T}(t) = \hat{U} \hat{T}(t) \). This unitary transformation with \( \hat{U} = e^{-i\hat{H}_0 t/\hbar} \) corresponds to a transfer from the Schrödinger representation to the interaction representation. The utility of this definition lies in the property of \( \hat{S}(t) \) that for either very early or very late times \( \hat{S}(\pm\infty) = \hat{1} \), the unit operator. In addition, if \( \hat{V} \) is very small then \( \hat{S} \) should be close to \( \hat{1} \) at all times. Using Eq. (2.2), and the definition of \( \hat{S}(t) \) it is easy to see that \( \hat{S} \) satisfies

\[
\frac{\partial \hat{S}}{\partial t} = \left( \frac{1}{i\hbar} \right) \hat{V}_I(t)\hat{S},
\] (2.3)

where \( \hat{V}_I(t) = \hat{U}^\dagger \hat{V}(t)\hat{U} \). Integrating both sides of Eq. (2.3) with respect to \( t \) and using the fact that \( \hat{S}(t = \infty) = \hat{1} \), one obtains

\[
\hat{S} = \hat{1} + \left( \frac{1}{i\hbar} \right) \int_{-\infty}^{t} \hat{V}_I(t_1)\hat{S}(t_1) \, dt_1.
\] (2.4)

It should be emphasized that Eq. (2.4) is exactly equivalent to Eqs. (2.1, 2.2, 2.3), but in a different form of presentation. Eq. (2.4) can be solved iteratively [77]. By replacing \( \hat{S}(t_1) \) on the right-hand side (RHS) of Eq. (2.4) with Eq. (2.4) itself, one obtains

\[
\hat{S} = \hat{1} + \left( \frac{1}{i\hbar} \right) \int_{-\infty}^{t} \hat{V}_I(t_1) \, dt_1 + \left( \frac{1}{i\hbar} \right)^2 \int_{-\infty}^{t} \hat{V}_I(t_1) \, dt_1 \int_{-\infty}^{t_1} \hat{V}_I(t_2) \, dt_2 \hat{S}(t_2).
\] (2.5)

Eq. (2.5) is still exact. This iterative process involving \( \hat{S}(t) \) can be carried out repeatedly until a designated accuracy of the perturbative calculation is achieved.

2.1.3. Effective two-state system coupled with two laser fields

In this subsection Eqs. (2.3)–(2.5) will be used to derive the equations for the time-dependent amplitudes of the ground state and the single resonantly coupled excited state of an effective two-state system under the action of an operator \( \hat{V}_I(t) \).

Before doing this, one must determine the appropriate form for the interaction operator \( \hat{V}_I \). For the effective two-level system, it is assumed that the upper state \( |2\rangle \) is coupled simultaneously by a three- and a one-photon processes (see Fig. 8a–c). The three-photon process is due to direct laser excitations whereas the one-photon process is due to a wave-mixing field. This field results from the fact that the transition \( |2\rangle \rightarrow |1\rangle \) is dipole allowed and a polarization, (and resultant field,) is generated at the transition frequency. For definiteness, it is assumed that two photons from the laser field \( E_{L1} \) plus one photon from the laser field \( E_{L2} \) form the three-photon excitation of the state, whereas one
photon from the wave-mixing field $E_{L3} = E_m$ is responsible for one-photon transitions between states $|1\rangle$ and $|2\rangle$ (see Fig. 8b,c). In the case of $E_{L1} = E_{L2} = E_L$, one has a third harmonic (TH) generation process $E_{L3} = \mathcal{E}_{TH}$ (Fig. 8a).

The interaction operator is given by

$$\hat{V}_I = \hat{V}_{I12} + \hat{V}_{I3}, \quad \hat{V}_{I12} = \hat{V}_{I1} + \hat{V}_{I2}, \quad (2.6a)$$

The unit operator is

$$\hat{1}$$

The interaction operator is given by

$$\hat{V}_I = -\hat{\mu} \cdot \bar{E}_{Lj0} \cos(\omega_L t - k_L z), \quad (j = 1, 2, 3). \quad (2.6b)$$

The reason that the interaction operators are grouped as in Eq. (2.6a) is to emphasize that the fields in $\hat{V}_{I12}$ are jointly responsible for the three-photon process whereas the field in $\hat{V}_{I3}$ participates the one-photon process only, as seen in Figs. 8b and c. Here, implicit assumptions are that the field at $\omega_{L1}$ is strong and the fields at $\omega_{L2}$ and $\omega_{L3}$ are weak, and that no other weakly coupled off resonant state can ever acquire any real population that does not go away adiabatically as the laser pulse dies out. Thus, one only keeps interaction linear in $\hat{V}_{I12}$ and up to the third order to $\hat{V}_{I12}$.

An isolated atom with Hamiltonian $\hat{H}_0$ has eigenstates $|j\rangle$ (i.e., $\hat{H}_0|j\rangle = \epsilon_j|j\rangle = \hbar \omega_j|j\rangle$) that form a complete set. The unit operator is $\sum_j |j\rangle \langle j| = \hat{1}$ with the summation over continuum states understood to switch over to an integral over energy. To derive the appropriate equations for the ground state and the resonantly coupled upper state, one applies the operator $\hat{S}$ to the ground state, which is the only state initially populated. The effect of $\hat{S}$ on the ground state can be expressed as a sum over the complete set, with time dependent coefficients $C_j(t)$:

$$\hat{S}(t)|1\rangle = \sum_j C_j(t)|j\rangle, \quad (2.7)$$

where within the topics of the present review only two or three of the states $|j\rangle$ will be coupled by resonant fields. These will be the only states whose amplitudes are of interest in the present context. However, the other off-resonant states must be included in deriving the appropriate multi-photon coupling between $|1\rangle$ and $|2\rangle$ and the proper optical shifts of these levels. Thus the formalism in this and the following subsections are “effective” two-state or three-state models.

If Eq. (2.6) is multiplied by $\langle 1|$, respectively, one obtains $C_1(t) = \langle 1|\hat{S}(t)|1\rangle$ and $C_2(t) = \langle 2|\hat{S}(t)|1\rangle$ which are the state amplitudes of interest. They are related to the coefficients in an expansion of state vector $|\Psi(t)\rangle$ by

$$|\Psi(t)\rangle = \hat{T}(t)|1\rangle = \hat{U} \sum_j C_j(t)|j\rangle = \sum_j C_j(t)e^{-iE_jt/\hbar}|j\rangle. \quad (2.8)$$

Thus, determination of the coefficients $C_j(t)$ is just as good as determining the amplitudes for any other alternative expansion of $|\Psi(t)\rangle$.

To derive equations for $C_1(t)$ and $C_2(t)$ one starts with Eqs. (2.3)–(2.5) which are exact. From Eq. (2.3) one can immediately obtain

$$\langle 1|\frac{d\hat{S}}{dt}|1\rangle = \frac{\partial C_1}{\partial t} = \left(\frac{1}{i\hbar}\right) \langle 1|((\hat{V}_{I12}(t) + \hat{V}_{I3}(t))\hat{S}(t))|1\rangle$$

$$= \left(\frac{1}{i\hbar}\right) \langle 1|\hat{V}_{I12}(t)\hat{S}(t)|1\rangle + \left(\frac{1}{i\hbar}\right) \langle 1|\hat{V}_{I3}(t)\hat{S}(t)|1\rangle. \quad (2.9)$$

To evaluate the matrix element of the second term on the RHS of Eq. (2.9), which is a product of operators, one inserts the unit operator $\sum_j |j\rangle \langle j| = \hat{1}$ between $\hat{V}_{I3}$ and $\hat{S}$. Note that $\hat{V}_{I3}$ is the dipole operator for the one-photon coupling of states $|1\rangle$ and $|2\rangle$, thus $\langle 1|\hat{V}_{I3}|1\rangle = 0$ and one has

$$\langle 1|\hat{V}_{I3} \left( \sum_{j=1}^2 |j\rangle \langle j| \right) \hat{S}|1\rangle = \langle 1|\hat{V}_{I3}|2\rangle C_2,$$

where $\langle 2|\hat{S}|1\rangle = C_2$ has been used.
To evaluate the first term on the RHS of Eq. (2.9) one replaces the operator \( \hat{S}(t) \) by its exact expansion given by Eq. (2.4). Eq. (2.9) becomes

\[
\frac{\partial C_1}{\partial t} = \left( \frac{1}{\hbar} \right) \langle 1| \hat{V}_{13}(t)|2 \rangle C_2 + \left( \frac{1}{\hbar} \right)^2 \langle 1| \hat{V}_{12}(t) \int_{-\infty}^{t} \hat{V}_{12}(t_1) \hat{S}(t_1) \, dt_1 \rangle |1\rangle,
\]

where terms containing the cross-product of \( \hat{V}_{12} \hat{V}_{13} \) have been neglected since these are 4th and higher order terms. Notice that the first term inside the square bracket on the RHS vanishes since \( V_{12} \) is a dipole operator. Now if one inserts the unit operator between the \( \hat{V}_{12} \) and \( \hat{S} \) operators in the integral in the square bracket one finds, by neglecting terms containing the cross-product of \( \hat{V}_{12} \hat{V}_{13} \) again,

\[
\frac{\partial C_1}{\partial t} = \left( \frac{1}{\hbar} \right) \langle 1| \hat{V}_{13}(t)|2 \rangle C_2 + \left( \frac{1}{\hbar} \right)^2 \langle 1| \hat{V}_{12}(t) \int_{-\infty}^{t} \hat{V}_{12}(t_1) \hat{S}(t_1) \, dt_1 \rangle |1\rangle,
\]

The next step is to investigate the second term on the RHS of Eq. (2.10). This is done by noting that while \( C_1(t_1) \) is a slowly varying function of time, the operator \( \hat{V}_{12}(t_1) \) contains very rapidly oscillating factors. Therefore, the integral can be evaluated asymptotically by integration by parts, with the rapidly oscillating complex exponential being integrated. This near-\( \delta \)-function behavior allows \( C_1(t_1) \) to be replaced by \( C_1(t) \).

The evaluation of the third term in Eq. (2.10) requires the use of Eq. (2.4) again to replace \( \hat{S}(t_1) \). In this further expansion of \( \hat{S} \) the term resulting from the unit operator vanishes and one finds

\[
\frac{\partial C_1}{\partial t} = \left( \frac{1}{\hbar} \right) \langle 1| \hat{V}_{13}(t)|2 \rangle C_2 + \left( \frac{1}{\hbar} \right)^2 \langle 1| \hat{V}_{12}(t) \int_{-\infty}^{t} \hat{V}_{12}(t_1) \hat{S}(t_1) \, dt_1 \rangle |1\rangle,
\]

To evaluate the integral over \( dr_2 \) in the double integral term in Eq. (2.11) one again inserts the unit operator between \( \hat{V}_{12}(t_2) \) and \( \hat{S}(t_2) \), and neglects terms containing the cross-product of \( \hat{V}_{12} \hat{V}_{13} \). Notice that in doing so the term \( |2\rangle \langle 2| \) in the unit operator, when combined with \( \hat{S}(t_2) \langle 1| \), leads to the possibility of a slowly varying coefficient times \( C_2(t_2) \).

Now the second integral in the last term in Eq. (2.11) contains the product of three \( \hat{V}_{12}(t_2) \) at different times. If the unit operator is inserted between each pair of these interaction operators one gets rapidly oscillating complex exponentials that result in \( C_2(t_2) \) being replaced by \( C_2(t) \) after the integration by parts method is used to evaluate the integrals. With this procedure and by defining laser fields detuning from exact resonance as \( \delta_2 = 2\omega_L \pm \omega_{L2} - (\omega_2 - \omega_1) \) (where ± represents sum and difference frequency generation processes), Eq. (2.11) becomes

\[
\frac{\partial C_1}{\partial t} = i(\Omega_{12}^{(1)} e^{i(\omega_{L3} - \omega_{21})} e^{-ik_{L3}z} C_2 + \Omega_{12}^{(3)} e^{i\delta_2 t} e^{-i(2k_{L2} \pm k_{L3})z} C_2 - iA_1(t) C_1),
\]

\[
A_1(t) = -i \left( \frac{1}{\hbar} \right)^2 \int_{-\infty}^{t} dt_1 \langle 1| \hat{V}_{12}(t_1) \hat{V}_{12}(t_1) |1\rangle,
\]

\[
\Omega_{12}^{(3)}(t) = \left( \frac{1}{\hbar} \right)^3 e^{i(2k_{L1} \pm k_{L3})z} e^{-i\delta_2 t} \times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dr_2 \langle 1| \hat{V}_{12}(t_1) \hat{V}_{12}(t_1) \hat{S}(t_2) |2\rangle.
\]

The term defined in Eq. (2.12b) is the a.c. Stark shift induced in \( |1\rangle \) by the laser fields. The quantity defined by Eq. (2.12c) is the three-photon half Rabi frequency for the three-photon resonant transition. When an actual calculation is carried out, one will keep only terms such as \( \hat{V}_{11} \hat{V}_{1} \hat{V}_{12} \). All other contributions lead to small amplitude rapidly oscillating terms on the RHS of Eq. (2.11), and hence neglected. This procedure corresponds to the multi-photon version of the rotating wave approximation (RWA, i.e., only the resonance terms are retained) where all far-off resonance terms have been neglected.
At this point clarifications on energy and momentum conservation laws should be discussed. One notices that in Eqs. (2.12a,c) the position dependent phase factors contain \(2\mathbf{k}_{L1} \pm \mathbf{k}_{L2}\). This relation comes from the wave vector relation (momentum conservation) describing the propagation geometry \(\mathbf{k}_{L3} = 2\mathbf{k}_{L1} \pm \mathbf{k}_{L2}\). This wave vector relation due to the propagation geometry is independent of the energy conservation relation \(\omega_{L3} = 2\omega_{L1} \pm \omega_{L2}\) where ± signs represent the sum/difference frequency generation processes. That is, for sum frequency generation of \(\omega_{L3} = 2\omega_{L1} + \omega_{L2}\), one can still have a wave vector sum \(2\mathbf{k}_{L1} \pm \mathbf{k}_{L2}\) depending on whether lasers with wave vectors \(\mathbf{k}_{L1}\) and \(\mathbf{k}_{L2}\) travel co-linearly or anti-co-linearly (counter-propagating). It will become clear later that these different propagation geometries correspond to two very different phase matching conditions and have profound consequences on the effectiveness of multi-photon destructive interference effects.

A further note on the expression of wave vectors is also necessary at this stage. In general, the magnitude of wave vector \(\mathbf{k}\) of an electric field at frequency \(\omega\) is defined as \(|\mathbf{k}| = n(\omega)\mathbf{v}/c\) where \(n(\omega)\) is the index of refraction of the medium at the frequency \(\omega\). Thus, one has \(\mathbf{k}_{L1} = n(\omega_{L1})\omega_{L1}/c\) and \(\mathbf{k}_{L2} = n(\omega_{L2})\omega_{L2}/c\) for the two laser fields, where the indices \(n(\omega_{L1})\) and \(n(\omega_{L2})\) are very close to unity since both lasers are very far from one-photon coupling of the transition \([1] \rightarrow [2]\). The wave vector for the generated field is very different as it is very close to direct one-photon pumping of the same transition of the resonant medium under investigation. In the case where buffer gases are mixed with the resonant medium to be studied, this very-near-resonance nature of the generated field indicates that the index of refraction is significantly different from unity. One proper way of treating such a situation is to separate the refractive index into near-resonance and non-resonant contributions, i.e., \(n(\omega_{L3}) = n_0(\omega_{L3}) + n_R(\omega_{L3})\). The resonant contribution will be specifically treated using the Maxwell wave equation whereas the non-resonant contribution can be viewed as an effective background refractive index. Thus, one writes \(\mathbf{k}_{L3} = n_0(\omega_{L3})\omega_{L3}/c\) with the understanding that the resonant part will be separately treated by using the Maxwell equation. With these clarifications of energy and wave vectors, one can now proceed to carry out detailed calculation in which all phase factors must be accurately tracked, a practice that will become evident in the derivation of the density matrix.

A corresponding derivation for \(C_2\) can be given to show that

\[
\frac{\partial C_2}{\partial t} = i(\Omega_{21}^{(1)}) e^{-i(\omega_{L3} - \omega_{L2})t} e^{i\mathbf{k}_{L3} z/c} C_1 + \Omega_{21}^{(3)} e^{-i\delta_2 t} e^{i(2\mathbf{k}_{L1} \pm \mathbf{k}_{L2}) z/c} C_1 - iA_2(t)C_2, \tag{2.13a}
\]

\[
A_2(t) = -i \left( \frac{1}{\hbar} \right)^2 \int_{-\infty}^{t} dt_1 (2|\hat{V}_{I12}(t)\hat{V}_{I12}(t_1)|2) \tag{2.13b}
\]

\[
\Omega_{21}^{(3)}(t) = \left( \frac{1}{\hbar} \right)^3 e^{-i(2\mathbf{k}_{L1} \pm \mathbf{k}_{L2}) z/c} e^{i\delta_2 t} \times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 (2|\hat{V}_{I12}(t)\hat{V}_{I12}(t_1)(\hat{1} - |2\rangle\langle 2|)\hat{V}_{I12}(t_2)|1), \tag{2.13c}
\]

where the term defined in Eq. (2.13b) is the a.c. Stark shift induced in [2] by the laser fields and cross-product terms such as \(\hat{V}_{I12}\hat{V}_{I3}\) have been neglected.

By using exact properties of \(\hat{S}(t)\) and ideas very similar to those described above, Eqs. (2.12) and (2.13) can be generalized to the case where the resonance excitation involves the simultaneous absorption of \(N\) photons of different colors coupling states \([1]\) and \([2]\) and one \((N + 1)\)-wave-mixing photon with the frequency of \(\omega_{Lm} = \sum_{j=1}^{N} \omega_{Lj}\) to couple the same transition. In all cases where narrow bandwidth lasers are used to study multiphoton process where \(N \geq 2\), the inclusion of the a.c. Stark shift is usually important unless the power densities of the laser fields are kept relatively low so that saturation effects are small. This follows from the fact that the a.c. Stark shift will almost always be larger than the power broadened width of the transition. Of course at low power densities, both the a.c. Stark shift and the inherent line width can, under some circumstances, be dominated by Doppler width, laser bandwidth, or the pressure broadened width. For the generalized multi-photon process, \(N \geq 2\), Eqs. (2.12) and (2.13) become

\[
\frac{\partial C_1}{\partial t} = i(\Omega_{12}^{(1)}) e^{i(\omega_{Lm} - \omega_{L2})t} e^{-i\mathbf{k}_{Lm} z} + \Omega_{12}^{(N)} e^{i\delta_2 t} e^{-i\sum_{j=1}^{N} \mathbf{k}_{Lj} z/c} C_2 - iA_1(t)C_1, \tag{2.14a}
\]

\[
\frac{\partial C_2}{\partial t} = i(\Omega_{21}^{(1)}) e^{-i(\omega_{Lm} - \omega_{L2})t} e^{i\mathbf{k}_{Lm} z/c} + \Omega_{21}^{(N)} e^{-i\delta_2 t} e^{i\sum_{j=1}^{N} \mathbf{k}_{Lj} z/c} C_1 - iA_2(t)C_2, \tag{2.14b}
\]
\[ A_n(t) = -i\left(\frac{1}{\hbar}\right)^2 \int_{-\infty}^{t'} dt_1 \langle n | \hat{V}_{112}(t) \hat{V}_{112}(t_1) | n \rangle, \quad (n = 1, 2) \]  

(2.14c)

\[
\Omega^{(N)}_{21}(t) = (-i)^{N+1} \left(\frac{1}{i\hbar}\right)^N e^{-i\sum_{j=1}^{N} k_{Lj} z} e^{i\delta_2 t} \times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{N-1}} dt_{N-1} \langle 2 | \hat{V}_{112}(t) \hat{V}_{112}(t_1) (\hat{1} - |2 \rangle \langle 2 |) \hat{V}_{112}(t_2) \cdots \hat{V}_{112}(t_{N-1}) | 1 \rangle. \]  

(2.14d)

where \( \delta_2 = \sum_{j=1}^{N} (\omega_{Lj} - (\omega_2 - \omega_1)) \) is the \( N \)-photon detuning. Again, Eq. (2.14c) defines the a.c. Stark shift induced in the state \( |n\rangle \) by laser fields and terms containing \( \hat{V}_{112} \hat{V}_{113} \) have been neglected. Eq. (2.14d) defined the \( N \)-photon half Rabi frequency. For the case of \( N = 1 \), it is easy to show that the half Rabi frequency is

\[ \Omega^{(1)}_{21} = -(1/\hbar) \langle 2 | \hat{V}_I(t) | 1 \rangle e^{-i k_{Lj} z/c} e^{i\delta_2 t} = \mu_{21} E_0 / (2\hbar), \]

where the RWA has used in the results for all \( N \)’s and \( \mu_{21} \) is the matrix element for the one-photon transition between states \(|1\rangle \) and \(|2\rangle \).

Typically, when unit operators are inserted between pairs of the \( \hat{V}_{112} \) and the time integrals evaluated, expressions for a.c. Stark shifts and multi-photon half Rabi frequencies are given in terms of the sums over intermediate states. In cases where \( N \) different colors are used to drive the \( N \)-photon-resonance transition and resonance is achieved only if \( \omega_{Lm} = \sum_{j=1}^{N} \omega_{Lj} \simeq \omega_2 \), one notices that in satisfying the resonance condition the \( N \) photons can be absorbed in many alternative orders. Thus, there are many sums over intermediate states to be carried out. This makes Eq. (2.14d) a particularly compact form for the multi-photon half Rabi frequency.

### 2.1.4. Effective three-state system coupled with two laser fields

Results similar to those of the previous subsection can be derived for an effective three-state system. A relevant example would be a system involving a two-photon resonance followed by a resonance coupling between the two-photon resonance level and a third state which is dipole allowed and one-photon coupled back to the ground state by an internally generated field (Fig. 9). This is the case of FWM generation. In this subsection a brief outline is given to show how this three-state generalization can be achieved.

Consider a three-level atomic system with energy level diagram as shown in Fig. 9 and with laser field couplings as described. In this case the interaction operator is given by

\[
\hat{V}_I = \hat{V}_{11} + \hat{V}_{12} + \hat{V}_{13},
\]

(2.15a)

\[
\hat{V}_{ij} = -\bar{\mu} \cdot \vec{E}_{Lj0} \cos(\omega_{Lj} t - k_{Lj} z) \quad (j = 1, 2, 3)
\]

(2.15b)

Here, it is assumed that the interaction operator \( \hat{V}_{11} \) is responsible for a two-photon process whereas the operators \( \hat{V}_{12} \) and \( \hat{V}_{13} \) each contribute to a separate one-photon processes. The initial equations, supplemented by Eqs. (2.3)–(2.6) as needed, are

\[
\hbar \frac{\partial}{\partial t} |j\rangle \hat{S} |1\rangle = \langle j | \hat{V}_I(t) \hat{S} |1\rangle = \langle j | (\hat{V}_{11}(t) + \hat{V}_{112}(t) + \hat{V}_{113}(t)) \hat{S} |1\rangle \quad (j = 1, 2, 3).
\]

(2.16)

Beginning with \( j = 1 \), one has

\[
\hbar \frac{\partial C_1}{\partial t} = \langle 1 | \hat{V}_{13} | 3 \rangle C_3 + \langle 1 | \hat{V}_I (\hat{1} - |3 \rangle \langle 3 |) \left( \hat{1} + \left( \frac{1}{i\hbar} \right) \int_{-\infty}^{t} dt_1 \hat{V}_I(t_1) \hat{S}(t_1) \right) | 1 \rangle,
\]

(2.17)

where Eqs. (2.5) and (2.4) have been used in calculating the first and the second terms. Notice that the \( |3 \rangle \langle 3 | \) has been subtracted from the term in \( \hat{V}_I \) and notice that the field at \( \omega_{L3} \) is weak. Thus bringing in the coupling between states \(|1\rangle \) and \(|3\rangle \) does not really change the a.c. Stark shift or the two-photon coupling between states \(|1\rangle \) and \(|2\rangle \). Neglecting the non-resonant term for the unit operator \( \hat{1} \) and cross-product terms such as \( \hat{V}_{11} \hat{V}_{12}, \hat{V}_{11} \hat{V}_{13} \) and \( \hat{V}_{12} \hat{V}_{13} \) (there are either far from the perspective resonance or of the higher order), and using Eq. (2.14), one obtains

\[
\frac{\partial C_1}{\partial t} = -i A_1(t) C_1 + i \Omega^{(1)}_{13} e^{i\delta_3 t} e^{-ik_{L3} z} C_3 + i \Omega^{(2)}_{12} e^{i\delta_2 t} e^{-2ik_{L1} z} C_2,
\]

(2.18)
At this stage of derivation, it is now convenient to introduce a unitary phase transformation to rewrite Eqs. (2.18), where the ionization out of the two-photon state is desired. Thus, a difference frequency mixing scheme is used. In most experimental cases involving suppression of a.c. Stark shift it is the ionization out of the two-photon state that is of particular interest. In the case of sum frequency mixing, selective ionization technique must be used if the ionization out of the two-photon state is desired.

where the field detunings are defined as $\delta_2 = 2\omega_{L1} - (\omega_2 - \omega_1)$ and $\delta_3 = 2\omega_{L1} + \omega_{L2} - (\omega_3 - \omega_1)$ (here the system under consideration is a sum frequency generation process). In addition, the same considerations as in deriving Eq. (2.14) have been used. If the third laser-like field (i.e., $\omega_{L3}$) is detuned from the $|1\rangle - |3\rangle$ resonance by exactly the amount that $2\omega_{L1} + \omega_{L2}$ differs from $\omega_3 - \omega_1$, (that is, $\omega_{L3} - \omega_{31} = 2\omega_{L1} + \omega_{L2} - \omega_{31}$), then this third laser-like light could be a FWM field. Letting $j = 3$ and recognizing that in this case the state $|3\rangle$ is only coupled to states $|1\rangle$ and $|2\rangle$ by one-photon processes, one obtains

$$
\frac{\partial C_3}{\partial t} = i\Omega_{31}^{(1)} e^{-i\delta_3 t} e^{i k_{L2} z} C_1 + i\Omega_{32}^{(1)} e^{i(\omega_3 - \omega_2 - \omega_{L2}) t} e^{\pm ik_{L2} z} C_2
$$

$$
+ \frac{1}{\hbar} (|3\rangle \langle 1| - |1\rangle \langle 3| - |2\rangle \langle 2|) \hat{S}(t).
$$

where the $\pm$ sign in front of $k_{L2}$ denotes the propagation direction of the laser at $\omega_{L2}$. Assuming that the lasers at $\omega_{L1}$ and $\omega_{L3}$ are much weaker than the laser pumping the two-photon resonance, one can use Eq. (2.4) to rewrite the third term in Eq. (2.19) into an a.c. Stark shift, $A_3(t)$, for state $|3\rangle$, i.e.,

$$
\frac{\partial C_3}{\partial t} = -iA_3(t) C_3 + i\Omega_{31}^{(1)} e^{-i\delta_3 t} e^{i k_{L2} z} C_1 + i\Omega_{32}^{(1)} e^{i(\omega_3 - \omega_2 - \omega_{L2}) t} e^{\pm ik_{L2} z} C_2.
$$

Following the similar procedures one can derive equation for $C_2(t)$ and obtain

$$
\frac{\partial C_2}{\partial t} = -iA_2(t) C_2 + i\Omega_{21}^{(2)} e^{-i\delta_2 t} e^{2ik_{L1} z} C_1 + i\Omega_{23}^{(1)} e^{i(\omega_2 - \omega_3 + \omega_{L2}) t} e^{\mp ik_{L2} z} C_3.
$$

At this stage of derivation, it is now convenient to introduce a unitary phase transformation to rewrite Eqs. (2.18), (2.20), (2.21) into a more familiar form. Take $A_1 = C_1$, $A_2 = C_2 e^{i\delta_2 t} e^{-2ik_{L1} z}$, and $A_3 = C_3 e^{i\delta_3 t} e^{-i(2k_{L1} \pm k_{L2}) z}$, one gets

$$
\frac{\partial A_1}{\partial t} = -iA_1 A_1 + i\Omega_{12}^{(2)} A_2 + i\Omega_{13}^{(1)} A_3 e^{-i[k_{L3} - (2k_{L1} \pm k_{L2})] z},
$$

Fig. 9. Energy level diagrams for three-state plus continuum models. Left panel: sum frequency mixing scheme. Right panel: difference frequency mixing scheme. In most experimental cases involving suppression of a.c. Stark shift it is the ionization out of the two-photon state that is of particular interest. Thus, a difference frequency mixing scheme is used. In the case of sum frequency mixing, selective ionization technique must be used if the ionization out of the two-photon state is desired.
\[ \frac{\partial A_2}{\partial t} = i[\delta_2 - A_2(t)]A_2 + i\Omega_{12}^{(2)}A_1 + i\Omega_{23}^{(1)}A_3, \]  
(2.22b)

\[ \frac{\partial A_3}{\partial t} = i[\delta_3 - A_3(t)]A_3 + i\Omega_{32}^{(1)}A_2 + i\Omega_{31}^{(1)}A_1e^{i[kL_3+(2kL_2\pm kL_2)]z}. \]  
(2.22c)

Clearly, except the last terms in Eqs. (2.22a,c) all other rapidly oscillating phase terms are eliminated from the equations of motion for the amplitudes \( A_j(t) \) \( (j = 1, 2, 3) \).

The last terms in Eq. (2.22a,c) are worth noting. Recall that the \( \pm \) represents the propagation geometry and the system under consideration is a sum frequency generation process where \( \omega_{L3} = 2\omega_{L1} + \omega_{L2} \), the non-resonant part (since \( k_{L3} = n_0(\omega_{L3}) \) \( \omega_{L3}/c \) includes only the non-resonant contribution to the index at the frequency of the generated field) of the phase mismatch between the generated field and the laser fields is

\[ \Delta K = k_{L3} - (2kL_2 \pm kL_2) = \frac{\omega_{L3}n_0(\omega_{L3}) - [2\omega_{L1}n(\omega_{L1}) \pm \omega_{L2}n(\omega_{L2})]}{c}. \]

This phase difference has profound effect on the behavior of the odd-photon destructive interference, as will be shown in Section 3.

Applying \( C_j \to A_j \) phase transformation described after Eq. (2.21) to Eq. (2.8) it follows that the state vector for this “effective” three-state system would be

\[ |\Psi(t)\rangle = A_1e^{-i\omega_1 t}|1\rangle + A_2e^{-i(\omega_2 + \delta_2)t}e^{2i\omega_{L1}z/c}|2\rangle + A_3e^{-i(\omega_3 + \delta_3)t}e^{i(2\omega_{L1} + \omega_{L2})z/c}|3\rangle. \]  
(2.23)

where \( A_j \) are the only real populations created. Of course, the off-resonant states must be retained in deriving the multi-photon half Rabi frequencies and the a.c. Stark shifts, but otherwise the last equation for the state vector, \( |\Psi(t)\rangle \), is valid. The half Rabi frequencies and the a.c. Stark shifts can be calculated theoretically, but this topic will not be covered here [78].

Before leaving this subsection, a useful rule of thumb may be worth pointing out. It was shown immediately after Eq. (2.22) that all fast oscillating factors can be removed from the resulting equations of motion for the amplitudes if the choice of state vector given in Eq. (2.23) is made. (For counter-propagation some rapid oscillation remains.) Consequently, one only needs to calculate these slowly varying quantities. Thus, to simplify the equations it is advisable to always start with the state vector for a near resonant \( M \)-level system expressed as

\[ |\Psi(t)\rangle = \sum_{m=1}^{M} A_m(t) e^{-i(\omega_m + \delta_m)t}e^{i\theta_m z}|m\rangle. \]  
(2.24)

Here, the rule of thumb for obtaining this state vector is that for the ground state one always has \( \delta_1 = 0 \) and \( \theta_1 = 0 \) (if one assumes that the ground state has zero energy, then one also takes \( \omega_1 = 0 \)). In addition, detuning \( \delta_m \) is always defined as the sum of all laser frequencies that contribute to the excitation \( |1\rangle \to |m\rangle \) minus the energy difference between the states \( |m\rangle \) and \( |1\rangle \) (i.e., \( \omega_m1 \)). Finally, \( \theta_m \) is always the sum of all wave vectors correspond to the laser frequencies used in the definition of \( \delta_m \). This rule of thumb will define the convention that will be consistently used throughout this review.

In the next subsection results derived in this subsection will be applied to derive and formulate the equations of motion for a density matrix treatment of few-state systems where some of the pairs of states are simultaneously coupled by one- and multi-photon processes. This density matrix treatment will then be chosen methodology to be used throughout this review.
2.2. Equations of motion for the density matrix

2.2.1. Justification for a density matrix formalism and brief discussions of resonance line broadening mechanisms

A density matrix formalism is necessary for a proper theoretical treatment of many effects in gaseous phase laser spectroscopy and nonlinear optical effects. In particular, this approach must be used in treating problems that require:

- The inclusion of Doppler effects in resonant one- or multi-photon excitation and multi-wave mixing processes.
- The inclusion of collisional dephasing effects on resonant one- or multi-photon excitation and multi-wave mixing processes.
- The inclusion of collisional dephasing effects on pressure dependent shifts of multiphoton resonances due to fields generated internally in the medium.

In all of the above situations there are rapid decay terms in the equations of motion for the off-diagonal elements of the density matrix that do not result in corresponding rapid rates of change of the diagonal elements of the density matrix. In these situations, the line widths for the excitation of the states are far broader than can be accounted for in terms of any changes of state populations. Consequently, no time dependent Schrödinger equation treatment can predict correctly both the polarization of the medium and the state populations. The missing ingredient in the time dependent Schrödinger equation treatment is the ability to deal with rapid loss of coherence between pairs of states due to processes that do not actually cause rapid changes in the state populations.

In the case of Doppler effects the rapid dephasing comes about because atoms in a laser beam have a continuous distribution of components of velocity parallel to the beam. Thus, if an atom with a zero component of velocity parallel to the direction of light propagation sees the light as exactly resonant, an atom moving with non-zero $V_{||}$ sees the light detuned in angular frequency by $-V_{||}c/\omega_L$. Since at room temperature the average $V_{||}$ might be around $3 \times 10^4$ cm/s and for a three-photon resonance $\omega_L$ might be $2 \times 10^{16}$ rad/s we have a Doppler spread of detunings of around $4 \times 10^{10}$ rad/s. This creates phase differences that become significant in about $1 \times 10^{-10}$ s. These Doppler shifts give a significant width to the excitation line shape and severely reduce the resulting polarization of the medium at the frequency of the wave-mixing field that might be generated. In effect, the Doppler shifts reduce the off-diagonal element of the density matrix that determines the polarization of the medium at the frequency of the generated light.

Collisional dephasing, on the other hand, comes about in two ways. The first mechanism of importance here is foreign gas broadening, which will be encountered in several topics of this review. For example, in investigations of the onset of a destructive interferences at low concentrations, where the total number of events per pulse were small, avalanche amplification was needed to observe signals. Thus, a buffer gas was introduced at concentrations much higher than the target species to serve as a “counting gas” with well defined and fixed gain. Collisional dephasing by a foreign gas results from collisions between a resonance atom in the ground state and a foreign gas atom. However, the pressure at which foreign gases give dephasing rates that are faster than the dephasing rate the Doppler effect are much higher than what was needed for a good counting gas, thus it was possible to avoid this effect in the published studies.

The second form of collisional dephasing occurs when the pressure of the resonance species is high, referred to as self pressure broadening. When an excited atom collides with a ground state atom of the same element a dipole–dipole interaction exists between the two colliding atoms. This interaction involves products of pairs of electron coordinates with the property that non-zero matrix elements exist only when an electron in each atom changes states. Energy is conserved by the ground state atom becoming excited and the excited partner dropping back to the ground state. That is, the excitation jumps between the two atoms. This process is usually accompanied by a change in the magnetic quantum number of the excited state. When this process occurs, no further correlation exists between the ground state and excited state. At a concentration where this rate of decay of coherence is fast compared with that induced by the Doppler shift, the excitation is collisionally exchanged back and forth between magnetic substates many times during a few nanosecond laser pulse, or during the lifetime of the excited state. Thus, in an inert gas where the ground state has $J = 0$ (ignoring hyperfine structure for these purposes) and the upper state in the three-photon excitation has $J = 1$, there will be $1/3$ of the excited atoms in each magnetic substate. With plane polarized laser light only one of these, $M_J = 0$, couples back to the ground state. Once this equilibrium is established there is no rate of change of state populations due to the energy transfer mechanism, but as the concentration is increased the line width and the rate of decay of coherence between pairs of states continues to increase proportionately. With large effects occurring with
impact parameters of as much as 10 nm, this pressure broadening effect becomes comparable with Doppler effects at concentrations of $10^{17}/\text{cm}^3$ and easily dominates the Doppler width by concentrations of $6 \times 10^{17} \text{--} 3 \times 10^{18}/\text{cm}^3$.

The broadening of the upper state in two-photon resonant excitation is also dominated by resonance energy transfer between the excited atom and ground state atoms, but with the coupling being due to the quadrupole–quadrupole interaction, which drops off much more rapidly with $R$. Typically, this rate of energy transfer is about a factor of 5–10 times smaller than the rate for one-photon resonance states [80].

These collisional energy transfer effects cause the probability amplitude for an atom in an excited state to decay exponentially with time. The energy transfer process introduces an exponential decay rate in the coherence between the excited state and any other state. Since coherence between a pair of states is measured by the corresponding off-diagonal element of the density matrix, the rate of energy transfer out of that state causes a corresponding contribution to each off-diagonal density matrix element involving the state in question. These will be the $\gamma_{mn}\rho_{mn}$ rates that enter as the $(\hat{c}\rho_{mn}/\hat{c}t)_{\text{coll}}$ terms in the equations of motion for the elements of the density matrix.

According to the NIST database on pressure broadening effects, the rate of resonance energy transfer, $\Gamma_{21}$, for states having allowed one-photon transitions back to the ground state is

$$\Gamma_{21} = 2.41 \frac{\kappa_{21}c}{2\omega_{21}},$$

(2.25)

where

$$\kappa_{21} = \frac{2\pi N_0\omega_{21}|\mu_{21}|^2}{\hbar c}.$$  

In the above expression $N_0$ is the concentration in cm$^{-3}$, $\mu_{21}$ is the electric dipole matrix element between states $|2\rangle$ and $|1\rangle$, $\omega_{21}$ is the resonance angular frequency of the light emitted in transitions between $|2\rangle$ and $|1\rangle$, and $c$ is the speed of light in vacuum. One of the first careful calculations of this rate that included all of the important details was carried out by Berman and Lamb [79].

In the following subsection a method for the derivation of equations of motion for the density matrix is described. This method will not be general enough to allow the calculation of laser cooling, or other processes where atomic recoil effects are of importance. It will, however, suffice for dealing with the problems that will be described in this review.

### 2.2.2. Derivation of density matrix and the corresponding equations of motion

The derivation of the density matrix begins with defining the density operator. At the level consistent with Section 2, there are two ways to define the density operator. The difference is in the choice of the state vector and, therefore, the order of application of a unitary phase transformation aimed at removing fast oscillating factors from the equations of motion of the density matrix. Of course, at the end they must yield the same equations of motion for the slowly varying part of the density matrix.

One way is to first define the state vector according to Eq. (2.8), i.e., using probability amplitudes $C_j(t)$. One then constructs a density operator according to the prescription given below. This will yield equations of motion for a quantity that still contain some relative oscillatory factors. One then applies a suitable unitary phase transformation to remove these oscillatory factors, resulting in equations of motion containing only the slowly varying components of the density matrix.

The second route to the equations is to first define the state vector according to Eq. (2.23), i.e., using probability amplitudes $A_j(t)$. One then follows the prescription given below to construct the density operator and hence derive the equations of motion that contains only slowly varying components of the density matrix. The only difference between these two methods is the order when the phase transformation is applied, i.e., to apply the phase transformation at the equations of motion stage or at the state vector stage. The final result should be the same, as they must be.

Since the equations of motion for coefficients $C_j$ have already been derived in the Section 2.1, it is convenient to use the probability amplitudes $C_j(t)$ and therefore, Eq. (2.8) to define the density matrix operator. It will be shown that with suitable unitary phase transformation the derived equations of motion do not contain fast oscillatory factors, and the same phase transformation maps the state vector with probability amplitudes $C_j(t)$ such as Eq. (2.8) into the state vector with probability amplitudes $A_j(t)$ as shown in Eq. (2.24).
The density operator is defined by
\[
\hat{\rho} = |\Psi(z, t)\rangle \langle \Psi(z, t)|,
\]  
(2.26)
with the bar representing an average over collision histories, or an average over the distribution of components of velocity parallel to the laser beam, or both. The coordinate \(z\) specifies the center of mass (c.m.) position of the atom in the laser beam.

To derive operator equations of motion for the density operator one uses the time dependent Schrödinger equation and its adjoint in order to evaluate \(i\hbar \hat{\rho} / \partial t\). Differentiating Eq. (2.26) with respect to time and using (in the interaction picture)
\[
i\hbar \frac{\partial}{\partial t} |\Psi(z, t)\rangle = \hat{V}_I |\Psi(z, t)\rangle,
\]  
(2.27a)
\[
-i\hbar \frac{\partial}{\partial t} \langle \Psi(z, t)| = \langle \Psi(z, t)| \hat{V}_I,
\]  
(2.27b)
one obtains,
\[
i\hbar \frac{\partial}{\partial t} \hat{\rho} = \hat{V}_I \hat{\rho} - \hat{\rho} \hat{V}_I + i\hbar \left( \frac{\partial}{\partial t} \right)_\text{coll} \hat{\rho},
\]  
(2.28)
where the subscript \(I\), denoting the interaction representation, for the density operator has been suppressed. In Eq. (2.28) an additional term \((\partial \hat{\rho} / \partial t)_\text{coll}\) has been added to properly account for relevant dephasing processes such as the effect of collisional destruction of coherence between pairs of states. These are measured by the off-diagonal elements of the density matrix.

Eq. (2.28) gives a start toward determining the density operator in terms of its matrix elements and the basis states chosen. In the following the same two sets of systems treated in Sections 2.1.3 and 2.1.4 will be retreated with the formalism of density matrix so that a comparison can be made.

### 2.2.3. Effective two-state system coupled with two laser fields

In order to make the comparison clear and concise, we cast the two-state problem given in Section 2.1.3 into a density matrix description. Using the definition Eq. (2.8) for the state vector one has
\[
\hat{\rho} = |\Psi(z, t)\rangle \langle \Psi(z, t)| = \sum_{m,n} C_m C_n^* e^{-i(\omega_m - \omega_n)H} |m\rangle \langle n| = \sum_{m,n} \tilde{\rho}_{mn} e^{-i(\omega_m - \omega_n)H} |m\rangle \langle n|,
\]  
(2.29)
where
\[
\tilde{\rho}_{mn} \equiv C_m C_n^*.
\]  
(2.30)
Multiplying Eq. (2.29) with \(\langle 2|\) from the left and \(|1\rangle\) from the right, one obtains
\[
\langle 2| \hat{\rho} |1\rangle = \tilde{\rho}_{21} e^{-i\omega_{21}t},
\]  
(2.31)
where \(\omega_{21} = (\epsilon_2 - \epsilon_1)/\hbar\).

Letting \(m = 2\) and \(n = 1\), differentiating Eq. (2.30) with respect to time and using Eqs. (2.14a,b), one arrives at
\[
\frac{\partial \tilde{\rho}_{21}}{\partial t} = i \left[ A_1(t) - A_2(t) + i \left( \gamma_{21} + \frac{\gamma_2}{2} \right) \right] \tilde{\rho}_{21} + \Omega^{(\text{eff})}_{21} (\tilde{\rho}_{11} - \tilde{\rho}_{22}),
\]  
(2.32a)
\[
\Omega^{(\text{eff})}_{21} = \Omega^{(1)}_{21} e^{-i(\omega_{L3} - \omega_{21})t} e^{ik_{L3}z} + \Omega^{(3)}_{21} e^{-i\delta_2 t} e^{i(2k_{L1} \pm k_{L2})z},
\]  
(2.32b)
where \(\delta_2 = (2\omega_{L1} + \omega_{L2}) - \omega_{21}\) and \(\omega_{L3} = 2\omega_{L1} + \omega_{L2}\), i.e., the system under consideration is that of a sum frequency generation process as given in Fig. 8b. The \(\pm\) sign appears in the exponential in Eq. (2.32b) specifies the co-propagation (i.e., \(+\)) or counter-propagation (i.e., \(-\)) of the laser at \(\omega_{L2}\) with respect the propagation direction of the laser at \(\omega_{L1}\).
In deriving Eq. (2.32) the collisional dephasing effect \((\hat{\rho}_{mn}/\hat{t})_{\text{coll}}\) is described by [81]

\[
\frac{\partial \rho_{mn}}{\partial t}_{\text{coll}} = -\left(\gamma_n + \gamma_m + \frac{\gamma_n \gamma_m}{2}\right) \hat{\rho}_{mn} \quad (m \neq n),
\]

(2.33a)

\[
\frac{\partial \rho_{mn}}{\partial t}_{\text{coll}} = \sum_{E_n > E_m} \Gamma_{mn} \hat{\rho}_{nn} - \sum_{E_n < E_m} \Gamma_{nm} \hat{\rho}_{mn},
\]

(2.33b)

where \(\gamma_n\) and \(\gamma_m\) denote the total decay rates of population out of levels \(n\) and \(m\). \(\Gamma_{mn}\) gives the rate per atom at which population decays from level \(m\) to level \(n\) whereas \(\gamma_{mn}\) gives the dipole dephasing rate due to processes that are not associated with the transfer of population. The combined coefficient on the RHS of Eq. (2.33a) describes the decay rate of the atomic coherence \(\rho_{mn}\). In the actual calculations where a real experimental situation has been specified, these relaxation rates will be modified to best describe the particular case in hand.

Eq. (2.32) still contains factors that oscillate rapidly in \(z\) and \(t\), thus the next step is to introduce a phase transformation to remove these factors. Letting \(\hat{\rho}_{21} = \rho_{21} e^{-i\delta z/c} e^{i(2kLz + kLz)/c}\) and \(\hat{\rho}_{mn} = \rho_{mn}\), Eq. (2.32) is transformed to

\[
\frac{\partial \rho_{21}}{\partial t} = i \left[\delta_2 + A_1(t) - A_2(t) + i \left(\gamma_2 + \frac{\gamma_2}{2}\right)\right] \rho_{21} + i\Omega^{(\text{eff})}_{21} (\rho_{11} - \rho_{22}),
\]

(2.34a)

\[
\Omega^{(\text{eff})}_{21} = \Omega^{(1)}_{21} e^{i[kL_3-(2kL_z+2kL_2)]z/c} + \Omega^{(3)}_{21}.
\]

(2.34b)

Recall that \(\omega_{L3} = 2\omega_{L1} + \omega_{L2}\). Then following the discussion given after Eq. (2.22) one immediately recognizes that for co-propagating beams

\[
e^{i[kL_3-(2kL_z+2kL_2)]z/c} = e^{i[2\omega_{L1}(n_0(\omega_{L3})-n(\omega_{L1}))+\omega_{L2}(n_0(\omega_{L3})-n(\omega_{L2}))]} \approx 1,
\]

so that \(\Omega^{(\text{eff})}_{21} \approx \Omega^{(1)}_{21} + \Omega^{(3)}_{21}\) for co-propagating beams. But for counter-propagating beams

\[
e^{i[kL_3-(2kL_z+2kL_2)]z/c} = e^{i[2\omega_{L1}(n_0(\omega_{L3})-n(\omega_{L1}))+\omega_{L2}(n_0(\omega_{L3})+n(\omega_{L2}))]} \approx e^{i2kL_2z/c}.
\]

Thus \(\Omega^{(\text{eff})}_{21} \approx \Omega^{(1)}_{21} e^{i2kL_2z/c} + \Omega^{(3)}_{21}\) for counter-propagating beams. This phase difference has important consequences for the interference effects to be described later. For co-propagating beams \(\Omega^{(\text{eff})}_{21}\) goes essentially to zero due to complete destructive interference between the two terms that comprise it. But in counter-propagating beams the phase difference between the two terms provides a phase matching point in \(\Omega^{(\text{eff})}_{21}\) at a frequency shifted from resonance, resulting in “restored” three-photon resonant absorption at a shifted frequency. This major point will be explained later.

Eq. (2.34) is the correct equation of motion for the slowly varying density matrix element \(\rho_{21}\). Note that the phase transformation introduced at this stage is consistent with \(C_1 = A_1 e^{-i\omega_{L1} t}\) and \(C_2 = A_2 e^{-i\omega_{L2} t} e^{i(2kL_1+kL_2)z/c}\), thus the state vector is given as

\[
|\Psi(t)\rangle = A_1(t) e^{-i\omega_{L1} t} |1\rangle + A_2(t) e^{-i(\omega_{L2}+\delta_2) t} e^{i(2kL_1+kL_2)z/c} |2\rangle.
\]

(2.35)

This implies that if one starts with Eq. (2.35) one will obtain Eq. (2.34) and also find that \(\rho_{mn} = A_m A_n^*\). Similarly, one obtains for the other relevant density matrix elements

\[
\frac{\partial \rho_{11}}{\partial t} = \Gamma_{12} \rho_{22} + i\Omega^{(3)}_{12} \rho_{21} - i\Omega^{(3)}_{21} \rho_{12},
\]

(2.36a)

\[
\frac{\partial \rho_{22}}{\partial t} = -\Gamma_{12} \rho_{12} + i\Omega^{(3)}_{12} \rho_{21} - i\Omega^{(3)}_{21} \rho_{12},
\]

(2.36b)

where \(\Gamma_{12} = \Gamma_{21}\) has been used. Obviously, the sum of Eqs. (2.36a,b) yield

\[
\frac{\partial \rho_{11}}{\partial t} + \frac{\partial \rho_{22}}{\partial t} = \frac{\partial (\rho_{11} + \rho_{22})}{\partial t} = 0,
\]

as it should since the population is conserved in a closed system.
2.2.4. Effective three-state system coupled with two laser fields

For the three-state system interacting with two laser fields as described in Section 2.1.4, the relevant equations for construction of the equations of motion for the density matrix elements are (2.18), (2.20), (2.21). Here, only the sum frequency generation scheme, i.e., $\omega_{13} = 2\omega_{11} + \omega_{L2}$, and co-propagating beams ($k_{L3} = 2k_{L1} + k_{L2}$) will be treated. Other variations can be derived similarly.

Setting $m = 3$ and $n = 1$, differentiating Eq. (2.30) with respect to time, and applying Eqs. (2.18) and (2.20), one obtains

$$\frac{\hat{\rho}_{31}}{\hat{t}} = i \left[ A_1(t) - A_3(t) + i \left( \gamma_{31} + \frac{\gamma_1 + \gamma_3}{2} \right) \right] \hat{\rho}_{31} + i \Omega_{31}^{(1)} e^{-i\delta_3 t} e^{i\hat{k}_{L1}\hat{z}} (\hat{\rho}_{11} - \hat{\rho}_{33})$$

$$+ i \Omega_{32}^{(1)} e^{i(\omega_1 - \omega_2 - \omega_3) t} e^{i\hat{k}_{L2}\hat{z}} \hat{p}_{21} - i \Omega_{21}^{(2)} e^{-i\delta_2 t} e^{i\hat{k}_{L1}\hat{z}} \hat{\rho}_{32}. \tag{2.37}$$

The phase transformation to remove fast oscillatory factors are given by

$$\hat{\rho}_{31} = \rho_{31} e^{-i\delta_3 t} e^{i\hat{k}_{L1}\hat{z}}, \quad \hat{\rho}_{32} = \rho_{32} e^{i(\delta_2 - \delta_3) t} e^{i\hat{k}_{L2}\hat{z}}, \quad \hat{\rho}_{21} = \rho_{21} e^{-i\delta_2 t} e^{i\hat{k}_{L1}\hat{z}},$$

$$\hat{\rho}_{mn} = \rho_{mn} \quad (m, n = 1, 2, 3).$$

Such a phase transformation can be easily deduced by observation of the various phase factors in equations such as Eq. (2.37). Using this transform, one immediately obtains

$$\frac{\hat{\rho}_{31}}{\hat{t}} = i \left[ \delta_3 + A_1(t) - A_3(t) + i \left( \gamma_{31} + \frac{\gamma_1 + \gamma_3}{2} \right) \right] \rho_{31}$$

$$+ i \Omega_{31}^{(1)} (\rho_{11} - \rho_{33}) + i \Omega_{32}^{(1)} \rho_{21} e^{-i\Delta K z} - i \Omega_{21}^{(2)} \rho_{32} e^{-i\Delta K z}, \tag{2.38}$$

where $\Delta K$ is defined just after Eq. (2.22). Note that the phase transformation introduced is consistent with $C_1 = A_1 e^{-i\omega_1 t}$, $C_2 = A_2 e^{-i\omega_2 t} e^{i\hat{k}_{L1}\hat{z}}$, and $C_3 = A_3 e^{-i\omega_3 t} e^{i\hat{k}_{L2}\hat{z}}$. Thus, the state vector is given as

$$|\Psi(t)\rangle = A_1(t) e^{-i\omega_1 t} |1\rangle + A_2(t) e^{-i(\omega_2 + \delta)} e^{i\hat{k}_{L2}\hat{z}} |2\rangle + A_3(t) e^{-i(\omega_3 + \delta)} e^{i\hat{k}_{L1}\hat{z}} |3\rangle. \tag{2.39}$$

Again, one identifies $\rho_{mn} = A_m A_n^*$.

One can determine equations of motion for the other elements of the density matrix through similar calculations, and find

$$\frac{\hat{\rho}_{32}}{\hat{t}} = i \left[ \delta_3 - \delta_2 + A_2(t) - A_3(t) + i \left( \gamma_{32} + \frac{\gamma_2 + \gamma_3}{2} \right) \right] \rho_{32}$$

$$+ i \Omega_{32}^{(1)} (\rho_{22} - \rho_{33}) e^{-i\Delta K z} + i \Omega_{31}^{(1)} \rho_{12} - i \Omega_{21}^{(2)} \rho_{31} e^{i\Delta K z}, \tag{2.40a}$$

$$\frac{\hat{\rho}_{21}}{\hat{t}} = i \left[ \delta_2 + A_1(t) - A_2(t) + i \left( \gamma_{21} + \frac{\gamma_1 + \gamma_2}{2} \right) \right] \rho_{21}$$

$$+ i \Omega_{21}^{(2)} (\rho_{11} - \rho_{22}) e^{-i\Delta K z} + i \Omega_{32}^{(1)} \rho_{31} e^{i\Delta K z} - i \Omega_{31}^{(1)} \rho_{23}, \tag{2.40b}$$

$$\frac{\hat{\rho}_{33}}{\hat{t}} = - \Gamma_{13} \rho_{33} - \Gamma_{23} \rho_{33} + i \Omega_{31}^{(1)} \rho_{13} - i \Omega_{13}^{(1)} \rho_{31}$$

$$+ i \Omega_{32}^{(1)} \rho_{23} e^{-i\Delta K z} - i \Omega_{23}^{(1)} \rho_{32} e^{i\Delta K z}, \tag{2.40c}$$

$$\frac{\hat{\rho}_{32}}{\hat{t}} = \Gamma_{32} \rho_{33} - \Gamma_{12} \rho_{22} + i \Omega_{21}^{(2)} \rho_{12} e^{-i\Delta K z} - i \Omega_{12}^{(2)} \rho_{21} e^{i\Delta K z}$$

$$+ i \Omega_{32}^{(1)} \rho_{23} e^{i\Delta K z} - i \Omega_{31}^{(1)} \rho_{32} e^{-i\Delta K z}, \tag{2.40d}$$

$$\frac{\hat{\rho}_{11}}{\hat{t}} = \Gamma_{12} \rho_{22} + \Gamma_{13} \rho_{33} + i \Omega_{12}^{(2)} \rho_{21} e^{i\Delta K z} - i \Omega_{21}^{(2)} \rho_{12} e^{-i\Delta K z}$$

$$+ i \Omega_{13}^{(1)} \rho_{31} - i \Omega_{31}^{(1)} \rho_{13}. \tag{2.40e}$$
Again, the sum of Eqs. (2.40c–e) yields (assuming \( \Gamma_{mn} = \Gamma_{nm} \))

\[
\frac{\partial \rho_{11}}{\partial t} + \frac{\partial \rho_{22}}{\partial t} + \frac{\partial \rho_{33}}{\partial t} = \frac{\partial (\rho_{11} + \rho_{22} + \rho_{33})}{\partial t} = 0,
\]
as it should.

In closing this subsection, readers are reminded that in dealing with the atomic density matrix the resonant contributions of the index of refraction have been left out. This part will be treated in accordance with Maxwell’s equation which will be discussed in the next subsection where the wave equation using slowly varying amplitude approximation will be presented.

2.3. Self consistent determination of the atomic response and the internally generated fields

In all problems of interest here, one of the fields that enter the equations describing the response of the subject system is not known at the outset. This added field is generated as a result of the response of the medium to all of the electromagnetic fields. Such internally generated fields must be determined by solving Maxwell’s equation with the source term appropriate to the given field. In this section the results of the earlier subsections will be combined with Maxwell’s equations, resulting in simultaneous solution of the equations of motion for the density matrix and Maxwell’s equations. Such self-consistent solutions lead to a satisfactory explanation for the destructive interferences that are the subject of the present review.

The discussion of wave propagation starts with the Maxwell’s equations involving the quantities; electric displacement vector, \( \vec{D} \), the magnetic inductance \( \vec{B} \), electric field, \( \vec{E} \), and magnetic field \( \vec{H} \). In the present context the equations are to describe wave propagation in a medium with no free charge density or free current density. The electrical and magnetic fields are in the optical frequency domain. The media of interest are neutral, isotropic and non-magnetic, but are nonlinear in response to an optical field, so that \( \vec{B} = \vec{H} \), and \( \vec{D} = \vec{E} + 4\pi \vec{P} \), where in general the polarization vector \( \vec{P} \) depends nonlinearly upon the local value of the electric field strength \( \vec{E} \).

The only currents and charge densities are those due to a polarization of the medium which are \[ J_P (z, t) = \frac{\partial P(z,t)}{\partial t}, \]

\[ \rho_P (z, t) = - \nabla \cdot \vec{P}(z, t). \]

In situations of interest here, the divergence of the polarization will be zero within the plane wave approximation, so \( \rho_P = 0 \). This yields electric fields in the medium that are plane polarized parallel to the incident laser fields, having no rapid dependence of the fields on the coordinates perpendicular to the direction of propagation. (Unfocused beams with diameter large enough that the beam does not expand appreciably within the resonance medium.)

Taking the direction of propagation to be the positive \( z \)-axis with plane polarization along the \( y \)-axis, the only source in Maxwell’s equations is the polarization induced current \( \vec{J}_P \) defined above. Typically, one defines the optical electric field by separating the positive and negative frequency part and by introducing the slowly varying amplitudes for each frequency component, i.e.,

\[
\vec{E}(z, t) = \vec{E}^{(+)}(z, t) + \vec{E}^{(-)}(z, t) = \hat{y} \frac{E_0^{(+)}}{2} e^{-i[\omega t - k(\omega)z]} + c.c.,
\]

where \( \hat{y} \) is the unit vector in the \( +y \) direction. In this expression \( k(\omega) = \omega / v = n(\omega) \omega / c \) and \( E_0^{(+)}(z, t) \) is the slowly varying amplitude of the electric field with positive frequency \( \omega \). This latter quantity is of primary interest as will be shown later. In the following, the derivation will be given for this positive frequency component of the electric field. The discussion and derivation of the negative frequency component can be obtained in the similar fashion.

Maxwell’s equations for the positive frequency component of the fields as stated take the form,

\[
\nabla \cdot \vec{B}^{(+)} = 0, \tag{2.44a}
\]

\[
\nabla \cdot \vec{E}^{(+)} = 0, \tag{2.44b}
\]
With this consideration Eq. (2.46) is modified to give

$$\nabla \times \vec{E}^{(+)} = -\frac{1}{c} \frac{\partial \vec{B}^{(+)}}{\partial t},$$

(2.44c)

$$\nabla \times \vec{B}^{(+)} = \frac{1}{c} \frac{\partial \vec{E}^{(+)}}{\partial t} + \frac{4\pi}{c} \frac{\partial \vec{P}^{(+)}}{\partial t}.$$  

(2.44d)

If one applies the curl operator to both sides of Eq. (2.44c), uses the identity \( \nabla \times \nabla \vec{A} = -\nabla \cdot \nabla \vec{A} + \nabla \nabla \cdot \vec{A} \), and applies Eqs. (2.44b), (2.44d), one gets

$$\frac{\partial^2 E^{(+)}(z, t)}{\partial z^2} - \frac{1}{v^2} \frac{\partial^2 E^{(+)}(z, t)}{\partial t^2} = -\frac{4\pi}{c^2} \frac{\partial^2 P^{(+)}(z, t)}{\partial t^2}.$$  

(2.45)

It is often possible to separate the polarization at a given frequency into a part that is linear in \( E^{(+)} \), and a nonlinear part that depends on higher order of the field, i.e.,

$$P^{(+)} = P_L E^{(+)} + P_{NL}^{(+)},$$

(2.46)

where \( P_{NL}^{(+)} \) is the nonlinear part of the polarization \( P^{(+)}(z, t) \). Substituting Eq. (2.46) into Eq. (2.45) and by combining the \( P_L \) term with the second derivative of \( E^{(+)} \) with respect to time, one gets an equation of the form

$$\frac{\partial^2 E^{(+)}(z, t)}{\partial z^2} - \frac{1}{v^2} \frac{\partial^2 E^{(+)}(z, t)}{\partial t^2} = -\frac{4\pi}{c^2} \frac{\partial^2 P_{NL}^{(+)}(z, t)}{\partial t^2},$$

(2.47)

where \( v \) is the modified group velocity of the field in the medium.

When working with a few-state resonant system, however, one cannot separate all of the linear part of the polarization and bring it to the LHS of Eq. (2.45) because the resonant contribution depends on the state amplitudes. In this case only the linear polarization contributions from all off-resonant states are incorporated as a background index of refraction. With this consideration Eq. (2.46) is modified to give

$$P^{(+)} = P_{L0} E^{(+)} + \varphi^{(+)},$$

where \( P_{L0} E^{(+)} \) is the non-resonant linear part of the polarization \( P^{(+)}(z, t) \) whereas \( \varphi^{(+)} \) is the part of the polarization \( P^{(+)}(z, t) \) that contains both the resonant linear contribution and all nonlinear contributions. Substituting the above equation into Eq. (2.45) and by combining the \( P_{L0} \) term with the second derivative of \( E^{(+)} \) with respect to time, one obtains

$$\frac{\partial^2 E^{(+)}(z, t)}{\partial z^2} - \frac{(n_0(\omega))^2}{c^2} \frac{\partial^2 E^{(+)}(z, t)}{\partial t^2} = -\frac{4\pi}{c^2} \frac{\partial^2 \varphi^{(+)}(z, t)}{\partial t^2},$$

(2.48)

where \( n_0(\omega) = 1 + 4\pi P_{L0} \) is the index of refraction at \( \omega \) with contributions only from all far-off resonance states including those contributed by any foreign gas that might be present.

The first step in solving Eq. (2.47) or Eq. (2.48) is to find the expression for the electric polarization. It is emphasized that all discussions given in this review will center on unfocused laser beams normally incident on the planar boundary between a non-resonant media and the atomic gas medium. If the thickness of this resonance medium, \( L \), satisfies \( L \ll R^2/\lambda \), with \( R \) the beam radius and \( \lambda \) the wavelength of the laser light, there will be very little expansion of the unfocused laser beam due to diffraction effects. Thus, if situations are avoided where resonance self-focusing effects can occur, the wavefronts in the medium will be nearly planar. Further, if all lasers (assuming all travel in \( \pm z \) directions) are plane polarized in the same plane, say along the \( z \) direction, then the plane of polarization will be preserved in the medium. In general, a component of the electric polarization such as \( P_y \) at an angular frequency, \( \omega \), can be determined as follows

$$P_y(z, t) = N_0 \langle \Psi(z, t)|\hat{\mu}_y|\Psi(z, t) \rangle = N_0 \sum_{m,n} \tilde{\rho}_{mn}(\mu_y)_{nm} e^{-i\omega mn t},$$

(2.49)

where Eqs. (2.8) and (2.30) have been used. Eqs. (2.47)–(2.49) are all for quantities that contain rapidly oscillating exponential factors (as evident from Eqs. (2.49)). In practice it is always desirable to deal with slowly varying quantities...
such as $E_0^{(+)}(z, t)$ defined in Eq. (2.43). This can be accomplished as described in the following subsection, where the slowly varying amplitude approximation and the justifications for using such a slowly varying quantity will be given.

2.3.1. The SVA approximation

2.3.1.1. Formal solution of the wave equation  

Formally, the wave-mixing field generated nonlinearly in the medium can be obtained by solving Eq. (2.47) exactly, resulting in (for the positive frequency part of the field)

$$ E^{(+)}(z, t) = E^{(+)}(0, t) - \frac{2\pi v}{c^2} \int_0^L dz' \frac{\partial}{\partial t} P^{(+)} \left( z', t - \frac{|z - z'|}{v} \right). $$

(2.50)

where $E^{(+)}(0, t)$ is the value of the field at the $z = 0$ boundary of the medium. In the case where the field is an internally generated wave-mixing field, one has $E_m^{(+)}(0, t) = 0$.

To see that Eq. (2.50) is the solution to the wave equation Eq. (2.47), consider the following function:

$$ E(z, t) = E(0, t_r) - \frac{v}{2} \int_0^L dz \frac{\partial}{\partial t} F(z', t - |z - z'|/v), $$

(2.51)

where $E(0, t_r)$ is the boundary value of the field in question and $t_r = t - n(\omega)z/c = t - z/v$.

Differentiating both sides of Eq. (2.51) twice with respect to $t$, gives

$$ \frac{1}{v^2} \frac{\partial^2 E}{\partial t^2} = \frac{1}{v^2} \frac{\partial^2 E(0, t_r)}{\partial t_r^2} + \frac{1}{2v} \int_0^L \frac{\partial^3 F(z', t - |z - z'|/v)}{\partial t^3} dz'. $$

(2.52)

Taking derivatives of Eq. (2.51) with respect to $z$ is more complicated because caution must be exercised in order to avoid the discontinuity with $|z - z'|$. This is done by breaking the integral into the integral from 0 to $z$, plus the integral from $z$ to $L$. One then finds,

$$ \frac{\partial^2 E}{\partial z^2} - \frac{1}{v^2} \frac{\partial E(0, t_r)}{\partial t_r^2} + \frac{\partial^2 E(z, t)}{\partial t^2} - \frac{1}{2v} \int_0^L dz' \frac{\partial^3 F(z', t - |z - z'|/v)}{\partial t^3}. $$

(2.53)

Subtracting Eq. (2.52) from Eq. (2.53), one arrives at

$$ \frac{\partial^2 E}{\partial z^2} \frac{\partial^2 E}{\partial t^2} = \frac{\partial^2 F(z, t)}{\partial t^2}. $$

Identifying $F = 4\pi P_{NL}^{(+)}/c^2$, and $E = E^{(+)}$, one recovers Eq. (2.47).

In the case of a near resonant field such as a wave mixing field the resonant part of the linear polarization must be separately treated. Thus only the non-resonant part of the index at the frequency of the generated field should be included in the retarded time $t_r = t - n_0(\omega)z/c$. It should be stressed that the generated wave does not travel with the velocity given simply by $c/n_0(\omega)$ because the resonant contribution is not included. A group velocity modifier due to the resonant part of the linear polarization will result from the polarization $g^{(+)}$ by self-consistent solution of the equations for the density matrix and wave-mixing field.

To recover Eq. (2.48), one starts with

$$ E^{(+)}(z, t) = E^{(+)}(0, t) - \frac{2\pi}{cn_0(\omega)} \int_0^L dz' \frac{\partial}{\partial t} P^{(+)} \left( z', t - n_0(\omega) \frac{|z - z'|}{c} \right). $$

(2.54)

Following the same procedure from Eq. (2.51) through Eq. (2.54), using $t_r = t - n_0(\omega)z/c$ and identifying $F = 4\pi g^{(+)}/c^2$, one arrives Eq. (2.48)

2.3.1.2. The slowly varying amplitude approximation  

The general solutions, Eq. (2.50) or Eq. (2.54), contains an element of the density matrix via the polarization $P_{NL}^{(+)}$ (or $g^{(+)}$ depending on the problems in hand) under the integral. In addition, all quantities contain fast time oscillation factors. Usually, an accurate but simpler form of Eq. (2.47) or Eq. (2.48) can be found where the problem is reduced to finding only the slowly varying amplitude of the field and the corresponding solution. This is the objective of the remainder of this subsection. In accord with what have been
treated throughout this review, i.e., few-state systems, the following derivation for the simplified wave equation will be applied to Eq. (2.48). Similar method can be applied to Eq. (2.47) as well.

The approximation needed to simplify Eq. (2.48) is called the slowly varying amplitude (SVA) approximation. The key assumptions of this approximation are: (1) the pulse length of the laser is very long as compared to the period of the optical fields, and (2) the wavelength of all light is very small as compared to either the spatial extent of the laser pulses or the distance over which the optical properties of the medium change appreciably.

In all cases discussed in the present review the pulse lengths of the lasers involved are typically several nanoseconds or longer and the spatial length of the pulses are correspondingly comparable to the length of the sample or greater. Further, except for the entrance and exit to the medium, the optical properties of the medium do not change.

The first step in developing the SVA approximation is to express the field and polarization in terms of a product of their slowly varying amplitudes and a rapidly oscillating time and position dependent exponential (see the discussion between Eq. (2.53) and Eq. (2.54)),

\[
E^{(+)} = \frac{E^{(+) 0}}{2} e^{-i\omega t - n_0(\omega) z/c},
\]

\[
\varphi^{(+)} = \varphi^{(+) 0} e^{-i\omega_{\text{mat}} t},
\]

where \(E^{(+) 0}(z, t)\) and \(\varphi^{(+) 0}(z, t)\) are the slowly time varying amplitudes of the field and relevant polarization (see Eqs. (2.48) and (2.49) and discussions there).

We now seek an approximation that will lead to a simpler yet accurate wave equation with respect to the slowly varying quantity \(E^{(+) 0}\). In doing so it is assumed that the following inequalities are very accurate for essentially all \(z\) and \(t\) (with any exceptions being over such small regions as to be negligible),

\[
\frac{2\omega}{\partial_t E^{(+) 0}} \gg 1, \quad \frac{\partial E^{(+) 0}}{\partial z^2} \gg 1,
\]

\[
\frac{2n_0(\omega)}{c} \frac{\omega}{\partial_t E^{(+) 0}} \gg 1, \quad \frac{n_0(\omega) \frac{\partial E^{(+) 0}}{c}}{\partial z} \gg 1,
\]

\[
\frac{2\omega_{\text{mat}}}{\partial_t \varphi^{(+) 0}} \gg 1, \quad \frac{\omega_{\text{mat}} \varphi^{(+) 0}}{\partial z} \gg 1.
\]

The above inequalities are mathematical statements of the key assumptions of the SVA approximation, which assumes that the complex exponential functions in Eq. (2.55) vary much more rapidly than the corresponding amplitudes.

Assuming the above inequalities are accurate, as they usually are, one finds

\[
\frac{\partial^2 E^{(+) 0}}{\partial z^2} \simeq -\left(\frac{n_0(\omega) \omega}{c}\right)^2 E^{(+) 0} + i \left(\frac{n_0(\omega) \omega}{c}\right) \frac{\partial E^{(+) 0}}{\partial z} e^{-i\omega t - n_0(\omega) z/c},
\]

\[
\frac{(n_0(\omega))^2}{c^2} \frac{\partial^2 E^{(+) 0}}{\partial t^2} \simeq -\frac{(n_0(\omega))^2}{c^2} E^{(+) 0} - i \frac{(n_0(\omega))^2 \omega}{c^2} \frac{\partial E^{(+) 0}}{\partial t} e^{-i\omega t - n_0(\omega) z/c},
\]

\[
\frac{\partial^2 \varphi^{(+) 0}}{\partial t^2} \simeq -\omega_{\text{mat}}^2 \varphi^{(+) 0} e^{-i\omega_{\text{mat}} t}.
\]
When these approximations are used in Eq. (2.48) one obtains

$$\frac{\partial E_0^{(+)}(z)}{\partial t} + \frac{n_0(\omega)}{c} \frac{\partial E_0^{(+)}(z)}{\partial z} = i \frac{4\pi \omega_{mn}^2}{c n_0(\omega) \omega} \psi_0^{(+)}(z) e^{i \delta_{nm} t} e^{-i n_0(\omega)\omega z/c},$$  

(2.58)

where $\delta_{nm} = \omega - \omega_{mn}$ has been used. In general, Eq. (2.58) can be approximated well by

$$\frac{\partial E_0^{(+)}(z)}{\partial t} + \frac{n_0(\omega)}{c} \frac{\partial E_0^{(+)}(z)}{\partial z} = i \frac{4\pi \omega_{mn}}{c} \psi_0^{(+)}(z) e^{i \delta_{nm} t} e^{-i n_0(\omega)\omega z/c},$$  

(2.59)

where approximations have been made on the RHS of Eq. (2.59) so that $n_0(\omega) \simeq 1$ and $\omega \simeq \omega_{mn}$.

Changing variables from $(z, t)$ to $(z, t_0)$ where $t_0 = t - \frac{z}{n_0(\omega)c}$, Eq. (2.59) becomes

$$\left(\frac{\partial E_0^{(+)}(z)}{\partial z}\right)_{t_0} = i \frac{4\pi \omega}{c^2} \psi_0^{(+)}(z) e^{i \delta_{nm} t} e^{-i n_0(\omega)\omega z/c}.$$  

(2.60)

Usually, Eq. (2.60) is the equation that will be combined with a few-state system in determining nonlinear fields generated in the medium.

### 2.3.2. Determination of the polarization $\psi_0^{(+)}$ used in the SVA equation

The remaining task is to determine the polarization $\psi_0^{(+)}$ for the wave equation of the generated field. In doing so, Eq. (2.60) must be solved self-consistently with the equations of motion for the density matrix described in Section 2.2.

With the use of Eq. (2.49) the $y$-component of the polarization (for simplicity the subscript $y$ will be suppressed in the following derivation) can be written as

$$P(z, t) = N_0 \langle \Psi(z, t) | \hat{y} | \Psi(z, t) \rangle = N_0 \sum_{m, n} \tilde{\rho}_{mn} \mu_{mn} e^{-i \omega_{mn} t}.$$  

(2.61)

Note that the summation must be carried over all possible $m$ and $n$ in Eq. (2.61). Thus there may be more than one internally generated field, and therefore more than one frequency term in this polarization. The key step is to collect the correct frequency term that corresponds to the corresponding generated field as this term is the source term for this generated field.

Consider an optical field at a frequency of $\omega_{L3}$ is generated at roughly the difference in energy between states $|m\rangle$ and $|n\rangle$. Assuming $E_m > E_n$ and $\omega_{L3} \simeq (E_m - E_n)/\hbar$, by comparing Eq. (2.61) and Eq. (2.55b) (the difference is the linear non-resonant part of the polarization at the frequency of the generated wave that does not contribute to the source term for the generated wave) the positive frequency part of Eq. (2.61) can be expressed as

$$\psi_0^{(+)} = N_0 \tilde{\rho}_{mn} \mu_{mn}.$$  

(2.62)

It is important to note that Eq. (2.62) contains both linear resonant and nonlinear contributions.

The next step is to express Eq. (2.62) in terms of $\rho_{mn}$ defined in Section 2.2.2–2.2.4. Specifically, using the phase transformation introduced after Eq. (2.37) (this is exactly the phase transformation $\tilde{\rho}_{mn} = \rho_{mn} e^{-i \delta_3 t + ik_{L3} z}$), Eq. (2.62) gives

$$\psi_0^{(+)} = N_0 \rho_{mn} \mu_{mn} e^{-i \delta_3 t + ik_{L3} z}.$$  

(2.63)

Note that for the generated field ($m = 3$ and $n = 1$) one has $\delta_{mn} = \omega_{L3} - \omega_{mn} = \delta_3 = \delta_3$ and $k_{L3} = n_0(\omega_{L3})\omega_{L3}/c$. Using these expressions and substituting Eq. (2.63) into (2.60) one obtains

$$\left(\frac{\partial E_0^{(+)}(z)}{\partial z}\right)_{t_0} = i \frac{4\pi N_0 \omega_{mn}}{c} \rho_{mn} \mu_{mn}.$$  

(2.64)

This is the desired SVA wave equation.
It should be stressed that phase mismatch between the generated field and the laser field, i.e., \( \Delta k \), is still contained in the equations of motion for the density matrix in the form of \( \Delta K \). That is, phase mismatch factors can be formally removed from the wave equation but they will appear in the equations of motion for the density, and vs visa.

Since the equations for the density matrix are written with coupling terms expressed in terms of half Rabi frequencies, it is convenient to express the Maxwell equation in terms of \( \Omega_{nn}^{(1)} \) in place of the electric field \( E \). These are equivalent since \( \Omega_{nn}^{(1)} = \mu_{nn} E^{(+)}/(2\hbar) \). Thus if Eq. (2.64) is multiplied through by \( \mu_{nn}/(2\hbar) \) one gets an equivalent equation

\[
\frac{\partial \Omega_{nn}^{(1)}}{\partial z} = 1 - \frac{2\pi N_0 \omega_{nn}}{\hbar c} \rho_{nn} |\mu_{nn}|^2. \tag{2.65}
\]

By making use of the ubiquitous parameter \( \kappa_{nm} = 2\pi N_0 \omega_{nm} |\mu_{nm}|^2/(\hbar c) \) Eq. (2.65) becomes

\[
\left( \frac{\partial \Omega_{nm}^{(1)}}{\partial z} \right)_{t_{\text{ref}}} = i\kappa_{nm} \rho_{nm}. \tag{2.66}
\]

This compact equation will be used throughout this review to treat propagation related effects.

With the mathematical preparation outlined in this section, the reader is ready to venture into the rest of the review where the density matrix formalism SVA approximation for Maxwell’s equations for the electromagnetic waves are applied to treat quantum destructive interference effects involving externally supplied laser fields and the internally generated coherent radiation fields.

3. Quantum interference effects in wave-mixing involving odd-photon resonant transitions

Section 3 is the first of two historical components that are devoted to the discussion of the major research work before mid-1990. This section is devoted to discussion of quantum interference effects where no intermediate near resonance is involved. The case of quantum interference effects in the presence of intermediate near resonance is topic of Section 4. As a rational for this separation we note that in most of the work to be reviewed in this section, interference effects are exhibited experimentally in photo–electron production, by photo-ionization. In the next section, spectroscopic detection of the photons is the main avenue for the detection and study of the interference effects.

In the course of the historical development of this field several different theoretical treatments of the “disappearing resonances” were published, following the initial papers on the subject. Due to different choices of formalism these may appear very dissimilar, but apart from pedagogical details and extensions to more general circumstances, the model originally proposed with the discovery of the effect [8,9] is common to all subsequent treatments. In this context we will not outline the alternative approaches, formalisms, notations that can be found in treating this subject. Rather, in the present review, we choose a specific density matrix formalism for treating all the subjects comprehensively. This choice is made for the following reasons:

1. The density matrix formalism is general enough to provide a basic set of equations that and be applied to all of the topics included in this review. As will be shown, some of the effects to be discussed can occur at low pressures where Doppler effects are nearly always of great importance. Other effects will involve concentration high enough for pressure broadened resonance widths to be come much larger than the Doppler widths. Both of these effects require a density matrix treatment. In order to be able to encompass the necessary range of possibilities the logical choice of methodology is to make use of a density matrix treatment.

2. From a modern theoretical physics perspective and for consistency, uniformity, clarity, and for future applications a density matrix formalism is preferred because the physical meanings of various coherence and population relaxation processes can be clearly demonstrated without ambiguity.

Based on these considerations, the authors have chosen the density matrix formalism with appropriate wave equations derived under SVA as the method of choice in describing the subject effects of this review.

Historically, almost all of the early experimental work in this field was carried out using multi–mode dye lasers with typical bandwidths of about 0.5 cm\(^{-1}\), and in many of the experiments lasers were often focused. With the use of such broadband laser sources the Doppler effect was usually unimportant. For this reason, all treatments given here and up to Section 4.4, which are relevant to the early work in the field, will not include the effect of Doppler broadening.
But from physics point of view it would be very desirable to re-examine several of the early experimental studies using unfocused lasers with very narrow bandwidths, perhaps even transform-limited bandwidths, which have now become routinely available in many research labs and facilities. For such laser systems the treatment involving Doppler broadening becomes directly relevant and important. For instance, the experimental lower limit on the concentrations for which odd-photon destructive interference can be induced has not been experimentally determined. With a strong transition in a room temperature gas contained in a cell with a length of a few centimeters, one can predict that the onset should occur at concentrations of a few times $10^{12}$ cm$^{-3}$. To make meaningful and quantitative comparison with such data, one must systematically include and correctly treat the Doppler broadening effect. Similarly, there are many other more interesting experimental effects related to pressure-induced shifts that could only be studied at relatively high concentrations in the past because of the large laser bandwidths. However, when these studies are carried out with narrow bandwidth lasers at lower concentrations Doppler effects will play an important role in determining the experimental outcome. It is the authors’ conviction that these also are worth revisiting using narrow bandwidth lasers. For these reasons Section 4.5 is devoted to analysis that includes the effect of Doppler broadening, and in conjunction with this treatment new experiments are suggested and discussed.

In this review the atomic states and laser couplings will be labeled in a convention where the numbering of the states begins with the ground state $|1\rangle$ and the numbering sequence is determined by the sequence of excitations or couplings taking place, starting from the single initially populated state. As stated above, all models and problems will receive the density matrix treatment, with phases of the off-diagonal components chosen so as to eliminate, as nearly as possible, all complex time and position dependent exponentials in the governing equations.

### 3.1. Basic results of an effective two-state plus continuum model

This subsection illustrates the basic results that one would expect from an effective two-state plus continuum model system under multi-photon resonant or near-resonant excitations (Fig. 8a–c). This system is mathematically simple but contains the essential ingredient for all the physics germane to this review, namely, quantum interference effects resulting from simultaneous excitation pathways involving both externally supplied and internally generated fields.

Effective two level atomic systems will be considered to interact with plane wave fields $E_j$ traveling in the $\pm z$ direction,

$$E_j(z, t) = E_{j0}(t) \cos \left( \omega_{Lj} t - \left[ \pm n(\omega_{Lj}) \right] \frac{\omega_{Lj} z}{c} \right).$$

Here, $E_{j0}(t)$ is the slowly-varying amplitude of the laser field with angular frequency $\omega_{Lj}$. The sign multiplying the refractive index $n(\omega_{Lj})$ is $+\left( -1 \right)$ if the direction of propagation of the corresponding field is in $+z (-z)$ direction. It has been assumed Doppler broadening can be neglected. With the stated convention it is straightforward to write the state vector so that the phases in the density matrix are chosen to agree with the phase relations in the following state vector

$$|\Psi(z, t)\rangle = A_1(z, t) e^{-i\omega_1 t}|1\rangle + A_2(z, t) e^{i\omega_m n_0(\omega_m) z/c} e^{-i(\omega_2 + \delta_2) t}|2\rangle.$$

Here $\omega_j = \epsilon_j/\hbar$, $(j = 1, 2)$, where $\epsilon_j$ is the energy of the states $|1\rangle$ or $|2\rangle$, and $\delta_2$ is the one-photon detuning from the state $|2\rangle$ by the generated field. $A_{1,2}$ are the amplitudes of state $|1\rangle$ and $|2\rangle$. The factor $n_0(\omega_m)$ is the index of refraction of the wave-mixing field with the resonant contribution for $|1\rangle - |2\rangle$ transition excluded. This omitted resonance contribution will be determined by calculating the resonant atomic response and will be included when the equations for the density matrix are solved self consistently with Maxwell’s equations. It should be noted that the effective two-state plus continuum model assumes that only the one-photon and the $N$-photon couplings (where $N$ is odd integer) of the electromagnetic fields are near-resonant. All other non-resonant orders and all transitions other than the $N$-photon resonance $|1\rangle - |2\rangle$ by any “distant” intermediate states are sufficiently far away so that the phase mismatch due to these far-off-resonance transitions remains fixed as the lasers are tuned near the $N$-photon resonance even though such a phase mismatch can include angles between laser beams or the presence of a fairly high pressure of positively dispersive buffer gas. The phase adopted in writing this state vector is appropriate to problems where it is necessary to solve Maxwell’s equation for the generation and propagation of the wave at $\omega_m$ but this is not necessary for the laser fields at $\omega_{Lj}$. In most cases of interest here, the order of nonlinearity is $N = 3$. 

---

Taking an undepleted ground state (i.e., \( \rho_{11}(z, t) \approx 1 \)) and using the SVA approximations given in Eq. (2.66), one obtains the following simultaneous differential equations with respect to the dimensionless retarded time \( t_r = t(z, t)/\tau \) (where \( \tau \) is a measure of the laser pulse length)

\[
\frac{\partial \rho_{21}}{\partial t_r} = i(\delta_2 \tau + i\Gamma) \rho_{21} + i \left( \Omega_{21}^{(N)} e^{-i\Delta K z} + \Omega_{21}^{(1)}(t) \right), \tag{3.1a}
\]

\[
\frac{\partial \rho_{22}}{\partial t_r} = -(\gamma_2 + \gamma_f) \rho_{22} - 2 \text{Im} \left( \Omega_{21}^{(N)} e^{-i\Delta K z} + \Omega_{21}^{(1)}(t) \right) \rho_{12}, \tag{3.1b}
\]

\[
\left( \frac{\partial \Omega_{21}(t)}{\partial z} \right)_{t_r} = i\kappa_{12} \rho_{21}. \tag{3.1c}
\]

In Eqs. (3.1a,c) the non-resonant part of the phase mismatch between the generated field and the laser fields is defined as

\[
\Delta K = \frac{\omega_m}{c} \left[ n_R(\omega_m) - 1 \right] - \sum_{j=1}^{N} P_{ej} \frac{\omega_{Lj}}{c} \left[ \pm n(\omega_{Lj}) - 1 \right]. \tag{3.2}
\]

The full phase mismatch between the generated field and the laser fields is defined as

\[
\Delta k = \frac{\omega_m}{c} n_R(\omega_m), \tag{3.3}
\]

where \( n_R(\omega_m) \) is the resonant part of the index of refraction at the frequency of the generated field. In Eq. (3.2) the constant \( P_{ej} = \pm 1 \) for an absorption (a stimulated emission) process, and the \( \pm \) sign in front of the index of refraction signifies that the propagation vector of the laser field \( \omega_{Lj} \) is in the \( +z \) or \( -z \) direction. In the applications that follow these signs will be explicitly written for individual cases. Throughout this review, \( \kappa_{jk} \equiv 2\pi(\omega_k - \omega_j)N_0 |\mu_{jk}|^2/(\hbar c) \) where \( N_0 \) is the concentration (in \( \text{cm}^{-3} \)) of the resonance medium and \( \mu_{jk} = \langle j | \hat{\mu} | k \rangle \) is the electric dipole matrix element between states \( |j \rangle \) and \( |k \rangle \). In addition, \( \omega_j = \epsilon_j/\hbar \) where \( \epsilon_j \) is the energy of the state \( |j \rangle \), \( 2\Omega_{jk}^{(1)} = \mu_{jk} E_L/\hbar \) and \( 2\Omega_{jk}^{(N)} \) are the one- and \( N \)-photon Rabi frequencies for the \( |j \rangle \to |k \rangle \) transition under the appropriate laser field \( (E_L) \) excitation. The relaxation rate \( \Gamma = (\gamma_2 + \gamma_f + 2\Gamma_P)/2 \) includes the population relaxation rate \( \gamma_2 \), the rate of ionization out of the state \( |2 \rangle \), i.e., \( \gamma_f \), and the collisional relaxation rate, \( \Gamma_P = \Gamma_{12} \), of the \( |1 \rangle \to |2 \rangle \) coherence due to self-broadening effect, as described in the Section 2.3. In pure inert gases the collisional dephasing/relaxation rate for the \( |1 \rangle \to |2 \rangle \) allowed transition is given by Eq. (2.35).

Eqs. (3.1a) and (3.1c) can be solved formally using the Fourier transform method. Define \( \lambda_{jk} \) as the Fourier transform of the density matrix \( \rho_{jk} \) and \( A_{21}^{(1)} \) as the transform of the Rabi frequency \( \Omega_{21}^{(1)} \) with respect to the dimensionless retarded time \( t_r \) (these notations will be used through out this review). Then the Fourier transform of Eqs. (3.1a) and (3.1c) gives the transformed equations:

\[
\lambda_{21}(\zeta, \eta) = -A_{21}^{(N)} e^{-i\Delta K \zeta} + A_{21}^{(1)}(t), \tag{3.4a}
\]

\[
\frac{\partial A_{21}^{(1)}(\zeta, \eta)}{\partial \zeta} = i\kappa_{12} \lambda_{21}, \tag{3.4b}
\]

where \( \eta = \omega \tau \) is the dimensionless Fourier transform variable and \( \tau \) is the the effective laser pulse duration.

With the initial condition \( A_{21}^{(1)}(0, \eta) = 0 \), the solution to Eq. (3.4b) can be expressed as

\[
A_{21}^{(1)} = \frac{A_{21}^{(N)} e^{-i\Delta K \zeta} - e^{-i\kappa_{12} \zeta/(\delta_2 \tau + \eta + i\Gamma \tau)}}{1 - \Delta K (\delta_2 \tau + \eta + i\Gamma \tau)/\kappa_{12} \tau}. \tag{3.5}
\]

Eq. (3.5) serves as the basis for all discussions for the remainder of Section 3. In fact, all cases discussed in Section 3 can be approached from the Eqs. (3.4a) and (3.4b) together with Eq. (3.1b) for \( \rho_{22} \).
Eq. (3.5) is remarkable in that many key physical observations can be extracted from it. To see this, first note that the field is pulsed with pulse length characterized by $\tau$, but the detailed pulse shape is not yet being specified. Whatever the shape, the integrand of the inverse transform integral is strongly dominated at small values of $|\eta|$. For a Gaussian type of pulse shape the most significant contribution in carrying out the inverse Fourier transform occurs for $|\eta| < 10$. However, if the collisional dephasing rate is large so that $I^\tau > |\eta|$, and $I^\tau > |\delta z|$ as was the case with all early experiments studying destructive interference effects, then the dominant contribution to the second exponential in the square bracket is $\simeq e^{-Kz}$. That is, the second exponential decays exponentially as a function of $z$. Moreover, even at pressures of $10^{-4}$ Torr in a typical resonant system, the mean-free-path of photons at line center is of the order of a centimeter, so that in a 20 cm cell there is strong absorption even at $10^{-4}$ Torr which means that the second exponential in the square bracket decays rapidly with propagation distance $z$. Consider a strong one-photon transition in a room temperature inert gas, one typically has $\kappa_{12} \simeq 2 \times 10^{14} P/(\text{cm s})$ where $P$ is the pressure in Torr. With $\tau = 10$ ns and $z = 10$ cm, one finds that the second term in the square brackets is about $e^{-10}$ for a pressure of $P \simeq 10^{-4}$ Torr (this corresponds to a concentration of a few times $10^{12}/\text{cm}^3$). If the temperature could be reduced to the point where the dominant width of the level was due to spontaneous decay this concentration would be reduced to about $10^9/\text{cm}^3$. Thus, even at very low concentrations the second exponential has quickly become negligible as a function of $z$. Further note that $\Delta K$ is the phase mismatch from lasers that are very far from any one-photon resonance, whereas $-\kappa_{12}/\delta z$ is the absorption coefficient that accounts for the absorption of the wave-mixing field when tuned close to a strong resonance. Typically, the ratio of $\Delta K/\kappa_{12}/\delta z$ is of the order of $10^{-5}$. In the presence of a buffer gas, this ratio would be even smaller. Indeed, it is small enough so that the denominator is affected by the second term by about a part in $10^6$ in absolute value. Thus, one can neglect $\Delta K (\delta z + \eta + i\Gamma z)/(\kappa_{12} z)$ in the denominator. Combining the above considerations and taking the inverse transform of both sides of Eq. (3.5) (for $z > 0$), one gets

$$
\Omega_{21}^{(1)}(z, t) \simeq -\Omega_{21}^{(N)}(z, t)e^{-i\Delta K z} \to \Omega_{21}^{(1)}(z, t) + \Omega_{21}^{(N)}(z, t)e^{-i\Delta K z} \simeq 0.
$$

From Eqs. (3.1a,b) it is immediately seen that at a propagation distance $z$ such that Eq. (3.6) is valid one has $\rho_{21} \simeq 0$, or the polarization is zero. If $\rho_{21} = 0$ then from Eq. (3.1b) $\rho_{22} \simeq 0$, since the initial value of $\rho_{22}$ is zero. The physical meaning of Eq. (3.6) is very clear: the excitation of the state $|2\rangle$ by the $N$-photon pumping from the laser field (i.e., $\Omega_{21}^{(N)}(z, t)e^{-i\Delta K z}$) and one-photon pumping due to the wave-mixing field (i.e., $\Omega_{21}^{(1)}(z, t)$) interfere destructively, leading to zero polarization at the frequency of $\nu_{0h}$ and very small population in $|2\rangle$. Additionally, the value of $|\Omega_{21}^{(1)}|_0$ is no longer dependent on $z$. Thus, a special regime has been reached, where $N$-photon destructive interference is effective and a multiphoton-interference-based transparency is established. It should be pointed out that this $N$-photon wave-mixing field at the one-photon resonance is far weaker than the corresponding field can be generated at a point where phase matching occurs in the wave-mixing process. In the phase-matched situation there is a constructive interference, which tracks precisely the phase of global polarization, between the wave-mixing fields generated by many atoms at all locations that have been traversed by the laser fields. Such constructive interference is almost entirely absent at small detunings where absorption is large and the wave-mixing field is almost entirely locally generated. Thus, the interference only tracks the phase and amplitude of the local polarization at the frequency of the wave-mixing field.

The effectiveness of Eq. (3.6), i.e., the onset of destructive interference, depends on the concentration. It should be noted that in room temperature and low pressure regime where the collisional dephasing rate is less important, the governing factor for the onset is the Doppler broadening neglected here. This effect is particularly important in finding the onset of the destructive interference in such a low concentration regime using lasers with transform-limited bandwidths. This aspect will be revisited in Section 4.3 where Doppler broadening and future experimental studies using narrow bandwidth lasers are discussed.

The first theoretical treatment of the destructive interference problem was given by Payne and Garrett [9]. By explicitly writing out the one-photon and three-photon coupling terms they showed that the contributions from the internally generated TH field and the externally provided laser fields were added to zero (the coupling term due to the TH field was expressed as an integral of the polarization at the TH frequency over position, which might not be immediately recognized as the coupling between the ground state and the upper state due to the TH field). Although this early paper spoke of collective effects, the only effects actually included in the mathematical model was the simultaneous response of the atoms interacting with both the laser field and the TH field, with the latter being determined self consistently. A short time later, Jackson and Wynne [13] presented a simpler general steady state susceptibility treatment of the problem. They assumed fast dephasing of the transition so that the polarization could be handled as a steady state.
problem. In this early work, these authors first explicitly spoke of destructive interference between the two excitation pathways, which was implicit in the work of Payne et al. [9] Agarwal and Tewari [16] later treated the same problem with focused beams using a fully quantum formulation. Their results are essentially the same as derived in Payne and Garrett’s 1983 semi-classical treatment [14] on the destructive interference problem with focused laser beams.

One of the features predicted by the more detailed theory [9,14], but not by the simpler susceptibility treatment [12,13] of “disappearing resonances”, was revealed in an experiment by Normand et al. [15] in Hg vapor. MPI and TH measurements (Fig. 10) were made in the vicinity of three-photon resonance with the strong $6s^1S_0 \rightarrow 6p^1P_1$ and very weak $6s^1S_0 \rightarrow 7p^1P_1$ optical transitions in Hg at 0.006 Torr vapor pressure utilizing a long focal length lens ($f = 350$ mm) and a fairly narrow-band laser source. They observed a strong ionization signal at the position of the weak $7p$ transition (oscillator strength $F \approx 0.03$) but no ionization signal at exact resonance for the strong $6p$ transition ($F \approx 1$). Though the authors did not recognize the fact [15] and its significance, this was the first confirmation of the predicted [8,9] oscillator strength dependence of the cancellation effect. Under the same concentrations and laser intensities the weaker transition showed no suppression, while the very strong one was suppressed by the TH field in the total transition amplitude. The effectiveness of destructive interference is directly proportional to oscillator strength. Thus, this counter-intuitive behavior, i.e., no signal at a strong resonance, strong signal at a weak resonance, was in complete agreement with theory [9,14]. The chosen pressure was such that one transition was below the concentration required for complete cancellation, and the other was above it. It is worth mentioning that in this study if a Doppler broadened line is assumed, the weaker resonance is not subject to the full destructive interference. This may be helped even further by a.c. Stark shifts due to the multi-mode dye laser causing further smearing of the transition.

3.2. Multiphoton ionization (MPI) profiles near wave-mixing phase-matching point with unfocused co-propagating beams and a positively dispersive buffer gas

In the previous subsection the fundamental mechanism of destructive interference was described in the circumstance where a fast collisional dephasing rate dominates the decoherence process, i.e., $\Gamma \tau \gg |\delta_2 \tau| > |\eta|$ and $\Gamma \tau \gg |\eta|$. In this subsection the focus is on the case of a mixture of low concentration of a resonant medium with a high concentration
of positively dispersive buffer gas, such as a Xe–Kr or Xe–Ar mixture [17]. The concentration of the resonant medium in these cases was typically on the level of \( \lesssim 10 \) Torr, whereas the concentration of the buffer gas might be 10 to 100 times higher. The problems of interest for MPI studies are the consequences of modifying the dispersive properties of a near-three-photon-resonant medium.

With co-propagating beams and at a sufficiently high partial pressure of the resonance medium, the discussion leading to Eq. (3.6) still apply. Thus one expects a destructive interference at three-photon resonance which results in \( \rho_{21} = 0 \) and \( \rho_{22} \simeq 0 \) at large \( z \). Note that this destructive interference is achieved even with the lasers are tuned so that the generated field is on one-photon resonance (i.e., \( \delta_2 = 0 \) which actually facilitates the effect because of strong absorption of the generated field as can be seen from Eq. (3.5)). Thus, no three-photon-resonant enhancement should occur with any arbitrary concentration of positively dispersive buffer gas.

Now we consider experiments in a three-photon-resonant medium with positively dispersive non-resonant additive, with the laser detuned from resonance so that the generated field is relatively far from one-photon resonance. Results for these cases have very different experimental features. The importance of these cases lie in the new possibility of tuning close to the phase matching point for efficient four wave mixing (FWM) generation. It will be shown below that if the detuning \( \delta_2 \) is close to the phase matching point for the wave-mixing field, then destructive interference is ineffective and MPI signals are large. More importantly, the line shape and width of the MPI signal will be shown to be identical that seen when the lasers were tuned near the \( N \)-photon resonance but part of the laser light is reflected back through the cell [17,27] (also see the next subsection).

Now consider Eq. (3.5) again but let \( \delta_2 \) be significantly larger than zero. As before, once \( \text{Re}[i\kappa_2 z/(\delta_2 \tau + \eta + i\Gamma \tau)] \gg 1 \), the second exponential term in Eq. (3.5) becomes negligible. However, large detuning from the resonance brings the possibility of making the denominator small. Since \( \delta_2 \tau \) will be much larger than other terms in the parenthesis, the real part of the denominator is \( 1 - \Delta K \delta_2/\kappa_{12} \). Thus, as \( \delta_2 \) is changed (scanned) one passes through a point \( \delta_{2m} \) where \( \kappa_{12}/\delta_{2m} = \Delta K \). Then the real part of the denominator is small, resulting in a maximum in the amplitude \( A_{21}^{(1)} \). This is the phase matching point for efficient production of the field \( E_m \). At this phase matching point one has \( \Delta K = 0 \) (see Eq. (2.59)). It occurs on the higher energy (blue) side of the resonance (since \( \delta_{2m} > 0 \)). Near this phase matching point, there will be no cancellation effect even though the generation of the wave-mixing field is most efficient. Indeed at this frequency the wave-mixing and laser fields interfere constructively where they destructively interfere at three-photon resonance.

For the circumstance where the laser is tuned through the region of phase matching, a rather remarkable property of the photoionization profile can now be demonstrated: In the region near the phase matching point the line shape of the ionization with an unfocused laser is very much like an atomic resonance line shape. Indeed, both theory and experiment [17,27] have demonstrated that the line shape of the photoinization signals look exactly like the signal that would occur at the \( N \)-photon resonance in the absence of the destructive interference.

To see these features let us define \( \delta = \delta_2 - \delta_{2m} \). Thus, \( \delta \) is the detuning from the exact phase matching point \( \delta_{2m} \).

With this new detuning the denominator of Eq. (3.5) becomes

\[
1 - \frac{\Delta K (\delta_2 \tau + \eta + i\Gamma \tau)}{\kappa_{12} \tau} = -\frac{(\delta \tau + \eta + i\Gamma \tau)}{\delta_{2m} \tau}. \tag{3.7}
\]

If Eq. (3.7) is inserted into Eq. (3.5) and the second exponential term is neglected (for sufficiently large \( z \)) one gets

\[
A_{21}^{(1)} = \frac{\delta_{2m} \tau}{\delta \tau + \eta + i\Gamma \tau} A_{21}^{(N)} e^{-i\Delta K z}. \tag{3.8}
\]

Using Eq. (3.8) in Eq. (3.4a) one obtains

\[
xz = \frac{A_{21}^{(N)} \tau e^{-i\Delta K z}}{\delta \tau + \eta + i\Gamma \tau}. \tag{3.9}
\]

It should be noted that when the dephasing rate \( \Gamma \) is larger than the Doppler width and \( \Gamma \tau \gg 1 \), this is exactly what one would expect for \( xz \) if this quantity was calculated at resonance with the multi-wave mixing field excluded (i.e., neglect the second term in the numerator in Eq. (3.4a)). Notice that Eq. (3.9) has the line shape of an atomic resonance with its amplitude identical to that expected in the absence of the destructive interference. The difference between \( \delta_2 \) in Eq. (3.4a) and \( \delta \) in Eq. (3.9), however, indicates that the resonance peak is centered at the wave-mixing phase matching point. In addition, when \( \gamma_1 \tau \gg 1 \) Eq. (3.9) simplifies to the steady state solution of Eq. (3.1a).
Now the inverse transforms of Eqs. (3.8) and (3.9) can be immediately carried out in the approximation appropriate to a pulse of length \( \tau \) (i.e. only small \( |\eta| \) contributes to the inverse so \( |\delta \tau| > |\eta| \) and \( I \tau > |\eta| \)) to yield

\[
\Omega_{21}^{(1)} = \frac{\delta_{2m} \tau}{\delta \tau + iI \tau} \Omega_{21}^{(N)} e^{-i\Delta K z},
\]

and

\[
\rho_{21} \simeq -\frac{\Omega_{21}^{(N)} \tau e^{-i\Delta K z}}{\delta \tau + iI \tau}.
\]

When the above results are inserted into Eq. (3.1b) one obtains

\[
\frac{\partial \rho_{22}}{\partial T_I} \simeq -(\gamma_2 + \gamma_1) \tau \rho_{22} + \frac{2|\Omega_{21}^{(N)}|^2 I \tau}{\delta^2 + I^2},
\]

which can be directly integrated over time, yielding the rate of ion production per unit volume

\[
R_I = N_0 \gamma_1 \rho_{22} = N_0 \gamma_1 \int_{-\infty}^{T_I} \frac{d\tau'}{2} \frac{2|\Omega_{21}^{(N)}|^2 e^{i\Delta K z}}{\delta^2 + I^2}.
\]

Notice that this ionization rate has a Lorentzian line shape centered at \( \delta = 0 \) or \( \delta_2 = \delta_{2m} \), the phase-matching point, with a width determined by \( I \), just like a pure atomic line. It should be noted, however, that Eq. (3.13) is only appropriate at sufficiently high concentrations which is necessary to make the other term in the multi wave mixing field be absorbed out in a small fraction of the gas cell length. Even then, it is hard to achieve phase matching at a point that is close enough to resonance for the impact theory of line broadening to hold at phase matching. Unlike self-broadening, where the functional form of the impact broadening theory and the statistical broadening limits have nearly equivalent line shapes, in the case of foreign gas broadening the far wing of the line is asymmetrical, and not Lorentzian on either side of the resonance. In addition, the absorption on the far wing tends to be dominated by the formation of mixed dimers, which makes the absorption on the far wing larger than that predicted by the impact theory. Thus, one should expect that when phase matching occurs at too large a detuning for impact broadening to be appropriate, the line width will be broader than predicted by Eq. (3.13), and the peak height will be correspondingly lower. This was discussed more thoroughly in connection with the original experiment.

The effect described above was first demonstrated with multi-mode lasers in the work of Payne et al. [17,27]. In the experimental study, ionization profiles were measured in regions near three photon resonance with the 6s \((J = 1)\) and 5d levels in Xe \((N = 3)\) in the nonlinear terms.) using Xe–Ar and Xe–Kr mixtures with co-propagating unfocused laser beams. By changing the ratio of the resonant species (Xe) to the positively dispersive non-resonant buffer species, (Kr or Ar), the phase matching point for third harmonic generation near the 6s resonance could be adjusted at will.

Fig. 11 shows the measurements of MPI in the vicinity of third harmonic phase matching point \((357.364 \text{ nm})\). By inserting a mirror into the path of the laser beam at the exit of the gas cell the three-photon-resonant MPI signals could be observed and studied with a counter-propagating beam geometry (also see the next subsection). This signal, at \((357.605 \text{ nm})\), is produced near three-photon resonance with the 5d level when about 50% of the laser beam is reflected back through the cell. With retro-reflected beams, three-photon excitation can occur by absorbing two photons propagating in one direction through the cell and one photon propagating in the opposite direction (see next subsection). Though the widths and strengths of the MPI signals are slightly different in the figure, similar signal size and similar line shapes for the two signal profiles are evident, as predicted.

It should be noted, however, that even though the widths and heights of the ionization signal, when the laser is tuned near phase matching and when the counter propagating laser is present and tuned to resonance, are similar there is a tendency for the signal near phase matching point to have a broader line width and a lower peak height. The closest the two signals come to being the same occurs near the minimum in Fig. 11 a, where one minimizes the width as much as possible yet without making the absorption coefficient too larger. It should be pointed out that in order to analyze the data shown in Fig. 11, both terms must be retained in Eq. (3.5) and second term must be replaced by an expression with the \( I \) being an empirical value appropriate for reproducing both the phase mismatch and the empirical absorption at the phase matching point. One can then obtain comparisons with the data like the solid curve in Fig. 11 a [17].
Fig. 11. Wavelength scan of ionization signals resulting from phase-matched third harmonic production in the negatively dispersive region of the Xe $5d$ level. Resonant signal for three-photon excitation of the $5d$ on the right. Phase matching occurs at detuning of $\delta_{2m} = -0.249 \text{ nm}$ ($P_{\text{Xe}} = 5.387 \text{ Torr}$, $P_{\text{Ar}} = 990.5 \text{ Torr}$), $\delta_{\text{FWHM}} = 0.135 \text{ nm}$. Reproduced from [18] with permission.

Fig. 12a shows MPI signals near the TH phase matching point when the ratio of the Xe and Ar pressures was fixed (to keep the phase matching point fixed), while the Xe pressure is increased. The MPI signal starts out broad with low amplitude, but as one approaches the limit where the second part of the TH field has completely decayed out the FWHM of the MPI becomes independent of Xe pressure until absorption by collision pairs of Xe–Ar start to play an important role. This behavior was in accord with theory. A detailed MPI line shape and fit at phase-matching with different functional forms is shown in Fig. 12b where the best fit is a Lorentzian.
The measured FWHM line width near the TH phase matching point as a function of pressure of the resonance medium also agreed well with the theoretical calculation described above. Near the TH phase matching point the ionization signals exhibit a line shape very much like an atomic resonance in cases where the phase matching point is relatively close to the three-photon resonance. Thus, the destructive interference cancels any resonant signal at the position of the atomic transition, but an ionization profile identical in shape and magnitude to the “invisible” atomic line is produced at the point of TH phase matching point with unfocused uni-directional beams.

It should be pointed out that although all of the three-photon excitation experiments showed that the interference phenomenon was operative over a wide range of experimental conditions, the use of focused unidirectional beams produced ionization signals with pressure dependent profiles that followed TH production profiles on the negatively dispersive (high energy) side of a resonant transition. Thus it was difficult to ascertain the true three-photon absorption behavior at the low pressure “onset” of the destructive interference. The observed “line shapes” and “blue shifts” were reflective of TH production with focused beams as opposed to resonantly enhanced ionization due to excitation of the atomic transition [5,7,9,12,13]. More detailed spectroscopic information is obtained from excitation by unfocused beams.

3.3. MPI when one laser beam counter-propagates relative to the others near a three-photon resonance

Historically, the use of counter-propagating laser beams to mediate three-photon excitation of an optical transition brought out two previously unknown consequences: (1) the restoration of the three-photon enhanced MPI and (2) a new pressure dependent frequency shift. The focus of this subsection is to examine effects associated with three-photon excitation of optical transitions by counter-propagating laser beams. The treatment presented here will include two-color, three-photon transitions in $2\omega_{L1} \pm \omega_{L2}$ type of FWM excitation schemes as in Figs. 8b and c. As will be seen, three-photon-resonant ionization signals reappear when one of the lasers counter-propagates relative to the other. In addition, a new pressure dependent frequency shift will appear in the MPI spectra. In the theoretical treatment presented here the difference between the space averaged field and the local field seen by the atom (neglected in the previous treatment) are important, resulting in a significant Lorentz frequency shift.

3.3.1. The restoration of MPI signal with counter-propagating beams: experiments

The first counter-propagating beam experiment was performed by Glownia and Sander [11], who showed that no cancellation effect occurred when counter propagating circular polarized beams were used (thus eliminating TH generation). Jackson and Wynne [12,13] performed a similar experiment, i.e., with retro-reflection, but with linearly polarized light. While the ionization signals disappeared in a co-propagating beam geometry, as had been reported by other groups, they discovered that when the laser beam was retro-reflected to form a “standing wave” field the ionization signal was restored (see Fig. 6). They noted that a retro-reflected beam allowed absorption of two photons from the forward beam and one photon from the retro-reflected beam. These observations were consistent with the earlier theory [8,9,14] which showed that a three-photon destructive interference effect leading to suppression of three-photon enhanced ionization requires a fixed phase relation between the three-photon excitation from the laser and one-photon pumping of the same state from the wave-mixing field. Much later it was shown that the destructive interference from FWM becomes constructive at a frequency that corresponds to phase matched FWM in the non-coaxial beam geometry [88].

Ferrell et al. [18] first utilized the cleaner geometry of unfocused beams in an MPI spectroscopic mode. They also implemented an internal X-ray calibration source (producing a known number of electrons) in a high-gain proportional counter gas cell to provide absolute laser-induced ionization yields at arbitrary gas pressures. The experiments were devoid of TH production on the negatively dispersive side of resonance (in the absence of a positively dispersive buffer gas), since there was no $\pi$ phase change associated with propagation through a focal volume to provide phase matching. When tuned to three-photon resonance for the $6s$ transition in single pass geometry, no resonant signal was observable at maximum laser power and maximum gain for any Xe pressure from 0.001 to 100 Torr. With a calibration of the absolute number of ions produced under a given circumstance, the study showed that the suppression of three-photon excitation in unfocused unidirectional beam geometry was at least a factor of 300–600 as compared to counter-propagating beam geometry at concentrations of $N_0 = 3 \times 10^{16}$ cm$^{-3}$ to $N_0 = 150 \times 10^{16}$ cm$^{-3}$ region [24] (see Fig. 13a). The excitation–ionization yield from the mixed beams (one photon from one beam and two from the opposite one) behaved normally, yielding a fifth order power dependence as expected. Shown in Fig. 13b is the MPI signal due to
counter-propagating beams with different laser power. The ratio of these signals is about 32 : 1, consistent with five-photon ionization when tuned to the 6s transition in Xe. The experiments with unfocused beams further confirmed that in the early experiments with focused beams, TH production on the blue side of the allowed transitions was responsible for the broadly shifting pressure dependent ionization profiles that were seen at lower pressures (before the complete suppression of near-resonant signals at higher pressures.) No resonantly enhanced signals at all were observable for any of the three-photon induced ΔJ = 1 transitions with unfocused beam geometry where no phase-matched TH field was produced, indicating just how efficient such a three-photon destructive interference can be. Indeed, a point of extreme interest in this experiment was to establish the lower bound on concentration of a resonant medium (Xe in this case) where three-photon destructive interference becomes effective. The observation of this onset requires that one be able to observe MPI signal with counter-propagating beams but to detect no MPI signals with co-propagating beams. For this study it was shown that a very sensitive proportional counter could be operated with Kr as the counting gas, with a small fraction of Xe added as the resonance medium. This proportional counter was calibrated by using an 55Fe X-ray source to produce a known number of electrons in the counting gas. By careful study of this ionization detector it was shown that less than 10 photoelectrons per pulse could be detected. The experiment was started with 1 Torr of Xe mixed with a much larger partial pressure of Kr. With 1 Torr of Xe the calibrated signal was 20,000 photoelectrons per laser pulse. The concentration of Xe was then reduced by pumping down the total pressure and adding back Kr to achieve the same proportional counter characteristics. The signal with counter-propagating beams should be reduced by an amount equal to the reduction in the Xe concentration. This was indeed found to be the case. When the Xe concentration was reduced in several stages to the point where the Xe partial pressure was 1 mTorr (concentration \( N_0 = 3.3 \times 10^{13} \text{ cm}^{-3} \)) 20 electrons per laser pulse (on average) was detected. At this level of resonant medium concentration, it was found that without retro-reflection, i.e., with only co-propagating photons present, no ionization could be measured. This was in accord with what theoretical analysis predicted for the broad bandwidth laser used in the experiment.

Another test of the robustness of the three-photon interference behavior was provided by Garrett et al. [25] in yet another experiment on three-photon-resonant transitions to the 6s state in Xe. Different from all previous experiments, this was a two-color experiment where two separate but simultaneous pulsed laser beams, frequencies \( \omega_{L1} \) and \( \omega_{L2} \), were used to drive the 6s transition in resonance, producing a FWM field of sum frequency \( \omega_m = 2\omega_{L1} + \omega_{L2} \). With Xe pressure of 250 Torr in an ionization cell, the two laser were arranged in three different geometries with results...
Fig. 14. MPI signals vs $\lambda_{\text{L1}}$ obtained through three-photon excitation of Xe $6s\left(\frac{3}{2}\right)(J = 1)$ in three different geometries. Top trace, counter-propagating beams. Bottom trace, single-pass co-propagating beams. Middle trace, co-propagating beams with a retro-reflection mirror to create counter-propagating beams at both frequencies. Insert shows excitation scheme and subsequent two-photon ionization out of the resonance level. Laser at $\lambda_{\text{L1}}$ is fixed at 387.900 nm, laser at $\lambda_{\text{L2}}$ is tuned around wavelength shown on abscissa. Reproduced from [25] with permission.

Signals in the top trace were produced by counter-propagating the two laser beams while tuning $\omega_{L1}$ through three photon resonance at FWM frequency $\omega_m = 2\omega_{L1} + \omega_{L2}$. The same beams were then co-propagated with the result shown in the bottom trace, where no ionization signal was detected. With co-propagation the destructive interference occurred as predicted, even with excitation from two independent laser sources having no phase relation between them. To show that the missing resonance signal was due to interference and not due to the lack of beam overlap, the co-propagating beams were retro-reflected to produce the middle trace in Fig. 14. The interference was complete with co-propagation (bottom trace), but was absent with counter-propagation (top trace). It was partially overcome with retro-reflection of both co-propagating beams (middle trace). An analogous two-color experiment was performed by Li et al. [26], where two separate pulsed laser sources were tuned to three-photon resonance at the sum frequency for excitation of the $4s'$ state in Ar. They obtained results similar to those of in Xe [25], i.e., no resonant signal with co-propagating beams, and strong three-photon resonant signals when retro-reflected.

Theory attests that the cancellation effect will occur under proper experimental parameters, when driving an optically allowed transition by any odd number of photons ($N=3, 5, \ldots$). This prediction was confirmed in experiments involving
five-photon-resonant excitation of the $5d\{3/2\}J = 1$ level in Xe and the $3d\{5/2\}J = 1$ level in Ar [84]. In both cases theory was confirmed and the five-photon-resonant signals were suppressed with uni-directional excitation and restored with retro-reflection excitation.

3.3.2. Pressure dependent frequency shift: experiments

In 1987 an experimental study by Ferrell et al. [19] revealed a feature in three-photon excitation with counter-propagating beams that was a departure from the good agreement between experiment and theory that existed at that time. This was the large pressure dependent resonant frequency shift of the three-photon resonant (counter-propagating) MPI signals in Xe. In Ferrell’s study counter-propagating beams were used to measure the self broadening of spectral lines corresponding to allowed resonant transitions between an excited state and the ground state. This problem is difficult to study because at low pressures the resonance line width is dominated by Doppler broadening. Self-broadening begins to dominate only at pressures of a few tens of Torr. When the pressure is high enough for self broadening to dominate Doppler broadening, the mean free path of a photon at line center is very small. Indeed “radiation trapping” has begun to be important at even $10^{-4}$ Torr. Ferrell et al. [19] reasoned that this type of pressure broadening could be measured by using three-photon excitation with counter-propagating laser beams, provided three-photon excitations are allowed for these transitions. Using a density matrix formalism and energy absorption rate as a measure of the coherence between states $|1\rangle$ and $|2\rangle$ and states $|2\rangle$ and $|3\rangle$, it was also shown that one could derive a theory that properly predicts the broadening of the resonance line width in agreement with three-photon excitation experiments using counter-propagating laser beams.

Ferrell et al. [19] measured a number of three-photon-resonant MPI line shapes and found that the theory of self-broadening accounted very well for the shapes and the widths up to surprisingly high pressures. However, in these relatively high pressure experiments there was an unexplained pressure dependent frequency shift of the resonance. With the use of a single laser, all four different transitions examined showed a blue pressure dependent frequency shift that was always about 50% of the FWHM of the nearly Lorentzian line shapes. In order to measure these shifts a double-cell apparatus (see Fig. 15) was used with a lower pressure sample of the inert gas present in the second cell and with the laser beams passing through both cells. Thus, simultaneous measurements were made of both the low pressure (reference) line shape from the second cell and the high pressure (signal) line shape from the first cell. When pulse-averaged signals at each wavelength were acquired, the line profiles obtained from two cells were compared and the shifts and widths at each pressure could be determined with reasonable accuracy. The data showed the unexplained shift to higher resonant frequency that were linear in Xe pressure.

Fig. 15. Schematic experimental apparatus used Ferrell et al. studies [19]. Reproduced from [19] with permission.
Figs. 16a and b show blue pressure dependent shifts in pure Xe (Fig. 16a) and Kr (Fig. 16b) as a function of gas pressure. The linearity of the shift as a function of pressure appears to extend to values as high as 1000 Torr.

Figs. 16c and d demonstrate the line shape (16c) and the pressure broadened width (16d) as a function of pressure of the resonance medium. The FWHM data also shows a solid line that is predicted from theory which makes an allowance for the fact that the laser bandwidth is large enough to hide any increase in width due to pressure broadening when the pressure is below 50 Torr. The allowance for the laser bandwidth gives rise to a slight curvature at the lower pressures.

The origin of the pressure dependent shift with counter-propagating excitation was first given by Friedburg et al. [20,21], who ascribed the shift to dispersion forces from polarization of the medium. Garrett et al. and Payne et al. [48,49] later provided theoretical treatments which discussed in detail the line shapes, line widths and amplitudes properties of the ionization signals including the pressure dependent resonance frequency shift. The differences between the works of Friedburg et al. [20,21] and Payne et al. [48,49] are in the treatment of the interference between two competing excitation pathways, and in the method of approach. In the treatment of the problem presented below, it will be shown that the magnitude of this shift is intimately tied in with the interference of excitation brought about by three-photon excitation from lasers and one-photon excitation from the FWM field. Thus, the FWM interference effect is still operative even with counter propagating beams, but with a different manifestation. Results show that the line shape, width, and amplitude of the ionization signals are the same as if the FWM was totally ignored in treating the problem. However, the peak in the signal is shifted, linearly in pressure, away from zero detuning due to the interference mechanism. Therefore, the MPI signal exhibits the same purely pressure broadened width and line shape as predicted from the theory of pressure broadening for self broadened resonance lines, with a quantitatively predicted pressure dependent frequency shift.

3.3.3. Theoretical treatment of counter-propagating beams and pressure dependent frequency shift

To describe the interference-based pressure dependent frequency shift in counter-propagating beams configuration, consider a sum frequency FWM ($\omega_m = 2\omega_{L1} + \omega_{L2}$) process where the laser beam at $\omega_{L1}$ propagates in the $+z$
direction and the laser beam at $\omega_{L2}$ propagates in the $-z$ direction. In this case the phase mismatch $\Delta K$, defined in Eq. (3.2), is dominated by the fact that one laser field counter-propagates relative to the other. That is,

$$\Delta K = \frac{\omega_m}{c} [n_0(\omega_m) - 1] - \frac{2\omega_{L1}}{c} [n(\omega_{L1}) - 1] - \frac{\omega_{L2}}{c} [-n(\omega_{L2}) - 1] \approx -\frac{2\omega_{L2}}{c},$$

where $\omega_m = 2\omega_{L1} + \omega_{L2}$ has been used and all indices are close to 1. Thus, Eqs. (3.1a) and (3.1c) can be rewritten as

$$\frac{\partial \rho_{21}}{\partial T_r} = i(\delta_2 \tau + i\Gamma \tau)\rho_{21} + iQ_{21}^{(3)} \tau e^{-2i\omega_{L2} z/c} + Q_{21}^{(1)} \tau,$$

$$\left(\frac{\partial Q_{21}^{(1)}}{\partial z}\right) = i\kappa_{12} \rho_{21}. \tag{3.14b}$$

In Eq. (3.14a) $Q_{21}^{(1)} = \mu_{21} E_{L0}/(2\hbar)$, where $E_{L0}$ is the amplitude of the local laser field seen by the atoms. In Eq. (3.14b), however, the Rabi frequency is due to the space averaged laser field. We make this distinction here since the two definitions are significant in the present context. That is, when the index of refraction deviates significantly from unity (due to a combination of high concentration and proximity to a resonance), the difference between the field seen by the atoms and the space averaged field that enters Maxwell’s equations can be significant. Under this circumstance the correction to the local field \[85\] can be shown to be increased by the Lorentz field, $(4\pi/3) P_m$, where $P_m$ is the polarization at the frequency of the wave-mixing field. For the positive frequency parts of the fields, the local field is given by

$$E_{L0}^{(+)} = \frac{E_{m0}^{(+)} e^{-i\omega_m (t-z/c)}}{2} = \frac{E_{m0}^{(+)} e^{-i\omega_m (t-z/c)}}{2} + \frac{4\pi}{3} P_m^{(+)} e^{-i\omega_m (t-z/c)},$$

where $E_{L0}^{(+)}$ and $E_{m0}^{(+)}$ are the amplitudes of the positive frequency component of the local and space averaged field at $\omega_m$, respectively. In addition, $P_m^{(+)}$ is the positive frequency component of the polarization at $\omega_m$, which must be determined by using the local field in the calculation of the atomic equations of motion. Using the relation $P_m^{(+)} = \mu_{12} N_0 \rho_{21} e^{-i\omega_m (t-z/c)} \[85\]$ and converting the $E_{L0}/2$ and $E_{m0}/2$ in the above equation into their equivalent half Rabi frequency form one immediately obtains $Q_{21}^{(1)}$ as

$$Q_{21} = \Omega_{21} + \frac{4\kappa_{12} \rho_{21}}{2\omega_m}.$$

Substituting this result into Eq. (3.14a) and defining $A_0 = \kappa_{12} c/(2\omega_m)$, one gets

$$\frac{\partial \rho_{21}}{\partial T_r} = i \left[ \delta_2 \tau + \frac{4}{3} A_0 \tau + i\Gamma \tau \right] \rho_{21} + i \left( \Omega_{21}^{(3)} \tau e^{-2i\omega_{L2} z/c} + \Omega_{21}^{(1)} \tau \right). \tag{3.15}$$

Note that the term $\frac{4}{3} A_0$ is a pressure dependent frequency shift since $\kappa_{12}$ contains the number density $N_0$. Actually an additional small frequency shift, derived from the theory of self-broadening, should be included here to be more accurate. This shift, which is quantitatively $-0.22 A_0$, can be included here, whereby the quantity inside the bracket $\delta_2 \tau + \frac{4}{3} A_0 \tau + i\Gamma \tau$ becomes $\delta_2 \tau + (\frac{4}{3} - 0.22) A_0 \tau + i\Gamma \tau$. Defining $d_2 = \delta_2 \tau + 1.11 A_0 \tau + i\Gamma \tau$ and taking the Fourier transform with respect to $T_r$, one arrives at

$$d_2 = A_{21}^{(3)} \tau e^{-2i\omega_{L2} z/c} + A_{21}^{(1)} \tau.$$

Substituting Eq. (3.16) into Eq. (3.14b) and using the initial condition for the generated field, i.e., $A_{21}^{(1)}(z = 0, \eta) = 0$, one arrives at a solution for the generated field

$$A_{21}^{(1)} = \frac{A_{21}^{(3)}}{1 - \omega_{L2} (d_2 + \eta)/\kappa_{12} \tau} \left[ e^{-2i\omega_{L2} z/c} - e^{-i\kappa_{12} z/c(d_2 + \eta)} \right]. \tag{3.17}$$
Again, at large $z$ such that $\text{Re}[i\kappa_1 \tau z/(d_2 + \eta)] \gg 1$, one has

$$A_{21}^{(1)} = -\frac{\mathcal{A}_{21}^{(3)}}{1 - [2\omega_{L2}(d_2 + \eta)/\kappa_1 \tau c]} e^{-2i\omega_{L2} z/c} = \left(\frac{\kappa_1 \tau c}{2\omega_{L2}}\right) \frac{\mathcal{A}_{21}^{(3)} e^{-2i\omega_{L2} z/c}}{d_2 - \kappa_1 \tau c/(2\omega_{L2}) + \eta}. \quad (3.18)$$

If this result is used in Eq. (3.16) one gets an equation for $x_{21}$ in the form

$$x_{21} = -\frac{\mathcal{A}_{21}^{(3)} e^{-i2\omega_{L2} z/c}}{d_2 - \kappa_1 \tau c/(2\omega_{L2}) + \eta}. \quad (3.19)$$

Replacing $d_2$ by its defined value, $d_2 = \delta_2 \tau + 1.11 A_0 \tau + i\Gamma_1$, and following the argument from Eqs. (3.9)–(3.13) for a pulsed field of length $\tau$ in the inverse Fourier transform (i.e. contribution only from $|\eta| \approx 0$), the inverse transform of Eqs. (3.18) and (3.19) gives

$$\Omega_{21}^{(1)} = \left(\frac{\kappa_1 \tau c}{2\omega_{L2}}\right) \frac{\mathcal{A}_{21}^{(3)} e^{-2i\omega_{L2} z/c}}{\delta_2 + 1.11 A_0 - \kappa_1 \tau c/(2\omega_{L2}) + i\Gamma_2}, \quad (3.20)$$

and

$$\rho_{21} = -\frac{\mathcal{A}_{21}^{(3)} e^{-i2\omega_{L2} z/c}}{\delta_2 + 1.11 A_0 - \kappa_1 \tau c/(2\omega_{L2}) + i\Gamma_2}. \quad (3.21)$$

The results in Eqs. (3.20) and (3.21) show a pressure induced frequency shift in the resonant denominator for $\rho_{21}$ and $\Omega_{21}^{(1)}$. That is, the real part of the denominator vanishes for $\delta_2 = \kappa_1 \tau c/(2\omega_{L2}) - 1.11 A_0$. Note that both Eq. (3.20) for $\Omega_{21}^{(1)}$ and Eq. (3.21) for $\rho_{21}$ have the same denominator and in both equations a maximum occurs at the same frequency. Also note that when the result of Eq. (3.18) was substituted in Eq. (3.16), the two terms in the numerator of (3.16) added together with the same sign. In the previous case (uni-directional beams) the two terms exactly canceled each other. This is an important point. With uni-directional beams the term contributing to $\rho_{21}$ from the wave-mixing field destructively interferes with the term due to three-photons from the laser field. With counter-propagating beams the two terms add constructively. Using the result for $\rho_{21}$ in Eq. (3.1b) to calculate $\rho_{22}$, one obtains the ionization rate per unit volume as

$$R_1 = N_0 \gamma_1 \rho_{22} = N_0 \gamma_1 \int_{-\infty}^{\tau} \frac{2\Gamma |\Omega_{22}^{(3)}|^2 e^{-\int_0^\tau (\gamma_1 + \gamma_2) dt}}{[\delta_2 + 1.11 A_0 - \kappa_1 \tau c/(2\omega_{L2})]^2 + \Gamma_2^2} \, dt. \quad (3.22)$$

If the pressure induced width is much larger than $\gamma_1$, this ionization profile has a Lorentzian line shape with FWHM of $2\Gamma$. The ionization profile peaks at a detuning $\delta_2 = \delta_{\text{shift}} = \kappa_1 \tau c/(2\omega_{L2}) - 1.11 A_0$. This peak corresponds to constructive interference (phase matching) between the two terms that couple levels $|1\rangle$ and $|2\rangle$. Thus with counter-propagating beams the shifted peak in the excitation profile corresponds to phase-matched wave mixing. This point was not realized in any of the early work in the field. Indeed it argued that counter-propagating beams produced poor phase matching and thus no interference. This was not the true picture. The proper account of the full behavior of the interference phenomena was first given by Payne [88] where it was shown by use of the Clausius–Mossotti equation that the peak occurred at the counter-propagating phase-matching point. In this context, of phase matching, we note the similarity between the ionization rate given in Eq. (3.22) and that in Eq. (3.13) obtained under the assumption of co-propagating beams with a high concentration of buffer gas to achieve phase matching. The equations are identical in form. Both involve a detuning about a phase-matching point.

As already noted earlier, Ferrell et al. [18,19] observed experimentally that the line shape and line width were identical to what was observed when the lasers were tuned near the three-photon resonance with part of the laser light reflected back through the cell and later the line shifts agreed very well with the theoretical predictions. Finally we note that if a difference frequency process $2\omega_{L1} - \omega_{L2}$ were considered in the above treatment, the pressure induced shift would have made the apparent position of $|3\rangle$ lower in energy so that $\omega_{L2}$ must supply a higher energy photon, just as in the case where $2\omega_{L1} + \omega_{L2}$ excitation was being carried out. Thus, for either $2\omega_{L1} + \omega_{L2}$ or $2\omega_{L1} - \omega_{L2}$ process, if one scans across the MPI resonance by tuning the second laser one will find that the frequency shift will always be on the blue (higher $\omega_{L2}$ frequency) side.
3.4. Shifting three-photon excitation profiles from two laser beams crossed at arbitrary angles

This subsection presents an expanded study of an effective two-state plus continuum model of a high pressure inert gas being excited by two transform limited bandwidth lasers, crossed at an arbitrary angle \( \theta \) (Fig. 17) \([47–49]\), in the region of a three-photon resonance. If the vector sum \( \vec{k}_T = 2\vec{k}_L_1 \pm \vec{k}_L_2 \) is defined as depicted in Fig. 17b, then a geometrical phase mismatch, \( K = k_m - k_{Tz} \), is introduced in the three-photon excitation modes \( 2\omega_{L_1} \pm \omega_{L_2} \), due to the angle between the two laser beams.

The theoretical treatment for this case follows exactly what has been shown in the end of the last subsection, i.e., from Eq. (3.14) through Eq. (3.22), except for the difference in the phase mismatch and hence the pressure dependent frequency shift.

From Fig. 17b it is readily shown that the \( z \)-component of \( \vec{k}_T \) is given as

\[
k_{Tz} = \frac{\omega_m}{c} \sqrt{1 \mp \frac{4\omega_{L_1}\omega_{L_2}}{\omega_m^2} (1 - \cos \theta)}.
\]

Since \( \Delta K = k_m - k_{Tz} = \omega_m/c - k_{Tz} \), one has

\[
\Delta K \simeq \frac{\omega_m}{c} \left[ 1 - \sqrt{1 \mp \frac{4\omega_{L_1}\omega_{L_2}}{\omega_m^2} (1 - \cos \theta)} \right].
\]

where \( \mp \) sign indicates a sum-(difference-) frequency-mixing process.

Thus, in the place of Eq. (3.17) one now has, for the Fourier transform of the generated field,

\[
A_{21}^{(1)} = -\frac{A_{21}^{(3)}}{1 - [\Delta K (d_2 + \eta)/\kappa_{12}\tau]} \left[ e^{-i\Delta K z} - e^{-i\kappa_{12}\tau z/(d_2 + \eta)} \right],
\]

with \( \Delta K \) given in Eq. (3.24). As before, the pressure broadened width is assumed to be very large compared with the laser bandwidths, and for the pulse length of several nanoseconds the spatial extent of the laser pulse is much larger than the length of the sample. Thus, at large enough concentrations \( N_0 \) and propagation depth \( z \) where \( \kappa_{12}\tau z (2.33\Delta_0\tau)[(\delta_2 \tau + 1.11\Delta_0\tau)^2 + (2.33\Delta_0\tau)^2] \geq 1 \), one can neglect the second exponential in the square bracket and find, after inverting Fourier transforms, that

\[
Q_{21}^{(1)} \tau = -\frac{Q_{21}^{(3)} e^{-i\Delta K z}}{1 - \Delta K d_2/\kappa_{12}\tau} = \left( \frac{\kappa_{12}\tau}{\Delta K} \right) \frac{Q_{21}^{(3)} e^{-i\Delta K z}}{d_2 - \kappa_{12}\tau/\Delta K}.
\]

\[
\rho_{21} = -\frac{Q_{21}^{(3)} e^{-i\Delta K z}}{d_2 - \kappa_{12}\tau/\Delta K}.
\]
As in the previous subsection, Eqs. (3.26) and (3.27) have the same denominator. Using Eq. (3.24) and the expression

Thus, the peak of the resonance is shifted to

for

matching occurs too far from the

absorption at large detunings is not given properly in terms of the detuning and relaxation rates. Also, when phase

position. No observable shift obtained for the 5

but the laser at \( \omega_{L2} \) was retro-reflected. (c), 200 Torr Xe, again with the second laser retro-reflected. The vertical line marks the unshifted resonance position. No observable shift obtained for the 5d[3/2](J = 3) level. Reproduced from [49] with permission.

As in the previous subsection, Eqs. (3.26) and (3.27) have the same denominator. Using Eq. (3.24) and the expression for \( d_2 \), this denominator becomes

where the total shift \( \Delta_p \) is given, using the definition of \( \Delta_0 \), as

Thus, the peak of the resonance is shifted to \( \delta_2 = \Delta_p \). The \( \mp \) sign in the denominator indicates that the sum-frequency-mixing gives a blue frequency shift of the ionization peak, whereas the difference-frequency-mixing gives a corresponding red frequency shift. That is to say, with sum-frequency-mixing the detuning from resonance to the phase matching point is positive, while for difference-frequency-mixing the detuning from resonance of the phase matching point is negative. Therefore, in both cases in order to tune laser at \( \omega_{L2} \) from the resonance to the phase matching point it must be tuned to the blue (higher energy photons).

### 3.4.1. The case of small \( 4\omega_{L1}\omega_{L2}/\omega_m^2 \)

It should be pointed out that when \( \theta \) is very small the approximation used in the above treatment is poor because the absorption at large detunings is not given properly in terms of the detuning and relaxation rates. Also, when phase matching occurs too far from the \( |1\rangle - |2\rangle \) resonance the phase matching point invariably gets almost as close to some other resonance as it is to the \( |1\rangle - |2\rangle \) transition. This necessitates inclusion of deviations from unity in \( n_0(\omega_m) \). Such deviations are not included in the above treatment. Never-the-less, aside from cases involving small \( \theta \), there are circumstances where the term \( 4(\omega_{L1}\omega_{L2}/\omega_m^2)(1 - \cos(\theta)) \ll 1 \) is very important. One of these cases frequently occurs in difference-frequency mixing where the wavelength of the laser at \( \lambda_{L2} \) is much longer than that of the FWM field. Other examples of this include SHR and amplified spontaneous emission (ASE). (See later section.)

As a test of the theory presented above, Garrett et al. [49] carried out a series measurements on suppression effects and pressure shifts for cross-beam configurations in pure Xe. The studies were experimentally attractive due to the large magnitude of expected MPI line-shifts. Fig. 18 shows the pressure shift at \( \theta = 22.8^\circ \). In this experiment one laser at \( \omega_{L1} \) had a fixed wavelength of \( \lambda_{L1} = 291.92 \) nm, while laser at second laser \( \omega_{L2} \) was scanned through the region of \( \lambda_{L2} = 620 - 651 \) nm. This covered the ground state to 5d[3/2](J = 1) transition region which is one-photon
Fig. 19. Pressure dependence of shift in the wavelength for resonance excitation for the angles $\theta = 10.1^\circ$, 18.1$^\circ$, and 28.4$^\circ$. Reproduced from [48] with permission.

resonant around $\lambda_m = 119.20$ nm. In this case, $4[\omega_{L1}\omega_{L2}/\omega_m^2](1 - \cos(\theta)) < 2.5 \times 10^{-3}$. In Fig. 18 curve (a), the Xe pressure was 100 Torr and both laser beams made a single pass through the medium, so that the only ionization seen was that at the $\theta = 22.8^\circ$ phase matching point. In Fig. 18 curve (b), 100% of the second laser beam was reflected back through the gas cell under the same pressure. In this case there is a phase matching point not only for beams crossing at $\theta = 22.8^\circ$, but also for $\theta = 157.2^\circ$ from the beam going in the opposite direction. For $\theta = 157.2^\circ$ the phase mismatch for the laser beams is large. Thus the phase matching point is extremely close to the three-photon resonance in order for the $-\kappa_{12}/\delta_{2m}$ term from the resonance to offset the laser $\Delta K$. Thus, there are two peaks, where one is only slightly shifted from three-photon resonance. Finally, in Fig. 18 curve (c) the situation is similar to Fig. 18 curve (b) except the Xe pressure was increased to 200 Torr. It should be noted that no shift was observed at 100 and 200 Torr for the $5d[5/2](J = 3)$ level where $\Delta J = 3$. For the $\Delta J = 3$ transition there is no third-harmonic coupling, no interference, and no shift, as expected.

Fig. 19 shows the position of phase matching, as monitored by four-photon MPI, as a function of Xe pressure for three different crossing angles, $\theta$. The dashed lines are based on Eq. (26), while the solid lines are obtained with $\Delta K$ being calculated without replacing the indices of the lasers and $n_0(\omega_m)$ by unity. The wavelengths chosen for the lasers in carrying out the data collection was the same as in Fig. 17a.

3.4.2. The case of large $\Delta K$

When $\Delta K$ is large enough so that $A_p$ is not much larger than the FWHM of the pressure broadened resonance, and the one-photon resonance has a strong oscillator strength ($F_{12} > 0.15$), then the pressure broadened width and the predicted shift are likely to be in reasonable agreement with experiment if the pressure of an inert gas is less than about 200 Torr. In the 20–100 Torr region the predictions about line width and line shape should be reasonably accurate, and
the ionization rate can be found as

$$ R_I = N_0 \gamma_1 \rho_{22} = N_0 \gamma_1 \int_{-\infty}^{t_f} dt' \frac{2\Gamma |\Omega_{21}^{(3)}|^2 e^{-\int_{t'}^{t_f}(\gamma_1+\gamma_2)} dt''}{(\delta_2 - \Delta_p)^2 + \Gamma^2}. $$

(3.30)

From this ionization line shape one can fit with a Lorentzian and compare the position of the peak with the corresponding signal from a low pressure cell to find $\Delta_p$. From the fit parameters in the Lorentzian one gets $\Gamma = \Gamma_p + (\gamma_2 + \gamma_1)/2$. This provides an accurate way of measuring pressure broadening of the $|1\rangle - |2\rangle$ transition.

From the point of view of the destructive interference between the one- and three-photon competing excitations of state $|2\rangle$ it is interesting to note that in all cases with only the two laser beams present there is just one peak which occurs at the point where phase matching occurs. In particular, with crossing angles up 0.5 radians, or so, the expected peak in the ionization signal is so far from resonance that no ionization peak is seen at all. On the other hand, when the angle between the beams is close to 180°, the peak in the ionization is still at the phase matching point, but the pressure broadened peak overlaps the resonance [47–49].

As an application of the phenomenon it might be noted that experiments like the study by Garrett et al. [49] can be used to determine accurate oscillator strengths and absorption coefficients of the medium far from resonance. Such studies carried out at large crossing angles provide an effective way of measuring self-pressure broadening in atomic species. These considerations will be seen later to be closely related to pressure shifts that are seen in backward SHR generation or ASE in high pressure inert gases.

### 3.5. Comments on suppression of off-resonance enhancements to MPI: suppression of four-photon resonant enhancements

In the late 1980s and early 1990s new consequences of the three-photon-FWM destructive interference were revealed. Several observations of the effects of a near three-photon intermediate resonance on four-photon resonance enhancements to MPI were reported [52–55]. The circumstance is depicted in Fig. 20, where intermediate level $|2\rangle$ provides near-three-photon resonant enhancement to four-photon excitation of level $|3\rangle$. In these experiments, measurements of four-photon-resonant enhancements in two-color-induced MPI spectra of Xe, revealed that a four-photon excitation could be suppressed if the excitation occurred near a three-photon intermediate resonance that supported the three-photon interference effect. With counter-propagating beams the resonant enhancement was restored [55]. Results of Charalambidis et al. (Fig. 21) show examples of the behavior for four-photon excitation of $4f$ and $5f$ states in Xe. This effect of four-photon cancellation through interference at a near-resonant three-photon intermediate was well described theoretically [35,36,56]. The role of interference near a three-photon intermediate state was delineated. A very important point of these studies was the demonstration that three-photon interference effect could, at high pressures, extend far away from the line-center of a three-photon resonance. Some of the theoretically predicted effects were experimentally tested in detail through studies with focused and unfocused laser beams by Hart et al. [54]. The theoretical studies by Payne et al. [35] and Tewari [56] were stimulated by some of the earlier experimental studies [52,53] that showed somewhat mysterious pressure effects on four-photon resonance enhanced five-photon ionization signals in Xe, under circumstances where the lasers were also near a three-photon resonance between the ground state and the $6s3/2(J = 1)$ state. These studies clearly demonstrated how three-photon destructive interference evolves at large phase mismatch for the wave-mixing field.

The influence of destructive interference at an intermediate three-photon near-resonance on a four-photon-resonant transition can be illustrated in a brief extension of results already presented. The four-photon excitation is mediated by a transform limited bandwidth laser source, detuned from an intermediate three-photon resonance by an amount $\delta_2$. The three-photon level is again coupled to the ground state by a generated TH field (see Fig. 20). The detuning $\delta_2$ is large as compared to the Doppler width or the pressure broadened width of the line. In the experiments the media were either Xe or Kr at 10–100 Torr pressure [52–55].

Fig. 22 shows two sets of data from Hart et al. [54] in Xe where the detuning from $6s$ three-photon resonance by the laser at $\omega_{L1}$ was held fixed, while the second laser at $\omega_{L2}$ was tuned through four-photon resonance, at 4 Torr Xe pressure. In both sets of graphs data in the upper curve was taken with a counter-propagating beam for the first laser, while the lower curve is without counter-propagation in the first laser field. Note that the ionization suppression is greater for the smaller detuning. With the first laser beam counter-propagating, the signal decreases as one detunes...
Fig. 20. Energy-level diagram showing the excitation of $|3\rangle$ by three laser photons at $\omega_{L1}$ plus one laser photon at $\omega_{L2}$. Also shown is the one-photon excitation of $|3\rangle$ by the third harmonic photon at $\omega_{TH} = 3\omega_{L1}$ plus a laser photon at $\omega_{L2}$. Note that three laser photons at $\omega_{L1}$ are nearly resonant with state $|2\rangle$ and the TH field is generated near state $|2\rangle$. Interference between these two pathways to $|2\rangle$ can suppress the excitation of $|3\rangle$ and thus the MPI signal.

Further from resonance. However, when there is no counter-propagating first laser present the signal initially increases as one tunes further from three-photon resonance.

Hart et al. [54] have also systematically studied four-photon MPI near three-photon resonance in focused beam geometry. Fig. 23 shows two sets of data for the same Xe transition. Fig. 23a details the four-photon-resonant MPI as a function of the detuning from the three-photon resonance whereas Fig. 23b shows the suppression of four-photon-resonant MPI vs phase mismatch. These observations agreed well with the theoretical predictions of Payne et al. [35].

Suppression of four-photon resonance enhancement can be understood on the basis of the three-photon destructive interference which is expected to occur because of the possibility of generating a FWM field that will compete with the laser excitation of the state $|2\rangle$. The simple analysis shows that the absorption of the generated FWM from the state $|2\rangle$ will lead to suppression of the three-photon excitation of the same state, eliminating the three-photon resonance enhancement to the excitation of the four-photon resonance. Hence, the enhancement to the MPI from the four-photon state $|3\rangle$ is suppressed. Detailed theoretical investigation has shown that this is indeed the physical mechanism that leads to the suppression of resonance enhancements to four-photon excitation and hybrid resonances, as seen in Hart et al. [54] and Charalambidis et al. [55]. In fact, this interference mechanism leads to the suppression of absorption on the wing of the upper state, and any other effect that this state might have on enhancing the further absorption of photons.

All cases and treatments described in this section assume that the excited state of primary interest is resonantly pumped by laser fields via an odd-photon process. There are no intermediate even-photon resonances that can be directly coupled by laser fields. Such intermediate resonant excitation schemes lead to new physical phenomena and will be the subject of the next section.

4. Expanded quantum interference effects in three-level systems

Destructive interference effects from wave-mixing fields, as treated in Section 3, were manifested in transitions that were observed through multi-photon ionization measurements. In every instance a multi-odd-photon driven
transition was suppressed by the interfering couplings between the resonant wave-mixing field and the resonant multiphoton excitation by the laser fields. However, in the late 1980s new manifestations of the odd-photon interferences were discovered, and a second class of interference effects that were even-photon-resonant were further explored. In the new categories, to be considered here, it was found that even-photon excitation could become suppressed \cite{28,30,32}. In addition, certain stimulated-emission-initiated processes could have their gain suppressed by a destructive interference involving a wave-mixing field resulted from polarization related to a stimulated emission process \cite{31,38,39}. The latter effects include gain suppression of OPSE or ASE \cite{45} propagating in the direction of the laser field, as well as forward propagating SHR emission \cite{31,38,39}. Furthermore, Autler–Townes splitting (and ac Stark shifts) could be suppressed by an effective odd-photon interference in the presence of even-photon resonance in a co-propagating beam geometry \cite{57,59–63}. The new class of even-photon-resonant interference effects were shown to cause gain saturation in parametric FWM processes \cite{28–30,32,33,40,46}. Further studies also showed that the new category of processes involve simultaneous two- and three-photon resonances were subject to the same underlying mixing wave destructive interference, but required different physical conditions.
In this section a three-state model is introduced and four subjects will be reviewed, though not in chronological order. The first two topics represent additional effects that ensue from odd-photon-based interference in the presence of even-photon resonance, while the last two describe the interferences involving two-photon transitions. More specifically, the following areas will be separately covered:

(A) Effects of three-photon destructive interference with a two-photon resonant intermediate state  
   (2) Suppression of forward SHR and ASE emissions by three-photon destructive interference
(B) Two-photon quantum interference effect in three level systems

1. Effects of two-photon destructive interference on parametric FWM.
2. Effects of two-photon destructive interference on FWM.

4.1. Effects of three-photon destructive interference with a two-photon resonant intermediate state

All of the problems of interest here involve the coupling of two different upper levels of an atomic system; one level coupled by a two-photon Rabi frequency and the other coupled by both three-photon and one-photon interactions. Thus, an effective three-state plus continuum model is appropriate (see Fig. 9). In all cases to be discussed in this section, the coupled by a two-photon Rabi frequency and the other coupled by both three-photon and one-photon interactions. Thus, the density matrix and Maxwell’s equations.

To begin, the state vector for the effective three-level system is expressed in the form

$$|\Psi(z, t)\rangle = A_1 e^{-i\omega_1 t}|1\rangle + A_2 e^{-i(\omega_2 + \delta_2)t} e^{i2\omega_1 n(\omega_1)z/c} |2\rangle + A_3 e^{-i(\omega_3 + \delta_3)t} e^{i\omega_m n(\omega_m)z/c} |3\rangle. \quad (4.1)$$

With the choices of relative phase made above and with the inclusion of relaxation rates for the different pairs of states, one obtains (within the RWA) the following set of equations for the density matrix elements (see Section 2),

$$\frac{\partial \rho_{21}}{\partial T_r} = i(\delta_2 \tau + i\gamma_{21} \tau) \rho_{21} - i\Omega_{31} \tau \rho_{23} + i\Omega_{21}^{(2)} \tau(\rho_{11} - \rho_{22}) + i\Omega_{23} \tau e^{i\Delta K z} \rho_{31}, \quad (4.2a)$$

$$\frac{\partial \rho_{31}}{\partial T_r} = i(\delta_3 \tau + i\gamma_{31} \tau) \rho_{31} - i\Omega_{31} \tau \rho_{32} + i\Omega_{31}^{(2)} \tau(\rho_{11} - \rho_{33}) + i\Omega_{32} \tau e^{-i\Delta K z} \rho_{21}, \quad (4.2b)$$

$$\frac{\partial \rho_{32}}{\partial T_r} = i(\delta_3 - \delta_2 \tau + i\gamma_{32} \tau) \rho_{32} + i\Omega_{32} \tau e^{-i\Delta K z}(\rho_{22} - \rho_{33}) + i\Omega_{31} \tau \rho_{12} - i\Omega_{31}^{(2)} \tau \rho_{31}, \quad (4.2c)$$

$$\frac{\partial \rho_{33}}{\partial T_r} = -i(\gamma_{2} + \gamma_{1}) \tau \rho_{22} - 2 \text{Im}[\Omega_{21}^{(2)} \tau \rho_{12} + \Omega_{23} \tau e^{i\Delta K z} \rho_{32}], \quad (4.2d)$$

where

$$\gamma_{21} = \frac{(\gamma_{2} + \gamma_{1} + 2I_{21})}{2}, \quad \gamma_{31} = \frac{(\gamma_{3} + 2I_{31})}{2}, \quad \gamma_{32} = \frac{(\gamma_{3} + \gamma_{2} + \gamma_{1} + 2I_{32})}{2}, \quad (4.3)$$

and as in Eqs. (3.2) and (3.3)

$$\Delta K = \frac{\omega_m}{c}[n(\omega_m) - 1] - 2\frac{\omega_{L1}}{c}[n(\omega_{L1}) - 1] - \frac{\pm \omega_{L2}}{c} [\pm n(\omega_{L2}) - 1]. \quad (4.4)$$

In deriving Eq. (4.2) a two-photon half Rabi frequency \(\Omega_{12}^{(2)}\) is introduced. This term represents the two-photon coupling of levels |1\rangle and |2\rangle. Also, from the earlier general definition of \(\Delta K\) it is understood that the ± sign in front of \(\omega_{L2}\) indicates that the transition involving \(\omega_{L2}\) is absorptive in nature, \(\omega_m = 2\omega_{L1} + \omega_{L2}\) (Fig. 9a), or emissive in nature, \(\omega_m = 2\omega_{L1} - \omega_{L2}\) (Fig. 9b). The ± sign in front of the refractive index designates different beam propagation geometries of the second laser field relative to the first laser field. These signs will be specified in each individual case. Again, \(n_0(\omega_m)\) is the non-resonant index of the medium at the wave-mixing frequency \(\omega_m\) including any contribution by the buffer gas, with the |1\rangle – |3\rangle resonance contribution excluded. As before, the resonant part is included directly through the self-consistent solution of the equations for the density matrix and Maxwell’s equations.

In accord with the actual experimental situations, the pressure of the resonance medium will be assumed to be large enough so that rapid relaxation of off-diagonal coherence induces pressure broadened widths that are larger than Doppler widths. Thus, any Doppler broadening effect will be ignored. However, in the case of transform limited lasers with less than about 50 Torr of a pure alkali vapor or inert gas (a strong |1\rangle – |3\rangle transition), Doppler effects would have to be included in the treatment. Indeed, in the case of the two-photon resonance in inert gases the Doppler effect
is important to around 300 Torr because of the shorter range quadrupole–quadrupole interactions involved, making the $\Gamma_{21}$ relaxation rate about a factor of five smaller than the dipole–dipole interactions for a strong transition [86].

The general procedure in solving each of the three-state problems discussed in this section is to first work out the relevant atomic response from the density matrix equations Eq. (4.2) with additional approximations appropriate to the particular problem being studied. Then, one uses the relevant coherence elements to construct necessary source terms for Maxwell’s equations appropriate to the internally generated fields. In the SVA approximation, the requisite Maxwell’s equations for all laser-like fields are given as

\[
\frac{\partial \Omega_{23}}{\partial z} + \frac{n_i(\omega_{L,2})}{c} \frac{\partial \Omega_{23}}{\partial t} = i\kappa_{32}\rho_{23}e^{-i\Delta K z},
\]

(4.5a)

\[
\frac{\partial \Omega_{31}}{\partial z} + \frac{n_0(\omega_m)}{c} \frac{\partial \Omega_{31}}{\partial t} = i\kappa_{13}\rho_{31},
\]

(4.5b)

With the assumption that the ground state population remains undepleted, one usually does not need to solve Maxwell’s equations for the input laser fields (i.e., Eq. (4.5a)). Thus, all external laser fields are assumed to propagate with group velocity close to c and without attenuation. In cases where the transition $|2\rangle - |3\rangle$ is coupled by an internally generated field (such as SHR emission or OPSE/ASE), however, Eq. (4.5a) for $\Omega_{23}$ will need to be solved simultaneously and self-consistently with the Maxwell’s equation for the field $\Omega_{31}$ generated at $\omega_m$ for the transition $|3\rangle - |1\rangle$.


In the early of 1990s it was realized [57] that multi-photon destructive interference is not always effective when an even-parity resonance transition forms the first leg of the excitation sequence. This belief was based on the concerns that the even-photon resonance excitation would promote and retain a population in the state $|2\rangle$. Such a cumulation of population in an even-photon terminal state would destroy the ability of the polarization to accurately and adiabatically follow the three-photon coupling due to the lasers, rendering the three-photon destructive interference impossible. It is now understood that the key to make the odd-photon destructive interference possible in the presence of an even-photon resonance is that $\rho_{21}$ must be able to adiabatically follow the laser couplings. One way to facilitate and achieve this is fast dephasing effects. Indeed, at high concentrations (about 50 Torr for strong one-photon transitions or about 300 Torr for two-photon transitions) collisional dephasing effects become fast enough to dwarf the Doppler width and bring about the adiabatic following of the off-diagonal elements of the density matrix. Furthermore, a large optical shift or splitting in level $|2\rangle$ can also bring about adiabatic following. It is the adiabatic following of the atomic coherence to the laser fields that preserves the effectiveness of the interference. In the following, a theoretical formulation of the problem will be presented first, followed by discussions on experimental observations.

The relevant case to be treated here is a classic two-color a.c. Stark shift, or Autler–Townes splitting experiment. It will be shown that in this category the large a.c. Stark shift and splitting can become suppressed when the two laser fields are co-propagating, but reappear when one of the beams is counter-propagated (or retro-reflected). This problem is somewhat simpler than other problems in the remainder of this section in that only one new field is generated, namely the FWM field. Thus this problem is closer to the previous examples of interference-based suppression.

Consider a three-level plus continuum model as shown in Fig. 9. Assume that a laser at $\omega_{L1}$ is tuned near the two-photon resonance between states $|1\rangle$ and $|2\rangle$. A second, more intense laser is kept tuned to the exact resonance between states $|2\rangle$ and $|3\rangle$. This intense laser field induces an Autler–Townes splitting in the two-photon resonant transition probability between $|1\rangle$ and $|2\rangle$ and in the enhanced three-photon photo-ionization of the atoms. Furthermore, assume that state $|3\rangle$ has dipole allowed transition back to the ground state. Since the combination of the first and second laser are tuned near a three-photon resonance which is also assumed to have allowed electric dipole transitions back to the ground state, one expects a FWM field to be generated at $\omega_m = 2\omega_{L1} \pm \omega_{L2}$. In the following, one will see both theoretically and experimentally that even with an intensity of $I_{L2}$ (for the laser at $\omega_{L2}$) that is sufficient to produce a large optical shift or Autler–Townes splitting of levels $|2\rangle$ and $|3\rangle$, a three-photon destructive interference involving FWM between $|1\rangle$ and $|3\rangle$ is still robust and effective, leading to striking new physical phenomena.

From the set of Eq. (4.2) for the three-level system the following set of equations of motion are appropriate to this two-color a.c. Stark shift problem,

\[
\frac{\partial \rho_{21}}{\partial \tau} = id_2\rho_{21} + i\Omega_{21}^{(2)}\tau + i\Omega_{23}^{(1)}\tau e^{i\Delta K z}\rho_{31},
\]

(4.6a)
radial and temporal variations of the splitting. Thus, if the laser at
where generalized detunings $d_2 = \delta_2 \tau + i(\gamma_2 + \gamma_I + 2\Gamma_2)\tau/2$ and $d_3 = \delta_3 \tau + i(\gamma_3 + 2\Gamma_3)\tau/2$ are introduced. This problem is made solvable and the predictions are made more striking if one assumes that the beam diameter and pulse length of the shift-inducing laser at $\omega_{L2}$ are much larger and longer respectively than that of the laser at $\omega_{L1}$. These assumptions imply that during the time of passage of the laser pulse at $\omega_{L1}$ the amplitude of the second laser at $\omega_{L2}$ remains essentially constant in time and is nearly constant over the beam waist of the first laser. This eliminates any radial and temporal variations of the splitting. Thus, if the laser at $\omega_{L1}$ is scanned through the two-photon resonance, one would expect to see two sharp ionization peaks, split from the unperturbed resonance by $|\Omega_2|$ on each side of the unperturbed resonance position. This is the well-known Autler–Townes splitting.

Taking Fourier transforms of Eqs. (4.6a–e) with respect dimensionless retarded time $T_r$, introducing $\eta = \omega \tau$ as the dimensionless transform variable, defining the transforms of the density matrix elements $\rho_{mn}$ and the half Rabi frequency $\Omega_{mn}$ as $\alpha_{mn}$ and $A_{mn}$, respectively as before, and defining $D_j = d_j + \eta$, one gets

$$\frac{\partial \rho_{31}}{\partial T_r} = id_3 \rho_{31} + i\Omega_{32} \tau e^{-i\Delta K_z} \rho_{21} + i\Omega_{31} \tau,$$  \hspace{1cm} (4.6b)

$$\frac{\partial \rho_{22}}{\partial T_r} = -(\gamma_2 + \gamma_I) \tau \rho_{22} - 2 \text{Im}[\Omega_{21}^{(2)} \tau \rho_{12} + \Omega_{23} \tau e^{i\Delta K_z} \rho_{32}],$$  \hspace{1cm} (4.6c)

$$\frac{\partial \rho_{33}}{\partial T_r} = -\gamma_3 \tau \rho_{33} - 2 \text{Im}[\Omega_{31} \tau \rho_{13} + \Omega_{32} \tau e^{-i\Delta K_z} \rho_{23}],$$  \hspace{1cm} (4.6d)

$$\left( \frac{\partial \Omega_{31}}{\partial z} \right)_{T_r} = i\kappa_{13} \rho_{31},$$  \hspace{1cm} (4.6e)

where $\kappa_{13} = \frac{\kappa_{13}}{\kappa_{13}}$. This

$$\omega_{21} = -\frac{A_{21}^{(2)} \tau + e^{i\Delta K_z} \Omega_{23} \tau \alpha_{31}}{D_2},$$  \hspace{1cm} (4.7a)

$$\omega_{31} = -\frac{A_{31} \tau + e^{-i\Delta K_z} \Omega_{32} \tau \alpha_{21}}{D_3},$$  \hspace{1cm} (4.7b)

$$\left( \frac{\partial \alpha_{31}}{\partial z} \right)_{T_r} = i\kappa_{13} \alpha_{31}.$$  \hspace{1cm} (4.7c)

Eqs. (4.7a,b) yield

$$\omega_{21} = \frac{D_3 A_{21}^{(2)} \tau - e^{i\Delta K_z} \Omega_{23} \tau A_{31} \tau}{W_2},$$  \hspace{1cm} (4.8a)

$$\omega_{31} = \frac{D_2 A_{31} \tau - e^{-i\Delta K_z} \Omega_{32} \tau A_{21}^{(2)} \tau}{W_2}.$$  \hspace{1cm} (4.8b)

where $W_2 = |\Omega_{23}|^2 - D_2 D_3$. Substituting $\alpha_{31}$ into the RHS of Eq. (4.7c) and using the initial condition for the generated field $A_{31}(z = 0, \eta) = 0$, one obtains the solution for $A_{31}$ as

$$A_{31}(z, \eta) = \frac{\Omega_{32} A_{21}^{(2)}}{D_2 M} e^{-i\Delta K_z} - e^{i\kappa_{13} \tau D_2 z/W_2},$$  \hspace{1cm} (4.9)

where

$$M = 1 + \frac{\Delta K W_2}{\kappa_{13} \tau D_2}.$$  \hspace{1cm}

For co-propagating beams (therefore $+n(\omega_{L2})$ in Eq. (4.4)) and for the lowest lying strongly resonant transitions in an inert gas with $P < 100$ Torr one would typically have $\Delta K < 0.2$ cm$^{-1}$. On the other hand, under the same circumstances, $\kappa_{13} \tau/|\Omega_{23}|^2$ can be very large. Thus, in the experiments (see below) the parameter $M$ would be very close to 1.
If one substitutes Eq. (4.9) into (4.8b), the expression for \( x_{31} \) becomes
\[
x_{31} = \frac{A_{21}^{(2)} \tau \Omega_{23 \tau}}{W_2 M} \left[ (1 - M)e^{-i\Delta K z} - e^{i\Delta K z} D_{23 \tau} / W_2 \right].
\] (4.10)

In Eq. (4.10) the value of \( M \) will generally be very close to 1, so the first term in the brackets is small for all values of \( z \). The second term in the brackets contains the exponential \(-\kappa_{13} \tau (\gamma_2 + \gamma_1 + 2 \Gamma_1 \tau) / 2 |\Omega_{23 \tau}|^2 \) which is negative, real, and large in magnitude for large \( z \). Thus, this term becomes very small for large \( z \), resulting in \( x_{31} \approx 0 \) at large \( z \). In the case where the laser at \( \omega_{L 2} \) is counter-propagated (therefore \(-n(\omega_{L 2})\) in Eq. (4.4)), however, \( \Delta K \) is large and \( M \) is not close to unity, therefore \( x_{31} \) is not small (see below).

To see the physical meaning of Eq. (4.10), consider \( x_{21} \) for \( z \approx 0 \) (i.e., near the entry point into the medium) where the FWM intensity is negligible. Set \( A_{31} \approx 0 \) at \( z \approx 0 \) in Eq. (4.8a), one has
\[
x_{21} = \frac{D_3 A_{21}^{(2)} \tau}{W_2} \simeq \frac{D_3 A_{21}^{(2)} \tau}{|\Omega_{23 \tau}|^2 - \delta_2^2}.
\] (4.11)

Since \( |D_3| \ll |W_2| \) this means that \( x_{21} \) is very small, like a dark state, except for two sharp peaks that occur at \( \delta_2 = \pm |\Omega_{23}| \) where the resonant denominator \( W_2 \) goes to zero. These two peaks are the members of the Autler–Townes doublet. The frequency separation between the two members of the doublet is frequently referred to as the “transparency window”. Thus, what has been achieved here is a two-photon induced transparency for the laser at \( \omega_{L 2} \). Indeed, if one solves the Maxwell equation for the laser field at \( \omega_{L 2} \), one will reach the conclusion that there is negligible absorption of the first laser when it is tuned to the line center of the level \( |2 \rangle \), exactly as the conventional three-state one-photon on resonance type of EIT [72–74].

For large \( z \) where \( \kappa_{13} \tau (\gamma_2 + \gamma_1 + 2 \Gamma_1 \tau) / (2 |\Omega_{23 \tau}|^2) \gg 1 \) and three-photon destructive interference is effective, one has \( M \approx 1 \) and from Eq. (4.10) \( x_{31} \approx 0 \). Using this relation in Eq. (4.7a), one obtains
\[
x_{21} = -\frac{A_{21}^{(2)}}{D_2},
\] (4.12)

which is exactly what would be obtained with \( \Omega_{23} = 0 \), indicating there is no coupling between states \( |2 \rangle \) and \( |3 \rangle \). With no coupling between \( |2 \rangle \) and \( |3 \rangle \) there can be no splitting in the \( |1 \rangle - |2 \rangle \) resonance. Consequently, sufficiently deep into the medium the ionization near the two-photon resonance shows no evidence of the Autler–Townes splitting and the two-photon induced transparency near the Autler–Townes splitting disappears. That is, a new, three-photon destructive interference is effective, and the corresponding inverse transform of Eq. (4.10) \( x_{31} \approx 0 \). Using this relation in Eq. (4.7a), one obtains
\[
x_{21} = -\frac{A_{21}^{(2)}}{D_2},
\] (4.12)

which implies that excitation to the FWM generating state \( |3 \rangle \) has been strongly suppressed at large \( z \), and the FWM field subsequently propagates freely in a highly absorptive and dispersive medium as if the medium was not there.

It is interesting to note that in this region of high pressure and large \( z \) where the three-photon destructive interference is effective, by substituting \( x_{31} = 0 \) and \( x_{21} = -\frac{A_{21}^{(2)}}{D_2} \) into Eq. (4.6c) one obtains
\[
\rho_{22} = \frac{2 \gamma_2 \tau}{(\delta_2 \tau)^2 + (\gamma_2 \tau)^2} \int_{-\infty}^{1/\tau} (dt') e^{-(\gamma_2 \tau + \gamma_1 \tau) t' (t' - t)/\tau} |\Omega_{21}^{(2)}(z, t'/\tau)|^2,
\] (4.14)

which is exactly what is expected for \( \rho_{22} \) in the absence of any coupling between states \( |2 \rangle \) and \( |3 \rangle \). Multiplying \( \rho_{22} \) by the concentration \( N_0 \) and the ionization rate \( \gamma_1 \) yields the ionization per unit volume in the laser beam. Thus, the MPI spectra also have Lorentzian line shapes, showing no effect of large optical shifts or Autler–Townes splitting, provided
Fig. 24. Left figure: MPI signal vs the wavelength of the first laser in co-propagating beams. Bottom trace: the second laser is blocked. Middle trace: the second laser is red-detuned by $10 \text{ cm}^{-1}$. Top trace: the second laser is blue-detuned by $10 \text{ cm}^{-1}$. There is no a.c. Stark shift observable. Right figure: MPI signal vs the wavelength of the first laser in counter-propagating beams. Top trace: the second laser is blocked. Middle trace: the second laser is red-detuned by $10 \text{ cm}^{-1}$. Bottom trace: the second laser is blue-detuned by $10 \text{ cm}^{-1}$. A large a.c. Stark shift are clearly seen in the two lower traces. The pressure is 5 Torr in both figures. Reproduced from [59] with permission.

the power density of the laser at $\omega_{L1}$ is kept at levels just sufficient to give a detectable MPI signal (typically a few thousand photoelectrons per laser pulse).

With counter-propagating laser beams the destructive interference will not occur, but there will be small shifts induced in the Autler–Townes doublet due to the effects discussed earlier on excitations with counter-propagating laser beams. One expects that the optical shift and Autler–Townes doublet will persist at all propagation depth and over a large range of concentrations when the counter-propagating laser beams are used.

It should be pointed out that there was no surprise that the three-photon destructive interference occurred when the first laser was tuned to exact resonance. After all, in this situation the large splitting leads to adiabatic following of $\rho_{21}$. Indeed, with $\rho_{21} \simeq 0$ (zero in lowest order adiabatic theory) state $|2\rangle$ is a “two-photon dark state”. However, the three-photon coupling between $|1\rangle$ and $|3\rangle$ is greatly enhanced by the two-photon resonance until the absorption of the FWM removes the second exponential term in this field (see Eq. (4.9)), thereby bringing about the destructive interference.

The effects on large optical shifts and Autler–Townes splittings described here were first predicted by Payne et al. [57] and were demonstrated for both two- and four-photon resonances by Deng et al. in a series experiments in 1994 and 1995. Fig. 24 [59,60] shows the first demonstration of the suppression of large optical shifts by odd-photon based destructive interference in the presence of a four-photon resonance. Here, the first laser was tuned near a four-photon resonance of Xe between the ground state $|1\rangle = |5P^6(J = 0)\rangle$ and an excited state $|2\rangle = |5p56p[1/2](J = 0)\rangle$, while the second laser was near one-photon resonance between states $|2\rangle = |5p56p[1/2](J = 0)\rangle$ and a lower excited state $|3\rangle = |5p56s[3/2](J = 1)\rangle$ which has dipole allowed transition back to the ground state. Both laser beams were focused to $250 \mu \text{m}$ to achieve four-photon excitations by the first laser and to generate large a.c. Stark shifts in the state $|2\rangle$ by the second laser. In the counter-propagating beams and with in the pressure range of $P = 1–250 \text{ Torr}$, a large a.c. Stark shifts can be clearly seen (Fig. 24b). In the co-propagating beams, however, no a.c. Stark shift due to the second laser
was detected (Fig. 24a). In this pressure region, the destructive interference between excitation pathways $|1\rangle - |3\rangle$ and $|1\rangle - |2\rangle - |3\rangle$ is so effective for co-propagating beams that it produces a pressure and power broadened line shape that exhibits no a.c. Stark shift even though the second laser was very intense and was tuned very close to a strong one-photon resonance.

An interesting yet very important piece of evidence that confirms the suppression due to destructive interference involving the generated field was demonstrated by Deng et al. [60], shown in the data of Fig. 25. In this study, Deng et al. compared a.c. Stark shift or lack of it using the set of transitions described above with a different set of transitions in Xe where the generation of FWM field is forbidden in co-propagating beam configuration. Indeed, the persistence of the a.c. Stark shift in co-propagating beam configuration where the FWM generation is forbidden (Fig. 25 right panel) demonstrates the importance of the generated field and the second excitation pathway it creates (Fig. 25 left panel). Without it there will be no destructive interference and the a.c. Stark shift will not be suppressed.

Fig. 26 demonstrates the suppression of Autler–Townes splitting of a two-photon transition by three-photon destructive interference. In this experiment, rubidium atomic vapor was used because of the large fine structure separation $\Delta \bar{\nu}_{\text{fs}} \simeq 240 \text{ cm}^{-1}$ between the $5p[1/2]$ and $5p[3/2]$ levels. With such large separation one can study the FWM process involving the $5p[3/2]$ level up to concentrations at which the interference occurs while neglecting the phase mismatch due to the $5p[1/2]$ fine structure level since the Autler–Townes splitting produced are sufficiently small compared with the fine structure splitting. The two-photon coupling between the ground states $|1\rangle = |5S[1/2]\rangle$ and $|2\rangle = |6d[3/2, 5/2]\rangle$ was provided by the first laser, whereas the Autler–Townes splitting was produced by a second, much more intense laser coupling states $|2\rangle = |6d[3/2, 5/2]\rangle$ and $|3\rangle = |5p[3/2]\rangle$. The latter state has large oscillator strength for the transition back to the ground state. At very low concentration and with the second laser turned off, the first laser produced two ionization peaks when scanned cross the region of state $6d$, (the top panel in Fig. 26). These two peaks correspond to transitions to $6d[3/2]$ and $6d[5/2]$. The latter level was used to produce an Autler–Townes splitting whereas the former provides a good calibration marker for the concentration of the vapor. When the second
laser was on, a large Autler–Townes splitting was produced in the $6d_{5/2}$ level and can be seen in both co-propagating (Fig. 26a) and counter-propagating (Fig. 26c) beam geometries. As the concentration was increased, however, the large Autler–Townes splitting remained in the counter-propagating beams geometry (Fig. 26d) but completely disappeared from the co-propagating beams geometry (Fig. 26b), leaving an ionization signal of pressure broadened atomic line shape as if the second laser was not there.

As has been shown in Eq. (4.13), the further excitation to the FWM generating state, therefore the generation of the FWM, is strongly suppressed when the three-photon destructive interference is effective. This prediction was first given by Payne et al. and was first demonstrated experimentally by Deng et al. [61–63]. Fig. 27 shows the behavior of the FWM field that was simultaneously measured with the photoionization signal described above. At low concentration, the generated field is weak and the destructive interference is ineffective. In this region the intensity of the generated wave grew quadratically, a well-known behavior (see the inset of Fig. 27). At high concentration where the three-photon destructive interference is effective the production of the generated field ceases to grow because of the strong suppression due to a three-photon destructive interference to the FWM generating state $|3\rangle$. Correspondingly, both the Autler–Townes splitting and the two-photon induced transparency disappear. The generated field travels thereafter dispersion free in a highly dispersive medium.

A key element demonstrated in the these experiments is the establishment of multi-photon destructive interference based two- and three-photon induced transparencies or in general, multi-photon induced transparency. These novel induced transparency effects are critically dependent upon the propagation of the internally generated fields, where a part of the generated fields must be strongly absorbed in order to make the three-photon destructive interference effective. Consequently, the population in the three-photon driven state, i.e., the FWM generating state, becomes independent of the concentration and propagation distance. In addition, the production and the absorption of the FWM field become independent of the concentration and propagation distance. As the result, the FWM field can propagate...
Fig. 27. FWM signal vs. \( P(\text{Torr})/T(\text{K}) \). Dashed curve: theoretical result based on the theory of three-photon destructive interference. Insert: low concentration behavior. The data shown in the insert is fitted with a quadratic curve. Reproduced from [61–63] with permission.

for an extended length of the medium without any appreciable attenuation. In Section 5, these novel properties will be further explored in the context of highly efficient multi-wave mixing processes in the presence of multi-photon induced transparencies.

Before leaving this subsection it should be pointed out that the multi-photon induced transparency effects described above, although were never directly demonstrated or pointed out before, were implied in the original experiments where the suppression of the photo-ionization signals was first observed. In the original three-photon ionization experiments, the destructive interference between a three-laser-photon pumping and a one-TH-photon pumping lead to vanishing excitation of the upper state where the ionization was originated. The fact that the population in this state is zero is indicative that this state is driven transparent by the two out-of-phase excitations. A complete destructive interference necessarily leads to the conclusion of a complete induced transparency. Indeed, should a set of optical fields satisfying the relation given in Eq. (4.13) have been injected in to the medium, one would have found that the field at frequency \( \omega_m \) would propagate through the medium losslessly even though it is very close to a strong one-photon transition.

4.1.2. Suppression of forward stimulated hyper-Raman (SHR) and optically pumped stimulated emissions (OPSE) by three-photon destructive interference

In the three-state model investigated in the last subsection, the first leg of the excitation sequence is a two-photon pumping of the state \( |2\rangle \). One of the facets of such a two-photon pumping is the strong tendency, when there is an optically allowed transition to a lower level \( |3\rangle \), of spontaneous-emission-initiated stimulated emission processes, such as SHR emission or OPSE. Consider a case where the laser at \( \omega_{L1} \) is the only external field. This scheme distinguishes itself from what have been reviewed so far in that more than one field is internally generated, as in SHR scattering process. The combined lasers and the internally generated fields (usually long wavelength fields in infrared) will act together to create a polarization at \( \omega_m \), leading to the generation of a wave-mixing field of shorter wavelength. Consequently, destructive interference effects may be present under certain conditions. Indeed, early experiments on SHR emission confirmed predictions that the same odd-photon destructive interference that suppressed odd-photon resonant laser-based excitation of allowed transitions would significantly diminish the gain for SHR emission [31,40,42,46,87] and OPSE [45,50] processes in the direction of the driving fields. That is, the effectiveness of the destructive interference acquires an “apparent polarity” in the sense of laser propagation direction. This was the first demonstration of the influence of a wave-mixing interference in a new context, i.e., in a coherent stimulated emission process.

The treatment of a wave-mixing interference involving a stimulated emission is more complicated than the problems considered and treated so far in this review in that the generation of two new electromagnetic fields must be treated self consistently and on an equal footing, by solving Maxwell’s equations for two separate frequencies, with polarizations generated by the atomic response at these frequencies. As a first step in the treatment of this process, a simplistic model of SHR generation near a two-photon resonance is presented here, followed by discussions of experimental studies and verifications of some most intriguing predictions. In the first instance it will be assumed that state \( |3\rangle \),
undergoing excitation by SHR scattering, does not have optically allowed transitions back to the ground state $|1\rangle$ (Fig. 28a). This simplest case exhibits the correct characteristic gain for a HR process. In the subsection following this simplistic treatment, a treatment is presented of the case where the optical transition $|3\rangle - |1\rangle$ back to the ground state is allowed. It is shown that the forward and backward HR components have very different characteristics with different interference effects. The forward SHR gain is canceled whereas a pressure dependent frequency shift is present in the backward stimulated electronic hyper-Raman emission/scattering (SEHRS). The treatment is then extended to describe similar behavior in OPSE.

4.1.2.1. Formulation of Stimulated hyper-Raman problems

(i) The SHR case where optical transition $|3\rangle - |1\rangle$ is not allowed

In this simplest case, with reference to Fig. 28a, it is assumed that the laser at $\omega_{L1}$ is the only external field and it is tuned near the two-photon resonance between states $|1\rangle$ and $|2\rangle$. It is further assumed that a spontaneously emitted HR photon at a frequency corresponding to near one-photon resonance between $|2\rangle$ and $|3\rangle$ is emitted parallel to the input laser beam. With the laser and this weak HR field propagating together one now considers the possibility that state $|3\rangle$ will become populated and the weak HR field will grow, since every time an excited atom in state $|3\rangle$ is produced there must be a HR photon generated. This is because the three-photon excitation process involves the absorption of two photons at $\omega_{L1}$ and a stimulated emission of a photon at $\omega_{L2} = \omega_{HR}$.

Now in a layer of the resonance medium with thickness of $\Delta z$, consider the number of excited atoms generated per unit time per unit area in state $|3\rangle$ as a result of the laser and the HR radiation passing through this thin layer. This rate will be equal to the increase in the flux, $F_{HR}$, of HR photons in passing between $z$ and $z + dz$. Thus, one gets

$$dF_{HR} = N_0 dz \frac{\partial \rho_{33}}{\partial t}. \quad (4.15)$$

To proceed further, two principal assumptions are made at this point in order to determine the rate of change of the population of $|3\rangle$ with respect to time. First, it is assumed that the laser is tuned far enough from two-photon resonance so that $|\delta_2 \tau + i(\gamma_2 + \gamma_L + 2\Gamma_{21})\tau/2| \gg \text{Max}(|\Omega_{21}^{(2)}\tau|, 1)$. This assumption permits one to adiabatically eliminate state $|2\rangle$ and look at the excitation of $|3\rangle$ as the result of simultaneous absorption of two photons and a stimulated emission of a HR photon. Second, it is assumed that the relaxation rate of the $|1\rangle - |3\rangle$ coherence is rapid, thereby allowing a rate for three-photon excitation of the state $|3\rangle$ to be calculated as

$$\frac{\partial \rho_{33}}{\partial t} = 2 \frac{\Omega_{31}^{(3)}|^2}{\Gamma_3}, \quad (4.16)$$
where \( \Gamma_3 \tau \gg 1 \) represents all of the relaxation effects that occur in the equation for \( \rho_{31} \). The three-photon half Rabi frequency can be written as

\[
\Omega^{(3)}_{31} = \frac{\Omega^{(2)}_{21} \Omega_{32}}{\delta_2},
\]

(4.17)

where the half Rabi frequency \( \Omega_{32} \) is that of the SHR field. Combing Eqs. (4.15)–(4.17) one gets

\[
\frac{\partial F_{HR}}{\partial z} = 2N_0 \frac{|\Omega^{(2)}_{21}|^2}{\delta_2^2} |\Omega^{(1)}_{32}|^2 = 2\kappa_{32} \frac{|\Omega^{(2)}_{21}|^2}{\delta_2^2} \Gamma_3 F_{HR},
\]

(4.18)

where the HR photon flux \( F_{HR} \equiv N_0 |\Omega_{32}|^2 / \kappa_{32} \) has been used.

Eq. (4.18) shows an exponentially growing flux of HR photons as a function of propagation distance \( z \), and a corresponding growth of population in state \( |3\rangle \). This is the gain that usually arises from a susceptibility and Maxwell’s equations treatment of this process.

The above described process will change if state \( |3\rangle \) has optically allowed transitions back to the ground state. In this case the generation of a wave-mixing field and OPSE/ASE, due to \( \rho_{31} \), and the corresponding occurrence of a three-photon destructive interference must be considered. This leads to the possibility that a suppression of any forward HR field may occur because of the close relation between forward HR generation and the three-photon excitation discussed in Section 3.1. In the next subsection, it will be shown that this is indeed what occurs.

(ii) The SHR case where optical transition \( |3\rangle - |1\rangle \) is allowed

In the case where dipole coupling of \( |3\rangle - |1\rangle \) is allowed (Fig. 28b), one must consider implications due to this coupling. As before, negligible ground state depletion is assumed in the following treatment. In addition, the spatial extent of the laser pulses are assumed to be much longer than the length of the gas cell. This latter assumption allows the possibility of significant gain for either forward or backward HR fields generated during the process. For clarity, the one-photon Rabi frequencies for the transition \( |2\rangle - |3\rangle \) due to forward (+) and backward (−) propagating HR fields are here-after separately designated by \( 2\Omega_{23}^{(\pm)} \). Correspondingly, the phase mismatch \( \Delta K \) for each propagation direction are separately defined as

\[
\Delta K = \frac{\omega_1}{c} [n_0(\omega_m) - 1] - 2 \frac{\omega_{L1}}{c} [n(\omega_{L1}) - 1] + \frac{\omega_{HR}}{c} [n(\omega_{HR}) - 1] \simeq 0, \quad \text{(forward SHR)},
\]

\[
\Delta K = \frac{\omega_1}{c} [n_0(\omega_m) - 1] - 2 \frac{\omega_{L1}}{c} [n(\omega_{L1}) - 1] + \frac{\omega_{HR}}{c} [-n(\omega_{HR}) - 1] \simeq - \frac{2\omega_{HR}}{c}, \quad \text{(backward SHR)},
\]

with the frequencies satisfying \( 2\Omega_{L1} = \omega_m + \omega_{HR} \). From the general set of equations (4.2) the following linearized equations for the density matrix elements \( \rho_{mn} \) and the wave-mixing field \( \Omega_{31} \) describing the processes depicted in Fig. 28b can be obtained

\[
\frac{\partial \rho_{21}}{\partial T_r} = id_2 \rho_{21} - i\Omega_{31} \tau \rho_{23} + i\Omega_{21}^{(2)} \tau + i(\Omega_{23}^{(2)} \tau e^{i\Delta K} + \Omega_{23}^{(2)} \tau e^{-2i\omega_{HR}/c}) \rho_{31},
\]

(4.19a)

\[
\frac{\partial \rho_{31}}{\partial T_r} = id_3 \rho_{31} - i\Omega_{21}^{(2)} \tau \rho_{32} + i\Omega_{31} \tau + i(\Omega_{32}^{(2)} \tau e^{-i\Delta K} + \Omega_{32}^{(2)} \tau e^{2i\omega_{HR}/c}) \rho_{21},
\]

(4.19b)

\[
\frac{\partial \rho_{32}}{\partial T_r} = id_3 \rho_{32} + i\Omega_{31} \tau \rho_{12} - i\Omega_{12}^{(2)} \tau \rho_{31},
\]

(4.19c)

where \( d_2 \) and \( d_3 \) are defined in Eq. (4.6) and \( d_{32} = -\delta_2 \tau + i\Gamma_4 \tau \). In addition, \( |\delta_3| \ll |\delta_2| \) has been assumed. Indeed, if it were not for a pressure dependent frequency shift that will be shown to occur for the backward propagating hyper-Raman, the value of \( \delta_3 \) would have been set to zero.

In order to solve this SHR problem an additional approximation will be invoked, namely we will seek a steady state solution to the equations of motion. This approximation has not been applied in previous sections which were somewhat less complicated than the present case. With the stated assumptions it is straightforward to obtain the solutions for \( \rho_{21} \) and \( \rho_{31} \) in a steady-state approximation and under the additional condition \( |\delta_2| \gg \Gamma_2 \) and \( |\delta_2| \gg \Gamma_4 \) (these conditions can
be removed in an inert gas with $P > 300$ Torr for some cases because of large relaxation rates and therefore accurate adiabatic following). One has

$$\rho_{21} = -\frac{\Omega_{21}^{(2)} r}{d_2} - (\Omega_{23}^{(+) r} e^{i\Delta K z} + \Omega_{23}^{(-) r} e^{-2i\omega_{HR} z/c}) \rho_{31},$$

(4.20)

and

$$\rho_{31} = -\frac{\Omega_{31} r}{(\delta_3 - A_3) r + i\Gamma_3 r} + \frac{\Omega_{31}^{(+) r} e^{-i\Delta K z} + \Omega_{31}^{(-) r} e^{2i\omega_{HR} z/c}) \Omega_{21}^{(2) r}}{d_2[(\delta_3 - A_3) r + i\Gamma_3 r]},$$

(4.21)

where $A_3 = (|\Omega_{23}^{(+) r}|^2 + |\Omega_{23}^{(-) r}|^2)/d_2 = A_3^{(+) r} + A_3^{(-) r}$ is the a.c. Stark-shift-like term in $|3\rangle$ due to both the components of the HR field. Note that $\rho_{31}$, which is proportional to the induced polarization, also has separate terms due the forward and backward SHR fields.

Now Maxwell’s equations must be simultaneously solved for the two SHR fields $\Omega_{23}^{(\pm)}$ and the corresponding two wave-mixing fields $\Omega_{31} = \Omega_{31}^{(+)} + \Omega_{31}^{(-)}$. Note that in the present case, the laser and HR fields travel at group velocities close to $c$, and the wave-mixing fields are strongly absorbed since the HR process terminates on resonance. Thus, at elevated concentrations the wave-mixing fields are generated locally (mean-free-path is less than $\lambda_m$) and it too can be taken to have a group velocity $c$ in this “local” generation. Thus, all fields are assumed to propagate at $c$. The SVA equation for field at $\omega_m = 2\omega_{L1} - \omega_{HR}$ is

$$\left( \frac{\partial \Omega_{31}}{\partial z} - T_r \right) e^{i\kappa_{13} \rho_{31}} = \frac{\kappa_{13}}{T_r + i(A_3 - \delta_3) T} \left[ \frac{\Omega_{21}^{(2) r} \Omega_{32}^{(+) r} e^{-i\Delta K z} + \Omega_{32}^{(-) r} \Omega_{21}^{(2) r} e^{2i\omega_{HR} z/c}}{d_2[(\delta_3 - A_3) r + i\Gamma_3 r}] - \Omega_{31} \right].$$

(4.22)

Note that the inhomogeneous term contains contributions from co-propagating (i.e., the forward component $\Omega_{32}^{(+)}$) and counter-propagating (i.e., the backward component $\Omega_{32}^{(-)}$) SHR fields with very different phase factors. Thus, these two sources generate fields $\Omega_{31}^{(+)}$ and $\Omega_{31}^{(-)}$ almost independently. Consequently, to a good approximation, Eq. (4.22) can be broken into two separate equations with each one containing only one type of source term. If this is done, solutions for the forward field $\Omega_{31}^{(+)}$ and the backward ($-\Delta z$) propagating field $\Omega_{31}^{(-)}$ can be found as

$$\Omega_{31}^{(+)} = \frac{\Omega_{32}^{(+)} \Omega_{21}^{(2) r}}{d_2} \left[ e^{-i\Delta K z} - e^{-i\kappa_{13} z / [(\delta_3 - A_3) r + i\Gamma_3 z]} \right],$$

(4.23a)

$$\Omega_{31}^{(-)} = K \frac{\Omega_{32}^{(-)} \Omega_{21}^{(2) r}}{d_2} \left[ e^{2i\omega_{HR} z/c} - e^{-i\kappa_{13} z / [(\delta_3 - A_3) r + i\Gamma_3 z]} \right],$$

(4.23b)

where

$$K = \frac{\kappa_{13} c / (2\omega_{HR})}{(\delta_3 + \kappa_{13} c / (2\omega_{HR}) - A_3 + i\Gamma_3).}$$

When the a.c. Stark shifts are not too large and $\Delta z$ is large enough so that the second exponential terms inside the brackets in Eqs. (4.23a,b) are negligible, the above relations simplify considerably. If the backward propagating HR is neglected, one has a wave-mixing field solution with phase driven by the forward SHR field only. This forward part is

$$\Omega_{31}^{(+)} = \frac{\Omega_{32}^{(+)} \Omega_{21}^{(2) r}}{d_2} e^{-i\Delta K z}.$$

(4.24)

If this result is inserted into Eq. (4.21) one immediately obtains the result that the forward part $\rho_{31} = \rho_{31}^{(+)} = 0$. Thus, a destructive interference between the three-photon pumping by the laser plus the forward HR field and the one-photon coupling due to the wave-mixing field has occurred. The polarization that is phased for production of forward
SHR vanishes. However, with both forward and backward components of the HR fields included, since the forward component vanishes, one gets, at large enough $z$

$$\rho_{31} = \frac{\Omega_{32}(-) \tau \Omega_{21}^{(2)} \exp(2i\omega_{HR} z/c) \tau}{d_2^* |\Omega_{21}^{(2)}|^2} = \frac{\Omega_{32}(-) \tau \Omega_{21}^{(2)} \exp(2i\omega_{HR} z/c) \tau}{d_2 d_{31}},$$

(4.25)

where $d_{31} = \delta_3 \tau - A_3 + \kappa_{13c}/(2\omega_{HR}) + i\Gamma_3 \tau$. Thus, the coherence $\rho_{31}$ is not zero but driven by the backward HR field. This coherence supports the growth of the backward propagating wave-mixing field.

To calculate the SHR fields $\rho_{HR}^{(\pm)} \equiv \Omega_{23}^{(\pm)}$ from the wave equation for each of these fields one must find the part of $\rho_{23}$ that has phase factor $\exp(i\Delta K z)$ for the forward propagating HR field and the part of $\rho_{23}$ that has phase factor $\exp(-2i\omega_{HR} z/c)$ for the backward propagating HR field. These components serve as the correct polarization-source terms for the two HR emissions. Thus, the two wave equations can be written in the forms

$$\left( \frac{\partial \Omega_{23}^{(+)}(z)}{\partial z} \right)_{Tr} = i\kappa_{32} \rho_{23}^{(+)} \exp(-i\Delta K z), \quad \left( \frac{\partial \Omega_{23}^{(-)}(z)}{\partial z} \right)_{Tr} = i\kappa_{32} \rho_{23}^{(-)} \exp(2i\omega_{HR} z/c),$$

(4.26)

where $\rho_{23}^{(\pm)}$ is the part of $\rho_{23}$ with the phase factor $\exp(i\Delta K z)$ and $\exp(-2i\omega_{HR} z/c)$, respectively. Using the steady-state solution of Eq. (4.19c) for $\rho_{23}$, one obtains $\rho_{32} \simeq \Omega_{12}^{(2)} \rho_{31}/d_{32}$ where $\rho_{31}$ is given in Eq. (4.21). After collecting terms for $\rho_{32}^{(+)}$, one arrives at the wave equation for the forward propagating component of the HR field

$$\left( \frac{\partial \Omega_{23}^{(+)}(z)}{\partial z} \right)_{Tr} = -i\kappa_{32} \frac{|\Omega_{21}^{(2)}|^2}{d_3^* (\delta_2 \tau + i\Gamma_4 \tau)} \Omega_{23}^{(-)},$$

(4.27)

Notice that there is no exponential growth for the forward propagating part of the SHR field, even at $\delta_2 = 0$. This is the direct consequence of the three-photon destructive interference.

For the backward propagating component of the HR field, one has

$$\left( \frac{\partial \Omega_{23}^{(-)}(z)}{\partial z} \right)_{Tr} = -\frac{i\kappa_{32} \tau S |\Omega_{21}^{(2)}|^2}{d_2^* (\delta_2 \tau + i\Gamma_4 \tau) (A_{3e}^* + \kappa_{13c} \tau / (2\omega_{HR}) - A_3^* \tau)} \Omega_{23}^{(-)},$$

(4.28)

where $S = 1 + \kappa_{13c} \tau / (2\omega_{HR} d_2)$. The largest gain occurs at the pressure shifted resonance position $\delta_3 = -\kappa_{13c} / (2\omega_{HR})$ as indicated by the resonant denominator (neglecting $A_3$, which is much smaller at small signal). It is worth pointing out that if this resonance is corrected for the difference between the local field seen by the atoms and the space averaged field the shift becomes $\delta_3 = -1.11 A_0 - \kappa_{13c} / (2\omega_{HR})$, where $A_0$ has been defined in Eq. (3.15). Evaluated at the peak gain Eq. (4.28) becomes

$$\left( \frac{\partial \Omega_{23}^{(-)}(z)}{\partial z} \right)_{Tr} = \frac{i\kappa_{32} \tau S |\Omega_{21}^{(2)}|^2}{d_2^* (\delta_2 \tau + i\Gamma_4 \tau) (A_{3e}^* \tau + i\Gamma_3 \tau)} \Omega_{23}^{(-)},$$

(4.29)

Eq. (4.29) can be expressed in terms of the flux of HR photons, analogous to Eq. (4.18). That is,

$$\frac{\partial F_{HR}^{(-)}(z)}{\partial z} = \frac{2\kappa_{32} S |\Omega_{21}^{(2)}|^2}{\delta_2^2 \Gamma_3^2 (1 + R^2)} F_{HR}^{(-)},$$

(4.30)

where

$$R = \frac{\kappa_{32} F_{HR}^{(-)}}{N_0 \delta_2 \Gamma_3},$$

where $|\delta_2| \gg \gamma_2$ and $|\delta_2| \gg \gamma_4$ have been used. In addition, small $F_{HR}^{(+)}$ has been neglected from the expression of $R$ since the forward component is strongly suppressed by the destructive interference, as evident in Eq. (4.27).

It is instructive to examine the $R \ll 1$ and $R \gg 1$ limits. At small $(L - z)$ (where $z$ is the propagation distance for the laser field and $L$ is the length of the medium, remember that the backward HR travels from the cell exit back to
Thus, in this high intensity region the backward HR photon flux does not grow exponentially. Instead, the gain is limited by the SHRS-induced Stark shifting and the intensity of SEHRS at the “exit window” (note that the “exit” for the backward propagating field is the entrance of the cell, therefore $z = 0$ in Eq. (4.33)) satisfies $I_{\text{HR}}^{(-)} = \sqrt{C_1 + C_2 P I_{L1}^2}$, where $C_1$ and $C_2$ are two constants. At higher pressures and power densities beyond where this onset occurs, $C_1$ will be small as compared to the $C_2 P I_{L1}^2$ term. Then $I_{\text{HR}}^{(-)} = \sqrt{C_2 P I_{L1}}$. This relation shows the $I_{\text{HR}}^{(-)} \propto \sqrt{P}$ when $I_{L1}$ is fixed and $I_{\text{HR}} \propto I_{L1}$ when $P$ is fixed.

It should be noted that Eq. (4.30) can be easily solved analytically, yielding a solution

$$
\ln \left[ \frac{F_{\text{HR}}^{(-)}(z)}{F_{\text{HR}}^{(-)}(0)} \right] + \left[ \frac{\kappa_{32}}{2N_0 \delta_2 \Gamma_3} F_{\text{HR}}^{(-)}(z) \right]^2 - \left[ \frac{\kappa_{32}}{2N_0 \delta_2 \Gamma_3} F_{\text{HR}}^{(-)}(0) \right]^2 = \frac{2\kappa_{32} S |\Omega_{21}^{(2)}|^2 L}{\delta_2 \Gamma_3}.
$$

In deriving this solution an assumption has been made that the initial flux satisfies $F_{\text{HR}}^{(-)}(0) = c/(AL)$ where $A$ is the laser beam cross-section. This assumption implies that initially there is one photon generated from a spontaneous HR process and this photon travels in the $-z$ direction.

In general, as the HR field grows in magnitude an appreciable a.c. Stark shift develops for the state $|3\rangle$. Thus, the HR field eventually grows to a magnitude such that it a.c.-Stark-shifts the resonance and limits the gain.

It is also interesting to examine the case where two-photon pumping occurs exactly on two-photon resonance, that is, where $\delta_2 = 0$. With assumptions of sufficiently high pressure so that approximations introduced are valid and in the limit of small signal theory ($A_{\lambda} = 0$), one obtains from Eq. (4.30)

$$
\left( \frac{\partial \Omega_{23}^{(-)}}{\partial z} \right)_{T_c} = \frac{\kappa_{32} S |\Omega_{21}^{(2)}|^2 \Omega_{23}^{(-)}}{\Gamma_2 \Gamma_3 \Gamma_4}.
$$

Note that the $\delta_2 = 0$ limit represents OPSE, also referred to as ASE instead of HR emission. Here, $S = 1 - i\kappa_{13} c/(2\omega_{\text{HR}} \Gamma_2)$. Thus one has a more general conclusion that there is no SHR or OPSE in the forward direction, though there is substantial gain for SHR and ASE in the backward direction. In addition, there is a pressure induced shift in the backward SHR and OPSE which should be corrected by the Lorentz shift, as explained earlier.

4.1.2.2. Experimental results exhibiting interference effect in SHR emissions and OPSE The first experimental observation of interference-based suppression of forward SHR emission was made in Na vapor by Moore et al. [31,38] and Garrett et al. [46]. In the experiments a laser was tuned near the 3s–4d $|3/2, 5/2\rangle$ and 3s–4d $|3/2, 5/2\rangle$ two-photon resonances with power densities of a few MW/cm$^2$ in a heat pipe oven of about 20 cm length. Forward and backward axial emissions were collected with equal collection efficiencies and spectrally recorded. Fig. 29 shows the results for
3d–3p SHR emissions at 2 Torr Na pressure. Clearly, the data exhibits very strong suppression of forward vs backward SHR profiles. Because of pressure limitations in a heat pipe oven, the pressure dependent shift, $\kappa_{13c}/(2\omega_{HR})$, of Eq. (4.28) was not easily measured. However, in subsequent experiments in Xe, Garrett et al. [41] easily verified the pressure dependent frequency shifts in SHR emissions associated with two-photon pumping near the $6P'[3/2]_2$ state. They also observed that the associated HR scattering produced excitation of the lower lying $6S'[1/2]_1$ state.

The first experiments on SHR suppression also revealed additional features of the process. They showed suppression/saturation behavior beyond the destructive interference in forward emission. Indeed, the backward SHR emissions are strongly influenced by a.c. Stark shifts, as well as being shifted by the interference effect (the pressure-dependent shift). Here, both of these features are quantitatively described.

For SEHRS generated through the $4d[5/2] - 4p[3/2]$ transition while the two-photon transitions are driven between $3s$ and $4d[5/2]$ in Na, the growth should be exponential as long as $|\delta_2| > \delta_{2c}$, where $\delta_{2c}$ is defined to satisfy

$$\frac{\kappa_{32} F_{HR}(L)}{N_0 \delta_{2c} I_3} = 1.$$ 

Physically, $\delta_{2c}$ corresponds to a critical detuning at which the growth of the SEHRS flux has just changed its characteristics from exponential to linear dependence on the propagation distance at the exit window where $z = L$. Once $|\delta_2| \ll \delta_{2c}$, the gain of the SEHRS will be dominated by the a.c. Stark shifts in state $|3\rangle$ due to this field, and Eq. (4.33) applies. Fig. 30 shows the backward HR energy per pulse versus energy per pulse of the laser. The solid line is a linear relation between the two, demonstrating the limiting effect of the a.c. Starks shifts, as predicted by Eq. (4.33). Fig. 31a shows the pressure dependence of the backward SEHRS signal with the laser intensity being fixed. Note that this behavior also agrees with Eq. (4.33).

The other outstanding feature of the SHR profiles is the “detuning widths” as a function of Na density, i.e., width of the emission profiles as a function of laser detuning from two-photon resonance. Once $|\delta_2| > \delta_{2c}$ even a 10% increase in detuning from two-photon resonance causes a very substantial decrease in SEHRS. This is because that the behavior is exponentially dependent on $1/\delta_{2c}^2$, and 20% of 30 or more e-folds is a substantial decrease. Eq. (4.33) can be used to estimate the FWHM of the SEHRS as a function of detuning from two-photon resonance. Graphically, the half width at half maximum is $\sqrt{3}\delta_{2c}/2$, so that the full width is

$$\delta_2^{FW}[\text{cm}^{-1}] = \sqrt{3}\delta_{2c} \simeq 3 \times 10^{-7} I_L [\text{W/cm}^2] \sqrt{P_{Na}[\text{Torr}]}.$$ 

(4.35)
Fig. 30. Energy per pulse, as a function of incident laser intensity, of backward stimulated hyper-Raman emission associated with pumping near the $4D$ states. $\lambda_{HR} \simeq 2.3 \mu m$. $P_{Na} = 0.07$ Torr. The solid line is a curve of slope $= 1.0$. Reproduced from [46] with permission.

Fig. 31. Upper figure: Intensity of the SHR emission as a function of Na pressure for fixed laser power. Solid line is the predicted $\sqrt{P_{Na}}$ form. Lower figure: effective width of the SHR emission profile as a function of Na pressure. Laser power density is $2.2 \times 10^7$ W/cm$^2$ at beam center. Solid line is the theoretically predicted $\sqrt{P_{Na}}$ form. Reproduced from [46] with permission.

Intuitively, the inclusion of the radial intensity profile will decrease the proportionality constant in Eq. (4.35) somewhat, but the general order of magnitude and the functional dependence given in Eq. (4.35) should be correct. In Fig. 31b the actual measured gain width versus $P_{Na}$ is shown. The solid line represents a fit with $const. \times \sqrt{P_{Na}}$, which is in general agreement with the expected behavior given in Eq. (4.35).

Caution should be made at this point that the omission of Doppler shifts and the likelihood of deviations from the steady-state approximation in calculating $\rho_{31}$ make the above formulation a poor approximation for most low pressure experimental studies in alkali metals. However, it should be appropriate for cases with HR generation when a laser is tuned near a two-photon resonance in Xe at pressures of 100 Torr or above. For instance, the OPSE/ASE treatment is probably only correct when $P > 300$ Torr. It should also be pointed out that the absence of forward HR is not dependent
**Fig. 32.** Scans of Xe $6p'(3/2)(J = 2) \rightarrow 6s'(1/2)(J = 1)$ OPSE at pressures, from right to left, of 20, 100, 200, 400, 600, and 800 Torr. The emission profile shifts to shorter wavelengths as Xe pressure is increased while other parameters are held constant. Inset: depiction of the three-level model for the OPSE process. Reproduced from [50] with permission.

on using a steady-state approximation in calculating $\rho_{31}$. However, the derivation of the proper gain for the backward HR field is tractable only in a steady-state treatment.

As noted in arriving at Eq. (4.34) the suppression of forward SHR emission can (under proper circumstances) be extended to similar behavior involving OPSE (also referred to as ASE). This is the case where the laser is tuned to an exact two-photon resonance. Currently there is no valid theory applicable to OPSE studies in low pressure alkali metals, but in the case of noble gases the relaxation rates $Γ_3$ and $Γ_4$ are easily larger than the Doppler widths before 100 Torr is reached. Thus, with a narrow bandwidth laser $ρ_{31}$ and $ρ_{23}$ adiabatically follow the driving field. Note that the $|1⟩ - |2⟩$ resonance requires pressures of around 300 Torr before pressure broadened widths make the Doppler width of the transition unimportant. The theory presented here predicts that there will be no forward OPSE in the proper pressure region due to the familiar destructive interference between the excitation by the wave-mixing field and the excitation by the direct three-photon pumping by laser fields. The important point is that memory effects can be subverted in the $|1⟩ - |2⟩$ resonance by the fast relaxation of coherence of the off-diagonal elements of the density matrix. That is, the fast relaxation leads to adiabatic following which preserves the memory of coherence, thus allowing coherent processes such as destructive interference. It is reasonable to suspect that this theory will work for multi-mode lasers as well, since in the linearized theory, each mode can be viewed as a narrow bandwidth source and the system response is the sum of the responses due to the individual modes. Thus, with a multi-mode laser the forward OPSE should still be suppressed. The gain that includes a detuning from two-photon resonance can be deduced from Eq. (4.29) and the backward gain for a multi-mode laser can be determined by superposition within the linearized theory in which there should be no depletion of the ground state population. For a narrow-bandwidth laser, however, the gain of the backward OPSE is given by Eq. (4.30).

Two studies by Garrett et al. focused on near-resonant [41] and resonant [50] two-photon pumping of the $5p - 6p'(3/2)_2$ transition in Xe. This was achieved with a 6-ns pulse length laser utilizing Coumarine 450 dye output at 448.6 nm doubled in barium borate crystal to obtain 900 μJ of light at 224.3 nm. The tunable light was injected into a gas cell through quartz windows, with the forward and backward propagating output from the cell being analyzed using a 0.5-m spectrometer operated at 0.09 nm resolution. The dominant backward emission was shown to be resulted from the $6p'(3/2)_2 - 6s'(1/2)_1$ backward SHR and OPSE processes, whereas the forward emissions were strongly suppressed. In order to obtain easily measurable signals, long focal length lenses were used to analyze the pressure dependent shifts. (This, seems to have introduced some small additional shift into the data.) Fig. 32 shows OPSE line shapes measured at six different pressures of Xe. Note that the shifts, unlike those in the study of Ferrell et al. [19], are much larger than the pressure broadened width. In Fig. 33 the shift $Δ_{\text{shift}} = -1.11K_{13}/(2ω_m) - K_{13}/(2ω_{HR}) = -(K_{13}/(2ω_{HR}))(1 + 1.11ω_{HR}/Ω_m)$ is compared with the shifts observed with 5, 10, and 20 cm focal length lenses.

Intuitively and theoretically speaking, the same suppression mechanism should hold for higher order wave-mixing interferences. Indeed, results for a five-photon SHR process confirmed the prediction. Fig. 34 shows forward suppression...
Fig. 33. Measured shift of OPSE as in Fig. 32, at Xe pressures from 10 to 800 Torr. Data are for focused pump beams with focusing lenses of 20 cm (triangles), 10 cm (circles), and 5 cm (squares). The dashed line is the shift predicted for unfocused beam pumping. Reproduced from [50] with permission.

Fig. 34. Scan of Na 4d pumping demonstrating parametric six-wave mixing (PSWM) and five-photon hyper-Raman processes. Upper trace: forward directed axially phase-matched PSWM process. Lower trace: backward propagating five-photon hyper-Raman emissions associated with the excitation of \( 3p[1/2] \) and \( 3p[3/2] \) states. Reproduced from [38] with permission.
of $3d-3p$ emissions when stimulated by two-photon pumping near the $4d$ state in Na at 3 Torr. The gain for forward emission is suppressed in this instance by destructive interference from six-wave mixing [38].

What has been treated so far in this subsection is a new type of destructive interference involving two-photon resonant excitation and SHR generation. The suppression of the forward directed SHR emission is due to three-photon destructive interference at the third level in the SHR generation scheme. In the next subsection, a different type of even-photon interference involving parametric FWM will be analyzed in detail.

### 4.2. Two-photon destructive interference in three-level systems

In all of the previous sections of this review the effects of wave-mixing fields on multi-photon induced processes have all involved quantum levels that were simultaneously coupled by two pathways: one by an odd-photon coupling and the other by a one-photon path (the wave-mixing path). It has been shown that the coupling by these two pathways can destructively interfere under a variety of circumstances. However, as mentioned in the introduction, the first realization of interference due to a transition being simultaneously coupled along two pathways was actually made in a second category of the phenomenon. This was the discovery by Manykin and Afanas’ev [32] that destructive interference could occur when two levels are coupled by two separate two-photon pathways. Here the two interfering paths occur near the resonant frequency for an even parity (two-photon) transition. The conditions for destructive interference are quite different for the pair of two-photon branches as compared to the coupling by two odd-photon branches. This second category will be subject of review in this subsection.

#### 4.2.1. Influence of two-photon interference on parametric four-wave mixing (PFWM) in gases

Consider a multi-photon process where a laser at $\omega_{L,1}$, being tuned very near a two-photon resonance between states $|1\rangle$ and $|2\rangle$, is the only external field. In this situation multiple internally generated fields can be produced (Fig. 35a).

There can be either a forward or backward emitted spontaneous HR photon that starts up the SHR process, as discussed in the previous subsection. There can also be a separate spontaneous down-conversion process where simultaneous spontaneous emissions of two photons occur. In this alternative process, also referred to as a parametric FWM (PFWM) process, no excitation of the third level occurs. Both generated photons propagate in the direction of the laser beam and have just the right frequencies to take the atoms back to the ground state while simultaneously satisfy the phase matching condition necessary for this parametric process to have high gain. Most often phase matching is achieved through conical emission of the pair of generated photons, whereby, the $k$-vectors of the two laser photons are balanced by a proper conical propagation angle for the parametric waves. However for certain systems having suitable dispersion properties at the PFWM frequency, phase matched production can occur for both parametric photons traveling parallel to the input beam. This is described as axial PFWM as opposed to conical PFWM. It was first described through
experiments in Na vapor [38] and later observed again in Na [43], potassium [44], and lithium vapors [42]. This process can occur when a two-photon resonance is pumped by two-photons \(2\omega_{L1}\) and two generated photons with frequencies \(\omega_{L2}\) and \(\omega_m\) can be produced, such that

\[
2\omega_{L1} = \omega_{L2} + \omega_m,
\]

with frequencies \(\omega_{L2}\) and \(\omega_m\) such that the additional condition

\[
\frac{\omega_{L2}}{c} n(\omega_{L2}) + \frac{\omega_m}{c} n(\omega_m) - \frac{2\omega_{L1}}{c} n(\omega_{L1}) = 0
\]

is satisfied. The last relation is the phase matching condition. As will be explained below, this can occur in certain media that exhibit special dispersive characteristics for the generated fields.

4.2.1.1. Theoretical treatment of co-axial PFWM problem Consider a situation where the PFWM has started up from noise but with just the right mix of frequencies for the two parametric waves to achieve co-axial phase matching. This process is possible, e.g., in a system as depicted in Fig. 35b. Co-axial propagation is required since angular phase matching is achieved by Moore et al. [31,38]. In addition, analysis has shown that the observed “suppression effect” by Malcuit et al. [28] is due to a lack of coherence, or the laser is detuned from the \(|1\rangle - |2\rangle\) resonance so that \(|Q_{12}\tau| \ll |d_2|\) and \(|d_2| \gg 1\). In addition, the concentration and \(|\delta_3|\) are such that absorption on the wing of the \(|1\rangle - |3\rangle\) resonance can be neglected. With these assumptions, and with \(|\delta_3|\gg|\delta_2|\), it is then possible to use the adiabatic following approximation to determine accurate values for \(\rho_{21}\), \(\rho_{31}\), and \(\rho_{23}\). These steady-state solutions of Eq. (4.2) can expressed as

\[
\rho_{21} = -\frac{Q_{21}^{(2)} \tau + Q_{23} \tau e^{i\Delta K \tau} \rho_{31}}{d_2},
\]

\[
\rho_{31} = -\frac{Q_{31} \tau + Q_{32} \tau e^{-i\Delta K \tau} \rho_{21}}{d_3},
\]

\[
\rho_{32} = -\frac{Q_{31} \rho_{12} - Q_{12}^{(2)} \tau \rho_{31}}{d_{32}},
\]

where \(d_2\) and \(d_3\) are defined in conjunction with Eq. (4.6) (also see Eq. (4.3)), and \(d_{32} = \delta_3\tau + i(\gamma_2 + \gamma_1 + \gamma_3 + 2\Gamma_3)\tau/2\) where \(|\delta_3| \gg |\delta_2|\) has been applied. Here

\[
\Delta K = \frac{\omega_m}{c} [n_0(\omega_m) - 1] + \frac{\omega_{L2}}{c} [n(\omega_{L2}) - 1] - \frac{2\omega_{L1}}{c} [n(\omega_{L1}) - 1],
\]

and in the present context \(\omega_{L2} = \omega_{IR}\) and \(\omega_m = \omega_{UV}\). This notation is chosen since the applications to follow involve generation of infra-red and UV photons.

As mentioned above we restrict ourselves to cases where co-axial phase matching is achievable. It is much harder to find proof of two-photon destructive interference in situations where angle phase matched PFWM dominates. In fact, \textit{no such proof exists to date}. It should be noted that there are experimental studies where some of the present assumptions may not apply. However, the clarity and simplicity of the treatments based on these assumptions serve the purpose of providing a cleaner and easy-to-follow picture of the key features of these complex processes.
With the above described assumptions, Eqs. (4.36a–c) yield

\[ \rho_{21} = -\frac{\Omega_{21}^{(\text{eff})} \tau}{d_2[1 - (|\Omega_{23}\tau|^2/d_2d_3)]}, \]

(4.37a)

\[ \rho_{31} = -\frac{\Omega_{31}\tau}{d_3} + \frac{\Omega_{32}\tau\Omega_{21}^{(\text{eff})}\tau e^{-i\Delta z}}{d_2d_3 - |\Omega_{23}\tau|^2}, \]

(4.37b)

\[ \rho_{23} = \left( \frac{d_3}{d_{32}} \right)^* \frac{\Omega_{21}^{(\text{eff})}\tau\Omega_{13}\tau}{d_2d_3 - |\Omega_{23}\tau|^2}, \]

(4.37c)

\[ \Omega_{21}^{(\text{eff})}\tau = \Omega_{21}^{(2)} e^{-i\Delta z\Omega_{23}\tau\Omega_{31}\tau}/d_3. \]

(4.37d)

Neglecting the imaginary parts of \(d_3\) and \(d_{32}\) systematically (because \(|\delta_3|\) is much larger than all \(I^\prime\)’s), assuming the speed of propagation is close to \(c\) for laser and all generated fields, and noting that \(\Omega_{21}^{(2)}\) depends only on \(T_r\), one arrives at the wave equations for the generated fields (see Eqs. (4.5a,b) and note that \(\omega_{L2} = \omega_{IR}\) and \(\omega_m = \omega_{UV}\))

\[ \left( \frac{\partial \Omega_{23}}{\partial z} \right) \bigg|_{T_r} = i\kappa_{32}\tau e^{-i\Delta z\Omega_{21}^{(\text{eff})}\tau\Omega_{13}\tau}/d_2\delta_3 - |\Omega_{23}\tau|^2, \]

(4.38a)

\[ \left( \frac{\partial \Omega_{31}}{\partial z} \right) \bigg|_{T_r} = -i\kappa_{13}\Omega_{31}\tau/d_3\delta_3 + i\kappa_{13}\Omega_{32}\tau\Omega_{21}^{(\text{eff})}\tau e^{-i\Delta K z}/d_2\delta_3 - |\Omega_{23}\tau|^2. \]

(4.38b)

Letting \(W_{31} = \Omega_{31}\tau e^{i\kappa_{13}z/\delta_3} = W_{31}^*\) and \(W_{23} = \Omega_{23}\tau\), noting that PFWM process requires phase-matched condition (i.e., \(\Delta k = 0\), or \(\Delta K = k_{13}/\delta_3\)), and neglecting any absorption of the light at \(\omega_{UV}\), one can rewrite Eqs. (4.38a,b) as

\[ \frac{\partial W_{31}}{\partial z} = i\kappa_{13}\tau \frac{\Omega_{21}^{(\text{eff})}\tau W_{32}}{d_2\delta_3\tau - |W_{23}|^2}, \]

(4.39a)

\[ \frac{\partial W_{23}}{\partial z} = i\kappa_{32}\tau \frac{\Omega_{21}^{(\text{eff})}\tau W_{13}}{d_2\delta_3\tau - |W_{23}|^2}. \]

(4.39b)

These are nonlinear equations for the pair of generated PFWM fields \(\Omega_{23} = \Omega_{IR}\) and \(\Omega_{31} = \Omega_{UV}\). Note that the “effective” two-photon Rabi frequency \(\Omega_{21}^{(\text{eff})}\) is comprised of a two-photon Rabi frequency due to laser pumping, \(\Omega_{21}^{(2)}\), and a negative term which is a two-photon Rabi frequency due to the two parametric fields, multiplied by a phase factor.

Now in the PFWM process the frequencies of the two generated fields are restricted only by the value of their sum \((2\omega_{L1} = \omega_m + \omega_{L2} \equiv \omega_{UV} + \omega_{IR}\)). But those frequencies correspond to phase matched wave generation are dominate since only the fields satisfying phase matching conditions have much higher gain. Thus the value of \(\delta_3\) that gives \(\Delta k = 0\) (i.e., \(\Delta K = k_{13}/\delta_3\)) determines the dominant pair of output frequencies. When axial phase matching is allowed, the gain length is very long as compared to conical generation (at other frequencies). Therefore, axial emission at phase matching strongly dominates the PFWM.

From Eq. (4.37d) one immediately sees the possibility of cancellation of the two terms, resulting in a two-photon destructive interference. This indeed can occur since the two fields represented by \(\Omega_{23}\) and \(\Omega_{31}\) can grow in magnitude to appropriate amplitudes to offset the first term due to the laser field. Indeed, when \(\Omega_{21}^{(\text{eff})} = 0\) is first reached, one has \(\rho_{12} = 0\), \(\rho_{31} = -\Omega_{31}\tau/d_3\), and \(\rho_{23} = 0\). These lead to \(\Omega_{21}^{(\text{eff})} = \Omega_{21}^{(2)} = e^{i\Delta K z\Omega_{23}\Omega_{31}/(\delta_3 + iI')}\) where the phase mismatch is \(\Delta k = \Delta K - k_{13}/\delta_3\) with the PMFW detuning \(\delta_3\) being fixed by the phase matching requirement. When phase matching is achieved one has \(\Delta k = 0\). Thus the \(z\)-dependent phase factor is canceled out, resulting a propagation independent, as it must be, two-photon destructive interference by the two pathways contained in \(\Omega_{21}^{(\text{eff})}\).
From Eqs. (4.39a,b) it is trivial to show that

$$\frac{\partial}{\partial z} \left( \frac{|W_{31}|^2}{k_{13}} - \frac{|W_{23}|^2}{k_{32}} \right) = 0.$$ (4.40)

For the parametric fields starting from noise this implies

$$|W_{31}| = \sqrt{k_{13}/k_{32}}|W_{23}|.$$ (4.41)

The two terms in Eq. (4.40) are each proportional to the photon flux of the respective PFWM field. That the two fluxes are equal is a direct result of the fact that these photons are always created in pairs. Hence, in the absence of significant absorption there are equal numbers of photons at the two frequencies, all traveling in the same direction at a speed close to $c$.

It is insightful to inspect the solutions to Eqs. (4.39a,b) when the parametric fields are small. Indeed, taking $Q_{21}^{(\text{eff})} \approx Q_{21}^{(2)}$ and assuming that $|d_2\delta_3\tau| \gg |Q_{23}\tau|^2$, one gets two coupled linear equations that have exponentially increasing solutions as a function of $z$. The small signal gain for both equations is found to be

$$g = \frac{\sqrt{k_{13}\kappa_{32}}|Q_{21}^{(2)}\tau|}{|d_2||\delta_3\tau|}.$$ (4.42)

Thus, the initial growth of the PFWM fields is exponential in nature.

The behavior of the nonlinear components can be analyzed by considering the start up of the generated fields with one photon at each of the two PFWM field frequency modes. One then asks when the nonlinear contribution to $Q_{21}^{(\text{eff})}$, i.e., the second term in Eq. (4.37d), from the medium becomes important. A simple analysis shows that one will need about $10^{14}$ photons at each frequency for the second term in $Q_{21}^{(\text{eff})}$, which is due to the parametric fields, to become comparable to the $Q_{21}^{(2)}$ which is a laser-driven term. Thus, after 34 e-folds of gain the PFWM fields become important in the nonlinear response. This implies that even at a point where a 33-e-fold gain has been achieved, this nonlinear term is still relatively unimportant. That is to say, the linear equations hold for about 97% of the depth of penetration required before the nonlinear contribution to the gain becomes appreciable. Note that when well phase matched, the phases of the $W_{23}$ and $W_{31}$ do not change in the linear regime. The amplitude just grows proportionally and exponentially with $z$.

Near the regime where the contribution from the nonlinear terms start to become important, PFWM fields quickly changes its character and becomes independent of $z$. Inspection of Eqs. (4.39a,b) clearly indicates that with the condition of $|d_2\delta_3\tau| \gg |Q_{23}\tau|^2$ it is $Q_{21}^{(\text{eff})} = 0$ that dominates the effectiveness of the nonlinearity. Thus, one is mostly interested in the situation that corresponds to $Q_{21}^{(\text{eff})} = 0$. This situation has very clear and important physical meaning: the two-photon Rabi frequency due to the PFWM fields destructively interferes with the two-photon Rabi frequency due to the laser field. It is because of this importance that the following analysis of the behavior of Eqs. (4.39a,b) focuses on a solution near this region of two-photon cancellation.

In order to investigate what to expect when the nonlinear terms start to become important, the behavior of solutions of Eqs. (4.39a,b) can be examined when the solution at a particular $z$ is near the “singular point” of the system. The term “singular point” implies that $Q_{21}^{(\text{eff})} = 0$ in Eq. (4.37d) and subsequently in Eqs. (4.39a,b). This is precisely the condition for two-photon destructive interference since at the “singular point” one has $\rho_{21} = 0$ (see Eq. (4.37a)). The following method of analyzing the solution of differential equations near the “singular point” was given by French mathematician Henri Poincaré about 90 years ago.

In the vicinity of the “singular point”, one writes the solution of Eqs. (4.39a,b) as

$$W_{31} = W_{31}^{(0)} + \epsilon_{31},$$ (4.43a)

$$W_{23} = W_{23}^{(0)} + \epsilon_{23},$$ (4.43b)
where $W_{31}^{(0)}$ and $W_{23}^{(0)}$ are the values of $W_{31}$ and $W_{23}$ at the “singular point”, therefore $W_{23}^{(0)} W_{31}^{(0)} / (\delta_3 \tau) = \Omega_{21}^{(2)}$. The small quantities $\epsilon_{31}$ and $\epsilon_{23}$ satisfy

$$\frac{\partial \epsilon_{31}}{\partial z} = -i z [W_{23}^{(0)} \epsilon_{31} + W_{31}^{(0)} \epsilon_{23}] \left( \frac{W_{23}^{(0)}}{W_{31}^{(0)}} \right),$$

(4.44a)

$$\frac{\partial \epsilon_{23}}{\partial z} = -i z [W_{23}^{(0)} \epsilon_{31} + W_{31}^{(0)} \epsilon_{23}],$$

(4.44b)

with

$$\alpha = \frac{\kappa_{32} \tau W_{31}^{(0)}}{(\delta_3 \tau)(d_2 \delta_3 \tau - |W_{23}^{(0)}|^2)}.$$

Now, if the “singular point” and the nearby point are both along a real solution curve in the solution space of the nonlinear equations and if these fields grew from noise one should have $\epsilon_{31}/\epsilon_{23} = W_{31}^{(0)}/W_{23}^{(0)}$. One sees immediately that this ratio is consistent with the equations for $\epsilon_{31}$ and $\epsilon_{23}$. Using this relation, Eqs. (4.44a,b) are decoupled, giving

$$\frac{\partial \epsilon_{31}}{\partial z} = -2i \frac{\kappa_{13} |W_{23}^{(0)}|^2}{(\delta_3 \tau)(d_2 \delta_3 \tau - |W_{23}^{(0)}|^2)} \epsilon_{31},$$

(4.45a)

$$\frac{\partial \epsilon_{23}}{\partial z} = -2i \frac{\kappa_{32} |W_{31}^{(0)}|^2}{(\delta_3 \tau)(d_2 \delta_3 \tau - |W_{23}^{(0)}|^2)} \epsilon_{23}.$$

(4.45b)

Notice that the denominators in parameter $\alpha$ and in Eqs. (4.45a,b) contain $d_2$ which has a positive imaginary part. Thus, the real part of the coefficients of $\epsilon_{31}$ and $\epsilon_{23}$ are negative, resulting in both $\epsilon_{31}$ and $\epsilon_{23}$ decay to zero as $z$ is increased. If the imaginary part of $d_2$ is considerably larger than the real part, the solution will be mostly an exponential decay to the “singular point”, and the solution is said to be a “fast destructive interference seeker”. On the other hand, if the laser for the two-photon transition is detuned from the two-photon resonance by an amount that is much larger than the combined width of the transition due to spontaneous decay, ionization rate, and collisional dephasing rate of the $|1 \rangle - |2 \rangle$ transition, the approach to the “singular point” will be slow and contain a rapidly oscillating complex exponential, thus termed as “slow destructive interference seeker”. This picture of what happens when one gets close to the situation where the two-photon cancellation occurs is found to be an accurate one when it is checked by numerical solutions to this system of nonlinear differential equations. Fig. 36 shows an example of a numerical solution to the nonlinear equations (4.39a,b).

Another manifestation of the two-photon destructive interference described above can also be argued similarly. Notice that when $\Omega_{21}^{(eff)} = 0$ one has $\rho_{21} = 0$ also, which leads to $\rho_{22} = 0$. Thus, if the PFWM were the only nonlinear process, then deep in the medium where the “singular point” of the system of differential equations has been reached there should also be a suppression of the enhancement to photoionization due to the two-photon resonance. The absence or presence of a two-photon resonantly enhanced MPI signal has not been established experimentally. This is partly due to the problems and difficulties with making ionization measurements in an alkali vapor environment.

It is worth pointing out an important difference between the two-photon destructive interference discussed here and the three-photon destructive interference review in the previous sections. The two-photon destructive interference in the PFWM process occurs only when the phase matching is fulfilled. On the other hand, it has been shown in Section 3.2 that three-photon destructive interference does not occur in the phase matching region.

In order to verify some of the predicted influences of the two-photon interference phenomenon on PFWM process, Wunderlich et al. [40] and later Garrett et al. [46] carried out experiments in Na vapor specifically designed to test some of the predicted behavior. Fig. 35b shows an energy level diagram appropriate to the $3s-4d$ [3/2, 5/2] two-photon resonance in the experimental studies [40,46]. This scheme was chosen because co-axial phase-matched PFWM process is operative [38] in this instance. The interference behavior is predictable only under this circumstance.

In the context of experimental verification of predicted results, let us consider the signature experimental tests for two-photon destructive interference in co-linearly phase matched PFWM process. Reasonably accurate comparison
with theoretical predictions require operation in a parameter region where the theory is valid. Population transfer must remain small since linearization in $\Omega_{21}^{(2)}$ neglects depletion of the ground state population.

First, the theory predicts that the onset of two-photon destructive interference should occur as a function of concentration (vapor pressure). Experimentally, the onset of two-photon destructive interference corresponds to $\Omega_{21}^{(2)} \tau = W_{23} W_{31} / (\delta_3 \tau) = 0$. When this occurs the product of $W_{23} W_{31}$ takes on a value that depends only on the power density of the laser, and therefore is independent of concentration for fixed laser intensity. Thus, if the laser power density is held fixed and the pressure is increased one will reach a point where quite suddenly the pressure dependence of the intensity of either parametric waves (i.e. the infrared (IR) or ultra-violet (UV) components) goes from being an exponential function of pressure to being pressure independent.

Second, neglecting absorption of the PFWM fields, the theory predicts that at fixed pressure, $\Omega_{21}^{(2)} \tau = W_{23} W_{31} / (\delta_3 \tau)$ implies that the intensity of either parametric wave is proportional to the intensity of the laser when two-photon destructive interference is operative. That is, when the two-photon destructive interference becomes operative the functional dependence of the intensity of either component of the PFWM output changes abruptly from exponential to a nearly linear behavior as a function of laser intensity. (This behavior will not be exactly linear as a function of the laser intensity in the actual experiments because of the absorption of the UV component of the PFWM.)

Finally, it is possible to predict fairly accurately where the onset of the two-photon interference will occur as a function of pressure and power density of the laser. The threshold for the interference will be reached when $\Omega_{21}^{(2)} \tau = W_{23} W_{31} / (\delta_3 \tau)$ at the exit end of the medium (at $z = L$, where $L$ is the length of the beam path in the medium). The magnitude of the fields (i.e. $W_{ij}$) at $z = L$ can be expressed as $W_{ij}(z = L) = W_{ij}(z = 0) e^{g L}$, where $g$ is the gain (which is the same for both fields). From Eq. (4.42) note that $g \propto N_0 L_1$. Thus, the interference condition is reached just at the exit (the threshold) when the following equation is satisfied

$$\frac{W_{31}(z = 0) W_{23}(z = 0) e^{2g L}}{\delta_3 \tau} = \Omega_{21}^{(2)} \tau.$$ 

A good approximation to the condition for the onset can be extracted from this relationship after noting that the RHS depends linearly on laser intensity while the LHS has the product of number density and laser intensity in an exponential. More specifically, one considers starting the process with values of $W_{31}$ and $W_{23}$ that correspond to
a single photon wave packet in each parametric frequency mode. One then attempts to find the gain needed to produce
enough parametric photons to match the value of the two-photon half Rabi frequency due to the parametric waves with
the two-photon half Rabi frequency due to the laser, i.e., $Q_{21}^{(2)}$.

Notice that the quantity in the exponent contains the product of pressure and laser power density. Thus, if the laser is
tuned on two-photon resonance, the only variable in the exponent is in the form of this product. Typically $I_{L1}$ will only
be changed by perhaps one or two orders of magnitude, yet during the buildup from noise to two-photon destructive
interference $e^{2gL}$ increases by more than 35 e-folds. Since a two-order of magnitude on the RHS corresponds to about
five e-folds on the LHS, one can get a general formula of 15–20% accuracy by putting a middle of the range value of
$I_{L1}$ into $Q_{21}^{(2)}$ and solving for the number of e-folds, $n_e$, required to reach interference. Thus, $2gL = n_e$ is a number
that is very insensitive to laser intensity. This gives $N_0 P I_{L1} = const.$ as a very acceptable relationship holding at the
threshold for two-photon cancellation. As an illustration of the appropriateness of the relationship, consider a factor of
2 change in laser intensity, the value of $2gL = n_e$ would need to change from $n_e = 35$ to 35.5 to satisfy the interference
condition, a change of only 1.5%, which is close to being constant, as expected.

4.2.1.2. Experimental studies of co-axial PFWM processes Prior to 1990, only one early gaseous phase experiment
had given signature evidence for the two-photon destructive interference effect. This is the work of Krasnikov
et al. [29]. In that study co-linearly phase matched four-wave sum-frequency mixing was produced while tuned onto
the $3S_{1/2} \rightarrow 4S_{1/2}$ two-photon resonance. One feature of the two-photon interference effect was demonstrated, as
described below. The experiment by Malcuit et al. [28] involving conical PFWM process did not show the signature
behavior of the two-photon destructive interference.

In the early 1990 Wunderlich et al. [40,46] reported a series of absolute measurements, demonstrating conclusively
the signature of the two-photon destructive interference with co-axially phase-matched Na vapor. The particular scheme
chosen to test the predicted behavior is depicted in Fig. 35b. Note that for frequency $\omega_{UV}$ the Na vapor exhibits its
full range of values of negative and positive dispersion between the fine structure components of the $p$ states. Thus
there is always a position between the $p$ substates where the dispersion of the output fields can match that of the
input laser fields in a co-propagating (axial) geometry [38]. Emissions associated with two photon pumping of the
$3S_{1/2} - 4S_{3/2}, 1/2$ transition were measured at pressures between 0.1 Torr $< P_{Na} < 5$ Torr using 6-ns pulses with
maximum energy per pulse of a few mJ and with an unfocused beam diameter of about 1 mm. The bandwidth of the
laser used was about 0.2 cm$^{-1}$. Forward and backward propagating (relative to the laser pulse) emission intensities were
measured with calibrated detectors and spectrally resolved. Angle phase matched conical emissions were discriminated
against by appropriate beam aperturing.

In their experiments, Wunderlich et al. [40,46] first quantitatively established that forward emissions indeed resulted
from co-axial PFWM processes. Fig. 37 shows spectrally resolved forward (Fig. 37a) and backward IR emissions
(Fig. 37b) from the Na heat pipe. For the backward emissions it was noticed that the 5.8 cm$^{-1}$ difference in frequency
coincides, within experimental accuracy, with the 5.6 cm$^{-1}$ separation between the $4p[1/2]$ and the $4p[3/2]$ fine
structure levels. Thus, this is the backward propagating HR or ASE. The forward propagating emissions with separation
of 7.0 cm$^{-1}$ are produced by PFWM process as evidenced by the fact that the separation of the two peaks coincides with
the two points where axial phase matching can occur on the blue side of the $4p[1/2]$ and $4p[3/2]$ levels. As expected,
no forward HR (or ASE) emissions (i.e., components separated by 5.8 cm$^{-1}$) are seen since the forward components are
suppressed by the three-photon interference as described earlier.

To see that the 7.0 cm$^{-1}$ separation is “just right” for PFWM involving two fine structure levels, note that the condition
for co-axial phase matching exists in this case. Since the medium is negatively dispersive at the laser wavelength
$\lambda_{L1} = 577.9$ nm (which is 307 cm$^{-1}$ on the blue side of the $3p[3/2]$ fine structure level), axial phase matching occurs
at frequencies where the dispersion of a photon at $\omega_{UV}$ matches that of two photons at $\omega_{IR}$ (the dispersion at $\omega_{IR}$ has
been neglected because of the assumption $n(\omega_{IR}) = 1$). The phase mismatch for the two laser photons is given by

$$2\Delta k_L = -2\frac{k_{3p} - 3p}{\delta_{3p}},$$

The phase matching condition is

$$\Delta k_{UV} + \Delta k_{IR} = 2\Delta k_L,$$
With this relation for the threshold of two-photon destructive interference the threshold pressure was found to be

Thus, the phase matching condition can be written as

where

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where \( 2F_{3s-3p} = 1.964 \), \( \delta_3 = 307 \text{ cm}^{-1} \), fine structure separation \( \Delta_{fs} = 5.6 \text{ cm}^{-1} \), \( F_{3s-4p[1/2]} = 0.00477 \), and \( F_{3s-4p[3/2]} = 0.0094 \). This is a quadratic equation for \( \delta_3 \) (in \text{ cm}^{-1} ) with one solution of \( \delta_3 = 0.65 \text{ cm}^{-1} \) above the \( 4p[1/2] \) fine structure level and another solution of \( \delta_3 = 7.31 \text{ cm}^{-1} \), which is \( 1.71 \text{ cm}^{-1} \) above the \( 4p[3/2] \) level. The difference between these two solutions is \( 6.67 \text{ cm}^{-1} \), which is close to the observed \( 7.0 \text{ cm}^{-1} \). Thus, the observations on the location of the peaks coincides well with the phase matched co-propagating laser and PFWM beams. Additional evidence is found in the correlated emission strengths of the UV and IR components. In detuning from two-photon resonance the intensities of the UV and IR beams rose and fell together indicating that the number of generated photons for the two frequencies must be the same.

From carefully calibrated measurements of the IR and UV PFWM output, direct comparison could be made between the calculated two-photon Rabi frequencies and the measured two-photon Rabi frequency of the laser. Extensive measurements were made of the pressure dependence of these outputs at different laser intensities, allowing the verifications of whether these two two-photon Rabi frequencies are nearly equal as required for two-photon destructive interference. Figs. 38a and b show the total IR (2.33 \text{ \mu m} ) and UV (330.3 \text{ nm}) forward axial emissions as a function of \( P_{Na} \). It should be noted that \( I_{IR} \) had become pressure independent by 0.4 Torr. Here the laser was tuned 1.2 cm\(^{-1}\) to the blue side of two-photon resonance and the laser power density was 35 MW/cm\(^2\). The absolute measurements of the intensity of the IR field gave \( I_{IR} = 1.7 \times 10^7 \text{ W/cm}^2 \), while for the UV field the measurements gave \( I_{UV} = 4.6 \times 10^5 \text{ W/cm}^2 \). Taking the appropriate experimental parameters for these Na data, one then has \( \Omega_{21}^{(2)} = 350I_{L1} [ \text{W/cm}^2 ] \), \( \Omega_{23} = 5.0 \times 10^8 \sqrt{I_{IR} [ \text{W/cm}^2 ]} \), \( \Omega_{31} = 2.0 \times 10^7 \sqrt{I_{UV} [ \text{W/cm}^2 ]} \), and \( N_0 = 1.3 \times 10^{16} P_{Na}. \) The product of pressure and laser intensity that corresponds to the threshold of two-photon destructive interference can then be found as

\[
P_{Na} [ \text{Torr} ] I_{L1} [ \text{W/cm}^2 ] = 2.28 \times 10^6 \sqrt{1 + (\delta_2 [\text{cm}^{-1}]/0.2)^2} [\text{Torr W/cm}^2].
\]

With this relation for the threshold of two-photon destructive interference the threshold pressure was found to be \( P_{Na} = 0.42 \text{ Torr}. \) This is about the point where the IR and the UV intensities have risen to 90% of their limiting...
Fig. 38. (a) Na pressure dependence of the forward axial component of the 2.33 μm emission. Pump laser intensity is 35 MW/cm², δ₂ = 1.2 cm⁻¹ on the high energy side of the 4d resonance; (b) output of the UV components of the axial PFWM process as a function of Na pressure for a fixed laser frequency. Pump laser intensity is 34.0 MW/cm², δ₂ = 0.1 cm⁻¹ on the high energy side of the 4d resonance. Reproduced from [40,46] with permission.

Fig. 39 shows the behavior of the forward axial IR component when the pressure is held fixed and the laser intensity changed. As expected, there is a sudden change in functional form at a critical laser intensity where the IR intensity shows approximately linear behavior at the higher laser power densities. At this point both the IR and UV components of the PFWM are each directly proportional to laser intensity. This is a clear signature of the two-photon interference. These cases agree fairly well with the predictions based on the simple theory described above. In Fig. 39a where δ₂ = 0 and P_{Na} = 2 Torr, the calculated value for the onset laser intensity is I_{L1} = 2.28 \times 10^6/2 = 1.14 MW/cm², which is quite close to the value obtained from the graph. In Fig. 39b, δ₂ = 0.35 cm⁻¹ and P_{Na} = 2 Torr. The threshold is estimated to occur at about 4.15 MW/cm², which agrees well with the 4 MW/cm² taken from the graph.

values as shown in Figs. 38a and b. Thus, there is good agreement between the prediction and the experimental observation.

Fig. 39 shows the behavior of the forward axial IR component when the pressure is held fixed and the laser intensity changed. As expected, there is a sudden change in functional form at a critical laser intensity where the IR intensity shows approximately linear behavior at the higher laser power densities. At this point both the IR and UV components of the PFWM are each directly proportional to laser intensity. This is a clear signature of the two-photon interference. These cases agree fairly well with the predictions based on the simple theory described above. In Fig. 39a where δ₂ = 0 and P_{Na} = 2 Torr, the calculated value for the onset laser intensity is I_{L1} = 2.28 \times 10^6/2 = 1.14 MW/cm², which is quite close to the value obtained from the graph. In Fig. 39b, δ₂ = 0.35 cm⁻¹ and P_{Na} = 2 Torr. The threshold is estimated to occur at about 4.15 MW/cm², which agrees well with the 4 MW/cm² taken from the graph.
Krasnikov et al. [29], in the first experiment study on two-photon interference effect, showed saturation with pressure of sum-frequency generation near $\lambda_{UV} = 330.0$ nm in Na vapor and termed the resulting two-photon interference phenomenon as “parametric brightening”. Their results were similar to the behavior in Fig. 39, though the figures were mis-labeled and mis-numbered.

Agarwal et al. [90] studied a quantum model for a similar PFWM process and discussed the statistical characteristics of the generated fields. Considering the mathematical similarity between this process and the parametric down-conversion process in solids such as nonlinear crystals, it is not surprising that co-axially phase matched PFWM fields are “squeezed” light and that some of the statistical properties of the light are effected by the two-photon destructive interference. Baker [91] discussed the consequences that destructive interference effects have on the statistics of internally generated fields for both two-photon destructive interference and odd-photon destructive interferences. His treatment of this problem [91] assumes a steady-state situation which permits a solution without the necessity of solving simultaneous differential equations for operator quantities. The treatment given here, being semi-classical, is closer to the original treatment by Manykin and Afanasev [32]. There have been several other treatments [30,92,93] of two-photon destructive interference associated with PFWM processes since the first study by Manykin and Afanasev [32].

### 4.2.2. Effect of two-photon cancellation on FWM processes

In this subsection another effect of two-photon cancellation on wave-mixing process will be discussed. This effect was originally predicted by Kildal and Brueck [94] and has been studied experimentally by Smith et al. [95] As will be shown that unlike the odd-photon destructive interferences, which is effective only when non-phase matched wave-mixing occurs, the two-photon variety requires that the related wave-mixing field be phase matched, as shown in the previous subsection. The key element in these two-photon interference problems is that the two-photon Rabi frequency due to the lasers destructively interferes with a different two-photon Rabi frequency involving at least one internally generated field. As will be seen that this interference can have a profound effect on the efficiency of a FWM generation scheme involving an intermediate two-photon enhancement.

Consider a FWM scheme where the first laser is tuned very near or onto a two-photon resonance between states $|1\rangle$ and $|2\rangle$, while a second laser is tuned in such a way that the combined excitation by these two laser fields is somewhat near a three-photon resonance so that proper phase matching is achieved (by the use of a properly chosen amount of positively dispersive buffer gas). Consequently, a FWM field can be efficiently generated. An appropriate energy-level diagram is given in Fig. 35a where the second laser has the frequency of $\omega_{21}$. The combination of the buffer gas and detuning of the second laser will be chosen so that the FWM process is phase-matched relatively far from resonance between states $|1\rangle$ and $|3\rangle$ to minimize the absorption of the FWM field generated. Readers may have already recognized that this condition is contrary to the case described in Section 3 where the second laser should be tuned near resonance between $|1\rangle$ and $|3\rangle$, a condition where substantial absorption of the wave-mixing field and large phase mismatch occur.

Technically, by using proper concentration ratios of a mixture of buffer gas to the resonant medium one can achieve phase-matching over a wide range of detunings, $\delta_3$, while still retain large nonlinear enhancements due to both two- and three-photon resonances.

The equations of motion for the present system can be easily obtained from Eqs. (4.6a–e)

\[
\frac{d\rho_{21}}{dT_f} = id_2\rho_{21} + i\Omega_{21}^2 \tau + i\Omega_{23}^2 e^{i\Delta K z} \rho_{31}, \tag{4.46a}
\]

\[
\frac{d\rho_{31}}{dT_f} = id_3\rho_{31} + i\Omega_{31} \tau + i\Omega_{32} e^{-i\Delta K z} \rho_{21}, \tag{4.46b}
\]

\[
\frac{d\rho_{22}}{dT_f} = -(\gamma_2 + \gamma_I)\rho_{22} - 2 \text{Im}[\Omega_{21}^2 \tau \rho_{12}], \tag{4.46c}
\]

\[
\frac{d\rho_{33}}{dT_f} = -\gamma_3\rho_{33} - 2 \text{Im}[\Omega_{31} \tau \rho_{13}], \tag{4.46d}
\]

\[
\left( \frac{d\Omega_{31} \tau}{dz} \right)_{T_f} = i\kappa_{13} \tau \rho_{31}, \tag{4.46e}
\]

where $d_2$ and $d_3$ are defined as in Eq. (4.6).
Assume that $|\delta_3 \tau| \gg 1$, $|\delta_3 \gg |\Omega_{L2}|$, but $|\Omega_{23}|^2/|\delta_3| \gg 1/\tau$ or $(\gamma_2 + \gamma_I + 2\Gamma_{21}) \tau/2 \gg 1$. These assumptions make a steady-state approximation applicable in solving for both $\rho_{21}$ and $\rho_{31}$, giving

$$
\rho_{21} = -\frac{\Omega_{21}^{(2)} \tau d_3 - \Omega_{23} \tau \Omega_{31} \tau e^{i\Delta K z}}{d_2 d_3 - |\Omega_{23}|^2},
$$

(4.47a)

$$
\rho_{31} = -\frac{\Omega_{31} \tau d_2 - \Omega_{32} \tau \Omega_{21}^{(2)} \tau e^{-i\Delta K z}}{(d_2 d_3 - |\Omega_{23}|^2)}. \quad (4.47b)
$$

In the actual experiments, one typically has $\delta_3 \gg \gamma_3$. Thus, by choosing the ratio of gas pressures to achieve exact phase matching, i.e., $\Delta K = k_{13}/\delta_3$, and by neglecting a small absorption term (that can be kept without changing the conclusions), one has

$$
\Omega_{31} = \frac{\Omega_{21}^{(2)} \tau d_3}{\Omega_{23} \tau} \left[ e^{-i\Delta K z} - e^{-ik_{13} \tau z d_2/(d_2 d_3 - |\Omega_{23}|^2)} \right]. \quad (4.48)
$$

At sufficiently high concentration and depth of propagation so that Re$[iK_{13} \tau z d_2/(d_2 d_3 - |\Omega_{23}|^2)] \gg 1$, one gets

$$
\Omega_{31} = \frac{\Omega_{21}^{(2)} d_3}{\Omega_{23} \tau} e^{-i\Delta K z} \rightarrow \Omega_{21}^{(2)} \tau - \frac{\Omega_{23} \tau \Omega_{31} \tau}{d_3} e^{i\Delta K z} = 0. \quad (4.49)
$$

Eq. (4.49) demonstrates the canceled excitation to the state $|2\rangle$ by a two-photon pumping from the laser at $\omega_{L1}$ (i.e., $\Omega_{21}^{(2)}$) and the two-photon pumping by a FWM photon plus a photon from the laser at $\omega_{L2}$ (i.e., $\Omega_{31} \Omega_{23}/\delta_3$). When this result is inserted into Eq. (4.47a), it follows that $\rho_{21} = 0$. That is, these two excitation pathways have destructively interfered to yield no coherence between $|1\rangle$ and $|2\rangle$. Using $\rho_{21} = 0$ in Eq. (4.46c) gives $\rho_{22} = 0$. Thus, MPI enhanced by the $|1\rangle - |2\rangle$ two-photon resonance will be absent at sufficiently large concentrations of the resonance gas and propagation depth $z$ where the destructive interference occurs.

The two-photon destructive interference discussed above has very different characteristics in comparison with the three-photon destructive interference discussed in Section 3. This type of two-photon destructive interference effect occurs only if the FWM process is phase matched. This is in contrast to the cases involving interference between one- and three-photon coupling as treated in Section 3, where maximum MPI signals, therefore minimum interference effects, are observed in the region where the FWM process is phase matched. Indeed, in those cases effective destructive interferences occur only in the region of three-photon resonance where phase mismatch occurs. It is important to realize that although the FWM field is an important part of the destructive interference loop, in the present case the absorption (i.e., the neglect of the second exponential term in Eq. (4.48)) required to bring about the effect is not the consequence of one-photon absorption of the FWM field. This can be seen clearly from Eq. (4.48) where the quantity involved in the absorption term are spontaneous decay rate and ionization rate out of state $|2\rangle$, indicating that two-photon absorption via a strongly a.c. Stark shifted resonance is responsible for the destructive interference.

Eq. (4.49) also indicates that if the intensity of the first laser (therefore, $\Omega_{21}^{(2)}$) is fixed, then when the destructive interference is effective, increasing the intensity of the second laser (therefore, $\Omega_{23}$) will lead to the decreasing of the intensity of the FWM field (therefore, $\Omega_{31}$). This characteristic lends a unique feature to the effect that can be easily verified. Experimentally, if the second laser has a non-uniform transverse beam profile, a spatial distribution that is complimentary to the intensity profile of the second laser will be developed in the transverse beam profile of the FWM field.

Before leaving this subsection, it is useful to note some differences between odd-photon and even-photon destructive interferences. What makes the odd-photon interferences discussed in Sections 3 and 4.1 very complete and robust is that their occurrence is independent of power density (as long as the ground state population is not depleted). Thus, the effect remains completely operative across the radial beam-intensity profile. In the case of the two-photon interference such as discussed in Sections 4.3 and 4.4 some effects depend on the transitions being pumped sufficiently hard. The odd-photon destructive interference effects, unlike the two-photon interference, is not dependent on phase matching for the FWM process. Thus, these effects are not only much more complete, but they require only that the FWM field be absorbed in a small fraction of the distance over which the laser propagates.
4.2.3. Future theoretical and experimental studies using narrow bandwidth lasers

In the past few decades, laser technology has progressed rapidly and many new laser radiation sources with novel properties and characteristics have become commercially available. One of these technological advances is the realization of high-brightness, very stable, yet very narrow bandwidth (near transform limited) laser systems by various injection-seeding techniques. Injection-seeded pulsed Nd:YAG lasers and injection-seeded pulsed dye lasers have revolutionized the field of nonlinear laser spectroscopy where the conventional single longitudinal mode dye lasers are not sufficiently strong, even when tuned on exact resonance, to bring out high order wave-mixing processes. These new type of very narrow bandwidth, yet high energy, pulsed lasers have expanded the horizons of research in nonlinear optics, and have ignited renewed interest in high precision pulsed laser spectroscopy. In the research field of propagation dependent quantum interference effects, which is the main topic of the present review, there has long been interest to revisit some of the early landmark experiments using very narrow bandwidth laser systems. For instance, all laser systems used in the experiments reviewed so far had rather broad bandwidths on the order of a few GHz or more. With such broad bandwidths, the Doppler broadening of transitions is dominated by laser bandwidth effects. Thus, even at low concentration where collisional dephasing is less important, the broad bandwidth of the laser will dominate and raise the onset concentration for the multi-photon destructive interference. The situation changes when very narrow bandwidth lasers are used, as the effect of Doppler broadening then becomes dominant. Consider the case when a transform limited bandwidth laser is tuned onto a two-photon resonance in Na at a concentration of 3 \times 10^{16}/cm^3. If the pulse length of the laser is \( \tau = 6 \) ns, the laser will have a bandwidth of around 30 MHz, which in terms of angular frequency is about \( 2 \times 10^8/s \). The fastest relaxation rate for the \( 4p \) state at 2 Torr pressure is probably \(< 1 \times 10^8/s \) due to the collisional relaxation rate originated from resonance energy transfer between excited atoms and atoms in the ground state. Thus, the collisional relaxation of the 4d state is much smaller than the average Doppler shift in the two-photon transition. Consequently, excitation due to both the wave-mixing field and the two-photon excitation are dominated by Doppler effects. This presents new challenges to both theoretical understandings of quantum destructive effects and experimental determinations of manifestations of various interference phenomena under low concentrations. In this subsection, the importance of the inclusion of Doppler broadening is first analyzed, followed by discussions of future experiments using narrow bandwidth laser systems. This subsection is aimed at providing readers some new ideas and future directions, and outlining the physical foundations behind some of the proposed studies.

4.2.3.1. Inclusion of Doppler broadening in the basic two-state model

Though they have not been included here-to-fore in formulations of the interference behavior, Doppler effects play an important role in problems where the collisional dephasing and laser bandwidth effects are small, such as the case of low concentrations and lasers with transform limited bandwidths. To include Doppler effects one may consider the effect of the center-of-mass motion of the atoms in terms of classical paths. At room temperature this will be accurate enough, as most atoms have de Broglie wave lengths that are short compared with range of the atom–atom interactions at such temperatures.

Consider an ensemble of effective two-state atoms that have velocities \( \vec{V} \), distributed according to the Maxwell distribution. The components of these velocities parallel to the laser fields is \( V_{||} \), and the group velocity distribution has a Gaussian \( G(V_{||}) = Ce^{-mV_{||}^2/(2k_B T)} \) form, with \( C \) being a normalization constant. Here, \( m \) is the mass of atom, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature in Kelvin. To a moving atom a plane wave optical field \( E_j \) from laser \( j \) traveling in the \( \pm \) direction appears as

\[
E_j(z, t) = E_j^{(0)} \cos \left( \frac{\omega_{L_j}}{c} t - \left[ \pm n(\omega_{L_j}) \right] \frac{\omega_{L_j} z}{c} \right).
\]

Thus, a moving atom “sees” a shifted frequency \( \omega^{(sh)}_{L_j} = \omega_{L_j}(1 - V_{||}/c) \). As before, the \( \pm \) sign in front of the refractive index \( n(\omega_{L_j}) \) indicate the direction of propagation of the corresponding field. For an atom with parallel component of velocity, \( V_{||} \), the state vector in the rest frame of the atom can be written as

\[
|\Psi(z, V_{||}, t)\rangle = A_1(z, V_{||}, t) e^{-i\omega_l t} |1\rangle + A_2(z, V_{||}, t) e^{i\omega_l n_0(\omega_{L_j}) z/c} e^{-i(\omega_2 - \omega_1) V_{||}/c} t |2\rangle,
\]

where the phase relations are chosen to agree with the phase in density matrix, as illustrated in Section 2. In the above expression of the state vector \( \epsilon_l = \hbar \omega_l \) (\( l = 1, 2 \)) is the energy of the state \( |l\rangle \), and again \( n_0(\omega_{L_j}) \) is the index of refraction of the wave-mixing field with the \( |1\rangle - |2\rangle \) transition excluded. As before, the resonant contribution will be determined by calculating the atomic response. It should be emphasized again that the effective two-state model assumes that
all transitions other than the \(N\)-photon resonance \(\ket{1} - \ket{2}\) are sufficiently far away so that the phase mismatch due to these far-off-resonance transitions remains fixed as the lasers are tuned near the \(N\)-photon resonance even though such a phase mismatch can include angles between laser beams or the presence of a fairly high pressure of positively dispersive buffer gas.

Expressing the multi-wave mixing field as

\[
E_m = E_m^{(0)} \cos \left[ \omega_m \left( 1 - \frac{V_{||}}{c} \right) t - n_0(\omega_m) \frac{\omega_m z}{c} \right],
\]

taking an undepleted ground state (i.e., \(\rho_{11}(z, V_{||}, t) \simeq 1\)) and using the SVA approximations, one obtains the following simultaneous differential equations with respect to the dimensionless retarded time \(T_r\) (see Eq. (3.3) and explanations there)

\[
\begin{align}
\frac{\partial \rho_{21}}{\partial T_r} &= i \left( \delta_2 \tau - (\omega_2 - \omega_1) \frac{V_{||}}{c} + i \Gamma \tau \right) \rho_{21} + i \left( \Omega_{21}^{(N)} e^{-i \Delta \kappa z} + \Omega_{21}^{(1)} \right), \\
\frac{\partial \rho_{22}}{\partial T_r} &= -(\gamma_2 + \gamma_1) \rho_{22} - 2 \frac{\text{Im}}{m^2} \left( \Omega_{21}^{(N)} e^{-i \Delta \kappa z} + \Omega_{21}^{(1)} \right) \rho_{12}, \\
\left( \frac{\partial \Omega_{21}^{(1)}}{\partial z} \right)_{T_r} &= \frac{\i \kappa_1 + \kappa_{12}}{2} \int_{-\infty}^{\infty} dV_{||} G(V_{||}) \rho_{21}(z, V_{||}, T_r),
\end{align}
\]

where \(\Gamma\) and phase mismatch are given in Eqs. (3.2) and (3.3). Comparing with Eqs. (3.1) and (3.2) one sees the appearance of Doppler shifted frequency in the off-diagonal density matrix and the velocity distribution integral in the source term of the Maxwell’s equation.

The procedure of solving Eq. (4.50) follows exactly the method described in Section 3. Define \(\alpha_{jk}, A_{21}^{(N)},\) and \(A_{21}^{(1)}\) as the Fourier transforms of \(\rho_{jk}, \Omega_{21}^{(N)},\) and \(\Omega_{21}^{(1)}\) with respect to the dimensionless retarded time \(T_r\) one obtains

\[
\begin{align}
\alpha_{21} &= -\frac{A_{21}^{(N)} e^{-i \Delta \kappa z} + A_{21}^{(1)}}{\delta_2 \tau + \eta - (\omega_2 - \omega_1) \frac{V_{||}}{c} + i \Gamma \tau}, \\
\frac{\partial A_{21}^{(1)}}{\partial \xi} &= -\frac{\i \kappa_1 + \kappa_{12}}{2} \int_{-\infty}^{\infty} dV_{||} G(V_{||}) A_{21}^{(N)} e^{-i \Delta \kappa z} - \frac{\i \kappa_1 + \kappa_{12}}{2} \int_{-\infty}^{\infty} dV_{||} G(V_{||}) A_{21}^{(1)},
\end{align}
\]

where \(\eta = \omega \tau\) is the dimensionless Fourier transform variable and

\[
Y = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{e^{-u^2}}{\delta_2 \tau + \eta - u \frac{\omega_2 - \omega_1}{c} + i \Gamma \tau} = -i \frac{\sqrt{\pi}}{A_D \tau} \frac{\partial \xi}{A_D \tau} W \left( \frac{\delta_2 \tau + \eta + i \Gamma \tau}{A_D \tau} \right).
\]

Here, \(V_0 = \sqrt{2kT/m}\) is the average thermal speed and \(u = V_{||}/V_0\). In addition, \(A_D = (\omega_2 - \omega_1) V_0/c\) is a measure of the mean Doppler width of the multi-photon resonance, and

\[
W(Z) = \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{e^{-u^2}}{Z - u} = e^{-Z^2} \left[ 1 + \frac{2i}{\sqrt{\pi}} \sum_{n=0}^\infty \frac{Z^2n+1}{(2n+1)n!} \right].
\]

It should be noted that when the laser has very narrow bandwidth and is tuned very near resonance, \(\delta_2 \tau\) will be small. Since the Doppler width is very large compared with the laser bandwidth or the lifetime broadened width of the line at low concentration, one has \(|Z| \ll 1\) and Eq. (4.50a) gives

\[
\rho_{21}(z, T_r) = \int_{-\infty}^{\infty} dV_{||} G(V_{||}) \rho_{21}(z, V_{||}, T_r) = i \frac{\sqrt{\pi}}{A_D \tau} \Omega_{21}^{(eff)},
\]

where \(\Omega_{21}^{(eff)} = \Omega_{21}^{(N)} e^{-i \Delta \kappa} + \Omega_{21}^{(1)}\). Thus, very near resonance the Doppler width brings about adiabatic following between \(\rho_{21}(z, T_r)\) and the effective half Rabi frequency coupling the two states. This is very similar to the effect that would
be brought about by a fast collisional dephasing rate, which would lead to the same relation with $\sqrt{\pi}/(\Delta D\tau)$ replaced by $1/(\gamma_{21}\tau)$, with $\gamma_{21}$ being the collisional relaxation rate.

The solution to Eq. (4.51b) can be expressed as

$$A_{21}^{(1)} = -\frac{A_{21}^{(N)}}{1 - (\Delta K/\Delta K_{12} Y)} \left[ e^{-i\Delta K z} - e^{-i\xi_{12} Y z} \right].$$

(4.53)

It should be noted that the imaginary part of $-\Delta K_{12} Y$ is the well known Voigt profile [97] for the absorption coefficient. The real part is the phase mismatch associated with the Doppler and lifetime broadened resonance. When the laser is tuned onto resonance the $A_D\tau$ will be much larger than either the laser bandwidth or $\gamma_1\tau/2$, so that $W(Z) \approx 1$. Thus,

$$Y \simeq -i\sqrt{\pi}/A_D\tau.$$

Note that $\Delta K_{12}\sqrt{\pi}/(A_D\tau)$ is the Doppler modified absorption coefficient for the wave mixing field. This absorption length is much larger compared with the value of $\Delta K$, which is the phase mismatch due to off resonance levels of the vapor. Thus, $A_{21}^{(1)}$ takes on the form

$$A_{21}^{(1)} = -A_{21}^{(N)} \left[ e^{-i\Delta K z} - e^{-i\gamma_{12} z\sqrt{\pi}/A_D} \right].$$

(4.54)

where at quite low concentrations but with longer propagation distance $z$ [98] the decaying exponential within the square brackets will become very small and can be neglected. Again, on carrying out the inverse Fourier transform, one finds

$$Q_{21}^{(1)} + e^{-i\Delta K z}Q_{21}^{(N)} = 0,$$

which makes the source term in the equation for $\rho_{21}$ have a value close to zero. In turn, this makes $\rho_{21} = 0$. At room temperature with one of the strong allowed transitions in Xe, Absorption will become strong with $z \approx 1$ cm at about $10^{-4}$ Torr, or $3 \times 10^{12}$/cm$^3$. Gilligan and Eyler [66] carried out an experiment in $H_2$ using transform limited bandwidth lasers. In that experiment the medium was cooled down to about $3^\circ$K in a pulsed supersonic nozzle jet and they observed the onset of three-photon cancellation at concentrations of around $5 \times 10^{11}$/cm$^3$, in good agreement with the corresponding onset of opacity for the TH field, as predicted above.

It should be emphasized again that the key for achieving multi-photon destructive interference effect is to have a mechanism to ensure that the atomic coherence of the laser coupled transition adiabatically follows the laser excitations. This has been the case with all examples of odd-photon destructive interference. In the case of low pressure and very narrow band width lasers, the mechanism for bringing about adiabatic following is the Doppler broadening effect.

4.2.3.2. Future experimental studies using narrow bandwidth laser systems

As the conclusion for this subsection, it is now appropriate to discuss some areas of the older research that may be interesting to revisit using narrow bandwidth laser systems. This list of possible experimental studies includes:

1. No experiments have been carried out, as yet, in cold alkali vapors with longer laser pulses. In this situation, it should be possible to demonstrate the onset of destructive interference at concentrations as low as a few times $10^{10}$/cm$^3$. Here, one would observe the quenching of fluorescence and scattered light from the upper state in the three-photon resonance as a signature of the destructive interference.

2. Nearly all of the studies of pressure dependent optical shifts observed, when counter-propagating laser beams drive three-photon resonances, have required pressures that are so high that the precise predictions are difficult. It would be possible to measure pressure dependent frequency shifts at much lower concentrations if the laser bandwidths were transform limited. In addition, one type of correction to these pressure induced frequency shifts has been neglected in older theories and has not been demonstrated experimentally.

3. The disappearance of forward hyper-Raman radiation is well understood when the driving laser is tuned well off two-photon resonance. The theory must be corrected when applied to alkali vapors where the dominant broadening mechanism is the Doppler effect, in particular when a transform limited bandwidth laser is used. Detailed experimental studies using narrow bandwidth lasers must be compared carefully with a proper theoretical treatment of the
effect. It should be noted that the current theory predicts large pressure dependent shifts in the wavelength of the
SEHRS, which should be accurately measurable with narrow bandwidth lasers at pressures as low as 10–20 Torr.

As with almost any area of physics, when new and better technologies are available new phenomena can often be
discovered by improving on older works. Only forty years ago, it seemed to many people that atomic spectroscopy
was a dead field, with almost everything being known. However, narrow bandwidth lasers have led to discoveries and
applications of high resolution spectroscopy. In addition, fast developed capability to prepare all the atoms in the same
quantum state, with almost no Doppler shifts, has resulted in a new medium with such sharp resonances that nearly
perfectly efficient nonlinear processes can be carried out. One could imagine new striking features in such a medium,
which are the subject of the next two sections.

5. Highly efficient multi-wave mixing processes in the presence of induced transparency

In Sections 3 and 4, multi-photon destructive interference from simultaneous couplings of two quantum states
(usually, but not necessarily, one is ground state) by externally supplied laser fields and by the internally generated
wave-mixing fields have been shown to be able to drastically modify the response of the system. In all the situations
discussed so far, however, there is no circumstance where the externally supplied fields are tuned close to a one-
photon resonance for the first step of the excitation sequence. This restriction was required by the assumption of a
non-depleted ground state, but the requirement also leads to very inefficient wave mixing. Clearly, when highly efficient
wave mixing processes are the objective it is desirable to have all laser fields tuned close to one-photon resonances, so
that the significant resonance enhancement to the transitions can be utilized. However, strong absorption occurs when
a pump laser field is tuned close to the first one-photon resonance in the excitation sequence, which necessarily starts
from a fully occupied ground state, causing significant pump field attenuation and distortion, and quickly diminishing
the advantages of resonance enhancement. Dispersion manipulation techniques, such as induced transparency, offer an
effective way to circumvent such a pump field dispersion problem, allowing almost negligible attenuation of the pump
field while staying tuned to a strong one-photon resonance, and thereby opening the possibility of efficient multi-wave
mixing processes. In this section several wave mixing schemes utilizing EIT [67–74,96,99–102] will be reviewed and
the role of multi-photon interference effects and the corresponding multi-photon induced transparency in these novel
wave mixing schemes will be discussed.

5.1. Early experimental evidence and theoretical studies related to multi-photon induced transparency

The earliest works that related to multi-wave mixing involving induced transparency can be traced back to the early
papers by Manykin and Afanas’ev [32] and by Aron and Johnson [5], Compton et al. [6], Miller et al. [7], and Payne
et al. [8,9,14,17] in the 1979–1983 time period, as discussed in Section 1. Although it was not specifically discussed
at that time, multi-photon induced transparency was actively involved in those experiments. A re-examination of these
early works made it clear that the observation of two- and three-photon destructive interferences, which reduced the
ionization signals to zero at higher concentrations due to the competing excitation processes between the lasers and the
internally generated field, necessarily implied that the generated fields propagated freely in highly dispersive media
even though these fields were very close to a strong one-photon allowed absorption line.

An insightful demonstration of this possibility was presented in experiments by Chen et al. [22,23]. In these studies
the TH field was one-photon resonant and the fundamental field was three-photon resonant with the 6s1S0 – 6p3P1
transition in low concentration Hg. By adjusting the relative amplitudes and relative phase of the fundamental and the
TH laser fields, it was shown that the resonant photoionization in an atomic Hg vapor cell could be reduced to zero.
Indeed, Chen et al. demonstrated (see Fig. 40) that as the relative phase, \( \theta \), was changed the MPI in the cell varied as
\( I = I_0[1 + \cos(\theta + \theta_0)]/2 \), giving a strong experimental indication that both fields can have a relative phase such
that they propagate together without absorption as soon as they enter the resonance medium. This occurs because the
relative phase of the one-photon and three-photon couplings is such that the two excitation pathways destructively
interfere. This effect can occur at exact resonance, or when the two fields are moderately detuned from resonance, with
the effect being largest at exact resonance.

In the mid-1990s, Deng et al. reported a series of experiments, using Xe gas in a 2nωL1 – ωL2 configuration
\( n = \text{integer} \) [59,60] and rubidium metal vapor in a 2ωL1 – ωL2 configuration [61–63], that gave clear experimental
evidence of multi-photon induced transparency in a mode where destructive interference were widely thought to be not possible. In these experiments where three-photon destructive interferences were studied in the presence of two- and four-photon intermediate resonances, Deng et al. showed the first direct evidence of multiphoton destructive interference with an intermediate even-photon resonance, simultaneous occurrence of the saturation of the FWM production and the collapse of the Autler–Townes splitting. Indeed, their observations clearly demonstrated that at lower concentration an induced two-photon transparency based on an Autler–Townes doublet in the two-photon terminal state was operative and no population was produced in this state even though the laser was on two-photon resonance. This is precisely the two-photon version of the one-photon electromagnetically induced transparency pioneered by Harris et al. (see discussion below). At higher concentrations, however, a new three-photon destructive interference was established due to the strong absorption of the generated FWM field, resulting in new phenomena such as the collapse of the Autler–Townes splitting and the suppression of FWM production at higher concentrations. It was shown clearly that a new three-photon induced transparency became operative, rendering the medium highly transparent to the field at FWM frequency even though the FWM field is very close to a strong one-photon resonance. This demonstration of the saturation of the FWM generation, which is more fundamental, is the first direct experimental evidence of the multiphoton induced transparency effect.

5.2. Early theoretical studies of index manipulation methods effecting FWM and four-photon resonantly enhanced MPI

There were early theoretical studies [8,9,14,103] related to multi-photon induced transparency effects, which also encompassed the concept of what is now referred to as an index manipulation technique. One of the first theoretical
considerations that employed index manipulation using a separate laser field in order to enhance or make possible frequency mixing processes was by Tewari et al.\cite{103}. In 1986, using a $\chi^{(3)}$ treatment Tewari et al. formulated a sum frequency ($2\omega_{L1} + \omega_{L2}$) mixing scheme very similar to the TH ($3\omega_{L1}$) generation problem studied by Aron et al.\cite{5}, Compton et al.\cite{6}, Miller et al.\cite{6}, and Payne et al.\cite{8,9,14}. The new element was the introduction of a second relatively intense laser tuned between the upper state of the three-photon $n$ transition and another excited state. This additional intense laser field can optically shift the nearby three-photon resonance or induce an Autler–Townes splitting. It can also provide effective means for more general manipulation of the phase matching and absorption of the generated field. This situation differs from the three-state problems described in Section 4.1, where the $|1\rangle - |2\rangle$ resonance was a two-photon resonance and the $|1\rangle - |3\rangle$ transition is a three-photon resonance. It is, however, close to the three-photon enhanced four-photon resonance discussed in Section 3.5. The difference is that the second laser is tuned on the $|2\rangle - |3\rangle$ resonance, i.e., $\omega_{L2} = \omega_3 - \omega_2$, and effectively splits the upper state of the three-photon resonance into an Autler–Townes doublet. In the following early work on index manipulation by Tewari and Agarwal\cite{103} is retreated using unfocused laser beams. It will be shown that with the assumption of long pulse length and uniform intensity distribution of the second laser, the enhancement of true phase matching can be achieved for efficient wave mixing using a positively dispersive buffer gas and by using properly chosen ratio of resonance medium to buffer gas concentrations. In particular, this enhancement of true phase matching can be achieved when $-|\Omega_{23}| < \delta_2 < 0$, but is not possible when $0 \leq \delta_2 < |\Omega_{23}|$, as the latter region is positively dispersive. Enhancements should be achievable where $|\Omega_{21}^{(1)}| > |\Omega_{21}^{(3)}|$. This implies that at the off-resonance point the one-photon coupling is far stronger than the three-photon coupling which caused it to be generated.

The system under consideration is an ensemble of atoms with energy levels and laser couplings as depicted in the inset of Fig. 41. Assuming small depletion of the ground state ($\rho_{11} \simeq 1$) and rapid relaxation of resonances due to pressure broadening, the relevant equations of motion for density matrix elements are

$$\frac{\partial \rho_{21}}{\partial T_r} = i(\delta_2 \tau + i\Gamma_2 \tau)\rho_{21} + i\Omega_{23} \tau \rho_{31} + i\Omega_{21}^{(eff)} \tau,$$

(5.1a)
\begin{equation}
\frac{\partial \rho_{21}}{\partial T_r} = i(\delta_2 \tau + i\Gamma_3 \tau) \rho_{21} + i\Omega_{32} \tau \rho_{21},
\end{equation}
\begin{equation}
\left( \frac{\partial \Omega_{21}^{(1)}}{\partial z} \right)_{T_r} = i\kappa_{12} \rho_{21},
\end{equation}
where \( \Omega_{21}^{(\text{eff})} = \Omega_{21}^{(3)} e^{-i\Delta K z} + \Omega_{21}^{(1)} \) and \( \delta_2 = \delta_3 \). When \( |\Omega_{32} \tau| > 100 \), steady state solutions for \( \rho_{21} \) and \( \rho_{31} \) are appropriate, and one has
\begin{equation}
\rho_{31} = -\frac{\Omega_{32} \tau}{\delta_2 \tau + i\Gamma_3 \tau} \rho_{21},
\end{equation}
\begin{equation}
\rho_{21} = G \Omega_{21}^{(\text{eff})} \tau,
\end{equation}
where dimensionless quantity \( G \) is defined as
\begin{equation}
G = \frac{\delta_2 \tau + i\Gamma_3 \tau}{|\Omega_{23} \tau|^2 - (\delta_2 \tau + i\Gamma_2 \tau)(\delta_2 \tau + i\Gamma_3 \tau)}.
\end{equation}
Using Eqs. (5.1c) and (5.2b), one obtains the solution of the TH field as
\begin{equation}
\Omega_{21}^{(1)} = -\frac{\kappa_{12} \tau G \Omega_{21}^{(3)} e^{-i\Delta K z}}{\kappa_{12} \tau G + \Delta K z}(1 - e^{i\Delta K z} e^{i\kappa_{12} \tau K z}).
\end{equation}
Writing
\[ \kappa_{12} \tau G = \Delta k_r + i\beta/2, \]
where \( \Delta k_r \) is the phase mismatch in the region near the Autler–Townes doublet, and \( \beta \) is the absorption coefficient in this region. Notice that in the region \( -|\Omega_{23} \tau| < \delta_2 \tau < 0 \) and \( \Gamma_2 \tau \simeq \Gamma_3 \tau \ll |\Omega_{23} \tau| \), one can approximate
\begin{equation}
G |\Omega_{23} \tau| \simeq \frac{\delta_2 + i\Gamma_2}{|\Omega_{23}|}.
\end{equation}
Notice that in writing the above equation it has been assumed that \( \Gamma_2 \simeq \Gamma_3 \). This is a reasonable approximation since both the transitions \( |1 \rangle - |2 \rangle \) and \( |2 \rangle - |3 \rangle \) are one-photon allowed and the fast dephasing effect in these transitions is the fast resonance energy transfer between ground state atoms and atoms in state \( |2 \rangle \). Using the above expression, one can write explicitly
\begin{equation}
\Delta k_r \simeq \frac{\kappa_{12} \delta_2}{|\Omega_{23}|},
\end{equation}
\begin{equation}
\beta \simeq \frac{2\kappa_{12} \Gamma_2}{|\Omega_{23}|}.
\end{equation}
Fig. 41 shows a plot of both \( \beta |\Omega_{23}|/\kappa_{12} \) (solid line) and \( \Delta k_r |\Omega_{23}|/\kappa_{12} \) (dot–dashed line) versus \( \delta_2/|\Omega_{23}| \) for \( (\Gamma_2 + \Gamma_3)/|\Omega_{23}| = 0.04 \) using the non-approximate Eq. (5.3). It is worth to point out that when \( |\delta_2 \tau| < 0.6 |\Omega_{23} \tau| \) one has \( |\Delta k_r| > \beta \) (whenever \( |\Omega_{23} \tau| \gg (\Gamma_2 \tau + \Gamma_3 \tau) \gg 1 \)). Thus, if the ratio of concentrations is such that \( \Delta K + \Delta k_r = 0 \) while \( |\delta_2| < 0.6 |\Omega_{23}| \), then at this phase matched point one has
\begin{equation}
\Omega_{21}^{(1)} \simeq \frac{i \Delta k_r}{\beta} \Omega_{21}^{(3)} (e^{-i\Delta K z} - e^{-\beta z} e^{i\Delta k r z}).
\end{equation}
Clearly, if \( \Delta K/\beta \gg 1 \) then the TH process is greatly enhanced by phase matching.
In cases where \( |\delta_2|/|\Omega_{23}| < 0.4 \) and \( (\Gamma_2 + \Gamma_3) \ll |\delta_2| \), Eqs. (5.5a,b) are accurate and one gets
\begin{equation}
\frac{\Delta k_r}{\beta} \simeq \frac{|\delta_2|}{2\Gamma_2}.
\end{equation}
Notice that this enhancement factor can be made large with properly chosen phase matching detuning. From an experimental demonstration viewpoint, one needs a strong narrow bandwidth laser to produce, for a strong resonance
in an alkali metal, $|\Omega_{23}| > 10^{12}$ rad/s. This laser should have a long pulse length and considerably larger beam radius than the lasers used for generating FWM/TH field in order to make the approximations applicable. The size of the enhancement due to phase matching will be dependent upon the size of the splitting divided by the transition line width. If this factor can be made very large the enhancement can be a factor perhaps even several hundred.

It should be pointed out that this enhancement requires that $\beta z \gg 1$ so that only one part of the FWM/TH field survives at exact phase matching. The enhancement can be substantial over most of the region of $-|\Omega_{23}| \leq \delta_2 < 0$ when the ratio of resonant medium concentration to buffer gas concentration is chosen properly in addition to the requirement that the concentrations are high enough to satisfy $\beta z \gg 1$. This is the region where FWM process cannot be phase matched without using this technique. To date, there is no detailed experimental verification of these predictions, aside from some indirect verification from experimental studies of the effects of destructive interference on four-photon resonances as described in Section 3.5.

The above results can be generalized to include the case where $\delta_3$ is not restricted to be equal to $\delta_2$. In fact, a theoretical formalism very similar to the treatment shown in Section 3.5 can be developed. In this case, Eqs. (5.2a,b) become

$$\rho_{31} = -\frac{\Omega_{23}}{\delta_3 + i\Gamma_3} \rho_{21},$$

$$\rho_{21} = G' G'_{21}^{(eff)} \tau,$$

where dimensionless quantity $G'$ is defined as

$$G' = \frac{\delta_3 + i\Gamma_3}{|\Omega_{23}|^2 - (\delta_2 + i\Gamma_2)\Gamma_3 \Gamma_2}. $$

Using Eqs. (5.1c) and (5.8b), one obtains the solution of the TH field as

$$Q_{21}^{(1)} = \frac{\kappa_{12} G' G'_{21} \Delta K}{\kappa_{12} G' + \Delta K} \left(1 - e^{i\Delta K z} e^{iK z} \right).$$

With Eqs. (5.8a,b) and (5.9) it is straight forward to determine $\rho_{22}, \rho_{23}$ and $\rho_{33}$, in addition to the MPI enhancement due to $|\Omega|$. It should be pointed out that having a high pressure buffer gas could lead to new and complex pressure dependent effects for four-photon resonance enhancement to MPI. In addition, it will lead to very complex dependence on the power density of the second laser which produces optical shifts and modifies the index of refraction at the FWM/TH frequency. Experimental studies in this regime, however, is not yet available at the present time.

### 5.3. Key differences between the three-state one-photon coupling electromagnetically induced transparency (EIT) and the multi-photon induced transparency

In the early 1990s, Harris et al. [72,73] studied a different type of induced transparency that results from a destructive interference between the amplitudes of the two members of a Autler–Townes doublet created by an intense externally supplied one-photon resonant field. Their pioneering work lead to a one-photon coupling induced transparency in a three-state $\Lambda$ scheme, commonly referred to as EIT. The key ingredient of this conventional EIT technique is also index manipulation, but in the form of two active, external-field produced, and one-photon coupled interference channels. This technique has lead to exciting new research activities in nonlinear optics and a flourish of applications in many other fields.

The conventional three-state one-photon coupling EIT schemes and related research and developments are not within the scope of the present review, which focuses on the role of destructive interference involving internally generated fields. However, it is important to point out some of the key and fundamental differences between the multi-photon induced transparency and the conventional three-state one-photon coupling EIT scheme such as three-state $\Lambda$ and ladder schemes.

In the conventional EIT, two externally supplied laser fields, each providing the coupling in a respective one-photon transition, interact with a three-state atomic system. The transparency to a probe field tuned on a strong one-photon resonance is produced by an intense on-one-photon-resonance control field that couples two empty states. Such a
strong and on-resonance laser field splits the one-photon terminal state into an Autler–Townes doublet. When an on-one-photon-resonance probe field is injected into the medium each member of the doublet forms its own transition pathway to an allowed two-photon transition terminal state. Because of destructive interference between the couplings involving the ground state and the two members of the Autler–Townes doublet of equal strength the state shared by the probe and control fields is driven to be a dark state. In the case of a \( A \) system, the resulting adiabatic response is a long-lived superposition state which is a linear combination of the ground state and the lower excited state. In the case of a ladder EIT scheme, however, the cascade transitions and the shorter life time of the two-photon terminal state significantly reduce the life time of this superposition state, giving a less effective induced transparency.

It should be pointed out that the above described situation occurs just as well in a low density medium where there are only slight propagation effects and the upper excited state is a dark state regardless the concentration as long as the intensities of the fields are appropriately adjusted. It is straight forward to show that at much higher concentrations, although propagation effects may significantly reduce the probe field propagation velocity, there is no pulse distortion in a true \( A \) system and the dark state remains a dark state. In fact, the transparency and the dynamics of the atomic system in a conventional EIT scheme do not rely on any probe field propagation dynamics and the transparency effects can be obtained simply by solving the atomic equations of motion only.

In the case of multi-photon induced transparency involving internally generated field, none of these features exists. First of all, this type of induced transparency is inherently multi-photon in nature, and it is critically dependent upon the generation and propagation dynamics of the wave-mixing field. Second, there is usually no Autler–Townes doublet or splitting. The interference pathway is brought about, in the case of the plane wave, by strong absorption of the generated field. A close relation between the three-photon Rabi frequency due to the external laser fields and the one-photon Rabi frequency due to the internally generated FWM field leads to identical amplitudes and a fixed phase relation at all points in space. As a consequence of occurrence of the destructive interference at all points in the beam, a multi-photon induced transparency is established, resulting in both external and internally generated fields propagating free of absorption and distortion in a highly dispersive medium. In addition, the usual dark state picture widely used in describing the conventional EIT phenomena cannot be directly applied here. In fact, there is no dark state prior to the establishment of the destructive interference. Indeed, at small values of \( N_0 z \), where \( N_0 \) and \( z \) are the concentration and propagation distance, the medium is highly absorbing and dispersive and there is no dark state until a propagating part of the FWM field is strongly diminished by absorption, leaving only an adiabatically following contribution. This is very different from the conventional EIT where a dark state is operative immediately after the two external fields enter the medium. No wave equation is ever needed to bring about the conventional EIT phenomena.

From the discussions presented above it is clear that there are fundamental differences between multi-photon induced transparency and the conventional EIT. Indeed, it is these fundamental differences that give multi-photon induced transparency rich properties and novel propagation dynamics. It should be noted that there are many excellent studies on conventional EIT enhanced or altered FWM processes. This extensive literature, however, will not be reviewed here since these studies give no consideration to the influence of the internally generated fields and the effects of destructive interferences resulted from their interactions with the media. For conventional three-state EIT and related works readers are recommended to consult the literature for relevant subjects, studies and progress reports.

To facilitate the investigation of efficient wave mixing processes where internally generated fields are involved in interference phenomena, such as highly efficient induced transparency, it is appropriate to divide the studies of wave mixing into two groups:

1. Studies in which the systems have initial populations that reside in a single state (usually the ground state).
2. Studies in which the systems are initially in a prepared superposition state.

The focus of investigation of this section is wave mixing effects in atomic media initially in a (ground) single state. The case of coherently prepared initial states will be treated in Section 6.

For the purpose of uniformity and versatility, a generic four-state life-time broadened atomic system will be used throughout the rest of this section to show that interesting multiple simultaneous induced transparency effects can occur at sufficient propagation distances in resonant media. It will be shown that multi-photon interferences can lead to many orders of magnitude suppression of populations in a pump-field-excitation terminal state and the state near three-photon resonance that is associated with mixing wave generation. It is remarkable that multiple simultaneous pathways and interference processes involving the externally supplied and internally generated fields can lead to such
efficient multiple simultaneous suppressions and induced transparencies. In Section 5.4, a unified theoretical framework on FWM generation in the context of induced transparency is given. In Section 5.5, several experiments on wave mixing using EIT are reviewed, and finally in Section 5.6 a different type of double-induced transparency scheme is discussed and the possibility of delaying the onset of the multi-photon destructive interference is demonstrated [68].

5.4. Theoretical treatment of multi-wave mixing processes in the presence of induced transparency

Consider a life time broadened four-state system that interacts with a pulsed (pulse length $\tau$) pump laser and two continuous wave (cw) control lasers (see Fig. 42). The pump laser is assumed to be tuned near the $|1\rangle - |2\rangle$ resonance, and the two cw control fields are assumed to be sufficiently intense to strongly saturate the $|2\rangle - |3\rangle$ and $|3\rangle - |4\rangle$ transitions, respectively. Thus, $|\Omega_{23}\tau| \gg 1$, $|\Omega_{34}\tau| \gg 1$, $|\Omega_{23}\tau|^2 \gg Max(\gamma_3\tau, \gamma_2\tau, |\delta_2\tau|, 1)$, and $|\Omega_{34}\tau|^2 \gg Max(\gamma_3\tau, \gamma_4\tau, |\delta_4\tau|, 1)$. These conditions lead to well-behaved adiabatic following that permits accurate predictions of the propagation dynamics. With appropriate laser polarizations and atomic angular momenta, a new wave at frequency $\omega_m$ will be generated as a result of the allowed transition $|4\rangle \rightarrow |1\rangle$. The objective of the following calculation is to seek a time dependent response of the system under the driving fields described above, and to investigate the propagation dynamics of both the pump and generated fields.

5.4.1. General formalism of multi-wave mixing in the presence of induced transparency

There are two arrangements of energy levels that are of particular interest. Fig. 42 left panel shows the ladder arrangement of energy levels that is useful for generating a wide range of FWM wavelengths that can be much shorter than the wavelength of any of the externally supplied fields. The disadvantage of a ladder system is the much shorter lifetime of coherence between states $|1\rangle$ and $|3\rangle$. This has consequences on the probe field propagation velocity and overall conversion efficiency. Fig. 42 right panel shows a double- $A$ scheme. With the two-photon state $|3\rangle$ being a member of the ground state manifold the lifetime of coherence between states $|1\rangle$ and $|3\rangle$ can be as long as milliseconds. This makes it possible to produce very slow optical waves, or perhaps even to store both the FWM and pump fields in the medium. The limitation is that if $|3\rangle$ is a hyperfine level of the ground state (to obtain long coherence time) then the FWM field always has a frequency that is just a side-band of one of the control lasers, thus not suitable for short wavelength conversion.

To encompass these excitation schemes in a conventional density matrix description, the atomic state vector is defined as follows:

$$|\Psi(z, t)\rangle = A_1(z, t) e^{-i\omega_1 t}|1\rangle + \sum_{k=2}^{4} A_k(z, t) e^{-i(\omega_k + \delta_k) t} e^{i(\omega_k + \delta_k - \omega_1) z/c} |k\rangle,$$

(5.10)
where \( \delta_2 = \omega_p - \omega_2 + \omega_1, \delta_3 = \omega_p + \omega_1 - \omega_3 + \omega_1, \) and \( \delta_4 = \omega_p + \omega_1 - \omega_2 - \omega_4 + \omega_1. \) The signs of the laser angular frequencies in the definition of the \( \delta_j \) depend on whether the light in question is absorbed or stimulates an emission. This definition of the atomic wave function allows a general treatment so that both ladder and double-\( A \) schemes can be contained naturally in a single framework. This type of choice of phase factors in the state vector has been used throughout this review.

Taking a non-depleted ground state approximation \( (\rho_{11} \simeq 1) \) and keeping only leading contributions, the set of equations of motion to be solved for the density matrix elements is given by

\[
\frac{\partial \rho_{21}}{\partial t_r} = i \left( \delta_2 + \frac{i \gamma_{21}}{2} \right) \rho_{21} + i \Omega_{23} \rho_{31} + i \Omega_{21} \rho_{11},
\]

\[
\frac{\partial \rho_{31}}{\partial t_r} = i \left( \delta_3 + \frac{i \gamma_{31}}{2} \right) \rho_{31} + i \Omega_{32} \rho_{21} + i \Omega_{34} \rho_{41},
\]

\[
\frac{\partial \rho_{41}}{\partial t_r} = i \left( \delta_4 + \frac{i \gamma_{41}}{2} \right) \rho_{41} + i \Omega_{41} \rho_{11} + i \Omega_{43} \rho_{31},
\]

where \( t_r = t - z/c \) and the phase mismatches due to off-resonant states of the atom have been neglected under the assumption that the resonances are dominant in a cold vapor driven by narrow bandwidth lasers and all fields travel in the \( +z \) direction. \( \gamma_{jk} \) is the decoherence rates of the relevant density matrix elements, and \( |\Omega_{12}| \ll |\Omega_{23}| \) is also assumed in accord with the assumption of non-depleted ground state. In addition, any propagation effects of the two cw control lasers have been neglected since there is never any appreciable population in states \( |2\rangle, |3\rangle, \) and \( |4\rangle \) to cause significant polarizations at the frequencies of the control lasers.

With co-propagating beam configuration the Maxwell equations for the pump (in accord with the convention of wave mixing, the first leg of excitation usually is referred as to a pump, therefore \( \Omega_{21} = \Omega_p \)) and FWM \( (\Omega_{41} = \Omega_m) \) fields in the SVA approximation are given as

\[
\left( \frac{\partial \Omega_p}{\partial z} \right)_{t_r} = i \kappa_{12} \rho_{21}, \quad \left( \frac{\partial \Omega_m}{\partial z} \right)_{t_r} = i \kappa_{14} \rho_{41}.
\]

Defining \( \omega_{jk}, A_p, \) and \( A_m \) as the time Fourier transforms of \( \rho_{jk}, \Omega_p, \) and \( \Omega_m, \) respectively, and taking Fourier transform of Eqs. (5.11), (5.12) with respect to \( t_r/\tau, \) one obtains [67]

\[
\omega_{21} = -\frac{W_{c2}}{A_0} A_p + \frac{\Omega_{23} \Omega_{34}}{A_0} A_m,
\]

\[
\omega_{31} = -\frac{\Omega_{32} D_4}{A_0} A_p - \frac{\Omega_{34} D_2}{A_0} A_m,
\]

\[
\omega_{41} = \frac{\Omega_{32} \Omega_{43}}{A_0} A_p - \frac{W_{c1}}{A_0} A_m,
\]

\[
\frac{\partial A_p(z, \eta)}{\partial z} = i \kappa_{12} \omega_{21}, \quad \frac{\partial A_m(z, \eta)}{\partial z} = i \kappa_{14} \omega_{41},
\]

where

\[
W_{c1} = |\Omega_{23}|^2 - D_2 D_3, \quad W_{c2} = |\Omega_{34}|^2 - D_2 D_4,
\]

\[
A_0 = D_4 |\Omega_{23}|^2 + D_2 |\Omega_{34}|^2 - D_2 D_3 D_4, \quad D_j = \delta_j + \eta + i \gamma_{j1} \tau/2, \quad (j = 2, 3, 4).
\]

The solutions for the pump and the FWM field can be analytically obtained as

\[
A_m(z, \eta) = A_p(0, \eta) \frac{K_2}{2K_3} (e^{i\delta_2 z} - e^{i\delta_4 z}),
\]

\[
A_p(z, \eta) = A_p(0, \eta) (B_+ e^{i\delta_2 z} + B_- e^{i\delta_4 z}),
\]
Assuming weak pump tuned between two intense, long pulsed lasers. In the latter scheme, as will be shown later, the possibility of stimulated HR from the pulsed FWM processes studied with two initial high-energy long pulsed lasers [96, 99–102] (see Sections 5.4). It should be emphasized that the FWM process described here starts with a weak pump laser. This is quite different from the pulsed FWM processes detected with two initial high-energy long pulsed lasers and strongly absorbed, however, stunning new effects occur, leading and evolving the system to double conventional EIT. When the internally generated mixing wave is sufficiently intense, it can be shown that in the early stage the cw control field strongly saturates the transition and the field is considered as the driving field which is assumed to strongly saturate the transition.

This intuitive picture of dual-conventional EIT, however, is not correct in the early stage of wave-mixing production. In fact, it can be shown that in the early stage the cw control field destroys the first ladder type conventional EIT, leading to the initial production of the mixing wave. When the internally generated mixing wave is sufficiently intense and strongly absorbed, however, stunning new effects occur, leading and evolving the system to double conventional EIT under suitable conditions, as will be shown below.

To demonstrate this feature, consider the complex exponents $e^{i\lambda_{\pm}z}$ in Eqs. (5.14a,b) under the conditions where $|\Omega_{34}\tau|^2 \gg |D_3D_4|$ and $|\Omega_{23}\tau|^2 \gg |D_2D_2|$. In this limit, the atomic response exhibits adiabatic behavior due to the fact that everywhere $\eta$ appears in $\Delta_0$ or $K_3$ it is dwarfed by terms involving Rabi frequencies of the driving fields. Thus, $\lambda_{\pm}$ can be expanded in a rapidly converging power series in $\eta$, yielding accurate results by keeping terms up to $\eta^2$. Assuming $\gamma_{21}\tau \gg 1$ and $\delta_4\tau \gg 1$, and letting

$$
\lambda_+ = \frac{D_+ + K_3}{\Delta_0} = a_{p0} + a_{p1}\eta + a_{p2}\eta^2, \quad \lambda_- = \frac{D_- - K_3}{\Delta_0} = a_{m0} + a_{m1}\eta + a_{m2}\eta^2,
$$

where

$$
a_{m0} = -\frac{M_m + M_p}{Z_0} + \frac{(T_2M_p + T_1M_m)d_3}{(M_m + M_p)Z_0},
$$

$$
a_{m1} = \frac{(M_m + M_p)(|\Omega_{23}\tau|^2 + |\Omega_{34}\tau|^2 - d_2d_4) + (T_2M_p + T_1M_m)}{(M_m + M_p)Z_0},
$$

$$
a_{m2} = -\frac{(M_m + M_p)(|\Omega_{34}\tau|^2 + |\Omega_{34}\tau|^2 - d_2d_4) + (T_2M_p + T_1M_m)}{(M_m + M_p)Z_0},
$$

$$
a_{p0} = \frac{(T_1M_p + T_2M_m)d_3}{(M_m + M_p)Z_0},
$$

$$
a_{p1} = \frac{(T_1M_p + T_2M_m)}{(M_m + M_p)Z_0},
$$

$$
a_{p2} = 0,
$$

where $\lambda_{\pm}$ is taken as known and $\lambda_{\pm}$ is taken as 0. In addition, the following notations have been used

$$
\lambda_{\pm} = (D_{\pm} \pm K_3)/\Delta_0, \quad B_{\pm} = (K_3 \pm D_{\pm})/(2K_3), \quad D_{\pm} = (K_p \pm K_m)/2,
$$

$$
K_2 = \kappa_{14\tau}\Omega_{32}\tau\Omega_{43}\tau, \quad K_3 = \sqrt{D_+^2 + \kappa_{12\tau}\kappa_{14\tau}\Omega_{23}\tau^2(\Omega_{34}\tau)^2},
$$

$$
K_p = -\kappa_{12\tau}W_{c2}, \quad K_m = -\kappa_{14\tau}W_{c1}.
$$

It should be emphasized that the FWM process described here starts with a weak pump laser. This is quite different from the pulsed FWM processes studied with two initial high-energy long pulsed lasers (see Section 6). A FWM process that starts with a weak pump tuned between $|1\rangle$ and $|2\rangle$, however, is better suited to cold and dense medium than a scheme that starts with two intense, long pulsed lasers. In the latter scheme, as will be shown later, the possibility of stimulated HR and parametric TWM out of state $|3\rangle$ could severely complicate the process unless a double-$A$ scheme without and intermediate states. Such a double-$A$ scheme, however, is not capable of generating shorter wavelength radiation. With a weak pump field scheme there is never any appreciable excited state population and the scheme can be used for efficient VUV conversion.
where \( d_j = \delta_j \tau + iv_j \tau / 2 \) (\( j = 2, 3, 4 \)), \( Z_0 = d_2 |\Omega_{43} \tau|^2 + d_4 |\Omega_{23} \tau|^2 \), \( T_1 = M_m d_4 / |\Omega_{43} \tau|^2 \), \( T_2 = M_p d_2 / |\Omega_{23} \tau|^2 \), \( M_p = \kappa_{12} \tau |\Omega_{23} \tau|^2 \), and \( M_m = \kappa_{14} \tau |\Omega_{23} \tau|^2 \), respectively.

The physical interpretation of \( a_{m1} \) and \( a_{pi} \) can be easily deduced by using Eqs. (5.14) and (5.15) in carrying out the inverse Fourier transform to find \( \Omega_p \) and \( \Omega_m \). First, note that \( a_{m0} \) and \( a_{p0} \) are related to phase factors and absorption coefficients for the two eigenfunctions involved in solving Maxwell’s equations. The expansion coefficients \( a_{m1} \) and \( a_{p1} \), on the other hand, are related to the group velocity for the two parts of the mixing wave and pump fields (see Eqs. (5.14a,b)). Finally, \( a_{m2} \) and \( a_{p2} \) are related to the rate at which the two pulse terms in the solutions for the pump and FWM fields broaden as a function of distance.

Detailed inspection of \( B_\pm \) and \( K_2 / (2K_3) \) reveal that these quantities depend only weakly on \( \eta \). Thus, to a very good approximation one has

\[
\frac{K_2}{2K_3} = \sqrt{\frac{\kappa_{14}}{\kappa_{12}}} B_+ B_- , \quad B_+ = \frac{M_m}{2K_3} , \quad B_- = \frac{M_p}{2K_3} , \quad 2K_3 = M_p + M_m .
\]

Further analysis of the two eigenvalues \( \lambda_\pm \) has shown that \( \lambda_- \) always has a much larger positive imaginary part. Thus, this term tends to decay out much faster than the corresponding term in the eigenvalue \( \lambda_+ \) after only a relatively short propagation distance. This differential decay behavior is the key element leading to multi-photon induced transparency after sufficient propagation distance. Indeed, once the \( \lambda_- \) term becomes unimportant, one has

\[
A_m(z, \eta) = A_p(0, \eta) \sqrt{\frac{\kappa_{14}}{\kappa_{12}}} B_+ B_- e^{i\lambda_+ z}, \quad (5.16a)
\]

\[
A_p(z, \eta) = A_p(0, \eta) B_+ e^{i\lambda_+ z}. \quad (5.16b)
\]

Taking Eq. (5.15) for \( \lambda_+ \) and assuming \( A_p(0, \eta) \) is of a Gaussian type, then by taking inverse transform one obtains from Eqs. (5.16a,b)

\[
\Omega_m(z, t) = \frac{K_2 e^{i\eta_0 z}}{2K_3} \Omega_p \left( 0, t - \frac{z}{V_{g+}} \right), \quad (5.17a)
\]

\[
\Omega_p(z, t) = \frac{\kappa_{14} |\Omega_{32} \tau|^2 e^{i\eta_0 z}}{2K_3} \Omega_p \left( 0, t - \frac{z}{V_{g+}} \right). \quad (5.17b)
\]

It is critically important to note that the ratio of \( \Omega_m / \Omega_p \) gives

\[
\frac{\Omega_m(z, t)}{\Omega_p(z, t)} \approx \frac{\Omega_{43}}{\Omega_{23}} \quad (5.18)
\]

Eqs. (5.17a,b) and (5.18) are the key results of the large differential decay behavior of the two eigenvalues. When these equations are satisfied the only absorption of the FWM and pump fields is due to the decay of coherence between states \( |1 \rangle \) and \( |3 \rangle \) that occurs during the time it takes for the pulse to propagate to \( z \). In addition, nearly all of the tendency for the pulse to spread has been removed, as if the two pulsed fields are propagating in a nearly loss free medium with the same group velocity

\[
\frac{1}{V_{g+} \tau} = \frac{1}{c \tau} + \text{Re}[a_{p1}] .
\]

This group velocity and other aspects of the problem look more familiar if one chooses \( M_p = M_m \) for optimized conversion efficiency. Indeed, one has

\[
\frac{1}{V_{g+} \tau} = \frac{1}{c \tau} + \frac{\kappa_{12} \tau}{2 |\Omega_{21} \tau|^2} .
\]
Correspondingly, \( \rho_{21} \) and \( \rho_{41} \) are given by

\[
\rho_{21}(z, t_r) = \frac{i}{2|\Omega_{23}|^2} \frac{\partial \Omega_p}{\partial t_r} + i \frac{\gamma_3}{4|\Omega_{23}|^2} \Omega_p,
\]

\( (5.19a) \)

\[
\rho_{41}(z, t_r) = \frac{i}{2|\Omega_{43}|^2} \frac{\partial \Omega_m}{\partial t_r} + i \frac{\gamma_3}{4|\Omega_{43}|^2} \Omega_m.
\]

\( (5.19b) \)

One immediately recognizes that the first terms on the RHS of Eqs. (5.19a,b), when moved to the LHS of Maxwell’s equation Eq. (5.12), leads to

\[
t_r - \frac{\kappa_{12} z}{2|\Omega_{23}|^2} = t - \frac{z}{V_{gs+}},
\]

which is a new retarded time for the wave with significantly modified group velocity, as expected.

Eqs. (5.19a,b) are of the exactly the form of dark states as in conventional EIT. When these eigen modes are achieved the multi-wave mixing process evolves into two conventional EIT processes, i.e., \(|1\rangle \rightarrow |2\rangle \rightarrow |3\rangle \) and \(|1\rangle \rightarrow |4\rangle \rightarrow |3\rangle \). In addition, the two EIT processes are longer interact with each other and both state \(|2\rangle \) and state \(|4\rangle \) are “dark states”, in the same sense as conventional EIT. When \( M_p \neq M_m \), the FWM process is not optimized, one has

\[
\rho_{21}(z, t_r) = \frac{i a_{p1} \kappa_{12} \Omega_p}{\partial t_r} + \frac{i a_{p0} \kappa_{12}}{\Omega_p},
\]

\( (5.20a) \)

\[
\rho_{41}(z, t_r) = \frac{i a_{p1} \kappa_{14} \Omega_m}{\partial t_r} + \frac{i a_{p0} \kappa_{14}}{\Omega_m}.
\]

\( (5.20b) \)

A simple and alternative way to understand these features can also be obtained by observing Eqs. (5.11a,c). It is seen that in order for \(|2\rangle \) to be a dark state one must have

\[
\Omega_{23} \rho_{31} + \Omega_p = 0 \rightarrow \rho_{31} = -\frac{\Omega_p}{\Omega_{23}}.
\]

Similarly, in order for \(|4\rangle \) to be a dark state simultaneously, \( \Omega_m \) has to grow until

\[
\Omega_{43} \rho_{31} + \Omega_m = 0 \rightarrow \rho_{31} = -\frac{\Omega_m}{\Omega_{43}}.
\]

These relations together require that

\[
\rho_{31} = -\frac{\Omega_p}{\Omega_{23}} = -\frac{\Omega_m}{\Omega_{43}} = \frac{\Omega_m}{\Omega_{43}} = \frac{\Omega_{43}}{\Omega_{23}},
\]

which is precisely the ratio obtained in Eq. (5.18) at large \( z \). Only when these conditions are satisfied will \(|2\rangle \) and \(|4\rangle \) evolve into two independent dark states. This requires propagation effect that is not essential in the conventional EIT schemes.

The accuracy involved in the conclusion drawn above depends strongly on the adiabatic conditions \(|\Omega_{23}^2 t_2^2| \gg |D_2 D_3| \) and \(|\Omega_{43}^2 t_2^2| \gg |D_3 D_4| \) and the other inequalities introduced at the beginning of the section. However, extensive numerics have shown that even when these inequalities for adiabatic behavior are only modestly satisfied, these destructive interferences indeed occur at large \( z \) once the fast decaying terms in Eqs. (5.14a,b) become negligible. Indeed, both \( \rho_{22} \) and \( \rho_{44} \) can be suppressed by as much as twelve orders of magnitude for a double-\( A \) system with slowly decaying \( \rho_{31} \). These dual-EIT based induced transparencies allow the pump and FWM fields to propagate with identical group velocity and with negligible absorption and distortion by maintaining a proper ratio of their amplitudes. Similar matched pulse propagation effect was also studied by Konopnicki and Eberly [104] and Oreg et al. [105] in early 1980s and by Harris [106,107] in early 1990s in the context of three-state \( A \)-schemes with externally supplied fields only. But the first studies of matched propagation in the context of multi-wave mixing and multi-wave induced transparency were carried out by Payne and Deng [67–69].
It is useful to provide a numerical example at this point. For this purpose let us consider a case with a Gaussian input probe pulse, i.e., \( \Omega_p(0, t) = \Omega_p(0, 0) \exp(-2(t/\tau)^2) \). Using the quadratic approximation given in Eq. (5.15), one obtains from Eqs. (5.14a,b)

\[
\Omega_m(z, t_r) = \frac{K_2}{2K_3} \Omega_p(0, 0)e^{i\alpha z} \left[ e^{-2(t_r/\tau - \alpha z)^2/(1 - 8\alpha^2 \tau^2)} - e^{i(\alpha m_0 - \alpha z)} e^{-2(t_r/\tau - \alpha z)^2/(1 - 8\alpha^2 \tau^2)} \right], \tag{5.21a}
\]

\[
\Omega_p(z, t_r) = \Omega_p(0, 0)e^{i\alpha z} \left[ B_+ e^{-2(t_r/\tau - \alpha z)^2/(1 - 8\alpha^2 \tau^2)} + B_- e^{i(\alpha m_0 - \alpha z)} e^{-2(t_r/\tau - \alpha z)^2/(1 - 8\alpha^2 \tau^2)} \right]. \tag{5.21b}
\]

From Eqs. (5.21a,b) it is clear that there are two propagation regimes where two different type of interferences occur.

In the short propagation regime, both terms in Eqs. (5.21a,b) are important and the group velocity difference has not caused the two terms to separate appreciably. This is the region where constructive–destructive recurrence, as a function of propagation distance, occur. It is in this region that the maximum conversion efficiency (near 100%) can be achieved. To accomplish this, one chooses the propagation distance such that the two terms in Eq. (5.21a) interfere constructively. This is a type of interference between two group velocity components of the same field. It should be noted that this recurrences, which are complementary in the pump and wave mixing fields, is not the competing-multiphoton-excitation-pathway based destructive effect that has been the subject of this review.

In the large propagation regime, the second exponential terms in Eqs. (5.21a,b) decay away because of the large differential decay rates of two eigenvalues. This is the region where the multi-photon destructive interference phenomena become effective. In this region, the two fields propagate freely in a highly dispersive medium by maintaining the proper ratio of amplitudes and proper phase relation. It is in this region that highly efficient multi-photon induced transparency can be achieved.

### 5.4.2. Small propagation regime: High photon flux conversion efficiency

To achieve maximum conversion efficiency in the small propagation region one first chooses \( k_{14} |\Omega_{23}|^2 = k_{12} |\Omega_{34}|^2 \). This choice makes \( |K_2/(2K_3)| = \sqrt{k_{14}/k_{12}}/2 \) which leads to a smaller \( D \). Consequently, \( K_3 \) dominates the coefficients of the complex exponentials, resulting in \( B_\pm \approx 1/2 \). Using these results one then chooses the propagation \( z \) so that the first constructive interference occurs in Eq. (5.21a), whereas the two terms in Eq. (5.21b) can destructively interfere to produce zero pump field. When this occurs, the same flux of photons exists in the FWM field. That is, all pump photons have been converted to FWM photons, corresponding a 100% photon flux conversion efficiency. In some experiments, this distance may be too small. Therefore, one should choose the propagation distance in such a way that the two terms in Eqs. (5.21a,b) interfere constructively and destructively, yet the attenuation of the two terms are not substantial.

**Case (a): A ladder system.**

Here, in addition to \( k_{12} |\Omega_{34}|^2 = k_{14} |\Omega_{32}|^2 \), the following experimentally relevant and achievable parameters appropriate to cold alkali vapors will be chosen: \( |\Omega_{23}| = 1000, \tau = 10 \mu s, \Omega_{34} = 100, k_{12} = 10000/cm, k_{14} = 1000/cm, \) and \( \gamma_{21} = 625, \gamma_{31} = 4, \gamma_{41} = 4, \delta_2 = \delta_3 = 0 \).

To achieve high conversion efficiency one chooses the thickness of the sample so that the two terms in Eq. (5.21a) interfere constructively, yet the peak attenuation and separation due to the different group velocities is minimal. This requires that \( \text{Re}(\alpha m_0 - \alpha z) = \pm \pi \) (for the smallest \( z \) corresponding to the first constructive-destructive recurrence). One must also choose \( \delta_4 = \Gamma \) large enough so that the real part of \( \alpha m_0 \) is much larger than the imaginary part. This means that \( z \) should be large enough to give \( \text{Im}(\alpha m_0 z) \ll 1 \), yet still small enough to give \( \text{Im}(\alpha m_0 z) \ll 1 \), and the attenuation of this part of the FWM field is not substantial. If one chooses \( \delta_4 = 160 \) then an efficiency of \( >80\% \) for a medium length of \( z = 0.2518 \text{ cm} \) can be obtained. These predictions agree well with a full numerical solution of Eqs. (5.11) and (5.12), which is shown in Fig. 43 (left panel).

**Case (b): A double-\( \Lambda \) system.**

The disadvantage of the ladder arrangement of the first four energy levels is that the state \( |3 \rangle \) will usually have a much shorter lifetime because of allowed one-photon cascade transitions back to the ground state. This will lead to, among other things, significant pump field attenuation. This problem is avoided with a double-\( \Lambda \) system where \( |3 \rangle \) is a member of the ground state hyperfine manifold. Thus, one has \( \gamma_{31} \ll 1 \). This leads to very small \( \alpha m_0 \) and a much greater reduction in absorption. In addition, smaller \( \gamma_{31} \) will greatly improve the adiabatic behavior of \( \rho_{21} \) and \( \rho_{41} \).
and hence more efficient conversion of pump beam to FWM can be obtained. Again, these predictions agree well with the numerical solution of Eqs. (5.11), (5.12), which is shown in Fig. 43 (right panel). The parameters used in producing this plot are $|\Omega_{23}| = 1000$, $|\Omega_{34}| = 100$, $\kappa_{12} = 10^5$/cm, $\kappa_{14} = 1000$/cm, $\delta_2 = \delta_3 = 0$, $\delta_m = 300$, $\gamma_{21} = 625$, $\tau = 10$ $\mu$s, $\gamma_{31} = 0.02$, and $\gamma_{41} = 4$. Eq. (5.21a) predicts that the first constructive interference in the FWM wave should occur at $z = \pi/6.6467 = 0.4714$ cm. This is indeed what is seen from the plot which shows that the peak height is about 0.97. If this were the total thickness of the medium, the conversion efficiency from pump photons to FWM photons would be 94%. Notice that if the same medium thickness and parameters (except $\gamma_{31}$) is applied to the ladder scheme where $\gamma_{31} = 4$, the generated field would have diminished to only 86%. Further more, if the control laser Rabi frequencies were reduced so that smaller group velocity is achieved, the difference between the efficiencies of the double-$A$ scheme and the ladder scheme would become much larger, with the double-$A$ scheme being much more efficient.

Extensive numerical calculations that integrate the full set of differential equations for all atomic and SVA field equations of motion show no visible difference from Eq. (5.21a,b) for the parameters chosen above. Examination of the actual numbers shows that the largest difference in producing these figures is less than 1%, demonstrating the accuracy and validity of the analytical solutions obtained.

5.4.3. Large propagation regime: Highly effective multi-photon induced transparency

As mentioned in Case (b), small $\gamma_{31}$ will greatly improve the adiabatic behavior of $\rho_{21}$ and $\rho_{41}$, leading to very high degree of cancellation. In fact, the cancellation effects that suppress $\rho_{21}$ and $\rho_{41}$ at large $z$ can be truly spectacular. In the following example it is shown that the slowly decaying parts of the pump and FWM fields can penetrate hundreds of centimeters without appreciable absorption and with almost no pulse spreading.

In the large propagation regime where the second exponential has decayed away a striking example of the destructive interference demonstrating the exceptionally effective multi-photon induced transparency can be obtained by taking $|\Omega_{34}| = 200$ and $\delta_4 = 10$ with all other parameters taken to be the same as in the Case (b) described above. With these parameters, $B_+ = 0.2$, $B_- = 0.8$, $C = 0.04$, $a_{m0} = -161.160 + 233.68i$, $a_{m1} = -5.97048 - 15.6888i$, $a_{m2} = 0.96188 + 0.231153i$, $a_{\rho0} = 0.000200i$, $a_{\rho1} = 0.0200$, and $a_{\rho2} = 0$. 

![Fig. 43. Surface plots of the conversion from a pump field to a FWM field vs. $z/L$ and $t_r/t$. (a) A ladder arrangement of energy levels. Parameters are: $\kappa_{12} = 1000$, $\kappa_{14} = 1000$ cm, $\kappa_{13} = 100000$ cm, $\delta_4 = 160$, and $L = 5$ cm. (b) A double-$A$ system with the same parameters as that of (a) except $\gamma_{31} = 0.02$, $\delta_4 = 300$, and $L = 10$ cm. Both graphs are generated by the numerical solution of Eq. (5.12), in conjunction of Eqs. (5.11a–c), subject to the condition that all of the population initially are in the ground state and the FWM field at $z = 0$ initially is zero. The numerical results are found to agree to at least two significant figures with the analytical results of Eqs. (5.21a,b) using the expressions given for the $a_{m1}$ and $a_{m2}$.
show that at large \( z \) the values of \( \rho_{21} \) and \( \rho_{41} \) correspond to the states \( |2\rangle \) and \( |4\rangle \) being dark states in the classic sense of EIT, agreeing well (to three significant figures) with the analytic results of Eqs. (5.19a,b). Since \( \rho_{21} \) and \( \rho_{41} \) determine the polarization at the probe and FWM frequencies, they are ideal indicators on the degree of transparency induced by the destructive interference, as also indicated in the plot of the diagonal elements (state population) \( \rho_{22} \) and \( \rho_{44} \).

From the values of \( a_{pi} \) it is already clear that the slowly decaying part propagates relatively fast and it can penetrate more than 100 cm without appreciable attenuation or change in pulse width. From the imaginary part of \( a_{m0} \) it is seen that after \( z = 0.05 \) cm the rapidly decaying part has decreased in amplitude by a factor of \( e^{-11.68} = 0.0000084 \). Thus, only two well-matched pulses, i.e., the first terms of Eq. (5.21a,b), exist in the medium.

In Fig. 44 elements of density matrix are plotted as a function of \( z/L \) at the times when the FWM and pump fields are maximum. Left panel: coherence \( \rho_{21} \) and \( \rho_{41} \) vs. \( z/L \). Right panel: populations \( \rho_{22} \) and \( \rho_{44} \) vs. \( z/L \). These results are obtained by numerically integrating Eqs. (5.11) and (5.12), subject to non-depleted ground state and SVA approximation. The numerical results shown agree very well (to three significant figures) with the analytical results using the \( a_{pi} \) and \( a_{mj} \) derived earlier. It can be seen that at large \( z \) where the interference is effective, both \( \rho_{21} \) and \( \rho_{41} \) decrease by more than six orders of magnitude as the coupled double-EIT is established and decoupled, exhibiting the characteristic dark state behavior of independent conventional EIT processes. Correspondingly, the residual populations \( \rho_{22} \) (in the pump field terminal state) and \( \rho_{44} \) (in the FWM generation state) are further suppressed by approximately a factor of \( 10^{14} \) and \( 10^{11} \), respectively. It is remarkable that such efficient multi-photon induced transparencies can be produced in such a short propagation distance.

It should be emphasized that although example demonstrated above has shown that approximations made in the present study work better for double-\( A \) systems than for ladder systems because of much smaller \( |D_3| \), it is important to realize that ladder systems are more important for applications such as frequency up conversion. This is due to the fact that double-\( A \) systems do not have the advantages of being widely tunable and being able to generate wavelengths very different from any laser used in the process.

### 5.5. Experimental studies of high efficiency FWM using the conventional three-state one-photon coupling EIT

In several pioneering studies by Jain et al. [96,99] and Merriam et al. [100–102] conventional three-state EIT has been used in achieving highly efficient FWM. In all of these studies two strong pulsed lasers (\( \Omega_p \) and \( \Omega_c \)) have been used to produce and maintain a strong coherence between states \( |1\rangle \) and \( |2\rangle \) (see Fig. 45. Note that the notations used in this subsection are that of [96,99–102]. Thus, state \( |3\rangle \) will be the dark state). A weak pulsed field \( \Omega_e = \Omega_{42} \), tuned close to resonance between states \( |2\rangle \) and \( |4\rangle \), is then introduced to generate a FWM field \( \Omega_h = \Omega_{41} \). These experiments demonstrated that this double-\( A \) scheme can produce close to 100% photon conversion efficiency between the injected weak pulse and the generated field. In addition, they demonstrated a type of interference after a sufficient depth of...
propagation once $\Omega_b \equiv \Omega_{41} = \Omega_c \Omega_p / \Omega_e = \Omega_{32}\Omega_{31} / \Omega_{32}$ is established. Under this condition, both fields can propagate almost indefinitely through the medium without pulse distortion or absorption. The main limitation on this decoupling from the medium is related to the absorption of the lasers that produce the coherence between states $|1\rangle$ and $|2\rangle$. The latter behavior is only remotely related to the “double EIT” phenomena described in the last section, but is closer to the decoupling from the medium experienced by the laser and the $(N + 1)$-wave mixing field in the odd-photon destructive interferences described in earlier sections.

In the experimental work of Jain et al. [96,99] and Merriam et al. [100–102], lasers were all tuned to resonance and the medium was $^{208}$Pb. The long pulsed probe and control lasers are tuned around $\lambda_p = 283$ nm $\lambda_c = 406$ nm, respectively. A weak and short pulsed laser field at $\lambda_e = 233$ nm is injected to the medium to generate a short pulsed FWM field at $\lambda_h = 186$ nm. The state designations are $|1\rangle = |6p^2(3 P_0)\rangle$, $|2\rangle = |6p^2(3 P_2)\rangle$, $|3\rangle = |6p 7s(3 P_1)\rangle$, and $|4\rangle = |6p 9s(3 P_1)\rangle$. The appropriate atomic equations of motion describing this system are given as

\[
\frac{\partial \rho_{31}}{\partial t_r} = -\Gamma_{31} \rho_{31} + i \Omega_{31}(\rho_{11} - \rho_{33}) + i \Omega_{32} \rho_{21} - i \Omega_{41} \rho_{34},
\]

\[
\frac{\partial \rho_{32}}{\partial t_r} = -\Gamma_{32} \rho_{32} + i \Omega_{32}(\rho_{22} - \rho_{33}) + i \Omega_{31} \rho_{12} - i \Omega_{42} \rho_{34},
\]

\[
\frac{\partial \rho_{11}}{\partial t_r} = -2 \text{Im}[\Omega_{13} \rho_{31} + \Omega_{14} \rho_{41}].
\]

where $\Gamma_{j k}$ is the decoherence rate between two relevant states. With the state $|3\rangle$ being the only state with a fast spontaneous decay rate, one can easily show that

\[
\rho_{11} = \frac{|\Omega_{23}|^2}{|\Omega|^2}, \quad \rho_{22} = \frac{|\Omega_{31}|^2}{|\Omega|^2}, \quad \rho_{33} = 0, \quad \rho_{21} = -\frac{\Omega_{31} \Omega_{23}}{|\Omega|^2},
\]

where $|\Omega|^2 = |\Omega_{31}|^2 + |\Omega_{23}|^2$. With the intensities used in the experiments these relations predict a substantial coherent population transfer from the ground state $|1\rangle$ to the lowest excited state $|2\rangle$, and a substantial coherence is maintained by the two long pulsed fields. Detailed theoretical analysis of these experiments have shown that a destructive interference occurs when relation $\Omega_h(L, t_r)/\Omega_e(L, t_r) = \Omega_p / \Omega_e$ is satisfied (see Eqs. (5.17a,b) and (5.18) in Section 5.4). Thus, one expects a hyperbolic relation and a linear relation when the ratio is plotted against $\Omega_e$ and $\Omega_p$, respectively, for the region of parameters where all the approximations used in the actual experiments are valid. This is demonstrated in Fig. 46 where the ratio $\Omega_h(L)/\Omega_c(L)$ is plotted as functions of $\Omega_p$ and $\Omega_c$, respectively. Furthermore, theoretical analysis shows that $\Omega_e(L, t_r)/\Omega_c(0, t_r) = 1/(1 + \kappa_{24}|\Omega_p|^2/(\kappa_{14}|\Omega_e|^2))$, in addition to a near 100% photon flux conversion efficiency. Fig. 47 shows the plots of $\Omega_e(L, t_r)/\Omega_c(0)$ and $\Omega_h(L, t_r)/\Omega_c(0)$ versus $\Omega_p/\Omega_e$. The latter plot
Fig. 46. Ratio of $O_{e}(z = L)/O_{e}(z = L)$, at the exit of the cell, as a function of the $O_{e}$ (left figures (a) and (b)) and $O_{p}$ (right figures (a) and (b)), respectively. In all figures, (a) For $N_{0}L = 1.2 \times 10^{14} \text{ cm}^{-2}$ and (b) For $N_{0}L = 5.6 \times 10^{14} \text{ cm}^{-2}$. The dashed vertical line in the left figures are the value of $O_{e}$ required for weak-probe EIT. The hyperbolic curves in the left figures are the $x_T L \rightarrow \infty$ theoretical prediction with (a) $O_{p} = 0.25 \text{ cm}^{-1}$ and (b) $O_{p} = 0.24 \text{ cm}^{-1}$. The solid lines in the right figures are the $x_T L \rightarrow \infty$ theoretical prediction with (a) $O_{e} = 0.33 \text{ cm}^{-1}$ and (b) $O_{e} = 0.35 \text{ cm}^{-1}$. Reproduced from [102] with permission.

Fig. 47. Ratios of $O_{e}(z = L)/O_{e}(z = 0)$ (left figures (a) and (b)) and $O_{h}(z = L)/O_{e}(z = L)$ (right figures (a) and (b)) as a function of $O_{e}/O_{p}$, respectively. In all figures, (a) For $N_{0}L = 1.2 \times 10^{14} \text{ cm}^{-2}$ and (b) For $N_{0}L = 5.6 \times 10^{14} \text{ cm}^{-2}$. The solid lines are the $x_T L \rightarrow \infty$ theoretical prediction. Reproduced from [102] with permission.
should exhibit a linear relation with unit slope (i.e., near 100% photon conversion efficiency) since as in the matched pulse region these quantities should be equal. The authors point out that at the lower concentration the power broadening of the $|2\rangle \rightarrow |4\rangle$ transition can reduce the absorption enough to block reaching the matched pulse region.

5.6. Inhibition of the onset of three-photon destructive interference

The discussions presented so far have shown that the internally generated fields play a critical role in many nonlinear optical processes where efficient optical wave generation and conversions occur as a result of strong and resonant excitation of the media. In particular, odd-photon destructive interference has been shown to be very robust in many wave mixing processes. The negative side and unwanted consequences of this novel effect is the suppression of mixing wave production, which significantly limits overall conversion efficiencies of some technologically important nonlinear devices operated under highly resonant conditions using gases media.

The main focus of this subsection is to discuss a multi-photon induced transparency based FWM scheme that is capable of substantially inhibiting the onset of three-photon destructive interference by actively weakening [68] and manipulating [68,71] the medium response. The idea is to achieve passive EIT at the three-photon resonance, but to come off resonance so that phase matching can still be achieved [68]. In addition, the passive EIT technique can be used to actively manipulate a strong one-photon resonance and therefore, the dispersion response of the medium. This can lead to an active channel opening for wave-mixing process in an otherwise totally optically opaque thick medium [71]. It will be shown that some of these novel schemes exhibit a new type of wave-matching condition that is fundamentally different from the conventional FWM process without induced transparency. This new wave-matching condition allows FWM field to be generated in a broad region that is not at all possible with conventional FWM process without induced transparency processes. Consequently, multi-wave mixing processes do not critically depend on the frequency detuning FWM field from the exact resonance for achieving constructive interference, as required in conventional FWM schemes. These are interesting new features that may find applications in opto-electronics engineering.

5.6.1. General treatment of the problem

Consider a life time broadened multi-level system interacting with four laser fields (Fig. 48). The equations of motion for the relevant density matrix elements to be solved are

\[
\frac{\hat{\rho}_{21}}{\hat{t}} = i \left( \delta_2 + i \frac{\gamma_{21}}{2} \right) \rho_{21} + i \Omega_{21} \rho_{21} + i \Omega_{23} \rho_{31} + i \Omega_{24} \rho_{41},
\]

(5.24a)

\[
\frac{\hat{\rho}_{31}}{\hat{t}} = - \frac{\gamma_{31}}{2} \rho_{31} + i \Omega_{32} \rho_{21},
\]

(5.24b)

\[
\frac{\hat{\rho}_{41}}{\hat{t}} = i \left( \delta_4 + i \frac{\gamma_{41}}{2} \right) \rho_{41} + i \Omega_{41} \rho_{41} + i \Omega_{42} \rho_{21} + i \Omega_{45} \rho_{51},
\]

(5.24c)

\[
\frac{\hat{\rho}_{51}}{\hat{t}} = - \frac{\gamma_{51}}{2} \rho_{51} + i \Omega_{54} \rho_{41}.
\]

(5.24d)

In deriving Eqs. (5.24a–d) the ground state has been assumed to be undepleted ($\rho_{11} \simeq 1$), which is ensured by the assumption $|\Omega_{21}|, |\Omega_{23}| \ll |\Omega_{23}|$, and only the leading contributions have been consistently kept. To reduce attenuation to the pump and the generated fields, it has been assumed that $\delta_2 = \omega_p - \omega_{21} = 0$, $\delta_3 = \omega_{21} - \omega_{23} = 0$, $\delta_5 = \omega_{21} - \omega_{45} = 0$, and $\gamma_{ii} = \gamma_4$. In addition, by assuming that the state $|3\rangle$ is a member of the ground state hyper-fine manifold with a very slow decay rate, $\gamma_{31} = 0$ will be used. The choice of the state $|5\rangle$ is of great importance. As will be shown later a slow decoherence rate $\gamma_{51} < 1$ will lead to partial inhibition of the early onset of multi-photon destructive interference. This condition may be achieved by carefully choosing the atomic angular momenta and ion-core configurations. Caution should also be exercised as to the choice of the state $|5\rangle$ so that the HR transition $|5\rangle \rightarrow |2\rangle$ is not allowed. Furthermore, the two-photon coupling $\Omega_{24}^{(2)}$ between states $|2\rangle$ and $|4\rangle$ is assumed to be relatively weak so that the following adiabatic solution is adequate for the pulsed pump field

\[
\rho_{21} \simeq \frac{i}{|\Omega_{21}|^2} \frac{\hat{t}}{\hat{t}} \left[ \Omega_p \left( 0, t - \frac{z}{V_g(p)} \right) \right],
\]

(5.25)
where the group velocity of the pulsed pump field is given by

\[
\frac{1}{V_g^{(p)}} = \frac{1}{c} + \frac{\kappa_{12}}{|\Omega_{c1}|^2}.
\] (5.26)

Note that for sufficiently high concentration the second term in Eq. (5.26) dominates, and one will have a significantly reduced group velocity

\[
V_g^{(p)} \simeq \frac{|\Omega_{c1}|^2}{\kappa_{12}}.
\]

In deriving Eqs. (5.25) and (5.26), notations \(\Omega_{21} = \Omega_p\), \(\Omega_{23} = \Omega_{c1}\), \(\Omega_{45} = \Omega_{c2}\), \(\Omega_{41} = \Omega_m\), and \(\Omega_{42}^{(2)} = \Omega_S^{(2)}\) have been introduced. In addition, adiabatic conditions \(|\Omega_{c1}\tau^2 \gg \text{Max}(\gamma_{21}\tau, |\delta_{21}|, 1)\) and \(|\Omega_{c2}\tau^2 \gg \text{Max}(\gamma_{41}\tau, \gamma_{51}\tau, |\delta_{41}|, 1)\) have been applied. These conditions ensure the validity of the adiabatic approximation, leading to the well behaved adiabatic solution of Eq. (5.25). The production and propagation effect of the FWM field at \(\omega_m = \omega_p + 2\omega_S\) can be obtained by solving the Maxwell’s equation for the generated wave, i.e.

\[
\frac{\partial \Omega_m}{\partial z} + \frac{1}{c} \frac{\partial \Omega_m}{\partial t} = i\kappa_{14} \rho_{41}.
\] (5.27)

Taking Fourier transform of Eqs. (5.24), (5.25), and (5.27) with respect \(t/\tau\), one obtains

\[
\alpha_{21} \simeq \frac{\eta}{|\Omega_{c1}|^2} A_p(0, 0) \tau e^{i\eta/(V_g^{(p)} \tau)},
\] (5.28a)

\[
\left(\eta + \delta_{41} \tau + \frac{i\gamma_{41}\tau}{2}\right) \alpha_{41} = -A_m \tau - \Omega_{S}^{(2)} \tau \alpha_{21} - \Omega_{c2} \tau \alpha_{51},
\] (5.28b)

\[
\left(\eta + \frac{i\gamma_{51}\tau}{2}\right) \alpha_{51} = -\Omega_{c2}^{*} \tau \alpha_{41},
\] (5.28c)

\[
\frac{\partial A_m}{\partial z} - \frac{i\eta}{c\tau} A_m = i\kappa_{14} \alpha_{41}.
\] (5.28d)
Assuming that $|\Omega_{c2}\tau| \gg \text{Max}(\gamma_{41}\tau, \gamma_{51}\tau, 1)$ which is also valid and consistent with the assumption on adiabaticity, one obtains

$$
\begin{align}
\alpha_{c1} & \simeq \frac{(\eta + i\gamma_{51}\tau/2)(A_{m} + \Omega_{S}^{(2)}g_{21})}{|\Omega_{c2}\tau|^2}, \\
\alpha_{51} & \simeq -\frac{\Omega_{c2}^{*}(A_{m} + \Omega_{S}^{(2)}g_{21})}{|\Omega_{c2}\tau|^2}, \\
A_{m}(z, \eta) & = \kappa_{14}\Omega_{S}^{(2)}\tau A_{p}(0, 0) e^{i\eta z/(V_{g}^{(p)}\tau)} \frac{(\eta + i\gamma_{51}\tau/2)}{|\Omega_{c2}\tau|^2} \frac{\eta}{|\Omega_{c1}\tau|^2} \left(1 - e^{-iK_{v}z}\right).
\end{align}
$$

(5.29a)

(5.29b)

(5.29c)

where

$$
K_{v} = \frac{\eta}{\tau} \left(\frac{1}{V_{g}^{(p)}} - \frac{1}{V_{g}^{(m)}}\right) - iK_{0}, \quad \frac{1}{V_{g}^{(m)}} = \frac{1}{c} + \frac{\kappa_{14}}{|\Omega_{c2}|^2}, \quad \frac{\kappa_{14}}{|\Omega_{c1}|^2}, \quad K_{0} = \frac{\kappa_{14}\gamma_{51}}{2|\Omega_{c2}\tau|^2}.
$$

(5.30)

For efficient FWM generation in slow propagation regime, the group velocity matching is of the primary importance. This is because that the group velocity matching corresponds to making the real part of $K_{v}$ zero. This matching condition significantly enhances the absolute value of Eq. (5.29c). Thus, one requires that the group velocities of the pump and the generated fields be closely matched, i.e.,

$$
\frac{1}{V_{g}^{(p)}} = \frac{1}{V_{g}^{(m)}} \rightarrow \frac{\kappa_{12}}{|\Omega_{c1}|^2} = \frac{\kappa_{14}}{|\Omega_{c2}|^2}.
$$

(5.30)

This relation demonstrates that in the case of dense media where the waves travel significantly slower than the speed of light in vacuum, group velocity matching can be achieved with two cw control fields.

It should be emphasized that this type of wave-matching is fundamentally different from the well-known phase-matching conditions usually seen in conventional FWM process. In the conventional FWM schemes, phase-matching conditions for efficient generation with parallel beams geometry require closely matched phase velocity only. This is because the group velocities of the waves involved are very close to $c$ and the separation between waves is not significant unless the pulses are very short and the medium is dense and very long. For an extended and dense resonant medium of length $L$ and where $V_{g}^{(p)} \ll L$, group velocity matching is of primary importance since the phase velocity matching near the resonance $|4\rangle - |1\rangle$ is always satisfied.

Furthermore, in the conventional FWM process, efficient generation is supported usually only at a specific phase velocity matching point (or a very narrow region near the phase velocity matching point). Thus, the choice of detuning for efficient FWM generation, which usually is pulsed in nature, is critically important. In the case of induced-transparency based FWM process, the presence of the second cw driving field has replaced the pulsed FWM detuning for group velocity matching. Thus, efficient FWM generation can be achieved on both sides of the three-photon resonant state over two broad regions near the FWM producing state. In the case where an extra level is in between the states $|2\rangle$ and $|4\rangle$ so that near resonance one-photon coupling is achieved, a similar conclusion can be reached where the FWM-matching region is even broader due to stronger one-photon coupling. These features of the present scheme raise an interesting possibility of active wave-matching control and widely tunable mixing wave generation technique that may have potential applications.

Taking the group velocity matching conditions given in Eq. (5.30), Eq. (5.29c) becomes

$$
A_{m}(z, \eta) = i\kappa_{14}\Omega_{S}^{(2)}\tau A_{p}(0, 0) e^{i\eta z/(V_{g}^{(p)}\tau)} \frac{(\eta + i\gamma_{51}\tau/2)}{|\Omega_{c2}\tau|^2} \frac{\eta}{|\Omega_{c1}\tau|^2} \left(1 - e^{-iK_{0}z}\right).
$$

(5.31)

In the next subsection it is shown that properly chosen state $|5\rangle$ can facilitate or inhibit the onset of multi-photon destructive interference, leading to different growth behavior of the FWM field.
Fig. 49. Plot showing the dimensionless Fourier transformed FWM field $|A_m(z, \eta)/(\Omega_S^{(2)} \tau)|$ as a function of propagation distance with fixed concentration. Dashed curve: $\gamma_{51} \tau = 0.157$, and the production of FWM saturates earlier because of a three-photon destructive interference. Solid curve: $\gamma_{51} \tau = 0.0157$, and the earlier onset of the three-photon destructive interference is delayed, leading to higher overall production of the FWM field. Reproduced from [68] with permission.

5.6.2. FWM production limited by three-photon destructive interference

Consider the case where $\gamma_{51} \tau \geq 0.157$. For $\gamma_{14} = 10^{11}$ cm$^{-1}$ s$^{-1}$, $\gamma_{12} = 10^9$ cm$^{-1}$ s$^{-1}$, and $z = 10$ cm, one has $K_0z \simeq 8$. Thus, the FWM production reaches saturation at this propagation depth and Eq. (5.31) gives

$$A_m(z, \eta) \simeq i\Omega_S^{(2)} \tau A_p(0, 0) e^{i\eta z/(V_g(\rho))} \left(\frac{\eta + i\gamma_{51} \tau/2}{\gamma_{51} \tau/2}\right) \frac{\eta}{|\Omega_{c1}|^2}.$$

(5.32)

Notice that this asymptotic solution for phase matched FWM generation is independent of concentration and propagation distance (except a $z$ dependent phase). This is the behavior of a destructive interference. Using Eqs. (5.28a) and (5.32), it is straightforward to show that

$$\Omega_m \simeq -\Omega_{42}^{(2)} \rho_{21} - \Omega_{45} \rho_{51}.$$

(5.33)

When this result is inserted into Eq. (5.24c), one immediately obtains $\rho_{41} \simeq 0$. Thus, at this depth and concentration there will be no further excitation to the state $|4\rangle$ and the generated field ceases to grow. This type of destructive interference limited behavior is clearly depicted in the Fig. 49 (the dashed curve) where the absolute value of Eq. (5.31) as a function of propagation distance is plotted. As expected, the absolute value of the Fourier transformed FWM field quickly reaches the saturation value given in Eq. (5.32) and is independent of the propagation distance after the destructive interference becomes effective.

5.6.3. Inhibiting the onset of three-photon destructive interference

From the standpoint of applications, inhibiting and delaying the onset of the destructive interference is of great importance. This allows one to reach higher overall conversion efficiency at much higher concentrations, both are necessary conditions for efficient radiation devices that rely on the principles of wave mixing. From Eq. (5.31) it is seen that if $\gamma_{51} \tau$ is such that $|K_0 z| \ll 1$ for the given concentration and propagation depth, the onset of the destructive interference can be delayed substantially. For such a small $|K_0|$ one has

$$A_m(z, \eta) \simeq i\kappa_{14} \tau z \Omega_S^{(2)} \tau A_p(0, 0) e^{i\eta z/(V_g(\rho))} \left(\frac{\eta + i\gamma_{51} \tau/2}{\gamma_{51} \tau/2}\right) \frac{\eta}{|\Omega_{c2}|^2}.$$

(5.34)

Compare Eq. (5.34) with Eq. (5.32) one immediately notices the multiplication factor $\kappa_{14} z$. Thus, the amplitude of the generated field will grow linearly as a function of concentration and propagation distance. This can lead to higher overall conversion efficiency under the same concentration and propagation distance where the destructive interference is effective (the thin solid curve in Fig. 49). The linear growth of the FWM field in the same region of propagation depth indicates the absence of the destructive interference. Notice that the FWM field amplitude in this case (thin solid curve) is about an order of magnitude larger than that achievable when the destructive interference is present (dashed curve).
It should be made clear that the induced-transparency based FWM scheme described here is capable of delaying the onset of the three-photon destructive interference, but in principle the destructive interference will still occur simply because of the nature of the back-coupling process in most frequency up-conversion schemes.

6. Highly efficient multi-wave mixing processes with coherently prepared states

One of many new surprises in multi-photon processes involving destructive interference effects from internally generated fields is that these interferences can occur with one-photon resonances if a long-lived coherent superposition of two states has been produced and maintained by previous application of coherent radiation fields. In such a coherently prepared medium, if a weak laser pulse, tuned near resonance between one of the prepared states and a higher lying excited state, (Fig. 45) is incident before the coherence between the prepared states decays appreciably, then a TWM field is generated so that the two fields lead to a two-photon resonance coupling between the two prepared states. With sufficient concentration the amplitude of the TWM field grows until sufficient absorption opens the back-coupling channel and a destructive interference is produced between the one-photon pumping by the laser and the one-photon pumping by the TWM field of the same upper state. The interference leaves no polarization at either the laser frequency or the frequency of the TWM field. At this point the remaining laser and TWM fields can propagate freely. Indeed, at large values of $z$, where interference is operative, there would be no population in the higher excited state and both on-one-photon-resonance fields propagate in this balanced condition indefinitely.

This intuitive consideration opens wide possibilities of quantum destructive interference participating multi-wave mixing process where a substantial atomic coherence has been prepared and maintained in the media. As will be shown, the feature of coherently prepared states can lead to efficient generation of coherent radiations.

The concept of coherently prepared states can be traced back to the early days of laser science. Bell and Bloom [108] first showed that it is possible to produce a coherence between the Zeeman sub-levels of alkali metal atoms by pumping the atoms with light modulated at the Zeeman resonance frequency. In 1976 Alzetta et al. [109,110] showed that different longitudinal modes of a laser, with frequencies differing by the hyperfine frequencies of alkali–metal atoms, could induce analogous coherences between the hyperfine sub-levels. Nearly at the same time, Arimondo et al. and Gary et al. [111,112] discussed the non-absorbing atomic state produced by coherent two-photon transitions. These pioneering works have lead to intensive research activities in the past 40 years, resulting in concepts and research discoveries such as coherent population trapping (CPT) [113] and the related effect of EIT [72–74], lasing without inversion (LWI) [114–118], velocity-selective laser cooling [119], and more recently, new CPT-based atomic frequency references [120], etc.

In the field of optical wave mixing, the technique of coherently prepared states has been applied to a broad range of topics such as EIT based optical phase conjugations [121], matched pulse propagations [104–107], phasorniums [122,123] and related phenomena, enhanced Kerr nonlinear phase shift [124,125], dark-state polaritons [126,127], generation of inelastic FWM [69], and temporal-amplitude-group-velocity matched pulses [128]. In this section, the concentration will be on progress in the field of optical wave mixing where initially prepared states, internally generated fields, and effects of quantum destructive interferences are the dominate features of the processes. Since the scope here is to discuss quantum destructive interference in a coherently prepared system for wave mixing processes, the broad field of coherently prepared states where internally generated field has not been a central feature will not be reviewed. For past progresses and new advances in coherent population trapping and related topics readers are recommended to many excellent research articles, review reports and classical textbooks.

6.1. Inelastic two-wave mixing (ITWM) in $A$ systems: destructive interference between one-photon resonant couplings

In Section 5.4 readers have seen discussions and reviews to a double-/$A$ FWM scheme where two intense long pulsed lasers were used to couple the two lowest states |1⟩ and |3⟩ (Fig. 45). The intensities and pulse lengths used in the related experiments [96,99–102] suggested that a nearly maximum atomic coherence was produced and maintained between these states. In this subsection it is shown that such an experimental situation can be viewed as an ITWM process with coherently prepared initial coherence. (Fig. 50 for a double-$A$ scheme and Fig. 51 for a ladder scheme.) In addition, new features of operation have been added to the analysis to further demonstrate the view of ITWM process. For instance, in the following treatment the possibility of abrupt (i.e., non-adiabatic) switching-off of the control laser
Fig. 50. A double-$A$ type energy-level diagram showing laser coupling for ITWM process: (a) coherence preparation process; and (b) ITWM generation process.

Fig. 51. A ladder type energy-level diagram showing laser coupling for ITWM process. (a) coherence preparation process and (b) ITWM generation process. Strong laser fields $\Omega_p$ and $\Omega_c$ should be on to maintain the coherence between the ground state $|1\rangle$ and the excited state $|3\rangle$ because of the latter has a relative fast decoherence rate through the cascade down transitions.

is also allowed. This operation freezes the density matrix elements at their value at the time of sudden switching-off. Consequently, the coherence between states $|1\rangle$ and $|3\rangle$ no longer propagates, but does decay slowly due to $\Gamma_{31}\tau \ll 1$. In an alkali such as $^{87}$Rb this decay rate is about $10^{3}$/s for a cold vapor at a concentration of $N_0 = 10^{13}$/cm$^3$ if the states $|1\rangle$ and $|3\rangle$ are both hyperfine states of the ground state manifold. (see Fig. 42 right panel) At $N_0 = 10^{12}$/cm$^3$ and at corresponding elevated temperatures, suitable inert gases can be used as buffer agents to reduce the escape rate of coherently prepared atoms from the laser beam due to thermal motion, and hence achieve a decoherence rate of kHz or less [129]. This slow decoherence rate permits one to introduce a weak short laser pulse, tuned near resonance between states $|3\rangle$ and $|4\rangle$ (see Fig. 50b), at a delayed time to generate a TWM field enabled by the allowed transition $|4\rangle - |1\rangle$. 
As will be explained, this TWM scheme involving prepared states is fundamentally different from the conventional three-states \( A \) type EIT schemes.

Consider a life time broadened four-level atomic system (such as a cold atomic vapor where the Doppler broadening can be neglected) interacting with three laser fields in a two-step laser excitation scheme: (1) coherence preparation step (Fig. 50a); and (2) TWM generation step (Fig. 50b). A similar energy level system has been used by several research groups for efficient wave mixing [96,99–102]. Assume that in the coherence creation phase a probe and a control laser have been used to establish a coherent superposition of states \([1]\) and \([3]\) uniformly through the medium. The control laser, followed by the probe laser, is rapidly switched off to store the light and the coherence at time \( t_0 \). The laser fields required for this operation are relatively intense in order to produce adequate uniformity in the excitation of the medium. In the TWM generation phase, with this coherent superposition established and a slowly decay, a weak short-pulsed source field, \( E_S \), is then introduced to initiate the TWM process. Physically, one expects no difference between the situation where both cw fields are left on and the situation where both cw fields are suddenly (i.e., the probe and control fields used in coherence creation phase) cut off before the arrival of the weak co-propagating pulsed laser. The only requirement is that the delay time \( t_D \) for the source laser to arrive plus the propagation time for it to traverse through the medium must be shorter than the decay time of the coherence \( 1/\Gamma_31 \).

If the pulse length of the field \( E_S \) and its medium transient time are shorter than the coherence decay time, one expects that the amplitudes of \( |3\rangle \) and \( \langle 3| \) will not change appreciably during the passage of the weak laser pulse, or during the delay following the shut-off of the strong cw fields. One thus considers a TWM picture with an initial condition where the atomic system is in a superposition state before the introduction of the pulsed source field. In this picture, state \([2]\) does not play any role as it is used only at the initial preparation stage. Thus, one has an effective three-state model (Fig. 50b) interacts with two weak pulsed fields under the condition that the following long-lived coherent superposition state has been created and maintained in the medium

\[
|\Psi\rangle = A_1 e^{-i\omega_1(t-t_0)}|1\rangle + A_3 e^{-i\omega_3(t-t_0)} e^{i(\omega_3-\omega_1)z/c} |3\rangle,
\]

as long as \( \Gamma_31(t - t_0) \ll 1 \) where \( t_0 \) is the time when the strong laser fields used for state preparation are abruptly switched-off.

When a weak pulsed laser field at frequency \( \omega_S \) is injected into the medium an additional term \( e^{-i(\omega_4+\omega_3)z/c} A_4|4\rangle \) with \( \omega_4 = \omega_S - \omega_4 + \omega_3 \) will be added to the above state vector. Defining \( \Omega_{43} = \Omega_S \) and \( \Omega_{41} = \Omega_{\text{TWM}} \), the equations of motion for the relevant density matrix elements and the wave equations for the pulsed source and TWM fields are given by

\[
\frac{\partial \rho_{41}}{\partial t_r} = i(\delta_4 + i\Gamma_{41})\rho_{41} + i\Omega_{\text{TWM}}\rho_{11} + i\Omega_S\rho_{31},
\]

\[
\frac{\partial \rho_{43}}{\partial t_r} = i(\delta_4 + i\Gamma_{43})\rho_{43} + i\Omega_S\rho_{33} + i\Omega_{\text{TWM}}\rho_{13},
\]

\[
\left( \frac{\partial \Omega_{\text{TWM}}}{\partial z} \right)_{t_r} = i\kappa_{14}\rho_{41}, \quad \left( \frac{\partial \Omega_S}{\partial z} \right)_{t_r} = i\kappa_{34}\rho_{43},
\]

where \( t_r = t - z/c \). In deriving these equations considerations have been taken into account that in a true four-state system the phase factors from the coherently prepared state exactly compensate the inelasticity of the two-wave mixing process. Note that without keeping track of the “grating” (i.e., the factor \( e^{i(\omega_3-\omega_1)z/c} \) appears in the second term in Eq. (6.1)) written on the medium, there would be a factor \( e^{i(\omega_3-\omega_1)z/c} \) multiplying the term \( i\kappa_{34}\rho_{43} \) in Eq. (6.2c) due to the fact that the TWM process is inelastic. In the case where the states \([1]\) and \([3]\) are members of ground state hyper-fine manifold and all fields are co-propagating the energy difference is too small to have an appreciable effect. However, it could be very important if the energy difference between \([1]\) and \([3]\) were much larger or when the cw fields are counter-propagating.
From Eqs. (6.2a–c) it is clear that this process should not be viewed as a conventional FWM process. Eqs. (6.2a–c) can be solved by standard method of Fourier transform with respect to \( t_r / \tau \). One has

\[
\begin{align*}
\chi_{41} &= -\frac{\rho_{41} A_S \tau + \rho_{11} A_{TWM} \tau}{\delta_4 \tau + \eta + i \Gamma_{41} \tau}, \\
\chi_{43} &= -\frac{\rho_{13} A_{TWM} \tau + \rho_{33} A_S \tau}{\delta_4 \tau + \eta + i \Gamma_{43} \tau}, \\
\frac{\partial A_{TWM}}{\partial z} &= i \kappa_{14} \chi_{41}, \quad \frac{\partial A_S}{\partial z} = i \kappa_{34} \chi_{43}.
\end{align*}
\]

(6.3a)

Here, \( \rho_{11}, \rho_{33}, \) and \( \rho_{31} \) are assumed to be constant over the period of propagation of the weak source and TWM fields through the medium. Solving Eqs. (6.3a–c) one obtains

\[
\begin{align*}
A_{TWM}(z, \eta) &= -\frac{\kappa_{14} \rho_{31}}{\kappa_{14} \rho_{11} + \kappa_{34} \rho_{33}} [1 - e^{-c_T z}] A_S(0, \eta), \\
A_S(z, \eta) &= \frac{\kappa_{14} \rho_{11} + \kappa_{34} \rho_{33}}{\kappa_{14} \rho_{11} + \kappa_{34} \rho_{33}} e^{-c_T z} A_S(0, \eta),
\end{align*}
\]

(6.4a, b)

where \( c_T = i (\kappa_{14} \rho_{11} + \kappa_{34} \rho_{33}) / (\delta_4 + \eta + i \Gamma_{41} \tau) \). From Eqs. (6.4a, b) it is straightforward to show that for sufficiently large \( z \) so that \( e^{-c_T z} \ll 1 \), one has

\[
\rho_{11} \Omega_{TWM}(z, t_r) + \rho_{31} \Omega_S(z, t_r) = 0.
\]

(6.5)

Substitute Eq. (6.5) into the RHS of Eq. (6.2a), it is seen that at large \( z \) when Eq. (6.5) is valid, \( \rho_{41} \) does not change in amplitude and this condition must persist even when \( |\delta_4| > 0 \). Thus, one should see no fluorescence or scattered light from the region of the beam at sufficiently large \( z \).

What has been demonstrated above is a very robust destructive interference between two odd-photon processes (both are one-photon in this case) involving internally generated fields where part of the internally generated TWM field must be absorbed before the destructive interference occurs. It leads to zero polarization of the medium at large \( z \) at the frequencies of \( \omega_S \) and \( \omega_{TWM} \), so that both the weak source laser and the generated field propagate as in free space.

Readers may think that the system discussed is the same as a conventional three-state \( \Lambda \)-type EIT scheme because the effective scheme is a three-state \( \Lambda \) type and the two channels involved in the destructive interference are both one-photon channels. This is, however, not correct. What has been demonstrated in Eqs. (6.4a, b) and (6.5) is a fundamentally different type of induced transparency that is closely related to odd-photon destructive interferences discussed in Section 3. Here, one has: (1) a large \( |\delta_4| \) population; (2) an internally generated field is required; (3) both fields involved are weak; and (4) there is no Autler–Townes splitting. Furthermore, the concept of a large transparency window does not apply, and it is the intricate destructive interference between two weak fields, even though in the form of one-photon resonance processes, that causes the reduction of absorption to both fields. This interference effect becomes important only after appropriate propagation so that a part of the generated field is strongly absorbed. These pulses are still “matched pulses” in the sense of earlier discussions. None of these features exist in the conventional three-state \( \Lambda \)-type EIT scheme.

To see how remarkable this interference effect is, one may consider the case where \( \delta_4 = 0 \). In this case light would ordinarily be absorbed in a very tiny distance for both frequencies (i.e., \( \omega_S \) and \( \omega_{TWM} \)). However, once Eq. (6.5) is satisfied both field propagate as in free space.

The phenomenon described above is reminiscent of what happens when one tunes a transform limited bandwidth pulsed laser near a three-photon resonance between a ground state \( |1\rangle \) and an excited state \( |2\rangle \) in an effective two-level system as described in Section 3. Thus, it is not surprising that destructive interference and hence induced transparency, which is fundamentally different from the conventional three-state EIT scheme, occur.

This treatment is readily extended to a ladder system which is much more useful for frequency up conversion to shorter wavelength regions. However, for such systems significant complications arise when the two-photon terminal state \( |3\rangle \) is above the first one-photon state \( |2\rangle \). For instance, in general the life time of the state \( |3\rangle \) is much shorter, leading to further attenuation of the wave mixing field that couples the transition \( |3\rangle - |4\rangle \). The cascade transitions...
Fig. 52. Spontaneous processes that could severely complicate the ITWM process as shown in Fig. 51. (a) SHR process with the HR terminal state not coupled to the ground state. (b) SHR process with the HR terminal state coupled to the ground state. This latter case will lead to processes such as OPSE or ASE.

$|3\rangle - |2\rangle - |1\rangle$ imply that the coherence between state $|3\rangle$ and $|1\rangle$ is very short lived and one must maintain the strong excitations of states $|1\rangle - |2\rangle - |3\rangle$. In addition, a more practical yet significant problem occurs in reality that will complicate the ladder scheme with such a strong excitation for atomic coherence preparation. This is the process of SHR generation associated with the large population created by the maximum atomic coherence. In the next subsection this process will be discussed and treated in more detail.

6.2. ITWM in ladder systems: generation of SHR radiation

The motivation for discussing a ladder scheme is rooted in the fact that it can generate a wide range of wavelengths that are much shorter than any of the field (probe, control, etc.) supplied externally. If one is mostly interested in generating a very different wavelength with high efficiency, then the ladder scheme is far more important than a $\Delta/\Delta$ scheme. The latter schemes can produce only side-bands of the frequencies of the externally supplied fields.

Consider a ladder type excitation scheme where a coherence is maintained by providing sufficiently intense fields $E_p$ and $E_c$ (shown in Fig. 52a). Here, it is assumed that the only new wavelength generated is the FWM field. In this case, following the treatment presented earlier it can be shown that nearly 100% photon flux conversion between the weak pulsed laser and the generated field can be obtained. The key difference, however, is that parameters such as $\gamma_{31}$, $\kappa_{14}$, and $\kappa_{34}$ are very different in magnitude from a $\Delta/\Delta$ scheme where states $|1\rangle$ and $|3\rangle$ usually are chosen to belong to the same ground state hyperfine manifold of a typical alkali metal vapor. For instance, in a ladder scheme the value of $\gamma_{31}$ might be 100 times larger than that of a $\Delta$ system at concentrations of $10^{14}$ cm$^{-3}$. Accordingly, the transition between the lowest $p$ and $d$ states, or the lowest $d$ and the second or third lowest $p$ states in an alkali is comparable to that between the ground state and the lowest $p$ state. However, the transition between the ground state and the second or third lowest $p$ state has an oscillator strength that is nearly two orders of magnitude smaller. Thus, it will be fairly typical in alkali vapors for $\kappa_{34}$ to be two orders of magnitude larger than $\kappa_{14}$. These differences in parameters imply that, with the ladder scheme, pulses shorter than 10 $\mu$s must be used because of the much more rapid decay of coherence $\rho_{31}$. One consequence of the large difference in $\kappa_{14}$ and $\kappa_{34}$ is that choosing to maximize the coherence, i.e., making $\rho_{11} = \rho_{33} = 1/2$, violates the condition for maximizing the conversion efficiency by a factor of around 100. Under this circumstance, the condition for achieving maximum amplitude for the generated wave, i.e., $\kappa_{14}\rho_{11} = \kappa_{34}\rho_{33}$, dictates that $\rho_{33} \gg \rho_{11}$. This implies that nearly all populations must be maintained in the state $|3\rangle$, corresponding to much smaller atomic coherence. Note that in this case if one has $\rho_{33} = 1$ (or even with $\rho_{33} \gg \rho_{11}$), then the process is clearly TWM in nature (i.e., $|3\rangle - |4\rangle - |1\rangle$) rather than a conventional FWM.

In reality, however, it is quite possible to have other states below state $|3\rangle$, especially for a ladder type scheme that encompasses large energy span for short wavelength generation. Some of these states may not radiate back to the ground state. This leads to the possibility that very high gain SHR generation may occur as a result of appreciable population of $|3\rangle$. The purpose of this subsection is to demonstrate such a complication indeed exists and it can even
been very efficient. Thus one should keep the possible complications by the SHR effect in mind when choosing the ladder scheme for ITWM so that the complication by SHR can be minimized or avoided.

Before starting the investigation of SHR process in a ladder system one should first note that if the maximum coherence is achieved then nearly 50% of all the population would be in state |3⟩. Secondly, it should be noted that the lasers at ωp and at ωc must be sufficiently intense in order to maintain a constant atomic coherence. Thus, if the field that couples state |3⟩ to either higher levels such as |4⟩ (as a prelude to prepared state two-wave mixing using externally supplied field ES) or to a lower level |5⟩ (by internally generated SHR field EHR) is very weak, then its effect on states |1⟩, |2⟩, and |3⟩ will not be appreciable. Consequently, ρ11, ρ33, ρ31 can all be treated as constants during the time when the weak field propagates in the medium, and one has an effective three-level system for a TWM process (|1⟩ → |3⟩ → |4⟩ → |1⟩ by ES + ETWM, Fig. 52b) or a HR process (|1⟩ → |3⟩ → |5⟩ → |1⟩ by EHR + ESP, Fig. 52c), respectively.

The relevant equations of motion for HR (Ω35 = ΩHR) and spontaneous emission generation (Ω51 = ΩSP) are given by

\[
\frac{\hat{c}\rho_{31}}{\hat{c}t_r} = -\frac{\gamma_{31}}{2} \rho_{31} + i\Omega_{SP}\rho_{11} + i\Omega_{HR}\rho_{31} e^{-i\Delta k z},
\]

(6.6a)

\[
\frac{\hat{c}\rho_{35}}{\hat{c}t_r} = -\frac{\gamma_{35}}{2} \rho_{35} - i\Omega_{SP}\rho_{31} - i\Omega_{HR}\rho_{33} e^{i\Delta k z},
\]

(6.6b)

\[
\left( \frac{\hat{c}\Omega_{SP}}{\hat{c}z} \right)_{t_r} = i\kappa_{15}\rho_{51}, \quad \left( \frac{\hat{c}\Omega_{HR}}{\hat{c}z} \right)_{t_r} = i\kappa_{35}\rho_{35} e^{-i\Delta k z},
\]

(6.6c)

where the phase mismatch is given by

\[
\Delta k = (k_{SP} \mp k_{HR}) - (\omega_3 - \omega_1) / c.
\]

with kSP and kHR being the wave vector of the spontaneously generated field and the SHR field, respectively.

Consider the case where the optical transition (|5⟩ − |1⟩) is not allowed. This is the case very frequently encountered in experimental studies where there will nearly always be such a state lying lower than |3⟩ with the ladder scheme. In this case, Ω51 = ΩSP = 0, ρ51 = 0, and ρ11, ρ33, and ρ31 are constant for small HR field. One has

\[
\frac{\hat{c}\rho_{35}}{\hat{c}t_r} = -\frac{\gamma_{35}}{2} \rho_{35} - i\Omega_{HR}\rho_{33} e^{i\Delta k z},
\]

(6.7a)

\[
\left( \frac{\hat{c}\Omega_{HR}}{\hat{c}z} \right)_{t_r} = i\kappa_{35}\rho_{35} e^{-i\Delta k z}.
\]

(6.7b)

The solution is simple and after inverse transform, one has

\[
\Omega_{HR}(z, t) = \Omega_{HR} \left(0, t - \frac{z}{V_{HR}}\right) e^{g z},
\]

(6.8)

where the group velocity and HR intensity gain are given by

\[
\frac{1}{V_{HR}} = \frac{1}{c} + \frac{4\kappa_{35}\rho_{33}}{\gamma_{35}}, \quad G_{HR} = 2g = \frac{4\kappa_{35}\rho_{33}}{\gamma_{35}},
\]

(6.9)

where γ35τ ≫ |η| has been assumed. Notice that if one makes ρ33 = 1/2, then if γ35τ = 5, N0 ≥ 3 × 10^14/cm^3, and pulse length τ = 10 μs, one will have κ35τ ≃ 10^6/cm. Thus, the gain could be close to GHR > 10^5/cm over distances of 0.003 cm. This indicates that the small signal theory, which would suggest a 300 e-folds of growth, is not a suitable treatment. However, if the condition for optimum efficiency is satisfied, one has κ35ρ33 = κ15ρ11. Thus, the population of |3⟩ will be around 50 times smaller, yielding a gain of GHR > 2000. Therefore, for a medium length of 0.003 cm a 6 e-folds of gain occurs and the small signal treatment is valid. Since κ35 ≫ κ15, ρ11 must be much larger than ρ33. Consequently, the atomic coherence is small. This is another situation where maximum coherence is not the suitable condition for high conversion efficiency. This example clearly shows it may be problematic using a ladder scheme in combination with strong and long pulse lasers for state preparation when HR generation may be present. The scheme with weak Ωp but strong Ωc and ΩS is a better scheme when applied to ladder configurations for efficient wave mixing.
6.3. Single photon ITWM and self-interference in a coherently prepared atomic medium

All previous subsections have focused on investigating several ITWM cases where the medium has been coherently prepared prior to the wave mixing processes. As the concluding discussion on ITWM processes it is appropriate to show in this subsection that the effects and phenomena described in the previous subsection are readily scalable to single photon level. Indeed, studies have shown that many destructive interference effects involving internally generated fields can be directly scaled to single photon level, leading to predictions such as efficient single-photon ITWM and IFWM, single photon self-interference effect, maximum entanglement of a few Fock states [130], and, etc. Here, the possibility of generating maximally entangled single-photon Fock state and near 100% conversion efficiency for generating a frequency shifted ITWM photon by proper choice of medium length and concentration will be discussed. As will be shown that highly efficient induced transparency occurs as the result of a novel single photon self-interference effect. This effect is again very different from the conventional EIT [72–74] where an intense control field is always required. Indeed, there will be no EIT in the conventional sense at single photon levels. It will be further demonstrated that maximally entangled Fock states can be generated using this single photon TWM process. In fact, a propagation distance dependent interference effect such as the constructive–destructive recurrence discussed previously allows one to tailor the degree of entanglement using the combination of density and propagation length.

Quantum entanglement [131–134] is one of the most striking features of quantum mechanics. The entanglement of the quantum states of separate particles, such as the entanglement of photon pairs [135], plays a crucial role in quantum information science [136], and has been intensively studied. The entanglement of multiple Fock states with a single slow or ultra-slow photon (or a few photons), however, has only recently been predicted using perfectly efficient, pair-wise FWM technique [130]. Rapid development in the design of single photon sources based on quantum dots coupled to optical cavities has opened the possibility of commercial pulsed sources emitting single photons on-demand with Fourier transform limited bandwidths. Such single photon sources with well defined polarization state, narrow spectra line width, and direction of propagation are likely in the near future. This is the part of the motivation for this subsection.

The system under consideration here for single photon ITWM process is an ensemble of life time broadened four-level atoms (Fig. 50) that has been coherently prepared so that a long-lived coherent superposition state can be written as follows:

$$|\Psi(z, t)\rangle = A_1 e^{-i\omega_1 t} |1\rangle + A_2 e^{-i\omega_2 t} e^{i(\omega_2 - \omega_1)z/c} |3\rangle. \quad (6.10)$$

Note that in forming the coherent superposition state a grating has been written to the medium to alleviate problems associated with phase mismatch when a pump photon at frequency $$\omega_p$$ is introduced at a later time to initiate the inelastic two-wave mixing.

The above described coherent superposition state can be produced with various coherent population transfer techniques routinely used in laboratories. For instance, in the optical frequency domain one may use a pair of collinear and circularly polarized lasers ($$\Omega_j \ (j = 1, 2)$$) with $$\Omega_1$$ and $$\Omega_2$$ being the Rabi frequencies of a pulsed (coupling transition |1⟩ − |2⟩) and a continuous wave (coupling |3⟩ − |2⟩) fields, respectively. Under this circumstances, a coherent mixture of the ground state |1⟩ and the lowest excited state |3⟩ can be created, yielding $$A_1 = \Omega_2/\Omega$$, $$A_2 = -\Omega_1/\Omega$$ where $$\Omega = \sqrt{\Omega_1^2 + \Omega_2^2}$$ [113,137]. The coherence is stored by rapidly switching off $$\Omega_2$$. Alternatively, in the radio-frequency domain one may use microwaves to achieve the direct non-electric dipole coupling of states |1⟩ and |3⟩. Once the coherence is established, state |2⟩ is no longer needed and an effective three-state system (i.e., |1⟩, |3⟩, and |4⟩) is sufficient for the following discussion of TWM process. Thus, the start point of the following treatment is such a coherently prepared three-state system with all atoms being in the prepared state in Eq. (6.10) with $$A_1$$ and $$A_2$$ given above.

Let us now inject a single pump photon wave packet into the coherently prepared system and investigate the corresponding system response. If the delay between the time when the pump-photon wave packet is introduced and the time when the coherent preparation is completed is small enough that the decay of the coherence is negligible, one effectively has a three-state system as shown in Fig. 50(b). It should be stressed that this is an effective three-state A-system, yet the conventional EIT process plays no role, as both the pump and the TWM fields are at single photon level. In the conventional EIT scheme, the control field (corresponding to the pump field $$\Omega_p$$ in the present case) couples two empty states and it must be sufficiently intense to drive the upper state |4⟩ transparent. In the single photon ITWM
scheme, however, a single photon pump field couples two states with one of the state having nearly all population. Second, in conventional EIT, the probe and control fields are externally supplied fields whereas in the ITWM case one of the participating fields is an internally generated single photon field. As will be shown below that near 100% single photon conversion from the pump to the ITWM field can be achieved. Furthermore, an efficient induced transparency produced by the single pump photon as a result of self-interference will become operative after sufficient propagation distance, resulting in a nearly lossless propagation of the single photon wave packet that is also oscillating between two single photon Fock states. This is a remarkable effect because the mechanism of producing the transparency is very different from that of conventional EIT scheme.

In order to be able to describe entangled state the Heisenberg representation will be used in the following calculation of the atomic dynamics and the electromagnetic fields. However, the elements of the density matrix \( \hat{\rho} \) distance, resulting in a nearly lossless propagation of the single photon wave packet that is also oscillating between two

where \( \hat{\rho}_{13}, \hat{\rho}_{33}, \) and \( \hat{\rho}_{11} \) will be treated as \( c\)-numbers whose values are not changed by the passage of a single-photon wave packet through the medium. This is consistent with the assumption of long-lived coherent superposition state. Taking the plane wave and SVA approximations the Maxwell’s equations of motion for the complex amplitudes of the pump and TWM field operators can be derived in the same fashion as one does before for the classical fields except that caution should be made in treating the orders of various operators. Thus, in the place of Eqs. (6.2a–c) one has the following four operator equations (here and after the subscript \( p \) (nt) denotes the single photon pump (TWM) field)

\[
\frac{\partial \hat{S}_m}{\partial t} = i d_4 \hat{S}_m + \frac{1}{|\Omega|^2} \hat{W}_m - i \frac{\Omega_1^2 \Omega_2}{|\Omega|^2} \hat{W}_p,  \tag{6.11a}
\]

\[
\frac{\partial \hat{S}_p}{\partial t} = i d_4 \hat{S}_p + \frac{1}{|\Omega|^2} \hat{W}_p - i \frac{\Omega_1^2 \Omega_2}{|\Omega|^2} \hat{W}_m,  \tag{6.11b}
\]

\[
\left( \frac{\partial \hat{E}_{m}^{(+)}(p)}{\partial z} \right)_t + 1 \left( \frac{\partial \hat{E}_{m}^{(+)}(p)}{\partial t} \right)_z = i \frac{\kappa_{14} \hbar}{\mu_{41}} \hat{S}_m,  \tag{6.11c}
\]

\[
\left( \frac{\partial \hat{E}_{p}^{(+)}(p)}{\partial z} \right)_t + 1 \left( \frac{\partial \hat{E}_{p}^{(+)}(p)}{\partial t} \right)_z = i \frac{\kappa_{34} \hbar}{\mu_{43}} \hat{S}_p,  \tag{6.11d}
\]

where \( \hat{S}_p \) and \( \hat{S}_m \) are the operators proportional to the polarization amplitudes at the frequencies of the pump and TWM fields. These operators can be found by straightforward calculation of the polarization operator \( \hat{P} = \langle \hat{\Psi} | \hat{\mu} | \hat{\Psi} \rangle \) using the dipole operator \( \hat{\mu} = \hat{r} \cdot \hat{E}_{p(m)} \). In addition, \( d_4 = \delta_4 + i \gamma_4 / 2 \) with \( \delta_4 \) being the pump/TWM field detuning, \( \gamma_4 \) being the total relaxation rate of the state \( |4 \rangle \), and

\[
\hat{W}_p = \mu_{43} \hat{E}_{p}^{(+)} / \hbar, \quad \hat{W}_m = \mu_{41} \hat{E}_{m}^{(+)} / \hbar, \quad \Omega^2 = |\Omega_1|^2 + |\Omega_2|^2,
\]

where \( \Omega_1 \) and \( \Omega_2 \) are the Rabi frequencies of the two classical fields used for the initial coherence preparation.

Following the same technique one carries out Fourier transforms with respect to time on the both sides of Eqs. (6.11a–d). This gives four linear inhomogeneous differential operator equations, completely in analogous to Eq. (6.3), that can be solved analytically. Assuming that \( |\delta_4 \tau| \gg 1 \) where \( \tau \) is the pulse length of the single pump photon wave packet (the pulse shape function of the pump photon source is defined as \( g(t) \)), one obtains, after taking the inverse Fourier transforms, the solution to Eqs. (6.11a–d) for arbitrary initial conditions of the pump and TWM field

\[
\hat{E}_{m}^{(+)} = \hat{z}_m \left[ \frac{P g(t_r) + e^{-iS_{0z}/d_4} M g(t_g)}{P + M} \right] + \hat{z}_p \frac{\mu_{43} \kappa_{14} \Omega_1 \Omega_2^2}{\mu_{41} (P + M)} [g(t_r) - e^{-iS_{0z}/d_4} g(t_g)],  \tag{6.12a}
\]

\[
\hat{E}_{p}^{(+)} = \hat{z}_p \left[ \frac{M g(t_r) + e^{-iS_{0z}/d_4} P g(t_g)}{P + M} \right] + \hat{z}_m \frac{\mu_{41} \kappa_{34} \Omega_1 \Omega_2^2}{\mu_{43} (P + M)} [g(t_r) - e^{-iS_{0z}/d_4} g(t_g)].  \tag{6.12b}
\]
where

\[
P = \kappa_{34} |\Omega_1|^2, \quad M = \kappa_{14} |\Omega_2|^2, \quad \hat{x}_p = \sqrt{\frac{2\pi \hbar \Omega_p}{A c \tau}} \hat{a}_p, \quad \hat{x}_m = \sqrt{\frac{2\pi \hbar \Omega_m}{A c \tau}} \hat{a}_m,
\]

\[
\frac{1}{V_g} = \frac{1}{c} + \frac{S_0}{d_4^2}, \quad S_0 = \frac{P + M}{|\Omega|^2}, \quad t_r = t - \frac{z}{c}, \quad t_g = t - \frac{z}{V_g},
\]

where \(\hat{a}_p\) and \(\hat{a}_m\) are the pump and TWM photon annihilation operators, respectively. In addition, \(A\) is the effective area for the photon pulse (beam), and the pulse shape function \(g(t)\) is normalized according to

\[
\int_{-\infty}^{\infty} \frac{dz}{c} |g(t_r)|^2 = 1.
\]

It should be emphasized that Eqs. (6.12a,b) contain no assumptions about the initial number of photons at either \(\omega_p\) or \(\omega_m\) frequency. Further, note also that if Eqs. (6.12a,b) operate on a state vector of \(|1_p; 0_m\rangle\), the second term in Eq. (6.12a) and the first term in Eq. (6.12b) survive the action of the annihilation operator \(\hat{a}_p\).

One can now use Eqs. (6.12a,b) to calculate various expectation values of products of \(\hat{E}_p, \hat{E}_m\), and their complex conjugates at the exit side of the medium. In doing so, one will make use of the fact that the initial state of the photon field before entering the medium is \(|\Phi(0, t)\rangle = |1_p; 0_m\rangle\) (i.e., 1 photon in the \(\omega_p\) mode and no photon in the \(\omega_m\) mode).

At the exit to the medium one is back in free space and the state of the field, in the Schrödinger representation, is given by

\[
|\Phi(z = L, t)\rangle = a_{10}(z, t) |0_p; 1_m\rangle + a_{01}(z, t) |1_p; 0_m\rangle,
\]

with the corresponding field operators given by \((z \geq L)\)

\[
\hat{E}_p^{(+)} = \hat{x}_p, \quad \hat{E}_m^{(+)} = \hat{x}_m.
\]

Let us calculate \((\langle \hat{E}_p^{(+)} \rangle)^\dagger \hat{E}_m^{(+)}\) and \((\langle \hat{E}_m^{(+)} \rangle)^\dagger \hat{E}_p^{(+)}\) using Eqs. (6.13) and (6.14). This involves of finding amplitudes \(a_{10}(z, t)\) and \(a_{01}(z, t)\). Once these amplitudes and expectation values are obtained, the amplitudes, conversion efficiency and entanglement for different choices of populations for states \(|1\rangle\) and \(|3\rangle\) and for different thickness of the resonance medium can be determined. Using Eqs. (6.13) and (6.14), one obtains

\[
|a_{10}|^2 = \frac{g^2(t_g) e^{-\beta z} P M}{(P + M)^2} + \frac{P M [g^2(t_r) - 2 g(t_r) g(t_g) e^{-\beta z} \cos(\Delta k z)]}{(P + M)^2},
\]

\[
|a_{01}|^2 = \frac{g^2(t_g) e^{-\beta z} P^2}{(P + M)^2} + \frac{M^2 g^2(t_r) + 2 P M g(t_r) g(t_g) e^{-\beta z} \cos(\Delta k z)}{(P + M)^2},
\]

where \(\beta = \gamma_4 S_0 / [d_4^2 + (\gamma_4 / 2)^2]\) and \(\Delta k = \delta_4 S_0 / [d_4^2 + (\gamma_4 / 2)^2]\).

Inspection of Eqs. (6.15a,b) reveals that three requirements should be satisfied in order to achieve 100% conversion efficiency of the pump photon to the TWM photon:

1. \(M = P\);
2. small absorption;
3. properly chosen propagation depth.

The first requirement leads to possible maximized amplitude of the TWM field. The second requirement limits \(\beta z\) which determines the significance of attenuation. The third requirement dictates the allowable peak separations due to the difference between \(c\) and \(V_g\). Essentially, it requires the difference between \(t_r\) and \(t_g\) be small compared with \(\tau\). It should be pointed out that \(\kappa_{14}\) and \(\kappa_{34}\) are in general not the same. This implies that in general the optimum condition for high conversion efficiency does not correspond to satisfying the condition for maximum atomic coherence, i.e., \(\rho_{13} \simeq 1/2\).
Fig. 53. Plot of the dimensionless quantities $|a_{10}|^2$ (solid line) and $|a_{01}|^2$ (dash–dotted line) as a function of $\Delta k z$. In this plot $P = M$ to make possible 100% conversion efficiencies and maximally entangled Fock states at small propagation distance. For the same purpose $\beta/\Delta k = \gamma_4/\delta_4 = 0.04$ in order to achieve $\Delta k L = \pm \pi/2$ and $\Delta k L = \pm \pi$, while $\beta L \ll 1$. Notice that for large $z$, the single photon self-interference effect have rendered the medium transparent with $|a_{10}|^2 \to 1/4$ and $|a_{01}|^2 \to 1/4$.

With $M = P$ and negligible absorption, Eqs. (6.15a,b) yield

$$|a_{10}|^2 = \frac{1}{2} g^2(t_r)[1 - \cos(\Delta k L)],$$

$$|a_{01}|^2 = \frac{1}{2} g^2(t_r)[1 + \cos(\Delta k L)].$$

Equations (6.17a,b) indicate that when the conditions described are well satisfied, choosing $\Delta k L = \pm \pi/2$ will result in the cosine terms being zero and the two coefficients being both equal to $g(t_r)/\sqrt{2}$ (up to a phase factor). Since the area under $|g|^2$ integrated over $z$ is unity, this yields a maximally entangled linear combination of $|1_p; 0_m\rangle$ and $|0_p; 1_m\rangle$.

If, on the other hand, one chooses $\Delta k L = \pm \pi$, then one obtains the state of the electromagnetic field at the exit of the cell as

$$|\Phi\rangle = |0_p; 1_m\rangle.$$ (6.17)

That is, there is exactly one photon in the TWM frequency mode at the exit and no photon in the pump frequency mode. This is a 100% conversion efficiency (see the inset of Fig. 53). Note that here one has the flexibility of choosing either the pump or the TWM photon by changing medium length or concentration, provided that the change will not significantly increase the absorption (see the small $k z$ region in Fig. 53).

In a real alkali medium it is possible to neglect $\beta L$ for the smallest distances over which $\Delta k L = \pm \pi/2$, or $\Delta k L = \pm \pi$. However, at large depths of propagation $z$ where the terms containing $\exp(-\beta z/2)$ decay out, one has

$$\langle(\hat{E}_m^{(+)}\dagger \hat{E}_m^{(+)}) = \frac{PM g^2(t_r)}{(P + M)^2},$$

$$\langle(\hat{E}_p^{(+)}\dagger \hat{E}_p^{(+)}) = \frac{M^2 g^2(t_r)}{(P + M)^2}.$$ (6.18b)

Eqs. (6.18a,b) suggest that at large $z$ there is no dispersion and absorption (see the large $\Delta K z$ region in Fig. 53), and the single photon wave packets travel with a modified group velocity that can be substantially smaller than $c$. In this large $z$ limit one has 25% probability of having a probe photon (i.e., state $|1_p; 0_m\rangle$), 25% probability of having the TWM photon (i.e., state $|0_p; 1_m\rangle$), and a 50% probability of finding no photon at either frequency (i.e., state $|0_p; 0_m\rangle$) every time when a measurement is performed. At large $z$, the probability no longer oscillates back and forth between the two frequency modes as a function of propagation distance. This situation should persist for large propagation distances as long as the residual absorption is small. Thus, in the large propagation limit, one has probabilistically well defined entangled and $z$-independent Fock states with no oscillation in probability amplitudes.
This is a remarkable single-photon induced transparency effect and, as will be explained below, it is due to a very efficient and robust single photon self-interference effect that is very different from the conventional EIT effect.

To understand how this remarkable phenomenon occurs let us consider the forms that the Heisenberg operators for \( \hat{E}_m^{(+)} \) and \( \hat{E}_p^{(+)} \) take on at large \( z \) values. Note that Eqs. (6.12a,b) are the solutions for the pump and TWM fields for arbitrary initial conditions. Consider the initial condition where the electromagnetic field has the form of \( \Phi(z = 0, t) = g(t_r)|1_p; 0_m\rangle \) before entering the medium. That is, initially one has a single pump photon only. Thus, in calculating expectation values of powers of the operator \( \hat{O} = (\hat{E}_m^{+}(p))\hat{E}_m^{(+)(p)} \), one can neglect terms containing \( \hat{a}_m \) in Eqs. (6.12a,b). This is because \( \hat{a}_m \) commutes with \( \hat{a}_p \). Furthermore, terms containing \( \hat{a}_m \) can always be moved to the right end position without encountering a non-zero commutator in any term contained in a power of this operator. Therefore, one can use \( \hat{a}_m|1_p; 0_m\rangle = 0 \). This implies that excluding the \( \hat{a}_m \) terms has no effect on the results when one calculates \( \langle \hat{I}_{p(m)} \rangle \), where \( \hat{I}_{p(m)} \) is the Heisenberg operator for the intensity of the pump (TWM) field at \( \omega_{p(m)} \). In addition, \( \langle (\hat{I}_{p(m)})^n \rangle \) is also unchanged by neglecting \( \hat{a}_m \) terms. One can thus calculate the average power density, and any of the moments related to fluctuations in these fields, without including the \( \hat{a}_m \) terms.

With the above consideration in mind and when \( \beta z \gg 1 \), one obtains, from Eqs. (6.12a,b)

\[
\begin{align*}
\hat{E}_m^{(+)} &= \frac{\mu_{43}}{\mu_{41}} \frac{\kappa_{14}}{P + M} \hat{g}(t_r) \hat{z}_p, \\
\hat{E}_p^{(+)} &= \frac{M}{P + M} \hat{g}(t_r) \hat{z}_p,
\end{align*}
\]

which lead to

\[
\frac{\hat{E}_m^{(+)}}{\hat{E}_p^{(+)}} = \frac{\mu_{43} \Omega_1}{\mu_{41} \Omega_2} \rightarrow \frac{\hat{W}_m}{\hat{W}_p} = \frac{\Omega_1}{\Omega_2}.
\]

Eqs. (6.19a,b) and (6.20) are just the operator analogous of Eqs. (6.4a,b) and (6.5) (also see Eqs. (5.17a,b) and (5.18)) in the semi-classical treatment for the case of sufficiently large \( z \). When Eq. (6.20) is used in Eqs. (6.11a,b), it is seen that the last two terms on the RHS cancel out. The remaining terms yield no contribution in evaluating \( \hat{S}_m \) and \( \hat{S}_p \), which will be used as sources for calculating the TWM and pump fields in Eqs. (6.11c,d). This remarkable cancellation implies that under the given initial conditions, and once \( \beta z \) is large enough that the relevant terms decay out, an interference occurs on the RHS of Eqs. (6.11a–d), resulting in a polarization that does not contribute to absorption or dispersion at either the pump or TWM frequency. Yet, there is only one photon at any given time in the medium. This single photon self-interference leads to vanishing source terms on the RHS of Eqs. (6.11a,b). Consequently, the pump or TWM single photon wave packets propagate absorption-free at the speed of light in vacuum.

Before leaving this subsection, it is important to point out some of the differences between this single photon self induced transparency effect and the induced transparency in the conventional three-state EIT scheme. In the latter scheme the transparency effect is the result of interference between two one-photon channels with one channel involves intense driving field, yet no propagation is necessary. In the case of single photon self induced transparency, there is no intense driving field and it is a propagation critical interference effect. In addition, the concept of transparency window created by the intense driving field does not have a correspondence in the present case.

7. Concluding remarks

The scope of this review has been delimited by several factors of practical importance. The subjects were chosen within a manageable and reasonably cohesive subset of a broader range of effects associated with optical interferences critically dependent on the internally generated fields. The treatment of the chosen subset of phenomena was further delimited by time, space, and the anticipated patience of the reader. However, in areas of research where multi-photon resonant phenomena are subject to strong influence by internally generated wave-mixing fields, a comprehensive review of experimental and theoretical consequences of such phenomena has been attempted. The common feature in all of the processes is the simultaneous optical coupling of two quantum states (usually, but not necessarily, one is the ground state) by two separate photon pathways: one pathway provided by input electromagnetic fields, and a second path provided, at least partially, by internally generated electromagnetic fields. Coupling by the two pathways can, under
This expression shows that for one-photon resonances strong saturation effects occur at power densities of only $\frac{I}{1 \text{W/cm}^2}$, others, in spite of language or formal mathematical differences that appear. It is hoped that the present overview will serve to further these and other such applications.

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Appendix A. Order of magnitudes for one- and multi-photon half Rabi Frequencies

This appendix gives some estimations on the magnitudes of one- and three-photon half Rabi frequencies frequently encountered in experiments in gaseous phase nonlinear optics.

First, consider the one-photon half Rabi frequency given by

$$\Omega_{21}^{(1)}[\text{rad/s}] = \mu_{21}E_{L0}/(2\hbar) \simeq ea_B E_{L0}/(2\hbar) \simeq 1.0 \times 10^8 \sqrt{I[\text{W/cm}^2]}.$$  

where the laser power density $I$ is in the unit of W/cm$^2$, $a_B$ is the familiar Bohr radius and $ea_B$ is of the order of magnitude of the transition dipole matrix element for a strong transition. Although the one-photon half Rabi frequency given above describes a fairly strong one-photon transition, this type of strength or magnitude occurs relatively frequently. This expression shows that for one-photon resonances strong saturation effects occur at power densities of only $I \simeq 1 \text{ W/cm}^2$.

With a two-photon processes the half Rabi frequency is given by

$$\Omega_{21}^{(2)}[\text{rad/s}] = i \int_{-\infty}^{t} \text{dt} \langle 2|\hat{V}_f(t')\hat{V}_f(t)|1 \rangle = \sum_j \frac{(\mu_{2j}E_{L0})(\mu_{j1}E_{L0})}{(2\hbar)^2(\omega_j - \omega_1 - \omega_L)},$$

$$\simeq 10^{17} \frac{I[\text{W/cm}^2]/(10^{16}) \simeq 10I[\text{W/cm}^2]}{(\omega_j - \omega_i - \omega_L)}, \quad (A.1)$$

where the summation was obtained by inserting $\hat{1} = \sum_j |j\rangle\langle j|$. The bar in the denominator indicates that an average value is taken. More precisely speaking, however, one should take a weighted average value of the denominator weighted by the size of the matrix elements. The integral over time was evaluated asymptotically by assuming a slowly varying amplitude for the fields. The factor of 10 comes from the consideration that this type of rough approximation is based on the estimate of a single typical term in the sum over the states. This is crude, but the approximation is usually within a factor of three or four for cases where the upper state is one of the lowest lying two-photon resonances,
with no contributing intermediate state being anywhere close to the resonance. This is usually true in the case in an inert gas where \( \Omega_{21}^{(2)} \simeq (1-10)I[W/cm^2]\) rad/s, but is generally not true in an alkali atom where the two-photon Rabi frequency is frequently around 500[I[W/cm^2]\) rad/s for transitions like 3s–4d in sodium. In the latter case, strong intermediate resonances exist that greatly enhance the two-photon Rabi frequency. Indeed, in an alkali the two-photon Rabi frequency is often dominated by a single term in the sum. Finally, similar arguments can be made for three-photon Rabi frequencies with no near intermediate resonance. One finds,

\[
\Omega_{21}^{(3)}[\text{rad/s}] \simeq (10^{-8} - 10^{-6})(I[W/cm^2])^{3/2}.
\]

Typically, for inert gases and unfocused lasers of a few nano-second pulse length and a beam diameters of 1 mm there should be very little depletion of the ground state population due to a three-photon resonance excitation. excited state populations will be small and measurements usually rely on the use of detectors with gains due to electron avalanche effect.

**References**

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[74] Perhaps the best way to calculate multi-photon half Rabi frequencies and a.c. Stark shifts is to make use of Green’s function methods. An elementary discussion of such calculations based of Talman’s optimized central potential can be found in a paper by Payne and Edwards (M.G. Payne and Mark Edwards, Comput. Phys. 7(4) (1993) 465–475.) The latter method gives an accuracy similar to what would be obtained from frozen core Hartree-Fock calculations. More accurate calculation requires many body calculations of the atomic structure.


Fortunately the required propagation distance $z$ is still relatively small. In the case of high concentration, destructive interference can occur for a very short distance of a few $\mu$m. At very low concentration such as $10^{-6}$ Torr, one may need about 1 mm propagation before the Doppler broadening of 1 GHz can bring about destructive interference.

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