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Vibrational Overtone Spectroscopy of Pyridine and Related Compounds

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Abstract

The vibrational overtone spectra of gaseous pyridine, 3-fluoropyridine, 2,6-difluoropyridine, and pyrazole have been recorded using photoacoustic absorption spectroscopy. The pyridine, 3-fluoropyridine, and 2,6-difluoropyridine overtone spectra exhibit two local mode progressions. These CH local modes are mixed and cannot be assigned to the separate CH oscillators at the 2,6 and 3,4 and 5 positions. The transition wavenumbers and peak widths are compared to those of benzene and pyrrole, both of which exhibit only one overtone peak at each quantum level. The fourth overtone spectrum of gaseous pyrazole displays two peaks. These spectra indicate that the presence of a lone pair perpendicular to the aromatic Π system in aromatic heterocycles removes the local mode equivalency of the CH oscillators.

Introduction

The visible vibrational overtone spectrum of benzene^{1,2} serves as a model for the local mode theory of overtone absorption spectra wherein the chemical equivalency of all six CH bonds leads to a single absorption feature for transitions to successively higher quantum levels. However the explanation for the location and shape of the absorption bands is still incomplete. Theoretical work³ modeled the widths of these overtone absorptions using intramolecular vibrational relaxation pathways. Experimental work⁴ on the second overtone spectrum of jet cooled benzene indicates homogeneous linewidths as small as 4 cm^{-1} . The absorption spectrum of jet cooled benzene displays as many as seven absorptions in the second overtone region⁵. These features are satisfactorily matched by a one dimensional vibron model calculation⁶ which includes coupling of the CH stretches, the CC stretches and the in-plane CH bends. In this model the most intense peak is assigned as the pure CH stretch overtone with 3 quanta and the weaker peaks are assigned to combinations of 2 quanta of CH stretch and the other two quanta in the CC stretches or CH bends⁷.

Pyridine, like benzene, is aromatic and a comparison of the spectra of these two molecules will contribute to the understanding of highly-excited vibrational states of polyatomic molecules. The overtone spectrum of pyridine displays two broad absorptions at each quantum transition^{8,9}. It is thought that the higher energy peak arises from the stretch of the CH furthest from the nitrogen atom, while the lower energy peak belongs to the CH stretches closest to the nitrogen. These assignments were made by comparison of the spectra of liquid pyridine and 2,6-lutidine.⁸ The higher energy peak at each vibrational level was present in the spectra of both compounds while the lower energy peak does not have a counterpart in the 2,6-lutidine spectrum. These workers also state that because the

C(3,5)-H and C(4)-H bonds are similar a small splitting of the higher energy peak is to be expected. They were, however, unable to observe this splitting in their spectra.

In a report⁹ of the $6\nu_{\text{CH}}$ of liquid pyridine, pyrazine, and related compounds, simple rules were presented to summarize the overtone spectral shifts when nitrogen is substituted for carbon in benzene. Furthermore, the overtone transition wavenumbers were compared to the nmr chemical shifts. Since the chemical shifts indicate the electron density around each of the protons they could be expected to correlate with the overtone stretching frequencies. For pyrimidine which has only two kinds of inequivalent CH bonds, the higher chemical shift corresponds to the higher transition wavenumber. In this case there are two different chemical shifts and two different overtone transitions. However pyridazine with two distinct chemical shifts displays only one CH stretch transition in the $6\nu_{\text{CH}}$ region and pyridine with three distinct chemical shifts displays two CH stretch peaks.

Mandal and Ray¹⁰ also reported the overtone spectrum of liquid pyridine up to $\nu=4$; however, in contrast to work presented in references 8 and 9, they observed only one peak at $\nu=3$ and 4. A nearest neighbor bond interaction model using five equivalent CH oscillators fit their results for the first overtone but found only one transition at $\nu = 3$ and 4. Because the nearest neighbor coupling constants, K_1 and K_2 , became insignificant at the higher levels of excitation only one transition appeared in the calculated spectrum at these levels.

We investigated pyrrole and pyrrolidine¹¹, observing multiple transitions indicative of vibrational coupling for the NH oscillator. Our work on pyrrole raises questions about the interpretation of the CH spectrum in pyridine. For pyrrole, also aromatic, one broad CH stretch transition occurs at each quantum transition similar to benzene. These protons have different chemical shifts indicating their unique electron density environment. This means that although the CH stretches are inequivalent by chemical shifts, the overtone spectrum does not distinguish between the two types.

Given the conflicting experimental results for pyridine and its importance as a comparison and test case to the spectrum of benzene, we have undertaken a study of nitrogen containing heteroaromatic ring compounds. We are interested in the influence of the nitrogen on the overtone spectrum of the nearly equivalent CH bonds. We present here the vibrational overtone spectrum of gaseous pyridine and the related compounds 2,6-difluoropyridine, 3-fluoropyridine and pyrazole. Applying the understanding gained in interpreting the spectrum of benzene^{6,7} to pyridine, there may be two sets of more or less isolated CH stretch, CC stretch and CH bend systems corresponding to the bonds closest and furthest to the nitrogen atom.

Experiment

The overtone absorption spectra were recorded using intracavity photoacoustic techniques. A Pyrex cell, 20 cm long and 1.3 cm I.D., outfitted with quartz windows oriented at Brewster's angle,

and a microphone (Knowles BT-1751) at the center, was aligned inside the cavity of a Spectra-Physics argon ion pumped dye laser. The microphone signal was directed to a lock-in amplifier (EG&G PAR model 5207) which was modulated at 250 Hz. The modulation frequency was provided by a mechanical chopper (PTI Inc. model 03-0C4000) which chopped the argon laser beam. A motor-driven three plate birefringent filter tuned the dye laser with 3 cm^{-1} resolution. The absorption wavelengths were measured with a Spex 1401 double monochromator with resolution of 1 cm^{-1} or with a McPherson model 270 monochromator with a resolution of $0.3\text{ \AA}$. Both the motor control unit (Oriel model 18007) and the lock-in amplifier were interfaced and controlled with an IBM PC computer.

The samples were purchased from Aldrich Chemical Co. The only other purification was freeze-pump-thawing on the vacuum line. Some of the samples were heated in an intracavity oven to increase the vapor pressure. Argon gas was added to the sample cell at 200-400 torr partial pressure to boost the acoustic signal in all the spectra.

Results and Discussion

The vibrational overtone spectrum of gaseous pyridine is shown in Figure 1. Two peaks are observed at each quantum level. The transition wavenumbers are tabulated and compared to those of the liquid in Table I. The absorptions at about 13800 , 14400 , and 16900 cm^{-1} are due to traces of water in the sample. In all cases the gaseous transitions lie to the blue of the corresponding transitions in the liquid. Fitting these transition wavenumbers, ΔE , to a Birge-Sponer plot³ for gaseous pyridine according to the equation

$$\Delta E = (w_e - w_e x_e)v - w_e x_e v^2$$

where w_e is the mechanical frequency, $w_e x_e$ is the anharmonicity and v is the local mode quantum number, yields two vibrational progressions. The mechanical frequencies of the higher- and lower-energy progressions, respectively, are 3105 and 3146 cm^{-1} while the anharmonicity for both progressions is 63 cm^{-1} (see Table 2). In these fits we used the wavenumber of the maximum intensity of the two features in the infrared spectrum¹²; these being 3043 and 3085 cm^{-1} . These average fundamental wavenumbers fell exactly on the Birge-Sponer line which fit the overtone transitions. The Birge-Sponer plots reported by Bini et al.⁸ for liquid pyridine included only $v = 3$ through 6, because the fundamental wavenumbers in the liquid are higher than those predicted by a Birge-Sponer fit to the overtone transitions. The liquid mechanical frequencies were 3105 and 3149 cm^{-1} almost identical to the gaseous values. The liquid anharmonicities were smaller, only 56 cm^{-1} ⁸.

Also listed in Table 1 are the overtone transitions in benzene. At each quantum level the absorption in benzene lies in between the two pyridine peaks. The presence of the electron attracting atom in the ring does not shift the absorption but splits it into two peaks.

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The widths of the pyridine absorption bands (summarized in Table 3) are similar to those reported for benzene, which are 82, 111, and 95 cm^{-1} for the $\nu = 4, 5$, and 6 transitions, respectively.² For pyridine the widths of the two $4\nu_{\text{CH}}$ peaks are 90 and 61 cm^{-1} for the lower and higher energy peaks, respectively. For $5\nu_{\text{CH}}$ both peaks are 110 cm^{-1} wide and for $6\nu_{\text{CH}}$ the lower energy peak is 102 cm^{-1} wide while the higher one is 130 cm^{-1} wide. The estimated error in these width measurements is ca. 6 cm^{-1} associated with the error in our intensity measurements and the assumption that the peaks are symmetric.

The relative intensities of the two peaks at each quantum level changes in going from the fundamental up through $6\nu_{\text{CH}}$. The higher energy peak is stronger in the fundamental but at $5\nu_{\text{CH}}$ the relative intensities switch leaving the lower energy peak the strongest.

The vibrational overtone spectra of gaseous 3-fluoropyridine and 2,6-difluoropyridine are shown in Figure 2 and summarized in Table I. These spectra are displayed to highlight the comparisons between them. The fundamental CH stretch region is included for completeness although these spectra have previously been reported^{13,14}. Fitting these transition energies to Birge-Sponer plots, we find the mechanical frequencies and anharmonicities listed in Table 2.

The vibrational spectra of both compounds display two prominent peaks at each quantum level. These two absorptions are blue-shifted with respect to those in pyridine. The shift is larger in the compound with two fluorine substituents on the ring. A similar relationship between aryl CH stretching frequency and the number of fluorine substituents in benzene was described by Gough and Henry¹⁵. Part of the blue shift comes from the higher fundamental frequencies in the fluorinated pyridines. Pyridine has CH stretches centered at 3040 and 3085 cm^{-1} , while in the 2,6 compound there is also a higher frequency absorption at 3110 cm^{-1} .

The widths for 3-fluoropyridine and 2,6-difluoropyridine are tabulated in Table 3. These widths are comparable to those in benzene with a few striking exceptions. The lower energy $4\nu_{\text{CH}}$ peak in 2,6-difluoropyridine at 124 cm^{-1} wide is significantly broader than its counterpart in benzene (82 cm^{-1} wide). At $5\nu_{\text{CH}}$ the width of the lower energy peak in 2,6-difluoropyridine is only 79 cm^{-1} compared to 111 cm^{-1} in benzene. Finally, the higher energy peak at $6\nu_{\text{CH}}$ in 3-fluoropyridine is 203 cm^{-1} wide, more than twice as wide as the corresponding peak in benzene (95 cm^{-1}).

The presence of two CH stretch overtone progressions in 3-fluoro- and 2,6-difluoropyridine calls into question their previous assignment⁸ to the CH stretches closest and furthest from the nitrogen. If this were the case the overtone spectrum of 2,6-difluoropyridine should contain only one vibrational progression. As a comparison to the present work, Sowa, Henry and Mizugai¹⁶ have investigated the vibrational spectra of some five membered heterocycles: 1 to $5\nu_{\text{CH}}$ of liquid furan and thiophene. The progressions of the two peaks for each compound were assigned to the two types of inequivalent CH oscillators. The 2,5 and 3,4-dibromothiophene spectra corroborate these assignments since each of these spectra possess only one absorption feature at $4\nu_{\text{CH}}$. The member of

the higher energy progression appears for 3,4-dibromothiophene and that of the lower energy progression appears for the 2,5-dibromothiophene. Of these five membered heterocycles, only pyrrole does not have two vibrational progressions following the local mode picture. In pyridine there are three types of local mode CH stretches. Fluorination at the 2 and 6 positions decreases the intensity of the lower energy peak and shifts both peaks to higher energy. It is possible that fluorination eliminates one of the three CH local modes and splits the remaining two which were previously unresolved in the spectrum of pyridine. Gough and Henry¹⁵ reported that in fluorobenzene the ortho CH stretch absorptions shifted to the blue further than the meta and para CH absorptions.

Another explanation can be offered for the appearance of multiple peaks by comparison to the theoretical model proposed for the benzene spectrum⁶. Because the intensity of the lower energy progression decreases but does not disappear completely, these absorptions could be the result of mixed mode states. The lower energy feature in pyridine could contain a large contribution from the CH stretch closest to the nitrogen but also involve combinations of other modes. In benzene there is one type of equivalent CH. The broad transitions at each overtone level, n , are due to combinations of modes of the pure stretch with other modes. The upper levels for these combinations can be designated as $\langle n, 0,0,0 \dots \rangle$, $\langle n-1, 2,0,0,\dots \rangle$, $\langle n-1, 1,1,0 \dots \rangle$ where the first quantum number represents the CH stretch and the subsequent numbers represent combination modes with the CC stretch and CCH bend. For pyridine there are three types of equivalent CH stretches. We would expect three systems of levels, one for each type of oscillator, involving the CC stretch and CCH bend modes. The overall appearance of only two broad peaks, which suggests two types of equivalent oscillators, would be the result of the overlap of these three systems of peaks. The switch in the relative intensities at the $v=5$ level could be due to relative shifts in the positions of the combination bands which have larger anharmonicities. This shift due to anharmonicity would favor the intensity of the red most absorption as is the case experimentally.

The spectrum of pyrazole, shown in Figure 3, is an intermediate case with two nitrogen atoms in the aromatic ring. One is protonated, similar to the nitrogen in pyrrole, while the other is unprotonated, analogous to the nitrogen in pyridine. In pyrazole the lone pair of the protonated nitrogen atom and one Π -bonded electron from the other nitrogen atom contribute to the aromaticity. While the CH spectrum of pyrrole displays only one peak at each quantum level, pyrazole, like pyridine, has two peaks in the CH spectrum.

The proton chemical shifts have been used to rationalize the overtone spectra of the nitrogen containing six membered rings⁹. In pyridine the nmr chemical shifts¹⁷ indicate two chemically different environments for the protons with chemical shifts of 5.942 ppm and two closer peaks at 6.982 and 7.383 ppm. In pyrazole the protons closest to the nitrogen shift all the way to 7.52 leaving the proton furthest from the nitrogen at 6.25 ppm¹⁷. This difference in the chemical environment of

the protons in pyrazole indicates that two of the protons are deshielded similar to the situation in benzene (7.23 ppm). Likewise for furan the chemical shifts of 6.30 and 7.37 ppm¹⁷ indicate two different proton environments for furan. However for thiophene, with two overtone progressions, the chemical shifts for the two types of protons are separated by only 0.20 ppm; while in pyrrole, where only one overtone band is observed, the proton chemical shifts are separated by 0.34 ppm. As discussed by Mizugai and Katayama¹⁸ the CH bond lengths are more consistent with the vibrational spectra. In pyrrole the CH bonds are essentially the same length at 1.077 Å,¹⁹ whereas the bonds in furan are 1.075 and 1.077 Å²⁰ and in thiophene they are 1.078 and 1.081 Å.²¹

Conclusions

The vibrational overtone spectra of gaseous pyridine, 3-fluoropyridine, 2,6-difluoropyridine, and pyrazole all possess two vibrational progressions. The progressions in the fluorinated compounds are shifted to the blue with respect to pyridine. It is possible that fluorination at the 2,6 position, while eliminating the CH oscillators located at the 2 and 6 positions, splits the CH frequencies for the 3, 5 and 4 positions restoring the pattern of two vibrational progressions. Alternatively the vibrational progressions may be the result of overlapping combination modes related to the different types of CH oscillators in these compounds.

In general the overtone spectra of cyclic heterocyclics display two vibrational progressions in the overtone spectra. The only exception to this is pyrrole with only one progression. Of the compounds studied, pyridine, 3-fluoro- and 2,6-difluoropyridine, furan, thiophene, pyrazole and pyrrole, only pyrrole does not have a lone pair perpendicular to the Π -bonding system. The lone pair exerts an effect on the CH stretches nearest to it which is observed in the overtone spectrum.

Table 1. Transition Wavenumbers (cm^{-1}) for Overtone Spectra of Gaseous Pyridine, 3-Fluoropyridine, 2,6-Difluoropyridine, Pyrazole, and Benzene.

ν	gaseous	pyridine			3-fluoro- pyridine	2,6-difluoro- pyridine	pyrazole	benzene ^a
		ref 8	liquid ref 9	ref 10				
1	3030(ν_{20a}) ^b	3004		3042.4	3054	3040		3047
	3042(ν_{7b}) ^b	3031		3030.1	3077	3089		
	3073(ν_{13}) ^b	3056		3072.8				
	3087(ν_{20b}) ^b	3080		3086.9				
	3094(ν_2) ^b			3094.2				
2		5835		5910				5972
		5867		5988				
		5907		6013				
		5956		6154 6231				
3	8719	8651		8842				8786
	8740	8785						
	8774							
	8826							
4	11417 $\pm$ 5	11296		11628	11489 $\pm$ 3	11590 $\pm$ 8		11498
	11555 $\pm$ 3	11474			11609 $\pm$ 3	11726 $\pm$ 4		
5	13941 $\pm$ 3	13810			14040 $\pm$ 5	14218 $\pm$ 5	13193 $\pm$ 3	14072
	14125 $\pm$ 3	14037			14244 $\pm$ 13	14375 $\pm$ 5	13279 $\pm$ 5	
6	16385 $\pm$ 3	16277	16300		16519 $\pm$ 3	16704 $\pm$ 5		16550
	16629 $\pm$ 3	16548	16570		16705 $\pm$ 3	16904 $\pm$ 3		

a) Data taken from reference 2.

b) Data taken from reference 12.

Table 2. Mechanical Frequencies and Anharmonicities in cm^{-1} .

	w_e	$w_e x_e$
pyridine	3105	-63
	3146	-63
3-fluoropyridine	3120	-63
	3136	-58
2,6-difluoropyridine	3094	-51
	3145	-54

Table 3. Widths of Gaseous Overtone Spectra in cm^{-1} .

	<u>Benzene</u>	<u>Pyridine</u>		<u>3-Fluoropyridine</u>		<u>2,6-Difluoropyridine</u>	
		low	high	low	high	low	high
4vCH	82	61	90	79	98	124	65
5vCH	111	110	110	120	153	79	99
6vCH	95	102	130	149	203	86	117

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Figure Captions

Figure 1. Spectra of the fundamental and second through fifth overtone CH stretch in gaseous pyridine. (Fundamental CH stretch spectrum taken from ref. 12.)

Figure 2. Spectra of fundamental and third through fifth overtone CH stretch in gaseous 3-fluoropyridine (upper) and 2,6-difluoropyridine (lower).

Figure 3. Spectrum of the fourth overtone CH stretch in gaseous pyrazole.





