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Methyl versus Aryl CH and CD Stretching Overtone Intensities in the Vapor Phase Spectra of Toluenes

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Room temperature vapor phase overtone spectra of toluene-d_0 and -d_8 have been recorded in the CH and CD stretching regions corresponding to $\Delta v_{CH} = 2-7$ and $\Delta v_{CD} = 2-6$. The vibrational overtone spectra are recorded by conventional near-infrared spectroscopy and by intracavity titanium:sapphire and dye laser photoacoustic spectroscopy. Absolute oscillator strengths are obtained from the conventional spectra and relative oscillator strengths within a given overtone from the photoacoustic spectra. Peaks corresponding to two nonequivalent aryl local modes are consistently assigned. The structure of the methyl band is complicated by methyl torsion. We show a simple method of calculating the absolute intensity of this methyl band. Oscillator strengths for both the aryl and the methyl transitions are calculated with an anharmonic oscillator local mode model and *ab initio* dipole moment functions. Our simple calculations show very good agreement between observed and calculated intensities, both for absolute total intensities and for relative intensities between the two aryl groups and between the aryl and methyl groups. This agreement indicates that most of the intensity in the methyl band arises from the CH or CD stretching transitions.

Introduction

In general, CH stretching overtone spectra are characterized by one peak for each of the nonequivalent CH oscillators in a molecule and can be interpreted within the local mode model of molecular vibration.[1,2] The model has been successful in assigning peak positions of the various XH bonds present in the molecule. Peak positions can be calculated with a harmonically coupled anharmonic oscillator (HCAO) local mode model with reasonable accuracy.[3−6] These peak positions are very sensitive to the CH bond lengths with the shortest bond length corresponding to the highest frequency CH stretching oscillator.[7] We have recently been able to distinguish experimentally between the CH bonds in naphthalene which have calculated bond lengths that differ by less than 1 mÅ.[8,9] In molecules with methyl groups, as the methyl group rotates, the CH bond lengths change slightly (a few milliangstroms).[10,11] This change can have a significant effect on the CH stretching frequencies.[7]

Microwave experiments show that toluene has a very low 6-fold torsional barrier of height 4.9 cm^{-1}.[12] Various *ab initio* calculations[10,11] determine the barrier height (excluding the zero-point vibrational energy correction) to be less than 10 cm^{-1} but do not agree on which of the two possible conformers, either the parallel (one α-CH (methyl CH) in the plane of the ring, $\|$) or the perpendicular (one α-CH perpendicular to the plane, $\perp$), is the lowest.

Molecules like propane and dimethyl ether have a high barrier to methyl torsion, and the methyl group does not rotate in the time frame of a CH stretching vibration. Thus, the methyl overtone region consists of only two peaks: one for the two out-of-plane CH bonds and one for the in-plane CH bond of the methyl group.[13,14] However, as the barrier height decreases, the methyl region changes shape. In particular, intensity begins to appear in the region between the in-plane and out-of-plane peaks. The overtone spectra of acetone and 2-*cis*-butene, which have intermediate barrier heights, clearly show this effect.[14,15] Toluene has one of the lowest torsional barriers, and in the overtone spectrum this center area becomes as intense as the in-plane and out-of-plane peaks[16,17] (if it is still meaningful to refer to in-plane and out-of-plane peaks). The center peak in the toluene spectrum was previously assigned as a free rotor peak.[17]

Surprisingly few overtone spectra of the toluenes have been published.[16,17] Berry *et al.* have recorded the $\Delta v_{CH} = 5$ region of the CH stretching overtone spectrum of vapor phase toluene at room temperature.[16] Gough and Henry recorded the $\Delta v_{CH} = 3$ and 4 regions of the spectrum of vapor phase toluene at an elevated temperature.[17] On basis of the local mode model, *ab initio* optimization, and the bond length frequency correlation, we would expect for a given overtone region of toluene that the spectrum would consist of a torsionally perturbed methyl region to the low-energy side and a higher-energy aryl region with two peaks.

Recently, CH stretching overtone intensities of useful accuracy have been calculated with the HCAO local mode model and *ab initio* dipole moment functions.[8,15,18,19] We use the HCAO approach and *ab initio* dipole moment functions to calculate absolute intensities of both the methyl and aryl regions in the CH and CD stretching overtone spectra of toluene-d_0 and -d_8. It is important to note that these calculations have no adjustable parameters. Very few calculations and measurements of CD stretching overtone intensities exist.[19,20] This is in part due to the fact that transitions for CD stretching oscillators are intrinsically weaker than those for CH stretching oscillators and in part due to the heavier D atom which leads to a smaller CD stretching frequency and increased coupling.[20] Thus, CD stretching overtone spectra deviate from what is expected on the basis of the simple local mode model and are more difficult to interpret.[20]

The HCAO local mode model neglects coupling to all lower frequency modes and approximates the coupling between CH bonds by harmonic terms. In 1,3-butadiene[19] and naphthalene,[8,9] we have observed that it is a good approximation to neglect coupling between CH oscillators where the hydrogens are bonded to different carbon atoms. In the present work we also neglect the coupling between the methyl CH oscillators and argue that this coupling primarily spreads out the intensity and

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contributes little to the total intrinsic methyl region intensity, except for the $v = 2$ region. Spectra of CH impurities in the deuterated samples are used to investigate the coupling between CH bonds.

In the present paper, we have not attempted to model the specific band profile of the methyl group. We have calculated the total intensity of the methyl group as an average over the torsional angle (*vide infra*). In the literature there have been a few attempts to calculate spectral profiles for methyl regions of molecules with low torsional barriers. Anastasakos and Wildman[21] were able to predict some of the features in the lower ($\Delta v_{CH} = 3$ and 4) methyl overtone spectra of toluene and *o*-xylene. Their model assumed only one rotating CH bond and a linear dipole moment function along this bond. Cavagnat *et al.*[22] calculated the profile of the methyl regions in the overtone spectra of monohydrogenated nitromethane, a molecule with only one CH in the methyl group. They used an *ab initio* dipole moment function expanded in both the CH stretching and the torsional angle and obtained impressive agreement with experiment. Zhu *et al.*[23] have used a model similar to the model by Cavagnat *et al.*[22] to calculate the methyl regions of 2,6-difluorotoluene with reasonable success. The model by Zhu *et al.* limits the expansion of the dipole moment function in the torsional angle but includes all three CH bonds of the methyl group.[23] They attribute the methyl profile to a large number of transitions that arise from terms involving torsion−stretching coupling, both in the Hamiltonian and in the dipole moment function.

Comparison of the total methyl to aryl intensity allows us to investigate whether or not the majority of intensity in the methyl band arises from CH stretching transitions. Alternatively, it may be necessary to include intrinsic intensity contributions (which would translate to dipole moment expansion terms) from other modes like torsion. We will also compare the relative intensities of the two aryl peaks in an attempt to confirm the previous assignment of the highest energy and most intense aryl peak to the $CH_{m,p}$ oscillators.

Experimental Section

Toluene-d_0 (spectroscopic grade) was obtained from Caledon Laboratories Limited. The 99+ atom % D toluene-d_8 was obtained from Aldrich, and the 100 atom % D toluene-d_8 was obtained from MSD isotopes. All samples were used without further purification except for degassing.

The room temperature vapor phase spectra of toluene and toluene-d_8 were recorded in the lower-energy overtone CH and CD stretching regions with conventional absorption spectroscopy and in the higher-energy overtone regions with intracavity laser photoacoustic spectroscopy (ICL-PAS).

A conventional spectrophotometer (Cary 5e UV−vis-near-IR) was fitted with a variable path length White cell (Foxboro variable path length cell fitted with BK7 Schott glass windows from Melles Griot). The wavenumber accuracy of the Cary 5e spectrophotometer is less than ±5 cm^{-1} in the near-infrared and visible regions. Background scans with an evacuated cell with a back pressure of 60 mTorr were recorded and subtracted for each of the Cary spectra. Cary spectra of toluene-d_0 were recorded in the $\Delta v_{CH} = 2-4$ regions, and of toluene-d_8 (99+ and 100%) in the $\Delta v_{CH} = 2$ and 3 regions and $\Delta v_{CD} = 2-4$ regions.

The experimental absolute oscillator strength f of an absorption band can be determined from these conventional spectra and the following equation[24]

$$f = 2.6935 \times 10^{-9}\ [\mathrm{K^{-1}\ Torr\ m\ cm}]\ \frac{T}{pl}\int A(\tilde{\nu})\, d\tilde{\nu} \qquad (1)$$

where T is the temperature, p is the sample pressure, l is the path length, A is the absorbance, and $\tilde{\nu}$ is the frequency in cm^{-1}.

Our version of ICL-PAS consists of an argon ion pumped titanium:sapphire solid state laser or dye laser and has been described in detail elsewhere.[25,26] An electret microphone (Knowles Electronics Inc., EK 3132) was used in the photoacoustic cell. As explained in detail in previous papers, the wavenumber accuracy of our ICL-PAS experiment was better than ±1 cm^{-1}. ICL-PAS spectra of toluene were recorded in the $\Delta v_{CH} = 4-7$ regions and of toluene-d_8 (99+ and 100%) in the $\Delta v_{CH} = 4$ region and $\Delta v_{CD} = 5$ and 6 regions. The spectrum of toluene-d_0 in the $\Delta v_{CH} = 6$ region was constructed from two overlapping spectra with the use of two different laser dyes (DCM and R6G). The spectrum of toluene-d_0 in the $\Delta v_{CH} = 7$ region was recorded with the use of the laser dye Coumarin 6, and a small amount of argon buffer gas was added to the cell with the sample both here and for the $\Delta v_{CH} = 6$ spectrum. The absolute absorbance is not known, and we can only obtain the relative oscillator strengths in the ICL-PAS spectra.[25,26]

The overtone spectra were decomposed into component peaks with a deconvolution program within Spectra Calc.[27] The spectra were deconvoluted with a number of Lorentzian peaks and a linear base line. The deconvolution provides peak positions and areas. Uncertainty in the deconvolution is very dependent on peak resolution. We generally estimate the uncertainty to be less than 5 cm^{-1} for peak positions and less than 10% for intensities of well-resolved peaks like the high-energy aryl peaks. However, for the poorly resolved peaks we estimate a much larger uncertainty. The total methyl band intensity is found as the sum of the areas of the deconvoluted peaks in the methyl band. We estimate the error in the methyl area to be less than 20% with a large portion of the error arising from uncertainty with the base line.

Calculation of Methyl and Aryl Overtone Intensities

The oscillator strength f of a vibrational transition from the ground vibrational state g to an excited vibrational state e is given by[24]

$$f_{e\leftarrow g} = 4.702 \times 10^{-7}\ [\mathrm{cm\ D^{-2}}]\ \tilde{\nu}_{eg}|\vec{\mu}_{eg}|^2 \qquad (2)$$

where $\tilde{\nu}_{eg}$ is the transition frequency in cm^{-1} and $\vec{\mu}_{eg} = \langle e|\vec{\mu}|g\rangle$ is the transition dipole moment in debye. Thus, in order to calculate vibrational intensities, we need both a dipole moment function and vibrational wave functions.

Toluene is well-known for its very small 6-fold barrier to internal methyl rotation (torsion). Thus, in the ground state the methyl group will rotate almost freely. As the vibrational energy is increased, the methyl torsion becomes more hindered but is still relatively free. This torsion of the methyl group will have an effect on the CH bond lengths in the molecule and thus also on the peak positions in the CH stretching overtone spectra. It will also affect the dipole moment function for each of the CH bonds. Both the variation of the CH oscillator potential and the dipole moment function with the torsional angle have to be considered in calculations of intensities for both the aryl and methyl CH bonds (*vide infra*).

We have used an axis system with the z axis along the CC bond around which the methyl group rotates, the x axis in the plane of the ring with the aryl CH in the 2-position at positive x, and the y axis perpendicular to the plane. The angles between the three methyl CH bonds are kept fixed. We define the position of the methyl group by the torsional angle, θ, which is defined as the angle between one α-CH bond and the plane of the ring. The two extremes on the potential energy curve are the parallel (||) and the perpendicular (⊥) conformers. Our *ab initio* calculations at the Hartree−Fock (HF)/6-31(d) and HF/6-311+G(d,p) levels predict in agreement with previous calculations[11] that the ⊥ conformer has the lowest energy. However, the energy difference is very small, and *ab initio* predictions of such small barriers are not conclusive.

We give here a brief outline of the models used to calculate intensities for a single isolated oscillator and refer to recent papers for more details of the HCAO local mode model and the procedures used to obtain *ab initio* dipole moment functions.[8,18,19] We use the local mode theory of anharmonic oscillators to obtain vibrational wave functions and energies. The Hamiltonian of an isolated CH oscillator that is described as a Morse oscillator can be written as

$$(H - E_{|0\rangle_j})/hc = v_j\tilde{\omega}_j - (v_j^2 + v_j)\tilde{\omega}_j x_j \qquad (3)$$

where $E_{|0\rangle_j}$ is the energy of the vibrational ground state and $\tilde{\omega}_j$ and $\tilde{\omega}_j x_j$ are the local mode frequency and anharmonicity of the CH$_j$ oscillator. The eigenstates of the Hamiltonian are denoted by $|v_j\rangle_j$ where v_j is the quantum number of vibrational excitation in the CH$_j$ oscillator. These eigenstates are thus Morse oscillator wave functions.

The dipole moment function is expressed as a series expansion in the internal CH displacement coordinate, q. For an isolated CH oscillator, we have

$$\vec{\mu}(q) = \sum_i \vec{\mu}_i q^i \qquad (4)$$

where

$$\vec{\mu}_i = \frac{1}{i!}\left.\frac{\partial^i \vec{\mu}}{\partial q_j^i}\right|_{\mathrm{e}} \qquad (5)$$

We have limited the expansion in eq 4 to fourth-order terms.[18] To determine the coefficients $\vec{\mu}_i$, we use *ab initio* molecular orbital theory to calculate dipole moment values at geometries in which one of the CH bonds in the molecule is displaced from equilibrium. This provides us with one-dimensional grids of the dipole moment as a function of q. For each of the CH bonds we calculate seven points with a maximum displacement of ±0.3 Å in steps of 0.1 Å. This assures a reasonable mapping of the dipole moment function and limits round-off errors.[18] All grid points and the optimized geometry are calculated with Gaussian 92.[28] The dipole moment coefficients $\vec{\mu}_i$, are found from standard numerical differential techniques.[29]

In this paper dipole moment functions have been calculated with the Hartree−Fock (HF) theory and both a 6-31G(d) and a 6-311+G(d,p) basis set. Previous work has suggested that the 6-311+G(d,p) basis set is the smallest basis set that is adequate for absolute intensities and that electron correlation has little effect on overtone intensities.[30,31]

Aryl CH Oscillators. *Ab initio* optimizations of toluene with the methyl group in the planar and the perpendicular conformers show that the aryl CH bonds change very little upon rotation of the methyl group. The calculations also show that, independent of θ, the CH bonds in the 3-, 4-, and 5-position have almost the same bond length and that the bond lengths in the 2- and 6-position are virtually the same.[10] Thus, independent of whether the || or the ⊥ conformer has the lowest energy, we would expect only two aryl peaks in the overtone spectra in agreement with what is observed.[16,17]

TABLE 1: *Ab Initio* HF/6-311+G(d,p) Dipole Moment Derivative Expansion Coefficients for Aryl and Methyl CH Bonds in Toluene[a]

$\vec{\mu}_i$	x/y^b	z	bond
$\vec{\mu}_1$/D Å^{-1}	−0.516	−0.330	CH$_o$
$\vec{\mu}_2$/D Å^{-2}	−1.020	−0.540	CH$_o$
$\vec{\mu}_3$/D Å^{-3}	−0.156	−0.0268	CH$_o$
$\vec{\mu}_4$/D Å^{-4}	−0.219	−0.155	CH$_o$
$\vec{\mu}_1$/D Å^{-1}	−0.509	0.400	CH$_m$
$\vec{\mu}_2$/D Å^{-2}	−1.054	0.653	CH$_m$
$\vec{\mu}_3$/D Å^{-3}	−0.118	0.0666	CH$_m$
$\vec{\mu}_4$/D Å^{-4}	−0.237	0.131	CH$_m$
$\vec{\mu}_1$/D Å^{-1}	−0.0119	0.599	CH$_p$
$\vec{\mu}_2$/D Å^{-2}	−0.0230	1.258	CH$_p$
$\vec{\mu}_3$/D Å^{-3}	−0.00216	0.130	CH$_p$
$\vec{\mu}_4$/D Å^{-4}	−0.00221	0.275	CH$_p$
$\vec{\mu}_1$/D Å^{-1}	−0.628	−0.560	α-CH$_{\parallel}$
$\vec{\mu}_2$/D Å^{-2}	−0.890	−0.783	α-CH$_{\parallel}$
$\vec{\mu}_3$/D Å^{-3}	−0.0490	−0.140	α-CH$_{\parallel}$
$\vec{\mu}_4$/D Å^{-4}	−0.300	0.230	α-CH$_{\parallel}$
$\vec{\mu}_1$/D Å^{-1}	−0.594	−0.550	α-CH$_{\perp}$
$\vec{\mu}_2$/D Å^{-2}	−1.059	−1.157	α-CH$_{\perp}$
$\vec{\mu}_3$/D Å^{-3}	−0.181	−0.365	α-CH$_{\perp}$
$\vec{\mu}_4$/D Å^{-4}	−0.365	0.0762	α-CH$_{\perp}$

[a] The indices refer to the order of the expansion coefficients. [b] For the CH$_p$ and the α-CH$_{\perp}$ it is the *y* component, the *x* component is zero. For the other bonds it is the *x* component, and the *y* component is either zero or very small due to fact that the ring is almost in the *yz* plane.

In 1,3-butadiene and naphthalene we found the coupling between the CH oscillators which were not attached to the same carbon atom to be negligible.[8,9,19] Since the aryl hydrogens in toluene are attached to different carbon atoms, the coupling between them will be small and our assumption of neglecting coupling between the aryl CH oscillators will be valid.

The dipole moment function of the aryl bonds changes very little with rotation of the methyl group. Furthermore, part of the change in each of the Cartesian components is due to a shift from one of the Cartesian components to another, and thus the effect is even less significant in the calculation of intensities. We found that the change in the calculated CH stretching intensities for the CH bond in the 2-position, the aryl bond most affected by the methyl group rotation, showed less than 5% variation with methyl torsion. The dipole coefficients for the CH bonds in the 2-, 3-, and 4-positions calculated at the HF/6-311+G(d,p) level are given in Table 1. It is not surprising that the electronic density around the aryl CH bonds is affected only minimally by the position of the hydrogen atoms in the methyl group which are quite distant on a molecular scale.

The overtone intensities of the high-energy aryl peak are calculated as the sum of three CH oscillators (the 3-, 4-, and 5-positions) with the same Morse parameters and dipole moment functions defined according to eqs 4 and 5. Similarly, the low-energy aryl peak intensity is the sum of the two ortho CH oscillators.

Methyl CH Oscillators. The *ab initio* optimizations of toluene at the planar and perpendicular conformers show, not surprisingly, that the methyl CH bond lengths change more than the aryl CH bond lengths with methyl torsion. The calculated variation of the methyl CH bond lengths depends on the level of calculation but is about 3 mÅ at both the HF/6-31G(d) and HF/6-311+G(d,p) levels. The change in the methyl CH bond length varies approximately as a sin^2 θ function.[21] Thus, the frequency and anharmonicity of the CH oscillator are expected to vary with θ. The intensity of a transition from the ground to excited state in a Morse potential depends on the anharmo-

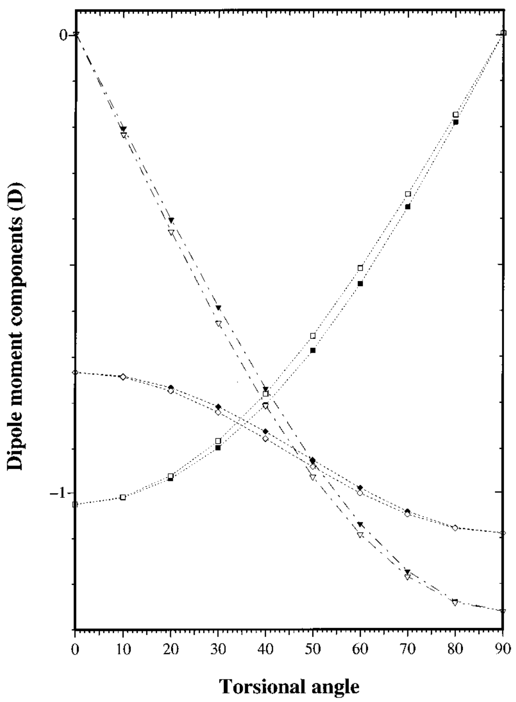

Figure 1. Three components (*x*, square; *y*, triangle; and *z*, diamond) of the second-order dipole moment expansion coefficients as a function of the torsional angle, θ. The filled symbols are the HF/6-31G(d) ab initio calculated points. The open symbols are from the approximations of eqs 6−8.

nicity and thus also depends on θ. However, a 5% change in anharmonicity leads to intensity changes of less than 10% for the CH stretching overtones with $v \leq 7$. It is thus a reasonable approximation to neglect the variation of the Morse potential with the torsional angle, and we have used an average Morse potential for the three methyl CH oscillators. The coupling between CH bonds which share the same carbon atom is approximated by harmonic terms in the HCAO local mode model. We have shown earlier[14] that this coupling is significant in the prediction of CH stretching overtone intensities for the local mode combination states, states whose components have the vibrational quanta spread over more than one oscillator. In particular, coupling effects on intensity are seen in the $\Delta v_{\mathrm{CH}} = 2$ region, where local mode combinations states can be more intense than the pure local mode transitions. However, at higher overtones the coupling and related mixed dipole terms do not contribute significantly to intensities. Thus, we can to a good approximation calculate total methyl overtone intensities with a simple one-dimensional model and neglect the harmonic coupling.

As mentioned earlier, the dipole moment function of the methyl CH bond is also expected to vary with methyl torsion. Figure 1 shows the variation of the second-order dipole moment derivatives as a function of θ calculated at the HF/6-31G(d) level. We see that the three Cartesian components of the dipole moment function can to a good approximation be written as:

$$\vec{\mu}^x = \sum_i a_i \cos(\theta) q^i \tag{6}$$

$$\vec{\mu}^y = \sum_i b_i \sin(\theta) q^i \tag{7}$$

$$\vec{\mu}^z = \sum_i (c_i + d_i \cos(2\theta)) q^i \tag{8}$$

The coefficients *a*, *b*, *c*, and *d* are defined by the following: $a_i = \vec{\mu}_i^x(||)$, $b_i = \vec{\mu}_i^y(\perp)$, $c_i = {}^1/_2(\vec{\mu}_i^z(||) + \vec{\mu}_i^z(\perp))$, and $d_i = {}^1/_2(\vec{\mu}_i^z(||) - \vec{\mu}_i^z(\perp))$, where $\vec{\mu}_i(||)$ are the dipole expansion coefficients according to eq 4 for a methyl CH bond in the parallel position, and similarly $\vec{\mu}_i(\perp)$ are the coefficients for a methyl CH bond in the perpendicular position. Thus, the coefficients necessary to describe the angular dependence of the dipole moment function for the methyl group can be obtained from only two one-dimensional grids. The calculations at the parallel and perpendicular positions of the methyl group have the advantage of both having C_s symmetry and also that the torsional angle is well-defined. The dipole coefficients $\vec{\mu}_i(||)$ and $\vec{\mu}_i(\perp)$ that are calculated at the HF/6-311+G(d,p) level are given in Table 1. The agreement between eqs 6−8 and *ab initio* calculated dipole moments decreases slightly with increasing expansion order.

The functional form of the dipole moment function, eqs 6−8, provides us with a simple method to calculate the methyl group intensity. The total intensity of the methyl group can be found by a simple integration (0 to $\pi/2$) and normalization over the torsional angle. Integration of the four terms gives $-2/\pi$ for $\cos(\theta)$, $2/\pi$ for $\sin(\theta)$, $\pi/2$ for 1, and 0 for $\cos(2\theta)$, which means that the *d* terms have no intensity contribution. To calculate the intensity, each of the three Cartesian dipole components, which corresponds to the *a*, *b*, and *c* terms, must be squared before they are summed and substituted in eq 2.

Results and Discussion

The room temperature vapor phase overtone spectrum of toluene-d_0 in the CH stretching regions corresponding to $\Delta v_{\mathrm{CH}} = 2-7$ is shown in Figures 2−7. Our spectrum in the $\Delta v_{\mathrm{CH}} = 3$ and 4 regions has an improved signal-to-noise ratio compared to the earlier spectra by Gough and Henry.[17] Changes due to the temperature difference between the spectral regions recorded by Gough and Henry,[17] and the present spectrum could not be detected. The spectrum in the $\Delta v_{\mathrm{CH}} = 5$ region is similar to the previously recorded spectrum[16] and is only shown here for completeness. The room temperature vapor phase overtone spectrum of toluene-d_8 in the CD stretching regions corresponding to $\Delta v_{\mathrm{CD}} = 2-6$ are shown in Figures 8−12. We have assigned two peaks in each of the aryl overtone regions of both the toluene-d_0 and -d_8 spectra. In Tables 2 and 3 we give the observed frequencies of the deconvoluted aryl peaks as well as the relative areas of the two aryl peaks and the methyl band for toluene-d_0 and -d_8, respectively.

The observed frequencies $\tilde{\nu}$ of the local mode peaks have been fitted to a two-parameter Morse oscillator energy expression

$$\tilde{\nu}/v = \tilde{\omega} - (v + 1)\tilde{\omega}x \tag{9}$$

in order to obtain values for the local mode frequency $\tilde{\omega}$ and anharmonicity $\tilde{\omega}x$ of the different CH and CD stretching oscillators. For the aryl regions the procedure is straightforward. The local mode parameters are given in Table 4, and the small size of the aryl uncertainties in Table 4 indicates that the two-parameter fit is excellent. For the CH stretching methyl region we have fitted the highest- and lowest-energy peaks to the two-parameter fit. These peaks do not necessarily represent pure local modes. However, they do seem to fit reasonably to the two-parameter fit. We take the methyl CH oscillator parameters to be the average of these two sets of values. In the toluene-d_8 spectra the methyl region is even more perturbed, and such a

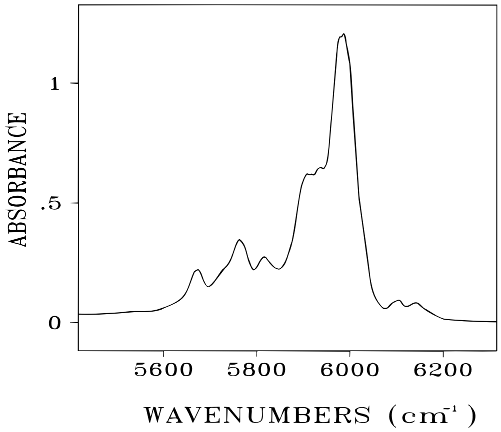

Figure 2. Room temperature vapor phase overtone spectrum of toluene in the $\Delta v_{CH} = 2$ region measured with a path length of 11.25 m and a pressure of 22 Torr.

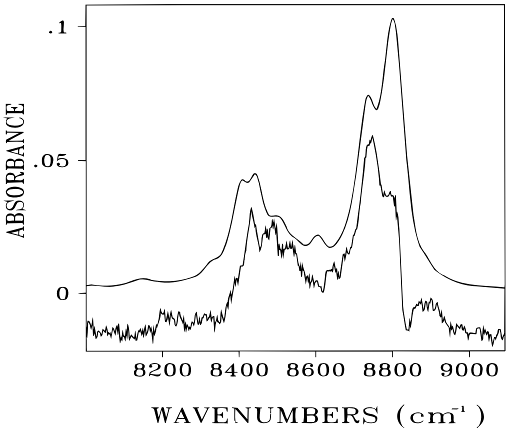

Figure 3. Room temperature vapor phase overtone spectrum of toluene in the $\Delta v_{CH} = 3$ region measured with a path length of 11.25 m and a pressure of 22 Torr (smooth curve). The spectrum of hydrogen impurities in the 99+ atom % D spectrum with the 100 atom % D spectrum subtracted has been scaled and offset (noisy curve).

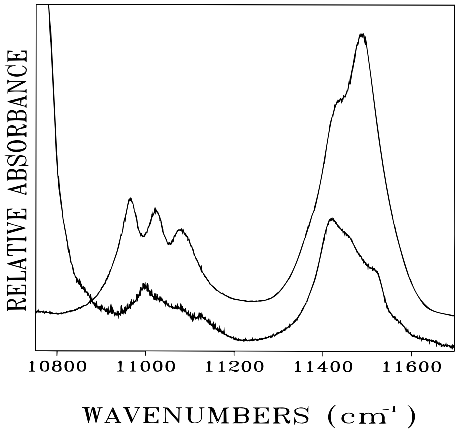

Figure 4. Room temperature vapor phase overtone spectra of toluene in the $\Delta v_{CH} = 4$ region. The spectrum was measured by ICL-PAS with a sample pressure of 20 Torr. The spectrum of hydrogen impurities in the 99+ atom % D spectrum has been scaled and offset (noisy curve). The intense peak at the low-energy side of the 99+% spectrum is the aryl $\Delta v_{CD} = 5$ peak (see Figure 11).

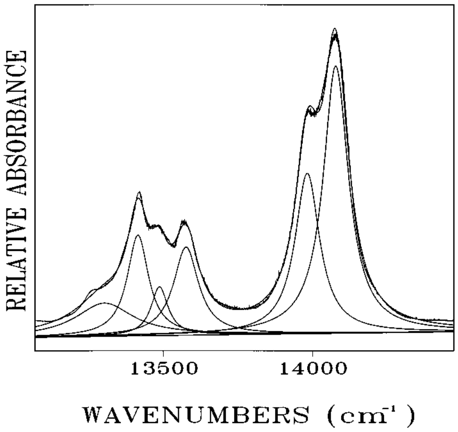

Figure 5. Room temperature vapor phase overtone spectra of toluene in the $\Delta v_{CH} = 5$ region. The spectrum was measured by ICL-PAS with a sample pressure of 20 Torr. The individual Lorentzian functions fit to the experimental spectrum (noisy spectrum) are also shown as well as their sum (smooth line).

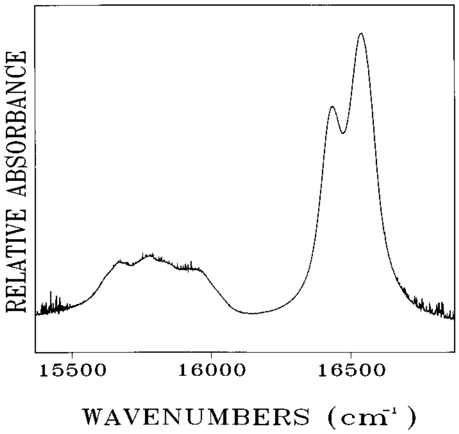

Figure 6. Room temperature vapor phase overtone spectrum of toluene in the $\Delta v_{CH} = 6$ region. The spectrum was measured by ICL-PAS with a sample pressure of 20 Torr of toluene and 85 Torr of Ar buffer gas. The spectrum was pieced together from two overlapping spectra recorded with the R6G and DCM dyes.

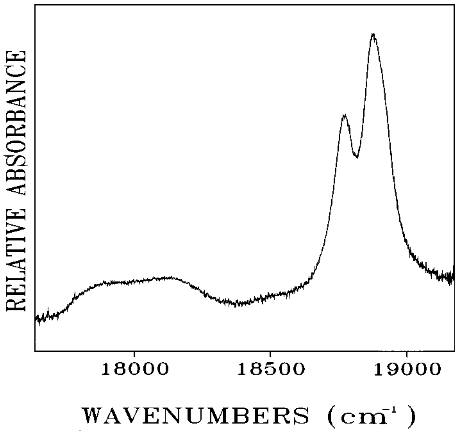

Figure 7. Room temperature vapor phase overtone spectrum of toluene in the $\Delta v_{CH} = 7$ region. The spectrum was measured by ICL-PAS with a sample pressure of 20 Torr of toluene and 100 Torr of Ar buffer gas.

procedure was not reasonable. We have found parameters for the methyl CD oscillator by scaling the CH values.[19] As mentioned in the theory section, a few percent variation in $\tilde{\omega}x$ does not alter the overtone intensities significantly. Our assignment of the local mode frequencies is in accord with what would be expected based on the *ab initio* bond lengths $R_{\mathrm{methyl}} > R_{\mathrm{o}} > R_{\mathrm{m,p}}$ and the bond length frequency correlation (the shorter the bond, the higher the local mode frequency)[7] and with previous results.[16,17]

The observed and calculated absolute total oscillator strengths for a few overtone regions are compared in Table 5. Experimental values can only be obtained from the Cary spectra which were recorded in the $\Delta v_{CH} = 2-4$ and $\Delta v_{CD} = 2-4$ regions.

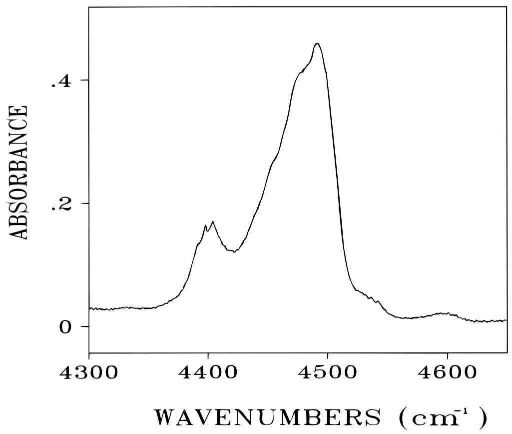

Figure 8. Room temperature vapor phase overtone spectrum of toluene-d_8 in the $\Delta v_{CD} = 2$ region measured with a path length of 3.75 m and a pressure of 19 Torr.

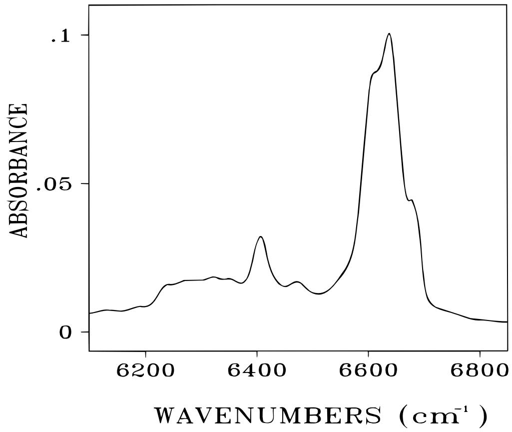

Figure 9. Room temperature vapor phase overtone spectrum of toluene-d_8 in the $\Delta v_{CD} = 3$ region measured with a path length of 20.25 m and a pressure of 19 Torr.

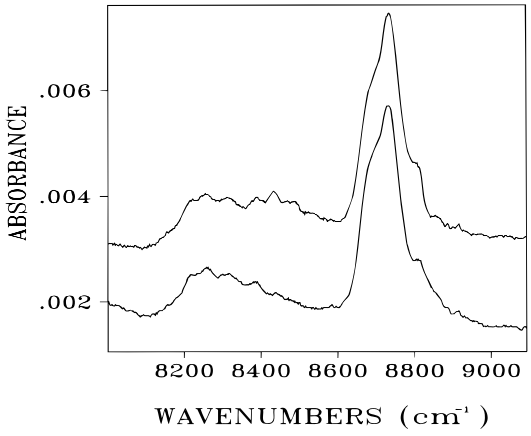

Figure 10. Room temperature vapor phase overtone spectra of toluene-d_8 in the $\Delta v_{CD} = 4$ region measure with a path length of 20.25 m. Lower trace: spectrum of the 100 atom % D sample recorded with a pressure of 18 Torr. Upper trace: spectrum of the 99+ atom % D sample offset for clarity. Ordinate scale is for the lower trace.

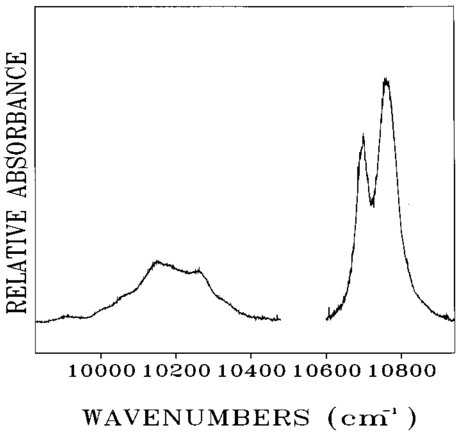

Figure 11. Room temperature vapor phase overtone spectrum of toluene-d_8 in the $\Delta v_{CD} = 5$ region. The spectrum was measured by ICL-PAS with a sample pressure of 20 Torr.

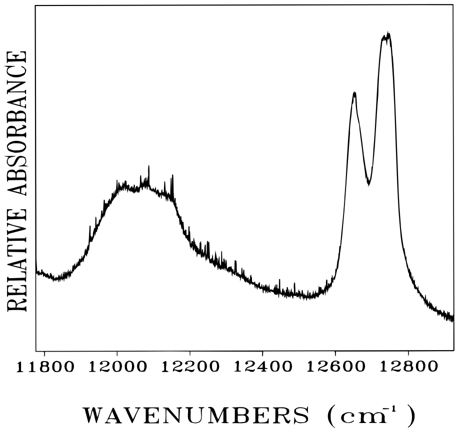

Figure 12. Room temperature vapor phase overtone spectrum of toluene-d_8 in the $\Delta v_{CD} = 6$ region. The spectrum was measured by ICL-PAS with a sample pressure of 20 Torr of toluene-d_8 and 80 Torr of Ar buffer gas.

TABLE 2: Observed and Calculated Relative Intensities, Observed Frequencies, and Peak Assignments for the CH Stretching Overtone Spectra of Vapor Phase Toluene-d_0

$\tilde{\nu}^a$/cm^{-1}	$f_{obs}{}^b$	$f_{calc}{}^c$	assignt
	(1.4)	1.64	$\|3\rangle_\alpha$
8 735	(1.0)	1.0	$\|3\rangle_o$
8 804	(1.4)	1.97	$\|3\rangle_{m,p}$
	1.2 (1.4)	1.55	$\|4\rangle_\alpha$
11 423	1.0 (1.0)	1.0	$\|4\rangle_o$
11 494	1.5 (2.1)	1.96	$\|4\rangle_{m,p}$
	1.6	1.51	$\|5\rangle_\alpha$
13 982	1.0	1.0	$\|5\rangle_o$
14 078	1.8	1.95	$\|5\rangle_{m,p}$
	1.4	1.55	$\|6\rangle_\alpha$
16 429	1.0	1.0	$\|6\rangle_o$
16 542	1.9	1.95	$\|6\rangle_{m,p}$
	1.6	1.65	$\|7\rangle_\alpha$
18 765	1.0	1.0	$\|7\rangle_o$
18 887	2.5	1.95	$\|7\rangle_{m,p}$

[a] The methyl band is broad and complex, and no one frequency is assigned to it. [b] Relative intensities within an overtone region, numbers in parentheses are from Cary spectra. [c] Local mode calculation with the parameters from Tables 1 and 4.

We see from Table 5 that the total calculated overtone intensity decreased as the basis set size was increased in agreement with earlier investigations.[8,15,30] Total overtone intensities calculated with the HF/6-311+G(d,p) dipole moment function are in good agreement with observed intensities for both the CH stretching and the CD stretching overtones.

In Tables 2 and 3 we also give the calculated relative intensities of transitions to the two aryl states and to the average methyl state. We have only shown the intensities obtained with the HF/6-311+G(d,p) dipole moment function, given in Table 1. The intensities with the smaller HF/6-31G(d) dipole moment function show similar relative intensities within a given overtone, but, as can be seen from Table 5, have larger absolute intensities. We have not shown the results for the first overtone

TABLE 3: Observed and Calculated Relative Intensities, Observed Frequencies, and Peak Assignments for the CD Stretching Overtone Spectra of Vapor Phase Toluene-d_8

$\tilde{\nu}$[a]/cm^{-1}	f_{obs}[b]	f_{calc}[c]	assign
	2.0	1.56	$\|4\rangle_\alpha$
8 683	1.0	1.0	$\|4\rangle_{\mathrm{o}}$
8 734	2.4	1.83	$\|4\rangle_{\mathrm{m,p}}$
	2.0	1.54	$\|5\rangle_\alpha$
10 696	1.0	1.0	$\|5\rangle_{\mathrm{o}}$
10 765	2.6	1.75	$\|5\rangle_{\mathrm{m,p}}$
	2.1	1.61	$\|6\rangle_\alpha$
12 653	1.0	1.0	$\|6\rangle_{\mathrm{o}}$
12 740	1.8	1.67	$\|6\rangle_{\mathrm{m,p}}$

[ã] The methyl band is broad and complex, and no one frequency is assigned to it. [b] Relative intensities within an overtone region. [c] Local mode calculation with the parameters from Tables 1 and 4.

TABLE 4: Local Mode Frequency and Anharmonicity of the CH and CD Stretching Modes in Vapor Phase Toluene-d_0 and -d_8[a]

	$\tilde{\omega}$[b]/cm^{-1}	$\tilde{\omega}x$[b]/cm^{-1}		$\tilde{\omega}$[b]/cm^{-1}	$\tilde{\omega}x$[b]/cm^{-1}
CH$_{\mathrm{o}}$	3144 ± 2	57.9 ± 0.3	α-CH$_{\mathrm{avg}}$	3060	60.6
CH$_{\mathrm{m,p}}$	3170 ± 2	59.1 ± 0.4	CD$_{\mathrm{o}}$	2326 ± 1	31.1 ± 0.2
α-CH	3053 ± 6	62.6 ± 0.9	CD$_{\mathrm{m,p}}$	2334 ± 1	30.1 ± 0.1
α-CH	3068 ± 6	58.7 ± 0.9	α-CD$_{\mathrm{avg}}$c	2246	32.6

[a] Uncertainties are one standard deviation. [b] From a fit of the local mode frequencies in the $\Delta v_{\mathrm{CH}} = 3-7$ and $\Delta v_{\mathrm{CD}} = 3-6$ regions. [c] Scaled from the α-CH$_{\mathrm{avg}}$ values (see ref 19).

TABLE 5: Observed and Calculated Total Oscillator Strengths of the CH and CD Stretching Regions in Vapor Phase Toluene-d_0 and -d_8

v	obs	HF/6-31G(d)[a]	HF/6-311+G(d,p)[a]	bond
1		4.3×10^{-5}	3.8×10^{-5}	CH
2	5.6×10^{-7}	5.9×10^{-7}	5.4×10^{-7}	CH
3	6.7×10^{-8}	12.7×10^{-8}	6.5×10^{-8}	CH
4	4.0×10^{-9}	16.0×10^{-9}	7.0×10^{-9}	CH
5		2.1×10^{-9}	8.7×10^{-10}	CH
1		2.2×10^{-5}	1.9×10^{-5}	CD
2	3.8×10^{-7}	2.6×10^{-7}	2.3×10^{-7}	CD
3	2.8×10^{-8}	3.9×10^{-8}	1.9×10^{-8}	CD
4	1.7×10^{-9}	3.4×10^{-9}	1.5×10^{-9}	CD
5		3.1×10^{-10}	1.3×10^{-10}	CD

[a] Calculated with the local mode parameters of Table 4 and the specified *ab initio* dipole moment function.

TABLE 6: Observed and Calculated Aryl to Methyl Intensity Ratios for the CH and CD Stretching Overtone Spectra of Vapor Phase Toluene-d_0 and -d_8

v	CH$_{\mathrm{obs}}$[a]	CH$_{\mathrm{calc}}$[b]	CD$_{\mathrm{obs}}$	CD$_{\mathrm{calc}}$[b]
3	1.7	1.80	1.9	1.76
4	2.1 (2.1)	1.92	1.7	1.81
5	1.7	1.96	1.8	1.78
6	1.9	1.90	1.3	1.65
7	2.2	1.79		1.48

[a] Ratio in parentheses from Cary spectra. [b] Local mode calculation with the parameters from Tables 1 and 4.

TABLE 7: Observed Spectral Width of the Aryl and Methyl Bands in the CH and CD Stretching Overtone Spectra of Vapor Phase Toluene-d_0 and -d_8[a]

	d_0		d_8	
v	methyl	aryl	methyl	aryl
3	156	126		
4	187	147	200	109
5	248	184	240	110
6	406	195	311	138
7	471	198		

[a] Fwhm bandwidths in cm^{-1} of the entire methyl or aryl band.

region (Δv_{CH} and $\Delta v_{\mathrm{CD}} = 2$) where we expect larger effective coupling both to lower frequency modes (local−normal mode combinations) and between the local modes (local mode combinations).[14,19] The spectra in the first and second overtone regions show overlap between the aryl and methyl regions which makes deconvolution more uncertain. The relative intensity between the two aryl CH or CD stretching peaks is predicted well by the anharmonic oscillator model and the HF/6-311+G-(d,p) dipole moment function as can be seen in Tables 2 and 3. This is not surprising as the aryl CH or CD oscillators are virtually decoupled from each other (*vide infra*).

A comparison of the total aryl to the total methyl intensities alleviates the problem associated with uncertainty in deconvolution of the aryl region and scaling intensities to one of the two aryl peaks. Table 6 shows the ratio of aryl to methyl intensity for both toluene-d_0 and -d_8. For toluene-d_0, the ratio of aryl to methyl intensity varies slightly with overtone. This variation is however less than the variation expected due to experimental uncertainty. For toluene-d_8, the calculated ratio decreases with increasing v. Experimentally, a decrease in the ratio is evident for the $\Delta v_{\mathrm{CD}} = 6$ region. It appears that the experimental and calculated ratios agree very well. Not surprisingly, the agreement is somewhat better for the CH bonds than for the CD bonds.

In Table 7 we compare the line width of the entire methyl and aryl bands for the different overtones. The methyl CH bond length stretches from 1.0839 Å in the || position to 1.0872 Å in the ⊥ position, whereas the spread in the aryl CH bond lengths is from 1.0754 to 1.0770 Å (HF/6-311+G(d,p)). Thus, as the variation in CH or CD bond lengths (the same within the Born−Oppenheimer approximation) is larger in the methyl group than between the two aryl CH bonds, it is expected that the width of the methyl band will be larger than the width of the aryl band. Moreover, since the barrier to rotation of the methyl group is small compared to kT, several torsional states will be populated at room temperature causing a widening of the CH or CD stretching transitions. This will be more pronounced for the methyl group which is more closely coupled to the torsional mode. We note that the width of the methyl band increases more rapidly with v than the width of the aryl band. Again, this is due in part to the greater spread in methyl bond lengths, which leads to a spread in frequencies that increases with v.

The width of the aryl band is consistently wider for the CH modes than for the CD modes. This is mainly because the CD peaks are closer to each other, as expected from the lower frequencies and anharmonicities, but also in part because the line width of the individual aryl peaks is about 100 cm^{-1} for the CH bonds but only about 60 cm^{-1} for the CD bonds.

We have observed the spectrum of hydrogen impurities in the 99+ atom % D toluene-d_8 sample. From our spectrum and intensity calculations, we estimate the 99+% sample to have 0.4% hydrogen impurity. No evidence for hydrogen impurities was observed in the overtone spectrum of the 100% toluene-d_8 sample. The hydrogen impurities are evident in the $\Delta v_{\mathrm{CH}} = 3$ and 4 regions. The $\Delta v_{\mathrm{CH}} = 3$ region overlaps significantly with the $\Delta v_{\mathrm{CD}} = 4$ region, and in Figure 3 we have subtracted the overtone spectrum of 100 atom % D toluene-d_8 from the 99+ atom % D toluene-d_8 spectrum. The residual spectrum is due to transitions in the $\Delta v_{\mathrm{CH}} = 3$ region from hydrogen impurities in the 99+% sample. The $\Delta v_{\mathrm{CH}} = 4$ region overlaps slightly with the $\Delta v_{\mathrm{CD}} = 5$ aryl peak that is seen at the low-energy side, and in Figure 4 we have not subtracted the spectrum of 100 atom % D toluene-d_8.

As the hydrogen impurity is less than 1%, it is very likely that the molecules in the 99+% sample have at most one hydrogen atom, and thus no coupling between CH stretching modes can occur. Compared to the spectra of toluene-d_0 it is apparent in Figures 3 and 4 that the methyl band is shifted to lower frequency in the d_0 spectrum relative to the impurity spectrum, whereas the frequency of the aryl transitions appears to be unshifted. We observed a similar effect in the overtone spectra of 1,3-butadiene.[19] This shift provides clear evidence for coupling between the methyl CH oscillators and indicates that a more complete treatment of the methyl group in toluene should include that coupling. Figures 3 and 4 also show significant changes in the band profiles. In the aryl band we see an increase in the relative intensity of the ortho peak in the CH impurity spectrum which indicates preferential substitution of the hydrogen atom in the ortho position. We observed a similar hydrogen atom preference for certain positions in 1,3-butadiene.[19] We believe that the change in the methyl band profile is due mainly to the fact that the CH_3 and the CHD_2 groups will provide different torsional potentials and different coupling within the methyl group, which in turn will lead to different band profiles.

Conclusion

We have used conventional and intracavity laser photoacoustic spectroscopy to measure the vapor phase overtone spectra of toluene-d_0 and -d_8 in the regions corresponding to $\Delta v_{CH} = 2-7$ and $\Delta v_{CD} = 2-6$. Oscillator strengths of the two aryl peaks and the methyl band have been determined from these spectra. The methyl band profile is complex, due in part to interactions with methyl torsion. We have used vibrational wave functions and eigenenergies from an anharmonic oscillator local mode model and a Taylor expanded *ab initio* dipole moment function to calculate oscillator strengths of the CH stretching aryl and methyl transitions. The total CH stretching intensity of the methyl band is obtained with a simplified model which averages over the methyl torsion.

The oscillator strengths were calculated with two different *ab initio* dipole moment functions, HF/6-31G(d) and HF/6-311+G(d,p), which both gave approximately the same relative intensities. However, comparison with observed absolute total oscillator strengths shows that the larger basis set calculation is closer to the observed values. Our calculated absolute total intensities, calculations which contain *no* adjustable parameters, are in good agreement with the observed absolute total intensities for both the CH and CD stretching overtone transitions.

Comparison of relative intensities between the two aryl transitions and between the aryl and methyl transitions shows excellent agreement between observation and experiment for the higher energy CH stretching overtones and good agreement for the higher energy CD stretching overtones. Thus, the intensity of the methyl band arises primarily from CH stretching transitions, and the methyl torsion and coupling between the three methyl CH bonds contribute to the band profile but do not contribute intrinsic intensity.

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