The Molecular Structures of HNC and HCN Derived from the Eight Stable Isotopic Species [1]

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Ground vibrational state rotational transitions have been measured for the following isotopic species of HNC: $H^{15}NC$, $H^{15}N^{13}C$, $DN^{13}C$, $D^{15}NC$ and $D^{15}N^{13}C$. Similar transitions have also been measured for $H^{13}C^{15}N$ and $D^{13}C^{15}N$. 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 $HN^{13}C$ [1]. This work, together with the recent interstellar observations [2], 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 [3]. Also the $J = 1 \leftarrow 0$ transitions of HNC, DNC and $HN^{13}C$ have been reported by Blackman, Brown, Godfrey and Gunn [4]. 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 [3] 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. [4] 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 [5].

Essentially identical molecular structures of HNC were reported by us and by Blackman et al. [4], 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 [6, 7], we have extended our study to include measurements of all eight possible isotopic species of HNC made from the ^1H, ^2H, ^{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 [1]. 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_3I, $^{13}CH_3I$, CD_3I or $^{13}CD_3I$. 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 $D^{15}N^{13}C$ and $D^{14}N^{13}C$ 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

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Table I. Observed transition frequencies [a] of isotopic species of HNC.

Isotopic Species	$J=1 \leftarrow 0$	$J=2 \leftarrow 1$	$J=3 \leftarrow 2$
HNC [b]	90663.593 (40)	181324.758 (50)	
$HN^{13}C$ [b]	87090.851 (40)	174179.411 (50)	
$H^{15}NC$	88865.715 (40)	177729.094 (50)	
$H^{15}N^{13}C$	85258.923 (40)	170515.680 (55)	
DNC [b]	76305.727 (40)	152609.774 (50)	
$DN^{13}C$		146734.002 (40)	220097.238 (60)
$D^{15}NC$		150571.926 (45)	225853.841 (60)
$D^{15}N^{13}C$		144620.101 (40)	216926.436 (50)

[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.

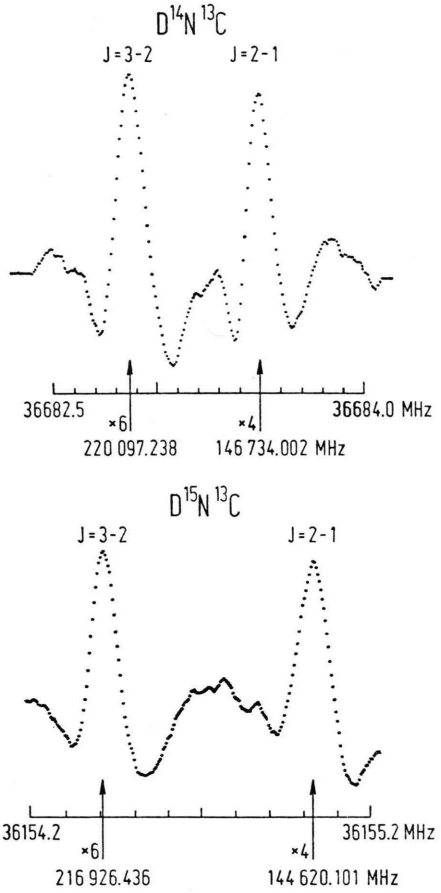

Fig. 1. The $J=2 \leftarrow 1$ and $3 \leftarrow 2$ transitions of $D^{14}N^{13}C$ and $D^{15}N^{13}C$ observed with the fourth and sixth harmonics of the klystron fundamental frequency. Each trace consists of 250 data points averaged over 1000 sweeps each of 15 ms duration followed by 25 point smoothing.

were calculated from the observed frequencies using the relationship:

$$\nu_{J+1 \leftarrow J} = 2B_0(J+1) - 4D_0(J+1)^3 .$$

Table II. Spectroscopic constants of isotopic species of HNC.

Isotopic Species	B_0/MHz (obs)	D_0/kHz (obs)	D_0/kHz (calc) [a]
HNC	45331.999 (40)	101.2 (50)	97.9
$HN^{13}C$	43545.616 (40)	95.5 (50)	90.7
$H^{15}NC$	44433.052 (40)	97.3 (50)	94.5
$H^{15}N^{13}C$	42629.642 (40)	90.2 (50)	87.3
DNC	38153.004 (40)	70.0 (50)	65.7
$DN^{13}C$	36684.003 (25)	62.8 (20)	60.8
$D^{15}NC$	37643.521 (30)	67.5 (20)	64.0
$D^{15}N^{13}C$	36155.521 (25)	61.9 (20)	59.1

[a] Calculated from the harmonic force field given by: D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 278 [1967]. The r_s structure of HNC given in Table V was used in this calculation.

Some transitions of the previously unreported $D^{13}C^{15}N$ and $H^{13}C^{15}N$ isotopic species of hydrogen cyanide have also been measured. In addition we have extended the measurements on $H^{13}C^{14}N$, $H^{12}C^{15}N$, $D^{13}C^{14}N$ and $DC^{15}N$, previously only the $J=1 \leftarrow 0$ transitions had been measured for these isotopic species [8]. A summary of all measurements, including the new ones made in the present work, for the eight species of HCN made of ^1H, ^2H, ^{12}C, ^{13}C, ^{14}N and ^{15}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 [a] of isotopic species of HCN.

Isotopic Species	$J=1 \leftarrow 0$	$J=2 \leftarrow 1$	$J=3 \leftarrow 2$	$J=4 \leftarrow 3$
HCN	88631.6024 (10) [b]	177261.1112 (20) [b]	265886.18 (55) [c]	
$H^{13}CN$	86339.944 (25)	172677.877 (50) [d]		
$HC^{15}N$	86054.961 (25)	172107.956 (45)		
$H^{13}C^{15}N$	83727.590 (25)	167453.285 (50)		
DCN	72414.6941 (7) [b]	144828.0003 (15) [b]	217238.40 (55) [c]	289644.67 (60) [c]
$D^{13}CN$	71175.01 (10) [e]	142348.808 (30) [d]	213519.926 (50)	284687.32 (20)
$DC^{15}N$	70339.48 (10) [e]	140677.446 (45)	211012.926 (65)	281344.550 (80)
$D^{13}C^{15}N$		138123.515 (30)	207182.140 (55)	276237.239 (70)

[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 ^{14}N nuclear quadrupole coupling, the above values represent hypothetical unsplit frequencies.

[b] F. C. De Lucia and W. Gordy, Phys. Rev. **187**, 58 [1969].

[c] C. A. Burrus and W. Gordy, Phys. Rev. **101**, 599 [1956].

[d] The following ^{14}N quadrupole coupling has been measured in the present work; for other quadrupole data see references.
$H^{13}CN$: $F=1 \leftarrow 1$ 86338.767 MHz, $F=2 \leftarrow 1$ 86340.184 MHz, $F=0 \leftarrow 1$ 86342.274 MHz.
$H^{13}CN$: $F=2 \leftarrow 2$ and $1 \leftarrow 0$ 172676.573 MHz, $F=2 \leftarrow 1$ and $3 \leftarrow 2$ 172677.959 MHz, $F=1 \leftarrow 1$ 172680.209 MHz.
$D^{13}CN$: $F=2 \leftarrow 2$ and $1 \leftarrow 0$ 142347.540 MHz, $F=2 \leftarrow 1$ and $3 \leftarrow 2$ 142348.883 MHz, $F=1 \leftarrow 1$ 142351.129 MHz.

[e] Reference 8.

Table IV. Spectroscopic constants of isotopic species of HCN.

Isotopic Species	B_0/MHz	D_0/kHz
HCN	44315.9757 (4)	87.24 (6)
$H^{13}CN$	43170.140 (20)	83.8 (40)
$HC^{15}N$	43027.644 (20)	81.9 (40)
$H^{13}C^{15}N$	41863.953 (20)	79.0 (40)
DCN	36207.4627 (2)	57.83 (4)
$D^{13}CN$	35587.619 (20)	53.3 (20)
$DC^{15}N$	35169.791 (20)	53.8 (20)
$D^{13}C^{15}N$	34531.276 (20)	50.7 (20)

Table V. Structures of HCN and HNC.

HCN	r(H−C)/Å	r(C−N)/Å
r_0	1.06236 (75) [a]	1.15679 (19)
r_s	1.06314 (11)	1.15512 (16)
r_e*	1.06255 (26)	1.15287 (7)
r_e experimental	1.06549 (24)	1.15321 (5)
r_e ab initio [b]	1.066	1.150
r_e ab initio [c]	1.064	1.149
r_e [c, d]	1.066	1.152
HNC	**r(H−N)/Å**	**r(N−C)/Å**
r_0	0.98623 (67)	1.17255 (16)
r_s	0.98607 (9)	1.17168 (22)
r_e*	0.99357 (117)	1.16453 (28)
r_e experimental		
r_e ab initio [b]	0.9955	1.1696
r_e ab initio [c]	0.993	1.164
r_e [c, d]	0.996	1.167

[a] Numbers in parentheses represent the range of values obtained from all calculations of the given parameter with the exception of the experimental r_e structure of HCN, in this case the uncertainty is obtained from estimated error limits of the experimental B_e values.

[b] Reference 6. [c] Reference 7.

[d] This value differs from the purely ab initio structures of Ref. 7 in that it includes an empirically determined increase of 2‰ in the structural parameters.

parameters from ground vibrational state rotational constants is by use of the substitution method [9, 10]. Although there exists a method, due to Watson [11], 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 [11]. 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 [12] 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 [13]. The r_s structure of HCN obtained previously by Winnewisser, Maki and Johnson [8] 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. [8] 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 [8], 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 α constants reported in reference [7] 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 [8] and this is listed in Table V together with the best available ab initio structures [6, 7] 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 α values were accurate. Unfortunately the calculated α 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 α 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 [13]. Further support for this possibility comes from the calculated potential surfaces [6, 7]. We are currently pursuing this possibility by investigating the spectra in excited states of the bending vibration.

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