

AD-A237 132



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REPORT DOCUMENTATION PAGE				Form Approved GMB No 0704-0188	
1a REPORT SECURITY CLASSIFICATION			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION / AVAILABILITY OF REPORT		
2b DECLASSIFICATION / DOWNGRADING SCHEDULE Unclassified					
4 PERFORMING ORGANIZATION REPORT NUMBER(S)			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a NAME OF PERFORMING ORGANIZATION Bowling Green State University		6b OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION		
6c ADDRESS (City, State, and ZIP Code) Bowling Green, Ohio 43403			7b ADDRESS (City, State, and ZIP Code)		
8a NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO	PROJECT NO	TASK NO
					WORK UNIT ACCESSION NO
11 TITLE (Include Security Classification) Vibrational Overtone Spectroscopy of Pyrrole and Pyrrolidine					
12 PERSONAL AUTHOR(S) D.L. Snively, F.R. Blackburn, Y. Ranatunga and V.A. Walters					
13a TYPE OF REPORT Technical Report		13b TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) May 23, 1991	15 PAGE COUNT
16 SUPPLEMENTARY NOTATION					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19 ABSTRACT (Continue on reverse if necessary and identify by block number) The gaseous near infrared and visible absorption spectra of pyrrole and pyrrolidine have been measured for the first through fourth N-H stretch vibrational overtones and the second through fourth C-H stretch overtones. The C-H overtone features follow the simple local mode expression with anharmonicities of 52 cm^{-1} for pyrrole and 55 cm^{-1} for pyrrolidine. Multiple transitions observed in the N-H stretching regions indicate the presence of vibrational coupling to other vibrational modes. For comparison, the visible spectra of neat liquid pyrrole, dilutions of pyrrole in carbon tetrachloride, and neat liquid pyrrolidine were obtained by direct absorption spectroscopy. The pattern of multiple peaks for the N-H absorption region appears (shifted 200 cm^{-1} to the red) in solution phase pyrrole. This shift of all the peaks results from the intermolecular interactions of the N-H in the liquid; however, the preservation of the peak splittings indicates that this splitting is a result of intramolecular vibrational coupling.					
20 DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED / UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a NAME OF RESPONSIBLE INDIVIDUAL			22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL	

OFFICE OF NAVAL RESEARCH
GRANT or CONTRACT N00014-88-K-0664

R&T Code 4131063
Technical Report No. 7

Approved for	
Dissemination	✓
Classification	
by	
Authority	
Small and/or	
Dist	Special
A-1	

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by

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Prepared for Publication
in
Journal of Physical Chemistry

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May 23, 1991

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91-02703



91 6 10 114

Vibrational overtone spectroscopy of pyrrole and pyrrolidine

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Abstract

The gaseous near infrared and visible absorption spectra of pyrrole and pyrrolidine have been measured for the first through fourth N-H stretch vibrational overtones and the second through fourth C-H stretch overtones. The C-H overtone features follow the simple local mode expression with anharmonicities of 52 cm^{-1} for pyrrole and 55 cm^{-1} for pyrrolidine. Multiple transitions observed in the N-H stretching regions indicate the presence of vibrational coupling to other vibrational modes. For comparison, the visible spectra of neat liquid pyrrole, dilutions of pyrrole in carbon tetrachloride, and neat liquid pyrrolidine were obtained by direct absorption spectroscopy. The pattern of multiple peaks for the N-H absorption region appears (shifted 200 cm^{-1} to the red) in solution phase pyrrole. This shift of all the peaks results from the intermolecular interactions of the N-H in the liquid; however, the preservation of the peak splittings indicates that this splitting is a result of intramolecular vibrational coupling. The spectrum of pyrrolidine is remarkably similar to that of pyrrole suggesting the same vibrational coupling exists for both compounds.

Introduction

The nature of individual bond oscillators has been revealed through the study of the near infrared and visible absorption spectra in polyatomic molecules. The strongest vibrational progressions are those corresponding to oscillators with the highest anharmonicities¹. The C-H, N-H and O-H stretching vibrations are more anharmonic than the stretching vibration between two heavy atoms. The anharmonicities for C-H, N-H and O-H oscillators range from 55 to 80 cm⁻¹. However, Yamasaki et al.² have determined the vibrational overtone spectrum of gaseous N₂O, finding the ν_3 mode (N-N stretching mode) to be nearly harmonic all the way through $v = 6$ with an anharmonicity of only 15 cm⁻¹. Bending and wagging motions tend to be harmonic so the direct overtone absorption of these modes is quite weak in the visible absorption spectrum.

If there is no strong vibrational mixing, the transition energies, ΔE , for these anharmonic oscillators can be fitted reasonably well to the following equation¹ which describes a single vibrational mode

$$\Delta E = (\omega_e - \omega_e x_e)v - \omega_e x_e v^2 \quad 1.$$

where v is the local mode vibrational quantum number, ω_e is the mechanical frequency for that particular local mode, and $\omega_e x_e$ is the anharmonicity for the local mode. Using this equation, a Birge-Sponer plot³ taking $\Delta E/v$ versus v yields the ω_e and $\omega_e x_e$ from measured ΔE values. These constants have been derived from overtone spectra for a number of amines including: liquid diethylamine⁴ and trimethylamine⁵, and gaseous ammonia^{6,7,8}, methylamine, dimethylamine, diethylamine and hydrazine⁹. Typical values for these constants range from 77 cm⁻¹ (ammonia) to 86 cm⁻¹ (hydrazine) for $\omega_e x_e$ and 3490 cm⁻¹ (hydrazine) to 3553 cm⁻¹ (ammonia) for ω_e .

Extensive investigations of the visible absorption spectrum of the C-H oscillator in CF₃H^{10, 11} and (CF₃)₃CH¹² have shown that a strong interaction exists between the C-H stretching and bending motion. Because the mechanical frequency for the stretch is approximately twice that of the bend, a Fermi resonance is observed in the vibrational overtone spectra of molecules which contain only one C-H oscillator. A seven parameter effective many level Fermi resonance Hamiltonian was used to fit the intensities and transition energies for CF₃H, (CF₃)₃CH and CD₃H. The off-diagonal effective stretch-bend-bend coupling constant, k_{sbb} , is 100 cm⁻¹ for CF₃H, 65 cm⁻¹ for (CF₃)₃CH¹² and only 30 cm⁻¹ for the case of CD₃H¹³. In order to better describe this stretch bend interaction, curvilinear coordinates^{14, 15} were used to describe the

CHX₃ spectrum in a similar way to that introduced for benzene¹⁶. A review of this area of research is recently available¹⁷.

The overtone spectrum of the N-H oscillator has received much less attention. The N-H stretch, with a fundamental transition energy at about 3500 cm⁻¹, is a weak feature in the infrared spectrum of most amines¹⁸. However, the N-H overtone absorption for simple amines is comparable if not stronger than the corresponding C-H stretching overtone absorptions in the visible region of the spectrum. The in-plane bends and out-of-plane bends are observed between 1650 to 1580 cm⁻¹ and 909 to 666 cm⁻¹, respectively¹⁸, for most amines. These bending absorptions are strong in the infrared spectrum but the pure overtone absorptions for these modes do not appear in the visible spectrum. Fermi resonance between the N-H stretch and bend in liquid infrared spectra has been discussed¹⁹ as it pertains to the frequency shifts with change in concentration of the amine diluted in CCl₄. The stretch-bend interaction in the N-H overtone spectrum has not been investigated.

The vibrational overtone spectrum of the heterocyclic aromatic compound pyrrole is presented in this report along with its saturated analog, pyrrolidine (Figure 1). Pyrrole was chosen for this work for several reasons: it contains only one N-H oscillator, the bond lengths for all four C-H oscillators are almost the same, its aromaticity guarantees a minimal contribution from low frequency torsional and bending modes, and its importance in developing technologies^{20,21,22,23}. The overtone spectrum is of particular interest in comparison to those of CD₃COH²³ and benzene¹⁶. As in CD₃COH, it might be possible in pyrrole and pyrrolidine for the in-plane bend and not the out-of-plane bend (since it is too low in energy) to couple to the stretch vibration. The importance of this difference for in-plane and out-of-plane bends has been discussed previously²⁴ with regard to the differences between benzene and CD₃COH; however, in the present case there is only one N-H oscillator (rather than six equivalent C-H oscillators in benzene) so the vibrational coupling to the bending mode will not be dominated by the like-bond coupling as in benzene.

Vibrational Spectrum of Pyrrole and Pyrrolidine

In 1942, the first rigorous study of the vibrational spectrum of liquid pyrrole and three of its deuterated analogs was carried out. In the study, twenty-three of the twenty-four vibrational modes were assigned²⁵. The symmetry indicated by this spectrum was C_{2v}; the planarity of pyrrole has been confirmed in subsequent work²⁶. The N-H stretch (A₁ symmetry) was assigned to a band at 3400 cm⁻¹. Lord assigned the in-plane N-H bend of B₁ symmetry to an absorption at 1146 cm⁻¹ which disappears upon deuteration and the out-of-plane N-H bend (B₂ symmetry) to the 565 cm⁻¹ absorption²⁵.

A revision of the vibrational analysis of pyrrole was undertaken by Scott in 1971²⁷ as a result of his harmonic force field computations. Two C-H stretching absorptions were assigned to the 3145 cm⁻¹ and 3129 cm⁻¹ bands. Attempts to assign the six modes of B₁ symmetry have been made^{27, 28}. Scott's normal mode analysis revealed that the N-H in-plane bend is strongly mixed with the C-H in-plane bend and the C-C and C-N stretch. Scott assigned the bands at 1526, 1412, 1284, 1148 and 1043 cm⁻¹ to these in-plane bending modes. In 1982, Navarro and Orza improved the accuracy of previously observed bands and observed many new weak features in the gas phase spectrum of pyrrole in a cell maintained at 70°C²⁹. Several new features in the C-H stretching region were identified. Xie et al.³⁰ assign the 3116, 3125, 3140 and 3148 cm⁻¹ peaks to the C-H fundamentals and the bands at 1287, 1424 and 1521 cm⁻¹ to the mixed in-plane bend and ring distortions.

The second N-H stretching overtone of pyrrole was first observed by Zumwalt and Badger³¹ and later Carlotti et al.³² resolved and analyzed the rotational structure. The R and P branches, with an average spacing of 0.30 cm⁻¹, were clearly resolved in this work giving an overall A-type contour, however the Q branch and K substructure were still unresolved. Douketis³³ reported the third N-H stretching overtone and suggested that the observed contour results from rotational structure and combination bands involving the C-H stretch. Douketis shows that the A, B and C rotational constants vary in a linear way going from v = 0, 1 and 3. The B and C constants decrease by about 1% while A shows almost no change. In addition, Douketis recorded at high resolution the fundamental C-H transition at room temperature and cooled in a supersonic jet.

The C-H stretching overtones from Δv = 2 - 6 have been reported for liquid pyrrole by Mizugai and Katayama³⁴ using a thermal lensing technique. They did not report the actual transition energies, only the following equation to which they fit their data

$$G_{v,0} = 3180 v - 59 v^2$$

From this expression the first through fifth overtone transitions should lie at 6,124, 9,009, 11,776, 14,425 and 16,956 cm⁻¹, respectively. Their observed C-H stretch band contours were about 200 cm⁻¹ wide. These workers did not mention the N-H transitions.

The fundamental spectrum of pyrrolidine in dilute carbon tetrachloride has been discussed³⁴ with regard to the effect of conformation on the fundamental frequencies. Pyrrolidine can exist in a chair conformation with the lone pair either axial or equatorial, or it can adopt a twist chair conformation in which the axial and equatorial designations are meaningless. The first N-H stretch overtone of gaseous pyrrolidine was reported³⁵ to consist of several absorption features, the

strongest of which appeared at 6590 cm^{-1} . These workers did not attempt to assign these multiple peaks.

Experimental

Pyrrole and pyrrolidine were obtained from Aldrich Company in 98% purity. Pyrrole was freshly distilled before use. For the liquid dilution spectra freshly distilled Aldrich CCl_4 was used. The liquid spectra were recorded on a Cary 219A spectrometer with a 10 cm path length.

The C-H fundamental transitions of pyrrolidine were recorded in a 10 cm pathlength cell on a Nicolet FTIR at 1 cm^{-1} resolution at 4 torr. Even with 20 torr of sample the N-H fundamental was not observed. A variable pathlength cell was required to record the N-H transition with a 9.75 m pathlength on a Cygnus 100 Mattson FTIR.

The NIR spectra were all recorded on the Cygnus 100 spectrometer outfitted with a quartz beamsplitter, InGaAs detector and tungsten lamp. These spectra were obtained using a variable pathlength cell with pathlengths ranging from 9.75 to 20 m.

The photoacoustic absorption spectra were obtained in a 1.5 cm by 20 cm vacuum cell outfitted with quartz windows oriented at Brewster's angle. A Knowles Electronics, Inc. Model 1751 microphone powered by a 1.5 V battery was set into a glass tee situated at the center of the cell. The signal from this microphone was detected by an EG&G Brookdeal Electronics PAR Model 5207 lock-in amplifier. The reference signal was provided by a Model 03-0C4000 PTI Inc. mechanical chopper which chopped the argon laser. The chopping frequency which resulted in the best signal-to-noise ratio was selected for each spectrum (frequencies ranged from 200 to 750 Hz). The photoacoustic cell was aligned intracavity in a Spectra Physics argon ion pumped dye laser. The dye laser wavelength was tuned with a 3-plate birefringent filter which resulted in a 3 cm^{-1} bandwidth of the laser output. An Oriel Company Model 18007 scanner was used to rotate the birefringent filter to select the laser output wavelength. The four dyes used in this work were Rhodamine 6G, DCM, Pyridine 2 and Styryl 9. The absorption wavelengths were measured with a Spex 1401 double monochromator which provides a 0.2 cm^{-1} resolution at $15,802\text{ cm}^{-1}$. The wavelength accuracy was limited to 3 cm^{-1} by the laser bandwidth.

Results

The overtone absorption spectra of pyrrole and pyrrolidine are shown in Figures 2 through 5. Figures 2 and 3 contain the first, second, third and fourth N-H stretch overtone spectra for pyrrole and pyrrolidine, respectively. The second, third, and fourth C-H stretch overtone spectra for pyrrole and second, fourth and fifth C-H overtone spectra for pyrrolidine are shown in Figures 4 and 5, respectively. The intensity scales on these figures are labeled either absorbance or PAS

intensity depending on whether the spectra were recorded on the FTIR spectrometer or by laser photoacoustic spectroscopy. These were the only absorption features found over the entire accessible spectroscopic range from 6,400 to 10,500 cm^{-1} and from 11,400 to 17,857 cm^{-1} .

The measured absorption frequencies and relative intensities for the observed transitions are listed in Table 1. The widths of the most intense peaks are also included for a rough comparison between the overtone transitions. Each of the strong N-H absorption bands in pyrrole (Figure 2) have distinguishable P, Q and R type rotational band contours typical of rotational band contours found in infrared spectroscopy. At our lower resolution, the rotational structure analyzed by Carloti et al.³² for the second N-H stretch overtone absorption is not resolved. The position of the Q branches, and when available the P and R branch maxima, are listed in Table 1. The strong absorption at 13,305 cm^{-1} appears to be the convolution of two rotational band contours. The strong absorption centered at 16,316 cm^{-1} also showed P and R type band structure with maxima at 16,310 and 16,331 cm^{-1} , respectively, with an overall width of 43 cm^{-1} . The C-H transitions at $\nu=3$ and 5 are single peaks consistent with aromaticity. However, the $\nu=4$ transition appears as a double peak. As seen in Table 1, the C-H stretch transitions are about twice as wide as the strongest peaks in the N-H overtone bands.

The most intense bands in the pyrrolidine N-H spectra shown in Figure 3 do not exhibit the P, Q, R type rotational structure. However, the band contours for the weaker transitions in the first and second overtones, which are remarkably similar to the band contour for the N-H fundamental, display interesting rotational structure. We will present the infrared absorption spectrum of pyrroline and pyrrolidine in another paper³⁷. The N-H first overtone transition wavenumbers presented in Table 1 agree with those reported by Baldock and Katritzky³⁵. The pyrrolidine $\nu=5$ C-H peak at 13,495 cm^{-1} is over 350 cm^{-1} wide and probably is a convolution of at least two transitions. The second overtone is better resolved and appears to be a convolution of three transitions, reflecting the differences in the C-H oscillators in the boat and twist boat conformations.

Figure 6 compares the liquid absorption spectra of neat pyrrole and pyrrolidine. Although the N-H third overtone band of liquid pyrrole (782 nm) is broad and structureless, the corresponding transition for pyrrolidine (centered 815 nm) appears to be three overlapping peaks. It is interesting this pyrrolidine band shows multiple peaks in both the gas and the liquid. Figure 7 shows the dilution effects for pyrrole in CCl_4 . As the dilution factor increases the broad, structureless N-H absorption disappears and as many as five peaks gain intensity on the blue side of the original broad neat liquid peak. Table 2 summarizes these liquid data.

Discussion

The band at $14,505\text{ cm}^{-1}$ of pyrrole ($14,368\text{ cm}^{-1}$ in the liquid) arises from the 5-0 C-H stretch overtone transition. We have confirmed this assignment by observing the overtone spectrum of pyrrole- d_5 wherein this band disappears. The corresponding C-H 5-0 peak in pyrrolidine appears at $13,495\text{ cm}^{-1}$ for the gaseous sample and $13,423\text{ cm}^{-1}$ for the liquid. This red shift going from pyrrole to pyrrolidine of 1000 cm^{-1} brings this absorption into the normal range of the 5-0 C-H stretching transitions in other nonaromatic hydrocarbons. Based on these assignments we can assign the other C-H transitions as designated in Table 1.

The anharmonicity for the C-H oscillator in gaseous pyrrole is $52.3 \pm 0.5\text{ cm}^{-1}$ using equation 1. Here the average value of the C-H stretching bands (3112 cm^{-1}) for the $\nu = 1$ level and the frequency for the strongest peak of the third overtone double peak was used. The liquid anharmonicity is $56 \pm 1\text{ cm}^{-1}$ (using the $\nu=1,4$ and 5 data) indicating very little change in the C-H vibrational potential. For gaseous pyrrolidine the anharmonicity is $55.5 \pm 0.5\text{ cm}^{-1}$. Once again, the average value of the four observed C-H stretching fundamentals was taken as the $\nu = 1$ level. Similar to the case for pyrrole the liquid anharmonicity increases slightly to 60 cm^{-1} , however only two levels ($\nu=1$ and 5) are known for liquid pyrrolidine.

The assignment of the other absorptions shown in Figures 2 and 3 is more problematic. The general pattern is a strong peak accompanied by two or three weaker peaks to lower energy. For instance, the $13,305\text{ cm}^{-1}$ band in pyrrole has three weaker transitions 103, 191 and 309 cm^{-1} to the red. The corresponding transition in pyrrolidine at $12,551\text{ cm}^{-1}$ has three weaker peaks shifted to the red by 82, 197 and 325 cm^{-1} . We believe these absorption features involve the N-H stretching motion which, similar to the C-H oscillator in CX_3H ¹³ interacts with the bend, causing new absorptions to appear. As shown in Table 1, the 4-0 N-H transitions appear at $13,305$ and $12,551\text{ cm}^{-1}$ for pyrrole and pyrrolidine, respectively. The 5-0 N-H transitions lie at $16,316$ and $15,298\text{ cm}^{-1}$ for pyrrole and pyrrolidine, respectively. The transitions for pyrrole are blue shifted due to aromaticity, while those in pyrrolidine are typical compared to other amines. For example, the N-H(5) level in ammonia and methylamine lies at $15,450$ ⁶ and $15,325\text{ cm}^{-1}$ ⁹, respectively.

Evidence that these multiple absorptions belong to intramolecular vibrational coupling in the N-H comes from the liquid spectra. The 4-0 N-H transition in the neat pyrrole spectrum shown in Figure 6 is shifted 500 cm^{-1} from the gaseous value. However, upon dilution in CCl_4 this broad red shifted peak shows structure reminiscent of the gaseous spectrum (Figure 7). Specifically, the splittings of 85, 186 and 303 cm^{-1} appear in the dilution spectra while the splittings in the gaseous spectrum are 103, 191 and 309 cm^{-1} . These numbers are in excellent agreement since the liquid spectra were recorded on a conventional absorption spectrometer at 1 nm (about 20 cm^{-1})

resolution. The intensity at the red side of the broad peak in neat pyrrole decreases at higher dilution and is probably due to inhomogeneous absorption of hydrogen bonded N-H oscillators. The values in the last column in Table 2 indicate that the entire N-H absorption at the $\nu=4$ level shifts about 200 cm^{-1} in the liquid 10% dilution. In contrast the C-H $\nu=4$ and 5 levels only shift about 100 cm^{-1} . For pyrrolidine neat liquid the 4-0 N-H transition is split. The comparison of dilution splittings to those of the gas for pyrrolidine is not as good as for the case of pyrrole, but does show the same trend.

The identity of the mode which mixes to the N-H stretch in pyrrole is difficult to determine with certainty. It is not possible for the interaction to involve strictly the N-H bend because in the normal coordinates the in-plane bend is always coupled to the C-H in-plane bends and the ring stretches. However, the vibrational spacing between the $\nu=3$ and $\nu=4$ quantum levels (using the two most intense peaks in each multiple absorption region) is 3122 cm^{-1} so we suspect the overtones of the mixed in-plane bend and ring distortions with frequencies of 1287, 1424 and 1521 cm^{-1} to be important. Taking a value of 1500 cm^{-1} for the fundamental frequency and an anharmonicity of about 10 cm^{-1} , we find the $\nu = 9$ level of this bending mode will lie at approximately $13,300\text{ cm}^{-1}$ and the $\nu = 11$ level at $16,300\text{ cm}^{-1}$, i.e. in the vicinity of the $\nu=4$ and 5 N-H overtones. This is a reasonable guess given the complicated nature of these in-plane bending modes. Because of the similarity of the spectra, we believe the same vibrational coupling mechanism occurs in pyrrolidine.

There is evidence that a perturbed vibrational level structure has been observed in other overtone spectra. For dimethylamine Fang *et al.*³⁸ have found that the $\Delta\nu=4$ transition does not fit a Birge-Sponer plot properly. In addition they noted that the N-H stretch has a low energy shoulder whose intensity decreases with increasing quantum number. The relative intensities of these bands were invariant to changes in pressure and temperature. These workers suggest that a Fermi resonance involving a stretch-bend interaction may be active in dimethylamine. Lehmann *et al.*³⁹ note that the rotational structure for the fifth and sixth quantum levels in ammonia are perturbed through Fermi resonance by some dark state. These workers suggest that the umbrella mode ν_2 is involved. The visible spectrum of several alcohols have been recorded^{38,40,41}, however this type of stretch-bend Fermi resonance has not been analyzed for these molecules. The possibility of a strong interaction between the O-H stretch and the O-H bend or C-O stretch was suggested as a possible explanation of the spectrum of methanol⁴¹.

Conclusion

The vibrational overtone spectra of gaseous and liquid phase pyrrole and pyrrolidine have been observed in the near infrared and visible region of the spectrum. The first, second, third and fourth

N-H stretch overtone transitions were observed. It is clear that the N-H stretch is coupled to some other vibrational mode and that the vibrational coupling pattern is similar for pyrrole and pyrrolidine. Several C-H stretch overtones for pyrrole and pyrrolidine were also observed. The C-H overtone spectra are simple and reflect the aromaticity of pyrrole and the boat conformation possible in pyrrolidine.

References

1. Henry, B.R. *Vib. Spectra Struct.* **1981**, 10, 269 .
2. Yamasaki, N.L.S.; Manzanares, C.; Baylor, I. L.C.; Schatz, G.C.; Weitz, E. *J. Phys. Chem.* **1989**, 93, 2204.
3. Birge, R.T.; Sponer, H. *Phys. Rev.* **1926**, 28, 259.
4. Weisman, R. B.; Rice, S. A. *Chem. Phys. Lett.* **1979**, 61(1), 15.
5. Fang, H.L.; Meister, D.M.; Swofford, R.L. *J. Phys. Chem.* **1984**, 88, 410.
6. Coy, S. L.; Lehmann, K. K. *J. Chem. Phys.* **1986**, 84(10), 5239 .
7. Hayward, R. J.; Henry, B.R. *J. Mol. Spectrosc.* **1974**, 50, 58.
8. Stella, G.; Gelfand, J.; Smith, W.H. *Chem. Phys. Lett.* **1976**, 39(1), 146.
9. Fang, H.L.; Swofford, R.L.; Compton, D. A.C. *Chem. Phys. Lett.* **1984**, 108(6), 539.
10. Dubal, H.-R.; Quack, M. *J. Chem. Phys.* **1984**, 81(9), 3779.
11. Segall, J.; Zare, R.N.; Dubal, H. R.; Lewerenz, M.; Quack, M. *J. Chem. Phys.* **1987**, 86(2), 634.
12. Baggott, J.E.; Chuang, M.-C.; Zare, R.N.; Dubal, H.R.; Quack, M. *J. Chem. Phys.* **1985**, 82 (3), 1186.
13. Lewerenz, M.; Quack, M. *J. Chem. Phys.* **1988**, 88(9), 5408.
14. Green Jr., W. H.; Lawrance, W.D., Moore, C.B. *J. Chem Phys.* **1987**, 86(11), 6000.
15. Halonen, L.; Carrington Jr., T.; Quack, M. *J. Chem. Soc. Faraday Trans. 2*, **1988**, 84(9), 1371.
16. Sibert III, E. L.; Reinhardt, W. P.; Hynes, J.T. *J. Chem. Phys.* **1984**, 81(3), 1115.
17. Quack, M.; *Annu. Rev. Phys. Chem.* **1990**, 41, 839.
18. *Spectrometric Identification of Organic Compounds*, Robert M. Silverstein, G. Clayton Bassler and Terence C. Morrill, ©1963 by John Wiley and Sons, Inc., Fourth Edition.
19. Wolff, H.; Schmidt, U.; Wolff, E. *Spectrochim. Acta.* 36A, **1980**, 899.
20. *Conductive Polymers*, Edited by Raymond B. Seymour, Polymer Science and Technology Vol.15, ©1981 Plenum Press.
21. *Electronic Properties of Polymers and Related Compounds*, Springer Series in Solid-State Sciences 63, Editors: H. Kuzmanov, M. Mehring, and S. Roth ©Springer-Verlag 1985.
22. Street, G.B.; Lindsey, S.E.; Nazzari, A.I.; Wynne, K.J. *Mol. Cryst. Liq. Cryst.* **1985**, 118, 137.

23. Dougherty, T. J.; Kaufman, J. E.; Goldfarb, A.; Weishaupt, K. R.; Boyle, D.; Mittleman, A. *Cancer Research* **1978**, 38, 2628.
24. Amrein, A.; Hollenstein, H.; Quack, M.; Zenobi, R.; Segall, J.; Zare, R.N. *J. Chem. Phys.* **1989**, 90(8), 3944.
25. Lord, Jr. R.C.; Miller, F. A. *J. Chem. Phys.* **1942**, 10, 328.
26. Nygaard, L.; Nielson, J.T.; Kirchheiner, J.; Maltesen, G.; Rastrup-Andersen, J.; Sorensen, G.O. *J. Mol. Struct.* **1969**, 3, 491.
27. Scott, D. W. *J. Mol. Spectrosc.* **1971**, 37,77.
28. Navarro, R.; Orza, J.M. *Anales de Quimica* **1984**, 80, 59.
29. Navarro, R.; Orza, J.M. *Anales de Quimica* **1982**, 79, 557.
30. Xie, Y; Fan, K.; Boggs, J., *Molec. Phys.* **1986**, 58(2), 401.
31. Zumwalt, L. R.; Badger, R.M. *J. Chem. Phys.* **1939**, 7, 629.
32. Carlotti, M.; Di Lonardo, G.; Galloni, G.; Trombetti, A. *J. Chem. Soc. Far.* **1977**, 2, 67 2852.
33. C. Douketis, Ph.D. thesis, Indiana University, 1990.
34. Mizugai, Y.; Katayama, M. *Chem. Phys. Letters* **1980**, 73(2), 240.
35. Krueger, P.J.; Jan, J. *Can. Jour. Chem.*, **1970**, 48, 3236.
36. Baldock, R.W.; Katritzky, A.R. *J. Chem. Soc. (B)*, **1968**, 1470.
37. Jeff Dage, Dave Brodin and D.L. Snavely, submitted to *Spectrochimica Acta*.
38. Fang, H.L.; Swofford, R.L. *Chem. Phys. Lett.* **1984**, 105(1), 5.
39. Coy, S. L.; Lehmann, K. K. *J. Chem. Phys.* **1986**, 84(19), 5239.
40. Jasinski, J. M. *Chem. Phys. Lett.* **1984**, 109(5), 462.
41. Fang, H. L. ; Meister, D. M.; Swofford, R. L. *J. Phys. Chem.* **1984**, 88,405.

Figure Captions

Figure 1 Pyrrole and pyrrolidine.

Figure 2 First, second, third and fourth overtone spectra for the N-H stretch in gaseous pyrrole.

Figure 3 First, second, third and fourth overtone spectra for the N-H stretch in gaseous pyrrolidine.

Figure 4 Second, third and fourth overtone spectra for the C-H stretch in gaseous pyrrole.

Figure 5 Second, fourth and fifth overtone spectra for the C-H stretch in gaseous pyrrolidine.

Figure 6 Liquid overtone spectrum of neat pyrrole and pyrrolidine.

Figure 7 Liquid overtone spectrum of the $\nu=4$ N-H transition of pyrrole diluted in CCl_4 .

Table 1 Observed gaseous peak transition frequencies (wavenumbers, cm^{-1})

	Pyrrole	Splitting	Width	Pyrrolidine	Splitting	Width
$\nu=1$ (C-H)	3116 ^c 3125 ^c 3140 ^c 3148 ^c			2818 2883 2970 2980		
$\nu=1$ (N-H)	3531 ^a			3364 ^b 4301 4373		
$\nu=2$ (C-H)	-			-		
$\nu=2$ (N-H)	6872 w	52		6483 Q 6494 Q 6505 Q 6519 Q	94	
	6924 vs	0	39	6588 6637	0 49	52
$\nu=3$ (C-H)	9034		87	7807 vw 8269 w 8478 vs		160
$\nu=3$ (N-H)				9265 9491 Q 9506 Q 9521 Q	381 140	
	10039 ^d 10111 ^d 10174 P 10183 Q 10193 R	146 74 0	40	9646 9697	0 51	57
$\nu=4$ (C-H)	11795 s 11836 vs		125			
$\nu=4$ (N-H)	12996 w 13114 vvw 13202 w 13305 vs 13350 w	309 191 103 0 45	53	12226 m 12354 m 12469 w 12551 vs 12600 s	325 197 82 0 49	75
$\nu=5$ (C-H)	14505		110	13495		350
$\nu=5$ (N-H)	16121 w 16180 vvw 16232 w 16310 P 16316 vs 16331 R	195 136 84 0	43	14980 m 15180 w 15254 s 15298 vs 15393 m 15473 w	274 118 44 0	77

$\nu=6$ (C-H)

15834

190

- a. R. Navarro and J.M. Orza, *Anales de Quimica* 79, 557 (1982).
- b. 9.75 m path length, position taken from the center of the rotational band contour
- c. Y. Xie and K. Fan, *J. Molec. Phys.* 59(2), 401 (1986).
- d. Zumwalt, L. R.; Badger, R.M. *J. Chem. Phys.* 1939, 7, 629.

Table 2. Observed liquid peak transition frequencies and frequency shifts for gas to 10% dilution (wavenumbers, cm^{-1})^a

Pyrrolidine

	Liquid	Dilution in CCl_4	Splitting	Gaseous	Splitting	$\Delta\nu_{\text{gas-10\%}}$
v=4 (N-H)	12165	12195 (251)	251	12226	325	159
	12270	12346 (100)	100	12354	197	123
	12422	12446 (0)	0	12469	82	105
				12551vs	0	
v=5 (C-H)	13245					
	13423	13368		13495		127

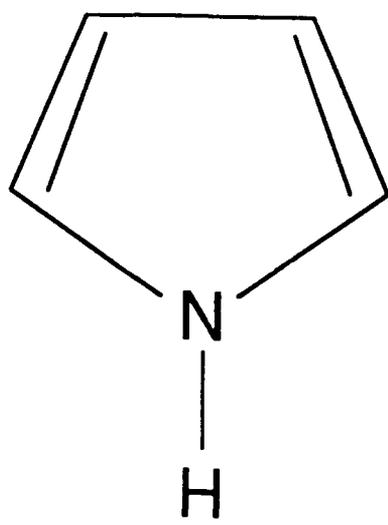
Pyrrole

	Liquid	Dilution in CCl_4	Splitting	Gaseous	Splitting	$\Delta\nu_{\text{gas-10\%}}$
v=4 (C-H)	11723	11765		11795		71
				11836		
v=4 (N-H)		12820	303	12996w	309	176
		12937	186	13114vww	191	
		13038 ^b	85	13202w	103	223
	12788	13123	0	13305vs	0	182
	13193 ^c	70	13350w	45		
	13263					
v=5 (C-H)	14368	14388		14505		117

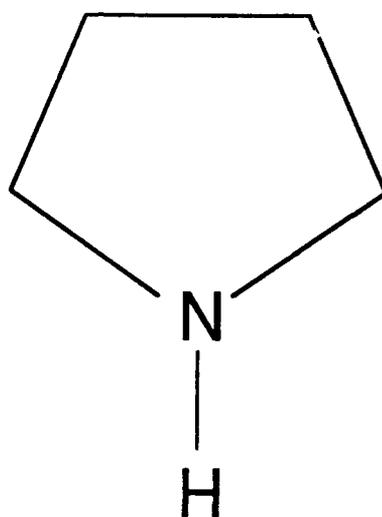
a. The splittings are measured relative to the strongest peak in each polyad.

b. This peak appears in a higher dilution spectrum (0.5%) not shown in Figure 7.

c. This is the first small peak just to the blue of the intense band at $13,123 \text{ cm}^{-1}$.



Pyrrole



Pyrrolidine

