The effect of internal rotation on the methyl CHstretching overtone spectra of toluene and the xylenes

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The effect of internal rotation on the methyl CH-stretching overtone spectra of toluene and the xylenes

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The structure of methyl CH-stretching overtone bands in the vibrational spectra of methylbenzenes was investigated theoretically. The anharmonic CH-stretching vibration, described by a Morse potential, was represented in terms of a harmonic basis while hindered internal rotation of the methyl group was represented by a rigid rotor attached to an infinitely massive frame. Relatively weak coupling between the anharmonic CH vibration and the hindered internal rotation is sufficient to shift the positions of rovibrational lines from a *PQR*-like rotational contour to patterns similar to those observed experimentally. For high rotational barriers, as in *o*-xylene, the rovibrational transitions form two bands associated with conformationally nonequivalent CH-bonds, consistent with the conformational preference established by microwave spectroscopy and molecular orbital calculations. For nearly free internal rotation, as in toluene, *m*-xylene and *p*-xylene, a prominent middle band is also present. This "free rotor" band corresponds to rotational transitions between states high above the barrier and disappears as the barrier height increases. The outer bands correspond to transitions for which either the initial or the final state is below or near the barrier height in energy. Contrary to earlier suggestions, the band structure is not indicative of the conformational preference of the methyl group in toluene. In fact, the calculated spectra of nearly free internal rotors are insensitive to this preference.

I. INTRODUCTION

Although chemical differences between conformationally nonequivalent CH-bonds may be concealed by rapid rotational averaging, high-resolution methyl-CH vibrational spectra often exhibit structure that can be attributed to the existence of distinct conformers on the vibrational timescale.[1-3] Such assignments are sensible if the rotational wave functions are highly localized in the potential wells that correspond to such conformers. On the other hand, the rotational wave functions for a free rotor are highly delocalized, all conformations being equally probable, and particular conformers cannot be identified.[4] The gas-phase methyl-CH vibrational spectra of nearly free CH_3–X internal rotors (X = NO_2,[5-7] BF_2,[8-10] phenyl[5,11-13]) are striking because they show multiple bands. In particular, the gas-phase methyl-CH overtone spectra of toluene, *m*-xylene, and *p*-xylene consist of three bands while the spectrum of *o*-xylene contains only two distinct bands that correspond closely to the outer bands in the toluene spectrum.[13] Similar band structure is found in the fundamental hydroxyl band of ethanol vapor,[14] and in the spectra of crystalline toluene[15] and durene,[16] although field effects complicate the latter two. It is tempting to assign such bands to nonequivalent bonds although it is not clear that such assignments can be justified.

The barrier to internal rotation in *o*-xylene, 1, is about 6 kJ·mol^{-1} (500 cm^{-1}) according to an analysis of the microwave spectrum.[17] Some STO-3G calculations[18] on

the coupled internal rotation yield 4.8 kJ·mol^{-1}, in good agreement with experimental data that suggest a threefold barrier near 5 kJ·mol^{-1}.[19] The preferred conformation has two methyl-CH bonds in the ring plane.

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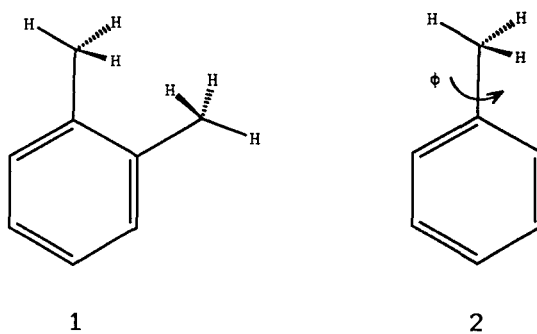
There are two conformationally nonequivalent CH-bond types, namely, the in-plane and out-of-plane CH-bonds, that correspond to the high- and low-frequency bands, respectively.[13] For toluene, 2, the barrier to rotation about the exocyclic CC-bond is merely 59 J·mol^{-1} (4.9 cm^{-1}) according to microwave analyses.[11,12] The preferred conformation has one methyl CH-bond either in the ring plane ($\phi = 0°$) or in the plane perpendicular to the ring plane ($\phi = 90°$). *Ab initio* molecular orbital calculations suggest that $\phi = 90°$ is slightly lower in energy, but such small differences are not reliable.[18,20] There is some experimental support for this preference from Raman/infrared[5] and fluorescence excitation[19,21] spectra, but the assignments depend upon small differences. On the basis of a comparison of overtone spectra, Gough and Henry assign the outer bands in the toluene spectrum to localized in-plane and out-of-plane CH-bonds as in *o*-xylene,[13] inferring a prefer-

ence for $\phi = 0°$ from relative intensities. The middle band is then attributed to "free" rotational states high above the barrier.

The origin of these bands remains unclear. The similarity of the toluene and xylene spectra suggests parallel assignments for the vibrational bands, but the low barrier in toluene seems to preclude the existence of distinguishable conformers. Indeed, if the "free rotor" band in the toluene spectrum is due to rapid averaging of the CH-bond environment, the identity of the outer bands presents the more perplexing question. The origins of these bands is the subject of this paper.

II. COMPUTATIONAL MODEL

The effect of internal rotation on the methyl-CH fundamental spectrum has been examined by several authors. Sheppard and Woodman showed that angular variation of the force constant during internal rotation can give rise to rotational wings.[22] In a study of $C_6D_5CHD_2$, in which the CH-bond is chemically isolated, Cavagnat and Lascombe took the rotational and vibrational motions to be adiabatically separable.[5] A similar approach was taken by Schiel and Richter in recent work on CH_3CH_2OD.[14] Averaging over the vibrational coordinate provided an additional angle-dependent contribution to the internal rotation potential. While this model led to acceptable fundamental infrared and Raman profiles of $C_6D_5CHD_2$, it predicted a qualitative change in the internal rotation potential upon isotopic substitution, as discussed below.

In the present work, we choose not to separate the vibrational and rotational motions, but to diagonalize a coupled Hamiltonian in the harmonic oscillator-rigid rotor basis. The objective is to construct a physically reasonable coupling which leads to acceptable CH-overtone spectra while remaining consistent with experimental and computational results.

A. The rotational Hamiltonian

The rotational Hamiltonian for a molecule that undergoes hindered rotation about an internal axis, ϕ, lying collinear with the principal z axis, may be written as[23]

$$\mathcal{H}_{\mathrm{rot}} = AP_x^2 + BP_y^2 + CP_z^2 - 2CpP_z + Fp^2 + V, \qquad (1)$$

where P is the overall angular momentum of the molecule, A, B, C, and F are rotational constants, p is the angular momentum about ϕ and V is the hindering potential. The first three terms on the right hand side of Eq. (1) are associated with overall rotations of the molecule and the last two terms are associated with hindered internal rotation. The remaining cross term corresponds to Coriolis coupling of these rotations. If the principal moments of inertia are large relative to the moment about ϕ, the terms involving P are small in comparison with the terms that describe internal rotation and $F \approx \hbar^2/2I_\phi$; the internal and overall rotations are adiabatically separable. The relevant Hamiltonian is then simply

$$\mathcal{H}_{\mathrm{rot}} = -(\hbar^2/2I)d^2/d\phi^2 + V(\phi), \qquad (2)$$

where $I = I_\phi$ and ϕ is the rotation angle about ϕ. In the case of toluene, for example, this approximation is quite good; A, B, C and F are about 0.057, 0.082, 0.191, and 5.44 cm^{-1}, respectively,[12] while internal rotation of a methyl group against an infinitely heavy framework yields a rotational constant of 5.25 cm^{-1}. As a periodic function of the angle ϕ, the hindering potential can always be expressed as a Fourier series,

$$V(\phi) = V_0 + \sum_{n=1}^{\infty} [V_n \cos(n\phi) + V'_n \sin(n\phi)], \qquad (3)$$

where n is the symmetry number (foldedness) for each component of the potential. For toluene, the potential has even parity so all of the coefficients V'_n vanish. The dominant term corresponds to $n = 6$.[11,12] Equation (2) becomes

$$\mathcal{H}_{\mathrm{rot}} = -\frac{(\hbar^2/2I)d^2}{d\phi^2} + \frac{1}{2} V_n[1 \pm \cos(n\phi)] = \mathcal{H}_{\mathrm{rot}}^0 + \mathcal{H}_{\mathrm{rot}}', \qquad (4)$$

where the negative sign applies if the most stable conformation of the toluene molecule has one CH-bond in the plane of the phenyl group and the positive sign applies if the most stable conformation has one CH-bond in the plane perpendicular to the phenyl group. In the absence of a hindering potential $\mathcal{H}_{\mathrm{rot}}'$, the eigenvalues of $\mathcal{H}_{\mathrm{rot}}^0$ are

$$F(m) = \hbar^2 m^2/2I. \qquad (5)$$

The normalized zeroth-order wave functions may be written as

$$\chi_{\mathrm{rot}}^+(m;\phi) = \pi^{-1/2}\cos(m\phi), \quad m = 1,2,3,\dots$$
$$= (2\pi)^{-1/2}, \quad m = 0 \qquad (6)$$

and

$$\chi_{\mathrm{rot}}^-(m;\phi) = \pi^{-1/2}\sin(m\phi), \quad m = 1,2,3,\dots, \qquad (7)$$

where m is a good quantum number only if $V_n = 0$. For small barriers, m is still useful as an index. The superscript $\pm$ corresponds to the parity of χ, denoted $\rlap{/}p_m$, which is either symmetric ($\rlap{/}p_m = +1$) or antisymmetric ($\rlap{/}p_m = -1$) with respect to inversion. Matrix elements of the even-parity potential vanish unless both wave functions have the same parity. By straightforward integration, the matrix elements of the perturbation $\mathcal{H}_{\mathrm{rot}}'$ are given by

$$H'_{m',m} = \tfrac{1}{4}V_n\{2\delta_{m',m} \pm [1 + (2^{1/2}-1-\rlap{/}p_m)\delta_{m,0}]$$
$$\times \delta'_{m',m+n} \pm \rlap{/}p_m \delta_{m'+m,n}\}, \qquad (8)$$

where the choice of positive or negative sign is determined by Eq. (4) and $\delta_{i,j}$ is the Kronecker delta. A basis consisting of the zeroth-order functions up to and including $m = 30$ is sufficient for the present purpose.[4]

B. The vibrational Hamiltonian

The vibrational Hamiltonian of interest is

$$\mathcal{H}_{\mathrm{vib}} = \tfrac{1}{2}g_{rr}p_r^2 + V(r), \qquad (9)$$

where g_{rr} is the G matrix element, i.e., the reciprocal reduced mass, and $p_r = -i\hbar d/dr$ is the momentum.[24] The vibrational potential $V(r)$ chosen here is the Morse potential

$$V_{\text{Morse}}(r) = D\{1 - \exp[-\alpha(r - r_e)]\}^2, \tag{10}$$

where D is the Morse oscillator dissociation energy and α is a scaling factor.[25] With this potential, the Schrödinger equation can be analytically solved approximately,[26] whereby the vibrational term values are

$$G(v) = \omega(v + 1/2) + \omega x(v + 1/2)^2, \tag{11}$$

where v is the vibrational quantum number, ω is the oscillator frequency, and x is the (dimensionless) anharmonicity. The parameters D and α are related to the frequency and anharmonicity by

$$D = \hbar\omega^2/4\omega x \tag{12}$$

and

$$\alpha = (2\omega x/\hbar g_{rr})^{1/2} \tag{13}$$

where all quantities are expressed in *Système International* (SI) units. The Morse wave functions are

$$\chi_{\text{Morse}}(v;z) = [v!/(2K - v - 1)!]^{1/2} e^{-z/2}$$
$$\times z^{K-v-1/2} L_v^{2K-2v-1}(z), \tag{14}$$

where $z = 2K \exp[-\alpha(r - r_e)]$, $K = (2D/g_{rr})^{1/2}/\alpha\hbar$, and $L_v^{2K-2v-1}$ is a generalized Laguerre polynomial.[27] The positions of CH-vibrational overtones of polyatomics are well described by Eq. (11), in which case ω and ωx are called the local-mode frequency and diagonal anharmonicity, respectively.

The Taylor series expansion of the Morse potential about $r = r_e$ may be written as

$$V_{\text{Morse}}(r) \approx (1/2)f_{rr}(r - r_e)^2 + (1/3!)f_{rrr}(r - r_e)^3$$
$$+ (1/4!)f_{rrrr}(r - r_e)^4 + \cdots, \tag{15}$$

where

$$f_{rr} = \omega^2/g_{rr} \tag{16}$$

and the nth-order force constant is given by

$$f_{r^n} = (-1)^n(2^{n-1} - 1)\alpha^{n-2}f_{rr}. \tag{17}$$

Upon substitution of Eq. (15), Eq. (9) becomes

$$\mathcal{H}_{\text{vib}} = \tfrac{1}{2}g_{rr}p_r^2 + (1/2)f_{rr}(r - r_e)^2 + (1/3!)f_{rrr}(r - r_e)^3$$
$$+ (1/4!)f_{rrrr}(r - r_e)^4 + \cdots = \mathcal{H}_{\text{vib}}^0 + \mathcal{H}_{\text{vib}}'. \tag{18}$$

If the expansion is truncated after the quartic term and the cubic and quartic terms are treated as perturbations to the zeroth-order harmonic oscillator Hamiltonian, term values are given exactly by Eq. (11). This is not a guarantee, however, that the truncated potential does not deviate strongly from Eq. (10).[28]

For the present work, the vibrational wave functions are described not by Eq. (14), but rather in a harmonic basis, viz.,

$$\chi_{\text{vib}}(v;q) = [(\gamma/\pi)^{1/2}/2^v(v!)]^{1/2}$$
$$\times \exp(-\tfrac{1}{2}\gamma q^2)H_v(\gamma^{1/2}q), \tag{19}$$

where $\gamma = \omega/\hbar$, q is the mass-weighted displacement, and H_v is a Hermite polynomial. This choice is computationally convenient and ensures that the vibrational wave functions go over smoothly to harmonic oscillator wave functions as the anharmonicity goes to zero. On the other hand, a relatively large harmonic basis is required in order to span (for practical purposes) the Morse function space. The required size of the basis is dependent upon the anharmonicity of the potential. If the temperature is sufficiently low, only the first few vibrational states will be significantly populated. However, a large basis is desirable in order to obtain reliable values for matrix elements involving highly vibrationally excited states, which have low thermal populations. Therefore, Eq. (15) was truncated after the ninth-order term and a basis of zeroth-order wave functions up to and including $v = 20$ was used. Matrix elements of terms up to q^4 have been tabulated.[24] Higher-order terms can be evaluated through repeated application of the recursion formula

$$H_{v+1}(z) = 2zH_v(z) - 2vH_{v-1}(z). \tag{20}$$

C. The rovibrational Hamiltonian

The hindered internal rotation and the CH-stretching vibration were coupled in the following manner. According to experimental and theoretical indications,[1,3] the CH-stretching frequency ω decreases approximately linearly as the equilibrium CH-bond length increases;

$$\omega - \omega_{\text{ref}} = -\alpha\Delta v(r_e - r_{\text{ref}}), \tag{21}$$

where α is an empirical proportionality constant and Δv is the change in vibrational quantum number for a given overtone. Concurrently, the bond length increases with the rotational angle ϕ as

$$r_e - r_i = \delta \sin^2 \phi, \tag{22}$$

where r_i is the length of the methyl CH-bond when it lies in the plane of the phenyl ring, which corresponds to $\phi = 0$. From the equilibrium bond lengths obtained from geometry-optimized molecular orbital (MO) calculations with the 4-21G and 4-31G bases,[18,20] δ is about 0.28 pm. For comparison, the empirical value of α and the frequency shifts observed experimentally for $\Delta v = 3-5$ of toluene[13] suggest that δ is 0.29 ± 0.03 pm. Of course, this estimate is not wholly independent because the bond lengths used to establish Eq. (21) are themselves from *ab initio* calculations. Because the changes in both frequency and equilibrium bond length with ϕ are due to changes in the molecular electronic structure, it is reasonable to expect that k and r_e are dependent.

With the in-plane methyl CH-bond as the reference in Eq. (21), the harmonic approximation yields

$$k(\phi) = [1 - (\alpha\delta/\omega_i)\sin^2 \phi]^2\omega_i^2/g_{rr} \approx k_i - \kappa \sin^2 \phi, \tag{23}$$

where $\kappa/k_i \ll 1$ and $k_i = f_{rr}$, the in-plane force constant. Because α is about $110 \text{ cm}^{-1} \cdot \text{pm}^{-1}$ experimentally[3] and ω_i is about 3083 cm^{-1} from a local-mode analysis,[13] κ/k_i is estimated to be 0.01, i.e., κ amounts to a few percent of k_i at most. This represents a very weak coupling between the rotational and vibrational motions. Such coupling was introduced by substitution of Eqs. (22) and (23) into *the harmonic term* in Eq. (15), which becomes

$$\frac{1}{2}k(\phi)(r-r_e)^2$$

$$=\frac{1}{2}k_i(r-r_i)^2-k_i\delta(r-r_i)\sin^2\phi$$

$$-\frac{1}{2}\kappa(r-r_i)^2\sin^2\phi+\kappa\delta(r-r_i)\sin^4\phi$$

$$+\frac{1}{2}k_i\delta^2\sin^4\phi-\frac{1}{2}\kappa\delta^2\sin^6\phi. \tag{24}$$

The first term on the right hand side is just the harmonic potential for the in-plane CH-bond. Therefore, the parameters for the Morse potential are associated with the reference in-plane CH-bond. The next three terms couple the vibrational and rotational motions. The last two terms shift the energy levels, but do not couple the motions because these terms depend upon the rotation angle only, i.e., they contribute to the rotational potential only. These terms are dropped for two reasons. Firstly, they are second- or third-order in the coupling parameters κ and δ. Secondly, it is well known that the rotational potential is dominated by

the V_6 term in toluene and by the V_3 term in o-xylene. However, the last two terms in Eq. (24) would introduce twofold, fourfold, and sixfold terms into these rotational potentials, contrary to the experimental findings and regardless of the degree of vibrational excitation of the CH-bond.

In apparent disagreement with the present approach, Cavagnat and Lascombe have indicated that the hindering potential for toluene-αd_2 is dominantly twofold[5] or three-fold,[15] even in the vibrational ground state. In general, rotational potentials correspond to sections through the potential energy hypersurface for all nuclear motions and represent the geometrical dependence of the total energy (electronic energy plus internuclear repulsions) within the Born–Oppenheimer approximation. Because this total energy does not depend on nuclear masses, a qualitative change in the symmetry of the toluene potential upon isotopic substitution is not expected. Indeed, asymmetrical substitution of the phenyl group and trideuteration of the methyl group have no apparent large-scale effects on the r_0-structure or the rotational barrier according to microwave investigations.[11,12]

In the basis of product functions $|v,m\rangle = |\chi_{\text{vib}}(v;q)\chi_{\text{rot}}(m;\phi)\rangle$, the matrix elements of these terms may be evaluated analytically to yield

$$\langle v',m'|(r-r_i)\sin^2\phi|v,m\rangle=\frac{1}{4}[v'g_{rr}/2\gamma]^{1/2}\delta_{v',v+1}\{(2-\hbar_m\delta_{m,1})\delta_{m',m}-[1+(2^{1/2}-1)\delta_{m,0}]\delta_{m',m+2}\}, \tag{25}$$

$$\langle v',m'|(r-r_i)^2\sin^2\phi|v,m\rangle=\frac{1}{4}(g_{rr}/\gamma)\{(v+\tfrac{1}{2})\delta_{v',v}+\tfrac{1}{2}[v'(v'-1)]^{1/2}\delta_{v',v+2}\}\{(2-\hbar_m\delta_{m,1})\delta_{m',m}$$

$$-[1+(2^{1/2}-1)\delta_{m,0}]\delta_{m',m+2}\}, \tag{26}$$

and

$$\langle v',m'|(r-r_i)\sin^4\phi|v,m\rangle=\frac{1}{8}[v'g_{rr}/2\gamma]^{1/2}\delta_{v',v+1}\{(3-2\hbar_m\delta_{m,1}+1/2\hbar_m\delta_{m,2})\delta_{m',m}$$

$$-[2+2(2^{1/2}-1)\delta_{m,0}-\tfrac{1}{2}\hbar_m\delta_{m,1}]\delta_{m',m+2}-\tfrac{1}{2}[1-(2^{1/2}-1)\delta_{m,0}]\delta_{m',m+4}\}, \tag{27}$$

where $v' \geqslant v$, $m' \geqslant m$ is assumed for illustration. Terms diagonal in m are dropped because they would be absorbed into the anharmonicity in a local-mode analysis. The coupled Hamiltonian is

$$\mathcal{H}_{\text{coup}}=-\tfrac{1}{2}\hbar^2[(1/I)\partial^2/\partial\phi^2+g_{rr}\partial^2/\partial r^2]+\tfrac{1}{2}V_6[1\pm\cos(6\phi)]+\tfrac{1}{2}k_i(r-r_i)^2-k_i\delta(r-r_i)\sin^2\phi$$

$$-\tfrac{1}{2}\kappa(r-r_i)^2\sin^2\phi+\kappa\delta(r-r_i)\sin^4\phi+(1/3!)f_{rrr}(r-r_i)^3+(1/4!)f_{rrrr}(r-r_i)^4+\cdots, \tag{28}$$

where practical necessity demands that the series be truncated at the Nth-order term. In the present work, tenth- and higher-order terms were excluded.

D. Calculation of the overtone spectrum

Only transitions from the ground vibrational manifold are considered here. Within the local-mode model, the highly vibrationally excited methyl-CH stretch is described by a linear combination of component Morse oscillators.[29] Within the dipole approximation, the transition moment operator generates only single particle excitations, i.e.,

$|v00\rangle \leftarrow |000\rangle$. In the absence of coupling between oscillators, the frequency distribution of the excitation spectrum is identical to that of the corresponding component oscillator. For the present work, the ground and excited vibrational states are described in terms of a single diatomic oscillator along the internal coordinate q.

According to first-order, time-dependent perturbation theory, the transition probability is proportional to the squared modulus of the electric dipole moment operator μ, which is represented by the MacLaurin series

$$\mu=\mu_0+\left(\frac{d\mu}{dq}\right)_0 q+\frac{1}{2}\left(\frac{d^2\mu}{dq^2}\right)_0 q^2+\cdots. \tag{29}$$

TABLE I. Parameter values for the calculation of overtone spectra of toluene and o-xylene.

	Toluene	o-xylene
ω_i/cm^{-1}	3125.0	3125.0
$\omega_i x/\text{cm}^{-1}$	−62.2	−62.2
Reduced mass, $\mu/\text{g} \cdot \text{mol}^{-1}$	0.93	0.93
Reduced moment, $I/10^{-47}\,\text{kg} \cdot \text{m}^2$	5.1	5.1
Force constant variation, κ/k_i	0.025	0.025
Bond length variation, δ/pm	1.0	1.2
Barrier height, $V_n/\text{kJ} \cdot \text{mol}^{-1}$	0.059	5.000
Barrier symmetry, n	6	3

There are some indications that second-order terms play a role in the determination of CH-overtone intensities, but this additional complication is deferred for the present. If electrical harmonicity is assumed, i.e., second- and higher-order terms in Eq. (29) are ignored, and if $(d\mu/dq)_0$ is independent of the dihedral angle ϕ, the intensity of a rovibrational transition $|\psi_{v,m'}\rangle \leftarrow |\psi_{0,m}\rangle$ is given by

$$I(v,m';0,m) = I_0 \exp[-(E_{v,m'} - E_{0,m})/k_B T]$$

$$\times \{[\,|\langle\psi_{v,m'}|q\cos\phi|\psi_{0,m}\rangle|^2$$

$$+ |\langle\psi_{v,m'}|q\sin\phi|\psi_{0,m}\rangle|^2]$$

$$\times\sin^2\theta + |\langle\psi_{v,m'}|q|\psi_{0,m}\rangle|^2\cos^2\theta\}, \quad (30)$$

where I_0 is a constant, $|\psi_{v,m}\rangle$ is an eigenfunction of the coupled Hamiltonian in Eq. (28) with eigenvalue $E_{v,m}$ and θ is the fixed angle between the methyl rotation axis and the CH-bond vector which is taken to be 70.53°. The indices v,m are clearly not good quantum numbers, but merely convenient labels. The relevant integrals are evaluated between eigenfunctions in the product basis.

Intensities were calculated for all transitions from the ground-state manifold with frequencies in the range $\omega[\Delta v + x\Delta v(\Delta v + 1)\pm 1/8]$. Transitions with relative intensity below 0.05 were ignored. This step of the calculation is the most time consuming and, for this reason, least-squares fitting procedures for parameter refinement were not attempted; the values of κ, δ, and ω_i were adjusted manually to obtain profiles similar to the experimental spectra. Consequently, the spectra and parameter values displayed here are illustrative and do not correspond to optimum values.

III. RESULTS AND DISCUSSION

The computed spectra are plotted as superpositions of Lorentzian lines of the calculated intensity and fixed width. The calculated spectra correspond to 359 K, the temperature at which the experimental spectra were recorded.[13] The full width at half maximum (FWHH) selected for the Lorentzian lines of the calculated spectra is 50 cm^{-1} for toluene and 30 cm^{-1} for o-xylene, which adequately represents the experimental envelopes of the inhomogeneously broadened bands. Differences in the homogeneous linewidths have been attributed to differing mechanisms for intramolecular vibrational energy redistribution (IVR). According to the local-mode analysis of the overtone spectra, ω_i is 3083 cm^{-1} and $\omega_i x$ is −62.2 cm^{-1} for toluene.[13]
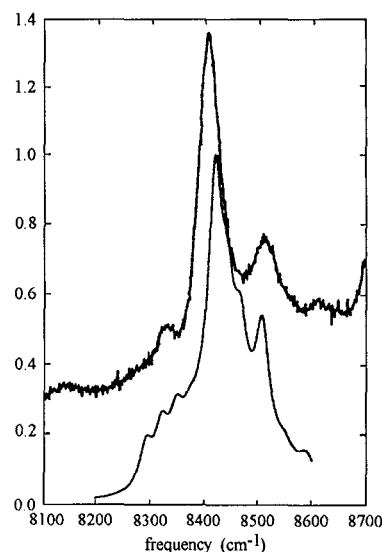

FIG. 1. The methyl-CH stretching band for o-xylene at $\Delta v=3$ and 359 K. The upper curve is the experimental spectrum from Ref. 13. The lower curve is the spectrum calculated on the basis of the parameters in Table I with Lorentzian lines having a FWHH of 30 cm^{-1}. For the synthetic spectrum, the bond length variation upon rotation is 1.2 pm and the threefold barrier height is 5 kJ · mol^{-1}. Other parameter values are the same as for toluene.

As noted above, these numbers also contain contributions from the coupling interaction. We have chosen to keep $\omega_i x$ at the measured value and increase ω_i to 3125 cm^{-1} in order to bring the calculated and experimental band profiles into coincidence. The same parameter values were used for o-xylene, but the potential was changed from sixfold to threefold, the barrier was increased from 59 J · mol^{-1} (Refs. 11 and 12) to 5 kJ · mol^{-1},[17-19] and the bond length variation is presumed to be slightly greater in o-xylene as a result of the strong interaction of the proximate methyl groups. (See Table I.)

A. o-xylene

Calculated methyl-CH overtone spectra for $\Delta v=3$ and 4 of o-xylene appear in Figs. 1 and 2, respectively. Most of the intensity of the high-frequency "in-plane" band at $\Delta v=3$ is associated with a simultaneous transition from the ground state to the first rotationally excited state of the methyl group, similar to an R-branch transition in which the quantum number for overall rotation of the molecule changes by $+1$. Of course, overall rotations are neglected in the present treatment and, in any case, further splitting of the calculated spectral lines would be masked by (and a source of) line broadening. Both the ground state and the upper state functions have probability maxima in the potential wells outside the plane of the aromatic ring. The prominent low-frequency "out-of-plane" band is dominated by a transition from the first rotationally excited state of the vibrational ground state, for which the probability maxima lie in the out-of-plane wells, to the rotational ground state of the vibrationally excited methyl rotor, for which the maxima lie similarly (P-like). In the $\Delta v=4$ re-
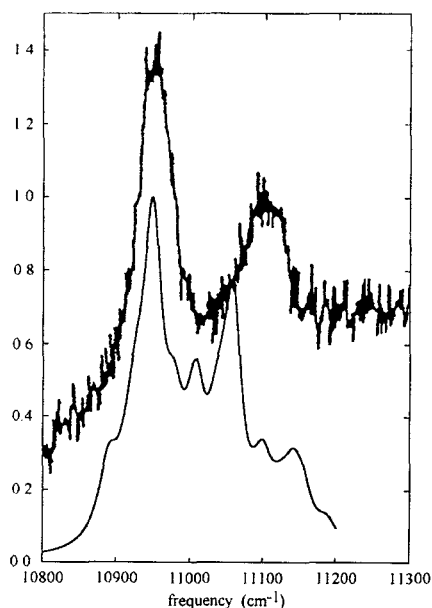
FIG. 2. The methyl-CH stretching band for o-xylene at $\Delta v = 4$ and 359 K. The upper curve is the experimental spectrum from Ref. 13. The lower curve is the spectrum calculated on the basis of the parameters in Table I with Lorentzian lines having a FWHH of 30 cm^{-1}. For the synthetic spectrum, the bond length variation upon rotation is 1.2 pm and the threefold barrier height is 5 kJ $\cdot$ mol^{-1}. Other parameter values are the same as for toluene.

gion, the prominent high- and low-frequency bands are dominated by the same rotational transitions. A smaller peak near 11 000 cm^{-1} in the calculated spectrum corresponds to a transition between the fourth rotational energy levels of the lower and upper manifolds (Q-like). This peak may be hidden under the low-frequency shoulder of the "in-plane" band in the observed spectrum.

B. Toluene

The toluene spectra in Fig. 3 and 4 show three prominent bands. In the absence of rovibrational coupling, the sixfold rotational potential splits the transitions involving the $m = 3$ levels.[12] The influence of κ or δ is to skew the distribution of lines toward lower frequencies, relative to the symmetrical rotational contour. Clearly, the band envelope conceals a wealth of detail. The following assignments can be made and apply to a range of parameter values about the selected values.

The principal contributions to the high- and low-frequency bands are due to transitions from the ground to the second rotationally excited state (S-like) and from the second rotationally excited state to the ground state of the vibrationally excited methyl rotor (O-like), respectively.

In addition, the so-called "free rotor" band appears between the outer bands. For $\Delta v = 3$ of toluene, this is composed principally of three transitions from the third, fifth, and tenth rotationally excited states into the first, third, and sixth rotationally excited states of the vibrationally excited rotor, respectively. Because these states are delocalized, the appellation "free rotor" seems appropriate.
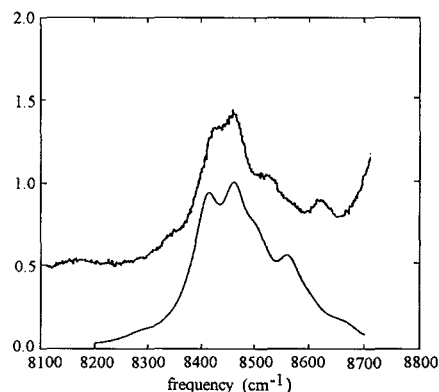

FIG. 3. The methyl-CH stretching band for toluene at $\Delta v = 3$ and 359 K. The upper curve is the experimental spectrum from Ref. 13. The lower curve is the spectrum calculated on the basis of the parameters in Table I with Lorentzian lines having a FWHH of 50 cm^{-1}. For the synthetic spectrum, the bond length variation upon rotation is 1.0 pm and the sixfold barrier height is 59 J $\cdot$ mol^{-1}. Other parameter values are the same as for o-xylene.

The high- and midfrequency bands in the $\Delta v = 4$ region are not resolved in the calculated spectrum, but comprise two sets of transitions. The high-frequency component is dominated by transitions from the ground to the second rotationally excited state (S-like) and from the first to the fifth rotationally excited state. The midfrequency or "free rotor" band consists principally of transitions from the third to the first rotationally excited state (O-like) and between fifth rotationally excited states (Q-like), well above the rotational barrier. The low-frequency band is most intense. It corresponds to the transition from the second rotationally excited state to the ground state of the vibrationally excited methyl rotor (O-like).

The calculated spectra are essentially unaffected by changing the sign of the cosine term in Eq. (4), which
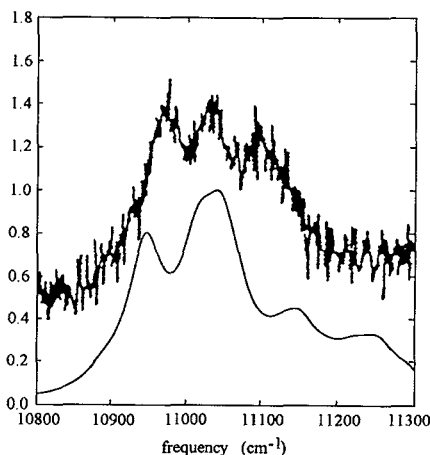

FIG. 4. The methyl-CH stretching band for toluene at $\Delta v = 4$ and 359 K. The upper curve is the experimental spectrum from Ref. 13. The lower curve is the spectrum calculated on the basis of the parameters in Table I with Lorentzian lines having a FWHH of 50 cm^{-1}. For the synthetic spectrum, the bond length variation upon rotation is 1.0 pm and the sixfold barrier height is 59 J $\cdot$ mol^{-1}. Other parameter values are the same as for o-xylene.

shifts the conformational preference from $\phi=0°$ to $\phi=90°$. Therefore, the similarity in peak positions between the toluene and o-xylene spectra does not imply that the "planar" $\phi=0°$ conformation is the more stable. Indeed, the spectra provide no apparent indication of the conformational preference if the barrier to internal rotation is small. The structure arises through redistribution of intensity in the rotational wings due to weak coupling between the vibrational and rotational motions. As other authors have already indicated, this is a sensitive probe of the electronic interactions between the methyl rotor and the phenyl ring.[30,31]

Gough and Henry have suggested[13] that this sensitivity may provide a method for estimation of the barrier to internal rotation. From Eq. (21) and (22)

$$\langle\omega-\omega_i\rangle=\langle\omega\rangle-\omega_i=\omega_{\text{free}}-\omega_i=-\alpha\delta(\Delta v)\langle\sin^2\phi\rangle, \tag{31}$$

i.e., the position of the "free rotor" peak measures $\langle\sin^2\phi\rangle$, which is related to the barrier height. Similar expressions that relate average values to NMR parameters have proved useful.[32] However, this expression also involves averaging over the vibrational coordinate and the values of α and δ are not sufficiently well defined to make Eq. (31) immediately useful.

Because the parameters are quite similar, the interpretation of the toluene spectra applies to m-xylene and p-xylene as well. In contrast, the o-xylene spectra show two prominent bands. The only differences between this parameter set and that for toluene are a change in the foldedness of the potential in Eq. (4) from $n=6$ for toluene to $n=3$ for o-xylene, a change in the barrier height in Eq. (4) from 59 J·mol^{-1} for toluene to 5 kJ·mol^{-1} for o-xylene, and an increase in the bond-length variation from 1.0 to 1.2 pm. These three changes, which are associated with strong interactions between the adjacent methyl groups, overshadow more subtle changes in the electronic interactions between the methyl and phenyl groups.

In this work, the homogeneous width of the lines that comprise the broad bands has been chosen to reproduce the experimentally observed envelopes. Relaxation processes have not been considered, although recent work has made progress in describing such processes.[33]

IV. SUMMARY

In conclusion, we have shown that the band structure of the methylbenzene spectra can be understood in a fashion consistent with the bond length-frequency shift correlation and with the conformational behavior. From the analytical viewpoint, we emphasize caution in the assignment and interpretation of such spectra. For a relatively high barrier to internal rotation of the methyl group, as in o-xylene, the wave functions are localized within potential wells associated with particular conformers and bands can be reasonably assigned to chemically distinct CH-bonds. On the other hand, for low barriers, as in toluene and the less hindered xylenes, the wave functions exhibit significant

dispersion and distinctions between classical conformers are artificial. From the physical viewpoint, the spectral data are a sensitive probe of the interactions between moieties. Although weak, these interactions can have profound photochemical and photophysical consequences, e.g., the acceleration of intramolecular vibrational redistribution[30] and the frustration of mode-selective photoreactions.

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