

High resolution infrared spectroscopy of the ν_1 (NH stretch) and ν_2 (CH stretch) bands of HCNH^+

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The infrared spectrum of the ν_1 band (NH stretch) and the ν_2 band (CH stretch) of protonated hydrogen cyanide HCNH^+ has been observed based on recent theoretical predictions. This is the first observed spectrum of this ion in any wavelength region. From a least-squares analysis of the rovibrational bands, the following spectroscopic constants have been obtained (in cm^{-1}):

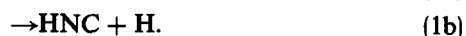
	ν_1 (NH stretch)	ν_2 (CH stretch)
ν_0	3482.844 1(10)	3187.863 8(4)
B_1	1.228 633(39)	1.228 494(19)
B_0	1.236 024(37)	1.236 067(18)
D_1	$1.574(43) \times 10^{-6}$	$1.610(22) \times 10^{-6}$
D_0	$1.596(42) \times 10^{-6}$	$1.620(21) \times 10^{-6}$

It is hoped that the rotational constants determined in this paper will lead to the identification of the microwave spectrum of this molecule in interstellar space.

I. INTRODUCTION

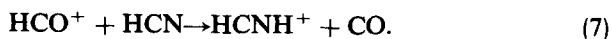
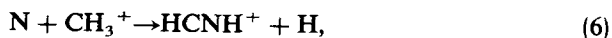
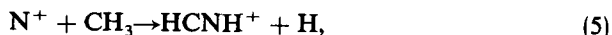
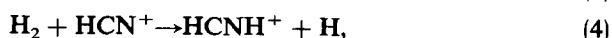
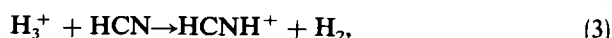
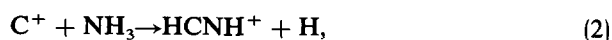
The protonated hydrogen cyanide ion, HCNH^+ , is a well bound system owing to the high proton affinity (7.5 eV) of HCN, and is observed prominently in the mass spectrum of HCN at relatively high pressure.¹⁻³ However, its spectrum had not been reported in any wavelength region until our recent observation⁴ of the infrared spectrum of the ν_2 (CH stretch) band. In this paper we present the follow-up of our work and report our observation in detail including that of the ν_1 (NH stretch) band.

The HCNH^+ molecular ion has drawn much attention in the last ten years because of its importance in the chemistry of interstellar space.⁵⁻¹⁵ In the scheme of ion-molecule reactions,^{5,6} HCNH^+ is a precursor of HCN and HNC both of which have been observed abundantly in interstellar space.^{16,17} These neutral species are generated by the dissociative recombination of HCNH^+ ,⁵⁻¹⁰



Herbst predicted from a statistical phase space theory of chemical reactions that the branching ratio of the reactions in Eq. (1) is 1. The carefully observed ratios of $[\text{HCN}]/[\text{HNC}]$ in various molecular clouds reported by astronomers^{18,19} show a large variation of the ratio demonstrating the complexity of the interstellar chemistry.

In interstellar space the HCNH^+ ion can be formed via the following ion-molecule reactions⁵⁻¹¹:



Of these, it is believed that Eq. (2) is the most prevalent in the formation of HCNH^+ .³ In this case the protonated hydrogen cyanide is likely to be produced initially in the formaldehyde-like structure $\text{H}_2\text{N} = \text{C}^+$ as suggested by Brown.⁹ Schaefer and his colleagues^{8,11,12} studied the stability of $\text{H}_2\text{N} = \text{C}^+$ as well as that of the other formaldehyde-like structure $\text{H}_2\text{C} = \text{N}^+$. Their conclusions, contrary to chemical intuition, imply that the latter is unstable but the former is a well bound system though 2 eV higher in energy than the most stable linear structure, HCNH^+ , which is isoelectronic to acetylene. Schaefer argued¹² that since the reaction (2) is highly exothermic, the $\text{H}_2\text{N} = \text{C}^+$ is produced with a large internal energy which enables the proton to cross the barrier of isomerization producing the linear HCNH^+ ion.

The molecular structure as well as the vibrational frequencies of HCNH^+ have been an active pursuit of theoreticians for the last ten years.^{11,14,20-25} The results are summarized later in Table IV. As in many previous cases, it is from these calculations that the spectroscopic search for HCNH^+ was initiated. In particular, the three theoretical predictions of vibrational frequencies obtained from Schaefer,²² DeFrees,²⁴ and Botschwina²⁵ were instrumental in the success of our work.

II. EXPERIMENTAL

The experimental apparatus has been described previously.^{4,26} Briefly, the continuously frequency tunable ($2300\text{--}4500 \text{ cm}^{-1}$) infrared radiation with a spectral purity of 2 MHz is generated by using the difference frequency technique which was developed by Pine.²⁹ The output of a ring dye laser (Coherent Associates model CR 699-21) is mixed with the output of a single mode Ar^+ laser in a temperature controlled LiNbO_3 crystal. Since the infrared power is proportional to the power of the dye laser (as well as the Ar^+ laser), the utilization of the ring dye laser has increased the infrared power significantly over what was obtained be-

TABLE I. Observed transition frequencies for HCNH^+ (in cm^{-1}) ν_1 (NH stretch).^a

R (1)	3487.743(0)	P (6)	3467.795(4)
R (2)	3490.017(- 1)	P (7)	3465.231(- 1)
R (3)	3492.584(0)	P (8)	3462.660(3)
R (4)	3494.976(- 6)	P (9)	3460.067(- 1)
R (5)	3497.363(- 2)	P (10)	3457.471(6)
R (6)	3499.735(3)	P (11)	3454.852(5)
R (7)	3502.084(- 1)	P (12)	3452.213(- 2)
R (8)	3504.423(0)	P (13)	3449.566(- 3)
R (9)	3506.747(2)	P (14)	3446.906(- 2)
R (10)	3509.054(1)	P (15)	3444.232(- 2)
R (11)	3511.342(- 3)	P (16)	3441.544(- 1)
R (12)	3513.623(1)	P (17)	3438.840(- 2)
R (14)	3518.129(- 2)	P (18)	3436.126(1)
R (16)	3522.581(3)	P (20)	3430.647(- 2)
R (18)	3526.965(1)	P (22)	3425.116(- 1)
R (20)	3531.293(5)	P (24)	3419.531(1)
R (22)	3535.543(- 7)	P (26)	3413.889(1)
R (23)	3537.660(2)		
R (25)	3541.827(0)		

^a Values in parentheses are (observed - calculated) $\times 10^3$.

fore.³⁰ An ac glow discharge was employed so as to make use of the powerful, high sensitivity velocity modulation method developed by Gudeman *et al.*³¹ The velocity modulation method also gives discrimination of ion transitions from neutral transitions. This was extremely useful in this study as transitions due to neutral species such as HCN, HNC, along with other possible reaction products appear in this wavelength region. The voltage of the discharge was 7.5 kV p-p with a current of 100 mA rms. This was applied to an 80 cm long water-cooled discharge cell with an inner diameter of 0.7 cm. To increase the effective path length of the radiation through the discharge cell, the infrared beam is cycled through the cell two times in the same direction so that the signals are still velocity modulated. The gas mixture used was H_2 and HCN in the ratio of 10 to 1 with a total pressure of 2 to 3 Torr. The signal to noise ratio of a typical transition was not very sensitive to the mixing ratio of the two gases. Halving or doubling did not cause appreciable degradation

TABLE II. Observed transition frequencies for HCNH^+ (in cm^{-1}) ν_2 (CH stretch).^a

R (0)	3190.321(0)	P (1)	3185.392(0)
R (1)	3192.763(0)	P (2)	3182.906(2)
R (2)	3195.189(0)	P (3)	3180.401(- 1)
R (3)	3197.601(1)	P (5)	3175.353(1)
R (4)	3199.995(- 1)	P (7)	3170.242(- 1)
R (5)	3202.378(1)	P (8)	3167.667(1)
R (6)	3204.741(- 1)	P (9)	3165.074(0)
R (7)	3207.091(- 1)	P (10)	3162.467(0)
R (9)	3211.746(0)	P (11)	3159.845(- 1)
R (11)	3216.338(1)	P (12)	3157.211(1)
R (12)	3218.611(2)	P (13)	3154.559(0)
R (13)	3220.865(- 1)	P (14)	3151.894(0)
R (14)	3223.106(- 1)	P (16)	3146.520(1)
R (15)	3225.330(- 2)	P (18)	3141.088(1)
R (16)	3227.541(0)	P (20)	3135.594(- 3)
R (20)	3236.225(3)	P (22)	3130.049(0)
R (22)	3240.469(2)	P (24)	3124.445(0)
R (24)	3244.645(- 3)	P (26)	3118.785(1)

^a Values in parentheses are (observed - calculated) $\times 10^3$.

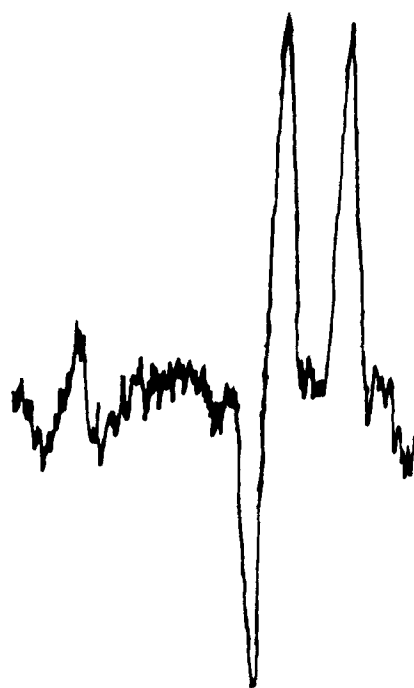


FIG. 1. A typical absorption line of HCNH^+ . The line with a derivative shape is the P(16) line of the ν_2 (CH stretch) band at 3146.520 cm^{-1} . The neighboring line with a nonderivative shape results from an incompletely suppressed absorption of some neutral molecule. The width of scanning is $\sim 0.2 \text{ cm}^{-1}$. A time constant of 1 s was used.

of the signal in sharp contrast to the case of HeH^+ .³² Transition frequencies were measured from simultaneously recorded reference gas lines which included C_2H_4 , N_2O , and NH_3 .

It should also be noted that other ion absorption lines were observed that were not part of the HCNH^+ vibration-rotation spectrum. In some cases these were unidentified but most were due to NH_4^+ ²⁶⁻²⁸ and were at least as strong as those of HCNH^+ .

III. OBSERVED RESULTS

The observed transition frequencies for the ν_1 (NH stretch) band and the ν_2 (CH stretch) band are listed in Tables I and II, respectively. Although the difference frequency laser is continuously tunable, it can be seen that some transitions are missing. For example, R (1) through P (5) of the ν_1 band were not observed due to the fact that not only are the low J spectral intensities dropping off, but there is a sharp decrease in infrared power in this immediate region. In certain other instances overlapping neutral or ion transitions precluded accurate measurement. A typical relatively strong

TABLE III. Spectroscopic constants of HCNH^+ (in cm^{-1}).^a

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ν_0	3482.844 1(10)	3187.863 8(4)
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^a Quoted errors are 1σ .

TABLE IV. Theoretical predictions for HCNH^+ .

	Exptl.	a	b	c	d	e
$\nu_0(\text{NH}) \text{ cm}^{-1}$	3482.844	3474	3435	3505		
$\nu_0(\text{CH}) \text{ cm}^{-1}$	3187.864	3201	3173	3202		
B_0 (GHz)	37.056	36.7	37.0	37.1	37.0	37.3
$\nu_{J=1\leftarrow 0}$ (GHz)	74.113	73.4	73.9	74.1	74.1	74.6
μ (D)		0.39	0.31		0.31	0.23

^a T. J. Lee and H. F. Schaeffer, *J. Chem. Phys.* **80**, 2977 (1984).

^b D. J. DeFrees, J. S. Binkley, and A. D. McLean (preprint) and D. J. DeFrees (private communication).

^c P. Botschwina (private communication).

^d P. S. Dardi and C. E. Dykstra, *Astrophys. J. Lett.* **240**, L171 (1980).

^e N. N. Haese, Ph.D. thesis, University of Wisconsin, 1981.

signal is shown in Fig. 1. The transition frequencies have been fit (by the method of least squares) to yield the spectroscopic constants of each band. These are given in Table III.

The assignment was first based on the observation of $R(0)$ and $P(1)$ and the lack of any transitions at the band origin for the ν_2 band. This was possible only after many long time-constant (10 s) scans in the low J region. The assignment was confirmed when the ν_1 band was measured and the method of "combination differences" was applied. The very similar α values for the ν_1 and ν_2 vibrational bands made it necessary to observe many high J transitions to arrive at a definite conclusion.

From the ground state rotational constants, the $J = 1\leftarrow 0$ microwave transition ($\nu_0 = 2B_0 - 4D_0$) can be calculated and is $74\,112.5 \pm 3.2$ MHz. The quoted error here is 3σ .

IV. DISCUSSION

The theoretical values of the vibrational band origins and the rotational constant (in the ground state) can now be compared to the experimental ones determined in this work. This is done in Table IV. It is evident from examination of this table that the quality of the *ab initio* calculation is extremely high. In some cases the band origins are predicted to within 10 cm^{-1} . The rotational constants that have been calculated are all quite close (the average is 74.0 GHz). Hopefully the precise value of the rotational constant determined here (and therefore the $J = 1\leftarrow 0$ transition frequency) will lead to the observation of this microwave transition in the laboratory and in space despite the small calculated dipole moment (see Table IV). With respect to HCO^+ , the HCNH^+ transition will be weaker by a factor of $(\mu^{\text{HCO}^+} / \mu^{\text{HCNH}^+})^2$ which is approximately 100–300 (for $\mu^{\text{HCO}^+} = 4D$).³³

The intensities of the two bands have also been calculated in two of the theoretical studies.^{22,25} The relative ordering

of the intensities for the ν_1 and ν_2 bands are different in each calculation. Although a quantitative assessment is difficult (because the bands occur at different frequencies) it does appear that the ν_2 band is slightly stronger than the ν_1 band as predicted by Botschwina.²⁵

Table V lists and compares the NH stretching frequencies of the molecular ions where this has been measured. Owing to the different bonding interactions of HCNH^+ , NH_4^+ , and HN_2^+ , the variation in stretching frequencies is about 150 cm^{-1} . Also listed in Table V are the proton stretching frequencies of the neutral precursors for HCNH^+ and NH_4^+ . In all cases the stretching frequency is seen to go down for the protonated species. In HCNH^+ , the ν_1 band and the ν_2 band are each 5% less than the proton stretch in HNC and HCN, respectively. In this case the bonds seem to be weakened equivalently.

The utility of high quality theoretical calculations should once more be stressed. The predictions for the small molecular ions have not only been accurate, but are partially responsible for the rate at which the field of infrared ion spectroscopy is advancing. Future challenges to the spectroscopists and the theoreticians may be: HCO_2^+ , CH_5^+ , C_2H_3^+ , and C_2H_5^+ to name a few.

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TABLE V. Stretching frequencies of several protonated molecular ions (in cm^{-1}).

HCNH^+ (ν_2 CH)	3188	HCN	(CH)	3369
HCNH^+ (ν_1 NH)	3483	HNC	(NH)	3653
NH_4^+ (ν_3 NH)	3343	NH_3	(ν_3)	3414
HN_2^+ (ν_1 NH)	3234			

¹T. W. Martin and C. E. Melton, *J. Chem. Phys.* **22**, 700 (1960).

²M. Inoue and M. Cottin, *Advances in Mass Spectrometry* edited by S. L. Fox (Academic, New York, 1966), Vol. 3, p. 339.

³W. T. Huntress, Jr., J. D. Baldeschwieler, and C. Ponnampereuma, *Nature* **223**, 468 (1969).

⁴R. S. Altman, M. W. Crofton, and T. Oka, *J. Chem. Phys.* **80**, 3911 (1984).

⁵E. Herbst and W. Klemperer, *Astrophys. J.* **185**, 505 (1973).

⁶W. D. Watson, *Astrophys. J. Lett.* **183**, L83 (1973).

⁷W. D. Watson, *Astrophys. J. Lett.* **188**, L35 (1974).

⁸P. K. Pearson and H. F. Schaefer III, *Astrophys. J.* **192**, 33 (1974).

⁹R. D. Brown, *Nature* **270**, 39 (1977).

¹⁰E. Herbst, *Astrophys. J.* **222**, 508 (1978).

¹¹M. P. Conrad and H. F. Schaefer III, *Nature* **274**, 456 (1979).

¹²H. F. Schaefer IV, *Acc. Chem. Res.* **12**, 288 (1979).

- ¹³S. S. Prasad and W. T. Huntress Jr., *Astrophys. J.* **239**, 151 (1980).
- ¹⁴T. L. Allen, J. D. Goddard, and H. F. Schaefer III, *J. Chem. Phys.* **73**, 3255 (1980).
- ¹⁵R. D. Brown and E. Rice, *Philos. Trans. R. Soc. London Ser. A* **303**, 523 (1981).
- ¹⁶L. E. Snyder and D. Buhl, *Astrophys. J. Lett.* **163**, L47 (1971).
- ¹⁷L. E. Snyder and D. Buhl, *Bull. A.A.A.S.* **3**, 388 (1971).
- ¹⁸A. Wooten, N. J. Evans, II, R. Snell, and P. Vanden Bout, *Astrophys. J. Lett.* **255**, L143 (1978).
- ¹⁹P. F. Goldsmith, W. D. Langer, J. Elder, W. Irvine, and E. Kolberg, *Astrophys. J.* **249**, 524 (1981).
- ²⁰P. S. Dardi and C. E. Dykstra, *Astrophys. J. Lett.* **240**, L171 (1980).
- ²¹D. J. DeFrees, G. H. Low, and A. D. McLean, *Astrophys. J.* **257**, 376 (1982).
- ²²T. J. Lee and H. F. Schaefer III, *J. Chem. Phys.* **80**, 2977 (1984).
- ²³D. J. DeFrees, J. S. Binkley, and A. D. McLean, *J. Chem. Phys.* (submitted).
- ²⁴D. J. DeFrees (private communication).
- ²⁵P. Botschwina (private communication).
- ²⁶M. W. Crofton and T. Oka, *J. Chem. Phys.* **79**, 3157 (1983).
- ²⁷E. Schäfer, M. H. Begemann, C. S. Gudeman, and R. J. Saykally, *J. Chem. Phys.* **79**, 3159 (1983).
- ²⁸E. Schäfer, R. J. Saykally, and A. G. Robiette, *J. Chem. Phys.* **80**, 3969 (1984).
- ²⁹A. S. Pine, *J. Opt. Soc. Am.* **64**, 1683 (1974).
- ³⁰T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980).
- ³¹C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, *Phys. Rev. Lett.* **50**, 727 (1983).
- ³²M. W. Crofton, R. S. Altman, N. N. Haese, and T. Oka (to be published).
- ³³N. N. Haese and R. C. Woods, *Chem. Phys. Lett.* **61**, 396 (1979).