# The Microwave Spectrum and Nuclear Quadrupole Coupling Constants of $HNC^{17}O$

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The microwave spectrum of $HNC^{17}O$ is reported for the first time. The measurements were made with both Stark modulated and microwave Fourier transform spectrometers. The $^{17}O$ and $^{14}N$ quadrupole hyperfine structure has been resolved and rotational, centrifugal distortion and $^{17}O$ and $^{14}N$ quadrupole coupling constants have been evaluated. The $^{17}O$ coupling constants are compared with those from an ab initio prediction.

## Introduction

Although the microwave spectrum of isocyanic acid, HNCO, has received much attention over the past forty years [1, 2], there has been no report of the spectrum of the $^{17}O$ isotopomer. Its spectrum should be of interest on two grounds. First, $^{17}O$ is a quadrupolar nucleus ($I = 5/2$), and the spectrum should show $^{17}O$ hyperfine structure, giving useful information about the electronic structure of the molecule. Secondly, HNCO is a known interstellar molecule [3], and $^{17}O$ is a known interstellar nucleus [4], so that the microwave spectrum should assist any radioastronomical searches.

In this paper we present the first measurements of the microwave spectrum of $HNC^{17}O$, made using both Stark modulated and Fourier transform spectrometers. It has been possible to obtain all three rotational constants and some centrifugal distortion constants. The quadrupole hyperfine structure has been resolved for several transitions, and has been fitted to all $^{17}O$ and $^{14}N$ coupling constants. The former are compared with those predicted ab initio.

## Experimental Methods

The isocyanic acid used in this work was prepared by the pyrolysis of its solid trimer, cyanuric acid, artificially enriched to 20% in $^{17}O$. The labelling was carried out by the base hydrolysis of cyanuric chloride, $(CNCl)_3$, with isotopically enriched water [1]. The solid cyanuric acid was precipitated by acidifying the solution, and was dried.

Initial measurements were made using a 100 kHz Stark modulated spectrometer at the University of British Columbia, in the frequency region 8–65 Ghz. The fundamental source was a Hewlett-Packard 8400 B Microwave Spectroscopy Source operating between 8–40 GHz. Power near 60 GHz was obtained by doubling from 30 GHz with a Space Kom DV-1 doubler. The 6 foot Hewlett-Packard 8425 B X band Stark cell was cooled with dry ice for all measurements.

Microwave Fourier transform (MWFT) measurements were made in G [5], X [6], K [7] and V [8] bands at the University of Kiel. Sample pressures were $\sim 1$ millitorr, and temperatures were $\sim 230$ K. Up to $33 \cdot 10^6$ cycles were obtained for individual transitions, covering averaging times of up to 45 minutes. The spectra were displayed by taking the Fourier transform of the decay. For the fully resolved transitions the frequencies were evaluated from the time domain signals using the least squares program written by Haekel [9].

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## Observed Spectrum and Analysis

Initially the rotational constants of $HNC^{17}O$ were predicted roughly as the averages of those of the $^{16}O$ and $^{18}O$ isotopomers. Searches were made for **a**-type R and Q branches, and for **b**-type P and R Branches, using the Stark modulated spectrometer. The **a**-type transitions were fairly easily identified from this prediction. Since the **b**-type lines were at high $J$, and the prediction could thus be in error by several hundred MHz, a broad band scan between 28–38 GHz was carried out. From this the peaks due to the species containing $^{16}O$ and $^{18}O$ (which was also enriched in the sample) were disregarded, and the lines of the $^{17}O$ isotopomer were relatively easily found. It helped greatly that the **b**-type lines are very strong. With the exception of $1_{01}$–$0_{00}$, which was partially resolved, no transition showed any $^{17}O$ or $^{14}N$ nuclear quadrupole hyperfine structure, even though the lines were broad. After the initial assignments it was relatively easy by "bootstrapping" to identify further transitions. At this point the consistency of the fit to rotational and centrifugal distortion constants was the only confirmation of the assignment.

The assignments were conclusively confirmed with the MWFT measurements. For $1_{01}$–$0_{00}$ the hyperfine structure was completely resolved to nine components, as is shown in Figure 1. The low J Q branch transitions were also essentially completely resolved; one of these, $8_{17}$–$8_{18}$, is in Figure 2. Several others, including **b**-type transitions, were partially resolved; their patterns could be predicted using the derived constants.

In spite of the complex hyperfine structure the analysis for the $^{17}O$ and $^{14}N$ quadrupole coupling constants was relatively easily done by least squares fitting. To make quantum number assignments, the patterns were predicted using a computer program written in the coupling scheme $I_1 + I_2 = I$; $I + J = F$. Atoms 1 and 2 were taken to be $^{17}O$ and $^{14}N$ respectively. In these predictions the $^{14}N$ constants were assumed to be unchanged from $H^{14}N^{12}C^{16}O$, and the $^{17}O$ constants were varied until good approximations to the observed patterns were produced. The lines were then assigned to the quantum numbers indicated in the prediction. The fit was then made in the same coupling scheme to the transitions $1_{01}$–$0_{00}$, $7_{16}$–$7_{17}$ and $8_{17}$–$8_{18}$; rotational constants from the Stark spectrum were entirely adequate for this purpose. The program included off-diagonal elements in the quantum number $I$ but not $J$. The resulting constants are in Table 1; they are essentially uncorrelated. Table 2 shows the measured transitions and assignments, and indicates the goodness of the fit.

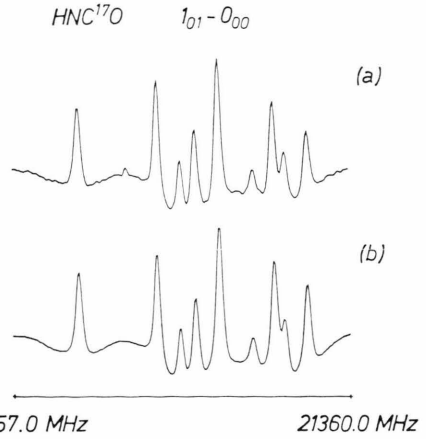


Fig. 1. The transition $1_{01}$–$0_{00}$ of $HNC^{17}O$, shown as an absorption spectrum [13]. $T = 240$ K, $P \sim 0.5$ mtorr, cycles averaged: $200 \cdot 32$ *k*. In part (a) the observed spectrum is given; in (b) it is compared with the spectrum calculated from the derived constants.

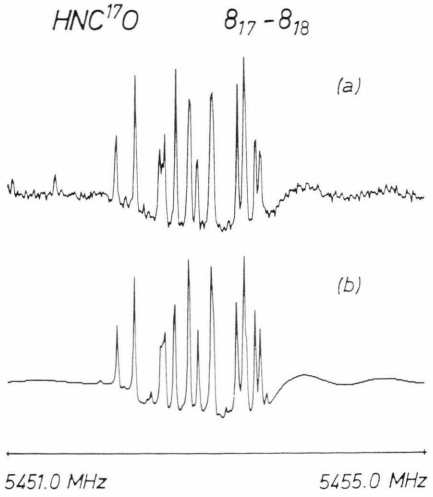


Fig. 2. The transition $8_{17}$–$8_{18}$ of $HNC^{17}O$, presented as an absorption spectrum [13]. $T = 236$ K, $P < 2$ mtorr, cycles averaged: $500 \cdot 32$ *k*. The observed spectrum, (a), is compared with that calculated from the derived constants, (b).

Fits to the rotational and centrifugal distortion constants were made to the transition frequencies with the hyperfine structure subtracted off – or, in the case of the lines measured only with the Stark spectrometer, to the measured centre frequencies. These were weighted according to the reciprocal of their esti-

Table 1. Spectroscopic constants of $HNC^{17}O$.

| Parameter | Value | |
|---|---|---|
| *Rotational constants/MHz* | | |
| $A$[a] | 912 665.4 | (29)[b] |
| $B$ | 10 755.14212 | (66) |
| $C$ | 10 603.65468 | (66) |
| *Centrifugal distortion constants/kHz* | | |
| $D_J$ | 3.401 | (25) |
| $D_{JK}$ | 875.3 | (84) |
| $d_1$ | −0.066846 | (81) |
| $d_2$ | −0.03106[c] | |
| $H_{JK}$ | −0.001323[c] | |
| $H_{KJ}$ | 21.7 | (34) |
| $h_J$ | $4.807 \times 10^{-7}$[c] | |
| *Nuclear quadrupole coupling constants/MHz* | | |
| $\chi_{aa}(^{17}O)$ | −3.276 | (24) |
| $\chi_{bb}(^{17}O)$ | −0.176 | (13) |
| $\chi_{aa}(^{14}N)$ | 2.051 | (13) |
| $\chi_{bb}(^{14}N)$ | −0.4725 | (68) |

[a] $D_K$ is assimilated into $A$.
[b] Numbers in parentheses are one standard deviation in units of the last significant figures.
[c] Fixed at the values for $HNC^{16}O$ [10].

mated uncertainty. Because as yet no millimetre wave spectrum has been measured, the model was abbreviated. It was essentially Watson's S-reduced Hamiltonian [10] with $d_2$, $H_{JK}$, and $h_J$ fixed at the values for $HNC^{16}O$ [11], and $D_K$ assimilated into $A$. The resulting constants are in Table 1, and the goodness of the fit is demonstrated in Table 3. The uncertainties in Table 1 should be viewed with caution, however, because there are two high correlations (coefficients $> 0.995$), between $A$ and $D_J$, and between $B$ and $C$.

## Discussion

This work presents the first measurements of spectroscopic constants of $HNC^{17}O$. The nuclear quadrupole coupling constants have been well determined, and reasonable values have been obtained for the rotational constants and some of the centrifugal distortion constants. With measurement of the millimetre wave spectrum it should be possible to obtain further distortion constants and to reduce the large correlations involving the rotational constants.

Gready [12] has recently published an ab initio prediction of the $^{17}O$ quadrupole coupling constants. Since her constants are in the principal quadrupole axis system and her calculation is based on a structure

Table 2. Rotational transitions of $HNC^{17}O$ resolved by $^{17}O$ and $^{14}N$ Quadrupole Coupling.

| $J'_{K_a K_c} - J''_{K_a K_c}$ $F'$ | $I'$ | $F''$ | $I''$ | Observed Frequency/MHz | Deviation/MHz |
|---|---|---|---|---|---|
| $1_{01}-0_{00}$ | | | | 21 358.783[a] | |
| 2.5 | 3.5 | 3.5 | 3.5 | 21 359.616 | 0.001 |
| 1.5 | 2.5 | 2.5 | 2.5 | 21 359.424 | 0.004 |
| 3.5 | 2.5 | 2.5 | 2.5 | 21 359.322 | −0.009 |
| 0.5 | 1.5 | 1.5 | 1.5 | 21 359.147 | 0.008 |
| 4.5 | 3.5 | 3.5 | 3.5 | 21 358.837 | −0.008 |
| 2.5 | 1.5 | 1.5 | 1.5 | 21 358.628 | 0.000 |
| 1.5 | 1.5 | 1.5 | 1.5 | 21 358.496 | 0.004 |
| 3.5 | 3.5 | 3.5 | 3.5 | 21 358.287 | 0.002 |
| 2.5 | 2.5 | 2.5 | 2.5 | 21 357.589 | −0.001 |
| $7_{16}-7_{17}$ | | | | 4 241.230[a] | |
| 6.5 | 2.5 | 6.5 | 2.5 | 4 241.791 | −0.001 |
| 8.5 | 3.5 | 8.5 | 2.5 | 4 241.739 | 0.000 |
| 7.5 | 2.5 | 7.5 | 2.5 | 4 241.654 | 0.002 |
| 5.5 | 3.5 | 5.5 | 3.5 | 4 241.634 | −0.001 |
| 7.5 | 1.5 | 7.5 | 1.5 | 4 241.610 | 0.001 |
| 9.5 | 3.5 | 9.5 | 3.5 | 4 241.574 | 0.004 |
| 7.5 | 3.5 | 7.5 | 3.5 | 4 241.326 | −0.002 |
| 6.5 | 1.5 | 6.5 | 1.5 | 4 241.301 | −0.002 |
| 4.5 | 3.5 | 4.5 | 3.5 | 4 241.281 | −0.005 |
| 6.5 | 3.5 | 6.5 | 3.5 | 4 241.153 | −0.009 |
| 8.5 | 2.5 | 8.5 | 3.5 | 4 241.127 | 0.004 |
| 8.5 | 1.5 | 8.5 | 1.5 | 4 241.113 | 0.013 |
| 10.5 | 3.5 | 10.5 | 3.5 | 4 240.981 | 0.010 |
| 5.5 | 2.5 | 5.5 | 1.5 | 4 240.866 | −0.001 |
| 3.5 | 3.5 | 3.5 | 3.5 | 4 240.838 | −0.004 |
| 5.5 | 1.5 | 5.5 | 2.5 | 4 240.783 | −0.012 |
| 9.5 | 2.5 | 9.5 | 2.5 | 4 240.599 | 0.010 |
| 4.5 | 2.5 | 4.5 | 2.5 | 4 240.406 | −0.007 |
| $8_{17}-8_{18}$ | | | | 5 452.854[a] | |
| 7.5 | 2.5 | 7.5 | 2.5 | 5 453.414 | 0.000 |
| 9.5 | 3.5 | 9.5 | 2.5 | 5 453.367 | 0.002 |
| 6.5 | 3.5 | 6.5 | 3.5 | 5 453.270 | −0.006 |
| 8.5 | 2.5 | 8.5 | 2.5 | 5 453.249 | −0.006 |
| 8.5 | 1.5 | 8.5 | 1.5 | 5 453.249 | 0.002 |
| 10.5 | 3.5 | 10.5 | 3.5 | 5 453.190 | 0.008 |
| 8.5 | 3.5 | 8.5 | 3.5 | 5 452.956 | −0.001 |
| 7.5 | 1.5 | 7.5 | 1.5 | 5 452.940 | 0.000 |
| 5.5 | 3.5 | 5.5 | 3.5 | 5 452.925 | −0.010 |
| 7.5 | 3.5 | 7.5 | 3.5 | 5 452.807 | −0.006 |
| 9.5 | 1.5 | 9.5 | 1.5 | 5 452.736 | 0.013 |
| 9.5 | 2.5 | 9.5 | 3.5 | 5 452.718 | 0.000 |
| 11.5 | 3.5 | 11.5 | 3.5 | 5 452.603 | 0.015 |
| 6.5 | 2.5 | 6.5 | 1.5 | 5 452.494 | 0.000 |
| 4.5 | 3.5 | 4.5 | 3.5 | 5 452.468 | −0.008 |
| 6.5 | 1.5 | 6.5 | 2.5 | 5 452.442 | −0.010 |
| 10.5 | 2.5 | 10.5 | 2.5 | 5 452.216 | 0.013 |
| 5.5 | 2.5 | 5.5 | 2.5 | 5 452.039 | −0.007 |

[a] Hypothetical unsplit line frequency obtained from the least squares fit to the nuclear quadrupole coupling constants.

Table 3. Observed unsplit line frequencies (in MHz) of $HNC^{17}O$.

| *Transition* $J'$ | $K'_a$ | $K'_c$ | $J''$ | $K''_a$ | $K''_c$ | Observed Frequency | Uncertainty | Deviation[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 1 | 0 | 0 | 0 | 21 358.783 | 0.002 | −0.001 |
| 3 | 0 | 3 | 2 | 0 | 2 | 64 076.06 | 0.100 | 0.113 |
| 3 | 1 | 3 | 2 | 1 | 2 | 63 844.02 | 0.400 | 0.354 |
| 3 | 1 | 2 | 2 | 1 | 1 | 64 298.14 | 0.100 | 0.026 |
| 3 | 2 | 1 | 2 | 2 | 0 | 64 057.18 | 0.300 | 0.001 |
| 7 | 1 | 6 | 7 | 1 | 7 | 4 241.230 | 0.002 | 0.001 |
| 8 | 1 | 7 | 8 | 1 | 8 | 5 452.854 | 0.002 | −0.001 |
| 11 | 1 | 10 | 11 | 1 | 11 | 9 995.72 | 0.250 | −0.121 |
| 12 | 1 | 11 | 12 | 1 | 12 | 11 812.55 | 0.250 | −0.215 |
| 13 | 1 | 12 | 13 | 1 | 13 | 13 780.65 | 0.250 | −0.276 |
| 14 | 1 | 13 | 14 | 1 | 14 | 15 900.07 | 0.250 | −0.212 |
| 15 | 1 | 14 | 15 | 1 | 15 | 18 170.79 | 0.020 | 0.004 |
| 16 | 1 | 15 | 16 | 1 | 16 | 20 592.39 | 0.020 | −0.002 |
| 17 | 1 | 16 | 17 | 1 | 17 | 23 165.05 | 0.030 | 0.002 |
| 19 | 1 | 18 | 19 | 1 | 19 | 28 763.19 | 0.250 | −0.095 |
| 20 | 1 | 19 | 20 | 1 | 20 | 31 788.91 | 0.250 | 0.163 |
| 21 | 1 | 20 | 21 | 1 | 21 | 34 965.05 | 0.250 | 0.031 |
| 36 | 1 | 36 | 37 | 0 | 37 | 62 148.02 | 0.100 | −0.013 |
| 37 | 1 | 37 | 38 | 0 | 38 | 38 127.67 | 0.030 | 0.003 |
| 38 | 1 | 38 | 39 | 0 | 39 | 14 044.75 | 0.050 | 0.020 |
| 40 | 0 | 40 | 39 | 1 | 39 | 10 100.10 | 0.030 | 0.013 |
| 41 | 0 | 41 | 40 | 1 | 40 | 34 306.08 | 0.030 | 0.002 |
| 42 | 0 | 42 | 41 | 1 | 41 | 58 572.46 | 0.100 | −0.065 |

[a] Observed frequency minus that calculated using the derived constants.

which is somewhat in error, a comparison between observed and calculated values is really only approximate. Since the molecule is planar, the best comparison is of the out-of-plane values.

Table 4 shows such a comparison. The agreement between the two sets of values is really only fair.

Table 4. Comparison of observed and calculated $^{17}O$ nuclear quadrupole coupling constants in $HNC^{17}O$ (in MHz).

| Parameter | Observed Value | Calculated Value |
|---|---|---|
| $\chi_{aa}(\chi_{zz})$[a] | −3.28 | −5.67 |
| $\chi_{bb}(\chi_{xx})$ | −0.18 | 0.44 |
| $\chi_{cc}(\chi_{yy})$ | 3.45 | 5.22 |

[a] The parameters $\chi_{aa}$, $\chi_{bb}$, $\chi_{cc}$ refer to the observed values in the principal inertial axis system. $\chi_{zz}$, $\chi_{xx}$, $\chi_{yy}$ refer to the calculated values, in the principal axis system of the quadrupole tensor. The angle between $a$ and $z$ is less than 10°; the out-of-plane $c$ and $y$ axes are parallel.

Gready did point out, however, that such disagreements are common for oxygen.

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