Implementation of Resonance Tracking for Assuring Reliability in Resonance Enhanced Photothermal Infrared Spectroscopy and Imaging

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Abstract [ABKWH]

Photothermal induced resonance (PTIR) is a method for optical spectroscopy that allows for infrared chemical imaging at spatial resolution below the limit of diffraction. By using the mechanical resonance of the cantilever for amplification the technique has been shown to allow sensitivity down to single mono-layers.

In this work we discuss the challenges that must be overcome for performing stable resonant PTIR measurements and how imprecise experimental procedures can lead to irreproducible or even erroneous results. We also present a controller design that continuously readjusts the excitation frequency of a PTIR setup back to the resonance frequency in order to allow for accurate resonance enhanced PTIR measurements. This controller can be used together with a broad range of atomic force microscopes. Schematics and program code for the controller are made freely available.

Introduction
Photo-thermal induced resonance (PTIR) is a well-established near-field method for mid-infrared (mid-IR) spectroscopic imaging at nanoscale spatial resolution. PTIR uses a pulsed, tunable infrared light source to cause local thermal expansion in the sample. A contact mode atomic force microscope (AFM) is used as a sensitive detector for this expansion. Upon each laser pulse, the bending modes of the AFM contact-mode cantilever are excited. The amplitudes of these modes have been shown to be proportional to the local infrared absorption. Due to the mechanical detection of infrared absorption PTIR can achieve spatial resolution of around 20 nm in the mid-IR and in the visible, far below the diffraction limit for far field optics. PTIR has been used in a wide range of fields ranging from biology, to material science and plasmonics, to name only a few.

Recently, Lu et al. demonstrated that the resonant excitation of the contact modes of the AFM cantilever in PTIR can significantly improve the detection limit of PTIR down to a monolayer sensitivity. This is achieved by tuning the repetition rate of the infrared light source to the frequency of the cantilever mode. Thus the energy transferred from the laser to the cantilever upon each pulse is accumulated in the cantilever, leading to higher cantilever amplitudes. The amplitude of the cantilever in this resonance enhanced (RE)-PTIR is given by \( A = \frac{2I_0}{\tau k} Q \). Here \( I_0 \) is the time average absorption force, \( \tau \) is the laser pulse duration, \( k \) is the cantilever force constant and \( Q \) is the quality factor of the resonance – in contact with the sample. As quality factors usually lie in the range of 50 to 100 for RE-
PTIR, the equilibrium amplitude of the excited cantilever is 50 to 100 times higher than that after single pulse excitation.

It is important to note that the frequencies of the contact resonances depend on the properties of the cantilever, of the tip and of the sample. Interactions between tip and sample are highly non-linear for larger deflections, precluding an analytical description of the behaviour of the cantilever. Instead, a linear approximation of the tip-sample force around the equilibrium position $z_{eq}$ of the tip can be used\textsuperscript{12} (see fig. 1 for a schematic depiction).

In such a linear approximation the tip sample force $F(z)$ is modelled as a spring connected to the tip of the cantilever, with the spring constant $k^*$ being

$$k^* = \left. \frac{\partial F(z)}{\partial z} \right|_{z=z_{eq}}$$

If the spring constant of the mode is larger than $k^*$ the shift of the resonance frequency can be described using a point mass on a spring model, which leads to the following expression\textsuperscript{12}

$$\frac{f_r}{f_0} = \sqrt{\frac{k_c + k^*}{k_c}}$$

$f_0$ is the resonance frequency of the free cantilever, $f_r$ is the resonance frequency of the cantilever in contact, $k_c$ is the spring constant equivalent to the cantilever in a point mass on a spring model. As can be seen in (2) the contact resonances have significantly higher frequencies than the free resonances of the cantilever. For higher modes, an approximate value for the equivalent spring constant can be calculated from the relation\textsuperscript{13}
and, as cantilevers are usually not mounted in parallel to the sample but at an angle $\alpha$ from the parallel plane $k^*$, has to be corrected by a factor of $\cos(\alpha)$.

As a result of the dependence of the contact resonance on the material properties parts of a sample consisting of different materials will have different contact resonances. This means, that the main requirement of RE-PTIR, i.e. excitation at the resonance maximum, cannot be fulfilled for all pixels in an RE-PTIR image, without modifying the excitation frequency while imaging. When the system is excited off resonance, then its maximum enhancement depends on the difference between the resonance frequency and the excitation frequency.

**Resonance enhancement is a mixed blessing**

As stated in the last section the enhancement in PTIR is described by the Q factor of the system. However, the Q factor not only describes the amplitude increase at the resonance but also relates its resonance frequency $f_r$ to the full width at half maximum (FWHM) of the resonance $\Delta f$ through $Q = \frac{f_r}{\Delta f}$. Hence, the stronger the RE-PTIR is enhanced the quicker the signal drops off resonance. As can be seen in figure 2, even materials commonly found in one sample can have resonance frequencies that do not overlap within FWHM. The problem posed by differences in the resonance position can be overcome when RE-PTIR is used to collect spectra at discrete points on the sample. Since acquiring a spectrum usually takes several seconds or more, depending on the needed
spectral resolution and wavelength range, spending a few additional seconds on recording a resonance curve and then readjusting the excitation frequency to the maximum in the recorded spectrum does not significantly increase the measurement time.

However, for imaging the RE-PTIR signal at a single wavelength is recorded at each pixel of the image. As the sample composition can change from pixel to pixel the contact resonance frequency of two consecutive pixels can also differ. Hence, to ensure resonant excitation, the resonance frequency has to be determined at each pixel, which entails a sweep of the lock-in amplifier across the full range within which the resonance frequency is expected to lie at every pixel of the image. The number of pixels that can be collected per unit of time is defined by the time it takes to perform one sweep of the lock-in amplifier.

The importance of detecting the amplitude of the cantilever at the resonance is demonstrated by the images AFM in figure 3. In these images the RE-PTIR signal of a sample consisting of a 180 nm high polystyrene film on gold was recorded. The tuneable external cavity quantum cascade laser (EC-QCL) was set to emit at a wavelength 1450 cm$^{-1}$, corresponding to an intense ring vibration of polystyrene$^{14}$.

When the repetition rate of the laser corresponds to the contact resonance of the cantilever on polystyrene (here 57 kHz first resonance, 176 kHz second resonance) the PTIR signal is strong when the AFM tip is placed on polystyrene and a significantly weaker when it is placed on gold, meaning that the imaging contrast is dominated by
chemical differences. As the laser repetition rate is increased the signal measured on polystyrene decreases relative to that measured on gold, leading to a loss of chemical contrast. In these conditions, (see fig. 2, 60kHz and 182 kHz) the imaging contrast is dominated by the sample topography and by the mechanical properties, rather than by chemical composition of the sample.

It is therefore clear, that RE-PTIR imaging necessitates constant tracking of the resonance frequency.

<Insert Figure 3 near here>

Resonance tracking for RE-PTIR

To the best of our knowledge, no resonance tracking method for PTIR has been published (although the commercially available PTIR instrument implements such a method in its latest iteration). Resonance tracking in contact mode AFM however, has been investigated by several researchers as a technique to gain insight into mechanical properties of a sample via the shift of the contact resonance. One group of reported techniques for resonance tracking are broadband excitation schemes, where the cantilever is excited at broad range of frequencies at once, and then the frequency and the amplitude of its vibrations are calculated from its ring down motion. Broadband excitation schemes use either a single pulse for excitation (essentially the method used in the original implementation of PTIR by Dazzi et al.\textsuperscript{15}) or a pre-calculated waveform that allows excitation of a more defined frequency range\textsuperscript{16}. Another technique that has been
successfully used to track the position of the resonance in AFM is dual amplitude resonance tracking (DART)\textsuperscript{17}, in which a shift in the position of the resonance is detected by comparing the amplitudes measured at two frequencies around the expected resonance frequency.

Finally, there are chirp based techniques which rapidly excite the cantilever at a range of frequencies around the expected resonance\textsuperscript{18}.

It is important to note that all the aforementioned techniques except for a single pulse broadband excitation use an analog signal to excite the cantilever. When using a pulsed light source for RE-PTIR these techniques cannot be used without modification.

Currently, commercially available broadly tuneable EC-QCLs, which are most commonly used for RE-PTIR, exhibit repetition rates in the same order of magnitude as the first few contact resonance bending modes of typical contact mode cantilevers, i.e. in the 100 kHz to 1 MHz range.

This imposes two important restrictions in their use for RE-PTIR: first it is not straightforward to approximate an analog excitation signal by using pulse width modulation or similar technique (as needed for band excitation techniques) and second, it is preferable not to apply multiple pulse trains at once (as would be needed for DART).

Hence, we propose to use a chirped technique for resonance tracking in RE-PTIR. These techniques can be performed by applying a train of laser pulses with chirped repetition rate to the RE-PTIR system. Through this type of excitation, it is also possible to track resonances at frequencies up to the maximum repetition rate permitted by the laser. By selectively pulsing the laser at a repetition rate corresponding to an integer fraction of the
targeted resonance, it is also possible to excite resonances with frequencies that exceed the repetition rate of the laser source.

**RE-PTIR setup**

The main parts of our self-built RE-PTIR setup are a commercially available, broadly tuneable EC-QCL source covering the mid-infrared spectral range of 889.7 cm\(^{-1}\) to 1766.8 cm\(^{-1}\) and 2770.1 cm\(^{-1}\) to 2932.6 cm\(^{-1}\) and a commercial AFM. The laser was focused onto the AFM cantilever using an off-axis parabolic mirror. The angle of incidence of the laser beam was 65°. To preclude absorption of laser light in the AFM cantilever gold covered contact mode cantilevers were used (resonance frequency 13 kHz, force constant 0.2 N/m).

We previously\(^{19}\) demonstrated that a generic AFM lock-in amplifier can be used to acquire RE-PTIR images and spectra with a minute modification, which is to pass its reference sine wave through a Schmitt-trigger to convert it to a rectangular 5V transistor-transistor logic (TTL) compatible signal. This signal can then be used to trigger the laser at the lock-in frequency.

**RE-PTIR controller**

In order to implement the chirped resonance tracking technique for RE-PTIR we built a designed a dedicated controller. For building the controller we used only components that are readily available and can be assembled without specialized equipment, in order to
make replication of this hardware by other researchers as easy as possible. Open software and freely available software were used to program the controller to facilitate modification of the software by others. We built the controller for maximum flexibility in the following ways:

1. The control logic is implemented on a field programmable gate array (FPGA), which can be easily reconfigured to perform a wide range of tasks. For example, it would be possible to use the same controller to perform ring-down PTIR measurements instead of RE-PTIR measurements.

2. Instead of building one monolithic program to control all aspects of the RE-PTIR measurement, the system was programmed as a collection of several small parts that can be reconnected - in software - easily and without influencing other parts of the controller.

3. Due to the highly parallel nature of FPGAs signal generation, processing and communication can happen at the same time and independent of each other.

4. The PC based user interface for the controller was designed to have several layers of abstraction, with the top layer offering a simple python based command line user interface and a display of the current resonance spectrum of the cantilever. Lower levels of the controller consist of C library to send and receive messages from the controller and a python module to parse raw data packets from the controller into data points for the resonance curve.

In order to perform chirped resonance tracking, the RE-PTIR has to

1. sweep the repetition rate of the laser across several tens of kilohertz,

2. calculate the cantilever amplitudes corresponding to each frequency and
3. output the maximum amplitude to the AFM controller.

All these operations have been implemented on the FPGA on our controller. To generate the trigger signal for the laser a pulse generator has been synthesized onto the FPGA. Pulses can be generated at a frequency resolution better than 0.5 kHz. An external high-speed level shifter is used to convert the laser trigger signal to a 5V TTL compatible signal that can be used directly for triggering e.g. an EC-QCL. The pulse generator can also be used to modulate the pulse length of the laser at a time resolution better than 9 ns. The laser repetition rate and pulse length can be switched at each pulse. Switching of the resonance frequency is performed by a central control process that receives settings (frequency step size, frequency starting point, sweep speed, sweep direction) from a personal computer (PC) via universal serial bus (USB) and sets the parameters of the pulse generator accordingly.

The controller uses the deflection signal of the AFM as input. This signal is passed through a pre-amplifier and band-pass filter, to remove slow changes in the signal that are introduced by the scanning of the cantilever (<35 kHz) and high frequency changes (>350 kHz). The output of amplifier is digitized by a 5 MHz 24 bit analog digital converter and read into the FPGA. On board the FPGA data pre-processing consists of high pass filtering of the data to remove a DC offset introduced by the amplifier. Then the modulus of samples is taken before low pass filtering to calculate the oscillation amplitude. The maximum amplitude of each frequency sweep is determined and then output via a digital analog converter (DAC; 16bit, 100kHz). An amplifier converts the 0 V to 3.3 V range of the DAC to the -10 V to +10 V range commonly found in AFM inputs. For a flow diagram of the program running on the FPGA see figure 4.
We use the mean modulus of the AFM deflection signal to record the amplitude of the oscillating cantilever. The advantage of the use of this type of amplitude detection, instead of the lock-in that is more commonly found in AFM setups, is its faster settling time which in turn allows for faster sweeping of the resonance. Furthermore, the mean modulus can be implemented on an FPGA in a very efficient way. The drawback of this type of detector, when compared to a lock-in amplifier, is its broad bandwidth, meaning that oscillations of a broad range of frequencies (down to DC signals) can contribute to the output. However, as has been demonstrated by Kos et al.\textsuperscript{18} when the cantilever is specifically excited at a single frequency, contributions from other frequencies can be neglected. While this is not entirely true for the pulsed excitation used to excite the PTIR signal, the analog band pass filter between raw deflection output and analog digital converter input in combination with the sparseness of mechanical modes in the relevant frequency range for the type of AFM cantilevers used, ensured, that no overlap of resonance frequencies was seen experimentally. Aliasing of the 2\textsuperscript{nd} mode (usually around 200 kHz in our system) to around 100 kHz was, however, observed.

The user communicates with the controller via a high-speed USB 2.0 chip from a Python program. From this program sweep parameters can be set and resonance curves can be inspected. The interface to the controller can easily be integrated with programs controlling other parts of the measurement setup to automate AFM measurements.
Results and discussion

Resonance tracking: RE-PTIR imaging

The output update rate of our controller is mainly limited by the duration of the sweep. Since, in its current implementation, the controller does not readjust sweep parameters without user input, parameters that cover all expected sample values have to be determined manually. First the user records relatively slow sweeps (≈ 20 ms) over a wide range of frequencies (≈ 100 kHz) at multiple points within the measurement area. From the resonance frequencies in these sweeps the minimum range of frequencies that need to be covered are then determined. After restricting the sweep range to minimum needed the sweep speed is increased until at least one sweep is performed per pixel at the wanted pixel rate. The pixel rate is determined by the number of pixels per line and the number of lines per second. As the sweep speed is increased, the detected resonance frequency is shifted in the direction of the sweep and the amplitude maximum of the resonance is decreased. The sweep speed has to selected so that these effects do not influence the measurement. In our experience, sweeps over a range of 25 kHz around a center frequency of 60 kHz can be performed at one sweep every 5 ms without significantly reducing the amplitude.

To show the improvement made possible by the RE-PTIR controller the sample depicted in figure 2 was imaged again with the controller (see fig. 5). Errors introduced by shifts of the resonance are now removed. A side by side comparison of cross sections along the horizontal shows the marked improvement in chemical contrast given through the use of frequency tracking measurements over single frequency measurements (see fig. 6).
Resonance tracking: RE-PTIR spectroscopy

In our previous work\textsuperscript{19} we demonstrated rapid acquisition of RE-PTIR spectra with an EC-QCL through continuously tuning the EC-QCL from one end of its spectral range to the other. To use the resonance tracking method together with rapid spectral acquisition the chirp duration has to be short enough so as to not reduce the spectral resolution of the laser. The fastest tuning rate supported by the laser used in this work was 100 cm\textsuperscript{-1}s\textsuperscript{-1}. Hence, one chirp has to be performed within 10 ms to still achieve the nominal spectral resolution of the EC-QCL. As stated in the previous section, this is entirely within the scope of the controller introduced in this work. Therefore, to convert the lock-in amplifier based setup that was used in our previous work\textsuperscript{19} to one using the resonance tracking demodulation introduced in this work, only the lock-in amplifier had to be replaced, no further modifications to the setup were necessary.

To evaluate the improvement in the stability of the signal achieved through the resonance tracking, RE-PTIR spectra of polystyrene were recorded repeatedly at the same sample position using a single frequency detection of the amplitude and resonance tracking detection of the amplitude. These measurements showed, that even for the same sample position the contact resonance frequency can drift, leading to changes in the height magnitude of the spectra recorded using single frequency amplitude detection (see fig. 7). The spectra recorded with active resonance tracking appeared significantly more stable.
In order to perform a numeric comparison of the stability of either method of performing RE-PTIR, the RE-PTIR signals measured at three polystyrene absorption bands were integrated. Since both methods of demodulation apply arbitrary scaling to the signal, the values were divided by their mean value before comparison (see table 1). For all three bands the relative standard deviation of the band integral is lower when using resonance tracking than without it. The improvement is in relative standard deviation is 8.7 to 9.4 fold.

<Insert Figure 7 near here>

<table>
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<tr>
<th>Band</th>
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<th>Single frequency rel. std. / 1</th>
<th>Ratio</th>
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<td>.46</td>
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<tr>
<td>1603 cm⁻¹</td>
<td>.047</td>
<td>.44</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table 1: Relative standard deviations (rel. std.) of the band integrals in the spectra depicted in figure 7. The last column is the ratio of the relative standard deviations measured with single frequency demodulation (lock-in amplifier) and with resonance tracking demodulation.

Conclusion

We are able to demonstrate how incorrect setting of the excitation frequency in RE-PTIR can lead to an incorrect imaging contrast dominated by changes in the contact resonance frequency instead of chemical composition differences. We are also able to show how a
controller implementing continuous resonance tracking can minimize this problem and is thus necessary for reliable RE-PTIR imaging.

Continuous resonance tracking demodulation even improves the stability of a RE-PTIR system used for spectroscopy. For the test sample used in this work a 8.7 to 9.6-fold reduction in the relative standard deviation of selected bands was achieved relative to lock-in demodulation measurements.

Finally, through the open nature of our controller design, it can serve as stepping stone for others to quickly convert an existing AFM to a RE-PTIR setup. It can also serve as a test bed that allows to compare several different evaluation methods (e.g. ring-down versus resonance excitation, different methods of resonance tracking, etc.) against each other. Schematics and source code for the controller are made available for free http://www.cta.tuwien.ac.at/division_environmental_and_process_analytics/process_analytics/downloads/ .

Contributions

The experiments were planned by BL and GR. Custom electronics for the setup were designed by WT and assembled by GR. VHDL and Python code for controlling PTIR measurements were developed by GR, BS developed C code and a VHDL code for rapid data transmission between PC and controller. FR performed PTIR measurements and improved the optical focusing in the setup. All planning, assembly and measurements were performed at TU Wien.

Conflict of Interest

The authors report there are no conflicts of interest.
Acknowledgements

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References


Figures

Figure 1: (a) Schematic depiction of replacing the tip-sample interaction with a spring. (b) The spring constant in (a) is derived from the first derivative of the tip sample force at the equilibrium position.

Figure 2: Comparison of resonance curves measured on gold substrate and a 180 nm polystyrene (PS) film. The softer polystyrene has a lower contact resonance frequency.
Figure 3: RE-PTIR and topography images of a sample consisting of 180 nm PS (left side) on a gold substrate (right side). The top image (gold) depicts the sample topography. RE-PTIR images (red) were recorded around the first (57 kHz to 60 kHz) and second (176 kHz to 182 kHz) resonance when illuminating the sample at 1450 cm\(^{-1}\) (corresponding to the aromatic ring absorption in PS).
Figure 4: Schematic description of data flow inside the resonance tracking controller. Boxes stand for different steps of data treatment, while labels on the connecters describe the data transferred from one step to the next.
Figure 5: RE-PTIR controller based images of the sample in figure 3. The image on the left side was taken at the first contact resonance. A sweep range of 50 kHz to 70 kHz at 1 sweep per 5.3 ms was used. For the image on the right side the second contact resonance was used. A range of 165 kHz to 200 kHz was swept once per 5.6 ms. All other experimental parameters were kept as for the images in figure 2 (i.e. illumination at 1450 cm\(^{-1}\), same cantilever, same set-point and feed-back, same scan rate). The images recorded with the controller correctly display contrast that reflect the chemical composition of the sample.
Figure 6: Horizontal cross-sections across the RE-PTIR images at the first contact resonance in figures 3 (left) and 5 (right). On the polystyrene film (marked in grey) a higher signal is expected than on the gold substrate.

Figure 7: Single channel RE-PTIR spectra of polystyrene taken at a fixed frequency using a lock-in amplifier (left) and with the newly developed frequency tracking controller (right). Negative peaks are due to water vapour absorption in the beam path.