The Molecular Structures of HNC and HCN Derived from the Eight Stable Isotopic Species


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Ground vibrational state rotational transitions have been measured for the following isotopic species of HNC: $^{13}$HNC, $^{15}$HNC, $^{13}$DNC, $^{15}$DNC, $^{12}$HNC and $^{15}$HNC. Similar transitions have also been measured for $^{13}$HC$^{15}$N and $^{15}$HC$^{13}$N. These measurements complete the set of rotational constants for the eight stable isotopic species of the two molecules. Molecular structures are calculated from these data in several ways and are compared with the results of recent ab initio calculations.

I. Introduction

In a recent paper we reported the observation of the $J = 1 \leftarrow 0$ and $2 \leftarrow 1$ rotational transitions of hydrogen isocyanide, HNC and its isotopic species DNC and HN$^{13}$C$^{15}$C. This work, together with the recent interstellar observations, showed conclusively that the interstellar absorption line U90.7, previously tentatively identified as HNC, was in fact due to this molecule. In addition to our work on HNC the $J = 1 \leftarrow 0$ transition of the parent isotopic species has been reported by Saykally, Szanto, Anderson and Woods. Also the $J = 1 \leftarrow 0$ transitions of DNC, HNC and HN$^{13}$C$^{15}$C have been reported by Blackman, Brown, Godfrey and Gunn.

A different method of HNC production was employed in each of these studies. In our work HNC was produced by the reaction of methyl bromide or methyl iodide with active nitrogen produced in a radiofrequency discharge. Woods and coworkers used a D.C. discharge through mixtures of nitrogen and acetylene, cyanogen and hydrogen or cyanogen and acetylene. The production method of Blackman et al. involved the thermal isomerisation of HCN at 1000 K; a previous attempt by these workers to see HNC absorption in a room temperature sample of HCN having failed.

Essentially identical molecular structures of HNC were reported by us and by Blackman et al., since the same isotopic species were measured in each case. In view of the astrophysical importance of this molecule and the need to obtain the best possible experimental structure for comparison with recent ab initio calculations, we have extended our study to include measurements of all eight possible isotopic species of HNC made from the $^{1}$H, $^{2}$H, $^{12}$C, $^{13}$C, $^{14}$N and $^{15}$N isotopes. These measurements and the improved molecular structure derived from them are reported in the present paper. Also, since hydrogen cyanide, HCN, is produced in the reaction scheme used to make HNC we have taken the opportunity to complete the measurements on the corresponding group of isotopic species of this molecule.

II. Experimental Procedures

The experimental apparatus and procedures were all as described and referenced in our previous paper. The various isotopic species of HNC were produced by the reaction of the appropriate combination of $^{14}$N$_{2}$ or $^{15}$N$_{2}$ with CH$_{3}$I, $^{12}$CH$_{3}$I, CD$_{3}$I or $^{13}$CD$_{3}$I. All enriched isotopic samples were purchased from Merck, Sharp and Dohme Ltd.

III. Results

The measured transition frequencies of the five isotopic species of HNC newly reported in the present paper, together with the frequencies reported for HNC, DNC and HN$^{13}$C in our previous paper, are listed in Table I. Figure 1 shows the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions of D$^{13}$NC$^{15}$C and D$^{15}$NC$^{13}$C observed with the fourth and sixth harmonics of the klystron fundamental frequency. The ground vibrational state rotational constants, $B_{0}$, and centrifugal distortion constants, $D_{0}$, listed in Table II...
Isotopic Species | \( J = 1 \leftarrow 0 \) | \( J = 2 \leftarrow 1 \) | \( J = 3 \leftarrow 2 \)
---|---|---|---
HNC | 90663.593 (40) | 181324.758 (50) |
\( \text{HN}^{13}\text{C} \) | 87090.851 (40) | 174179.411 (50) |
\( \text{H}^{15}\text{NC} \) | 88865.715 (40) | 177729.094 (50) |
\( \text{HN}^{13}\text{C} \) | 85258.923 (40) | 170515.680 (55) |
\( \text{DN}^{13}\text{C} \) | 76305.727 (40) | 152609.774 (50) |
\( \text{DN}^{15}\text{C} \) | 146734.002 (40) | 220097.238 (60) |
\( \text{DN}^{13}\text{C} \) | 150571.926 (45) | 225853.841 (60) |
\( \text{DN}^{15}\text{C} \) | 144620.101 (40) | 216926.436 (50) |

Table I. Observed transition frequencies \(^a\) of isotopic species of HNC.

\(^a\) Frequencies are in MHz. The numbers in parentheses correspond to the estimated experimental uncertainties in the last digits of the quoted frequencies.

\(^b\) Data taken from Reference 1. The \( J=1 \leftarrow 0 \) transition of the parent isotopic species has been remeasured in the present work.

Some transitions of the previously unreported \( \text{D}^{13}\text{C}^{15}\text{N} \) and \( \text{H}^{13}\text{C}^{15}\text{N} \) isotopic species of hydrogen cyanide have also been measured. In addition we have extended the measurements on \( \text{H}^{13}\text{C}^{14}\text{N} \), \( \text{H}^{12}\text{C}^{15}\text{N} \), \( \text{D}^{13}\text{C}^{14}\text{N} \) and \( \text{DC}^{15}\text{N} \), previously only the \( J = 1 \leftarrow 0 \) transitions had been measured for these isotopic species \(^a\). A summary of all measurements, including the new ones made in the present work, for the eight species of HCN made of \( 2\text{H}, 12\text{C}, 13\text{C}, 14\text{N} \) and \( 15\text{N} \) is given in Table III. Rotational and centrifugal distortion constants derived from these data are listed in Table IV.

The errors listed in Tables II and IV for the derived constants, in the cases where only two transitions were measured, were calculated assuming an uncertainty in the measured transition frequency equal to one tenth of the observed line width.

**IV. Structure and Discussion**

It is widely recognised that the most consistent and generally applicable way of obtaining structural
Table III. Transition frequencies of isotopic species of HCN.

<table>
<thead>
<tr>
<th>Isotopic Species</th>
<th>J=1 ← 0</th>
<th>J=2 ← 1</th>
<th>J=3 ← 2</th>
<th>J=4 ← 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>88631.6024(10) b</td>
<td>177261.1112(20) b</td>
<td>265886.18 (55) c</td>
<td></td>
</tr>
<tr>
<td>H^2CN</td>
<td>86339.944 (25)</td>
<td>172677.877 (50) d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC^14N</td>
<td>86054.961 (25)</td>
<td>172107.956 (45)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H^3CN</td>
<td>83727.590 (25)</td>
<td>167453.285 (50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCN</td>
<td>72414.6941(7) b</td>
<td>144828.0003(15) b</td>
<td>217238.40 (55) e</td>
<td>289644.67 (60) c</td>
</tr>
<tr>
<td>D^2CN</td>
<td>71175.01 (10) e</td>
<td>142348.808 (30) d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DC^14N</td>
<td>70339.48 (10) e</td>
<td>140677.446 (45)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D^3CN</td>
<td>138123.515 (30)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Frequencies are in MHz. The numbers in parentheses correspond to the estimated experimental uncertainties in the last digits of the quoted frequencies, where the observed transitions are split by D and or ^14N nuclear quadrupole coupling, the above values represent hypothetical unsplit frequencies.

d The following ^14N quadrupole coupling has been measured in the present work; for other quadrupole data see references.

Table IV. Spectroscopic constants of isotopic species of HCN.

<table>
<thead>
<tr>
<th>Isotopic Species</th>
<th>B_0/MHz</th>
<th>D_0/kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>44315.9757(4)</td>
<td>87.24 (6)</td>
</tr>
<tr>
<td>H^13CN</td>
<td>43170.140 (20)</td>
<td>83.8 (40)</td>
</tr>
<tr>
<td>HC^14N</td>
<td>43027.644 (20)</td>
<td>81.9 (40)</td>
</tr>
<tr>
<td>H^3CN</td>
<td>41863.953 (20)</td>
<td>79.0 (40)</td>
</tr>
<tr>
<td>DCN</td>
<td>36207.4627 (2)</td>
<td>57.83 (4)</td>
</tr>
<tr>
<td>D^13CN</td>
<td>35587.619 (20)</td>
<td>53.3 (20)</td>
</tr>
<tr>
<td>DC^14N</td>
<td>35169.791 (20)</td>
<td>53.8 (20)</td>
</tr>
<tr>
<td>D^3CN</td>
<td>34531.276 (20)</td>
<td>50.7 (20)</td>
</tr>
</tbody>
</table>

parameters from ground vibrational state rotational constants is by use of the substitution method. Although there exists a method, due to Watson, of obtaining near-equilibrium structures from ground state rotational constants, it is not applicable to the case of hydrogen-deuterium substitution and so the r_s method remains the best currently available for HNC and HCN. With the rotational constants for HNC and HCN listed in Tables II and IV it is possible to calculate the r_s structures of these molecules in eight different ways although only two of the resulting structures for each molecule are completely independent. The average value and the range of values obtained from such a calculation are given in Table V. It should be observed that the range of values for the r_s structural parameters in each molecule are similar. A similar range of variation of r_s parameters was found by Pearson and McCormick in their work on thioborine HBS. However, this close agreement among the various ways of calculating the r_s structure of HNC cannot be taken as evidence that the molecule shows no tendency to quasilinear behaviour, since the structure is based entirely on absorption lines arising from K=l=0.
ground vibrational state rotational levels. The \( r_s \) structure of HCN obtained previously by Winnewisser, Maki and Johnson is essentially identical to that given here in Table V. With the present sets of rotational constants it is possible to calculate twenty-eight different \( r_0 \) structures for both HNC and HCN. Winnewisser et al. reported such a calculation in their paper on HCN. However, a similar calculation on HNC will not be reported here in detail since the results mainly serve to demonstrate the limitations of \( r_0 \) structures. The \( r_0 \) structures given in Table V are averages of the sixteen possible \( r_0 \) structures which may be calculated from pairs of rotational constants involving different hydrogen isotopes. As observed previously, the structures calculated in this way show much less scatter than the complete set of \( r_0 \) structures. The structure called \( r_e^* \) in Table V was calculated from \( B_e^* \) values obtained by combining the ab initio \( \alpha \) constants reported in reference with the experimental \( B_0 \) values reported in this paper; again only H, D isotopic pairs were used. A purely experimental \( r_e \) structure is available for HCN and this is listed in Table V together with the best available ab initio structures for both HCN and HNC. For HCN it may be observed that the \( r_e^* \) structural parameters have a smaller range than the \( r_0 \) parameters, as would be expected if the calculated \( \alpha \) values were accurate. Unfortunately the calculated \( \alpha \) values are not so successful in improving the consistency of the HNC structure, since in this case the \( r_e^* \) structure shows larger scatter than the \( r_0 \) structure. The \( r_e^* \) structure seems to be in generally better agreement with the experimental \( r_e \) structure in the case of HCN and the ab initio \( r_e \) structure in the case of HNC than is either the \( r_0 \) or the \( r_s \) structure. However, it is still clearly desirable to have experimental values for the \( \alpha \) constants for the purposes of calculating equilibrium structures. Finally we would like to point out the large difference between both the \( r_0 \) and \( r_s \) values for the H – N distance in HNC and both the ab initio \( r_e \) values and the \( r_e^* \) value. Such an apparent shortening of the internuclear distance would be expected if the hydrogen atom were undergoing a large amplitude motion. Further support for this possibility comes from the calculated potential surfaces. We are currently pursuing this possibility by investigating the spectra in excited states of the bending vibration.

Acknowledgements

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