REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

(2)

AD-A265 524

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
5/27/93	Technical Report

4. TITLE AND SUBTITLE

Vibrational overtone spectroscopy of cyclic amines: Pyridine and related compounds

5. FUNDING NUMBERS

N00014-88-K-4130
4131063

6. AUTHOR(S)

Joyce Overly and D.L. Snavely

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Bowling Green State University
Bowling Green, OH 43403

8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report
No. 13

DTIC
ELECTE
JUN 9 1993
S C D

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

This document has been approved for public release and sale: its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The vibrational overtone spectra of gaseous pyridine, 2,6-difluoropyridine, and pyrazole have been recorded using photoacoustic absorption spectroscopy. The pyridine overtone spectrum shows a progression of two peaks at each vibrational level. The widths of the overtone absorptions are compared to the known peak widths in the overtone spectrum of benzene. The spectrum has been analyzed in terms of a local mode model and, taken separately, the two peaks fit well to a Birge-Sponer plot. The v=4 overtone spectrum of 2,6-difluoropyridine is similar to that of pyridine but the peaks are shifted to higher energy. The presence of two peaks in this spectrum refutes a previous assignment of the liquid pyridine overtone spectrum in which the two peaks were attributed to structurally different C-H oscillators in the molecule. The overtone spectrum of pyrazole also shows two peaks.

93-12860

93

14. SUBJECT TERMS	15. NUMBER OF PAGES
Overtone spectroscopy, Pyridine	8
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT N00014-88-K-4130

R&T Code 4131063

Technical Report No. 13

Vibrational overtone spectroscopy of cyclic amines: Pyridine and related compounds

by

Joyce Overly and Deanne Snavely

Prepared for Publication

in

Journal of Chemical Physics

Center for Photochemical Sciences
Bowling Green State University, Bowling Green, Ohio 43403

May 27, 1993

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale: its distribution is unlimited.

DTIC QUALITY INSPECTED 2

Accesion For
NTIS CRA&I
DTIC TAB
Unannounced
Justification
By
Distribution /
Availability Codes
Dist | Avail and/or Special
A-1

Vibrational Overtone Spectroscopy of Pyridine and Related Compounds

Joyce A. Overly and Deanne Snavely
Center for Photochemical Sciences
Bowling Green State University
Bowling Green OH 43403

Abstract

The vibrational overtone spectra of gaseous pyridine, 2,6-difluoropyridine, and pyrazole have been recorded using photoacoustic absorption spectroscopy. The pyridine overtone spectrum shows a progression of two peaks at each vibrational level. The widths of the overtone absorptions are compared to the known peak widths in the overtone spectrum of benzene. The spectrum has been analyzed in terms of a local mode model and, taken separately, the two peaks fit well to a Birge-Sponer plot. The v=4 overtone spectrum of 2,6-difluoropyridine is similar to that of pyridine but the peaks are shifted to higher energy. The presence of two peaks in this spectrum refutes a previous assignment of the liquid pyridine overtone spectrum in which the two peaks were attributed to structurally different C-H oscillators in the molecule. The overtone spectrum of pyrazole also shows two peaks.

Introduction

The visible vibrational overtone spectrum of benzene was first recorded in 1979[1] and has been the subject of a great deal of work since then.[2] The explanation for the location and shape of the absorption bands is still incomplete. As an extension of earlier work in our laboratory on cyclic amines[3] we have recorded the vibrational overtone spectrum of pyridine and the related compounds 2,6-difluoropyridine and pyrazole. 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 infrared, near-infrared, and visible vibrational spectra (v = 1 to 6) of liquid pyridine and 2,6-lutidine[4] were recorded by Bini, et.al., using infrared and near-infrared spectrometers and laser thermal lensing techniques for the visible region (v = 5,6). They observed two peaks in the high overtone spectrum (v = 3 to 6) of pyridine. Their results are shown in Table I. These two peaks

were assigned by comparison to the spectrum of 2,6-lutidine. The higher energy peak at each vibrational level was present in the spectra of both compounds and therefore was assigned to the C(3)-H, C(4)-H, and C(5)-H stretches. The lower energy peak at each vibrational level was assigned to the C(2)-H and C(6)-H stretches since it 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 differ slightly some small splitting of the higher energy peak is to be expected. They were, however, unable to observe this splitting in their spectra.

Katayama, et. al.,[5] observed the fifth overtone spectra of the C-H stretch in pyridine, pyrazine, and related compounds using photoacoustic spectroscopy of liquid samples. They report two peaks in the v = 6 overtone spectra of pyridine, at 16300 cm^{-1} and 16570 cm^{-1}. They developed general rules for the vibrational overtone frequency shifts in molecules derived from benzene by substituting nitrogen atoms for the carbon atoms.

The overtone spectrum of pyridine up to v=4 was recorded by Mandal and Ray[6] using a conventional spectrophotometer and neat liquid or solution samples. Their results are tabulated in Table I. Only one peak in the v=4 overtone spectrum was reported. They fit their results to a Hamiltonian for a system of five coupled C-H oscillators with nearest-neighbor ring C-H bond interactions.

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 mesured with a Spex 1401 double monochromator with resolution of 1 cm^{-1}. Both

the motor control unit (Oriel model 18007) and the lock-in amplifier were interfaced and controlled with an IBM PC computer.

Results and Discussion

The vibrational overtone spectrum of gaseous pyridine is shown in Figure 1. The apparent 'noise' which can be seen at about 13800 and 16900 cm^{-1} in the spectrum is due to absorption by traces of water in the sample. Our results are compared to those of other researchers in Table I. A Birge-Sponer plot[3] of the pyridine data (see Figure 4) gives the mechanical frequencies of the higher- and lower-energy progressions, respectively, as 3100 cm^{-1} and 3148 cm^{-1}. The anharmonicities are -62 cm^{-1} and -64 cm^{-1}. The widths of the absorption bands are in the same range as those reported for benzene, which are 82, 111, and 95 cm^{-1} for the v=4,5,6 transitions, respectively.[2]

The vibrational overtone spectrum of gaseous 2,6-difluoropyridine is shown in Figure 2. The results are summarized in Table II. This spectrum also contains two peaks but they are blue-shifted by 171 and 173 cm^{-1}. There may also be a third peak but it is very weak and its exact position is difficult to determine. The presence of two peaks in the C-H stretch overtone of this compound refutes the assignment of the pyridine overtone spectrum made by Bini, et. al.[1] Based on their assignment the overtone spectrum of 2,6-difluoropyridine should contain only one peak. This is not the case and therefore our results point to a more complex explanation for the appearance multiple peaks.

The vibrational overtone spectrum of pyrazole is shown in Figure 3 and the results are listed in Table III. There appear to be two peaks in this spectrum also. Work on this compound is incomplete at this time. Additional work will be done to improve the signal-to-noise ratio of this spectrum as well as record the spectrum of the other overtones for both this compound and for 2,6-difluoropyridine.

Table I. Overtone Spectrum of Pyridine: Comparison of Results

v	This Work	Bini, et.al.[1]	Katayama, et.al.[2]	Mandal & Ray[3]
	energy(width)			
1		3004 3031 3056 3080		
2		5835 5867 5907 5956		5910 5988 6013 6154 6231
3		8651 8785		8842
4	11417±5(90) 11555±3(61)	11296 11474		11628
5	13941±3(110) 14125±3(110)		13810 14037	
6	16385±2(102) 16629±3(130)		16277 16548	16300 16570

Values are given in wavenumbers (cm^{-1}).

Table II. Vibrational Overtone Data for Pyrazole

energy	
13202±2	weak
13279±6	

Values are given in wavenumbers (cm^{-1}).

Table III. Vibrational Overtone Data for 2,6-Difluoropyridine

v	energy(width)	
4	11413±2(81)	very weak
	11590±8(124)	
	11726±4(65)	

Values are given in wavenumbers (cm^{-1}),

References

1. Bray, R.G.; Berry, M.J. *J. Chem. Phys*. **1979**, *71*, 4090.

2. For example see:
Reddy, K.V.; Heller, D.F.; Berry, M.J. *J. Chem. Phys*. **1982**, *76*, 2814.
Sibert, E.L.; Reinhardt, W.P.; Hynes, J.T. *J. Chem. Phys*. **1984**, *81*, 1115.
Page, R.H.; Shen, Y.R.; Lee, Y.T. *J. Chem. Phys*. **1988**, *88*, 4621.
Scotoni, M.; Boschetti, A.; Overhofer, N.; Bassi, D. *J. Chem. Phys*. **1991**, *94*, 971.
and references therein.

3. Snavely, D.L.; Blackburn, F.R.; Ranasinghe, Y. Walters, V.A.; Gonzalez del Riego, M. *J. Phys. Chem.* **1992**, *96;* 3599.

4. Bini, R.; Foggi, P.; Della Valle, R.G. *J. Phys. Chem.* **1991**, *95*, 3027.

5. Katayama, M.; Itaya, K.; Nasu, T.; Sakai, J. *J. Phys. Chem.* **1991**, *95*, 10592.

6. Mandal, D.K.; Ray, A.K. *Indian J. Chem.* **1991**, *30A*, 109.

7. Wong K.N.; Colson, S.D.; *J. Mol. Spectrosc.* **1984**, *104*, 129.

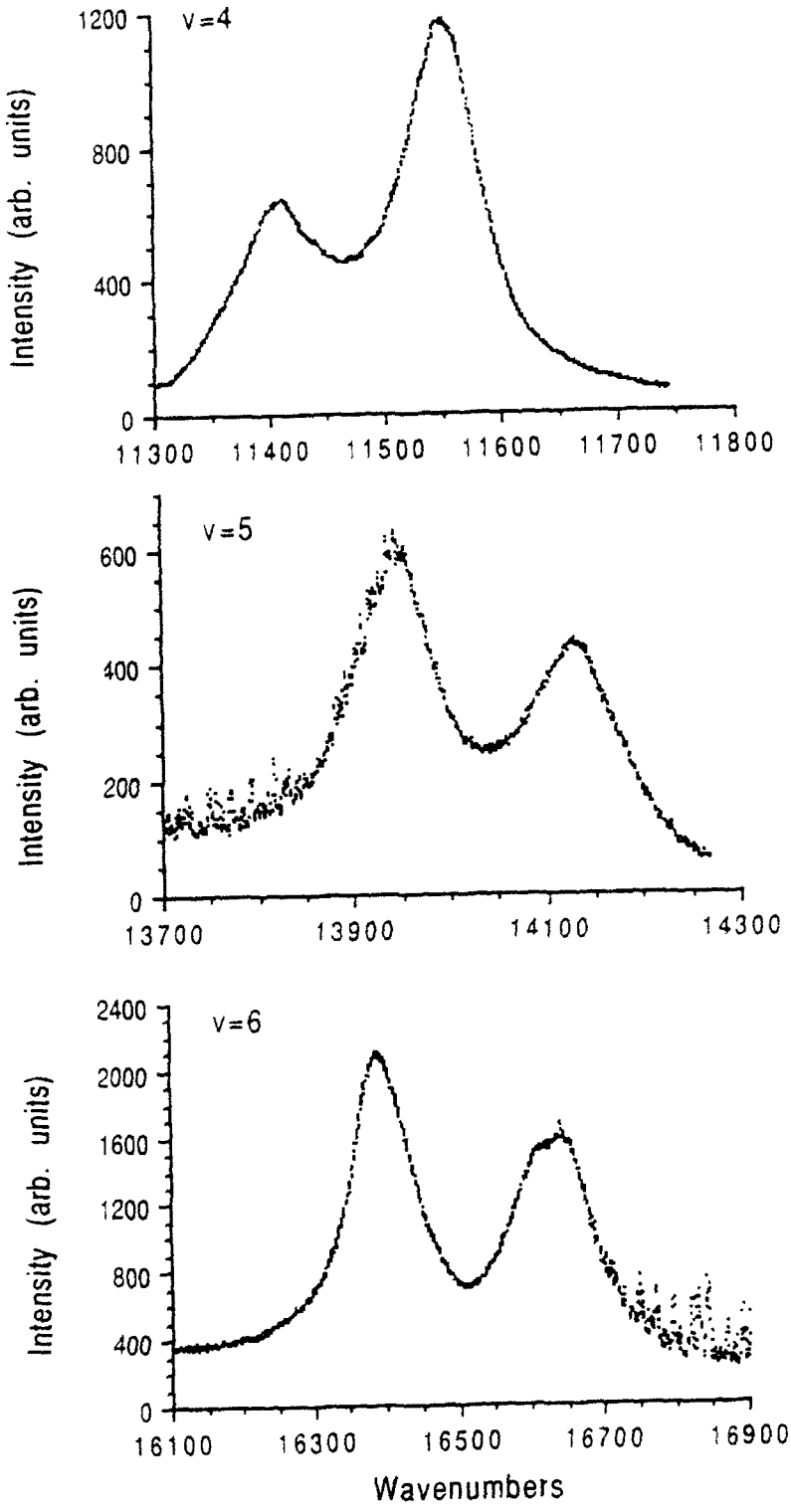

Figure 1. Vibrational overtone spectrum of gaseous pyridine.

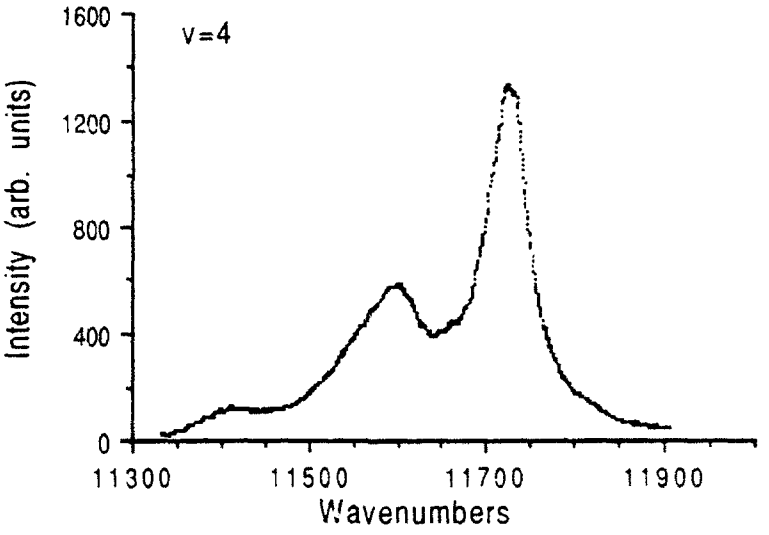

Figure 2. Vibratonal overtone spectrum of gaseous 2,6-difluoropyridine.

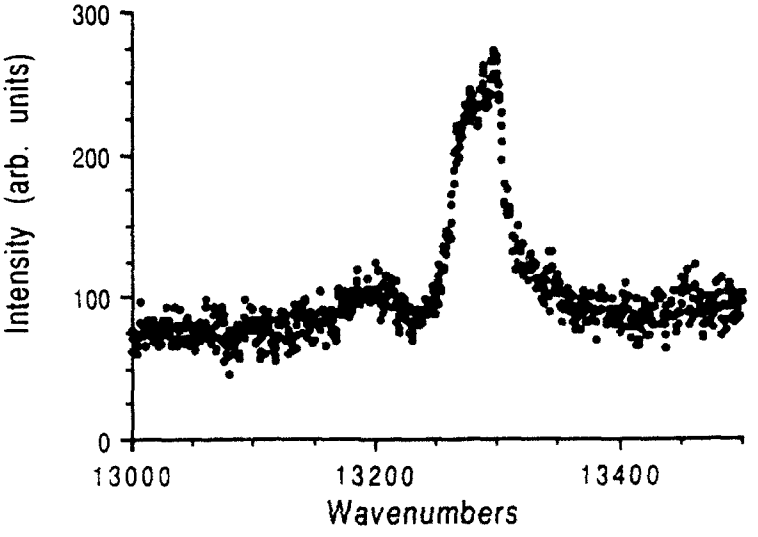

Figure 3. Vibrational overtone spectrum of gaseous pyrazole (72°C).

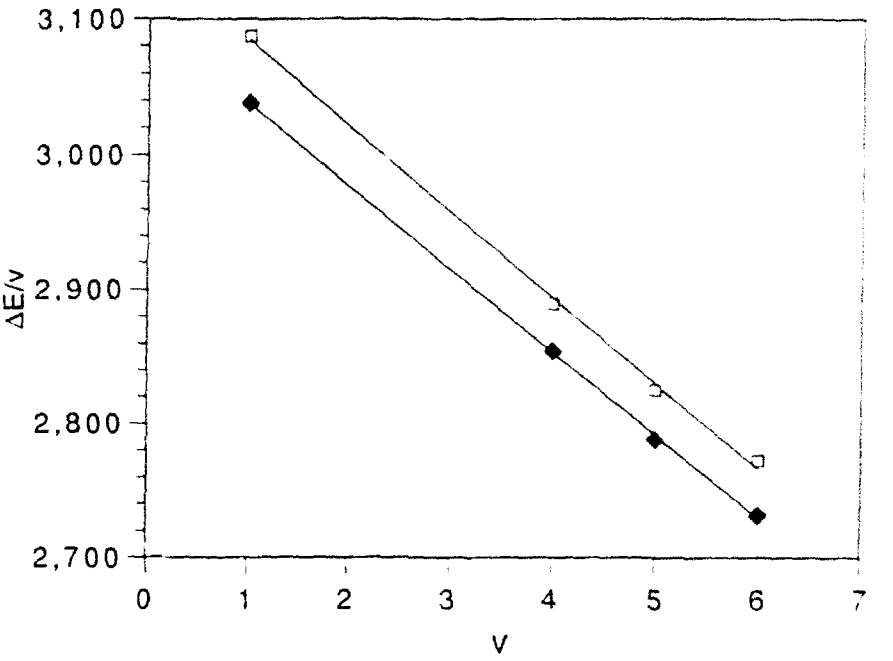

Figure 4. Birge-Sponer plot for pyridine. Data for the infrared transitions is taken from reference 7.