High-Resolution Studies of Tropolone in the $S_0$ and $S_1$ Electronic States: Isotope Driven Dynamics in the Zero-Point Energy Levels

John C. Keske
Wei Lin
The University of Texas Rio Grande Valley, wei.lin@utrgv.edu
Wallace C. Pringle
Stewart E. Novick
Thomas A. Blake

See next page for additional authors

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Authors
John C. Keske, Wei Lin, Wallace C. Pringle, Stewart E. Novick, Thomas A. Blake, and David F. Plusquellic

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High-resolution studies of tropolone in the $S_0$ and $S_1$ electronic states: Isotope driven dynamics in the zero-point energy levels

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High-resolution studies of tropolone in the $S_0$ and $S_1$ electronic states: Isotope driven dynamics in the zero-point energy levels

John C. Keske
Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8441

Wei Lin,a) Wallace C. Pringle, and Stewart E. Novick
Wesleyan University, Middletown, Connecticut 06459

Thomas A. Blake
Pacific Northwest National Laboratory, Richland, Washington 99352

David F. Plusquellicb)
Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8441

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Rotationally resolved microwave (MW) and ultraviolet (UV) spectra of jet-cooled tropolone have been obtained in $S_0$ and $S_1$ electronic states using Fourier-transform microwave and UV-laser/molecular-beam spectrometers. In the ground electronic state, the MW spectra of all heavy-atom isotopomers including one $^{18}$O and four $^{13}$C isotopomers were observed in natural abundance. The OD isotopomer was obtained from isotopically enriched samples. The two lowest tunneling states of each isotopomer except $^{18}$O have been assigned. The observed inversion splitting for the OD isotopomer is 1523.227(5) MHz. For the asymmetric $^{13}$C structures, the magnitudes of tunneling-rotation interactions are found to diminish with decreasing distance between the heavy atom and the tunneling proton. In the limit of closest approach, the 0+ state of $^{18}$O was well fitted to an asymmetric rotor Hamiltonian, reflecting significant changes in the tautomerization dynamics. Comparisons of the substituted atom coordinates with theoretical predictions at the MP2/ aug-cc-pVTZ level of theory suggest the localized 0+ and 0− wave functions of the heavier isotopes favor the C–OH and C=O forms of tropolone, respectively. The only exception occurs for the $^{13}$C=O structures which correlate to the 0− and 0+ states, respectively. These preferences reflect kinetic isotope effects as quantitatively verified by the calculated zero-point energy differences between members of the asymmetric atom pairs. From rotationally resolved data of the 0+ ← 0+ and 0− ← 0− bands in $S_1$, line-shape fits have yielded Lorentzian linewidths that differ by 12.2(16) MHz over the 19.88(4) cm$^{-1}$ interval in $S_1$. The fluorescence decay rates together with previously reported quantum yield data give nonradiative decay rates of 7.7(5) × 10^7 and 8.5(5) × 10^8 s$^{-1}$ for the 0+ and 0− levels of the $S_1$ state of tropolone. © 2006 American Institute of Physics.

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I. INTRODUCTION

Tropolone (2-hydroxy-2,4,6-cycloheptatriene-1-one) has served as a prototypical molecule for proton transfer. Facile intramolecular proton transfer occurs between the two carbonyl oxygens during the tautomerization of the seven-member carbon ring. A schematic diagram of the potential-energy surfaces associated with the proton transfer coordinate is shown in Fig. 1. The symmetric double-minimum potentials have sufficiently low barriers that tunneling splittings are resolved in both the $S_0$ ($\chi\chi^1A_1$) and $S_1$ ($\hat{A}^1B_2$) electronic states at modest resolution. The vibrational wave functions of the two lowest-energy tunneling components, designated as the 0+ and 0− states, have $A_1$ and $B_2$ symmetry in the $C_{2v}$ point-group symmetry of the transition state.

Tropolone has been the subject of numerous experimental $^{1-7}$ and theoretical $^{8-12}$ studies in matrix and gas-phase environments. Tanaka et al. have accurately determined tunneling splitting to be 0.973 799 95(87) cm$^{-1}$ from jet-cooled microwave (MW) studies of the ground state.$^2$ Doublets arising from the difference in the tunneling splittings in $S_1$ and $S_0$ were first reported by Alves and Hollas in the vapor-phase absorption spectrum.$^{13,14}$ More recently, high-resolution degenerate four-wave mixing experiments of bulk-gas-phase samples$^{15}$ have been made near the $S_1$←$S_0$ ($\pi^+ ← \pi^-$) electronic origin. Accurate excited-state parameters analogous to those obtained for the ground state have been reported. From these results, the tunneling split-
In $S_1(\Delta_1)$ undergoes a drastic increase to $\Delta_1 > 19 \text{ cm}^{-1}$, illustrating the importance of the $\pi$ electron system on the tautomerization dynamics.

Additional studies have examined the dependence of the tunneling splitting on the vibrational mode excited in both $S_0$ (Refs. 4, 7, 11, and 16) and $S_1$. These investigations have shown that the splitting decreases with increasing vibrational excitation along other vibrational coordinates, highlighting the sensitivity of the tunneling dynamics to nuclear displacements of the frame. For example, it was found that vibrations involving the motion of the oxygen atoms and out-of-plane modes affecting the planarity of the molecule have the largest impact on the proton-tunneling dynamics. The influence of the tropolone-ring substitutions on the tunneling splittings has also been investigated using laser-induced fluorescence (LIF) techniques for several symmetric and asymmetric analogues. Like tropolone, tunneling doublets are observed in the spectra of the symmetric forms. The proton-tunneling dynamics is, however, effectively quenched with asymmetric substitution as a result of the loss of symmetry along the tunneling coordinate.

In this study, we have obtained rotationally resolved spectra of tropolone in the ground and first electronically excited states. In $S_0$, the analysis of the symmetric isotopomers ($^{12}$C, $^{13}$C, and OD forms) has permitted an estimate of the ground-state tunneling barrier. For the other asymmetric heavy-atom isotopomers, we find that the tautomerization dynamics becomes rapidly quenched with increasing proximity of the isotopic label to the tunneling proton, causing, in effect, a preferential selectivity for one of the two resonance structures in each tunneling state. The selectivity is shown to depend on the substituted atom position and reflect kinetic isotope effects that are quantitatively explained in terms of the calculated zero-point energies. In the $S_1$ state, the fluorescence lifetimes have been used to estimate the radiative and nonradiative decay rates of tropolone and their dependence on tunneling state.

### II. EXPERIMENT

Pure rotational spectra of tropolone and its isotopomers were obtained using two different Fourier-transform microwave spectrometers. In the NIST spectrometer, tropolone (95% purity) was resistively heated to 110 °C in a reservoir nozzle and expanded with a He/Ne gas mixture through a 1.2 mm pulsed nozzle operating at 6 Hz. For each scan, 30 free-induction decays were averaged and Fourier transformed at stepped intervals of 0.5 MHz. In the Wesleyan spectrometer, the tropolone or deuterated tropolone sample was placed in a tube directly upstream of the 0.5 mm pulsed nozzle and 1 atm of a He/Ne gas mixture flowed over the unheated sample and into the nozzle. For each scan, 50 shots at 10 Hz were averaged and transformed at intervals of 0.3 MHz.

Fluorescence excitation spectra of the $S_1 \rightarrow S_0$ transitions of tropolone near 370 nm were measured at NIST using a UV-laser/molecular-beam spectrometer described in detail elsewhere. Briefly, an Ar+-pumped cw ring Ti-sapphire laser generated 500 mW of narrow-band light near 740 nm. Approximately 5 mW of the UV light at 370 nm were generated in an external resonant cavity containing a lithium borate crystal. Tropolone was heated to 120 °C in a three-chamber quartz source. The vapor was mixed with 29 kPa (220 Torr) of Ar and expanded into a source chamber through a 125 μm nozzle. The molecular beam was skimmed and crossed at right angles with a slightly focused UV beam 18 cm downstream of the source. Laser-induced fluorescence at the beam crossing was collected with 20% efficiency using two spherical mirrors and detected using a photomultiplier and computer-interfaced photon counter. The Doppler-limited resolution of the spectrometer at 330 nm was 18 MHz. Relative frequency calibration was performed using a HeNe-stabilized reference cavity, and absolute frequencies were obtained using a wavemeter accurate to ±0.02 cm$^{-1}$.

### III. RESULTS

#### A. The $0^+$ and $0^-$ ground states of the $^{13}$C isotopomers of tropolone

The schematic diagram of the proton-tunneling surfaces of tropolone along the symmetric double-minimum poten-
tute and therefore nine additional states are expected. This number would be expected to double if, like the parent, both tunneling states are observed. However, from Fig. 1, the structural features that distinguish, for example, $^{13}$C$_1$ and $^{13}$C$_3$ in structure I are interconverted in structure II. Therefore, the $^{13}$C$_1$ and $^{13}$C$_3$ isotopomers will correlate to the two lowest-energy tunneling states, 0$^+$ and 0$^-$, or vice versa, where the state labels are retained for clarity (and the implied parity of the symmetric forms is no longer valid). The same holds true for the other three asymmetric pairs: $^{13}$C$_2$, $^{13}$C$_4$, and $^{18}$O$_8$. From these considerations, ten states are expected, eight for the asymmetric atoms, and two more for the symmetry position, $^{13}$C$_5$. From our data, only nine states were observed including the four pairs of $^{13}$C$_1$ states plus the 0$^+$ level of $^{18}$O obtained under colder expansion conditions. Both tunneling states of the OD isotopomer were also obtained from enriched samples. The 11 parameter sets obtained from the fits using SPFIT are given in Tables II–IV. Simulated spectra of the four $^{13}$C isotopomers are shown below the experimental trace in Fig. 2.

Correlations between the specific locations of the heavy-atom isotopes in the structure of tropolone and the parameter sets are easily drawn from simple comparisons of the rotational constants with those of the parent isotopomer, ignoring for the moment small changes in the principal-axis orientation with $^{13}$C or $^{18}$O substitution. No attempt is made at this time to distinguish between the two subscript labels. For example, the A constants of the $^{13}$C$_1$ data in Table I are nearly identical with those of $^{13}$C data in Table II indicating that the isotope is on or near the $a$ axis as is the case only for the $C_5$ position. Likewise, the $^{13}$C$_2(7)$ position is near the $b$ axis, identifying it with the second data set in Table III. The three remaining identifications are made based on the differences in the $B$ rotational constants as follows. Although of similar distance from the $b$ axis, the O$_8$ atom is heavier than C$_4$ associating the former with the second data set in Table IV. The remaining correlations are easily made from similar arguments that distinguish between the C$_{1(2)}$ and C$_4$ positions.
The tunneling-rotation interaction terms were well fitted to a standard asymmetric rotor Hamiltonian, including hyperfine splittings. Except for the $^{18}\text{O}_8$ isotopomer, the locations of several $0^− \leftrightarrow 0^+$ transitions were predicted and assigned following initial fits of the pure rotational transitions of the $0^+$ and $0^−$ states. The assignment of these nominally forbidden transitions substantially improved the fit quality of the tunneling parameters. However, even in their absence, accurate determinations of the tunneling parameters for the $^{13}\text{C}_3(7)$ and $^{13}\text{C}_4(6)$ isotopomers have been possible as evident from the following example.

The dependence of the tunneling parameters on the observed rotational energy levels is readily apparent for a two-
TABLE IV. $S_0$ rotational constants of the asymmetric $^{13}$C and $^{18}$O isotopomers of tropolone obtained from fits of the FTMW spectra.

<table>
<thead>
<tr>
<th></th>
<th>$^{13}$C$_{2\bar{1}}$(i)</th>
<th>$^{18}$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0$^+$</td>
<td>0$^-$</td>
</tr>
<tr>
<td>$A$ (MHz)</td>
<td>2 734.751 ± 9 (34)</td>
<td>2 735.591 ± 8 (66)</td>
</tr>
<tr>
<td>$B$ (MHz)</td>
<td>1 656.269 ± 12 (73)</td>
<td>1 656.447 ± 4 (18)</td>
</tr>
<tr>
<td>$C$ (MHz)</td>
<td>1 031.825 ± 35 (34)</td>
<td>1 032.026 ± 1 (37)</td>
</tr>
<tr>
<td>$\Delta u (\AA)$</td>
<td>−0.138 ± 63</td>
<td>−0.144 ± 29</td>
</tr>
<tr>
<td>$\Delta_1$ (kHz)</td>
<td>0.991 ± 3 (85)</td>
<td>0.141 ± 59</td>
</tr>
<tr>
<td>$\Delta_{Mr}$ (kHz)</td>
<td>2.996 ± (30)</td>
<td>−4.140 ± (41)</td>
</tr>
<tr>
<td>$\delta_1$ (kHz)</td>
<td>0.157 ± (45)</td>
<td>0.76 ± (72)</td>
</tr>
<tr>
<td>$\delta_2$ (kHz)</td>
<td>0.036 ± 6 (46)</td>
<td>0.026 ± (13)</td>
</tr>
<tr>
<td>$\Delta_0$ (MHz)</td>
<td>2.139 ± (42)</td>
<td>−0.714 ± (95)</td>
</tr>
<tr>
<td>$F_{ab}$ (MHz)</td>
<td>±1.226 ± (37)</td>
<td>±1.226 ± (37)</td>
</tr>
<tr>
<td>$\Delta_0$ (MHz)</td>
<td>26.819 ± (91)</td>
<td>26.819 ± (91)</td>
</tr>
<tr>
<td>Assigned</td>
<td>27</td>
<td>13</td>
</tr>
<tr>
<td>0$^+$ ← 0$^-$ assigned</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\sigma$ (kHz)</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>$\sigma$ (kHz$^2$)</td>
<td>11.2$^a$</td>
<td>11.2$^a$</td>
</tr>
</tbody>
</table>

$^a$Additional terms used $C_{2\bar{1}}$/$0^+$ $H_{J_{1}}$=0.70 (57) Hz and $0^+$/0$^+$ $H_{J_{2}}$ = 18.3 (70) Hz.

|                  | 0$^+$                   | 0$^-$       | 0$^+$       |
|------------------|-------------------------|-------------|
|                  | 0$^+$                   | 0$^-$       | 0$^+$       |
| $\sigma$ (kHz) | 2.5                     | 2.5          | 2.2           |
| $\sigma$ (kHz$^2$) | 11.2$^a$              | 11.2$^a$     | ...           |

$^b$Uncertainties are type A, $k=1$, or $1\sigma$ (Ref. 29).

$^c$Experimental uncertainty of all assigned lines is 4 kHz.

$^d$Observed minus calculated standard deviation of fits that exclude $F_{ab}$ and $\Delta_0$.

$^e$Same $\sigma$ is obtained when 0$^+$ and 0$^-$ states are reversed in the fits that include $F_{ab}$ and $\Delta_0$.

level system. For $J=1$, the operator $F_{ab}(P_aP_a+P_bP_b)$ couples the two asymmetric rotor wave functions [111] and [101] ($JK_aK_bK_c$) of the 0$^+$ and 0$^-$ tunneling states. The Hamiltonian matrix of one of these pairs has the standard form

$$\hat{H} = \begin{bmatrix} E^{(+)}_{[111]} & F_{ab} \\ F_{ab} & E^{(-)}_{[111]} + \Delta_0 \end{bmatrix}. \quad (1)$$

Analytical solution of the corresponding secular equation of Eq. (1) yields the following eigenvalues:

$$E^{(\pm)} = E^{(+)}_{[111]} \pm \sqrt{(E^{(-)}_{[111]} + \Delta_0 - E^{(+)}_{[111]})^2 + 4F_{ab}^2}. \quad (2)$$

In the absence of tunneling-rotation interactions (i.e., $F_{ab}=0$), the eigenvalues are simply those of the asymmetric rotor with the 0$^+$ state offset by the vibrational energy difference. However, depending on the measurement precision and their relative magnitudes, $F_{ab}$ and $\Delta_0$ may be reliably obtained from the pure rotational transitions alone. For example, the asymmetric rotor levels in the $S_0$ state of tropolone are shifted by −9 and +8 kHz for the [(0,101) and (1,111) ($JK_aK_bK_c$)] levels, respectively. Of course, when the much weaker level-crossing transitions are observed, the value of $\Delta_0$ is determined directly and significantly decreases the correlation of these two parameters. To illustrate the impact of these terms, the observed-minus-calculated (OmC) standard deviations from fits without them are given in the lower parts of the Tables I–IV. The overall fit quality decreases by roughly an order of magnitude or more even for the two cases where the level-crossing transitions were not observed.

As a final note, the sign of the parameter $F_{ab}$ does not affect the rotational energies and consequently, is not determined from the frequency fits. However, the operator $P_aP_a+P_bP_b$ is the same as that used to model rotational transition intensity perturbations arising from inertial axis reorientation effects. While this operator is a necessary condition for observing quantum interference effects, it is not sufficient for tropolone because of the additional requirement of hybrid band character. For the effective $C_{2v}$ structure of tropolone on the time scale of a rotational period, the dipole moments lie along the $a$ inertial axes, and consequently, the transition intensities will be insensitive to the sign of $F_{ab}$. The $b$-axis components present in the asymmetric structures are too small to make appreciable intensity differences in the MW spectra. These same arguments apply to the electronically excited states of tropolone discussed in the next section.

B. $S_1$ state of tropolone

The two lowest-energy features in the $S_1$ spectrum of tropolone have been assigned by Alves and Hollas to the 0$^+\rightarrow 0^-$ and 0$^+\rightarrow 0^-$ transitions at 27 017.54 and 27 036.47 cm$^{-1}$, respectively.13,14 The rotationally resolved UV spectra of these bands are shown in Fig. 3. Each spectrum spans more than a 7 cm$^{-1}$ spectral region at a rotational temperature of $\approx$9 K. As apparent from the absence of $a$-type $Q$-branch transitions near the electronic origins, the rotational spectra of 0$^+\rightarrow 0^-$ and 0$^+\rightarrow 0^-$ bands are 100% $S_1$ type in character. The band polarizations are consistent with the $C_{2v}$ symmetry of the transition state and the $B_2$ electronic symmetry of the $S_1$ state. A number of $a$-type transitions are also observed for the much weaker 0$^+\rightarrow 0^-$ and 0$^+\rightarrow 0^+$ vibronic bands. These transitions are shifted to the red and blue of the 0$^+\rightarrow 0^-$ and 0$^+\rightarrow 0^-$ bands, respectively, as a result of the much smaller $\approx$1 cm$^{-1}$ ground-state splitting and therefore, are nested within these main bands. Nominally forbidden because of parity selection rules, the appearance of the $a$-type transitions is a result of the mixed nature of the rovibrational wave functions from tunneling-rotation interactions between the 0$^+$ and 0$^-$ levels of both electronic states. Rovibronic transitions of this latter kind are $a$ type in character because of the $B_3$ symmetry of the 0$^-$ levels. The relative contributions of the 0$^+\rightarrow 0^-$ and 0$^+\rightarrow 0^+$ bands are shown in Fig. 4.

The assigned line sets of the 0$^+\rightarrow 0^-$ and 0$^+\rightarrow 0^+$ bands were simultaneously fitted using the SPFIT program.28 To aid in the assignment and fitting of these spectra, the predicted line sets generated by SPFIT were overlayed with the experimental data using the JB95 program.32 The assigned line sets included 129 and 102 transitions from the 0$^+\rightarrow 0^+$ and 0$^+\rightarrow 0^+$ bands, respectively. The assigned frequencies were then used to refine the relative frequency calibration of the UV spectra by means of a lower-state combination difference analysis.25 All fits discussed below include the pure rotational transitions of the $S_0$ state weighted in
The quartic distortion parameters were not reliably fitted for either state. The OmC standard deviation of the overall fit was 5.5 MHz which is <1/20 of the observed linewidths. Fits that included the tunneling-rotation term gave \( F(S_i) = -6.9(9) \) MHz and reduced the standard deviation only marginally to 5.4 MHz. The analysis was repeated using the ten distortion constants and \( F(S_i) = -4.28(24) \) MHz previously reported for the \( S_1 \) state.\(^{15} \) The OmC standard deviation increased slightly to 6.8 MHz. Upon including all of the \( S_1 \) parameters in Ref. 15, the OmC standard deviation rose to 65 MHz. Except for the latter case, the changes in the overall fit quality are not statistically meaningful for our data sets. Therefore, the parameters reported in Table V are based on the initial fits that exclude \( F(S_i) \) and the distortion constants. We also note that changes in the rotational constants for fixed values of \( |F(S_i)| < 10 \) MHz are less than the reported uncertainties in the constants.

Additional fits of the LIF intensities were performed using genetic algorithms\(^{33} \) (GA) and nonlinear least-squares-fitting routines based on the Levenberg-Marquardt

![FIG. 3. Rotationally resolved UV spectra of the 0+−0+ (0−−0+) and 0−−0− (0−−0+) transitions at \( \lambda = 370.128 \) and 369.869 nm, respectively. Both bands span more than 5 cm\(^{-1} \) at rotational temperatures of \( -10 \) K. Residuals are shown to illustrate the quality of the frequency and intensity fits.](image)

![FIG. 4. Expanded region near the electronic origin illustrating contributions from the 0+−0+ and 0+−0− vibrational transitions.](image)

<table>
<thead>
<tr>
<th>Origin (cm(^{-1} ))</th>
<th>Band type</th>
<th>( \Delta V \text{(u \AA)} )</th>
<th>( T_1 : T_2 : \text{wt(K)} )</th>
<th>Assigned(^e )</th>
<th>( \sigma ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27 017.67(2)</td>
<td>100% ( b ) type</td>
<td>0.70669</td>
<td>9.0(1):33(1):0.08(1)</td>
<td>129</td>
<td>5.1</td>
</tr>
<tr>
<td>27 036.58(2)</td>
<td>100% ( b ) type</td>
<td>-0.94203</td>
<td>9.5(1):46(1):0.07(1)</td>
<td>102</td>
<td>5.1</td>
</tr>
</tbody>
</table>

\(^a\)Uncertainties are type A, \( k = 1 \), or 1\( \sigma \) (Ref. 29).

\(^b\)Two-temperature model from Ref. 35: \( \exp(-\Delta E/kT_1) + \text{wt}\exp(-\Delta E/kT_2) \).

\(^c\)Experimental uncertainty of all assigned lines is 5 MHz.
TABLE VI. Observed changes in the $S_0$ rotational constants, $\Delta A=A^+−A^−$, etc., of the two tunneling states of each isotopomer and the tunneling parameters relative to the parent isotopomer. All values are in MHz except where noted.

<table>
<thead>
<tr>
<th>$0^−/0^+$</th>
<th>$^{12}\text{C}$</th>
<th>OD</th>
<th>$^{11}\text{C}_3$</th>
<th>$^{12}\text{C}_3$</th>
<th>$^{12}\text{C}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta A$</td>
<td>−0.373 90</td>
<td>−0.010(3)</td>
<td>−0.373 2</td>
<td>−0.176 6</td>
<td>−0.7415</td>
</tr>
<tr>
<td>$\Delta R$</td>
<td>−0.026 750</td>
<td>−0.0019(5)</td>
<td>−0.027 02</td>
<td>−0.081 81</td>
<td>−0.1937</td>
</tr>
<tr>
<td>$\Delta C$</td>
<td>−0.059 435</td>
<td>−0.0050(3)</td>
<td>−0.058 20</td>
<td>−0.052 39</td>
<td>−0.1689</td>
</tr>
<tr>
<td>$\Delta \Delta F^a$</td>
<td>−1.42</td>
<td>+1.392(2)</td>
<td>−2.11</td>
<td>−2.15</td>
<td>−6.66</td>
</tr>
</tbody>
</table>

$^a$Inertial defect in units of $\mu$ Å$^2$ MHz.$^1$
quenching, the data sets in Tables III and IV are arranged in order of decreasing distance of the substituted atom to the tunneling proton. The changes in the rotational constants and tunneling parameters relative to those of the parent isotopomer are summarized in Table VI.

The $^{13}$C$_{4(6)}$ isotopomer appears to retain much of the character of the symmetric structures. However, the tunneling splitting increases from that of the $^{12}$C parent by >0.5%, offsetting the expected decrease from the kinetic isotope effect on symmetric forms. The perturbations of the remaining three isotopomers become increasingly more severe for positions approaching the tunneling proton. The tunneling splitting increases by 15% and then decreases by 8% for the $^{13}$C$_{3(7)}$ and $^{13}$C$_{2(1)}$ isotopomers, respectively. The magnitude of $F_{ab}$ decreases by 15% for the $^{13}$C$_{3(7)}$ and then by more than ten fold for $^{13}$C$_{2(1)}$. The Coriolis interactions are completely absent for the $^{18}$O isotopomer suggesting that the tunneling is completely quenched and that the $0^+$ and $0^-$ wave functions are highly localized. Finally, notice that in sharp contrast to the other isotopomers (including the parent), the three rotational constants of $^{13}$C$_{2(1)}$ increase in the $0^-$ state.

The anomalous changes in the rotational constants and tunneling splitting for the $^{13}$C$_{2(1)}$ isotopomer are two of the more intriguing aspects of tropolone’s tunneling dynamics. One explanation might be that the state labels were reversed in the fit. This, however, proved not to be the case. The Omc standard deviation from such fits increased to 11 kHz, a result identical to fits that excluded $F_{ab}$ and $\Delta_0$. A second explanation might involve a reversal of the localized probability amplitudes of the $0^+$ and $0^-$ wave functions relative to those of the other asymmetrically substituted atoms.

In order to explore this second possibility further, the in-plane center-of-mass (COM) coordinates of the substituted atoms were determined using Kraitchman’s equations$^{38}$ and are given for each state and each isotopomer in

![FIG. 5. The two curves represent the locus of $V_0$/$\mu$ pairs that give the experimental values of the inversion splittings for H- and D-tropolone. The model on which these curves are based is given in the text. However, the various points on the curves give varying values for the Coriolis coupling constants $F_{ab}$. The vertical lines represent the points on the curves where the experimental values of $F_{ab}$ are predicted. Those two points, one for each curve, are the values of $V_0$ and $\mu$ which correctly predict the experimental values of the inversion splittings and the Coriolis coupling constants for the two isotopomers. Ideally, the two predicted values for $V_0$ should be identical for both H- and D-tropolone. The difference of 405 cm$^{-1}$ between the two values of $V_0$ is an indication of the limitations of the simple one-dimensional linear inversion model.](image)

**Table VII.** Experimentally derived in-plane substitution coordinates of the heavy atoms in tropolone. Planar structures are assumed. Theoretical values were obtained at the MP2/aug-cc-pVTZ level of theory for resonance structure I of Fig. 1.

<table>
<thead>
<tr>
<th></th>
<th>Experimental*</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$0^+$</td>
<td>$0^-$</td>
</tr>
<tr>
<td>$C_3$</td>
<td>$a$ (Å)</td>
<td>−2.3059(6)</td>
</tr>
<tr>
<td></td>
<td>$b$ (Å)</td>
<td>0$^a$</td>
</tr>
<tr>
<td>$C_{4(6)}$</td>
<td>$a$ (Å)</td>
<td>−1.6908(9)</td>
</tr>
<tr>
<td></td>
<td>$b$ (Å)</td>
<td>−1.2601(1)</td>
</tr>
<tr>
<td>$C_{3(7)}$</td>
<td>$a$ (Å)</td>
<td>−0.311(5)</td>
</tr>
<tr>
<td></td>
<td>$b$ (Å)</td>
<td>−1.575(1)</td>
</tr>
<tr>
<td>$C_{2(1)}$</td>
<td>$a$ (Å)</td>
<td>+0.806(2)</td>
</tr>
<tr>
<td></td>
<td>$b$ (Å)</td>
<td>+0.753(2)</td>
</tr>
<tr>
<td>$O_{8(9)}$</td>
<td>$a$ (Å)</td>
<td>+2.0032(7)</td>
</tr>
<tr>
<td></td>
<td>$b$ (Å)</td>
<td>+1.227(1)</td>
</tr>
</tbody>
</table>

*Signs assigned to the experimentally derived coordinates are included to clarify associations made in the text. Uncertainties are type B and $k=1$ (Ref. 29) based on Costain’s criteria from Ref. 39.

*Small imaginary coordinate obtained.
Table VII. These are compared with the atomic coordinates predicted for structure I in Fig. 1 at the MP2/aug-cc-pVTZ level of theory. Notice first that these coordinates unambiguously confirm the semiquantitative arguments given above to identify each isotopomer. The predicted coordinates of $^{13}$C$_4$ and C$_4$ are in excellent agreement with experiment. For the C$_4$ structure, the experimental b coordinates differ, however, by 0.011 Å versus the difference of 0.016 Å found theoretically. This would suggest that $^{13}$C$_4$ substitution causes the $^0\tilde{g}$ wave function to become somewhat localized on the negative b axis or C–OH side of the ring and the $^0\tilde{g}$ wave function on the C=O side. A comparison of the C$_3$ coordinates reveals a similar association with tunneling state.

This trend changes abruptly for the C$_2$ coordinates. The coordinate differences in a and b are somewhat larger; 0.026 and 0.057 Å versus predicted values of 0.052 and 0.049 Å, respectively. More importantly, their absolute magnitudes suggest that the probability amplitudes of the $^0\tilde{g}$ and $^0\tilde{g}$ states are reversed, i.e., the $^{13}$C$_1$ atom on the C=O side is more favored in the lower-energy $^0\tilde{g}$ state and $^{13}$C$_2$ on the C–OH side is the preferred structure in the $^0\tilde{g}$ state.

C. Isotope driven dynamics in the zero-point energy levels of $S_0$

Within the Born–Oppenheimer approximation, the structures favored by the partially or completely localized wave functions of each asymmetric pair are determined by the relative magnitudes of their zero-point energies (ZPEs). The ZPE of each isotopomer includes contributions from 39 vibrational degrees of freedom. The heavier isotopomers will have larger reduced masses and therefore, diminished ZPE contributions along one or more of these normal-mode coordinates.

Insight into the magnitude of the asymmetry and its impact on the tunneling dynamics may be obtained from a simple two-state model. Since the ZPE difference for each $^{13}$C pair introduces, in effect, an asymmetry to the tunneling potential, the perturbations may be treated by adding a term to the diagonal elements of the symmetric two-state Hamiltonian matrix [very similar in form to that given in Eq. (1)]. As shown previously, the eigenvalues are related to the experimental tunneling splitting $\Delta_A$ using

$$\Delta_{A}^2 = \Delta_{S}^2 + \Delta_{ZPE}^2,$$

where $\Delta_{S}$ is the splitting observed for the symmetric form and $\Delta_{ZPE}$ is the ZPE difference of a given asymmetric pair. Furthermore, the probability of tunneling into the higher energy well is obtained from $P_{rel}=\left[1+\Delta_{ZPE}/\Delta_{S}\right]^{-1}$. The results given in the fourth column of Table VIII illustrate that the $\Delta_{ZPE}$ accounts for only 1/5 of the observed splitting for the $^{13}$C$_4$ pair, and therefore, the probability density of the wave function in each well is nearly equal with $P_{rel}=98\%$. For the $^{13}$C$_3$ pair, $\Delta_{ZPE}$ is more important, accounting for roughly half of the observed splitting and leading to increased wave-function asymmetry where now $P_{rel}=74\%$. However, the two-state model fails for C$_2$ asymmetric pair since the $\Delta_{ZPE}$ can never be less than $\Delta_{S}$. The off-diagonal terms in the Hamiltonian matrix that describe the tunneling interaction are assumed to remain unaltered in this model. The greater than 10 fold reduction in $F_{ab}$ observed for the $^{13}$C$_2$ isotopomer versus the other $^{13}$C isotopomers (see Tables II–IV) indicates that this assumption is not valid and that the magnitudes of the off-diagonal terms must also decrease. In the event of an equivalent 13-fold reduction in the off-diagonal term $\Delta_{S}/2$, $\Delta_{ZPE}$ would account for 99% of the observed splitting.

Estimates of the $\Delta_{ZPE}$ may also be obtained from ab initio theory. The calculated decreases in the zero-point energies relative to the parent are given in Table VIII for the nine heavy isotopomers of reference structure I. These are the harmonic values obtained at the MP2/6-311++G(d,p) level using tight convergence criteria. All values are negative for the heavier isotopes (as expected from the product rule) and range between −37 and −53 cm$^{-1}$. Of particular interest are the changes within each asymmetric pair given in the third column. The negative $\Delta_{ZPE}$'s of the asymmetric
pairs $^{13}$C$_4$/^{13}$C$_6$, $^{13}$C$_3$/^{13}$C$_7$, and $^{18}$O$_8$/^{18}$O$_9$ indicate that the lower-energy 0$^+$ wave function is preferentially localized on the C–OH side of the ring and the 0$^-$ wave function on the C–O side. In contrast, this association is reversed for the $^{13}$C$_4$/^{13}$C$_7$ pair, indicating also a side reversal of the probability densities of the wave functions. These conclusions are entirely consistent with those based on the substituted atom coordinates. Although the $\Delta$ZPE's are small (<0.01% of the total ZPE), it is clear that subtle perturbations within the frame of tropolone can have a remarkable impact on the average location of the proton in the two tunneling states of tropolone.

### D. Nonradiative decay dynamics of tropolone in the S$_1$ state

Many of the photophysical properties of the S$_1$ state of tropolone have been previously interpreted from vibronically resolved measurements performed in jet-cooled expansions$^{17,19,44,45}$ and from high-resolution four-wave mixing data obtained at room temperature.$^{15}$ The important S$_1$ property uncovered in the rotationally resolved studies is directly relevant to the nonradiative decay dynamics of the S$_1$ state. We find all of the rotational lines in both tunneling states to be smooth Lorentzian shapes (after deconvolution of the small 18 MHz Gaussian component arising from residual Doppler broadening). Furthermore, the Lorentzian widths are different for the two states but constant across each band and therefore, lack any J or $K_a$ dependence for J=0–22 and $K_a$=0–22 sampled at $\approx$9 K. The fluorescence decay rates $k_F$ that correspond to the observed widths of 131.1(8) and 143.3(8) MHz for the 0$^+$ and 0$^-$ states are 8.23(1)$\times$10$^8$ and 9.00(1)$\times$10$^8$ s$^{-1}$, respectively. The rate increase of 0.77(2)$\times$10$^8$ s$^{-1}$ over the $\approx$20 cm$^{-1}$ energy interval is slightly larger than that previously obtained from fluorescence lifetime measurements.$^{44}$

The relative changes in a related quantity $\varphi_F$, the fluorescence quantum yield, have been measured by Hagemeister et al.$^{45}$ for the 0$^+$ and 0$^-$ states and other vibronic levels in S$_1$ up to $\Delta E$=+650 cm$^{-1}$ above the origin using cavity ring down methods. The quantum yield $\varphi_F$ is $k_F/(k_F+k_{nr})$ is defined as the ratio of radiative decay rate $k_F$ to the fluorescence decay rate $k_F$, which includes contributions from both $k_F$ and the nonradiative rate(s) $k_{nr}$. The relative quantum yield reported for the 0$^+$ and 0$^-$ levels is $\varphi(0^+)/\varphi(0^-)=0.89(6)$ which together with the $k_F$ values measured here determine the ratio $k_F(0^+)/k_F(0^-)=0.97(6)$.

The absolute quantum yield has not been measured for gas-phase tropolone and therefore, $k_{nr}$ is not known. However, the results from two other studies of the tropolone-water complex (TW) permit rigorous limits to be set on $k_{nr}$ (and $k_F$) in tropolone. The quantum yield of TW obtained from the cavity ring down measurements$^{45}$ is reported to undergo eight-fold increase relative to the tropolone origin, i.e., $\varphi(TW)/\varphi(0^+)=8.1$. Rotationally resolved measurements of the S$_1$ origin of TW have also been performed and will be reported elsewhere. From the line-shape fits of TW, the Lorentzian width obtained is 68(1) MHz, yielding a fluorescence decay rate $k_F(TW)$ of 4.27(6)$\times$10$^8$ s$^{-1}$. Substituting the known quantities into the quantum yield ratio

$$\varphi(TW) = \frac{k_F(TW)}{k_F(0^+)}$$

reveals that the eight-fold larger quantum yield for TW is principally a result of the radiative rate increase where $k_F(TW)/k_F(0^+)=4.1(6)$, with the remainder of the increase appearing in $k_F(0^-)/k_F(TW)=1.93(3)$. Under these constraints, decay rates relevant to tropolone may be obtained upon expanding and rearranging the ratio $k_F(0^+)/k_F(TW)$ to give

$$k_{nr}(TW) = \frac{8.23(1)\times10^8 s^{-1}}{1.93(3)} - 4.1(6)k_F(TW).$$

While this expression does not uniquely determine $k_F(0^+)$ [and therefore, $k_{nr}(0^+)$], it provides for a rather restrictive range on the possible values. The few important limiting cases are tabulated in Table IX. For example, in the extreme case where $k_{nr}(TW)$=0, then the maximum value that $k_F(0^+)$ may assume from Eq. (7) is 1.0(2)$\times$10$^8$ s$^{-1}$ and therefore, $k_{nr}(0^+)=7.2(2)\times$10$^8$ s$^{-1}$. In the other unrealistic limits where $k_F(0^+)=0$ s$^{-1}$, $k_F(0^-)=8.23(1)\times10^8$ s$^{-1}$. The values for the 0$^-$ state follow immediately from similar expressions for $k_F(0^-)/k_F(0^+)$ and are also listed. Clearly, from Table IX, conservative estimates for $k_{nr}(0^+)$ and $k_{nr}(0^-)$ are 7.7(5)$\times$10$^8$ and 8.5(5)$\times$10$^8$ s$^{-1}$, respectively, with a further restriction that $k_{nr}(0^+)/k_{nr}(0^-)=1.10(1)$. (Here, the ranges are specified as an error since values approaching the limits become increasingly unlikely.) Finally, we note that the radiative rate of 0.5$\times$10$^8$ s$^{-1}$ found for tropolone in cyclohexane is near the center of this range.$^{44,46}$ The excited-state properties that impact the nonradiative decay behavior of tropolone will be addressed in a forthcoming article on tropolone-H$_2$O.

### TABLE IX. Range of values that are possible for the radiative decay rates $k_r$, nonradiative rates $k_{nr}$, and quantum yields $\varphi$ based on the measured lifetimes and relative fluorescence quantum yields (Ref. 45 of tropolone and tropolone-H$_2$O and Eq. (7)).

<table>
<thead>
<tr>
<th>$k_r(0^+)$</th>
<th>$k_r(0^-)$</th>
<th>$\varphi(0^+)$</th>
<th>$k_r(0^+)/k_{nr}(0^+)$</th>
<th>$\varphi(0^-)$</th>
<th>$k_r(0^-)/k_{nr}(0^-)$</th>
<th>$k_{nr}$</th>
<th>$k_r$</th>
<th>$\varphi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>8.23</td>
<td>0.00</td>
<td>0.00</td>
<td>9.00</td>
<td>0.00</td>
<td>1.10</td>
<td>0.00</td>
<td>4.26</td>
</tr>
<tr>
<td>0.50$^a$</td>
<td>7.73</td>
<td>0.06</td>
<td>0.49</td>
<td>8.51</td>
<td>0.05</td>
<td>1.10</td>
<td>2.05</td>
<td>2.22</td>
</tr>
<tr>
<td>1.04</td>
<td>7.19</td>
<td>0.12</td>
<td>1.00</td>
<td>8.00</td>
<td>0.11</td>
<td>1.11</td>
<td>4.26</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$^a$Radiative rate estimated for tropolone in cyclohexane.

$^b$Establishes upper bounds on $k_r(0^+)$ and $k_r(0^-)$. 

The ranges are specified as an error since values approaching the limits become increasingly unlikely.
V. SUMMARY AND CONCLUSIONS

High-resolution spectroscopic studies of jet-cooled tropolone and its isotopomers have permitted a detailed examination of the proton transfer dynamics in the zero-point states of the ground and first electronically excited singlet states. In $S_0$, rovibrational spectra have been obtained for three symmetric and four asymmetric forms of tropolone. In $S_1$, the rotationally resolved spectra of the $0^+$ and $0^-$ states have been obtained.

In the ground electronic state, a linear inversion model predicts inversion barriers for the three symmetric isotopomers $^{12}$C, OD, and $^{13}$C$_5$, ranging between 1883 cm$^{-1}$ for the parent isotopomer to 2288 cm$^{-1}$ for tropolone-OD. Since the tunneling dynamics in tropolone involves the cooperative motion of all atoms, the isotope dependence of the barrier height, like the observed vibrational-mode-specific tunneling splittings in the $S_0$ and $S_1$ states, suggests the need to treat the tautomerization coordinate as a multidimensional surface that includes other vibrational degrees of freedom.$^{11,12}$

Such mode-specific effects are also manifested in the observed changes in the coupling matrix elements and splittings of the asymmetric $^{12}$C and $^{18}$O forms, illustrating the extreme sensitivity of the dynamics to even the zero-point energies. The kinetic isotope effect impacts the zero-point energies. The kinetic isotope effect impacts the zero-point energies. The kinetic isotope effect impacts the zero-point energies.

From rotationally resolved studies in $S_1$, the lifetime-limited linewidths have been used to place restrictive ranges on the radiative and nonradiative decay rates of tropolone when combined with previous quantum yield data on tropolone-OD.$^{15}$ The rotational parameters, smooth line shapes, decay rates, and ratio determined for the two inversion levels reveal intrinsic properties needed to arrive at a better understanding of the $S_1$ photophysics and tropolone's complexes.

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