JOURNAL OF MOLECULAR SPECTROSCOPY **123**, 251–253 (1987)

The Infrared ν_5 Band (HNC Bend) of Protonated Hydrogen Cyanide, $HCNH^+$

The first spectroscopic observation of $HCNH^+$ was reported by Altman, Crofton, and Oka three years ago (*1, 2*). They used a difference frequency laser system to observe the ν_1 (NH stretch) and the ν_2 (CH stretch) bands in an A.C. glow discharge of H_2 and HCN. On the basis of this result, millimeter-wave rotational transitions of $HCNH^+$ were observed by Bogey, Demuynck, and Destombes (*3*) in the laboratory and by Ziurys and Turner (*4*) in interstellar space. More recently, Amano and Tanaka utilized the high ion concentration in a hollow cathode discharge cell to observe isotopic species and the hot bands $\nu_4 + \nu_1 \leftarrow \nu_4$ and $\nu_5 + \nu_1 \leftarrow \nu_5$ and thus determined rotational constants in these states (*5*). Tanaka, Kawaguchi, and Hirota used a diode laser to study the ν_4 fundamental (HCN bend) in the 12-μm region (*6*). In this paper we report our observation of the ν_5 fundamental band (HNC bend) using a diode-laser system.

The apparatus is similar to that used for the study of the ν_2 band of H_3O^+ (*7*). $HCNH^+$ was produced in

TABLE I

Observed Wavenumbers of the ν_5 Fundamental Band of $HCNH^+$ (cm^{-1})

Transition	Wavenumber[a]
P(23)	587.259 (2)
P(22)	589.774 (-2)
P(16)	604.850 (-1)
P(13)	612.361 (-2)
P(12)	614.860 (-3)
P(8)	624.846 (6)
P(7)	627.328 (-1)
Q(2)	644.711 (0)
Q(3)	644.735 (-1)
Q(4)	644.769 (-1)
Q(5)	644.811 (-1)
Q(6)	644.862 (-1)
Q(7)	644.924 (3)
Q(8)	644.988 (-1)
Q(9)	645.064 (0)
Q(11)	645.243 (2)
Q(12)	645.343 (1)
Q(13)	645.450 (-1)
Q(26)	647.627 (-2)
Q(27)	647.854 (0)
Q(28)	648.089 (1)
R(7)	664.364 (-3)
R(10)	671.702 (1)
R(11)	674.140 (0)
R(12)	676.578 (3)
R(14)	681.439 (1)

[a] Values in parentheses are (observed − calculated) × 10^3.

0022-2852/87 $3.00

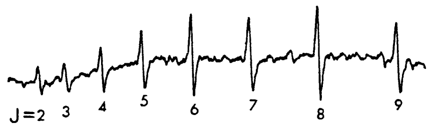

FIG. 1. The first eight Q-branch lines of the ν_5 fundamental band of $HCNH^+$. A time constant of 3 sec was used.

a water-cooled A.C. discharge cell (1.2 cm i.d., 1 m in length) using a mixture of HCN and H_2 (~1:5) with a total pressure of 1.5 to 2 Torr, a voltage of ~4 kV, and a current of ~100 mA. The velocity modulation technique of Gudeman, Saykally, and others (*8*) was used to discriminate the ion signals from the stronger neutral signals and to increase the sensitivity of detection. The signal-to-noise ratio of absorption lines was considerably lower (by a factor of ~5) in an air-cooled cell. Three mesa-stripe geometry diodes were used to cover the region from 500 to 700 cm^{-1}, where the ν_5 band was theoretically predicted (*9–11*).

A total of 26 transitions were observed. Figure 1 shows the observed spectral lines of the first eight Q branch lines ($Q(2)$–$Q(9)$). The measured wavenumbers of the lines are listed in Table I. The spectrum was fitted using least-squares method to the energy expression for the excited state:

$$E' = B'[J(J+1)-1] - D'[J(J+1)-1]^2 \pm \tfrac{1}{2}[q + q_J J(J+1)]J(J+1),$$

where q and $q_J J(J+1)$ are the ℓ-doubling constant and its rotational dependence, respectively. The ground state rotational constants B'' and D'' were fixed at the values given by Bogey *et al.* (*3*). The determined molecular constants are listed in Table II together with the values obtained by Amano and Tanaka (*5*). The theoretical predictions by Lee and Schaefer (*9*), DeFrees and McLean (*10*), and Botschwina (*11*) are given in the footnote of the table. The observed value of the ℓ-doubling constant is very close to the approximated value (*12*) $q \sim 2.6B_e^2/\omega_5$.

TABLE II

Molecular Constants of $HCNH^+$ ν_5 (in cm^{-1})[a]

	This Result[b]	Ref 5
ν_0	645.9233(88)[c]	
B'	1.237 507(10)	1.237 527(15)
D'	$1.619(15)\times10^{-6}$	$1.644(67)\times10^{-6}$
q	0.005 492(11)	0.005 480(29)
q_j	$-2.7(20)\times10^{-8}$	$1.1(13)\times10^{-7}$

[a] Quoted errors are 1σ.
[b] Fitting is done with B'' and D'' fixed at 1.236046 and 1.6068×10^{-6} cm^{-1}, respectively.
[c] Theoretical prediction of ν_0 (HNC bend) (cm^{-1}): Lee *et al.* (*9*), 700; DeFrees and McLean (*10*), 699; Botschwina (*11*), 620.

ACKNOWLEDGMENTS

This work was supported by the NSF grant PHS-84-08316 and was also partially supported by the donors of the Petroleum Research Fund administered by the American Chemical Society. One of us (C.E.B.) gratefully acknowledges the travel grant for this study by Deutsche Forschungsgemeinschaft.

REFERENCES

1. R. S. ALTMAN, M. W. CROFTON, AND T. OKA, *J. Chem. Phys.* **80**, 3911 (1984).
2. R. S. ALTMAN, M. W. CROFTON, AND T. OKA, *J. Chem. Phys.* **81**, 4255 (1984).
3. M. BOGEY, C. DEMUYNCK, AND J. L. DESTOMBES, *J. Chem. Phys.* **83**, 3703 (1985).
4. L. M. ZIURYS AND B. E. TURNER, *Astrophys. J.* **302**, L31 (1986).
5. T. AMANO AND K. TANAKA, *J. Mol. Spectrosc.* **116**, 112 (1986).
6. K. TANAKA, K. KAWAGUCHI, AND E. HIROTA, *J. Mol. Spectrosc.* **117**, 408 (1986).
7. D. J. LIU, N. N. HAESE, AND T. OKA, *J. Chem. Phys.* **82**, 5368 (1985).
8. C. S. GUDEMAN, M. H. BEGEMANN, J. PFAFF, AND R. J. SAYKALLY, *Phys. Rev. Lett.* **50**, 727 (1983).
9. T. J. LEE AND H. F. SCHAEFER III, *J. Chem. Phys.* **80**, 2977 (1984).
10. D. J. DEFREES AND A. D. MCLEAN, *J. Chem. Phys.* **82**, 333 (1985).
11. P. BOTSCHWINA, *Chem. Phys. Lett.* **124**, 382 (1986).
12. C. H. TOWNES AND A. L. SCHAWLOW, "Microwave Spectroscopy" McGraw-Hill (1955).

WING-CHEUNG HO
CORNELIS E. BLOM[1]
DI-JIA LIU
TAKESHI OKA

Department of Chemistry and
Department of Astronomy and Astrophysics
The University of Chicago
Chicago, Illinois 60637
Received October 23, 1986

---

[1] Permanent address: Physikalisch-Chemisches Institute, Justus-Liebig-Universitat Giessen, D-6300 Giessen, West Germany.