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## COMMUNICATIONS

## Observation of the infrared $\nu_2$ band (CH stretch) of protonated hydrogen cyanide, $\text{HCNH}^+$

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In our recent paper<sup>1</sup> on the infrared spectrum of the  $\nu_3$  band of  $\text{NH}_4^+$ , we called for theoretical predictions of the vibrational frequencies of other ions, in particular, protonated hydrogen cyanide  $\text{H}_2\text{CN}^+$ , protonated methane ( $\text{CH}_5^+$ ), and protonated acetylene ( $\text{H}_3\text{C}_2^+$ ). Three theorists (P. Botschwina, D. De Frees, and H. F. Schaeffer) have responded to this call and have provided us with predictions of the vibrational frequencies of the  $\text{HCNH}^+$  ion. In this Communication, we report the first successful observation of the infrared vibration-rotation spectrum of the fundamental  $\nu_2$  band (CH stretch) of this molecular ion. The search and discovery of this spectrum was greatly facilitated by the accurate theoretical predictions cited above. To the best of our knowledge, there has previously been no spectroscopic observation of this molecular ion in any wavelength region.

The  $\text{HCNH}^+$  ion is a well bound system owing to the high proton affinity (7.5 eV) of HCN.<sup>2</sup> It is isoelectronic to acetylene and therefore a linear structure is predicted.<sup>3</sup> Formaldehyde structures  $\text{H}_2\text{CN}^+$  and  $\text{H}_2\text{NC}^+$ , which are higher in energy (by 3.1 and 2.0 eV, respectively), have also been considered.<sup>3,4</sup> This molecular ion is particularly important in the chemistry of interstellar space. It is the precursor of HCN and HNC<sup>5,6</sup> which have been found to exist abundantly in interstellar space and it also is considered in detailed studies of interstellar chemistry.<sup>7-9</sup> It is hoped that the rotational constants determined in this paper will lead to the identification of the microwave spectrum of this molecular ion in interstellar space in spite of the predicted small dipole moment.<sup>10,11</sup>

The apparatus used is similar to that used for  $\text{NH}_4^+$ . A difference frequency laser system developed by Pine<sup>12</sup> gives frequency tunable, high resolution, infrared radiation, and the ac Doppler modulation method developed by Gudeman *et al.*<sup>13</sup> gives the high sensitivity and discrimination of ion spectral lines from the much stronger neutral lines. A mixture of  $\text{H}_2$  and HCN(10:1) was used for the ac discharge at a pressure of 2–3 Torr. A discharge voltage of 7.5 kV *p-p* and

current of 100 mA rms was applied to an 80 cm long water-cooled absorption cell with an i.d. of 0.7 cm. The  $\nu_2$  band (CH stretch) was chosen for the search because the range of the estimated vibrational frequencies (3201,<sup>11</sup> 3202,<sup>14</sup> 3172  $\text{cm}^{-1}$ <sup>15</sup>) was much smaller than that of the  $\nu_1$  band (NH stretch) although the intensity of the former is predicted to be approximately 30% weaker than the latter.<sup>11</sup>

The observed spectral lines which fit a linear molecule are listed in Table I. The stronger lines ( $J \sim 10$ ) had signal-to-noise ratios of up to 10 with a 3 s time constant. The transitions missing from Table I were ones obscured by strong neutral absorptions. The assignment of rotational quantum numbers is based on the absence of the "zero line" at the band origin  $\nu_0$ . The very low intensities of the low  $J$  lines combined with the interfering neutral absorption lines near the band origin complicated this determination. The present

TABLE I. Observed frequencies of the  $\nu_2$  band (CH stretch) of  $\text{HCNH}^+$  (in  $\text{cm}^{-1}$ ).

Transition	Frequency <sup>a</sup>	Transition	Frequency
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(0)		
R (15)	3225.330(– 2)		
R (16)	3227.542(1)		

<sup>a</sup> Observed minus calculated frequencies for the last digits are given in parentheses.

TABLE II. Vibration-rotation constants of HCNH<sup>+</sup>.

Observed constants (cm <sup>-1</sup> ) <sup>a</sup>	
$\nu_0 = 3187.863\ 82(39)$	
$B' = 1.228\ 493(30)$	$B'' = 1.236\ 067(32)$
$D' = 1.632 \times 10^{-6}(92)$	$D'' = 1.640 \times 10^{-6}(115)$
Predicted $\nu_0 = 3201,$ <sup>b</sup> $3202,$ <sup>c</sup> $3174$ <sup>d</sup>	

<sup>a</sup> Value in parentheses is  $1\sigma$ . <sup>c</sup> Reference 14.<sup>b</sup> Reference 11.<sup>d</sup> Reference 15.

assignment was reached after scanning the region many times with a long time constant. We are attempting to confirm this by measuring the  $\nu_1$  band (NH stretch) of this molecular ion. The frequencies of the absorption lines were measured using the standard spectrum of ethylene compiled by Pine.<sup>16</sup>

The vibration-rotation constants determined from the least squares fit of the data are summarized in Table II. The agreement between the observed band origin and the predicted vibrational frequencies is excellent. While the determination of the detailed molecular structure has to await observation of other isotopic species, the obtained rotational constant  $1.236\ 067 \pm 0.000\ 10\ \text{cm}^{-1}$  is consistent with the theoretical values reported.<sup>11,14,15,17,18</sup> Our results give the frequency of  $74\ 112.5 \pm 6\ \text{MHz}$  for the  $J = 1 \rightarrow 0$  microwave transition where the quoted error is three times the standard deviation of fitting.

The excellent agreement between the theoretical and experimental constants shows the quality and value of *ab initio* calculations now possible. Further predictions of vi-

brational frequencies and intensities of protonated CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>CO, CO<sub>2</sub>, H<sub>2</sub>S, PH<sub>3</sub>, etc. are eagerly awaited.

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*Note added in proof:* Since submitting this Communication we have completed studying the  $\nu_1$  (NH stretch) band of this molecular ion. This work confirms our assignment for the  $\nu_2$  (CH stretch) band and gives a band origin for  $\nu_1$  of  $3482.844\ \text{cm}^{-1}$  which is again in excellent accord with the theoretical predictions. This will appear shortly as a full paper in this journal.

<sup>1</sup>M. W. Crofton and T. Oka, *J. Chem. Phys.* **79**, 3157 (1983).<sup>2</sup>R. Walden and J. L. Franklin, *Int. J. Mass Spectrom. Ion Phys.* **36**, 85 (1980).<sup>3</sup>P. K. Pearson and H. F. Schaeffer III, *Astrophys. J.* **192**, 33 (1974).<sup>4</sup>M. P. Conrad and H. F. Schaeffer III, *Nature* **274**, 456 (1978).<sup>5</sup>E. Herbst and W. Klemperer, *Astrophys. J.* **185**, 505 (1973).<sup>6</sup>W. D. Watson, *Astrophys. J. Lett.* **183**, L17 (1973).<sup>7</sup>E. Herbst, *Astrophys. J.* **222**, 508 (1978).<sup>8</sup>W. T. Huntress, Jr. and G. F. Mitchell, *Astrophys. J.* **231**, 456 (1978).<sup>9</sup>S. S. Prasad and W. T. Huntress, Jr., *Astrophys. J. Suppl. Ser.* **43**, 1 (1980).<sup>10</sup>N. N. Haese and R. C. Woods, *Chem. Phys. Lett.* **61**, 396 (1979).<sup>11</sup>T. J. Lee and H. F. Schaeffer III (preprint).<sup>12</sup>A. S. Pine, *J. Opt. Soc. Am.* **64**, 1683 (1974).<sup>13</sup>C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, *Phys. Rev. Lett.* **50**, 727 (1983).<sup>14</sup>P. Botschwina (private communication).<sup>15</sup>D. De Frees (private communication).<sup>16</sup>A. S. Pine, M. I. T. Lincoln Laboratory Report No. NSF/ASRA/DAR-78-24562 (1980).<sup>17</sup>N. N. Haese, Ph. D. Thesis, University of Wisconsin, 1981.<sup>18</sup>P. S. Dardi and C. E. Dykstra, *Astrophys. J.* **240**, L171 (1980).