Overtone Investigation of Methyl-Substituted Pyridines

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Conventional near-infrared absorption spectroscopy and intracavity laser photoacoustic spectroscopy have been used to record the room temperature vapor phase overtone spectra of 4-methylpyridine-d_0, 3-methylpyridine-d_0, and 2-methylpyridine-d_0 in the $\Delta v_{CH} = 2-6$ regions. These methods are also used to record the hydrogen impurity spectra of 4-methylpyridine-d_7 and 3-methylpyridine-d_7 in the $\Delta v_{CH} = 2-5$ regions. Oscillator strengths are calculated using an anharmonic oscillator local mode model and ab initio dipole moment functions. Ab initio geometries and intensity calculations, which contain no adjustable parameters, are used to assign spectral peaks in the aryl regions. Peaks corresponding to two nonequivalent aryl local modes are assigned in the spectrum of 4-methylpyridine. Peaks corresponding to four nonequivalent aryl local modes are assigned in the spectra of 3-methylpyridine and 2-methylpyridine. The effects of a change in barrier type and size to internal methyl rotation on the complicated methyl band profile are examined. The aryl regions of the hydrogen impurity spectra are similar to the undeuterated compounds, but a significant change is observed in the methyl regions.

Introduction

The overtone spectra of molecules containing XH bonds (X = C, O, N, ...) are dominated by the transitions involving XH stretching vibrations. Vibrational overtone spectra are generally found to contain a Lorentzian peak for each of the nonequivalent XH bonds in a molecule. These transitions are well described by the local mode model.[1−5] The harmonically coupled anharmonic oscillator (HCAO) model[6−9] has proven successful in the prediction of overtone peak positions and in the determination of vibrational wave functions. When combined with ab initio dipole moment functions, overtone intensities can be successfully predicted.[10−17]

A correlation between bond length and frequency has been established for overtones where the local mode frequency varies inversely with equilibrium bond length.[18] While there is no simple direct relationship of frequency to absolute bond length, this is still a very useful relationship. Different XH bonds within a molecule will be ordered in an overtone spectrum from highest to lowest energy for the shortest to longest relative bond lengths, and overtone spectroscopy has proven to be a very sensitive technique for probing these small changes in bond lengths. Intracavity dye/titanium:sapphire laser photoacoustic spectroscopy (ICL-PAS) has been able to detect CH bond length differences as small as 0.0006 Å.[19,20] CH bonds with 1 mÅ difference in length in pyridine have recently been studied using the HCAO model with ICL-PAS vibrational overtones.[21] Overtone vibrations occur on a very short time scale, and information regarding molecular geometries and conformations unavailable through other slower techniques becomes obtainable. Thus, overtones can be used to examine structural and conformational differences, as well as intramolecular vibrational energy redistribution (IVR).[22,23]

The overtones of toluene[24,25] revealed a complex profile in the methyl regions of the spectra. This complexity was atypical of most XH bonds at similar overtones. The methyl group of toluene has a very low energy barrier to internal rotation (4.9 cm^{-1})[26] and can be considered a free rotor. Further investigation into the vibrational overtones of molecules also containing rotating methyl groups showed complex structure similar to toluene.[23,25,27−29] In these molecules, the CH bond lengths in the methyl group change with the group's rotation. This is a partial cause for the complex structure as the CH stretching frequency is related to the bond length.[30,31] The overtone spectra of methyl groups restricted from rotating do not show this complex structure.[12,32−35] These spectra show the typical series of one peak for each conformationally nonequivalent CH in the methyl group.

Partial deuteration of methyl groups can change or remove coupling between CH oscillators on the methyl group. Studies of the overtone spectra of these partially deuterated molecules reveal different methyl band profiles from the undeuterated compounds.[28,36,37] It was shown that both vibrational−vibrational coupling between methyl CH oscillators and vibrational−torsional coupling between the CH oscillators and methyl rotation contribute to the complex structure observed. Attempts to reproduce the spectral profiles have been included in some of these studies[27,29,36,38] and have met with reasonable success. These models account for the changes in the bond parameters and dipole moment functions with rotation, and include various couplings.

This work investigates the vibrational overtones of the methylpyridines, a series of molecules with a rotating methyl group. Neither the vapor phase overtone spectra of the monosubstituted methylpyridines nor experimentally determined geometries have been published. The CH bonds attached to the ring of these molecules (aryl bonds) provide an interesting study. The lengths of these bonds have very small differences, on the order of mÅ (ab initio). Analyses of the aryl CH bonds in the methylpyridines are studied using a combination of overtone spectra and intensities from the HCAO model.

4-Methylpyridine is very similar to toluene and contains a methyl group with a very low energy (4.75 cm^{-1})[39] 6-fold barrier to rotation. The methyl groups of 3-methylpyridine and 2-methylpyridine have 3-fold barriers to rotation of ∼50 cm^{-1} (ab

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initio) and 90.4 cm^{-1},[40] respectively. The increase in barrier height is significant while still allowing rotation at room temperature. The effects of a small change in barrier size on the overtones are examined.

The CH vibrational overtones of the hydrogen impurities in 3-methylpyridine-d_7 (98%) and 4-methylpyridine-d_7 (98%) are investigated in transitions involving up to five vibrational quanta of CH stretch. The methyl regions of these spectra are used to investigate the importance of coupling within the methyl group as well as the importance of barrier size and type.

Experimental Section

The compounds 2-methylpyridine-d_0 (Aldrich), 3-methylpyridine-d_0 (Matheson Coleman & Bell), 4-methylpyridine-d_0 (Matheson Coleman & Bell), 3-methylpyridine-d_7 (Cambridge Isotope Laboratories, 98%), and 4-methylpyridine-d_7 (Cambridge Isotope Laboratories, 98%) were used without further purification with the exception of degassing using freeze−pump−thaw cycles.

The vapor phase overtone spectra were recorded using conventional absorption spectroscopy for the $\Delta v_{CH} = 2-4$ regions of the d_0 compounds and for the $\Delta v_{CH} = 2$ and 3 regions of the d_7 compounds. ICL-PAS was used for the $\Delta v_{CH} = 4-6$ regions of the d_0 compounds and for the $\Delta v_{CH} = 4$ and 5 regions of the d_7 compounds.

The IR absorption spectroscopy was performed on a Varian CARY 5E UV−vis−NIR spectrophotometer. A White variable path length cell (Wilks variable path length cell with BK7 Schott glass windows from Melles Griot) was used for all spectra recorded on the Cary 5E. Background spectra of the evacuated cell were taken either immediately before or after the sample spectra, and were subtracted from the sample spectra. All spectra of these compounds using the Cary were taken after allowing the gaseous sample to fill the evacuated Wilks cell at a path length of either 21.75 m or 23.25 m (see figure captions). The spectra were taken at temperatures between 21.4 and 23.0 °C.

The photoacoustic spectra were recorded using an ICL-PAS spectrometer constructed in the laboratory. This setup has been described in detail previously.[5,41] An argon ion laser was used to pump either a solid-state titanium:sapphire tunable laser (Coherent 890) or a dye laser (Coherent CR-599) with the dyes R6G or DCM. The titanium:sapphire laser was used to record the spectra in the $\Delta v_{CH} = 4$ and 5 regions and the dye lasers in the $\Delta v_{CH} = 6$ region. The $\Delta v_{CH} = 6$ spectra consist of the overlapping regions of these two dyes. The sample cell was fitted with a microphone (Knowles Electronics Inc., EK-3132). All spectra were recorded at room temperature (between 21 and 25 °C), and sample liquid was present in a sidearm for all scans. Thus, all spectra were measured at the equilibrium vapor pressure. Argon buffer gas (150 Torr) was present in all scans to aid in heat transfer. The absolute overtone intensity is unknown in ICL-PAS; however, the relative intensities within a spectrum were measured.[5,41]

The spectra were analyzed using a deconvolution program in Spectra Calc,[42] which uses a nonlinear, least-squares fitting algorithm.[43] The spectra were deconvoluted into component Lorentzian peaks with a linear baseline, providing peak positions and areas. The uncertainties of well-resolved peaks are generally estimated to be within 5 cm^{-1} for the energies and within 10% for the intensities. For greatly overlapping peaks these uncertainties are significantly larger. In particular, the only physically meaningful intensity result from deconvolution of such spectra is the total intensity of the overlapping peaks.

Theory

The intensity of a local mode overtone transition is given in terms of the unitless quantity of oscillator strength, f, by the expression[44]

$$f_{e\leftarrow g} = 4.70175 \times 10^{-7}[cmD^{-2}]\tilde{\nu}_{eg}|\vec{\mu}_{eg}|^2 \tag{1}$$

where the subscripts e and g correspond to the excited and ground states, respectively, $\tilde{\nu}_{eg}$ is the transition frequency in wavenumbers, and $\vec{\mu}_{eg} = \langle e|\vec{\mu}|g\rangle$ is the transition dipole moment in debye.

To calculate the intensity of a transition we must know the transition frequency, the vibrational wave functions of the two states, and the transition dipole moment. Vibrational wave functions and transition frequencies are obtained using the HCAO model, of which a brief description is given here.

It has been found that coupling between XH oscillators which are not attached to the same X atom is negligible.[16,19,20] It is therefore valid to neglect coupling between the aryl CH oscillators of the methylpyridines and treat them as independent oscillators.

In the HCAO model, XH oscillators are approximated as Morse oscillators. The Hamiltonian of a Morse oscillator is given by the expression

$$(\boldsymbol{H} - \boldsymbol{E}_{|0\rangle_j})/\boldsymbol{hc} = v_j\varpi_j - (v_j^{\,2} + v_j)\varpi x_j \tag{2}$$

where $\boldsymbol{E}_{|0\rangle_j}$ is the energy of the ground vibrational state, ϖ_j and ϖx_j are the local mode frequency and the local mode anharmonicity of the XH$_j$ oscillator, and v_j is the number of vibrational quanta in the XH$_j$ oscillator. The eigenstates of this Hamiltonian are denoted by $|v\rangle_j$.

A transition dipole moment can be found ab initio by expanding the dipole moment in a Taylor series as a function of displacement of the XH bond about equilibrium. For an isolated XH bond system, with the displacement coordinate q

$$\mu(q) = \sum_{i=0}^{n} \mu_i q^i \tag{3}$$

with the coefficients μ_i given by

$$\mu_i = \frac{1}{i!}\frac{\partial^i \mu}{\partial q^i} \tag{4}$$

Expansion and compression of the XH bond by ±0.4 Å in steps of 0.1 Å give values of the dipole moment. These in turn lead to the coefficients μ_i which are evaluated using standard numerical techniques. In this work eq 3 is truncated at seventh order. All ab initio calculations were performed using *Gaussian 98*.[45] This method of calculating overtone intensities has proven successful in providing a fit of experimental intensities over a range of 6 orders of magnitude for several molecules.[10,16,46−49]

Results and Discussion

The room temperature vapor phase overtone spectra of 2-methylpyridine-d_0, 3-methylpyridine-d_0, and 4-methylpyridine-d_0 in the CH stretching regions corresponding to $\Delta v_{CH} = 2-6$ are shown in Figures 1−5. The room temperature vapor phase overtone spectra of 3-methylpyridine-d_7 (98%) and 4-methylpyridine-d_7 (98%) corresponding to the $\Delta v_{CH} = 2-5$ regions are shown in Figures 6−9. Each of these spectra can be generally described as having a lower energy methyl CH band and a higher energy aryl CH band.

TABLE 1: Ab Initio CH Bond Lengths (Å) and Rotational Barriers (cm^{-1}) in 4-Methylpyridine

	6-31G(d)		6-31+G(d,p)		6-311++G(2d,2p)	
angle[a]	0°	90°	0°	90°	0°	90°
C_2H	1.0764	1.0763	1.0769	1.0768	1.0742	1.0740
C_3H	1.0751	1.0753	1.0751	1.0754	1.0723	1.0726
C_5H	1.0756	1.0753	1.0757	1.0754	1.0728	1.0726
C_6H	1.0762	1.0763	1.0767	1.0768	1.0739	1.0740
$C_{me}H_1$	1.0835	1.0860	1.0837	1.0863	1.0809	1.0835
$C_{me}H_2$	1.0852	1.0840	1.0855	1.0842	1.0828	1.0815
$C_{me}H_3$	1.0852	1.0840	1.0855	1.0842	1.0828	1.0815
barrier	1.2		3.4		0.8	

[a] Angle of the $C_{me}H_1$ bond with the plane of the pyridine ring.

The spectra are analyzed with the aid of ab initio calculations as experimentally determined structures are not available. The only restriction in the calculated geometries was a difference of 120° in the dihedral angles of the methyl CH bonds and the molecular ring. The barriers to internal methyl rotation in the three methylpyridines are significantly smaller than kT at room temperature (207 cm^{-1}). As a result, the methyl groups will not exist in the form of lowest energy stable conformations. Geometries have been calculated at the Hartree−Fock level using three basis sets. The CH bond lengths and barriers to rotation are presented in Tables 1−3. Rotation of the methyl group has a small effect on the aryl CH bond lengths; however, the ordering of the relative CH bond lengths remains consistent with the three basis sets.

4-Methylpyridine. The aryl regions of 4-methylpyridine show a simplification to a two-peak structure, one peak for each of the two nonequivalent CH oscillators. As expected, the splitting between the two peaks increases with increasing Δv_{CH}. The assignment is based on the ab initio bond lengths and identifies the highest energy peak as corresponding to the C_3H and C_5H bonds and the lower energy of the two aryl peaks as corresponding to the C_2H and C_6H bonds. The observed peak energies, relative intensities within each overtone, and spectral assignments are given in Table 4.

The observed peak energies from the two-peak deconvolution of the aryl regions of 4-methylpyridine have been fitted to the two parameter Morse oscillator energy expression

$$\tilde{\nu}/v = \varpi - (v + 1)\varpi x \tag{5}$$

to obtain values for the local mode frequencies and anharmonicities which are given in Table 5. The small values of the uncertainties of these parameters support the assumption to neglect coupling between aryl CH oscillators.

These values of the local mode frequency and anharmonicity were used to calculate the overtone intensities with dipole moment functions calculated with an HF/6-31G(d) basis set. Our past experience has shown that the use of larger basis sets can provide agreement with the absolute total intensity. However, only relative intensities are measured with ICL-PAS and the HF/6-31G(d) basis set is sufficient to predict correctly the relative intensities within an overtone.[10,19,21,28,47,50]

As the aryl CH bonds change by small amounts with methyl group rotation, intensities were calculated for conformations with one methyl CH bond in the molecular plane and with a methyl CH perpendicular to the molecular frame. These two conformations represent the methyl group at 30-degree intervals during rotation. The calculated aryl intensities of the two conformers were either identical or varied by less than 1%. The values were averaged with equal weight as each conformation is encountered an equal number of times upon full rotation. These averaged intensities and their relative intensities within each overtone are given in Table 4.

The agreement of the calculations with the experimental values for the relative intensities is excellent with the exception of $\Delta v_{CH} = 3$, where local mode combinations from the methyl group are expected to overlap with and contribute to the aryl band. The agreement of the relative intensities supports the assignment of the lower energy aryl peak to the C_2H and C_6H oscillators and the higher energy peak to the C_3H and C_5H oscillators.

3-Methylpyridine. The aryl bands of the 3-methylpyridine spectra are more complicated than those of 4-methylpyridine. 3-Methylpyridine contains four nonequivalent aryl CH bonds, with a general three-peak structure through the overtones and a center peak with roughly double the intensity of the high and low energy peaks. A summary of the observed frequencies and their assignments (based on the ab initio geometries) is given in Table 6.

The lowest energy aryl peak is assigned to the C_2H oscillator, and the high-energy peak assigned to the C_5H oscillator. The C_4H and C_6H average bond lengths differ by only 0.0004 Å (HF/6-311++G(2d,2p)), and we would not expect resolution into two peaks until the higher overtones. In a study on pyridine,[21] where the meta and para CH bonds differ in length by approximately 0.001 Å, separation of the peaks in the overtone spectra did not become clear by visual inspection until $\Delta v_{CH} = 6$. In 3-methylpyridine the difference in bond length is less; however, the local environments of the C_4H and C_6H bonds are different. In pyridine,[21] the para CH bond was calculated to be 0.0013 Å (HF/6-311++G(2d,2p)) longer than the meta CH bond. The bond lengths were also calculated with additional HF basis sets, as well as at the MP2 and QCISD levels of theory. All of the calculations agreed with the relative ordering of the meta and para CH bonds and were supported by the experimental and intensity results.[21] In 3-methylpyridine the relative ordering of the aryl CH bond lengths remains constant with the different basis sets. Ab initio calculations on this type of CH bond have been shown to be accurate in the ordering of relative bond lengths. The middle aryl peak structure is assigned as the overlapping peaks corresponding to the C_4H and C_6H oscillators.

The aryl regions of the spectra have been deconvoluted using a four-peak structure except at $\Delta v_{CH} = 4$ where a five-peak deconvolution was used. In the deconvolution of the $\Delta v_{CH} = 4$ spectrum, the highest energy peak has split into two peaks of nearly equal intensity (0.55 and 0.49). It is likely that a Fermi resonance is occurring between states involving three quanta of CH stretch and two quanta of CH bend and four quanta of CH stretch. The stretching bending resonant state will steal intensity from the pure local mode stretching state. Such Fermi resonances are known to tune in and out as the number of vibrational quanta changes and have been observed in the CH stretching overtone spectra of other molecules.[51,52]

A fitting of the peak frequencies to eq 5 to obtain the local mode bond parameters has been done with the average of the two highest energy peaks in the $\Delta v_{CH} = 4$ region used to fit the Morse oscillator expression. The middle peak structure is deconvoluted as two peaks, with the lower energy of these assigned to the C_4H oscillator based on the ab initio bond lengths. The results are summarized in Table 5. The uncertainties in ϖ and ϖx were small for C_2H and C_5H. The slightly larger uncertainties in the C_4H and C_6H parameters reflect the lack of resolution in the corresponding peaks.

TABLE 2: Ab Initio CH Bond Lengths (Å) and Rotational Barriers (cm^{-1}) in 3-Methylpyridine

	6-31G(d)			6-31+G(d,p)			6-311++G(2d,2p)		
angle[a]	0°	90°	180°	0°	90°	180°	0°	90°	180°
C_2H	1.0769	1.0773	1.0777	1.0773	1.0778	1.0782	1.0746	1.0750	1.0754
C_4H	1.0768	1.0765	1.0763	1.0771	1.0768	1.0765	1.0742	1.0740	1.0737
C_5H	1.0744	1.0745	1.0744	1.0746	1.0746	1.0745	1.0717	1.0717	1.0717
C_6H	1.0760	1.0759	1.0758	1.0765	1.0763	1.0762	1.0737	1.0736	1.0735
$C_{me}H_1$	1.0838	1.0864	1.0838	1.0839	1.0867	1.0840	1.0811	1.0839	1.0813
$C_{me}H_2$	1.0857	1.0843	1.0856	1.0860	1.0845	1.0859	1.0832	1.0817	1.0831
$C_{me}H_3$	1.0857	1.0844	1.0856	1.0860	1.0846	1.0859	1.0832	1.0819	1.0831
barrier		25.9	52.8		23.2	52.3		30.2	59.4

[a] Angle of the $C_{me}H_1$ bond with the plane defined by $C_{me}C_3C_2$, with 0° corresponding to syn to nitrogen.

TABLE 3: Ab Initio CH Bond Lengths (Å) and Rotational Barriers (cm^{-1}) in 2-Methylpyridine

	6-31G(d)			6-31+G(d,p)			6-311++G(2d,2p)		
angle[a]	0°	90°	180°	0°	90°	180°	0°	90°	180°
C_3H	1.0751	1.0748	1.0744	1.0752	1.0748	1.0744	1.0723	1.0719	1.0715
C_4H	1.0756	1.0757	1.0756	1.0759	1.0759	1.0759	1.0731	1.0731	1.0731
C_5H	1.0741	1.0741	1.0741	1.0741	1.0741	1.0741	1.0712	1.0713	1.0712
C_6H	1.0762	1.0764	1.0764	1.0767	1.0768	1.0769	1.0739	1.0740	1.0742
$C_{me}H_1$	1.0811	1.0861	1.0842	1.0813	1.0865	1.0846	1.0786	1.0836	1.0817
$C_{me}H_2$	1.0859	1.0819	1.0841	1.0862	1.0821	1.0845	1.0834	1.0794	1.0818
$C_{me}H_3$	1.0859	1.0848	1.0841	1.0862	1.0851	1.0845	1.0834	1.0823	1.0818
barrier	74.2	40.8		113.8	58.6		111.6	58.6	

[a] Angle of the $C_{me}H_1$ bond with the plane defined by $C_{me}C_2N$, with 0° corresponding to syn to nitrogen.

TABLE 4: Observed and Calculated Frequencies, Intensities, and Peak Assignments for the Aryl Regions of the CH Stretching Overtone Spectrum of 4-Methylpyridine

obsd		calcd			
$\tilde{\nu}/cm^{-1}$	I_{rel}[a]	$\tilde{\nu}/cm^{-1}$	f	I_{rel}[a]	assignment[b]
8714	1.0	8714	4.8×10^{-8}	1.7	$\|3\rangle_{2,6}$
8773	1.0	8775	2.7×10^{-8}	1.0	$\|3\rangle_{3,5}$
11377	2.0	11380	5.9×10^{-9}	1.8	$\|4\rangle_{2,6}$
11471	1.0	11469	3.3×10^{-9}	1.0	$\|4\rangle_{3,5}$
13929	1.6	13926	8.0×10^{-10}	1.8	$\|5\rangle_{2,6}$
14048	1.0	14047	4.5×10^{-10}	1.0	$\|5\rangle_{3,5}$
16353	1.9	16354	1.2×10^{-10}	1.8	$\|6\rangle_{2,6}$
16507	1.0	16509	6.7×10^{-11}	1.0	$\|6\rangle_{3,5}$

[a] Relative intensities within an overtone. [b] Defined as $|v\rangle$ the number of vibrational quanta, with the subscripts denoting the assigned number of the ring carbon of the CH oscillator.

Dipole moment functions at the HF/6-31G(d) level were calculated for the four aryl CH oscillators for three conformations of 3-methylpyridine. These conformations correspond to a methyl CH in the molecular plane on the nitrogen side of the molecule, perpendicular to the molecular plane, and in the molecular plane on the non-nitrogen side. These three conformations represent the molecule at 30-degree intervals during methyl rotation with the perpendicular conformation occurring twice as often as either of the other two conformers. As with 4-methylpyridine, the calculated aryl intensities were found to change very little with methyl rotation. A weighted average of 1:2:1 for the three conformations as listed above was used to obtain the averaged relative intensities given in Table 7. Agreement between calculated and observed relative intensities is excellent.

The aryl regions of the spectra of 3-methylpyridine were also analyzed using a three peak deconvolution and a four peak deconvolution without the Fermi resonance. The local mode parameters from these two methods have much larger uncertainties (25% and 209% greater, respectively), and the calculated relative intensities did not always agree with the observed values. The intensity disagreement with these alternate analyses and the differences in the uncertainties of the local mode parameters support our assignment of the overtones of 3-methylpyridine as a four-peak progression with a splitting at $\Delta v_{\mathrm{CH}} = 4$ due to a Fermi resonance.

2-Methylpyridine. In 2-methylpyridine there are four nonequivalent aryl CH bonds. Thus the aryl regions of the overtone spectra will consist of a series of four peak progressions, which, given the small differences in bond lengths, are expected to have considerable overlap. Though the differences in the aryl CH bond lengths are small, the relative ordering of the bond lengths is reproduced with various basis sets (Table 3). In the aryl regions of the spectra it is clear that there is a low energy peak separated from the rest. The high-energy peak of the aryl band has an overlapping structure. The aryl regions of the spectra have been analyzed assuming a four peak structure. The observed peak energies and their assignments (based on the ab initio geometries) of the aryl regions are given in Table 8. The peak frequencies are fit to eq 5 to obtain the local mode parameters, which are given in Table 5.

The spectra show an apparent increase in relative height of the middle peak with increasing v. The two middle energy peak progressions are becoming closer in energy and increasing their overlap. This occurs because the higher energy of the two peaks is associated with a higher anharmonicity. Also witnessed in the spectra is the separation of the highest energy peak from the middle energy overlapping peaks.

Dipole moment functions were calculated for the same three conformers as in 3-methylpyridine. Intensities were calculated using these assignments at the HF/6-31G(d) level and averaged with the same weighting as in 3-methylpyridine. Again, only very small changes in intensity with methyl rotation were found. The averaged calculated relative intensities are given in Table 9 along with the experimental values. Once again agreement is excellent.

Analysis of the 2-methylpyridine aryl regions with a three-peak structure provides the local mode frequency and anharmonicity with average uncertainties 62% larger than from the four peak analysis. Intensity calculations assuming the three peak analysis do not reproduce the observed relative intensities. This evidence supports our assignment of a four-peak progression.

TABLE 5: Local Mode Frequencies and Anharmonicities (cm^{-1}) of the Aryl CH Stretching Modes of the Methylpyridines[a]

4-methylpyridine			3-methylpyridine			2-methylpyridine		
	ϖ	ϖx		ϖ	ϖx		ϖ	ϖx
$C_{2,6}H$	3143 ± 1	59.7 ± 0.3	C_2H	3134 ± 4	61.8 ± 0.6	C_3H	3192 ± 6	62.0 ± 1.0
$C_{3,5}H$	3156 ± 2	57.8 ± 0.3	C_4H	3152 ± 5	60.5 ± 1.0	C_4H	3168 ± 1	59.3 ± 0.2
			C_5H	3178 ± 1	58.9 ± 0.1	C_5H	3198 ± 8	60.8 ± 1.5
			C_6H	3165 ± 7	61.2 ± 1.3	C_6H	3150 ± 3	60.9 ± 0.5

[a] Uncertainties are one standard deviation.

TABLE 6: Observed Frequencies and Peak Assignments for the Aryl Regions of the CH Stretching Overtone Spectrum of 3-Methylpyridine

$\tilde{\nu}$/cm^{-1}	assignment	$\tilde{\nu}$/cm^{-1}	assignment
8659	$|3\rangle_2$	13817	$|5\rangle_2$
8726	$|3\rangle_4$	13938	$|5\rangle_4$
8762	$|3\rangle_6$	13975	$|5\rangle_6$
8825	$|3\rangle_5$	14121	$|5\rangle_5$
11311	$|4\rangle_2$	16212	$|6\rangle_2$
11408	$|4\rangle_4$	16369	$|6\rangle_4$
11444	$|4\rangle_6$	16433	$|6\rangle_6$
11508	$|4\rangle_5$	16591	$|6\rangle_5$
11559	$|4\rangle_5$		

TABLE 7: Observed and Calculated Relative Aryl Peak Intensities for 3-Methylpyridine

assignment	obsd	calcd	assignment	obsd	calcd
$|3\rangle_2$	1.0	1.0	$|5\rangle_2$	1.0	1.0
$|3\rangle_{4+6}$	2.08	2.02	$|5\rangle_{4+6}$	1.89	1.96
$|3\rangle_5$	0.96	0.88	$|5\rangle_5$	0.72	0.80
$|4\rangle_2$	1.0	1.0	$|6\rangle_2$	1.0	1.0
$|4\rangle_{4+6}$	1.86	2.00	$|6\rangle_{4+6}$	2.49	1.92
$|4\rangle_5$ [a]	0.94	0.85	$|6\rangle_5$	1.00	0.76

[a] Experimental intensity is the combination of the two Fermi resonant peaks.

TABLE 8: Observed Frequencies and Peak Assignments for the Aryl Regions of the CH Stretching Overtone Spectrum of 2-Methylpridine

$\tilde{\nu}$/cm^{-1}	assignment	$\tilde{\nu}$/cm^{-1}	assignment
8717	$|3\rangle_6$	13914	$|5\rangle_6$
8792	$|3\rangle_4$	14062	$|5\rangle_4$
8837	$|3\rangle_3$	14091	$|5\rangle_3$
8866	$|3\rangle_5$	14145	$|5\rangle_5$
11383	$|4\rangle_6$	16342	$|6\rangle_6$
11489	$|4\rangle_4$	16519	$|6\rangle_4$
11523	$|4\rangle_3$	16558	$|6\rangle_3$
11576	$|4\rangle_5$	16646	$|6\rangle_5$

TABLE 9: Observed and Calculated Relative Intensities for the Aryl Regions of 2-Methylpyridine

assignment	obsd	predicted	assignment	obsd	predicted
$|3\rangle_6$	1.0	1.0	$|5\rangle_6$	1.0	1.0
$|3\rangle_{4,3,5}$	2.25	2.14	$|5\rangle_{4,3,5}$	2.15	2.10
$|4\rangle_6$	1.0	1.0	$|6\rangle_6$	1.0	1.0
$|4\rangle_{4,3,5}$	1.87	2.12	$|6\rangle_{4,3,5}$	2.25	2.07

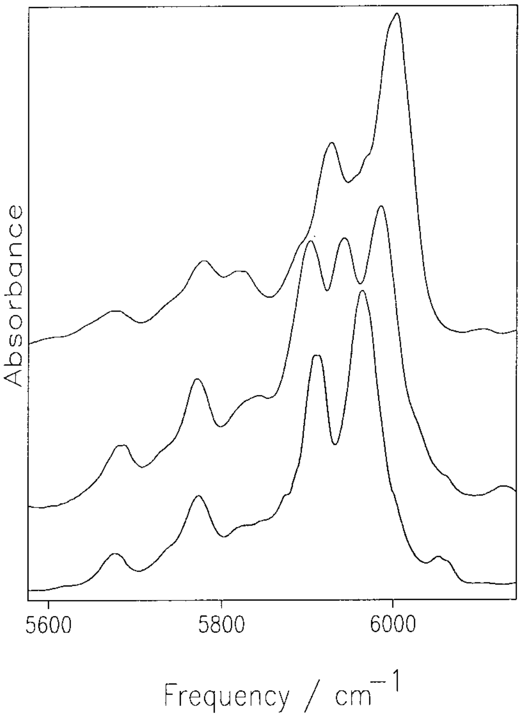

Figure 1. The room temperature vapor phase spectra in the $\Delta v_{CH} = 2$ region of 2-methylpyridine (top trace) with a path length of 21.75 m and a pressure of 8 Torr, 3-methylpyridine (middle trace) with a path length of 23.25 m and a pressure of 6 Torr, and 4-methylpyridine (bottom trace) with a path length of 21.75 m and a pressure of 6 Torr.

Methyl Regions. Comparison of the methyl bands in the $\Delta v_{CH} = 2-6$ regions of the three methylpyridines is shown in Figures 1−5. The methyl region of 4-methylpyridine is very similar to that of toluene[28] as would be expected. These molecules both have a methyl rotor attached to the ring with a very low energy 6-fold barrier to rotation. The change in methyl CH bond length with rotation is predicted to be smaller in 4-methylpyridine (0.0025 Å) than in toluene (0.0033 Å) (HF/6-31G(d)). The spectral profile can be described as nearly identical.

The methyl group of 3-methylpyridine has a 3-fold barrier to rotation on the order of 50 cm^{-1}. This barrier appears to have only a small effect on the methyl group, as the spectral profile is similar to that of 4-methylpyridine. A sharpening of the peaks and a narrowing of the band is observed while the overall shape is maintained. A barrier of only 50 cm^{-1} is still small relative to the thermal energies of the molecule, and the methyl group can be considered to be a nearly free rotor. A change in the barrier from 6-fold to 3-fold appears to have no effect on the spectral profile.

The methyl group of 2-methylpyridine has a 3-fold barrier to rotation on the order of 100 cm^{-1}. The barrier to rotation does not prevent the methyl group from rotating, but it does present a hindrance. The increased barrier size appears to have an effect. The overall methyl profile is similar to the other two methylpyridines but there are clear differences between the band profile in 2-methylpyridine and those of the other methylpyridines and toluene. The type of barrier had little effect in changing the profile between 4-methylpyridine and 3-methylpyridine. The barrier type remains the same in 3-methylpyridine and 2-methylpyridine, yet the methyl profiles are different. Thus, the change in the methyl profile would appear to be due to the increase in barrier size.

The predicted changes in methyl CH bond lengths (HF/6-31G(d)) with rotation in these three molecules are 0.0025 Å for 4-methylpyridine, 0.0026 Å for 3-methylpyridine, and 0.0050 Å for 2-methylpyridine. The expected effect of a change in

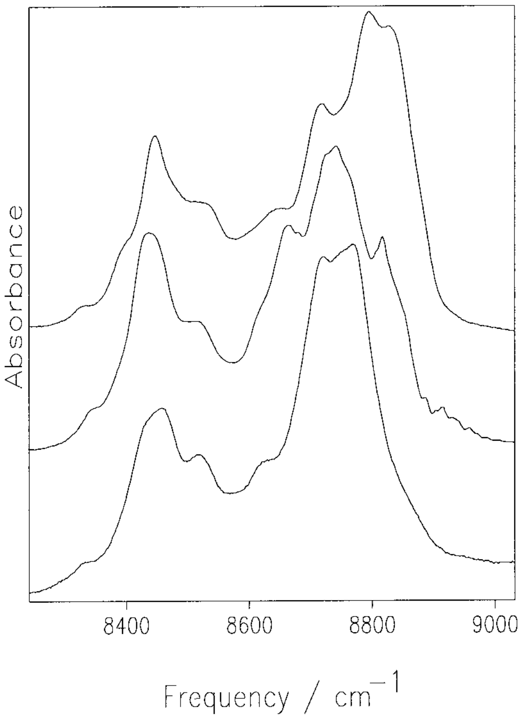

Figure 2. The room temperature vapor phase spectra in the $\Delta v_{\mathrm{CH}} = 3$ region of 2- methylpyridine (top trace) with a path length of 21.75 m and a pressure of 8 Torr, 3-methylpyridine (middle trace) with a path length of 23.25 m and a pressure of 6 Torr, and 4-methylpyridine (bottom trace) with a path length of 21.75 m and a pressure of 6 Torr.

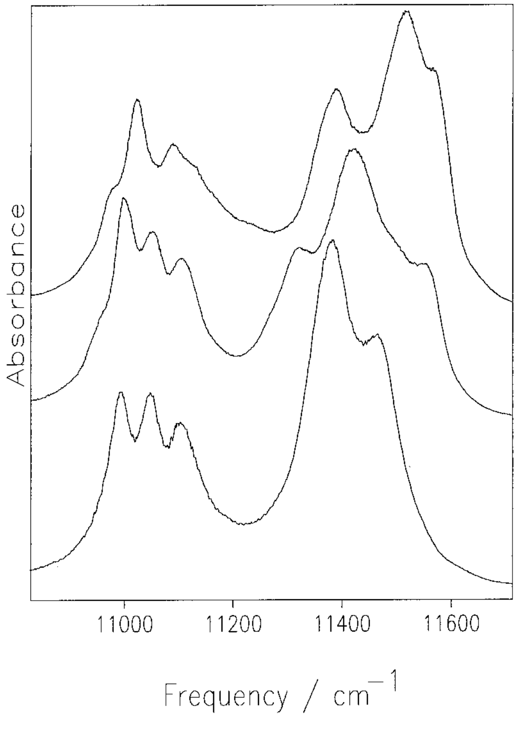

Figure 3. The room temperature vapor phase spectra in the $\Delta v_{\mathrm{CH}} = 4$ region of 2-methylpyridine (top trace), 3-methylpyridine (middle trace), and 4-methylpyridine (bottom trace). The spectra were recorded by ICL-PAS with 150 Torr of Ar buffer gas.

methyl bond length is a greater variation in ϖ and ϖx with rotation. The methyl regions are all at similar energies. Surprisingly, the greater bond length change in 2-methylpyridine has no apparent effect on the overall bandwidth. However, it is possible that the greater change in bond length could contribute to the change in the band profile in 2-methylpyridine.

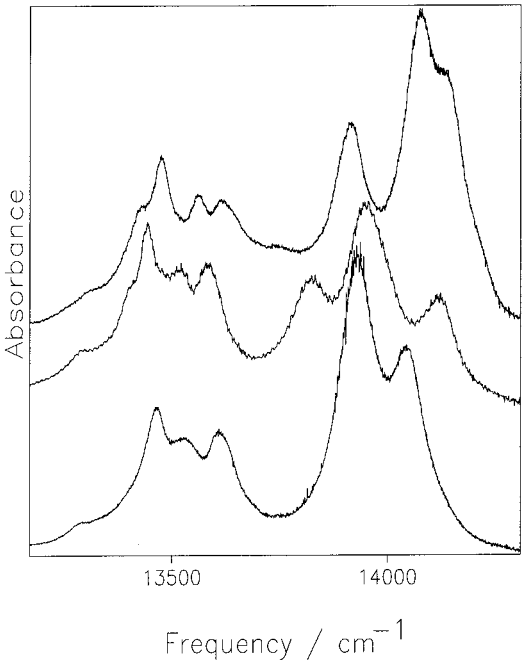

Figure 4. The room temperature vapor phase spectra in the $\Delta v_{\mathrm{CH}} = 5$ region of 2-methylpyridine (top trace), 3-methylpyridine (middle trace), and 4-methylpyridine (bottom trace). The spectra were recorded by ICL-PAS with 150 Torr of Ar buffer gas.

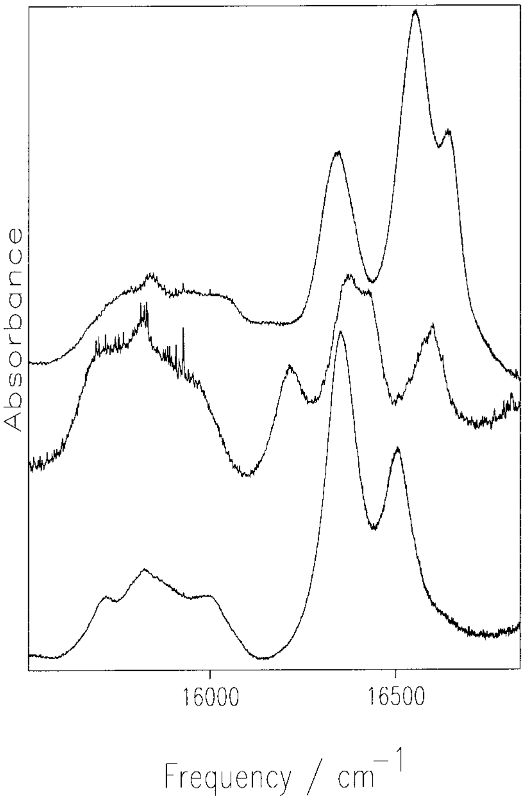

Figure 5. The room temperature vapor phase spectra in the $\Delta v_{\mathrm{CH}} = 6$ region of 2-methylpyridine (top trace), 3-methylpyridine (middle trace), and 4-methylpyridine (bottom trace). The spectra were recorded by ICL-PAS with 150 Torr of Ar buffer gas, and are the addition of overlapping spectra using DCM and R6G dyes.

Deuterated Methylpyridines. The compounds 3-methylpyridine-d_7 and 4-methylpyridine-d_7 were obtained at 98% purity. As a hydrogen impurity of approximately 2% is present, the most common nonfully deuterated molecules will only have

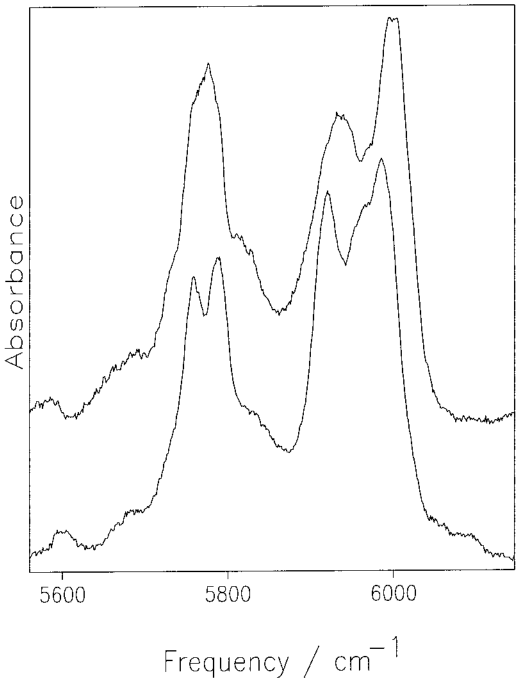

Figure 6. The room temperature vapor phase spectra in the $\Delta v_{CH} = 2$ region of 3-methylpyridine-d_7 98% (top trace) and 4-methylpyridine-d_7 98% (bottom trace). The spectra are additions of 3 scans recorded with a 21.75 m path length at 6 Torr pressure.

one hydrogen atom. The vibrational overtone spectra of the deuterated compounds will consist of the CH and CD stretching overtones of 3-methylpyridine-d_6 and 4-methylpyridine-d_6, and the CD stretching overtones of the d_7 compounds. The spectra in the regions of $\Delta v_{CH} = 2-5$ are presented in Figures 6−9.

The stretching overtones of CD bonds occur at lower energies and at lower intrinsic intensities than for CH bonds of the same manifold. When overlap of CD and CH overtones does occur, the CD overtones are from a higher manifold and will have significantly lower oscillator strengths. The lower oscillator strength does not allow the CD overtones to be ignored, as the number of CD oscillators in the samples is much higher than the number of CH oscillators.

The $\Delta v_{CD} = 2-6$ overtone spectra of toluene have been previously recorded[28] and local mode parameters obtained. As toluene is a similar compound, with the CH overtones having very similar energies, it can be assumed that the CD overtones will be similar to those of the methylpyridines as well. Thus it is expected that the $\Delta v_{CD} = 4$ region will overlap with the $\Delta v_{CH} = 3$ region and that the $\Delta v_{CD} = 7$ region will overlap with the $\Delta v_{CH} = 5$ region.

The aryl regions have been deconvoluted and the peak energies and assignments based on the d_0 compounds are given in Table 10.

Aryl Region − 4-Methylpyridine. The aryl region of the $\Delta v_{CH} = 3$ spectrum is more complicated than in the undeuterated compound. As the $\Delta v_{CD} = 4$ manifold is of similar energy we expect there to be additional peaks present. However two of the deconvoluted peaks do have energies similar to the aryl CH peaks of 4-methylpyridine-d_0 and are assigned as the aryl CH overtone peaks of the d_6 compound.

The $\Delta v_{CH} = 4$ region does not have any overlap with CD stretching transitions, and the aryl region is expected to be similar to that of the d_0 compound. The spectrum consists of two main peaks matching the spectrum of the undeuterated compound. There are also small shoulders on either side of the aryl band. Overall this region has reasonable agreement with undeuterated 4-methylpyridine.

The $\Delta v_{CH} = 5$ spectrum is predicted to overlap the $\Delta v_{CD} = 7$ manifold. The two aryl CH peaks in the 4-methylpyridine-d_6

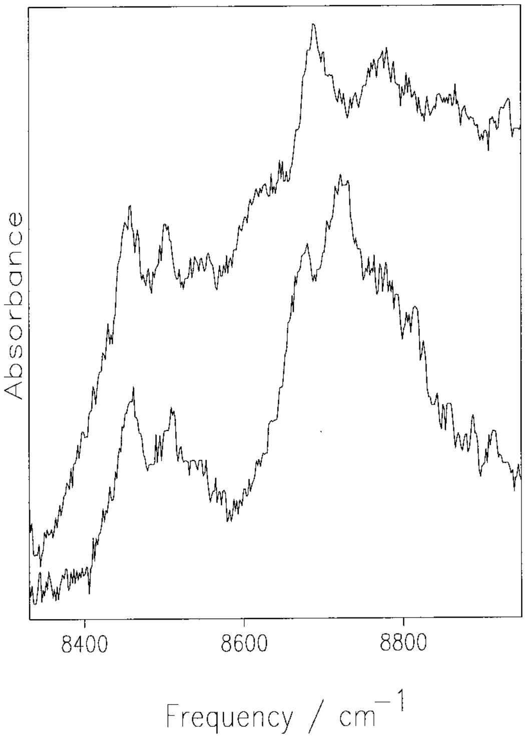

Figure 7. The room temperature vapor phase spectra in the $\Delta v_{CH} = 3$ region of 3-methylpyridine-d_7 98% (top trace) and 4-methylpyridine-d_7 98% (bottom trace). The spectra are additions of 3 scans recorded with a 21.75 m path length at 6 Torr pressure.

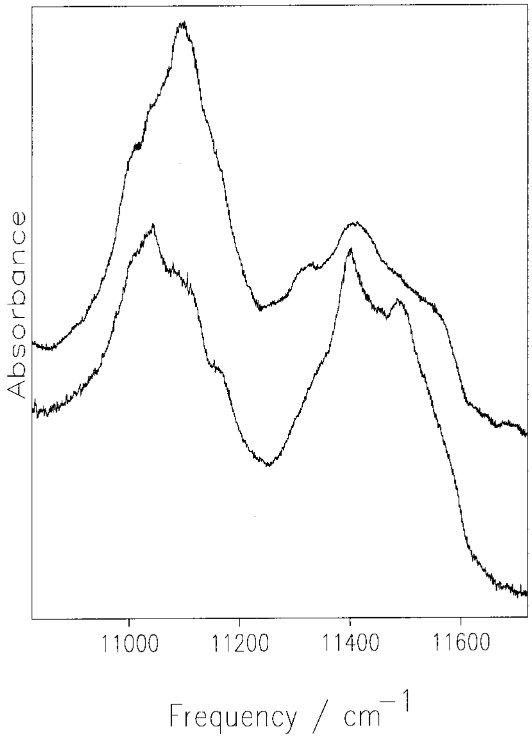

Figure 8. The room temperature vapor phase spectra in the $\Delta v_{CH} = 4$ region of 3-methylpyridine-d_7 98% (top trace) and 4-methylpyridine-d_7 98% (bottom trace). The spectra were recorded by ICL-PAS with 150 Torr of Ar buffer gas.

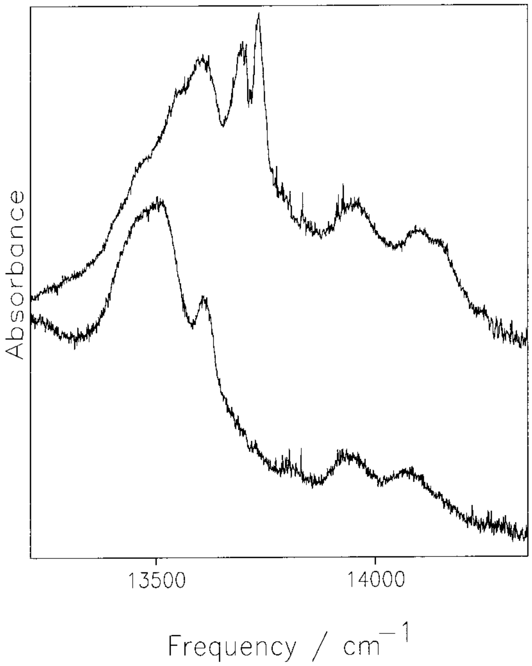

Figure 9. The room temperature vapor phase spectra in the $\Delta v_{CH} = 5$ region of 3-methylpyridine-d_7 98% (top trace) and 4-methylpyridine-d_7 98% (bottom trace). The spectra were recorded by ICL-PAS with 150 Torr of Ar buffer gas.

TABLE 10: Observed Frequencies and Peak Assignments for the Aryl CH Regions of the Hydrogen Impurities of 4-Methylpyridine-d_7 and 3-Methylpyridine-d_7

4-methylpyridine-d_7 (98%)			3-methylpyridine-d_7 (98%)		
$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm$^{-1\,a}$	CH assignment		$\tilde{\nu}$/cm$^{-1\,a}$	CH assignment
8671			8617	8659	$\|3\rangle_2$
8723	8714	$\|3\rangle_{2.6}$	8689	8726	$\|3\rangle_4$
8768	8773	$\|3\rangle_{3,5}$	8771	8762	$\|3\rangle_6$
8796			8856	8825	$\|3\rangle_5$
11322			11316	11311	$\|4\rangle_2$
11403	11377	$\|4\rangle_{2,6}$	11406	11408	$\|4\rangle_4$
11492	11471	$\|4\rangle_{3,5}$	11456	11444	$\|4\rangle_6$
11560			11516	11508	$\|4\rangle_5$
			11564	11559	$\|4\rangle_5$
			13804	13817	$\|5\rangle_2$
13938	13929	$\|5\rangle_{2,6}$	13928	13938	$\|5\rangle_4$
14081	14048	$\|5\rangle_{3,5}$	13976	13975	$\|5\rangle_6$
			14120	14121	$\|5\rangle_5$

[a] Frequency of the d_0 compound from Tables 4 and 6.

spectrum are at slightly higher energies than in 4-methylpyridine-d_0. This is consistent with the $\Delta v_{CH} = 4$ aryl peaks. Between the aryl and methyl bands there is a small peak in the spectrum, which is not present in the spectrum of the d_0 compound. As this peak is not present in the spectrum of the undeuterated compound it can be assigned as part of the $\Delta v_{CD} = 7$ region. It is unclear whether the peak corresponds to the CD methyl or aryl band.

Aryl Region − 3-Methylpyridine. The aryl peak structure in the $\Delta v_{CH} = 3$ spectrum is different from the undeuterated spectrum. This is due in part to an overlap with the $\Delta v_{CD} = 4$ spectrum. Assignment of the deconvoluted peaks for this spectrum is not straightforward and it is unclear whether the peak positions given correspond to CH or CD vibrations. The noise and the sloping baseline in the spectrum will increase the uncertainty in the peak positions.

The $\Delta v_{CH} = 4$ spectrum has a good signal-to-noise ratio, only a small slope in the baseline, and does not overlap with a CD stretching manifold. Not surprisingly the deconvoluted aryl peak positions closely match positions for the undeuterated compound. The splitting of the high-energy peak supports the view that it is a Fermi resonance and not a combination peak. Coupling of the high-energy peak to another stretching vibration is unlikely as there are no CD stretches predicted to occur in this energy range, and there is only one CH.

The $\Delta v_{CH} = 5$ spectrum is predicted to overlap the $\Delta v_{CD} = 7$ manifold. In the spectrum two sharp peaks appear in the region between the aryl and methyl bands. Intramanifold coupling occurring between XH oscillators attached to the same central atom is known to shift the peak positions to lower energies. Substituting all but one of the hydrogen atoms on a common central atom causes a shift to higher energy of the overtone peaks.[16,28] In 1,3-butadiene this shift was approximately 30 cm^{-1} at $\Delta v_{CH} = 5$.[16] If these two peaks were part of the methyl profile, the shift in energy would be around 200 cm^{-1}. As these peaks are of similar energy to the additional peak which appeared in the 4-methylpyridine-d_6 $\Delta v_{CH} = 5$ spectrum, it is more likely that these peaks are part of the $\Delta v_{CD} = 7$ spectrum.

The aryl peak positions at $\Delta v_{CH} = 5$ have excellent agreement for the two highest energy peaks. The two lowest energy aryl peaks have good agreement with peak positions from the undeuterated compound. The swamping of these peaks by the CD peaks increases the uncertainty in the deconvoluted peak positions.

Methyl Region − 4-Methylpyridine. The complex structure in the methyl band is due in part to coupling between vibrational and torsional states. The replacement of hydrogen with deuterium will change the torsional states and the vibrations that participate in the coupling. As a result, a change in the methyl profile is expected when the methyl group is partially deuterated.

In the methyl overtones of 4-methylpyridine-d_6 there is an obvious change in the band profile from the d_0 compound. The methyl regions also show a shift to higher energies for $\Delta v_{CH} = 2-4$. This is expected from the decrease in vibrational−vibrational coupling (such coupling lowers the overtone energy). The shift is further evidence for the existence of such vibrational−vibrational coupling in the methyl group which has been assumed in previous work on the band profiles of methyl rotors.[29] The methyl band in the $\Delta v_{CH} = 5$ spectrum does not appear to be significantly shifted to higher energy, though the most intense point of the band has shifted from 13456 to 13512 cm^{-1}.

The methyl bands of the $\Delta v_{CH} = 3$ and 4 spectra of 4-methylpyridine-d_6 are similar to the CH methyl bands in toluene-d_7[28] in the profiles and in the shifts from the undeuterated compounds. This is not unexpected as the methyl groups of these two compounds have much in common. The methyl bands were nearly identical for 4-methylpyridine-d_0 and toluene-d_0, implying that the methyl groups in the two molecules will have very similar dipole moment functions, local mode parameters, and couplings. In both cases, the methyl group changes from CH_3 to CHD_2. In the Born−Oppenheimer approximation the dipole moment function will be the same for CH_3 and CHD_2 groups. The local mode frequency and anharmonicity will not change for the lone CH bond upon substitution of the other two hydrogen atoms with deuterium. The loss of vibrational−vibrational coupling, vibrational−(CH_3)torsional coupling, and the addition of vibrational−(CHD_2)torsional coupling will all be similar. The methyl groups in 4-methylpyridine and toluene both have very low energy 6-fold barriers to rotation. As the dipole moment functions, wave functions, and couplings are all similar, the spectra of the methyl regions of these molecules are expected to be similar as well.

Methyl Region − 3-Methylpyridine. The methyl overtones of 3-methylpyridine-d_6 are also different than the undeuterated compound. The methyl bands are shifted to higher energies than in 3-methylpyridine-d_0 as was the case for both 4-methylpyridine and toluene.[28]

The methyl profiles of 3-methylpyridine-d_0, 4-methylpyridine-d_0 and toluene-d_0 are all similar. The small increase in barrier size and the change to a 3-fold barrier did not have a significant effect on the methyl profiles in the undeuterated spectra. However, in the monohydrogenated impurity spectra, the methyl profile of 3-methylpyridine is distinctly different from the methyl profiles of 4-methylpyridine and toluene[28] in the $\Delta v_{CH} = 2$, 4, and 5 regions.

In the deuterated compounds coupling in the CHD_2 group will involve CD vibrations in addition to the CH vibrations. It appears in this more complicated coupling situation that a change in the type and an increase in size of the barrier to internal rotation does affect the methyl profile.

The change in the relative intensities of the aryl and methyl bands in the d_6 compounds is from an uneven distribution of the hydrogen impurities. The preference of the hydrogen impurities to be on the methyl group arises from the method of synthesis.

Conclusion

The overtone spectra of the methylpyridines have been recorded and studied in the $\Delta v_{CH} = 2-6$ regions using conventional absorption and ICL-PAS techniques. These molecules each contain a rotating methyl group attached to a pyridine ring. The barrier to rotation increases as the methyl substitution site becomes closer to the nitrogen.

The aryl regions of the overtones show a simplified structure having one peak progression for each nonequivalent CH oscillator. These peak progressions are well described as uncoupled anharmonic Morse oscillators and fit the two parameter Morse oscillator expression which provides values of ϖ and ϖx with small uncertainties. The relative intensities of the aryl peaks in 4-methylpyridine agree very well with the calculated relative intensities from the HCAO model and HF/6-31G(d) dipole moment functions. In 3-methylpyridine and 2-methylpyridine, the agreement of the relative intensities of the lone aryl peaks to overlapping aryl peaks within the vibrational manifolds is again excellent.

The methyl regions of the methylpyridines show a complex band profile. The band profile in 4-methylpyridine is very similar to that of toluene. This is an expected result as the methyl groups of these two compounds are free rotors, both having a very low energy 6-fold barrier to rotation. The methyl band profiles of 3-methylpyridine are similar to the profiles in 4-methylpyridine and toluene, which is an indication that changing to a low energy 3-fold barrier has little effect on the band profile. The methyl band profiles of 2-methylpyridine are changed from those of 3-methylpyridine, 4-methylpyridine, and toluene. A change in the torsional states with a 3-fold barrier of 100 cm^{-1} does affect the band profile, which indicates that vibrational−torsional coupling is an important contributor to the complex structure.

The $\Delta v_{CH} = 2-5$ spectra of the hydrogen impurities in 3-methylpyridine-d_7 and 4-methylpyridine-d_7 have also been recorded. The aryl regions of the monohydrogenated spectra are similar to those of the undeuterated compounds with additional structure where CD stretching peaks overlap. This correspondence supports the assignment of pure local modes in the aryl regions, and the assignment of a Fermi resonance in the $\Delta v_{CH} = 4$ spectrum of 3-methylpyridine.

The methyl band profiles in the d_6 compounds are from CHD_2 groups, which have different torsional states from the CH_3 group. The methyl band profiles are significantly changed from those of the undeuterated compounds. The methyl profiles of the two methylpyridines are not similar to one another as they are in 3-methylpyridine-d_0 and 4-methylpyridine-d_0. The change in barrier has a pronounced effect on the methyl band profile in the presence of the additional coupling involving methyl CD bonds.

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