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Theoretical and Spectroscopic Study of Gaseous Monohydrogenated Toluene and 4-Methylpyridine

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The infrared and Raman spectra of gaseous monohydrogenated toluene and γ-picoline are recorded. They are analyzed with a theoretical model that takes into account, in the adiabatic approximation, coupling between the internal rotation of the methyl group and the methyl CH stretching vibration. Ab initio calculations at the HF/6-31G** level of theory are performed to determine the principal parameters used in this model and their variation with the internal rotation coordinate. Reconstruction of the ν(CH) fundamental spectra of both compounds and the two first ν(CH) overtone spectra of toluene present a good agreement with the experimental findings. Both molecules exhibit almost the same spectral profiles, a signature of similar internal dynamics of the methyl group essentially governed by the internal rotation potential. Comparison of these results with those previously obtained for monohydrogenated nitromethane reveals that the molecular environment of the methyl group (NO_2, C_6D_5, and C_5ND_4) is at the origin of some spectral differences, essentially related to differences in electric anharmonicity.

Introduction

The flexibility of a molecule, characterized by a large-amplitude, very anharmonic motion (e.g., internal rotation of CH_3 group, ring puckering of small cycles, isomerization), is an important factor in chemical reactions. These types of motions are generally coupled with vibrational motions, particularly with the CH stretching vibrations.[1−14]

This coupling induces a conformational dependence of the CH vibrators, which become nonequivalent during the large-amplitude motion, and leads to complex features observed in the fundamental Raman and infrared spectra.[1−6,8−10]

The internal rotation of the methyl group in toluene and γ-picoline in the gas phase is a quasifree motion, with barriers of 4.9 and 4.75 cm^{-1} for toluene[15] and γ-picoline,[16] respectively as determined by microwave. Analysis of vibrationally excited CH stretching spectra of toluene[11,13] and some of its fluoro derivatives[12,14] (from $\Delta v = 3$ to 7) shows that the complex structure is conserved in the excited states. The spectra can also be perturbed by the presence of strong CH stretch−bend Fermi resonance phenomena, leading to intramolecular vibrational energy redistribution (IVR). Some studies of fluorescence spectra of various fluorotoluenes show that a quasifree rotating methyl group acts as an accelerator of IVR in the electronic excited state.[17−19]

The potential of internal rotation of the CH_3 group has a 6-fold symmetry in the case of toluene and γ-picoline, according to both the symmetry of its environment and the planarity of the benzene and pyridine moieties.[15,16]

The aim of this work is to simulate vibrational CH-stretching spectra, reflecting the coupling between the methyl CH vibrators and the internal rotation, according to a quantum theory presented in the next part of this paper. Comparison of these simulated spectra with the spectra found experimentally enables us to evidence and quantify possible Fermi resonance phenomena in highly vibrationally excited states.

We are especially interested in the CHD_2 derivatives of toluene and γ-picoline, because the CH vibrator so isolated is very sensitive to intramolecular dynamics. The fundamental IR and Raman CH-stretching spectra of these molecules are reconstructed, as are the two first ν(CH) overtone spectra of toluene, and are compared with the experimentally determined spectra.

Effective potentials of CHD_2 internal rotation are determined from ab initio calculations at the Hartree−Fock (HF) level in the 6-31G** basis set. The conformational dependence of the CH vibrational energy is obtained from a precise correlation between CH bond length calculated both ab initio and by its stretching frequency.[20−22]

The effect of the environment of the methyl group on the internal rotation is studied by comparing the results obtained for toluene and γ-picoline and for the already analyzed internal rotation of the methyl group in nitromethane, CH_3NO_2,[2] and its partially deuterated derivatives.

Experimental Section

Synthesis and Spectra. The isotopic derivatives were synthesized according to the previously published procedure.[1,5]

The Raman spectra were recorded with a Raman multichannel spectrometer DILOR OMARS 89 equipped with a liquid N_2-cooled charge-coupled device EG&G Princeton Applied Research and a Spectra Physics 2017 argon ion laser (514.5 nm beam at 4 W) as exciting radiation. The gaseous compounds were transferred under vacuum into a cylindrical Pyrex cell equipped with two windows tilted at the Brewster angle for multiple reflections. The resolution was 1 cm^{-1}. The infrared spectra were recorded with a Fourier-transform infrared (FTIR) spectrometer (Bio-Rad FTS-60A) and gas cells equipped with

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CaF_2 windows: a homemade cell ($l = 10$ cm) and an Infrared Analysis long path cell ($l = 1-7$ m).

In the cells, the gas was at equilibrium pressure at room temperature (29 mmHg for toluene, 6 mmHg for 4-methylpyridine).

Method of Calculation. All the calculations were performed with the GAUSSIAN 92 program[23] at the HF level, in the 6-31G** basis set. Vibrational frequencies were obtained by determining second derivatives of energy analytically with respect to geometry distortions.

As we are interested in the variations of the geometrical parameters and not in their exact values, we show that this level of calculation is sufficient to obtain results in good agreement with experimental ones.

Theoretical Approach

The basic idea of the theory developed to simulate the CH-stretching spectra is to suppose that the fast methyl group vibrations, and particularly the ν(CH) stretching vibration, are coupled to the much slower internal rotation motion of the methyl group. These vibrations then depend on the rotation coordinate. In a first approximation, the internal rotation motion may be described by a Hamiltonian of the form:

$$\frac{H_1}{hc} = -\frac{\partial}{\partial\theta}\,\mathrm{B_v}(\theta)\,\frac{\partial}{\partial\theta} + \mathrm{V}(\theta) \qquad (1)$$

where θ is the internal rotation coordinate, $\mathrm{V}(\theta)$ the rotational potential energy, and $\mathrm{B_v}(\theta)$ the reduced rotational constant of the methyl rotor. $\mathrm{B_v}(\theta)$ varies with θ and with the vibrational quantum number v as $\mathrm{B_v}(\theta) = \mathrm{B}_e(\theta) - \alpha(v + 1/2)$. $\mathrm{B}_e(\theta)$ and α are determined from ab initio calculations.[24,25]

The vibrational Hamiltonian for polyatomic molecules can be written in terms of curvilinear internal coordinates q_i and their conjugate moments p_{q_i}:

$$\frac{H_2}{hc} = \Sigma\left\{\frac{1}{2}\,p_{q_i}^{+}\,\mathrm{g}(q_i)\,p_{q_i} + \mathrm{V}(q_i,\theta)\right\} \qquad (2)$$

where the Wilson matrix $g(q_i)$ is function of internal curvilinear coordinates and atomic masses.[26]

The coupling of the vibrational and large-amplitude motions is modeled by the total Hamiltonian $H_T = H_1 + H_2$, which is solved in the adiabatic approximation. The total wave function ϕ_T is written as a product of two wave functions, $\varphi(q_i,\theta)$, which describes the fast vibrational motions and depends slowly on θ, and $\psi(\theta)$, which describes the much slower internal rotation motion. Thus, the Schrödinger equation can be separated into two equations, one describing the vibrations of the molecule for each θ value, the other describing the large-amplitude motion and depending on the vibrational energy $e(\theta)$:

$$\begin{cases} H_2(q_i,\theta)\varphi(q_i,\theta) = e(\theta)\,\varphi(q_i,\theta) \\ [H_1(\theta) + e(\theta)]\,\psi(\theta) = E\,\psi(\theta) \end{cases} \qquad (3)$$

The vibrational energy $e(\theta)$ acts as an additional potential for the rotational motion. Thus, even in the ground vibrational state, the effective potential of the rotation motion depends on the molecular energy:

$$\mathrm{V_{eff}}(\theta,0) = \mathrm{V}(\theta) + \frac{1}{2}\sum_i e_i(\theta) \qquad (4)$$

where $1/2\,\sum_i e_i(\theta)$ is the zero-point vibrational energy (ZPVE) of the $3N - 7$ vibrations other than the internal rotation.

When the CH bond is excited by v quanta of energy, the effective potential of the internal rotation is increased by the corresponding vibrational part:

$$\mathrm{V_{eff}}(\theta,\mathrm{v}) = \mathrm{V_{eff}}(\theta,0) + e_{\mathrm{CH}}(\theta) \qquad (5)$$

The Fermi resonance phenomena, resulting from the anharmonic coupling of degenerated vibrational states [e.g., $n\nu$(CH) and $(n - 1)\nu$(CH) + 2δ(CH)], can perturb this vibrational energy contribution. They can be modeled with a first-order perturbative treatment, as has been done previously.[3,4,9,10] In the absence of strong coupling perturbation, which is the case for the CH stretching of the CHD_2 methyl group, at least for the first excited vibrational states, this vibrational energy can be approximated by

$$e_{\mathrm{CH}}(\theta) = \mathrm{v}\Delta\bar{\omega}_{\mathrm{CH}}(\theta) + \mathrm{v}(\mathrm{v} + 1)\Delta\bar{\chi}_{\mathrm{CH}}(\theta) \qquad (6)$$

where $\Delta\bar{\omega}_{\mathrm{CH}}(\theta)$ and $\Delta\bar{\chi}_{\mathrm{CH}}(\theta)$ are the variations of harmonic frequency and anharmonicity, respectively, of the CH bond stretch.

The Schrödinger equations of the internal motion corresponding to the two vibrational levels v = 0 and v are diagonalized on a basis set of 85 free rotors. They give the internal-rotation energy levels and their corresponding wave functions in the two CH-stretching vibrational states. The CH bond-stretching spectra are reconstructed by adding the CH-stretching transitions calculated between the energy levels of the two rotational potentials $\mathrm{V_{eff}}(\theta,\mathrm{v})$ and $\mathrm{V_{eff}}(\theta,0)$, separated by an arbitrary energy corresponding to the CH-stretching frequency in its equilibrium position.

The intensities of these transitions are calculated from the following relationship:

$$I_{|0,n\rangle\rightarrow|\mathrm{v},n'\rangle} = P\left(\iint \varphi_{\mathrm{v}}^{*}(q,\theta)\,\psi_{\mathrm{v}n'}^{*}(\theta)\,A(q,\theta)\,\varphi_0(q,\theta)\,\psi_{0n}(\theta)\,\mathrm{d}q\mathrm{d}\theta\right)^2 \qquad (7)$$

where P is the Boltzmann factor, $\exp[-(E_{0n} - E_{00})/kT]$, and $|0,n\rangle$ and $|\mathrm{v},n'\rangle$ are the nth and n'th rotational levels, respectively, in the ground and excited states of the CH bond-stretching. $A(\mathrm{q},\theta)$ is the transition operator, that is, the mean polarizability for the isotropic Raman spectrum and the dipole operator μ for the infrared one.

In the adiabatic approximation, the two integrals of eq 7 can be separated to obtain the following expression:

$$\mathrm{I}_{|0,n\rangle\rightarrow|\mathrm{v},n'\rangle} = P\left\{\int \varphi_{\mathrm{v}}^{*}(q,\theta)\,\varphi_0(q,\theta)\,\mathrm{d}q \int \psi_{\mathrm{v}n'}^{*}(\theta)\,A_0(q,\theta)\,\psi_{0n}(\theta)\,\mathrm{d}\theta + \sum_i \int \varphi_{\mathrm{v}}^{*}(q,\theta)\,q^i\,\varphi_0(q,\theta)\,\mathrm{d}q \int \psi_{\mathrm{v}n'}^{*}(\theta)\left(\frac{\partial^i A(q,\theta)}{\partial q^i}\right)_0 \times \psi_{0n}(\theta)\,\mathrm{d}\theta\right\}^2 \qquad (8)$$

in which the transition operator $A(q,\theta)$ is expanded in Taylor series around its equilibrium position:

$$A(q,\theta) = A_0(q,\theta) + \left(\frac{\partial A(q,\theta)}{\partial q}\right)_0 q + \left(\frac{\partial^2 A(q,\theta)}{\partial q^2}\right)_0 q^2 + \ldots \qquad (9)$$

TABLE 1: Matrix Elements $\langle \mathrm{v} | q^n | 0 \rangle$ for a Morse Oscillator (in Å^n) for a CH Bond in Monohydrogenated Toluene

v	$n = 1$	$n = 2$	$n = 3$	$n = 4$	exponent
1	7.7970	0.4245	0.1638	0.0188	−2
2	−7.7325	8.0827	0.8196	0.3830	−3
3	1.2642	−2.0017	0.9092	0.1296	−3
4	−2.7108	5.2427	−4.1734	0.9847	−4
5	0.7000	−1.5334	1.5923	−0.7826	−4
6	−2.0830	4.9800	−6.0920	4.1570	−5

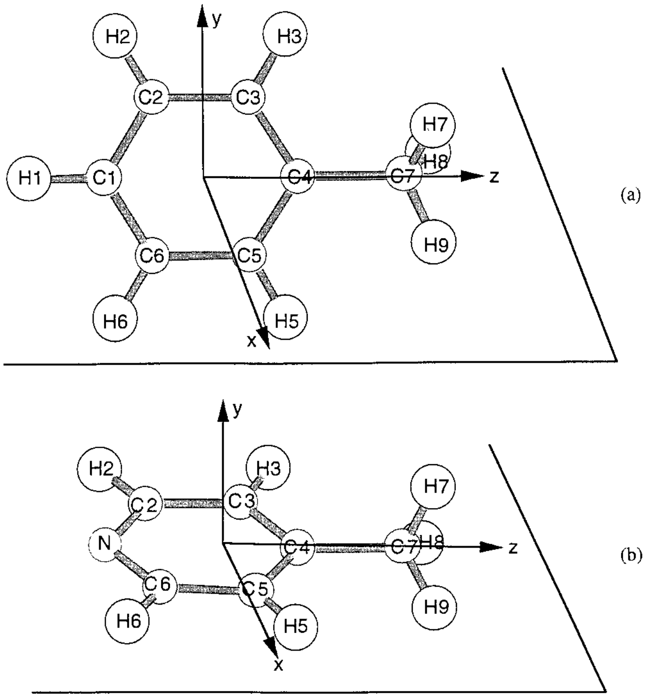

Figure 1. Equilibrium structures of toluene (a) and γ-picoline (b) and the numbering of the atoms.

The first term of eq 8 is zero because of the wave functions' orthogonality, so the intensity of a transition can be written:

$$I_{|0,n\rangle \to |\mathrm{v},n'\rangle} = P\left\{\sum_i \int \varphi_{\mathrm{v}}^*(q,\theta)\, q^i\, \varphi_0(q,\theta)\, \mathrm{d}q \int \psi_{\mathrm{v}n'}^*(\theta) \left(\frac{\partial^i A(q,\theta)}{\partial q^i}\right)_0 \times \psi_{0n}(\theta)\, \mathrm{d}\theta\right\}^2 \quad (10)$$

Two factors are thus important in this intensity calculation: The first integral is determined by the matrix elements over the Morse oscillator wave functions (used to describe the very anharmonic CH vibrators) and the power of the CH coordinate (Table 1); the second integral depends on the size of the transition operator derivatives.

Infrared Spectrum. In this case, A is the dipole moment vector μ, which can be decomposed along the three inertia axes of the molecule x, y, and z, shown in Figure 1. The infrared intensity is the result of the combination of the three contributions $\mu_x(\theta)$, $\mu_y(\theta)$, and $\mu_z(\theta)$, varying with the rotational coordinate θ. Equation 10 may then be written:

$$I_{|0,n\rangle \to |\mathrm{v},n'\rangle} = P \sum_{j=1}^{3} \{\sum_i \int \varphi_{\mathrm{v}}^*(q,\theta)\, q^i\, \varphi_0(q,\theta)\, \mathrm{d}q \times \int \psi_{\mathrm{v}n'}^*(\theta)\, \mu_j^i(\theta)\, \psi_{0n}(\theta)\, \mathrm{d}\theta\}^2 \quad (11)$$

with $j = x$, y, and z.

TABLE 2: Ab Initio HF/6-31G Dipole Moment Derivative Expansion Coefficients for the CH Bond in Monohydrogenated Toluene: $\mu'^j_i(\theta) = a + b \cos 2\theta + c \cos 4\theta$ (in D·Å^{-i})**

	a	b	c
$\mu'^1_x(\theta)$	0.641	0.024	−0.005
$\mu'^1_y(\theta)$	−0.675	−0.010	−0.006
$\mu'^1_z(\theta)$	0.554	−0.013	0.008
$\mu'^2_x(\theta)$	1.011	−0.028	−0.004
$\mu'^2_y(\theta)$	−1.165	0.013	−0.013
$\mu'^2_z(\theta)$	0.861	−0.186	0.010
$\mu'^3_x(\theta)$	−0.058	−0.052	−0.002
$\mu'^3_y(\theta)$	0.112	0.051	0.002
$\mu'^3_z(\theta)$	0.051	−0.120	−0.009
$\mu'^4_x(\theta)$	−0.179	0.000	−0.004
$\mu'^4_y(\theta)$	0.261	0.037	0.011
$\mu'^4_z(\theta)$	−0.275	0.059	−0.017

TABLE 3: Ab Initio HF/6-31G Dipole Moment Derivative Expansion Coefficients for the CH Bond in Monohydrogenated γ-Picoline: $\mu'^j_i(\theta) = a + b \cos 2\theta + c \cos 4\theta$ (in D·Å^{-i})**

	a	b	c
$\mu'^1_x(\theta)$	0.616	0.025	0.000
$\mu'^1_y(\theta)$	−0.574	−0.001	0.001
$\mu'^1_z(\theta)$	0.436	0.046	0.000
$\mu'^2_x(\theta)$	0.947	−0.015	0.005
$\mu'^2_y(\theta)$	−1.053	0.027	−0.006
$\mu'^2_z(\theta)$	0.745	−0.092	0.003
$\mu'^3_x(\theta)$	−0.098	−0.034	0.000
$\mu'^3_y(\theta)$	0.132	0.032	−0.002
$\mu'^3_z(\theta)$	0.003	−0.093	−0.005
$\mu'^4_x(\theta)$	−0.180	0.008	0.008
$\mu'^4_y(\theta)$	0.241	0.024	0.008
$\mu'^4_z(\theta)$	−0.226	0.043	−0.010

At $\Delta \mathrm{v} = 1$, the first-order term of the dipole moment derivatives is the most important one (Table 1), but the contributions of the high-order terms become increasingly important as the vibrational energy increases.

The coefficients $\mu_j^i(\theta)$ are calculated by fitting a three-dimensional grid of dipole moments with a fourth-order Taylor series expansion. The grids are constructed by displacing serially from their equilibrium position each of the three CH or CD coordinates, by steps of 0.1 Å in a range of ±0.3 Å, the rest of the molecule staying in its optimized conformation.[3,9,27−32] This leads to grids of dimensions 7 × 7 × 7. Because dipole moment derivatives depend on the rotation angle of the methyl group, these calculations are realized for several values of the θ coordinate. The values of the coefficients $\mu'^i_x(\theta)$ ($\mu^i_x(\theta) = \mu'^i_x(\theta) \cos \theta$), $\mu'^i_y(\theta)$ ($\mu^i_y(\theta) = \mu'^i_y(\theta) \sin \theta$), and $\mu'^i_z(\theta)$ ($\mu^i_z(\theta) = \mu'^i_z(\theta)$), and their variations with the rotation angle are given in Tables 2 and 3.

We have neglected any interaction between methyl internal rotation and rotation of the whole molecule. To account for the effect of the overall rotation of the molecule, each transition is convoluted by a theoretical vibration−rotation profile corresponding to each component of the spectrum (A, B, or C type, depending on whether the considered transition involves the μ_z, μ_x, or μ_y dipole component). To calculate the spectra, we have assigned to each transition its corresponding vibration−rotation theoretical profile, calculated in the harmonic approximation from rotational constants determined by ab initio calculations.[33−35]

TABLE 4: Geometric Parameters of Toluene and γ-Picoline (Bond Lengths in Å, Angles in deg, Energies in hartrees)

	toluene				γ-picoline	
	6-31G**	6-31G**	6-31G*[a]	exp[b]	6-31G**	6-31G**
angle	0°	90°	90°		0°	90°
XC_2[c]	1.3826	1.3849	1.385	1.3976	1.3187	1.3206
C_2C_3	1.3876	1.3851	1.386	1.3976	1.3857	1.3836
C_3C_4	1.3877	1.3901	1.390	1.3976	1.3862	1.3882
XC_6[c]	1.3872	1.3849	1.385	1.3976	1.3230	1.3208
C_5C_6	1.3827	1.3851	1.385	1.3976	1.3814	1.3834
C_4C_7	1.5112	1.5112	1.516	1.509	1.5082	1.5081
C_1H_1	1.0757	1.0757	1.075	1.098		
C_2H_2	1.0761	1.0761	1.076	1.098	1.0770	1.0770
C_3H_3	1.0766	1.0769	1.076	1.098	1.0753	1.0756
C_5H_5	1.0772	1.0769	1.077	1.098	1.0759	1.0756
C_6H_6	1.0761	1.0761	1.075	1.098	1.0770	1.0769
C_7H_7	1.0839	1.0868	1.086	1.145	1.0834	1.0861
C_7H_8	1.0860	1.0846	1.084	1.145	1.0855	1.0841
C_7H_9	1.0860	1.0845	1.083	1.145	1.0853	1.0840
XC_2C_3[c]	120.22	120.22	120.2	120.0	123.83	123.83
$C_2C_3C_4$	120.95	120.95	121.0	120.0	119.20	119.20
C_2XC_6[c]	119.38	119.38	119.4	120.0	117.04	117.04
XC_6C_5[c]	120.21	120.21	120.2	120.0	123.84	123.83
$C_7C_4C_3$	121.33	120.87	120.8	120.0	121.99	121.56
$H_1C_1C_6$	120.27	120.31	120.3	120.0		
H_2C_2X[c]	120.09	120.05	120.1	120.0	116.25	116.21
$H_3C_3C_2$	119.46	119.51	119.5	120.0	119.84	119.88
$H_5C_5C_4$	119.48	119.53	119.5	120.0	120.89	120.92
$H_6C_6C_5$	119.78	119.73	119.7	120.0	120.00	119.96
$H_7C_7C_4$	111.19	111.11	108.4	107.6	111.15	110.65
$H_8C_7C_4$	111.18	111.22	110.0	107.6	110.94	111.10
$H_9C_7C_4$	111.17	111.22	108.5	107.6	110.79	111.11
energy	−269.7538858	−269.7538945			−285.7465554	−285.7465651

[a] Reference 36. [b] Reference 37. [c] $X = C_1$ for toluene, N for γ-picoline.

These profiles are convoluted by a Lorentzian whose half-width is adjusted for each spectrum.

Raman Spectrum. The transition operator is here the mean polarizability $\bar{\alpha}$, associated with the CH bond. As shown by the Morse coefficients (Table 1), the first term of the development of the transition operator is preponderant at $\Delta v = 1$. So, neglecting the conformational dependence of the polarizability, eq 10 may be written as:

$$I_{|0,n\rangle\to|v,n\rangle} = P\left(\frac{\partial\bar{\alpha}}{\partial q}\right)^2 \langle 1,n'|0,n\rangle^2 \qquad (12)$$

The isotropic Raman spectrum is calculated by assigning a Lorentzian profile to each transition between the potential energy levels of the first excited vibrational ν(CH) state and the ground state of internal rotation.

The parameters used to reconstruct the CH-stretching spectra (the variations of $r(\theta)$, $\omega(\theta)$, $\mu_x(\theta)$, $\mu_y(\theta)$, $\mu_z(\theta)$, and ZPVE) are determined from ab initio calculations.

Results

Geometry Optimizations and Frequency Calculations. *Toluene*: The geometry of toluene has been optimized for several values of the rotation angle θ of the methyl group. The calculated parameters for $\theta = 90°$ and 0° are reported in Table 4, along with those determined in a 6-31G* basis set,[36] and the experimental values.[37] In these calculations, the ring was constrained to be planar, to reduce the computational effort. This is an inconsequential approximation, the energy difference between the full optimization and this constrained optimization being only 1 cm^{-1}.

The major parts of the calculated parameters (in the 6-31G** basis set) present a small variation when going from the 0° to the 90° conformations. The angles formed by the C atoms of the ring remain constant, as do the C4—C7 (Figure 1) and the C*i*—H*i* (*i* = 1, 2, and 6) bond lengths of the ring. However, the two C—H bonds adjacent to the methyl group (C3H3 and C5H5) are weakly affected by the internal rotation ($\Delta r_{CH} = 0.6 \times 10^{-3}$ Å). The methyl CH bonds show a strong perturbation related to the internal rotation.

The addition of polarization functions on the H atoms, when going from the 6-31G* to the 6-31G** basis set, improves the reproduction of experimental parameters, especially for the CH bonds and the ring angles. Although the methyl C—C—H angles are badly reproduced, the regularity of experimental values is retrieved in our parameters.

γ-Picoline: Very few calculations have been performed on γ-picoline,[38,39] and no experimentally determined structure is available with which to compare our results. The geometrical parameters we calculated in a 6-31G** basis set are reported in Table 4 for two values of the internal rotation angle θ: 0° and 90°. The ring was constrained to be planar in the optimizations. As in the toluene case, the C—C—C angles of the ring remain unchanged when going from 0° to 90°. The two C—H bonds far away from the methyl group (C2H2 and C6H6) (Figure 1) are unperturbed too, as is the C4C7 bond length. On the other hand, the C3H3 and C5H5 bonds of the ring adjacent to the methyl group are perturbed by exactly the same amplitude as those in toluene. This may be due to weak van der Waals interactions between these methyl and aliphatic CH bonds. Finally, the methyl C7H*i* (*i* = 7 to 9) bonds are strongly affected by the internal motion.

We conclude from these findings that toluene and γ-picoline have very similar behavior and that we will achieve a parallel treatment for both molecules. The equilibrium conformation corresponds to $\theta = 90°$ for both compounds (Table 4), that is,

TABLE 5: Parameters Involved in Calculating the Spectra of Monohydrogenated Toluene and γ-Picoline

		toluene	γ-picoline
barrier	calc	$V_6 = 1.9$	$V_6 = 2.1$
(cm^{-1})	exp	$V_6 = 4.9^a$	$V_6 = 4.75^b$
$r_{CH}(\theta)$	(Å)	$r_0 = 1.0853$	$r_0 = 1.0848$
		$r_2 = -1.46 \times 10^{-3}$	$r_2 = -1.65 \times 10^{-3}$
		$r_4 = 0.06 \times 10^{-3}$	$r_4 = 0.08 \times 10^{-3}$
$E(\theta)$	(cm^{-1})	$E_0 = 22347.5$	$E_0 = 20586.9$
		$E_2 = 12.4$	$E_2 = 15.0$
$V_{eff}(\theta,0)$	(cm^{-1})	$V_2^0 = 12.4$	$V_2^0 = 15.0$
		$V_6^0 = 4.9$	$V_6^0 = 4.75$
$\Delta\omega_{CH}(\theta)$	(cm^{-1})	$\omega_2 = 36.0$	$\omega_2 = 33.0$
		$\omega_4 = -1.2$	$\omega_4 = -2.0$
$\Delta\nu_{CH}(\theta)$	(cm^{-1})	$\nu_2 = 40.0$	$\nu_2 = 40.0$
		$\nu_4 = -1.2$	$\nu_4 = -2.0$
$V_{eff}(\theta,1)$	(cm^{-1})	$V_2^1 = 52.4$	$V_2^1 = 55.0$
		$V_4^1 = -1.2$	$V_4^1 = -2.0$
		$V_6^1 = 4.9$	$V_6^1 = 4.75$
$V_{eff}(\theta,2)$	(cm^{-1})	$V_2^2 = 96.4$	
		$V_4^2 = -2.4$	
		$V_6^2 = 4.9$	
$V_{eff}(\theta,3)$	(cm^{-1})	$V_2^3 = 144.4$	
		$V_4^3 = -3.6$	
		$V_6^3 = 4.9$	

[a] Reference 15. [b] Reference 16.

when a CH bond is in the plane perpendicular to the molecular plane. The calculated potential energy of internal rotation has a 6-fold symmetry, with an electronic barrier of 1.9 cm^{-1} for toluene (Table 5) (4.9 cm^{-1} experimentally[15]). This value is very close to the 2 cm^{-1} calculated in a 6−311G** basis set[40] and shows that the use of a larger basis set leads to no real improvement.

To compare precisely the calculated barrier with the experimental one, we have to take into account the vibrational contribution from ZPVE of all the modes except internal rotation ($3N - 7$ modes). From frequency calculations of toluene C_6D_5-CH_3 performed for several θ values in the 6-31G** basis set, we obtain a difference of ZPVE between the perpendicular and parallel conformations (i.e., for a CH bond being in the plane perpendicular or parallel, respectively, to the molecular plane) of 0.6 cm^{-1}, the same as that determined by Hameka and Jensen[40] with a 6−311G** basis set. Such a value is within the limits of calculations accuracy and thus we do not include it in the barrier height. More-sophisticated calculations have shown that the addition of electronic correlation via MP2 (second-order Møller−Plesset perturbation) methods greatly affect the electronic barrier, the agreement with experiment being very good when the ZPVE contribution is added.[40] However, for our purposes in this paper, we can consider that our calculations lead to a correct order of magnitude when compared with the experimentally determined[15] barrier (4.9 cm^{-1}).

The barrier height calculated for γ-picoline is 2.1 cm^{-1} (Table 5), and constitutes only the electronic contribution, the variation of ZPVE for $NC_5D_4CH_3$ being zero. The agreement with the experimental data[16] (4.75 cm^{-1}) is similar to that obtained for toluene.

In the following, we will use the more reliable experimental values of the barriers to define the internal rotation potential energy $V(\theta)$ for both compounds (Table 5):

$$V(\theta) = \frac{V_6}{2}(1 + \cos 6\theta) \qquad (13)$$

The calculated variation of the methyl CH bond length during the internal motion can be fitted by the expression:

$$r_{CH}(\theta) = r_0 + r_2 \cos 2\theta + r_4 \cos 4\theta \qquad (14)$$

The parameters reported in Table 5 display a very small contribution in cos 4θ for both molecules, showing there is essentially a two-order symmetry with respect to the molecular plane. The maximum lengthening difference is of 2.9×10^{-3} and 3.3×10^{-3} Å for toluene and γ-picoline, respectively. In Figure 2, where these variations are represented, we can see that the CH bond is the longest for a θ angle of 90°, corresponding to the equilibrium conformation, and the shortest for $\theta = 0°$. As in the nitromethane case,[2] this behavior can be explained by a hyperconjugation effect of the benzene or pyridine electronic cloud on the methyl CH bond.

Vibrational frequency calculations have been performed on monohydrogenated derivatives at several θ values. Because ab initio frequencies are always overestimated at the HF level, they have been scaled by factors of 0.911 for ν(CH), 0.921 for ν(CD), and 0.9 for the others. The two first factors are those previously determined for nitromethane,[2] with the last one being typically used in this basis set.[41−43] The calculated and scaled frequencies are reported for $\theta = 0°$ and 90° in Tables 6 and 7, respectively, for toluene and γ-picoline. The infrared and Raman experimental frequencies recorded in gas phase are also reported in these Tables.

The scaled ZPVE (i.e., one-half the sum of the $3N - 7$ vibrations other than the internal motion) also presents a conformational dependence that can be expressed (Table 5) according to the following relation:

$$E(\theta) = E_0 + \frac{1}{2}(E_2 \cos 2\theta + E_4 \cos 4\theta) \qquad (15)$$

The effective potential of internal rotation in the ground-vibrational state can then be calculated from eq 4, taking only the nonconstant part of ZPVE into account (Table 5):

$$V_{eff}(\theta,0) = \frac{1}{2}(V_2^0 \cos 2\theta + V_6^0 \cos 6\theta) \qquad (16)$$

To determine the effective potential of internal rotation in the first excited ν(CH) vibrational state, we have to know the variation of the CH vibrational energy. The variation during the internal rotation motion of the scaled calculated harmonic CH-stretching frequencies can be fitted by the following expression, reported in Table 5 (the constant part is omitted because it does not enter in effective potential calculations):

$$\Delta\omega_{CH}(\theta) = \frac{1}{2}(\omega_2 \cos 2\theta + \omega_4 \cos 4\theta) \qquad (17)$$

Comparison of the parameters involved in eqs 14 and 17 shows that a variation of CH bond length of 10^{-3} Å leads to a harmonic vibrational frequency shift of 12.3 and 10.9 cm^{-1} for toluene and γ-picoline, respectively. These values are in good agreement with those found for a large range of molecules,[20−22] and particularly for nitromethane.[2]

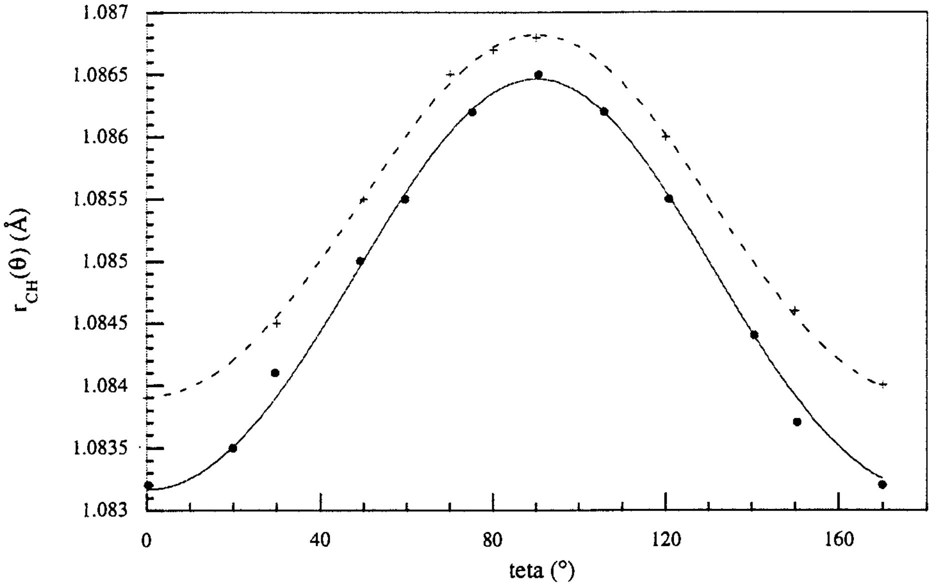

Figure 2. Calculated CH bond lengths of toluene (+) and γ-picoline (●) for various torsional angles and their parametrization by a cos 2θ and cos 4θ function (- - - for toluene, ___ for γ-picoline).

TABLE 6: Experimental and Calculated Vibrational Frequencies for Toluene ($C_6D_5CHD_2$) and Scaled by Factors of 0.911 for ν(CH), 0.921 for ν(CD), and 0.9 for the Others (in cm^{-1})

0°	90°	0° scaled	90° scaled	exp	assignment
3248.2	3211.2	2959.1	2925.4	2970/2947.5/2934	νCH
2500.1	2500.1	2302.6	2302.6	2312	7a
2486.7	2486.7	2290.2	2290.2	2295	2
2476.5	2476.4	2280.8	2280.8	2276	20a
2463.4	2463.6	2268.8	2269.0	2267	20b
2455.9	2456.2	2261.9	2262.2		7b
2400.9	2418.1	2211.2	2227.1	2206	νaCD$_2$
2323.4	2335.2	2139.8	2150.7	2148	νsCD$_2$
1768.8	1768.7	1591.9	1591.8	1590	8a
1738.4	1735.0	1564.6	1561.5	1573	8b
1537.4	1537.0	1383.7	1383.3	1391	19a
1491.7	1469.7	1342.5	1322.7	1311	19b
1430.0	1429.4	1287.0	1286.5	1284.5	δHCD
1419.0	1417.4	1277.1	1275.7	1267.5	δHCD
1263.9	1265.3	1137.5	1138.8	1156	14
1254.5	1263.5	1129.0	1137.1	1146	13
1159.7	1159.1	1043.7	1043.2	1047	δCD$_2$
1153.6	1156.0	1038.2	1040.4	1004	3
1042.8	1042.5	938.5	938.2	962	12
989.3	1032.5	890.4	929.2	889.5	rCHD$_2$
947.4	952.4	852.7	857.2	871.5	9a
922.6	931.0	830.3	837.9	841	5
920.6	922.1	828.5	829.9		18b
913.3	920.5	822.0	828.4		18a
899.5	899.7	809.5	809.7		15
892.5	892.5	803.2	803.2		17a
959.3	856.1	863.4	770.5		rCHD$_2$
806.6	825.3	725.9	742.8	722	1
778.3	781.5	700.5	703.3	698	10b
743.2	743.2	668.9	668.9	656	10a
669.3	680.2	602.4	612.2	610.6	11
652.9	653.0	587.6	587.9	599	6b
607.2	608.2	546.5	547.4	543	4
534.1	533.9	480.7	480.5	495	6a
450.1	456.3	405.1	410.7	403	16b
396.2	396.4	356.6	356.8		16a
328.8	322.9	295.9	290.6	304	9b
210.2	209.2	189.2	188.3	188	17b
−21.0	9.6				τCHD$_2$
		22353.7	22341.3		ZPVE

TABLE 7: Experimental and Calculated Vibrational Frequencies for γ-Picoline ($NC_5D_4CHD_2$) and Scaled by Factors of 0.911 for ν(CH), 0.921 for ν(CD), and 0.9 for the Others (in cm^{-1})

0°	90°	0° scaled	90° scaled	exp	assignment
3257.7	3218.5	2967.8	2932.0	2984/2956/2943	νCH
2496.5	2496.1	2299.3	2298.9		7b
2490.6	2490.7	2293.8	2293.9		7a
2467.9	2467.8	2273.0	2272.9	2279	20b
2464.4	2464.3	2269.7	2269.7	2254.5	20a
2407.4	2427.6	2217.2	2235.8		νaCD$_2$
2329.6	2340.0	2145.6	2155.1	2155.5	νsCD$_2$
1776.4	1776.2	1598.7	1598.6	1576	8a
1743.6	1739.1	1569.3	1565.2	1548	8b
1562.7	1562.7	1406.4	1406.4	1398	19a
1471.5	1437.2	1324.3	1293.5	1332	19b
1427.6	1424.4	1284.8	1282.0	1285	δHCD
1408.1	1416.6	1267.3	1274.9	1245	δHCD
1271.1	1281.2	1144.0	1153.1	1170	14
1229.8	1228.6	1106.8	1105.8	1095	13
1157.1	1165.5	1041.4	1049.0	1054	δCD$_2$
1142.6	1141.8	1028.3	1027.6		9a
1063.3	1062.7	957.0	956.4	976	1
1026.3	1041.2	923.6	937.1	942	rCHD$_2$
994.8	1017.2	895.3	915.5	916	15
949.3	928.5	854.4	835.6	852	17a
928.3	923.0	835.5	830.7	839	5
916.9	919.3	825.3	827.4	831	1
909.2	907.3	818.3	816.6	813	18a
906.1	858.4	815.5	772.6	761	rCHD$_2$
792.9	799.5	713.6	719.5	738	18b
761.3	761.3	685.2	685.2	674	10a
712.8	717.6	641.5	645.9	654	10b
706.6	712.9	635.9	641.6		6b
681.7	693.3	613.5	624.0		4
531.3	531.4	478.2	478.2	493	6a
476.0	483.0	428.4	434.7	440	16b
378.5	378.7	340.7	340.8		16a
328.3	322.0	295.4	289.8	302	9b
215.1	214.1	193.6	192.7	190	17b
−23.4	20.0				τCHD$_2$
		20594.4	20579.4		ZPVE

Study of the CH overtone-stretching spectra of toluene (up to $\Delta v = 6^{44}$) shows that, as in the case of nitromethane,[3] the anharmonicity of the CH bond presents a conformational dependence, which can be estimated by: $\Delta\chi_{CH}(\theta) = 1.0 \cos 2\theta$. This value will also be used for γ-picoline.

The variation of the vibrational CH-stretching energy can then be calculated from eq 6 and parametrized according to the

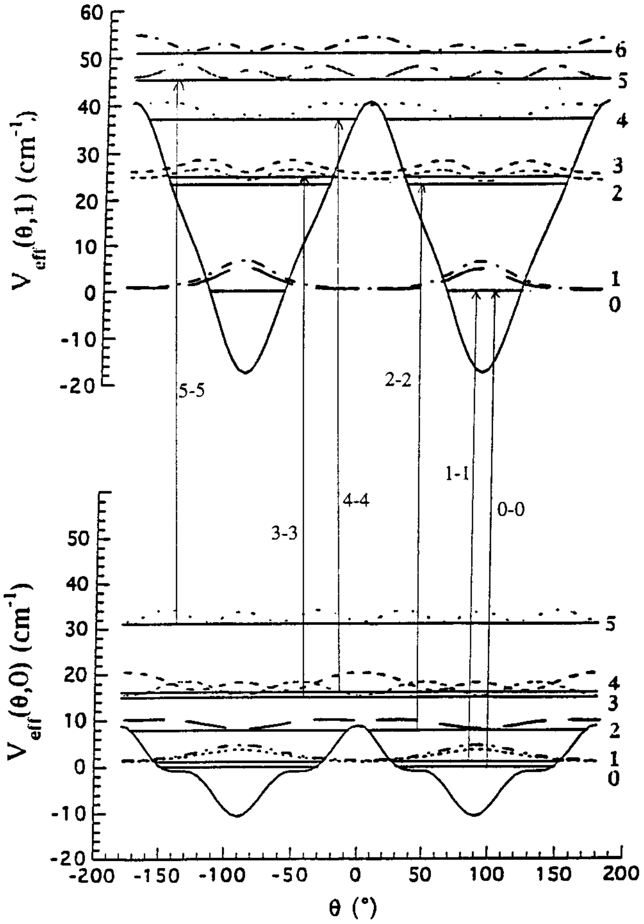

Figure 3. Effective potential of internal rotation in toluene, in the ground and in the first excited CH-stretching vibrational states.

following form (Table 5):

$$\Delta\nu_{CH}(\theta) = \frac{1}{2}(\nu_2 \cos 2\theta + \nu_4 \cos 4\theta) \qquad (18)$$

$V_{eff}(\theta,1)$ is then determined from eq 5 and now contains a contribution from cos 4θ (Table 5):

$$V_{eff}(\theta,1) = \frac{1}{2}(V_2^1 \cos 2\theta + V_4^1 \cos 4\theta + V_6^1 \cos 6\theta) \qquad (19)$$

$V_{eff}(\theta,0)$ and $V_{eff}(\theta,1)$ are represented in Figure 3 for toluene. We have calculated the energy levels of internal rotation in the two considered vibrational states, by diagonalization of the Schrödinger equation of internal rotation, the corresponding wave functions, and the transitions between these levels. Because the parameters of effective potentials are almost the same in toluene and γ-picoline, we have not included a graph for the latter compound, which is identical to Figure 3. The following analysis is thus valid for both molecules.

The wave functions of the two first rotational levels in the two vibrational states considered are localized in the potential wells. They give rise to two intense transitions, $|0,0\rangle \rightarrow |1,0\rangle$ and $|0,1\rangle \rightarrow |1,1\rangle$ corresponding to a CH vibrator in perpendicular position. The $|0,n\rangle \rightarrow |1,n\rangle$ transitions for $n \geq 5$, between roational energy levels above the barrier, correspond to a CH vibrator in free rotation, and the $|0,n\rangle \rightarrow |1,n\rangle$ transitions for $n = 2, 3, 4$ correspond to a CH vibrator in parallel position.

Comparison between Experimental and Calculated Spectra. The Raman CH-stretching spectra are reconstructed for toluene (Figure 4) and γ-picoline (Figure 5), the intensities having been calculated from Franck−Condon recoveries. These spectra exhibit two bands. The less intense one, at 2934 and 2944 cm^{-1} for toluene and γ-picoline, respectively, corresponds to a CH vibrator in perpendicular position, and the other one (at 2947.5 and 2956 cm^{-1}, respectively) corresponds to a mean frequency for a CH vibrator in free rotation. The calculated spectra are in good agreement with the experimental ones. However, comparing experimental and scaled ab initio frequencies (Tables 6 and 7), we observe a frequency shift toward high energy for the CH stretching of the methyl group. Such a shift was not present in nitromethane (CHD_2NO_2), in which the same scaled factors gave rise to calculated frequencies in very good agreement with the experimental ones.[2] The present frequency shift is due to weak anharmonic coupling with methyl CHD_2 group-bending overtones. This coupling becomes very strong for the CH_3 toluene derivatives and leads to strong Fermi resonance perturbation.[44] As expected, the spectra of the two molecules are very similar and in every respect resemble the spectrum of nitromethane.[2] This shows that the environment of the methyl group has nearly no influence on the fundamental Raman spectra.

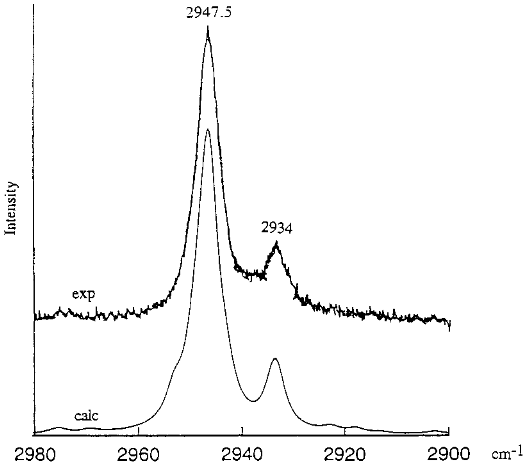

Figure 4. Experimental (top curve) and calculated (bottom curve) Raman spectra of the fundamental CH-stretching vibration of gaseous toluene, $C_6D_5CHD_2$, at 300 K.

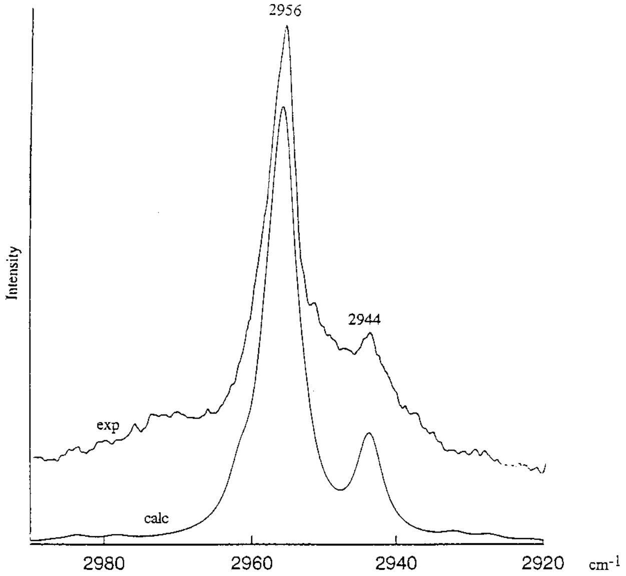

Figure 5. Experimental (top curve) and calculated (bottom curve) Raman spectra of the fundamental CH-stretching vibration of gaseous γ-picoline, 4-$CHD_2C_5ND_4$, at 300 K.

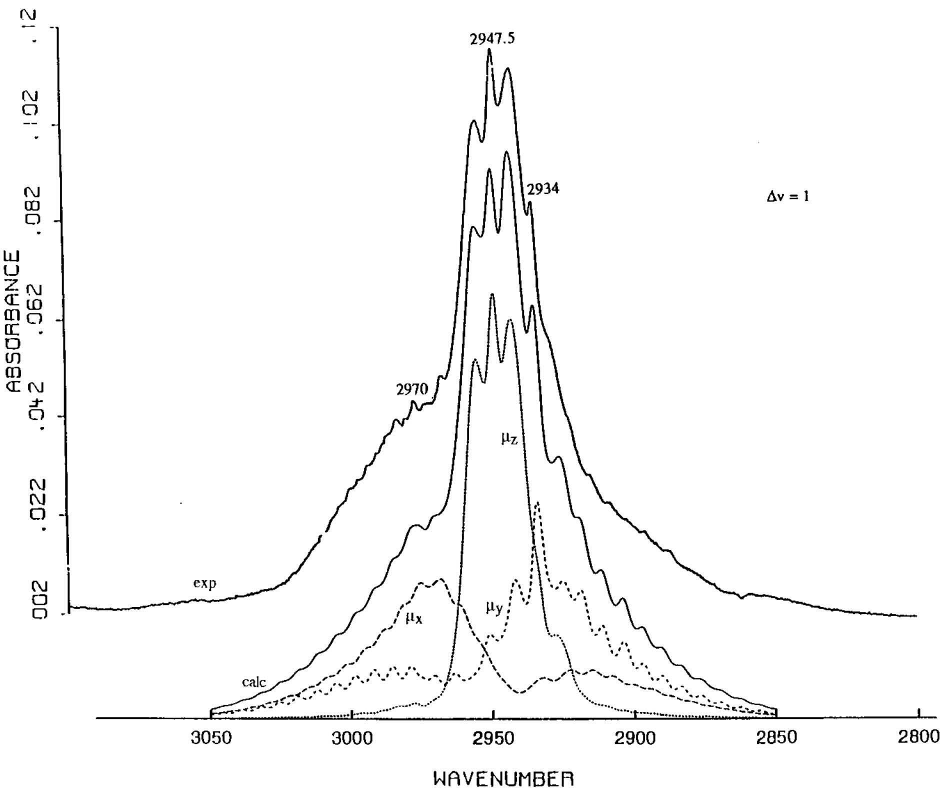

Figure 6. Experimental (top curve) and calculated (next lower curve) infrared spectra of the fundamental CH-stretching vibration of gaseous toluene, $C_6D_5CHD_2$, at 300 K. The experimental spectrum was obtained by FTIR with a 10-cm-path cell and a resolution of 0.5 cm^{-1}. The calculated spectrum (lower solid line) was obtained by summing the contributions of the three dipole moment components (shown by the bottom three dashed lines).

To reconstruct the fundamental ν(CH) infrared spectra, we calculated the intensity of each transition, taking into account the dipole moment derivatives through the fourth order (Tables 1−3), and convoluted these transitions by the corresponding vibration−rotation profile. The spectra so calculated are displayed in Figures 6 and 7 for toluene and γ-picoline respectively, with the spectra corresponding to each of the three dipole moment components; the experimental spectra are also shown. The major part of the intensity of the band comes from the μ_y component of the dipole moment for the CH bond in perpendicular position (2934 and 2941 cm^{-1}), from the μ_x component for the CH bond in parallel position (2970 and 2984 cm^{-1}), and from the μ_z component for the free rotor (2947.5 and 2956 cm^{-1}) (Figure 1). The fundamental calculated spectra are again in good agreement with the experimental ones. We can notice here an interesting difference from nitromethane,[3] the band corresponding to the CH vibrator in parallel position is visible here, but is almost absent in the corresponding spectrum of nitromethane, CHD_2NO_2. Indeed, in this latter compound, the μ_x^1 component of the dipole moment has a value very close to zero, thus extinguishing the corresponding transitions.

A further analysis of the dipole moment derivatives of the three compounds (Tables 2 and 3 here and Table 4 from our previous report[3]) shows they are very similar for toluene and γ-picoline only slightly higher for toluene. This explains the similarity of the IR spectra intensities (Figures 6 and 7). On the other hand, the dipole moment derivatives of nitromethane are much smaller. This can be related to the polarizability[45] of the X moiety for molecules X-CH_3 (where X = C_6H_5, NC_5H_4, or NO_2). The mean molecular polarizabilities $\bar{\alpha}$, where $\bar{\alpha} = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$, determined from ab initio calculations are 10.6, 9.8, and 4.1 × 10^{-40} C^2 m^2 J^{-1} for toluene, γ-picoline, and nitromethane, respectively. These polarizabilities follow the same order relation as the magnitude of dipole moment derivatives. We thus conclude that the greater the polarizability of the X substituent, the greater the induced dipole moment, and the greater the electric anharmonic contribution to intensity.

For toluene, we have also studied the spectra for Δv = 2 and 3. The effective potential of internal rotation in these vibrational states can be expressed according to the same relation as eq 19, and the parameters are given in Table 5.

The calculated spectra are represented in Figures 8 and 9, which show the contributions from the three components of the dipole moment in comparison and with the experimental spectra. Again, our model gives a good reproduction of the experimental spectra.

We can observe the same complex features as in the fundamental spectrum. The three bands at 5742, 5776, and 5806 cm^{-1} at Δv = 2 and at 8430, 8480, and 8528.5 cm^{-1} at Δv = 3 can respectively be assigned to the CH vibrator in perpendicular position, in free rotation, and in parallel position. The intensity contributions are comparable with those of the previous spectrum, except for that of the μ_y component, which is more intense. This results not only from the greater splitting of the two low-frequency profiles but also from to the increase of the internal rotation barrier with the increase in the vibrational quantum number v, inducing a more important localization of the wave functions in the potential wells. Actually, from v = 0 to v = 3, the barriers of hindered rotation are at 17.3, 57.3, 101.3, and 149.3 cm^{-1}. Furthermore, the μ_z component contribution presents, at the frequency corresponding to that of the μ_y component contribution, an intense peak not observed in the nitromethane spectra.[3] Again, the difference in electric anharmonicity can explain this difference, the component of

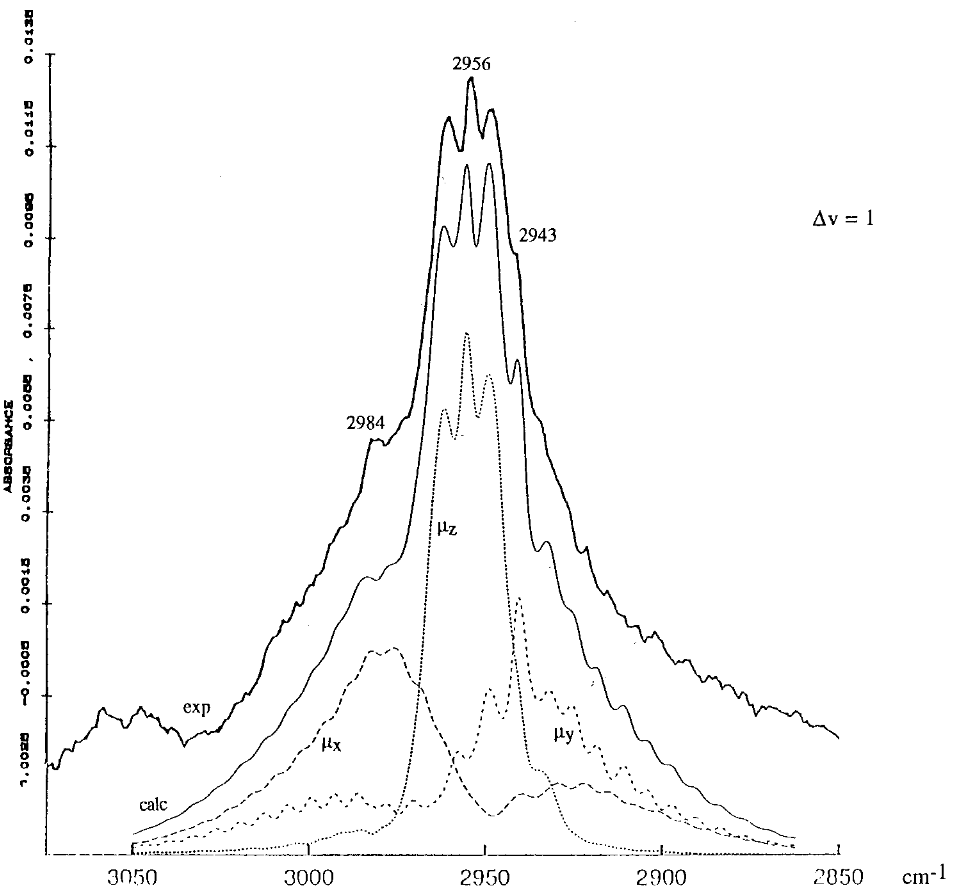

Figure 7. Experimental (top curve) and calculated (next lower curve) infrared spectra of the fundamental CH-stretching vibration of gaseous γ-picoline, 4-$CHD_2C_5ND_4$, at 300 K. The experimental spectrum was obtained by FTIR with a 10-cm-path cell and a resolution of 0.5 cm^{-1}. The calculated spectrum (lower solid line) was obtained by summing the contributions of the three dipole moment components (shown by the bottom three dashed lines).

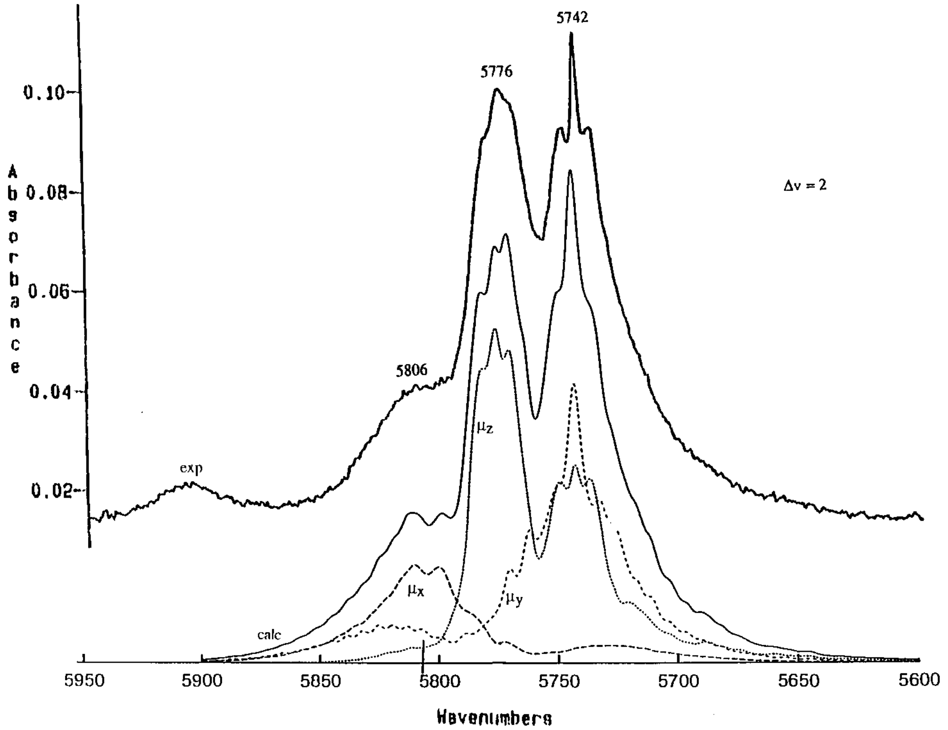

Figure 8. Experimental (top curve) and calculated (next lower curve) infrared spectra of the first overtone (Δv = 2) of the CH-stretching vibration of gaseous toluene, $C_6D_5CHD_2$, at 300 K. The experimental spectrum was obtained by FTIR with a 6.3-m-path cell and a resolution of 1 cm^{-1}. The calculated spectrum (lower solid line) was obtained by summing the contributions of the three dipole moment components (shown by the bottom three dashed lines).

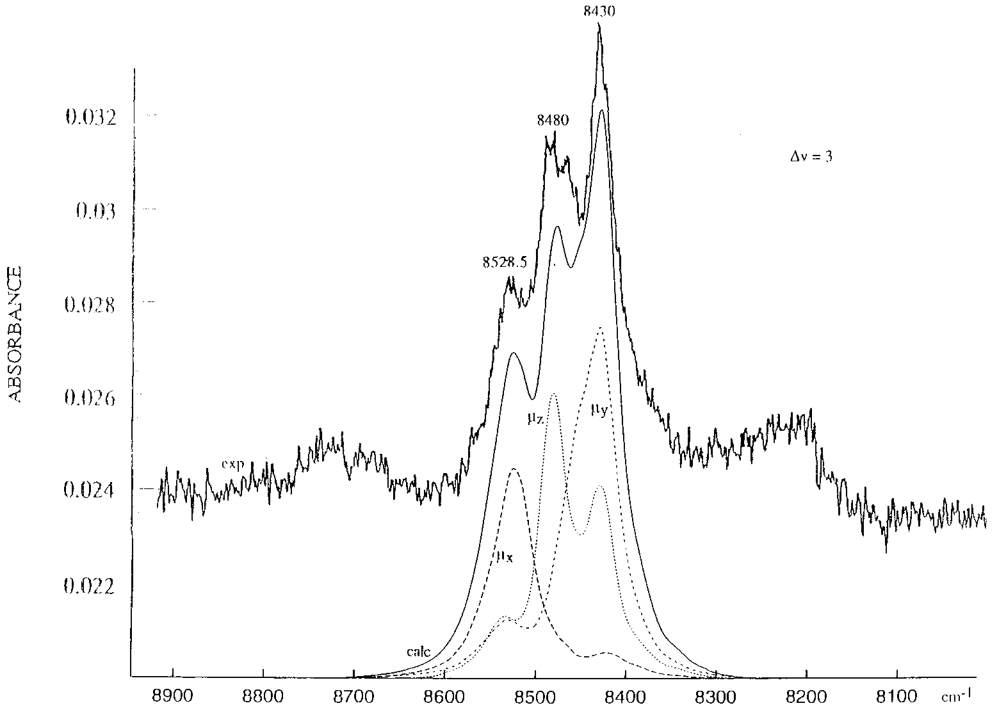

Figure 9. Experimental (top curve) and calculated (next lower curve) infrared spectra of the second overtone ($\Delta v = 3$) of the CH-stretching vibration of gaseous toluene, $C_6D_5CHD_2$, at 300 K. The experimental spectrum was obtained by FTIR with a 6.3-m-path cell and a resolution of 2 cm^{-1}. The calculated spectrum (lower solid line) was obtained by summing the contributions of the three dipole moment components (shown by the bottom three dashed lines).

the dipole moment showing a greater variation of cos 2θ in toluene (22%) (Table 2) than in nitromethane[3] (13%). This variation becomes even greater than the constant part for the μ_z^3 component (Table 2). This illustrates that the major part of the differences between toluene (or γ-picoline) and nitromethane spectra comes from electric anharmonicity of the CH vibrator during its internal rotation, which can be effectively related to different molecular environments.

Conclusion

We have studied the coupling between the CH-stretching vibration and the internal rotation motion of the monohydrogenated methyl group in monohydrogenated toluene and γ-picoline. These two molecules have very similar symmetries and heights of the hindered rotation barrier (4.9 and 4.75 cm^{-1} for toluene and γ-picoline, respectively). From a quantum theory we have developed, the Raman and infrared CH stretching spectra are reconstructed, reflecting the coupling of the CH vibrator with the internal motion. Raman and fundamental infrared ν(CH) spectra are very similar for both compounds and both display complex features owing to the presence of different pseudo-conformers. Calculation of the overtone spectra $\Delta v = 2$ and 3 for toluene shows there is no important Fermi resonance phenomenon until the second overtone in this molecule.

All the simulated spectra are in good agreement with the experimental ones, demonstrating the ability of our simple theory to model this way of energy redistribution.

The results obtained in the present work are very similar to those obtained for monohydrogenated nitromethane,[1,2] indicating that, in the first excited CH-stretching states, the principal factor governing IVR is the internal rotation barrier. Nevertheless, some differences can be observed in these spectra that can be explained by differences in the electric anharmonicity of these two groups of molecules. This can effectively be attributed to the differences in molecular environment.

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