The Infrared $\nu_5$ 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 $\nu_1$ (NH stretch) and the $\nu_2$ (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, Demuyck, 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 $\nu_2 + \nu_1 \leftrightarrow \nu_4$ and $\nu_3 + \nu_1 \leftrightarrow \nu_5$ and thus determined rotational constants in these states (5). Tanaka, Kawaguchi, and Hirota used a diode laser to study the $\nu_4$ fundamental (HCN bend) in the 12-$\mu$m region (6). In this paper we report our observation of the $\nu_5$ fundamental band (HNC bend) using a diode-laser system.

The apparatus is similar to that used for the study of the $\nu_2$ band of H$_2$O$^+$ (7). HCNH$^+$ was produced in

\begin{table}
\centering
\caption{Observed Wavenumbers of the $\nu_5$ Fundamental Band of HCNH$^+$ (cm$^{-1}$)}
\begin{tabular}{ll}
\hline
Transition & Wavenumber$^a$ \\
\hline
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)  & 627.320 (-1) \\
Q(2)  & 644.711 (0)  \\
Q(3)  & 644.735 (-1) \\
Q(4)  & 644.769 (-1) \\
Q(5)  & 644.811 (-1) \\
Q(6)  & 644.852 (-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)  \\
\hline
\end{tabular}
\end{table}

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

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a water-cooled A.C. discharge cell (1.2 cm i.d., 1 m in length) using a mixture of HCN and H₂ (≈ 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 r₃ 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:

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

where \( q \) and \( q_J(J+1) \) are the \( \ell \)-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 Botschwinia (11) are given in the footnote of the table. The observed value of the \( \ell \)-doubling constant is very close to the approximated value (12) \( q \approx 2.6B'_2/\omega_2 \).

**Table I**

<table>
<thead>
<tr>
<th>Molecular Constants of HCN⁺ r₃ (in cm⁻¹)*</th>
</tr>
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<tr>
<td>This Resultb</td>
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<tr>
<td>( \gamma_0 )</td>
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<tr>
<td>( B' )</td>
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<tr>
<td>( D' )</td>
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<tr>
<td>( q )</td>
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<td>( q_J )</td>
</tr>
</tbody>
</table>

*Quoted errors are 1σ.

b Fitting is done with \( B' \) and \( D' \) fixed at 1.236046 and 1.6068x10⁻⁶ cm⁻¹, respectively.

c Theoretical prediction of \( \gamma_0 \) (HNC bend) (cm⁻¹): Lee et al. (9), 700; DeFrees and McLean (10), 699; Botschwinia (11), 620.

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1. R. S. Altman, M. W. Crofton, AF
2. R. S. Altman, M. W. Crofton, AF
3. M. Bogey, C. Demuyck, and J.
4. L. M. Ziurys and B. E. Turner, A
5. T. Amano and K. Tanaka, J. Mol
6. K. Tanaka, K. Kawaguchi, and 1
7. D. J. Liu, N. N. Hase, and T. Ok
8. C. S. Gudeman, M. H. Begemann
9. T. J. Lee and H. F. Schaefer III, J
10. D. J. DeFrees and A. D. McLean
12. C. H. Townes and A. L. Schawlo

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REFERENCES


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1 of HCNH'. A time constant of 3 sec

A mixture of HCN and H₂ (≈1:5) with a time constant of 3 sec

10 of absorption lines was nes-stripe geometry diodes were used co-euently predicted (9-11).

erved spectral lines of the first eight are listed in Table I. The spectrum was cited state:

\[ \nu(J+1)[J(J+1)] \]

1 dependence, respectively. The ground by Bogey et al. (5). The determined attained by Amano and Tanaka (5). The

in (10), and Botschwa (11) are given stant is very close to the approximated

1 cm⁻¹)²

Ref 5

1.237 0.27(15)
1.64(67)×10⁻⁶
0.005 480(29)
1.1(13)×10⁻⁷

0.4 cm⁻¹, respectively,

700; Defrees and McLean (10), 699;