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A study of nonrigid aromatic molecules by supersonic molecular jet spectroscopy. II. Propyltoluenes

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Dispersed emission (DE) and time of flight mass spectra (TOFMS) are presented for supersonic molecular jet-cooled *o*-, *m*-, and *p*-*n*-propyltoluene. The spectra exhibit multiple origins which are assigned to *anti* and *gauche* conformations of the propyl group relative to the aromatic ring. The TOFMS of *m*-*n*-propyltoluene rules out an eclipsed propyl conformation as a populated conformation. Empirical force field (EFF) calculations are presented which support these assignments. The spectra also exhibit features, typically within 100 cm^{-1} of the origin, which are assigned to transitions associated with the internal rotation of the ring methyl group. A model which treats this methyl motion as a one-dimensional rigid rotor is used to solve for the rotational constant B of the methyl rotor, and for the size and shape of the barrier to rotation. The barrier for *p*-*n*-propyltoluene is found to be small in both the ground ($S_0 - V_6 = 5\text{ cm}^{-1}$) and excited ($S_1 - V_6 = 20\text{ cm}^{-1}$) electronic states. For *m*-*n*-propyltoluene, the ground state is again found to have a low barrier ($V_6 = 23\text{ cm}^{-1}$), but the excited state has a potential barrier of $V_3 = 75\text{ cm}^{-1}$. The barrier for *o*-*n*-propyltoluene in the ground state is observed to be higher ($V_3 = 64\text{ cm}^{-1}$) than for the other two isomers. The first excited electronic state of this latter compound displays a multitude of levels in the TOFMS which are explained by a double-rotor model involving the ring methyl group ($V_3 = 72\text{ cm}^{-1}$, $V_6 = -14\text{ cm}^{-1}$) and terminal methyl group of the propyl chain ($V_3 = 106\text{ cm}^{-1}$, $V_6 = -13\text{ cm}^{-1}$). The results are indicative of an interaction between the ring methyl group and the propyl chain. In all three *n*-propyltoluene isomers, more than one origin peak is present in the TOFMS, indicating the presence of multiple stable propyl conformations for each isomer. The propyltoluenes thus demonstrate two types of nonrigid molecular behavior: internal rotational motion associated with the ring methyl group, and potentially three stable conformations of the propyl chain with respect to the aromatic ring.

I. INTRODUCTION

A thorough understanding of the conformational analysis of organic molecules is essential for the evaluation and prediction of physical and chemical properties of these molecules.¹ Important issues which must be addressed for specific compounds include the determination of the number of accessible stable ground state conformations, the nature of the potential energy barriers/surfaces which connect the various conformations, and the determination of the important torsional vibrations which are characteristic of these conformations.² Nuclear magnetic resonance, microwave, and infrared spectroscopy have made conspicuous experimental contributions to this area. More recently, a wide range of theoretical and calculational methodologies have been exploited to describe the ground state structures of organic molecules.³ Conformational analysis and structures in the excited states of molecules are not nearly as well investigated or understood.

The ground (S_0) and excited (S_1) state potentials for the internal rotation of an aromatic ring methyl group, such as the one in toluene, can be characterized by laser supersonic molecular jet spectroscopy.⁴⁻⁷ The fluorescence excita-

tion (FE) or time of flight mass spectrum (TOFMS) of aromatic molecules containing a methyl substituent often show weak features within the first 100 cm^{-1} to the blue of the 0_0^0 transition corresponding to internal rotational transitions of the methyl group. Treating this methyl substituent as a one-dimensional rigid rotor and fitting a secular equation to the observed spectrum, one can find values for the size and shape of the potential well for internal rotation, and for the rotational constant B .

This paper presents the laser molecular jet TOFMS of the $S_1 \leftrightarrow S_0$ origin bands for the three *n*-propyltoluenes. Two types of motion and nonrigid molecular behavior can be explored in this series of molecules: rotation of the ring methyl group; and conformations of the propyl chain with respect to the aromatic ring. In addition, any interactions which may take place between these two dynamical or nonrigid components of the molecules are of interest. Definitive experimental evidence elucidating the structures of the propyl conformations has not been presented in the past. The experimental data presented here are supplemented by theoretical empirical force field calculations which are employed herein to predict the existence of different stable propyl conformations and methyl rotor dynamics for each molecule.

II. EXPERIMENTAL PROCEDURES

The TOFMS chamber has been described previously.⁸ TOFMS experiments utilize an R. M. Jordan pulsed valve. Helium is used as the carrier gas except where specified, with backing pressures of 50–100 psig. All compounds are purchased from Wiley Organics (purity > 99.5%).

Dispersed emission (DE) experiments are carried out in a fluorescence excitation chamber, using the optical setup described in the previous paper (I). Expansion of the gas into the chamber is achieved with a Quanta Ray PSV-2 pulsed valve with a 500 μm pinhole located ~ 1 cm from the laser beam. Samples are usually placed inside the head of the valve and heated to 70 $^{\circ}\text{C}$ to achieve a greater concentration in the jet. Helium is used as the carrier gas at a pressure of ~ 50 psig.

III. CALCULATIONS

As given in I, the energy levels for the internal rotation of the ring methyl group are found by treating the methyl group and the benzene ring as rigid rotors⁷:

$$\left[-B \frac{\partial^2}{\partial \phi^2} + V(\phi) \right] \Psi_s(\phi) = E_m \Psi_s(\phi). \quad (1)$$

The potential $V(\phi)$ is, in this instance, given by

$$V(\phi) = \frac{V_3}{2} (1 - \cos 3\phi) + \frac{V_6}{2} (1 - \cos 6\phi). \quad (2)$$

With $V(\phi) = 0$ the free rotor states $\Psi_m(\phi)$ and energy levels ($E_m = m^2 B$) are recovered.

The eigenvalues for Eq. (1) are determined by expanding $\Psi_s(\phi)$ into typically 21 free-rotor wave functions and diagonalizing the Hamiltonian matrix numerically. The parameters B , V_3 , and V_6 are adjusted to fit the experimentally observed spectrum.

Empirical force field molecular orbital–molecular mechanics calculations using the MOMM-85 algorithm are performed to obtain lowest energy configurations for the *n*-propyltoluenes. These calculations are carried out in a fashion similar to that described in Ref. 9.

IV. RESULTS AND DISCUSSIONS

A. Conformations of the propyl group

The TOFMS of *p*-*n*-propyltoluene and *n*-propylbenzene are presented in Figs. 1(a) and 1(b), respectively. Both spectra show two prominent peaks, at 36 811.2 and 36 860.5 cm^{-1} for *p*-*n*-propyltoluene, and at 37 533.9 and 37 583.1 cm^{-1} for *n*-propylbenzene. These two sets of features are due to the existence of two stable and distinct conformations of the propyl group in both molecules. The exact nature of these conformations is still in question.^{10,11}

The α and β carbon atoms of the ethyl group in ethylbenzene are thought, from theoretical and experimental data,^{9,12} to lie in the plane perpendicular to the plane of the benzene ring, passing through the 1 and 4 positions of the ring; this is generally assumed to be the case for C_α and C_β of sterically unhindered *n*-alkylbenzenes.

For *n*-propylbenzene and related compounds, the orientation of the C_α – C_β bond of the propyl group is much less

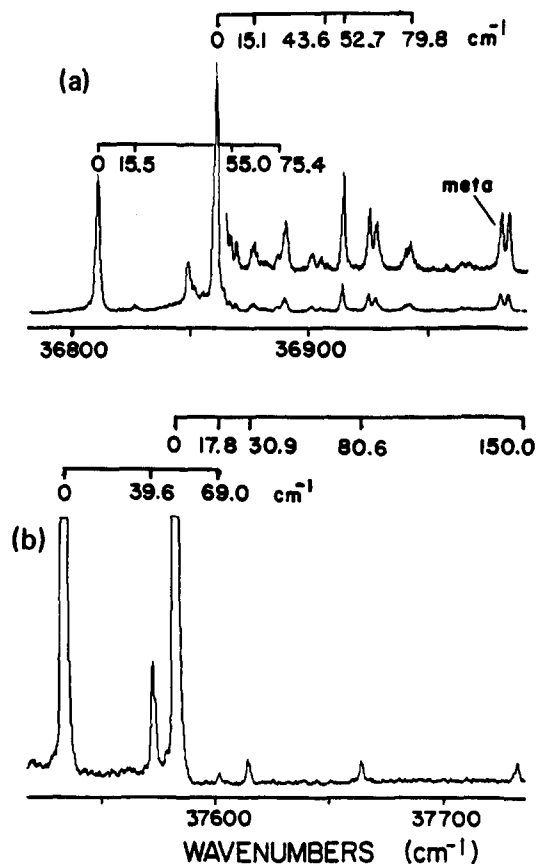
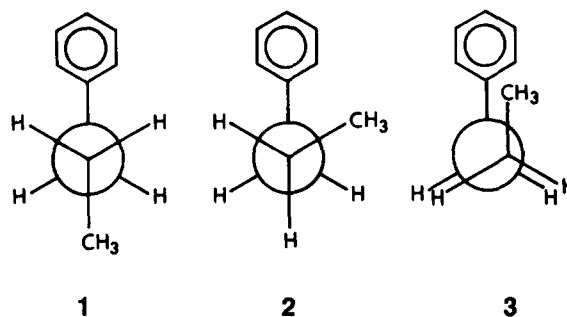


FIG. 1. One-color TOFMS of the 0_0^0 region of (a) *p*-*n*-propyltoluene and (b) *n*-propylbenzene. Both spectra display two origins corresponding to different conformations of the propyl group (*gauche* and *anti*, see Ref. 6). Weak features to higher energy of the origins in (b) are assigned as propyl torsions, and correspond with similar features in (a). Additional features in (a) not seen in (b) are assigned as methyl torsions. Table III lists the specific assignments for the methyl torsions.

clear, due to a lack of definitive experimental data. However, three distinct conformations have been proposed^{10,11}: *anti* 1, *gauche* 2, and eclipsed 3.¹³



Eclipsed conformations have been typically considered to be energy maxima. In a recent series of papers, Hirota *et al.*¹⁰ postulated the importance of $\text{CH} \cdots \pi$ attractive interactions which increase the stability of eclipsed conformations relative to *anti* conformations. Indeed, Hopkins *et al.*¹¹ suggested that the eclipsed conformation could actually be preferred over the *gauche* conformation, pending unambiguous experimental verification.

Our EFF calculations and those previously reported in the literature¹⁰ favor the *gauche* conformation over the eclipsed, but do not specifically take into account the $\text{CH}\cdots\pi$ attractive interactions postulated by Hirota *et al.*¹⁰ Thus, the calculations may be quantitatively unreliable pending additional parametrization. The assignments of the two origins for *p-n*-propyltoluene and *n*-propylbenzene in Figs. 1(a) and 1(b) are therefore somewhat ambiguous; one corresponds to either a *gauche* or an eclipsed conformation, the other to the *anti* conformation. The *gauche*, or eclipsed, conformation should be red shifted in either case relative to the *anti* conformation due to a "self-solvation" of the aromatic ring by the propyl group.^{11,14} For this reason the peaks at 36 860.5 and 37 583.1 cm^{-1} in Figs. 1(a) and 1(b), respectively, are assigned as the *anti* conformer origins. The other origin in these two spectra must be associated with either a *gauche* or an eclipsed conformer. The correct choice can be made with the help of the TOFMS for *m-n*-propyltoluene.

The TOFMS of *m-n*-propyltoluene is presented in Fig. 2. The spectrum consists primarily of a number of intense doublet features. The origins occur as doublets due to torsions of the aromatic ring methyl group: this doublet methyl rotation structure will be discussed in the next section. The doublet features centered at 36 981.2, 37 039.0, and 37 058.4 cm^{-1} are all assigned as separate *m-n*-propyltoluene origins, while the remaining two doublets centered at 37 014.9 and 37 087.2 cm^{-1} , which are noticeably weaker, are assigned to torsions of the propyl group. These latter two doublets are spaced roughly 30 cm^{-1} from their respective origins and correspond to features observed in the *p-n*-propyltoluene and *n*-propylbenzene spectra.

The presence of the ring methyl group in the meta, rather than the para position results in an *anti* conformation 4 and two possible, distinct *gauche* conformers: a *syn-gauche* 5, with the propyl chain pointing towards the aromatic methyl group, and an *anti-gauche* 6, with the propyl chain

pointing away from the aromatic methyl group. Thus, if the *gauche* conformation is favored over the eclipsed conformation 4, three origins (including the *anti*-conformer 6 origin) should be observed in the TOFMS. If the eclipsed conformation 7 were preferred, only two origins would be observed. Since it has already been shown that the former, not the latter, case prevails (Fig. 2), the *gauche* conformer must be a stable conformation, and the eclipsed conformation is not a minimum. This is the only definitive experimental finding to unambiguously define the geometry of the *n*-propyl chain in an aromatic system. In addition, this represents the first experimental observation of the three distinct stable conformations in nonsymmetrically substituted propyl aromatics.

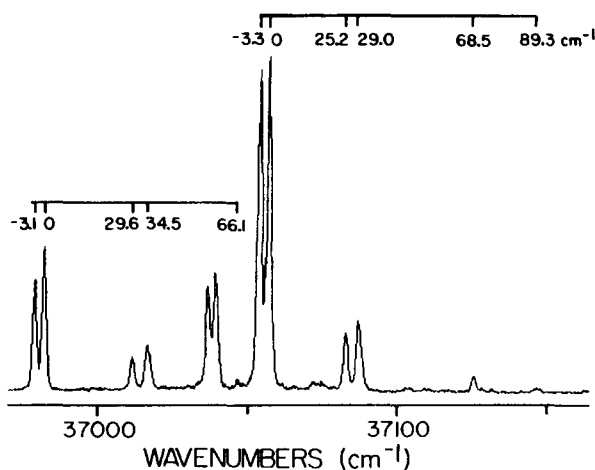
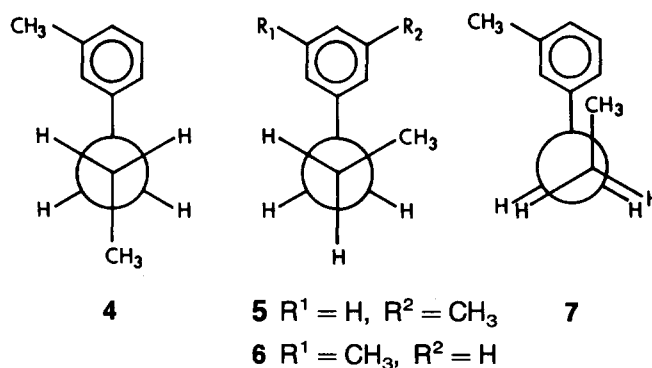


FIG. 2. One-color TOFMS of the 0_0^0 region of *m-n*-propyltoluene. The spectrum contains three origins at 36 982.8, 37 040.4, and 37 060.1 cm^{-1} , corresponding to three different propyl group conformations. Accompanying each origin peak is a second peak, forming a doublet, which is assigned as a methyl torsion. The doublet structures are indicative of differences in the potential barrier height to methyl rotation in S_1 and S_0 .

Since the *gauche* conformer origins should appear to the red of the *anti* conformer origin, as in, for example, *n*-propylbenzene, the intense doublet feature centered at 37 058.4 cm^{-1} in Fig. 2 is assigned as the *anti* conformer origin. Our EFF calculations predict this to be the most stable conformer and it indeed shows the most intensity in the spectrum. Of the two remaining origins, the one centered at 37 039.0 cm^{-1} is somewhat less intense than the origin at 36 981.2 cm^{-1} . Due to steric repulsion between the terminal propyl methyl and the ring methyl, the *syn-gauche* conformation should be less effectively solvated (have a higher transition energy) than the *anti-gauche* conformation. On this basis, the doublet centered at 37 039.0 cm^{-1} is assigned as the *syn-gauche* conformer origin, and the doublet centered at 36 981.2 cm^{-1} is assigned as the *anti-gauche* conformer origin.

The TOFMS of jet-cooled *o-n*-propyltoluene is presented in Fig. 3. The spectrum is noticeably different from that of *m-n*-propyltoluene, although three propyl conformations (*anti*, *syn-gauche*, and *anti-gauche*) are again expected. The most intense feature of the spectrum occurs at 37 195.1 cm^{-1} and is assigned as the origin of the *anti* conformer. This assignment is put forward for two reasons: (1) the *anti* conformer, being the most stable conformer, should occur with the greatest abundance and should therefore show the greatest intensity in the TOFMS; and (2) the *anti* conformer should have the highest energy origin transition of the three possible conformers, as discussed above and in Refs. 4 and 10. The weaker feature at 37 186.4 cm^{-1} , 8.4 cm^{-1} to red of the *anti* origin, is either another origin due to a different conformer of the propyl group, or is due to a methyl torsion. The feature at 37 186.4 cm^{-1} cannot, however, be assigned in this latter manner for reasons that will be discussed in the

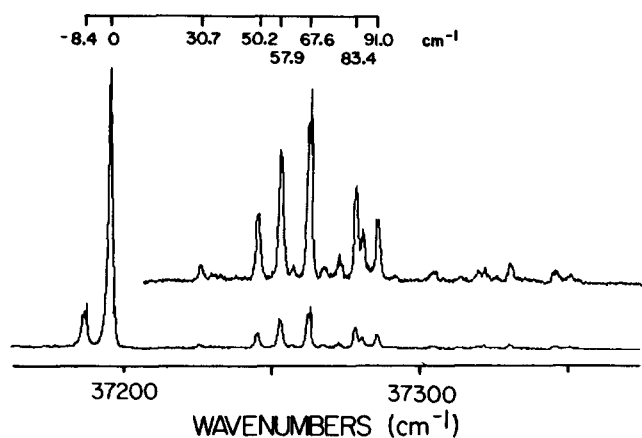


FIG. 3. One-color TOFMS of the 0_0^0 region of *o-n*-propyltoluene. The features at 37 186.4 and 37 195.1 cm^{-1} are separate origins belonging to the *anti-gauche* and *anti* conformers, respectively. The *syn-gauche* conformation is not observed. The large number of peaks in the grouping centered at $\sim 65 \text{ cm}^{-1}$ to higher energy of the *anti* origin strongly implies that the methyl group interacts strongly with the propyl group. Assignments are given in Table VII.

following section dealing with rotation of the methyl group. The feature is $37\,186.4 \text{ cm}^{-1}$ is thus assigned as a separate conformer origin. This conformer is taken to be the *anti-gauche* conformer. No feature corresponding to the origin of the *syn-gauche* conformer is observed in the TOFMS. Two different possibilities could explain this result: (1) the conformational preferences of *o-n*-propyltoluene are different from those of the other compounds so far discussed; or (2) an experimental artifact exists which causes the observation of only two origins. These two possibilities will be discussed in turn.

EFF calculations for the *n*-propyltoluene indicate only a slight dependence of the relative steric energy of the different conformers on the relative position (ortho, meta, para) of the ring methyl group. The EFF results are summarized in Table I. In all of the three cases shown in Table I, the *anti* conformer is the most stable (lowest steric energy), with little difference ($\sim 35 \text{ cm}^{-1}$ or less) between the two *gauche* conformers of any particular isomer.

The EFF calculations, however, indicate little about the nature of the conformational energy wells. The calculations are performed with the β -carbon of the propyl group at $\sim 90^\circ$ with respect to the plane of the benzene ring; the bond angles and lengths are then optimized about the geometry.

The effects of ring librations are not taken into account although the calculations are parametrized for nonsolvated molecules at 298 K.

The absence of a *syn-gauche* origin in the TOFMS of *o-n*-propyltoluene (Fig. 3) may also be a result of a kinetic effect in the expansion of the molecular beam, whereby collisions with expansion gas and other solute molecules displace the *syn-gauche* conformer from a relatively shallow potential well and into more stable *anti-gauche* and *anti* conformer wells. A similar argument¹⁵ has been used previously to explain cluster nucleation processes involved in the molecular jet formation of solute-solvent clusters between toluene and simple hydrocarbons.

Presently we favor a combination of both energy and kinetic effects as the best explanation for the large disparities in intensity between the *syn-gauche*, *anti-gauche*, and *anti* conformer origins in the TOFMS spectrum of *o-n*-propyltoluene.

B. Rotational states of the ring methyl group

1. *p-n*-Propyltoluene

Aside from two intense origin features in the TOFMS for *n*-propylbenzene [Fig. 1(b)], several weak features are seen to appear in the spectrum. These are presumably due to torsional modes of the propyl group and correspond quite well with similar features in the TOFMS of *p-n*-propyltoluene [Fig. 1(a)]. This latter spectrum, however, also displays several features not seen in the *n*-propylbenzene spectrum, which must be due to rotation of the ring methyl group.

The molecular symmetry group¹⁶ for the *anti* conformer of *p-n*-propyltoluene is G_6 , which is isomorphic to C_{3v} , and the appropriate symmetry labels for the internal rotational levels are therefore a_1 , a_2 , and e . The selection rules for internal methyl rotor transitions polarized along the x , y , and z principal axes of inertia of the molecule are as follows:

$$x, y: A_1 \leftrightarrow A_1, A_2 \leftrightarrow A_2, E \leftrightarrow E,$$

$$z: A_1 \leftrightarrow A_2, E \leftrightarrow E.$$

The *gauche* conformation of *p-n*-propyltoluene has no nontrivial symmetry elements (as is also the case for all conformers of *o*- and *m-n*-propyltoluene) and the appropriate molecular symmetry group accounting for internal methyl rotations is thus isomorphic to C_3 . The internal rotational

TABLE I. MOMM-85 calculated steric energy in kcal/mol for *gauche* and *anti* conformations of the *n*-propylbenzenes.

Compound	<i>Syn-gauche</i> ^{a,b}	<i>Anti</i> ^a	<i>Anti-gauche</i> ^a
<i>n</i> -Propylbenzene ^c	17.71 (62°/103°)	17.36 (190°/90°)	...
<i>o-n</i> -Propyltoluene	18.39 (63°/89°)	17.80 (180°/95°)	18.28 (297°/110°)
<i>m-n</i> -Propyltoluene	17.41 (62°/78°)	17.08 (180°/90°)	17.41 (298°/101°)

^a The angles indicated (Y°/X°) define the orientation of the propyl group. X° refers to the torsion angle $\tau(C_0-C_i-C_\alpha-C_\beta)$ and Y° refers to the torsion angle $\tau(C_i-C_\alpha-C_\beta-C_\gamma)$.

^b See structures 5 and 6 for illustrations of *syn-gauche* and *anti-gauche* conformations of these compounds.

^c Due to symmetry, *anti*- and *syn-gauche* are not possible, only *gauche*.

levels are labeled simply *a* or *e*. The selection rules permit only $a \leftrightarrow a$ and $e \leftrightarrow e$ transitions.

In Fig. 1(a), the peak at 52.7 cm^{-1} to higher energy of the *anti* conformer origin at $36\,860.5 \text{ cm}^{-1}$ is readily assigned as the $0a_1 \rightarrow 3a_1$ transition of the methyl rotor, and the peak at 15.5 cm^{-1} to higher energy of the *gauche* conformer origin at $36\,811.2 \text{ cm}^{-1}$ is assigned as the $1e \rightarrow 2e$ transition based on the calculations outlined. These two peaks indicate that the ring methyl group in both conformations has a low barrier to rotation in S_1 .

The internal rotational levels of the ring methyl group should, in addition to being built on the two origins in the spectrum, be built upon all the torsional features of the propyl group. This results in the fairly congested spectrum observed for *p-n*-propyltoluene [Fig. 1(a)], with many overlapping weak features. Nevertheless, identifiable features appear at 55.0 and 75.4 cm^{-1} to higher energy of the *gauche* origin and at 15.1 and 79.8 cm^{-1} to higher energy of the *anti* origin and support the contention that the methyl group is essentially a free rotor in S_1 . Table II lists the energy levels for S_1 calculated using parameters $B = 5.2 \text{ cm}^{-1}$ and $V_6 = 20 \text{ cm}^{-1}$. The zero-point energy in this potential well is 9.7 cm^{-1} . The transition energies are listed in Table III and closely match the observed spacings from both conformer origins in the TOFMS.

Figures 4(a) and 4(b) show the DE spectra obtained by exciting each of the two origin features observed in the TOFMS. Figure 4(a), the origin excited DE spectrum of the *gauche* conformer, displays features at ~ 45 and 80 cm^{-1} to lower energy of the origin, corresponding to the $0a \rightarrow 3a$ and $1e \rightarrow 4e$ transitions. Figure 4(b), the DE spectrum of the *anti* conformer, shows only very weak features to lower energy of the origin, but again centered near ~ 49 and 79 cm^{-1} , corresponding also to the $0a_1 \rightarrow 3a_1$ and $1e \rightarrow 4e$ transitions. Good fits to both spectra are obtained with parameters $B = 5.2 \text{ cm}^{-1}$ and $B_6 = 5 \text{ cm}^{-1}$. The calculated zero-point energy is 2.5 cm^{-1} . The calculated energy levels for S_0 are listed in Table II, while Table III lists the calculated and observed transition energies for $S_0 \leftarrow S_1$.

2. *m-n*-Propyltoluene

The nature of the doublets observed in the TOFMS of *m-n*-propyltoluene is best understood from examination of

TABLE II. Internal rotational levels of *p-n*-propyltoluene in the S_0 and S_1 states.

Ground state S_0^a		Excited state S_1^b	
Level	Energy (cm^{-1})	Level	Energy (cm^{-1})
$0a_1$	0	$0a_1$	0
$1e$	5.20	$1e$	5.17
$2e$	20.79	$2e$	20.59
$3a_2$	45.56	$3a_2$	42.00
$3a_1$	48.06	$3a_1$	52.00
$4e$	83.24	$4e$	83.81
$5e$	130.03	$5e$	130.47

^a $B = 5.2 \text{ cm}^{-1}$, $V_3 = 0 \text{ cm}^{-1}$, $V_6 = 5 \text{ cm}^{-1}$.

^b $B = 5.2 \text{ cm}^{-1}$, $V_3 = 0 \text{ cm}^{-1}$, $V_6 = 20 \text{ cm}^{-1}$.

TABLE III. Energies of allowed transitions between internal rotational levels in the S_0 and S_1 states for *p-n*-propyltoluene.

Transition ($S_1 \rightarrow S_0$)	Calculated E (cm^{-1})	Observed E (cm^{-1}) by DE	
		0^a	0^b
$0a_1 \rightarrow 0a_1$	0	0^a	0^b
$0a_1 \rightarrow 3a_2$	45.56
$0a_1 \rightarrow 3a_1$	48.01	45	49
$1e \rightarrow 1e$	0.03	0	0
$1e \rightarrow 2e$	15.62
$1e \rightarrow 4e$	78.07	80	79

Transition ($S_0 \rightarrow S_1$)	Calculated E (cm^{-1})	Observed E (cm^{-1}) by TOFMS	
		0^a	0^b
$0a_1 \rightarrow 0a_1$	0	0^a	0^b
$0a_1 \rightarrow 3a_2$	42.00	...	43.6
$0a_1 \rightarrow 3a_1$	52.00	55.0	52.7
$1e \rightarrow 1e$	-0.03	0	0
$1e \rightarrow 2e$	15.39	15.5	15.1
$1e \rightarrow 4e$	78.61	75.4	79.8

^a Measured from the *gauche* origin.

^b Measured from the *anti* origin.

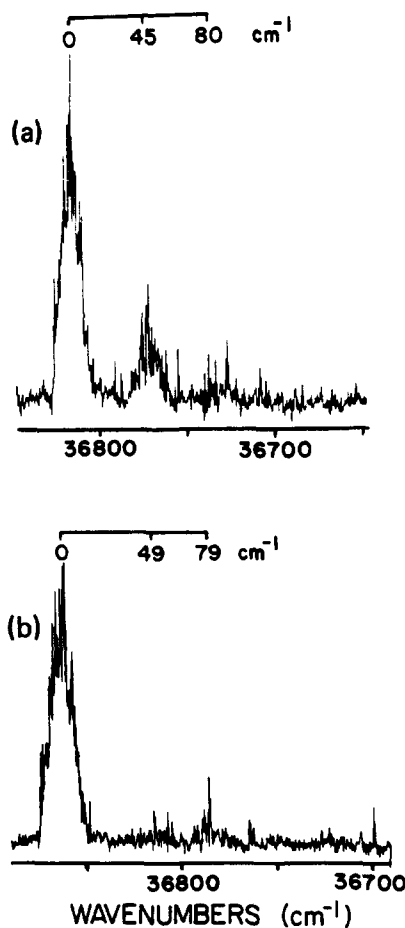


FIG. 4. DE spectra at the 0_0^0 region of *p-n*-propyltoluene obtained by pumping the two origins in Fig. 1 at (a) $36\,811.2 \text{ cm}^{-1}$ and (b) $36\,860.5 \text{ cm}^{-1}$. Resolution in these figures is 13.0 and 15.2 cm^{-1} , respectively. Assignments are given in Table III.

the DE spectra obtained by exciting each half of a given doublet origin. Figures 5(a) and 5(b) are the DE spectra associated with the two components of the *anti-gauche* conformer 6 origin. Figures 5(c) and 5(d) are the DE spectra obtained by exciting the two components of the *anti* conformer 4 origin. When the low energy component of the *anti-gauche* 6 ($\nu_{\text{ex}} = 36\,979.7\text{ cm}^{-1}$) or *anti* 4 ($\nu_{\text{ex}} = 37\,056.8\text{ cm}^{-1}$) conformer origin is excited, a peak appears in the DE spectra at $\sim 15\text{ cm}^{-1}$ [Figs. 5(b) and 5(d)]. This feature is absent from the DE spectra if the high energy component of each doublet origin is excited, at $36\,982.8$ and $37\,060.1\text{ cm}^{-1}$ for the *anti-gauche* and *anti* conformers, respectively [Figs. 5(a) and 5(c)]. The DE spectra for the *syn-gauche* conformer 5 origin show weak but similar results. 15 cm^{-1} matches the separation between the $1e \rightarrow 1e$ and $1e \rightarrow 2e$ transition energies for a free rotor rather closely, and thus when the low energy components of the doublet origins are being excited in a DE experiment, the $1e$ level in S_1 must be populated since the $1e \rightarrow 2e$ transition is observed. The low energy components of the doublet origins observed in the TOFMS must correspond then to the $1e \rightarrow 1e$ transition. The high energy components must represent the $0a \rightarrow 0a$ transitions and may therefore be regarded as the true origins.

Note that the different nuclear spin states associated with the a and e rotational levels of the methyl rotor give rise to hot bands in the spectra of the n -propyltoluenes which cannot be depopulated by normal cooling techniques. Essentially two types of n -propyltoluene molecules exist in the cooled beam; those in the $0a$ state and those in the $1e$ state.

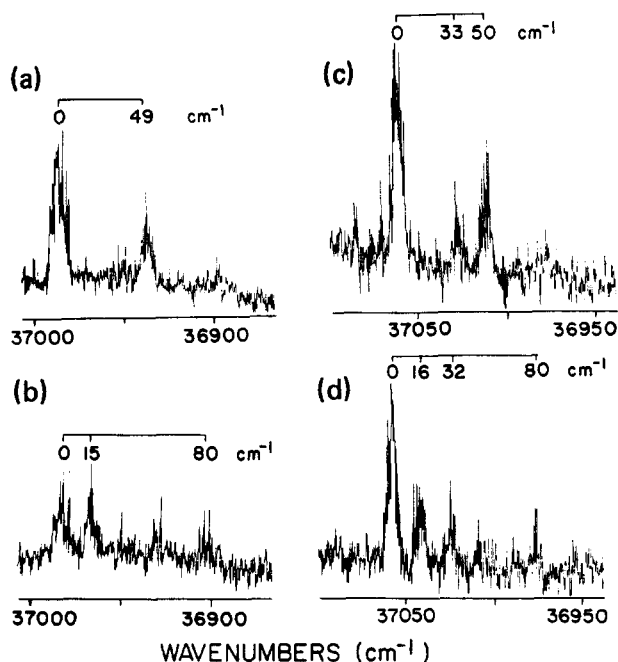


FIG. 5. DE spectra of the 0_0^0 region of m - n -propyltoluene obtained (resolution 7 cm^{-1}) by pumping at (a) $36\,982.8\text{ cm}^{-1}$, (b) $36\,979.7\text{ cm}^{-1}$, (c) $37\,060.1\text{ cm}^{-1}$, and (d) $37\,056.8\text{ cm}^{-1}$. Note the similarities between (a) and (c) (origin transition pumped) and (b) and (d) (transition involving a torsionally excited methyl rotor pumped). Assignments are given in Table V.

The doublet "origins" observed for the various conformers of m - n -propyltoluene, for example, are illustrative of this.

Table IV lists the energy levels calculated for internal rotation of the methyl group in the ground state of m - n -propyltoluene, with $B = 5.0\text{ cm}^{-1}$, $V_6 = 23\text{ cm}^{-1}$, and a resultant zero-point energy of 11.1 cm^{-1} . Table V lists the allowed transitions along with their calculated and observed energies. As is seen for p - n -propyltoluene, the different conformations display similar behavior with respect to the internal rotational levels of the methyl rotor in S_0 , since both the *anti* and *anti-gauche* data are fit by the same potential.

Information about the internal rotational levels of the ring methyl rotor in S_1 can be readily obtained upon inspection of the TOFMS (Fig. 2). The fact that the $1e \rightarrow 1e$ transition is red shifted by several cm^{-1} from the $0a \rightarrow 0a$ origin means that the rotational barrier has increased in S_1 . Also, the doublet features centered at $37\,014.9$ and $37\,087.2\text{ cm}^{-1}$, corresponding to propyl torsions, appear in the TOFMS of the meta isomer as doublets since they have the ring methyl torsional levels built on them. The corresponding feature for the *syn-gauche* conformation is apparently too weak to be observed in the TOFMS.

The two components of the *anti-gauche* origin feature are separated by 3.1 cm^{-1} . The propyl feature centered at $37\,014.9\text{ cm}^{-1}$ is, however, split by 4.9 cm^{-1} . This difference is indicative of an interaction in S_1 between the propyl and methyl group motions. The increased splitting of the doublet corresponding to the $0a \rightarrow 0a$ and $1e \rightarrow 1e$ transitions implies an increased barrier to rotation of the methyl group in S_1 . This effect seems to be substantially reduced for the *anti* conformation, since the spacings of the origin doublet feature (3.3 cm^{-1}) and the corresponding propyl feature (3.8 cm^{-1}) are almost the same.

The TOFMS (Fig. 2) contains additional weak features which are roughly 65 cm^{-1} to the blue of both the *anti-gauche* and *anti* conformer origins. These are assigned as the $0a \rightarrow 3a$ transitions of the two conformers, shifted to higher energy in S_1 , relative to S_0 , by the increased potential barrier to rotation. Table IV lists the energy levels for internal rotation of the methyl group in S_1 and Table V lists the calculated and observed transition energies. The barrier to rotation in S_1 is calculated to be $V_3 = 75\text{ cm}^{-1}$, with $B = 5.2\text{ cm}^{-1}$ and a calculated zero-point energy of 25.2 cm^{-1} , for both the *anti-gauche* and *anti* conformers. Thus, if the propyl group

TABLE IV. Internal rotational levels for S_0 and S_1 of m - n -propyltoluene.

Ground state S_0^a		Excited state S_1^b	
Level	Energy (cm^{-1})	Level	Energy (cm^{-1})
$0a$	0	$0a$	0
$1e$	4.95	$1e$	1.55
$2e$	19.71	$2e$	41.14
$3a$	39.53	$3a$	56.59
$3a$	51.02	$3a$	68.80
$4e$	80.83	$4e$	98.02

^a $B = 5.0\text{ cm}^{-1}$, $V_3 = 0\text{ cm}^{-1}$, $V_6 = 23\text{ cm}^{-1}$.

^b $B = 5.2\text{ cm}^{-1}$, $V_3 = 75\text{ cm}^{-1}$, $V_6 = 0\text{ cm}^{-1}$.

TABLE V. Energies of allowed transitions between internal rotational levels in the S_0 and S_1 states for *m-n*-propyltoluene.

Transition ($S_1 \rightarrow S_0$)	Calculated E (cm^{-1})	Observed E (cm^{-1}) by DE	
0a \rightarrow 0a	0	0 ^a	0 ^b
0a \rightarrow 3a	39.53	...	33
0a \rightarrow 3a	51.02	49	50
1e \rightarrow 1e	0	0	0
1e \rightarrow 2e	14.76	15	16
1e \rightarrow 4e	75.88	80	80

Transition ($S_0 \rightarrow S_1$)	Calculated E (cm^{-1})	Observed E (cm^{-1}) by TOFMS	
0a \rightarrow 0a	0	0 ^a	0 ^b
0a \rightarrow 3a	56.59
0a \rightarrow 3a	68.80	66.1	68.5
1e \rightarrow 1e	-3.40	-3.1	-3.3
1e \rightarrow 2e	36.19
1e \rightarrow 4e	93.07	...	89.3

^a Measured from the *trans-gauche* origin.^b Measured from the *anti* origin.

is not torsionally excited, the S_1 potential for internal rotation of the methyl group in both the *anti* and *anti-gauche* conformer appears to be approximately the same. If the propyl group is torsionally excited, however, it appears to be able to interact with the ring methyl group in the *anti-gauche* conformer, resulting in a somewhat ($\sim 10 \text{ cm}^{-1}$) higher barrier to rotation for the methyl group.

3. *o-n*-Propyltoluene

The feature at $37\,186.4 \text{ cm}^{-1}$ (to the red and the *anti* conformation's origin) in the TOFMS for *o-n*-propyltoluene (Fig. 3) cannot be assigned as the $1e \rightarrow 1e$ methyl rotational transition: the maximum amount that the $1e \rightarrow 1e$ transition can be shifted from the origin (0a \rightarrow 0a transition) is $B \text{ cm}^{-1}$ (the rotational constant) and B for a methyl group rotation cannot equal 8.4 cm^{-1} . If the $37\,186.4 \text{ cm}^{-1}$ peak is a hot band, it must correspond to a different transition such as the $1e \rightarrow 2e$ or $2e \rightarrow 2e$ transitions. If this were the case, then the $1e \rightarrow 1e$ transition should fall between $37\,186.4 \text{ cm}^{-1}$ and the origin at $37\,195.1 \text{ cm}^{-1}$, yet absolutely no sign of another peak in this region in the TOFMS can be found. In addition, a fairly large ($\sim 100 \text{ cm}^{-1}$) V_6 potential would be required to shift the $2e$ level in S_1 down relative to the 0a and $1e$ levels so that the 8.4 cm^{-1} spacing would be obtained. A large V_6 potential is physically inappropriate to describe the potential for methyl rotation in *o-n*-propyltoluene. These arguments lead to the conclusion that the feature in Fig. 3 at $37\,186.4 \text{ cm}^{-1}$ is in fact a separate origin, as discussed previously, belonging to a different conformer of *o-n*-propyltoluene. It is interesting to note that such a feature is absent from the TOFMS of *o*-ethyltoluene, for which *gauche* and *anti* conformation cannot occur.¹⁷

The remaining portion of the TOFMS of *o-n*-propyltoluene is highly unusual in that a large number of peaks occur in the region between 50 and 90 cm^{-1} to higher energy of the *anti* origin. Five strong features, and four weak ones occur in this interval.¹⁸ A V_3 potential alone or in combina-

tion with a V_6 potential can account for, at best, three of the features within this interval. Two possibilities exist to explain the remaining peaks. The first of these is that the ring methyl torsions couple with torsions of the propyl chain, resulting in more peaks in the TOFMS. The second explanation is that the extra peaks in the TOFMS are due to methyl torsions of the terminal methyl group of the propyl chain. The first possibility is worthwhile to consider, but without detailed knowledge of the propyl chain motion, quantitative predictions are difficult to make. This is, of course, not true for the second explanation. Table VI lists the internal rotational levels for both rotors (terminal methyl and ring methyl) in S_1 with $V_3 = 72 \text{ cm}^{-1}$, $V_6 = -14 \text{ cm}^{-1}$, and $B = 5.0 \text{ cm}^{-1}$ for the ring methyl group, and $V_3 = 106 \text{ cm}^{-1}$, $V_6 = -13 \text{ cm}^{-1}$, and $B = 5.0 \text{ cm}^{-1}$ for the terminal methyl group of the propyl chain. The calculated zero-point energy for the ring methyl rotor is 18.0 cm^{-1} and for the terminal methyl group is 25.7 cm^{-1} . Together the two rotors account for the TOFMS of *o-n*-propyltoluene quite well, as shown in Table VII in which the calculated and observed transition energies are given for $S_0 \rightarrow S_1$.

While this double methyl rotor model fits the TOFMS (Fig. 3) quite well, it does possess some puzzling aspects. For example, the potential barrier to rotation of the terminal methyl group of the propyl chain decreases from $\sim 1000 \text{ cm}^{-1}$ (calculated value based on the EFF/MOMM-85 algorithm) in S_0 to 106 cm^{-1} in S_1 . Moreover, the appearance in the TOFMS of transitions between internal rotational levels of the terminal methyl group is contrary to what was observed for *m*- and *p-n*-propyltoluene. Finally, the necessity of adding a small amount of V_6 potential to the V_3 potential well is unexpected.

TABLE VI. Internal rotational levels from proposed double rotor model for *o-n*-propyltoluene.

Ring methyl group			
Ground state S_0^a		Excited state S_1^b	
Level	Energy (cm^{-1})	Level	Energy (cm^{-1})
0a	0	0a	0
1e	1.95	1e	1.64
2e	37.03	2e	37.04
3a	54.33	3a	50.14
3a	63.63	3a	67.58
4e	94.38	4e	93.69
5e	140.44	5e	137.60
Terminal methyl group of propyl chain			
Ground state S_0^c		Excited state S_1^d	
Level	Energy (cm^{-1})	Level	Energy (cm^{-1})
0a	0	0a	0
1e	0	1e	0.81
2e	203.9	2e	48.72
3a	203.9	3a	57.67
3a	394.1	3a	83.99
4e	394.1	4e	106.33
		5e	149.38

^a $B = 5.2 \text{ cm}^{-1}$, $V_3 = 64 \text{ cm}^{-1}$, $V_6 = 0 \text{ cm}^{-1}$.^b $B = 5.0 \text{ cm}^{-1}$, $V_3 = 72 \text{ cm}^{-1}$, $V_6 = -14 \text{ cm}^{-1}$.^c $B = 5.2 \text{ cm}^{-1}$, $V_3 = 1000 \text{ cm}^{-1}$, $V_6 = 0 \text{ cm}^{-1}$.^d $B = 5.0 \text{ cm}^{-1}$, $V_3 = 106 \text{ cm}^{-1}$, $V_6 = -13 \text{ cm}^{-1}$.

TABLE VII. Energies of allowed transitions between internal rotational levels in S_1 and S_0 states of *o-n*-propyltoluene.

Transition ($S_0 \rightarrow S_1$)	Calculated E (cm^{-1})	Observed E (cm^{-1}) by TOFMS
$0a \rightarrow 0a^a$	0	0
$0a \rightarrow 3a$	50.14	50.2
$0a \rightarrow 3a$	67.58	67.6
$1e \rightarrow 1e$	-0.31	0
$1e \rightarrow 2e$	35.09	c
$1e \rightarrow 4e$	91.74	91.0
$1e \rightarrow 5e$	135.65	135.8
<hr/>		
$0a \rightarrow 0a^b$	0	0
$0a \rightarrow 3a$	57.67	57.9
$0a \rightarrow 3a$	83.99	83.4
$1e \rightarrow 1e$	0.81	0
$1e \rightarrow 2e$	48.72	...
$1e \rightarrow 4e$	106.33	110.0
$1e \rightarrow 5e$	149.38	150.8

^a Transitions involving the ring methyl group.

^b Transitions involving the terminal methyl group of the propyl chain.

^c Feature at 30.7 cm^{-1} is most likely a propyl torsional mode.

While a two-rotor model is proposed for the excited state, the ground state of *o-n*-propyltoluene presents quite a different situation. Figure 6 presents the DE spectrum obtained by exciting the *anti* conformer origin at $37\,195.1 \text{ cm}^{-1}$. The feature at 63 cm^{-1} to lower energy of the origin is presumably the $0a \rightarrow 3a$ transition, and can be fit by a single rotor potential with $B = 5.2 \text{ cm}^{-1}$, $V_3 = 64 \text{ cm}^{-1}$, and $V_6 = 0 \text{ cm}^{-1}$, resulting in a zero-point energy of 22.7 cm^{-1} . The energy levels for this calculated potential are listed in Table VI.

Based on the above proposed models for the *o-n*-propyltoluene, two primary conclusions can be drawn from the data presented: (1) the terminal methyl group of the propyl

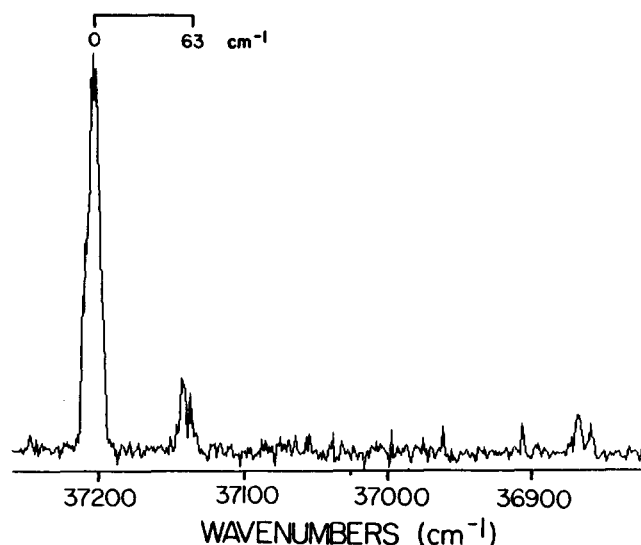


FIG. 6. DE spectrum of the 0_0^0 region of *o-n*-propyltoluene obtained (resolution 15.2 cm^{-1}) when the *anti* origin at $37\,195.1 \text{ cm}^{-1}$ is pumped. Note the absence of a large number of features in the spectrum, unlike Fig. 3, indicating that the methyl group does not interact with the propyl group in the ground state.

chain and the ring methyl group both undergo rotational transitions in the S_1 excited state, and (2) the terminal methyl group on the propyl chain has a smaller ($V_3 = 106 \text{ cm}^{-1}$, $V_6 = -13 \text{ cm}^{-1}$) barrier to rotation in S_1 than in S_0 .

The differences between the TOFMS and DE spectrum of *o-n*-propyltoluene imply that the interaction between the methyl and propyl groups of the molecule in S_1 comes about as a result of changes in the electron densities of *o-n*-propyltoluene. The TOFMS of *o-n*-propyltoluene is therefore different from those of all of the other molecules presented because of the close proximity of the methyl and propyl groups.

V. SUMMARY AND CONCLUSIONS

The existence of various stable conformers of the propyl group for each isomer of *n*-propyltoluene has been demonstrated through the use of supersonic molecular jet spectroscopy. In particular, transitions for three specific conformations of *m-n*-propyltoluene are observed and assigned as the *anti-gauche*, *syn-gauche*, and *anti* conformations. This confirms the predictions of EFF/MOMM-85 calculations for these molecules. These studies validate the use of such calculations for predicting the geometry of nonrigid molecules. This work also recommends supersonic molecular jet spectroscopy for the observation and identification of conformations which interconvert with very low energy barriers between them.

Table VIII summarizes the rotational constants and potential energy parameters for the methyl rotor(s) of toluene, the xylenes and the *n*-propyltoluenes. The data presented show that the methyl rotor experiences a decreasing barrier to rotation in the order ortho > meta > para. This trend, which is substantially stronger in the S_1 excited state relative to the ground state, is presumed to be due to steric hindrance between the two substituents. The size of this interaction does not seem to depend significantly on the conformation of the propyl group.

TABLE VIII. Potential energy parameters and rotational constants for the ring methyl group of the *n*-propyltoluenes and xylenes.

Compound	Ground state S_0	Excited state S_1
Toluene	$B = 5.2$ $V_6 = 10$	$B = 5.2$ $V_6 = 25$
<i>p</i> -Xylene	$B = 5.2$ $V_6 = 10$	$B = 5.2$ $V_6 = 25$
<i>m</i> -Xylene	$B = 5.2$ $V_6 = 25$	$B = 5.2$ $V_3 = 81$ $V_6 = -30$
<i>o</i> -Xylene	$B = 5.2$ $V_3 = 425$ $V_6 = 18$	$B = 5.5$ $V_3 = 166$ $V_3' = -25$
<i>p-n</i> -Propyltoluene	$B = 5.2$ $V_6 = 5$	$\chi = 0.72$ $B = 5.2$ $V_6 = 20$
<i>m-n</i> -Propyltoluene	$B = 5.0$ $V_6 = 23$	$B = 5.2$ $V_3 = 75$
<i>o-n</i> -Propyltoluene	$B = 5.2$ $V_3 = 64$	$B = 5.0$ $V_3 = 72$ $V_6 = -14$

The TOFMS and DE spectra presented for *m*- and *p*-propyltoluene are devoid of transitions to the $5e$ or higher rotational levels. The rapid falloff of intensity indicates that the equilibrium positions of the nuclei do not change much on going from S_0 to S_1 . Transitions between populated low-lying internal rotational levels in S_0 to similar low energy levels in S_1 will have the best Franck–Condon overlaps and show the most intensity; thus the relative orientations of the S_0 and S_1 potential wells are similar.

The TOFMS and DE spectra of *o*-*n*-propyltoluene contain features assigned to levels corresponding to a high degree of internal rotational excitation. Whether this is indicative of a change in the methyl group orientation in S_1 relative to S_0 cannot be proven; however, such a conclusion seems somewhat reasonable given the interaction changes that occur in the potential upon excitation from S_0 to S_1 .

In general, an inspection of the features within the first $100\text{--}200\text{ cm}^{-1}$ of the 0_0^0 origin peak of a given nonrigid molecule can yield much qualitative information about the nature of the potential well for internal rotation of a particular substituent such as, for example, a methyl group on an aromatic ring. For this specific case, the presence of a feature at $\sim 50\text{ cm}^{-1}$ to higher energy of the origin is indicative of a low ($\sim 10\text{--}20\text{ cm}^{-1}$) barrier to rotation, since such a feature is most likely due to the $0a_1 \rightarrow 3a_1$ transition which falls at 45 cm^{-1} for a free methyl rotor. Doublet features at the origin, as are observed for *m*-*n*-propyltoluene, are indicative of significant differences in the barrier to rotation of the methyl group in S_0 and S_1 . A rapid falloff in the intensity of the internal rotational transitions in, for example, the TOFMS can be taken as an indication that little change takes place in the equilibrium positions of the nuclei in S_1 with respect to S_0 . Large gaps in the spectrum can suggest that a high potential barrier to methyl rotation is present. Studying the internal rotations of a ring methyl group in this way yields information that is useful and necessary in understanding the interactions that occur between such a methyl group and other substituents, and should lead to an improved understanding of the chemistry of the molecule.

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¹³Although other eclipsed conformations can be envisioned in which, for example, a methylene hydrogen is eclipsing the benzene ring, such conformations lack the $\text{CH} \cdots \pi$ attractive interactions which led to the postulation of **3** as a stable conformer in the first place. For this reason, these other eclipsed conformations are not considered to be important. This conclusion is supported by our EFF calculations.

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¹⁸One or more of these bands could be associated with the *cis-gauche* conformer; however, we fully expect that all stable conformations of the propyl group which involve self-solvation of the ring will have origin transitions red shifted with respect to an intense origin associated with the *anti* conformer. We therefore conclude that these features are associated with the *trans-gauche* and *anti* conformers and we assume that most belong to the latter on the basis of the relative intensities of their origin bands.