Deuterium Isotope Effects on the CH Stretching Overtone Spectrum of Toluene-α-d_1

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The room-temperature vapor phase overtone spectrum of toluene-α-d_1 has been recorded in the CH stretching regions corresponding to $\Delta v_{CH} = 2-7$. 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 both the conventional and photoacoustic spectra. The aryl region of the spectrum is nearly identical to the aryl region of the spectrum of toluene-d_0 and can be understood on the basis of two nonequivalent aryl local modes. The methyl band differs markedly from the methyl band in toluene-d_0 in relative intensity, in line width, and in structure. We use an anharmonic oscillator local mode model and an *ab initio* dipole moment function to calculate oscillator strengths for the aryl and methyl transitions. As was the case for toluene-d_0, these simple calculations show good agreement between observed and calculated intensities both in absolute total intensities and for relative intensities between the two aryl groups and between the aryl and methyl groups. We explain the differences between the methyl bands in the -α-d_1 and -d_0 spectra on the basis of our intensity calculations and on the basis of coupling between CH and CD stretching vibrations and methyl torsions.

Introduction

In a previous paper,[1] we have reported the overtone spectra of toluene-d_0 and toluene-d_8 in the regions corresponding to $\Delta v_{CH} = 2-7$ and $\Delta v_{CD} = 2-6$. The aryl regions of the spectra could be interpreted straightforwardly within the local mode model.[2,3] One peak was observed corresponding to aryl CH bonds at the 2- and 6- positions (ortho) and one peak to the aryl CH bonds at the 3-, 4-, and 5- positions (meta and para). The assignment was in accord with ab initio calculations of the relative bond lengths[4] and with our calculations of relative intensities.[1] The methyl band has a much more complex structure which we interpreted on the basis of interaction between methyl CH stretching and methyl torsion.

We measured oscillator strengths of the two aryl peaks and of the methyl band. We used an extension of our previous model, which was based on the HCAO local mode approach[5−8] and ab initio dipole moment functions,[9−12] to calculate oscillator strengths for the methyl and aryl transitions. The total CH stretching intensity of the methyl band was obtained with a simplified model which averaged over methyl torsion.

Toluene has a very low 6-fold barrier to methyl torsion.[13] For molecules with a high barrier like propane and dimethyl ether, the methyl overtone region consists of two peaks, one associated with two out-of-plane CH bonds and one for the in-plane CH bond of the methyl group.[14,15] The resolution of these peaks is in accord with their difference in bond lengths. Thus, the torsion of the methyl group affects the CH bond lengths. It will also have an effect on the dipole moment function for each of the CH bonds. A full analysis of the methyl profile requires consideration of coupling between stretching vibrations and between the stretching vibrations and torsion. The torsional dependence of the dipole moment function must also be incorporated. We have used such a model to account for the methyl profiles in the overtone spectrum of 2,6-difluorotoluene.[16]

In our work on toluene,[1] we adopted a simpler approach. We were interested in calculating the total methyl intensity and comparing it to the calculated aryl intensity and to our observations. We used a simple one-dimensional model that neglected the harmonic coupling between the methyl CH bonds. The variation of the dipole moment function with methyl torsion was approximated by a simple functional form. Thus, we were able to obtain the total intensity of the methyl group through integration from 0 (in plane) to $\pi/2$ and normalization over the torsional angle. Our calculated absolute intensities are in good agreement with the observed CH and CD stretching overtone intensities. Moreover comparison of relative intensities between the two aryl transitions and between the aryl and methyl transitions shows very good agreement between observation and experiment.

An interesting feature of our previous work on toluene-d_8 involved the appearance of impurity peaks due to the spectra of molecules in which all but one hydrogen had been replaced by deuterium. Although these molecules were present in very low concentration, and the resultant overtone spectra had a low signal-to-noise ratio, it appeared that the methyl spectral profile was significantly altered. In other words, the methyl regions of the overtone spectrum of a CHD_2 group differed markedly from the corresponding spectrum of a CH_3 group.

In this work we investigate the effect of deuterium substitution through a study of the overtone spectrum of toluene-α-d_1, where α refers to the methyl position. We again use our simple model

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and average over the methyl group to calculate total and relative intensities and compare the results to our measured values. We make a detailed comparison between the overtone spectra of toluene-d_0 and toluene-α-d_1, both for the aryl regions and for the methyl regions. We use our intensity calculations and coupling considerations to explain qualitatively the differences between the methyl regions of the overtone spectra for these two molecules.

Experimental Section

Toluene-α-d_1 was prepared by a method similar to that described by Trevoy and Brown.[17] A 5 g amount of lithium aluminum deuteride (Aldrich, 98%) was added to 75 mL of dimethyl ether under nitrogen. A 15 mL volume of benzyl chloride (Aldrich) was added dropwise and the mixture was refluxed for 3 h. The reaction was quenched with 5 mL of D_2O, 5 mL of 15% NaOH in D_2O, and 15 mL of D_2O. The toluene-α-d_1 was isolated through distillation, drying over 3 Å molecular sieves, and several pump−freeze−pump−thaw cycles on the vacuum line. The product was characterized with NMR, near-IR, and GC/MS. The near-IR spectrum at $\Delta v_{CH} = 6$ demonstrated the absence of dimethyl ether, as did GC/MS and NMR. Both GC/MS and NMR demonstrated the absence of benzyl chloride. Integration of the aryl and methyl peaks in the NMR yielded an aryl:methyl ratio of 2.52, in agreement with the expected ratio of 2.5 in toluene-α-d_1. Our estimated error in integration is ∼5%, and on this basis we believe the purity of toluene-α-d_1 to be >95%.

The room-temperature vapor phase overtone spectrum of toluene-α-d_1 was recorded in the $\Delta v_{CH} = 2-4$ regions by conventional absorption spectroscopy and in the $\Delta v_{CH} = 4-7$ regions by intracavity laser photoacoustic spectroscopy (ICL-PAS). The conventional spectra were recorded with a Cary 5e and a variable path length cell (see our previous work for details[1]). The experimental absolute oscillator strength f of an absorption band can be determined from these conventional spectra and the equation[18]

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

where T is the temperature, p is the 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 ($\Delta v_{CH} = 4$ and 5) or dye laser ($\Delta v_{CH} = 6$ and 7), and details can be found in our previous work.[1,19,20] The spectrum in the $\Delta v_{CH} = 6$ region was recorded with the dye R6G. However the dye DCM gave a better signal-to-noise ratio in the methyl region of the spectrum, and the DCM spectrum was used in a comparison of the detailed methyl band shape. The spectrum in region of $\Delta v_{CH} = 7$ was recorded with the dye Coumarin 6, and a small amount of argon buffer gas (100 Torr) was added to the cell here and at $\Delta v_{CH} = 4$ to improve the photoacoustic signal. The laser power in the methyl region at $\Delta v_{CH} = 7$ is very low. We have used the aryl peak positions in our analysis (vide infra); however, both the methyl band shape and the comparison of methyl and aryl intensities are subject to large uncertainties and have not been used.

Just as in our previous work,[1] the overtone spectra were decomposed into component peaks with a deconvolution program within Spectra Calc.[21] The spectra were deconvoluted with a number of Lorentzian peaks and a linear baseline. Uncertainty in the peak positions and areas obtained from the aryl region of the spectrum are typically ±5 cm^{-1} for peak positions and less than 10% for relative intensities. In the regions $\Delta v_{CH} = 3-7$, the aryl band could be deconvoluted into two peaks. However deconvolution of the broad methyl band leads to much larger uncertainties. From two to five peaks were used in the methyl deconvolution, and the total methyl band intensity is found as the sum of the areas of these deconvoluted peaks. We estimate the error in the methyl area to be less than 20%, where a large part of the error arises from uncertainty in the baseline.

Theory and Calculations

The theoretical models which we have used in the present paper are similar to the models we used in our previous work on toluene-d_0.[1] Thus only a brief outline is given here with reference to recent papers for more details of the vibrational model and the procedures used to obtain the dipole moment functions.[9,11,12] Within the Born−Oppenheimer approximation the ab initio calculations for toluene-α-d_1 and toluene-d_0 will be identical. Thus the previously optimized geometry and dipole moment functions can be used for the present work on toluene-α-d_1.

The oscillator strength f of a transition from the ground vibrational state g to an excited state e is given by[18]

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

where $\tilde{\nu}_{\mathrm{eg}}$ is the vibrational wavenumber of the transition and $\vec{\mu}_{\mathrm{eg}}$ is the transition dipole moment matrix element in Debye (D).

Vibrational Model. The aryl CH bonds change very little upon rotation of the methyl group.[1] The three $\mathrm{CH}_{m,p}$ bonds (meta and para positions) have almost the same bond length as have the two CH_o bonds (ortho position). Thus we expect two peaks in the aryl region of the overtone spectra of toluene-d_0 and -α-d_1. The coupling between the aryl CH oscillators will be negligible as the aryl CH bonds are not attached to the same carbon atom.[12] We treat the aryl CH oscillators as five isolated CH oscillators with one set of local mode parameters for the two CH_o oscillators and one set for the three $\mathrm{CH}_{m,p}$ oscillators.

We use the local mode theory of anharmonic oscillators to obtain vibrational wave functions and energies for each of the CH oscillators. 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 vibrational quantum number. These eigenstates are thus Morse oscillator wave functions.

We have used the same axis system as in our previous work.[1] The z-axis is along the CC bond around which the methyl group rotates, the x-axis in the plane of the ring, and the y-axis perpendicular to the plane. The torsional angle, θ, is defined as the angle between one α-CH bond and the plane of the ring. The calculated variation in the methyl CH bond length with methyl torsion is about 3 mÅ at the HF/6-311+G(d,p) level.[1] The parallel (||) CH bond has an ab initio calculated shorter CH bond length, higher local mode frequency, and lower local mode anharmonicity than the perpendicular (⊥) CH bond. The change in unscaled calculated frequency and anharmonicity is about 40 and 1 cm^{-1} at the HF/6-311+G(d,p) level. The intensity of a transition from the ground state to a vibrationally excited state of a typical CH stretching oscillator changes less

TABLE 1: Observed and Calculated Relative Intensities, Observed Frequencies, and Peak Assignments for the CH Stretching Overtone Spectra of Vapor Phase Toluene-α-d_1 and Toluene-d_0

toluene-α-d_1					toluene-d_0	
$\tilde{\nu}^a$/cm^{-1}	$f_{obs}{}^b$	$f_{calc}{}^c$	$f_{calc}{}^d$	assign	$f_{obs}{}^e$	$f_{calc}{}^e$
	(1.1)	1.10	1.09	$\|3\rangle_\alpha$	(1.4)	1.64
8 740	(1.0)	1.00	1.00	$\|3\rangle_o$	(1.0)	1. 0
8 806	(1.3)	1.96	1.97	$\|3\rangle_{m,p}$	(1.4)	1.97
	0.89 (1.1)	1.06	1.03	$\|4\rangle_\alpha$	1.2 (1.4)	1.55
11 424	1.0 (1.0)	1.00	1.00	$\|4\rangle_o$	1.0 (1.0)	1.0
11 496	1.5 (1.6)	1.94	1.96	$\|4\rangle_{m,p}$	1.5 (2.1)	1.96
	1.4	1.06	1.01	$\|5\rangle_\alpha$	1.6	1.51
13 979	1.0	1.00	1.00	$\|5\rangle_o$	1.0	1.0
14 075	1.9	1.92	1.95	$\|5\rangle_{m,p}$	1.8	1.95
	0.8	1.11	1.03	$\|6\rangle_\alpha$	1.4	1.55
16 430	1.0	1.00	1.00	$\|6\rangle_0$	1.0	1.0
16 543	2.1	1.90	1.95	$\|6\rangle_{m,p}$	1.9	1.95
		1.21	1.10	$\|7\rangle_\alpha$	1.6	1.65
18 766	1.0	1.00	1.00	$\|7\rangle_o$	1.0	1.0
18 895	1.6	1.89	1.95	$\|7\rangle_{m,p}$	2.5	1.95

[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 calculations with dipole moment from ref 1 and local mode parameters from Table 2. [d] Calculated relative intensities from ref 1 except that the intensity for $|i\rangle_a$ is given as two-thirds the value for toluene-d_0 in ref 1. [e] From ref 1.

than 10% with a 5% change in anharmonicity. Thus it seems reasonable, for intensity purposes, to neglect the variation in Morse potential with the methyl group rotation. We have also neglected the coupling between the methyl CH oscillators. This will have an effect in the $\Delta v_{CH} = 2$ region where local mode combination states can carry significant intensity that is obtained both from vibrational coupling and mixed dipole moment terms (vide infra).[15] However, at higher overtones the local mode combination states carry insignificant intensity. This approach worked well for our recent toluene-d_0 calculations. Thus we treat the methyl group in toluene-α-d_1 as two noncoupled CH oscillators with an average Morse potential.

Dipole Moment Function. For an isolated CH oscillator, we express the dipole moment function as a series expansion in the internal CH displacement coordinate, q,

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

where $\vec{\mu}_i$ is $1/i!$ times the ith order derivative of the dipole moment function with respect to q. We limit the expansion in eq 4 to fourth-order terms.[11] The coefficients are determined from ab initio calculated one-dimensional grids of the dipole moment function as a function of q with standard numerical differential techniques.[22] To ensure a reasonable mapping and to limit round off errors, seven points with a maximum displacement of ±0.3 Å in steps of 0.1 Å are calculated.[11] All grid points and optimized geometries are calculated at the Hartree–Fock (HF) level with a 6-311+G(d,p) basis set, with Gaussian 92.[23] Previous work has suggested that this method is adequate for absolute overtone intensities.[24,25]

Average dipole coefficients for the aryl CH$_o$, CH$_m$, and CH$_p$ are given in Table 1 of ref 1. There is only a small variation in dipole coefficients between the two CH$_o$ bonds. We have calculated the intensity of the high energy aryl peak as the sum of three CH oscillators (the 3-, 4-, and 5- positions) with the local mode parameters from Table 2 and dipole moment functions defined according to eq 4. The low energy aryl peak is calculated as the sum of two ortho CH oscillators (positions 2 and 6).

TABLE 2: Local Mode Frequency and Anharmonicity of the CH Stretching Modes in Vapor Phase Toluene-α-d_1^{a} and Toluene-d_0^{a}

	toluene-α-d_1		toluene-d_0	
	$\tilde{\omega}^b$/cm^{-1}	$\tilde{\omega}x^b$/cm^{-1}	$\tilde{\omega}^c$/cm^{-1}	$\tilde{\omega}x^c$/cm^{-1}
CH$_o$	3146 ± 2	58.2 ± 0.3	3144 ± 2	57.9 ± 0.3
CH$_{m,p}$	3169 ± 3	58.9 ± 0.4	3170 ± 2	59.1 ± 0.4
α-CH	3066 ± 7	63.8 ± 1.1	3053 ± 6	62.6 ± 0.9
α-CH	3084 ± 9	61.5 ± 1.5	3068 ± 6	58.7 ± 0.9
α-CH$_{av}$	3075	62.6	3060	60.6

[a] Uncertainties are one standard deviation. [b] From a fit of the local mode frequencies in the $\Delta v_{CH} = 3-7$ regions. [c] From ref 1.

We have shown previously that the variation of the dipole moment function of the methyl CH bond can to a good approximation be written as[1]

$$\vec{\mu}^x = \sum_i a_i \cos(\theta) q^i \tag{5}$$

$$\vec{\mu}^y = \sum_i b_i \sin(\theta) q^i \tag{6}$$

$$\vec{\mu}^z = \sum_i (c_i + d_i \cos(2\theta)) q^i \tag{7}$$

The coefficients a, b, c, and d are defined by the following:

$$a_i = \vec{\mu}_i^{\,x}(||) \quad b_i = \vec{\mu}_i^{\,y}(\perp) \quad c_i = {}^1/_2(\vec{\mu}_i^{\,z}(||) + \vec{\mu}_i^{\,z}(\perp))$$
$$d_i = {}^1/_2(\vec{\mu}_i^{\,z}(||) - \vec{\mu}_i^{\,z}(\perp))$$

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 it is only necessary to calculate two dipole moment grids, one each for the || and ⊥ conformers, to describe the dipole moment function of the rotating methyl CH oscillator. The HF/6-311+G(d,p) calculated dipole moment coefficients are given in Table 1 of ref 1.

The total intensity of a methyl CH oscillator can be found by averaging over the methyl torsion. We do this by a simple integration and normalization of the dipole components. Integration from 0 to $\pi/2$ and normalization (division by $\int_0^{\pi/2} d\theta = \pi/2$) of the four terms in eqs 5–7 gives $2/\pi$ for $\cos(\theta)$, $2/\pi$ for $\sin(\theta)$, 1 for 1, and 0 for $\cos(2\theta)$. (Our previous paper had a typographical error in these integrals, but the correct values were used in our calculations.[1]) To calculate the intensity of a rotating methyl CH oscillator, the three Cartesian components, including the integration and normalization factors, must be squared and then summed and substituted into eq 2. We calculate the total intensity of the partially deuterated methyl group CH$_2$D as the sum of two rotating average CH oscillators.

Results and Discussion

The room-temperature vapor phase overtone spectrum of toluene-α-d_1 in the CH stretching regions corresponding to $\Delta v_{CH} = 2-6$ is shown in Figures 1–5. The figures also show the overtone spectrum of toluene-d_0 from our previous work[1] and is presented here for comparison. In the toluene-d_0 spectrum, the intensity of the high energy aryl peak maximum has been scaled to match the corresponding peak in the toluene-α-d_1 spectrum.

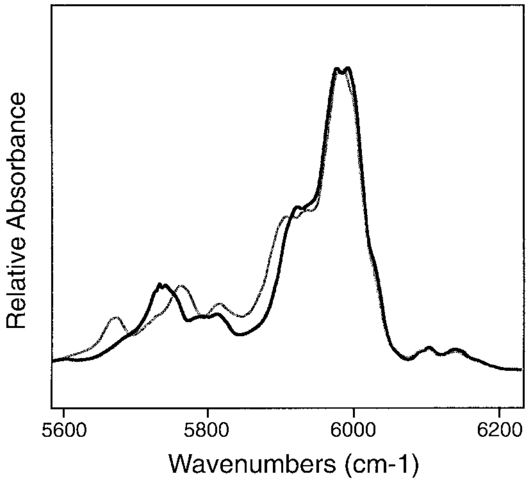

Figure 1. Room-temperature vapor phase overtone spectrum of toluene-α-d_1 (solid line) in the $\Delta v_{CH} = 2$ region measured with a path length of 11.25 m and a pressure of 17 Torr. The scaled spectrum of toluene-d_0 (dotted line) is taken from ref 1 (see text).

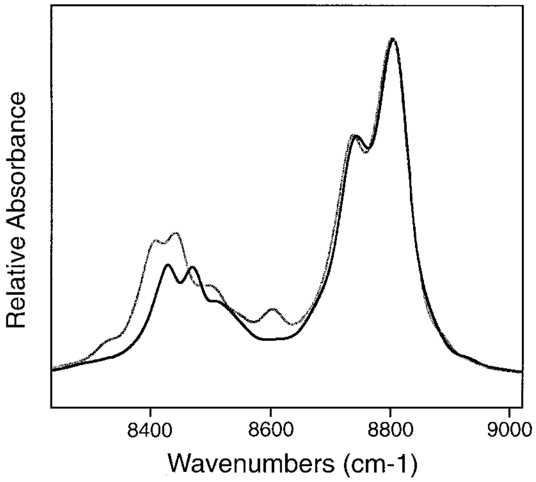

Figure 2. Room-temperature vapor phase overtone spectrum of toluene-α-d_1 (solid line) in the $\Delta v_{CH} = 3$ region measured with a path length of 11.25 m and a pressure of 17 Torr. The scaled spectrum of toluene-d_0 (dotted line) is taken from ref 1 (see text).

The aryl regions of the toluene-α-d_1 spectrum have been decomposed into three peaks at $\Delta v_{CH} = 2$ and two peaks at $\Delta v_{CH} = 3-7$. In Table 1 we give the observed frequencies of the two aryl peaks ($\Delta v_{CH} = 3-7$) as well as the relative areas of the two aryl peaks and the methyl band.

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

$$\tilde{\nu}/v = \tilde{\omega} - (v + 1)\tilde{\omega}x \tag{8}$$

to obtain values for the local mode frequency $\tilde{\omega}$ and anharmonicity $\tilde{\omega}x$ for the different CH stretching oscillators. For the aryl regions the procedure is straightforward and the local mode parameters are given in Table 2. The very small uncertainties in the aryl parameters indicate that the two-parameter fit is excellent. For the CH stretching methyl region, we have fitted peaks from the deconvolution that correspond to high- and low-energy maxima in the broad unresolved methyl band. These peaks do not represent pure local modes. However they do fit reasonably well to eq 8, and we take the methyl CH oscillator parameters to be the average of these two sets of values.

The observed and calculated absolute total oscillator strengths are compared in Table 3 for those regions where we have conventional spectra ($\Delta v_{CH} = 2-4$). The total observed overtone intensities in toluene-d_0 are also given for comparison.[1] The total overtone intensities calculated with the HF/6-311+G(d,p) dipole moment function are in good agreement with the observed intensities. In Table 4 we compare the line widths of the entire methyl and aryl bands for the different overtones in the spectrum of toluene-α-d_1. We also present the results for toluene-d_0[1] for comparison.

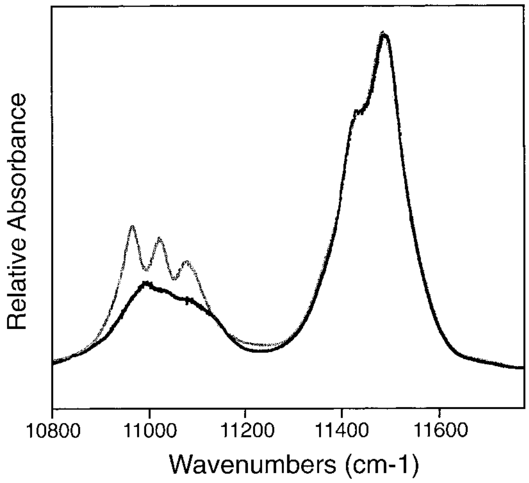

Figure 3. Room-temperature vapor phase overtone spectrum of toluene-α-d_1 (solid line) in the $\Delta v_{CH} = 4$ region. The spectrum was measured by ICL-PAS with a sample pressure of 17 Torr of toluene-α-d_1 and 100 Torr of argon buffer gas. The scaled spectrum of toluene-d_0 (dotted line) is taken from ref 1 (see text).

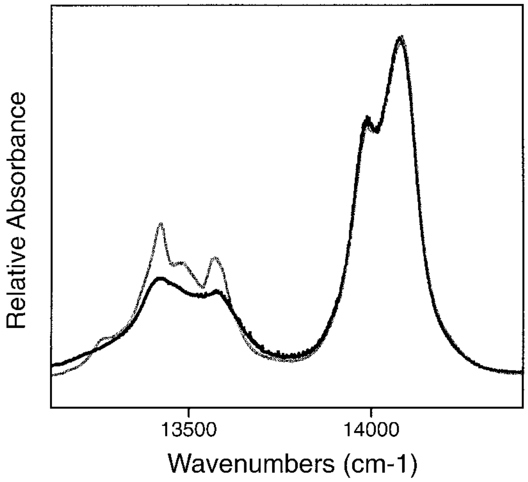

Figure 4. Room-temperature vapor phase overtone spectrum of the toluene-α-d_1 (solid line) in the $\Delta v_{CH} = 5$ region. The spectrum was measured by ICL-PAS with a sample pressure of 16 Torr. The scaled spectrum of toluene-d_0 (dotted line) is taken from ref 1 (see text).

Perhaps the most striking feature in comparing the overtone spectrum of toluene-α-d_1 and toluene-d_0 is that while the aryl region of the spectrum is virtually identical, the methyl region of the spectrum is significantly different. Inspection of Figures 1−5 shows identical aryl regions for $\Delta v_{CH} = 4-6$ in Figures 3−5. In the construction of these figures, only the intensity of the higher energy aryl peak was matched. No change was then made in the relative intensity of the other peaks in the toluene-d_0 spectrum, nor was any attempt made to shift the wavenumber position of the toluene-d_0 spectrum.

There are small changes in the low-energy side of the aryl peak at $\Delta v_{CH} = 2$ (Figure 1). These arise not from the aryl peaks themselves but from differences in the methyl local mode

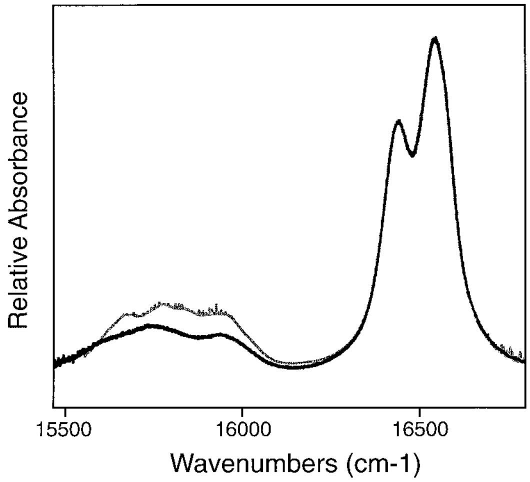

Figure 5. Room-temperature vapor phase overtone spectrum of toluene-α-d_1 (solid line) in the $\Delta v_{CH} = 6$ region. The spectrum was measured by ICL-PAS with a sample pressure of 20 Torr. The scaled spectrum of toluene-d_0 (dotted line) is taken from ref 1 (see text).

TABLE 3: Observed and Calculated Total Oscillator Strengths of the CH Stretching Regions in Vapor Phase Toluene-α-d_1

v	obs (toluene-α-d_1)	calc[a] (toluene-α-d_1)	obs[b] (toluene-α-d_0)
1		3.1×10^{-5}	
2	4.7×10^{-7}	4.7×10^{-7}	5.6×10^{-7}
3	6.2×10^{-8}	5.7×10^{-8}	6.7×10^{-8}
4	3.6×10^{-9}	6.2×10^{-9}	4.0×10^{-9}
5		7.8×10^{-10}	

[a] Calculated with the local mode parameters of Table 2 and the HF/6-311+G(d,p) dipole moment function of ref 1. [b] From ref 1.

TABLE 4: Observed Spectral Widths of the Aryl and Methyl Bands in the CH Stretching Overtone Spectra of Toluene-α-d_1 and -d_0[a]

	methyl		aryl	
v	toluene-α-d_1	toluene-d_0[b]	toluene-α-d_1	toluene-d_0[b]
3	156	156	120	126
4	221	187	142	147
5	290	248	182	184
6	434	406	196	195
7	493	471	220	198

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

TABLE 5: Observed and Calculated Aryl to Methyl Intensity Ratios in the CH Stretching Overtone Spectra of Vapor Phase Toluene-α-d_1 and -d_0

	toluene-α-d_1		toluene-d_0	
v	obs[a]	calc[b]	obs[c]	calc[c]
3	(2.1)	2.7	(1.7)	1.80
4	2.8(2.3)	2.8	2.1(2.1)	1.92
5	2.1	2.75	1.7	1.96
6	3.8	2.6	2.1	1.90
7			2.2	1.79

[a] Ratios in parentheses are from Cary spectra. [b] Local mode calculation from the parameters of Table 2 and the dipole moment function of ref 1. [c] From ref 1.

combination peaks that are predicted to appear in this area. In the region of $\Delta v_{CH} = 2$ in the spectrum of toluene-α-d_1, the peak $|11\rangle$ is predicted (eq 8) to lie at 5900 cm^{-1} on the basis of the average values of the local mode parameters in Table 2. The corresponding methyl local mode combinations in toluene-d_0 are the symmetrized combinations of the $|110\rangle$, $|101\rangle$, and $|011\rangle$ states, and in zeroth order, these are predicted to start about 20 cm^{-1} lower in energy than $|11\rangle$ on the basis of the corresponding local mode parameters from ref 1. A very slight shift on the low-energy side of the aryl peak at $\Delta v_{CH} = 3$ (Figure 2) arises for the same reason. Local mode combination states decrease in relative intensity compared to pure local mode states ($|v0\rangle_{\pm}$) with increasing v. This is why the aryl regions at $\Delta v_{CH} = 3$ are only slightly changed from the toluene-d_0 to the toluene-α-d_1 spectrum and are identical for higher overtones. At $\Delta v_{CH} = 3$ the local mode combination states corresponding to $|210\rangle$, $|201\rangle$, etc., in toluene-d_0 are expected at slightly lower energies than the states corresponding to $|21\rangle$ and $|12\rangle$ in toluene-α-d_1.

Not surprisingly the aryl local mode parameters in Table 2 are virtually identical to the corresponding parameters for toluene-d_0.[1] Moreover the aryl bandwidths in Table 4 are the same as the toluene-d_0 aryl bandwidths, with the exception of $\Delta v_{CH} = 7$ where the uncertainty is much larger. Finally the observed relative intensities of the ortho and meta/para peaks, 1:x, as given in Table 1, compare almost exactly to the values for toluene-d_0 ($x = 1.3$, 1.5, 1.8, and 1.9 for $\Delta v_{CH} = 3-6$).[1] Any differences here probably relate to uncertainties in our deconvolution procedure. In our calculations, we assume the aryl vibrations are not coupled to the methyl vibrations, and this approximation appears to be correct given the similarity in the aryl overtones in toluene-α-d_1 and toluene-d_0.

By contrast the methyl region of the overtone spectrum changes significantly between the toluene-α-d_1 and toluene-d_0 spectra. The most obvious change is a decrease in the relative intensity of the methyl as compared to the aryl spectral regions from toluene-d_0 to toluene-α-d_1. The observed relative intensities for the methyl group in Table 1 are approximately two-thirds of the values from the toluene-d_0 spectrum. The decrease in intensity also shows up in the absolute total oscillator strengths given in Table 3. The calculated intensities change very slightly because of the change in local mode parameters. Apart from this small change due to the changed parameters, on the basis of the Born–Oppenheimer approximation, we expect the only change in intensity to come from a reduction of one-third in the methyl intensity. Table 1 gives calculated relative intensities based on our local mode model and the same dipole moment as in the toluene-d_0 calculation.[1] We have also given calculated relative intensities taken directly from our toluene-d_0 work with the toluene-d_0 methyl intensities multiplied by two-thirds. As expected the change in intensities due to the small change in parameters is not significant. The relative intensity between the two aryl CH stretching peaks is predicted well by the anharmonic oscillator model and the HF/6-311+G(d,p) dipole moment function. The agreement occurs despite the fact that these peaks overlap and thus make the deconvolution procedure somewhat uncertain, especially for the lower overtones.

A comparison of total aryl to total methyl intensities should alleviate much of the problem associated with uncertainties in deconvolution. Observed and calculated values for this ratio are presented in Table 5 and compared to the corresponding data for toluene-d_0. Just as in the toluene-d_0 case, the calculated ratios are predicted to be approximately constant and agree reasonably well with the observed ratios. Due to the inherently lower intensity of the methyl region in toluene-α-d_1, uncertainties in total aryl to total methyl ratios are larger for toluene-α-d_1 than for toluene-d_0. Note that in all cases the observed aryl to methyl intensity ratio is larger in toluene-α-d_1 in accord with expectations.

The other marked change between the -α-d_1 and -d_0 overtone spectra is a change in the methyl profile. At $\Delta v_{CH} = 2$ and 3 the methyl profiles are clearly different for -α-d_1 and -d_0. Beginning at $\Delta v_{CH} = 4$, the toluene-α-d_1 methyl profile broadens significantly and loses structure relative to the toluene-d_0 profile. This difference can be seen in Table 4, where the methyl bandwidths are equal at $\Delta v_{CH} = 3$ but are greater for -α-d_1 from $\Delta v_{CH} = 4-7$.

In our previous paper,[1] we also presented the overtone spectrum of toluene-d_8, which was obtained from 99+ atom % D toluene-d_8 as well as from 100% toluene-d_8. In the 99+% sample we were able to observe the spectra of hydrogen impurities from molecules with only one hydrogen atom. Such a hydrogen impurity spectrum was observed in the regions of $\Delta v_{CH} = 3$ and 4. Thus the methyl regions of these spectra correspond to transitions involving the CD_2H group as compared to a CH_2D group in toluene-α-d_1. However if one compares the profile at $\Delta v_{CH} = 3$ and 4 of the hydrogen impurity spectra with the methyl profiles for toluene-α-d_1, they are very similar.

In our recent work on the overtone spectrum of 2,6-difluorotoluene[16] we were able to calculate the methyl profiles. The model was based on a local mode treatment of the three methyl CH stretching modes and a simple one-dimensional rigid rotor for torsion. Interaction between torsion and stretching occurs through angular-dependent terms involving both frequency and anharmonicity. Angular-dependent terms were also included in the dipole moment function. Because of coupling between torsion and stretching, both in the Hamiltonian and through the dipole moment function, a very large number of transitions were predicted to carry intensity and to contribute to the overall spectral profile.

On the basis of this work[16] we can provide a qualitative explanation of the changes in methyl profile from -α-d_1 to -d_0 and of the similarity in the -α-d_1 and -α-d_2 (hydrogen impurity) methyl profiles. The width of the methyl band is dependent on the difference in energy of the methyl vibrational states at a given overtone and the coupling between vibrational and torsional states. As we noted in the toluene-d_0 paper, the predicted difference in methyl CH bond lengths as the methyl group rotates is greater than the predicted difference in aryl CH bond lengths. This factor would predict a greater width in the methyl band relative to the aryl band. Moreover the methyl bandwidth should increase more rapidly with increasing v than the aryl bandwidth. Both of these characteristics are observed in the spectra of -α-d_1 and -d_0.

Torsional coupling is expected to increase methyl bandwidths even further. However no coupling is expected between methyl torsion and aryl CH stretching. In comparing the CH_2D group of -α-d_1 to the CH_3 group of toluene-d_0, the spread in vibrational frequencies will be slightly larger in the CH_3 group due to a greater spread in the energies of local mode combination states. However, as we have noted previously, these combination states carry very little intensity for $\Delta v_{CH} \geq 3$. The greater methyl bandwidth implies greater torsional coupling in -α-d_1 relative to -d_0. The presence of a deuterium atom increases the density of CH or CD stretching vibrational states that carry intensity from the ground state and couple to torsion. On this basis one might expect that since both CH and CD oscillators are present in toluene-α-d_1 and toluene-α-d_2, the methyl profiles in the spectra of these two molecules would have common features and would differ from the methyl profiles in the spectra of toluene-d_0 where only CH oscillators are present.

Conclusion

We have used conventional and intracavity laser photoacoustic spectroscopy to measure the vapor phase overtone spectrum of toluene-α-d_1 in the regions corresponding to $\Delta v_{CH} = 2-7$. Oscillator strengths of the two aryl peaks and the methyl band have been measured absolutely for $\Delta v_{CH} = 2-4$ and relatively for $\Delta v_{CH} = 2-6$.

We have used a similar model to that used for our previous work on toluene-d_0[1] to calculate oscillator strengths of the CH stretching aryl and methyl transitions. Just as in our previous study,[1] our calculated absolute total intensities are in good agreement with the observed absolute CH stretching overtone intensities. Similarly, observed relative intensities between the two aryl transitions and between the aryl and methyl transitions agree well with calculated relative intensities, particularly for higher overtones.

A detailed comparison has been made between the spectrum of toluene-α-d_1 and the spectrum of toluene-d_0. The aryl regions of the spectrum are unchanged. In accord with expectations, the methyl region of the spectrum decreases in relative intensity for toluene-α-d_1. Both the spectral bandwidth and the band profile change for the methyl regions of toluene-α-d_1. This change is explained in terms of differences in coupling between the CH/CD stretching vibrations and methyl torsion.

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