

A microwave study of hydrogen-transfer-triggered methyl-group rotation in 5-methyltropolone

Vadim V. Ilyushin,^{1,a)} Emily A. Cloessner,² Yung-Ching Chou,³ Laura B. Picraux,⁴ Jon T. Hougen,⁵ and Richard Lavrich^{2,b)}

¹*Institute of Radio Astronomy of NASU, Chervonopraporna 4, 61002 Kharkov, Ukraine*

²*Department of Chemistry and Biochemistry, College of Charleston, Charleston, South Carolina 29424, USA*

³*Department of Natural Science, Taipei Municipal University of Education, Taipei 10048, Taiwan*

⁴*Sun Chemical, Cincinnati, Ohio 45232, USA*

⁵*Optical Technology Division, NIST, Gaithersburg, Maryland 20899-8441, USA*

(Received 13 October 2009; accepted 3 September 2010; published online 11 November 2010)

We present here the first experimental and theoretical study of the microwave spectrum of 5-methyltropolone, which can be visualized as a seven-membered “aromatic” carbon ring with a five-membered hydrogen-bonded cyclic structure at the top and a methyl group at the bottom. The molecule is known from earlier studies in the literature to exhibit two large-amplitude motions, an intramolecular hydrogen transfer and a methyl torsion. The former motion is particularly interesting because transfer of the hydrogen atom from the hydroxyl to the carbonyl group induces a tautomerization in the molecule, which then triggers a 60° internal rotation of the methyl group. Measurements were carried out by Fourier-transform microwave spectroscopy in the 8–24 GHz frequency range. Theoretical analysis was carried out using a tunneling-rotational Hamiltonian based on a G_{12}^m extended-group-theory formalism. Our global fit of 1015 transitions to 20 molecular parameters gave a root-mean-square deviation of 1.5 kHz. The tunneling splitting of the two $J=0$ levels arising from a hypothetical pure hydrogen-transfer motion is calculated to be 1310 MHz. The tunneling splitting of the two $J=0$ levels arising from a hypothetical pure methyl top internal-rotation motion is calculated to be 885 MHz. We have also carried out *ab initio* calculations, which support the structural parameters determined from our spectroscopic analysis and give estimates of the barriers to the two large-amplitude motions. © 2010 American Institute of Physics. [doi:10.1063/1.3493336]

I. INTRODUCTION

Intermolecular and intramolecular hydrogen transfers often serve as triggers for more extensive chemical or conformational changes in molecules, and such systems are therefore of importance for molecular dynamics and biochemistry. An early example of a spectroscopic study at rotational resolution on such a system is the microwave work by Sanders¹ on 2-methylmalonaldehyde, where an intramolecular hydrogen transfer in one part of the molecule triggers the internal rotation of a methyl group in another part. At almost the same time, de la Vega² published a theoretical discussion of various differences in the quantum mechanical treatment of tunneling between equivalent and nonequivalent wells, including a discussion of Sanders' 2-methylmalonaldehyde case.

The electronic spectrum in a jet-cooled beam of the closely related molecule 5-methyltropolone (5MT), which again involves internal rotation of a methyl group triggered by an intramolecular hydrogen transfer, was extensively

studied at vibrational resolution by Sekiya and co-workers.³ Extensive tunneling and other information were obtained, but primarily for the excited electronic state S_1 , since splittings in the ground S_0 state were below the limit of the available experimental resolution. A theoretical study of the experimental splittings observed in the S_1 state of 5-methyltropolone was carried out by Vendrell, Moreno, and Lluch⁴ based on a reduced dimensionality treatment of the potential energy surface. These authors also discussed “the present difficulties to obtain excited state potential energy surfaces with great accuracy beyond the Franck–Condon vertical excitation region.”

In this paper, we report a microwave study on the S_0 state of 5-methyltropolone, similar to that carried out^{1,5,6} for 2-methylmalonaldehyde. The goals of the present study are twofold: (i) to provide a set of accurate energies and secure quantum number assignments for the tunneling-rotational levels of 5-methyltropolone that can serve as the experimental basis for comparison with any future quantum chemistry calculations and (ii) to show that a group-theoretically derived effective tunneling Hamiltonian formalism already in the literature^{5,7} is capable of fitting the microwave spectrum to its experimental error and is thus capable of providing secure quantum number assignments for all observed levels.

^{a)}Guest worker, Summer 2009, Optical Technology Division, NIST, Gaithersburg MD 20899-8441, USA.

^{b)}Author to whom correspondence should be addressed. Department of Chemistry and Biochemistry, College of Charleston, 66 George Street, Charleston, SC 29424, USA. Electronic mail: lavrichr@cofc.edu.

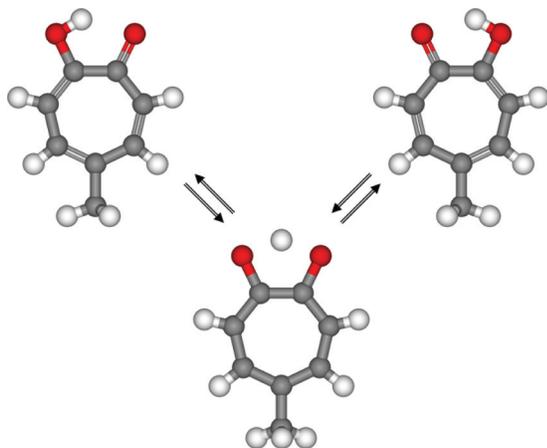


FIG. 1. A sketch of two equilibrium conformations of 5MT and the transition state for the tunneling path involving hydrogen transfer and corrective internal rotation. Conformations in the upper left and right are two of the six equilibrium conformations of a 5MT molecule with labeled atoms, while the structure in the lower center is the transition state of the tunneling path in the group-theoretical formalism. The methyl rotor experiences a threefold torsional barrier in the equilibrium conformations and a sixfold torsional barrier in the more symmetric transition state.

We report in addition quantum chemistry calculations in support of our experimental molecular constants.

From a spectroscopic point of view, the current study of the 5MT microwave spectrum was motivated by recent progress^{5,6} in our quantitative understanding of the analogous tunneling system, 2-methylmalonaldehyde,¹ and by the associated question of how the system will behave when the hydrogen to be transferred and the methyl top to be rotated are well separated from each other in the molecule. Microwave spectroscopy is well suited to quantitatively determine the energy splittings associated with the intramolecular motions under discussion. Theoretical processing of the full set of rotational energy levels should then lead to good experimental values for internal-rotation and hydrogen-transfer barriers, though as we shall see below, some problems remain in the reduced-dimension theoretical models used at present for 5MT.

Figure 1 shows the equilibrium structure of 5MT (Ref. 4) and the transition state in the tunneling path involving hydrogen transfer.⁴ As is well known, the act of hydrogen transfer induces a tautomeric rearrangement of the CC and CO single and double bonds in the molecule¹⁻⁴ and triggers a subsequent 60° internal rotation of the methyl group, which we refer to here as a “corrective internal rotation.” (One C—H bond of the methyl group prefers to lie in the ring plane and adjacent to the C=C bond at equilibrium.) This combined motion, together with the pure methyl top internal rotation, gives rise to a two-dimensional tunneling problem, with two distinct tunneling frequencies. The question of whether an effective Hamiltonian can be devised to fit this rather complicated microwave spectrum to experimental error is, of course, of theoretical interest for high-resolution studies of other molecules with two strongly coupled large-amplitude motions.

II. EXPERIMENTAL

Since 5MT is not available commercially, it was synthesized from tropolone. The first step was to brominate tropolone in methanol at $-10\text{ }^{\circ}\text{C}$ by dropwise addition of Br_2 following the methodology in Ref. 8. Upon warming to room temperature, a mixture of 3,7-dibromo and 3,5,7-tribromotropolone precipitated from the solution.⁸ Recrystallization of this mixed precipitate from methanol gave 3,7-dibromotropolone (yield: 31%). Next, the Mannich reaction was utilized to place a morpholinomethyl group in the 5-position of the 3,7-dibromotropolone⁹ (yield: 89%). The final step was to hydrogenate 3,7-(dibromo)-5-(morpholinomethyl)tropolone with Pd:C to remove all bromine and convert the Mannich residue to a CH_3 group.⁹ Because the bromines are removed from the ring as HBr , it was found that the solution was slowly neutralized, causing incompletely hydrogenated intermediates to precipitate from solution, at which point further hydrogenation ceases. Therefore, the solution was kept basic (as indicated by pH paper) by adding a few milliliters of 6M NaOH during the hydrogenation. The yield of this step was 38%.

The measurements were made using two nearly identical Fourier transform microwave (FTMW) instruments equipped with a heated reservoir nozzle,¹⁰ one at the College of Charleston and the other at the National Institute of Standards and Technology (NIST). The estimated measurement precision is 2 kHz for both instruments. We used Ne gas as a carrier at a backing pressure of about 100 kPa. A nozzle temperature of $110\text{ }^{\circ}\text{C}$ gave a reasonable signal-to-noise ratio and an optimum trade-off between signal to noise and the time of measurement for one load of sample. Initial searches and a part of the measurements were carried out at College of Charleston. Measurements at NIST aimed at extending the data set, in particular at recording more b-type transitions across the tunneling splittings. No previous microwave measurements for this molecule could be found in the literature.

Measurements were made in the frequency range from 7 to 26 GHz and transitions up to $J=17$ and $K_a=10$ were observed. Some low- J transitions were clearly broadened, presumably by spin-spin hyperfine interactions, but this broadening was not investigated in detail, and these transitions were simply given an uncertainty of 4 kHz, just as for very weak transitions. All lines were weighted in our fits by the inverse square of their assigned uncertainties.

III. EFFECTIVE HAMILTONIAN

We use here the same high-barrier tunneling formalism Hamiltonian as for 2-methylmalonaldehyde,^{5,6} which is described in detail in Refs. 5 and 7. We also used the same fitting program, i.e., a slightly modified version of the program obtained from Ohashi.¹¹ The reader is referred to Ref. 5 and references therein for a detailed description of this formalism. We give here only a brief summary of the important physical ideas, which are individually numbered in the next two paragraphs for clearer conceptual separation.

(i) Since we desire an effective Hamiltonian to fit rotational energy levels, the Hamiltonian is expressed as a series in powers of the three molecule-fixed components J_x , J_y , and

J_z of the total angular momentum operator \mathbf{J} . (ii) For treatments of the electronic ground state, coefficients of the variational operators in the power series are considered to be functions only of the vibrational variables. (iii) At this point, we depart from traditional vibration-rotation Hamiltonians and divide vibrational variables into small-amplitude vibrations (SAVs), which can be treated as harmonic oscillators with small anharmonic corrections, and large-amplitude motions (LAMs), which involve atomic excursions comparable to or larger than typical molecular bond lengths. (iv) For treating the ground state (as here), the SAVs are ignored (or, more correctly, the coefficients of the terms in the J_x , J_y , and J_z power series are implicitly averaged over Gaussian harmonic oscillator wave functions corresponding to $v=0$ for each SAV). (v) If there were no LAMs, all coefficients would be constants at this point, and we would use traditional spectroscopic theory to set up and diagonalize a rotational Hamiltonian matrix of dimension $(2J+1) \times (2J+1)$ for each J to obtain the desired rotational energy levels.

(vi) However, the LAMs are present and all coefficients are not constants, and in fact their magnitudes and signs can vary greatly when the molecule carries out its LAMs. Some scheme for dealing with the effects of this large variation to within microwave measurement accuracy must be devised. (vii) To accomplish this, we restrict consideration to situations where the molecule carries out many LAM oscillations in a given local minimum and only occasionally tunnels to a “nearby” local minimum, i.e., we restrict consideration to “high-barrier tunneling problems.” In such a tunneling formalism, all details of the strong coefficient variation along the LAMs are converted to J and K dependent contributions to the tunneling splittings (somewhat like various details of a diatomic molecule potential curve can be converted to B , D , H , etc. rotational constants). (viii) Such a tunneling formalism also allows us to use a basis set (for given J) that consists of a full set of $2J+1$ rotational basis functions in each of the n local minima and further allows us to set up a tunneling-rotational Hamiltonian matrix of dimension $(2J+1)n \times (2J+1)n$. (ix) Since the local minima between which tunneling takes place are by hypothesis equivalent, there are numerous symmetry restrictions leading to tunneling matrix elements with the same magnitude, but often with a different complex phase, distributed appropriately throughout the $(2J+1)n \times (2J+1)n$ array. Permutation-inversion group theory and time reversal procedures (often rather lengthy) are used to determine these symmetry restrictions. The permutation-inversion group theory is also used to block-diagonalize the full matrix into submatrices labeled by appropriate symmetry species before numerical diagonalization is carried out. (x) The final result is a $(2J+1)n$ -dimensional Hamiltonian matrix, which has been block-diagonalized by symmetry and which has the proper number of symmetry allowed terms, whose coefficients are now treated as “molecular constants” to be determined from a least-squares fit to experimental data.

The question now arises of why one would bother with such a complicated effective tunneling-rotational Hamiltonian treatment when these same rotational levels can all be calculated using commercial quantum chemistry packages.

The answer, of course, is that during initial spectroscopic studies of a complicated and dense LAM-rotational spectrum, when no clear patterns are evident and when no line assignments are certain, it is necessary to have a Hamiltonian that is capable of fitting the correctly measured and assigned LAM-rotational lines with J up to 20 or 30 to experimental accuracy (often a few kilohertz in modern microwave studies), but that is also capable of rejecting with reasonable reliability the mismeasured and misassigned lines in the data set. At present, this task is better performed for most polyatomic molecules by “effective spectroscopic Hamiltonians,” such as we now describe below, than by *ab initio* spectroscopic Hamiltonians.

For notational purposes, we repeat here only the linear and quadratic terms in Eq. (1) of Ref. 5 (after putting a factor of $\frac{1}{2}$ in front of the last term to correct an omission there).

$$H = h_v + h_j \mathbf{J}^2 + h_k J_z^2 + (f_+ J_+^2 + f_- J_-^2) + q J_z + (r_+ J_+ + r_- J_-) + (1/2)[s_+(J_+ J_z + J_z J_+) + s_-(J_- J_z + J_z J_-)]. \quad (1)$$

Apart from some symmetry restrictions, each term in Eq. (1) gives rise^{5,7} to matrix elements within the n “nontunneling” $(2J+1) \times (2J+1)$ blocks on the diagonal of the full $(2J+1)n \times (2J+1)n$ Hamiltonian matrix, as well as giving rise to matrix elements within each of the $n(n-1)$ off-diagonal $(2J+1) \times (2J+1)$ “tunneling blocks” connecting rotational manifolds localized in different local LAM minima. As a consequence, each coefficient in Eq. (1) is represented in the fit by a nontunneling value (its value in the diagonal blocks), as well as by a number of different “tunneling” values (one value for each symmetrically inequivalent off-diagonal tunneling block). Each of the fitting constants (i.e., each of the letters h , f , q , r , and s) will thus acquire an additional subscript $n=1-6$, which indicates that they represent Hamiltonian matrix elements associated with no tunneling ($n=1$) or tunneling from framework 1 to framework $n > 1$.

The nontunneling value of h_v , which does not multiply any total angular momentum operator in Eq. (1), corresponds to a spectroscopically uninteresting absolute energy offset for all levels, but the tunneling values of h_v represent the tunneling frequencies in the nonrotating molecule for each symmetrically inequivalent tunneling path. The nontunneling values of h_j , h_k , and f correspond physically (approximately) to the usual asymmetric-rotor rotational constants $(1/2)(B+C)$, $A - (1/2)(B+C)$, and $(B-C)/4$, while the tunneling values of h_j , h_k , and f correspond to tunneling corrections to these rotational constants. The linear terms q and r in Eq. (1) correspond physically to the interaction of components of the total angular momentum with any angular momentum generated in the molecule-fixed axis system by the two LAMs in the molecule. Symmetry and/or time reversal requirements appropriate for 5MT allow contributions from these linear terms only in the off-diagonal tunneling blocks. The nontunneling quadratic s term allows physically for the fact that molecule-fixed components J_x , J_y , and J_z of the total angular momentum \mathbf{J} are not expressed in the principal-axis system of the molecule. Instead, as is common in internal-rotation problems,¹² the z axis is chosen⁷ to lie along the $\boldsymbol{\rho}$ vector.¹² Higher-order J and K_a dependences of the h , f , q , r , and s

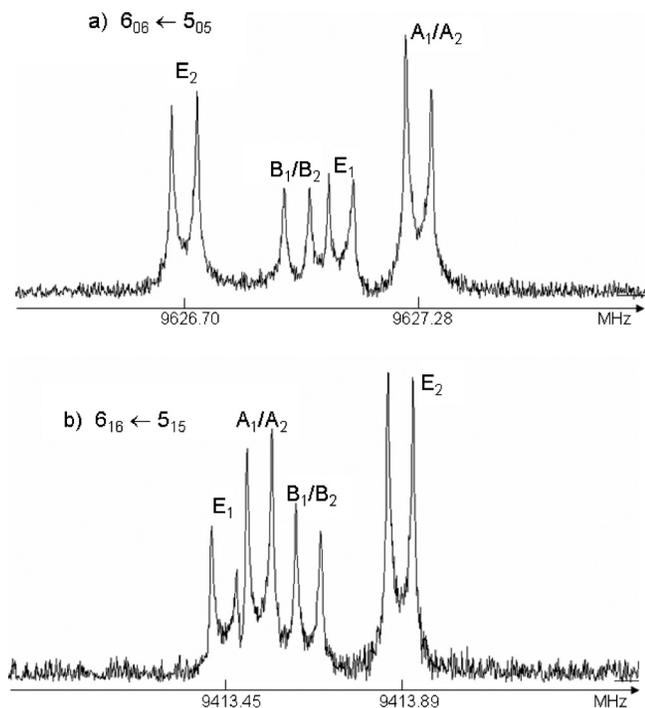


FIG. 2. Two representative tunneling splitting patterns in the microwave spectrum of 5MT, with J_{KaKc} and G_{12} symmetry species labels. All lines consist of Doppler doublets (e.g., the E_2 line at 9626.70 MHz) because the microwave radiation in the cavity propagates parallel and antiparallel to the unidirectional molecular beam. In addition, each transition has four components because of the interplay of hydrogen-transfer and internal-rotation tunneling splittings in this molecule. The four tunneling components all have different symmetry species in the permutation-inversion group appropriate for 5MT, and these symmetry species in turn have different nuclear-spin statistical weights, resulting in the approximate 5:3 intensity ratio evident in the figure. Such intensity ratios are a great help in assigning correct symmetry species to the various components.

parameters [i.e., centrifugal distortion corrections that are not shown in Eq. (1)] are indicated by adding subscripts j and k , as illustrated by the series h_v , $h_j J^2$, $h_k J_z^2$, $h_{jj} J^4$, $h_{jk} J^2 J_z^2$, $h_{kk} J_z^4$, etc.

IV. SPECTRAL FITS

Since there was no previous microwave study reported for 5MT, we first performed broadband scans of some parts of the 9–16 GHz region of the spectrum, guided by A , B , and C rotational constants from a low-level *ab initio* calculation. These broadband scans revealed a sequence of quartet lines, which were attributed to tunneling-split components of low K_a transitions of the 5MT vibrational ground state. Two of these quartet patterns are shown in Fig. 2. A fit performed for some components of the observed quartets using a Watson Hamiltonian gives us a preliminary assignment of rotational quantum numbers for about 16 transitions with K_a up to 2. Further progress with the pure asymmetric-rotor Hamiltonian was stopped by the increasing residuals in the fit when we tried to add new lines so that from this point forward, we turned to the high-barrier tunneling formalism Hamiltonian described in the previous section.

Our initial assumptions for this tunneling Hamiltonian fit were based on the following observations. An inspection of the three other molecules where ground state rotational tran-

sitions were treated using the same formalism (namely CH_3NH_2 ,¹³ 2-methylmalonaldehyde-d0 and 2-methylmalonaldehyde-d1^{5,6}) showed that for R -type $K_a=0$ transitions [like those shown at Fig. 2(a)], the A -species components of the split rotational transitions always lie at the highest frequency, even though the order of the other symmetry components varied among the three cases mentioned. Consideration of the relative intensities for components of different symmetry species, based on our calculated nuclear-spin statistical weights of 5 for A and E_2 levels and 3 for B and E_1 levels, confirmed this assumption, as illustrated in Fig. 2(a), and also gave us tentative assignments for the E_2 components of these transitions. The assignment of the weaker B and E_1 symmetry components of R -type $K_a=0$ transitions as well as of the $K_a \neq 0$ transitions was carried out by trial-and-error, i.e., various possibilities were tested. Final assignments for tunneling components of the $6_{06} \leftarrow 5_{05}$ and $6_{16} \leftarrow 5_{15}$ transitions are shown in Fig. 2.

Initial values for rotational constants in our tunneling Hamiltonian fits were taken from our preliminary asymmetric-rotor fits. The pure internal-rotation tunneling splitting parameter h_{3v} was fixed at the value obtained for 2-methylmalonaldehyde-d0 since from a chemical point of view, the torsional motion in 2-methylmalonaldehyde and 5MT seem quite similar. The H-transfer plus corrective internal-rotation tunneling splitting parameter h_{2v} was manually adjusted from its 2-methylmalonaldehyde-d0 value until the calculated 5MT splittings were comparable in magnitude to those obtained in our experiments. An initial ρ value of 0.017 was estimated from $\rho \approx I_a/I_a$ using the preliminary A rotational constant to determine I_a and an assumed moment of inertia $I_a=3.18 \text{ u}\text{\AA}^2$ for the methyl top. After a number of attempts, we obtained a fit within experimental error (within 2.9 kHz) for the 94 $\Delta K_a=0$ R -type transitions present in our initial scans. Several further iterations of predictions and new measurements gave us the final fit described in the next paragraph.

A final least-squares fit of 1015 5MT transitions to 20 parameters was carried out, giving a root-mean-square (rms) deviation of 1.5 kHz. A copy of the input and output files is deposited in the supplementary material²⁴ (Appendix). A copy of the fitting program is deposited in Appendix A of Ref. 6. The data set contains 648 $\Delta K=0$ and 135 $\Delta K=2$ a -type transitions, which connect energy levels within each vibrational tunneling state, as well as about 232 $|\Delta K|=1$ b -type transitions, which go across the tunneling splittings. The transitions are evenly distributed among the four symmetry species of the molecule. The $\Delta K \neq 0$ transitions include about 167 Q -branch lines. All these data are fit to a weighted rms deviation of 0.64, which from our point of view is excellent. The rms deviation of 1.5 kHz demonstrates that the hydrogen-transfer-internal-rotation tunneling Hamiltonian used here is capable of describing energy levels and their splittings to better than 2 kHz.

The molecular parameters from our final fit are shown in Table I. The upper part contains linear combinations of the three usual rotational constants, the five quartic centrifugal distortion constants, an off-diagonal rotational constant s_1 (see Eq. (1)), and the value of the usual internal-rotation

TABLE I. Molecular parameters from our least-squares fit of tunneling-rotational transitions in the ground vibrational state of 5-methyltroplone. Numbers in parentheses denote one standard deviation (type A, $k=1$) (Ref. 14) and apply to the last digits of the parameters. All parameters and the rms deviation of the fit are in megahertz, except for ρ , which is unitless. $\bar{B} \equiv (B+C)/2$. Transition frequencies used in the fit are given in the supplemental material (Ref. 24).

Parameter	Value
$A-\bar{B}$	1847.451 966(30)
\bar{B}	865.648 126 9(64)
$(B-C)/4$	66.215 244 3(25)
s_1	12.396 601(28)
ρ	0.017 096 909(29)
$D_J \times 10^4$	0.156 69(29)
$D_{JK} \times 10^4$	0.4062(13)
$D_K \times 10^4$	2.353(11)
$\delta_J \times 10^4$	-0.044 37(14)
$\delta_K \times 10^4$	-0.5103(36)
h_{2v}	-654.950 244(65)
h_{2j}	0.000 446 62(71)
h_{2k}	0.009 045 7(54)
f_2	-0.000 138 47(46)
h_{4v}	0.362 221(25)
h_{3v}	-295.0732(19)
h_{3j}	-0.000 117 1(15)
h_{3k}	-0.000 122 1(93)
f_3	-0.000 027 20(74)
r_3	0.025 55(34)
Number of lines ^a	1015
rms	0.0015

^aNumber of transitions included in the fit.

moment-of-inertia ratio ρ . The lower part contains parameters associated with the large-amplitude tunneling motions.

The first five nontunneling constants in Table I can be converted to five quantities having somewhat more physical meaning,¹² as shown in Table II. The principal-axis rotational constants A_p , B_p , and C_p are obtained by diagonalizing the 3×3 matrix containing A , B , and C on the diagonal and s_1 in the AB off-diagonal position. The quantity ρ (representing the ratio of the moment of inertia of the methyl top to a moment of inertia of the whole molecule pointing nearly along the principal a axis¹²) is transferred directly from Table I. The angle θ between the methyl top symmetry axis and the principal a -axis of the molecule is obtained by manipulating Eq. (2-30) and some of its neighbors in Ref. 12. We have carried out quantum chemistry calculations for these five structural parameters (all of which can be obtained from the equilibrium structure of the molecule) using the GAUSSIAN 03 suite of programs^{15,16} at the B3LYP and MP2 levels. Values from two such calculations are shown in Table II. The excellent agreement between our experimental values and the quantum chemistry values for all five of these structural parameters gives good support for the tunneling-rotational Hamiltonian used for the spectroscopic analysis here.

The parameters h_{nv} for $n=2$ and 4 represent the nearest-neighbor and next-next-nearest-neighbor tunneling frequencies associated with the H-transfer motion plus corrective internal rotation (see the schematic potential surface in Fig. 2 of Ref. 5 for the definition of “nearest-neighbor” minima etc.). Table I shows that $|h_{2v}|/|h_{4v}| \approx 1800$, and this large ratio justifies the high-barrier tunneling formalism used here. The parameter h_{nv} for $n=3$ represents the next-nearest-neighbor tunneling frequency associated with the pure internal-rotation motion of the methyl group.

For a one-dimensional tunneling problem between two equivalent wells, a tunneling frequency of $|h_v|$ would lead to a tunneling splitting of $2|h_v|$. For the six equivalent wells and

TABLE II. Comparison of experimental and theoretical values for five structural parameters and two tunneling barriers in 5MT. A_p , B_p , and C_p are the principal-axis rotational constants in megahertz. The other two structural parameters are the unitless ratio ρ [approximately equal (Refs. 12 and 20) to the moment of inertia of the methyl top divided by the a -axis moment of inertia of the whole 5MT molecule] and the angle θ between the internal-rotation axis of the methyl top and the principal a -axis of the molecule (in degrees). All barriers are in cm^{-1} . V_3 and V_3^0 represent the threefold barrier for the pure internal-rotation motion, without and with zero-point vibrational corrections, respectively. V_H and V_H^0 represent the barrier for the H-transfer motion with corrective internal rotation, without and with zero-point corrections, respectively.

	A_p (MHz)	B_p (MHz)	C_p (MHz)	ρ (unitless)	θ (°)	V_3 (cm^{-1})	V_3^0 (cm^{-1})	V_H (cm^{-1})	V_H^0 (cm^{-1})
Experiment ^a	2713.2	998.0	733.2	0.01710	1.126		321		
RB3LYP/6-311+G(2df,2pd) ^b	2741.3	1000.2	736.1	0.01694	0.880	240	188		
RMP2(FC)/6-311G(2d,2p) ^c	2736.6	997.6	734.4	0.01689	0.891	211	181	2066	1303
RMP4(FC)/6-311G(2d,2p) ^d						266		2453	
RMP2(FC)/6-31G(d,p) ^d						229	198	1969	1213
RMP4(FC)/6-31G(d,p) ^d						275		2402	

^aExperimental values for the five structural parameters are obtained from the first five fitting parameters in the left column of Table I (see text). The experimental value for V_3^0 is obtained using Eq. (2).

^bAll theoretical values in this table were obtained using the GAUSSIAN suite of programs (Ref. 15). This row illustrates structural parameters obtained from our largest RB3LYP calculation. The first four structural parameters, which depend on moments-of-inertia at the minimum-energy (equilibrium) geometry, agree with experiment to within 1%.

^cStructural parameters obtained from our largest RMP2 calculation. The first four structural parameters agree with experiment to within 1.2%.

^dCalculations used to obtain estimates of the barrier heights (see text). The two RMP4 calculations use the structure from the corresponding RMP2(FC) immediately above. Barriers calculated with zero-point vibrational energy contributions (V_3^0 and V_H^0) are considerably smaller than barriers calculated without such corrections (V_3 and V_H).

two different tunneling pathways considered here, the energies of the four splitting components are given⁵ by the somewhat more complicated expressions $(\pm 2h_{2v} + 2h_{3v})$ and $(\pm h_{2v} - h_{3v})$. Using the values in Table I, we see that the total width of the splitting pattern arising from the six-well problem in 5-methyltropolone is $4|h_{2v}| = 2620$ MHz, a value consistent with the upper bound estimate of <0.1 cm⁻¹ obtained from the S₁-S₀ fluorescence spectrum of 5MT.³

For the purpose of comparison with other molecules, it is often convenient to focus on only one of the tunneling frequencies at a time. Thus, using the hypothetical two-well hydrogen-transfer splitting of $2|h_{2v}| = 1310$ MHz from Table I, we see that just as for 2-methylmalonaldehyde^{1,5,6} versus malonaldehyde,¹⁷ the additional effort required to rotate the methyl group in conjunction with the hydrogen-transfer tunneling causes the hydrogen tunneling splitting for 5-methyltropolone to be much smaller than the value of 29193.79(3) MHz obtained for tropolone.¹⁸ For the pure internal-rotation tunneling (with no migration of the hydroxyl hydrogen), the quantity $|3h_{3v}|$ corresponds to the usual E-A internal-rotation splitting of $J=0$ torsional levels in a methyl top molecule.⁵ For 5MT, we obtained a value of $3|h_{3v}| = 885.220(6)$ MHz, which is about three times larger than the corresponding quantity in 2-methylmalonaldehyde.⁶

As a final point in this section, we note that no parameters of the type q_n occur in Table I. It turns out that $q_1=0$ by symmetry and time reversal arguments,⁷ corresponding physically to the fact that vibronic angular momentum cannot be generated in nondegenerate vibronic states. As discussed in detail in Ref. 19, the three parameters q_2 , q_3 , and ρ were highly correlated in the least-squares fit of spectral data for the group-theoretically related molecule methylamine so that q_3 was set equal to zero there, corresponding physically to the fact that linear terms in the internal-rotation angular momentum can be removed from the torsion-rotation Hamiltonian by using a suitable contact transformation²⁰ to change from the “principal-axis-method” coordinate system to the “internal-axis-method” coordinate system.¹² A nonzero value for the parameter q_2 was in fact determined for methylamine.¹⁹ The fact that we found q_2 unnecessary in our fit for 5MT probably arises because the tropolone “frame” has a much larger moment of inertia than the amine frame, when both are compared to the moment of inertia of the methyl top involved in the corrective internal rotation. We note in passing that the q_n terms were also not required to fit⁶ the microwave spectra of the related molecules 2-methylmalonaldehyde-d0 and 2-methylmalonaldehyde-d1.

V. HYDROGEN-TRANSFER TIME SCALES

It is well known from treatments of the two-well tunneling problem that high-resolution spectroscopy measures the energy difference between the two stationary state levels, but that this energy difference Δ in the frequency domain can be converted to the time interval $\tau \approx 1/\Delta$ required for a full-cycle nonstationary state motion of a wave packet from one of the two wells to the other and back. The situation is more complicated for a multiwell, multidimensional tunneling problem since a given energy difference is in general deter-

mined by more than one tunneling frequency and a wave packet starting out from one well has several possible final destinations, but in the $J=0$ tunneling Hamiltonian used to treat energy levels in the present study, we consider (by analogy with the two-well problem) twice the matrix element between a given pair of localized minima to represent the energy splitting between their sum and difference wave functions and then further interpret the reciprocal of this energy splitting as the time required for an idealized round-trip wave packet trajectory involving only these two minima, i.e., $\Delta = 2|h_{2v}|$ and $\tau \approx 1/(2|h_{2v}|)$. In this idealized two-well sense, we have thus determined that H-transfer from one oxygen to the other (with corrective internal rotation) takes place (in the ground vibrational state) approximately every $1/(4|h_{2v}|) \approx 0.4$ ns, while pure internal-rotation tunneling from one torsional well to another occurs approximately every $1/(4|h_{3v}|) \approx 0.8$ ns.

These time intervals differ greatly from the time intervals determined for a hydrogen-transfer event in the work of Ushiyama and Takatsuka,²¹ who carried out full dimensional *ab initio* molecular dynamics for 5MT at the RHF level with a 6-31G basis set, and this discrepancy requires an explanation. In brief, Ushiyama and Takatsuka sampled 50 trajectories each for total energies of 1.25, 2.75, and 4.25 times the vibrational zero-point energy, starting from zero momentum and random initial atom positions in the vicinity of the equilibrium structure. If, for those trajectories where H transfer actually occurs, one “starts the clock” when the hydroxyl H has moved to a position halfway between the two oxygen atoms, then their results can be roughly summarized as follows: at about 10 fs, the reorganization of the electronic structure begins; at about 30 fs, the rotation of the methyl group begins; at about 100 fs, the 60° corrective rotation of the methyl group is complete. As is evident, our nanosecond time scale does not correspond to the femtosecond scale of Ushiyama and Takatsuka. In fact, their time intervals are not directly comparable to ours for two reasons. (i) Total energies far above the zero-point level were considered in Ref. 21, and (ii) Ushiyama and Takatsuka were essentially trying to determine theoretically the duration and detailed time-sequence of a tunneling event once it actually starts, while the measurements here give only an estimate of the average interval between tunneling events. (To calculate the latter, techniques like those recently reviewed in Ref. 22 are required.)

A somewhat different point is raised by comparing the thought processes in Ref. 21 with those here. In (traditional) tunneling thinking, there is a single path between any two localized minima, which is traversed in the forward or in the backward direction, depending on which minimum the localized wave packet is launched from. However, in the path described in Ref. 21, the hydrogen transfer and reorganization of the electrons always precede the methyl top rotation, meaning that there is actually a kind of hysteresis effect, so that the forward (e.g., 1→2) tunneling path in a two-dimensional H-transfer and methyl-rotation space (see Fig. 2 of Ref. 5) does not coincide with the backward path (e.g., 1←2). Does this “hysteresis” have to be incorporated in multidimensional tunneling models, and if so how? This

question may be related to some isotopic anomalies in “experimentally determined” multidimensional tunneling frequencies mentioned in Sec. VII.

VI. BARRIER HEIGHTS FROM OBSERVED TUNNELING SPLITTINGS AND ASSUMED TUNNELING PATHS

An experimental estimate of a barrier height can be obtained from an observed tunneling splitting if the following additional information is available: (i) the shape of the potential energy surface above the tunneling path connecting the two equivalent minima, (ii) the length of the tunneling path connecting the two minima, and (iii) the amount of mass that must be moved at each step along the tunneling path.

A. Internal-rotation barrier

The situation for pure internal-rotation motion of a methyl top is relatively simple. Following numerous examples in the literature, (i) the barrier is assumed to have a cosine shape, (ii) the tunneling path is assumed to have a length of $2\pi/3$ radians, i.e., to be equal to the angular rotation taking the top from one minimum to the next, and (iii) the amount of mass to be moved is assumed to be nearly constant along the path and to correspond to a moment of inertia for the CH_3 top of $I_\alpha \approx 3.18 \text{ u}\text{\AA}^2$. (See, however, the next section for some unexpected problems with V_3 in the closely related molecule 2-methylmalonaldehyde.) As mentioned, the quantity $|3h_{3v}|$ corresponds to the usual E-A internal-rotation splitting in a methyl top molecule.⁵ This observed quantity can thus be combined with a calculated value for the internal-rotation parameter F to obtain a barrier height from the usual internal-rotation Hamiltonian

$$H = T + V = Fp_\alpha^2 + (1/2)V_n(1 - \cos n\alpha), \quad (2)$$

where α is the internal-rotation angle and $n=3$ for the methyl torsion. Expressions near Eq. (2-30) in Ref. 12 allow us to determine from the first five fitting parameters in Table I a value for the moment-of-inertia of the top about its symmetry axis $I_\alpha = 3.1851 \text{ u}\text{\AA}^2$, and thus a value for $F = 5.3847 \text{ cm}^{-1}$ in Eq. (2) above. The value for I_α lies in the normal range (the first two quantum chemistry calculations shown in Table II, for example, both give $3.12 \text{ u}\text{\AA}^2$), which further supports the validity of the present analysis. The value for F leads to a barrier of $V_3 = 321 \text{ cm}^{-1}$ for the pure internal-rotation motion. This value is in good agreement with the value of $V_3 = 329 \text{ cm}^{-1}$ obtained from the S_1 - S_0 fluorescence spectrum of 5MT.³

Theoretical barrier heights require a difference in energy between the saddle point at the top of the barrier and the minimum at the bottom of the barrier. Furthermore, the small-amplitude vibrational frequencies can be significantly different at these two stationary points, so zero-point vibrational corrections are frequently important. Table II shows theoretical barriers obtained for the pure internal-rotation motion without zero-point corrections (V_3) and the same barriers with zero-point corrections included (V_3^0), obtained from RMP2 and RMP4 calculations with two different basis

sets. It can be seen that the experimental barrier determined independently here and in Ref. 3 is nearly a factor of two higher than these theoretical estimates. Improvement of the theoretical internal-rotation barrier by higher level calculations is beyond the scope of this work (which is primarily a spectroscopic study of 5MT).

B. H-transfer barrier

As discussed at some length for the H-transfer motion in 2-methylmalonaldehyde,⁶ we were only able to arrive at experimental barrier heights in reasonable agreement with theoretical expectations by “hiding” the mass of the three methyl protons, i.e., by assuming that only the mass of the hydroxyl hydrogen atom was being moved along the tunneling path.² At the moment, we do not know what the cause of this difficulty is, so we do not attempt to calculate a H-transfer barrier here from our least-squares determined value for the H-transfer tunneling frequency. Our quantum chemistry calculations, as shown in Table II, give values in the range of 1200 or 1300 cm^{-1} for this barrier. Our values uncorrected for zero-point motion are in the range of 2000 cm^{-1} , which are comparable to the value of 0.219 eV ($\approx 1770 \text{ cm}^{-1}$) given in Ref. 21. At the moment, these theoretical values are probably the best estimates for the H-transfer barrier height.

VII. DISCUSSION

It would be interesting to study the 5MT-d1 spectrum to shed more light on some anomalies in the h_{2v} and h_{3v} parameters obtained for 2-methylmalonaldehyde. For the latter molecule, deuteration of the hydroxyl H led to a change in the torsional splitting parameter h_{3v} , which was both unexpectedly large and in the “wrong” direction.^{5,6} While the correct explanation for this observation is still unknown, one possibility is the “leakage” of the large H-transfer tunneling splitting parameter h_{2v} in 2-methylmalonaldehyde into the much smaller torsional tunneling splitting parameter h_{3v} ,^{5,6} caused by some “coupling” of these two motions that was not properly included in the model. If this explanation is correct, then deuteration of the hydroxyl H in 5MT should produce a much smaller change in h_{3v} since the h_{2v}/h_{3v} ratio is only 2.2 for 5MT compared to 188 for 2-methylmalonaldehyde and a small leakage of one splitting parameter into the other (nearly equal) splitting parameter should be much less noticeable.

It is possible to unify our understanding of competing tunneling splittings in a variety of molecules exhibiting a methyl-group rotation triggered by some back-and-forth large-amplitude motion elsewhere in the molecule by using a diagram such as Fig. 3, where the $J=0$ energy level splitting pattern is plotted against the unitless parameter $(h_{2v} - h_{3v})/(h_{2v} + h_{3v})$. If the back-and-forth triggering motion tunnels at a much faster rate than the pure internal-rotation tunneling, then (when the corrective methyl-group rotation is considered) the tunneling splittings have the same spacings as the Hückel π orbitals in benzene, with levels at $-2|h_{2v}|$, $-|h_{2v}|$, $+|h_{2v}|$, $+2|h_{2v}|$. This situation is shown on the right of Fig. 3. If the internal-rotation tunneling of the methyl group

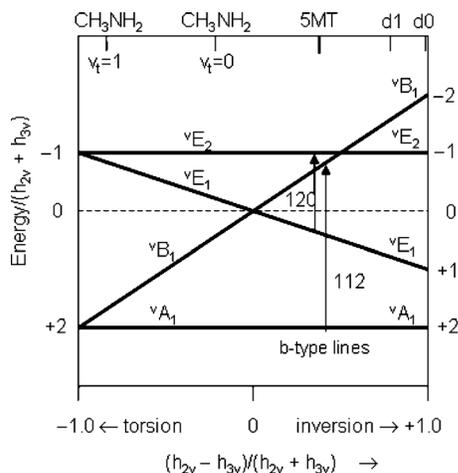


FIG. 3. Schematic illustration of energy level splittings arising from a back-and-forth LAM tunneling motion and an internal-rotation LAM tunneling motion, according to Eq. (5) in Ref. 5. The diagram has been drawn with unitless abscissa and ordinate, obtained by dividing both scales by $h_{2v} + h_{3v}$. At the pure torsional splitting limit, shown on the left ($h_{2v}=0$), the unitless energy levels consist of two superimposed nondegenerate levels at $+2$ separated from two doubly degenerate levels at -1 . At the limit of only back-and-forth motion ($-NH_2$ inversion or H-transfer) plus corrective internal-rotation splittings, shown on the right ($h_{3v}=0$), the unitless energy levels consist of a benzene- π -orbital-like pattern, with the two nondegenerate levels at the bottom and top (at ± 2) and the doubly degenerate levels in between (at ± 1). At the center, where the inversion and torsion splitting parameters are equal ($h_{2v}-h_{3v}=0$), the lowest level is nondegenerate (at $+2$), the highest is doubly degenerate (at -1), and the middle level is accidentally triply degenerate (at 0). Markers at the top of the diagram indicate the position along the abscissa appropriate for 5MT, as well as positions appropriate for 2-methylmalonaldehyde-d0 and -d1 (Refs. 5 and 6) and for the first two torsional levels of methylamine (Refs. 19 and 23). Note that the unitless energies in this figure must be multiplied by $h_{2v}+h_{3v}$ and that the values of these two parameters for these examples are either both positive or both negative so that the denominators are never zero. Vertical arrows (slightly offset from the true 5MT position) and their associated integers indicate the number of $\nu E_2-\nu E_1$ and $\nu B_1-\nu A_1$ b-type transitions observed in this work.

is much faster than the back-and-forth tunneling motion, then the tunneling splitting looks like an ordinary A-E internal-rotation splitting, with a magnitude of $3|h_{3v}|$, as shown on the left of Fig. 3. A given molecule, e.g., 5MT, can obviously change its position on the horizontal axis if either the OH or the CH_3 group or both are deuterated or if some combination of the OH stretching and bending vibrations and/or the CH_3 torsional vibration is excited. Furthermore, molecules with very different chemical functional groups can be included in Fig. 3 as long as some back-and-forth large-amplitude motion triggers a 60° methyl-group rotation.

VIII. CONCLUSIONS

The main conclusions from the present work can be divided into three categories. From the point of view of spectroscopic analyses, the present high-barrier two-dimensional tunneling formalism has now been used successfully for molecules with a variety of ratios for the back-and-forth versus internal-rotation tunneling splittings since the ratios plotted in Fig. 3 sample more or less uniformly all positions along the abscissa. The 1015 microwave lines of 5MT measured and fit to experimental error in this work have confirmed one more time the ability of the present model to

handle microwave measurements at the 2 kHz level of accuracy. The capability thus exists to produce extensive and accurate lists of microwave and millimeter-wave transitions for molecules of this type should the need arise (e.g., for astrophysical searches).

There is excellent agreement between our experimental values and the quantum chemistry values for all five structural parameters of 5MT, which gives good support for the tunneling-rotational Hamiltonian used for the spectroscopic analysis here. From the point of view of barrier determinations, the situation is less satisfactory. Quantum-chemistry estimates for the pure internal-rotation barrier are almost a factor to two lower than two independent experimental determinations. A definitive experimental determination of the more interesting H-transfer barrier does not seem possible at the present time, so all that is available are the theoretical estimates.

From the point of view of molecular structure and dynamics, this study confirms that the energy levels of 5-methyltropolone and 2-methylmalonaldehyde are indeed quite similar and can be described by the same theoretical formalism. The resulting quantitative description of the stationary state energy levels in these two molecules with a strongly coupled pair of large-amplitude motions, one of which is reciprocal and the other of which is angular, is clearly only a first step to a detailed understanding of the non-stationary-state dynamical processes that can occur in these “molecular machines.”²¹

ACKNOWLEDGMENTS

This program was supported in part by a grant to the College of Charleston from the Howard Hughes Medical Institute through the Undergraduate Science Education Program. R.L. thanks Research Corporation for funding. Y.-C.C. thanks the National Science Council of Taiwan (Grant No. NSC 96-2113-M-133-001-MY2) for support and the National Center for High-performance Computing of Taiwan for computer time and facilities. V.V.I. expresses his appreciation to Dr. Frank J. Lovas for guidance with the FTMW measurements at NIST.

APPENDIX: SUPPLEMENTARY DATA

The supplementary data for this paper contain a copy of input and output files with the final data set and fit. A copy of the fitting program is deposited in Appendix A of Ref. 6.

- ¹N. D. Sanders, *J. Mol. Spectrosc.* **86**, 27 (1981).
- ²J. R. De la Vega, *Acc. Chem. Res.* **15**, 185 (1982).
- ³K. Nishi, H. Sekiya, H. Kawakami, A. Mori, and Y. Nishimura, *J. Chem. Phys.* **111**, 3961 (1999).
- ⁴O. Vendrell, M. Moreno, and J. M. Lluch, *J. Chem. Phys.* **117**, 7525 (2002).
- ⁵Y.-C. Chou and J. T. Hougen, *J. Chem. Phys.* **124**, 074319 (2006).
- ⁶V. V. Ilyushin, E. A. Alekseev, Y.-C. Chou, Y.-C. Hsu, J. T. Hougen, F. J. Lovas, and L. B. Picraux, *J. Mol. Spectrosc.* **251**, 56 (2008).
- ⁷N. Ohashi and J. T. Hougen, *J. Mol. Spectrosc.* **121**, 474 (1987).
- ⁸D. Ménard, M. St-Jacques, and J. F. Bagli, *Can. J. Chem.* **60**, 231 (1982).
- ⁹S. Seto and K. Ogura, *Bull. Chem. Soc. Jpn.* **32**, 493 (1959).
- ¹⁰R. D. Suenram, J. U. Grabow, A. Zuban, and I. Leonov, *Rev. Sci. Instrum.* **70**, 2127 (1999).
- ¹¹N. Ohashi (private communication).

- ¹²C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.* **31**, 841 (1959).
- ¹³V. V. Ilyushin, E. A. Alekseev, S. F. Dyubko, R. A. Motiyenko, and J. T. Hougen, *J. Mol. Spectrosc.* **229**, 170 (2005).
- ¹⁴B. N. Taylor and C. E. Kuyatt, NIST Technical Note No. 1297 (1994). This publication may be downloaded from <http://physics.nist.gov/Pubs/guidelines/contents.html>.
- ¹⁵M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.
- ¹⁶Certain commercial products are identified in this paper in order to specify adequately the experimental or theoretical procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.
- ¹⁷T. Baba, T. Tanaka, I. Morino, K. M. T. Yamada, and K. Tanaka, *J. Chem. Phys.* **110**, 4131 (1999).
- ¹⁸K. Tanaka, H. Honjo, T. Tanaka, H. Kohguchi, Y. Ohshima, and Y. Endo, *J. Chem. Phys.* **110**, 1969 (1999).
- ¹⁹N. Ohashi, K. Takagi, J. T. Hougen, W. B. Olson, and W. J. Lafferty, *J. Mol. Spectrosc.* **126**, 443 (1987).
- ²⁰J. T. Hougen, I. Kleiner, and M. Godefroid, *J. Mol. Spectrosc.* **163**, 559 (1994).
- ²¹H. Ushiyama and K. Takatsuka, *Angew. Chem., Int. Ed.* **44**, 1237 (2005).
- ²²U. Lourderaj and W. L. Hase, *J. Phys. Chem. A* **113**, 2236 (2009).
- ²³N. Ohashi, S. Tsunekawa, K. Takagi, and J. T. Hougen, *J. Mol. Spectrosc.* **137**, 33 (1989).
- ²⁴See supplementary material at <http://dx.doi.org/10.1063/1.3493336> for input/output files from least-squares fit.