Deuterium Nuclear Quadrupole Coupling in Deutero-Isocyanic Acid

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The deuterium quadrupole hyperfine structure has been resolved in the 6(1, 5)–6(1, 6) transition of deutero-isocyanic acid (DNCO), and has been used to evaluate the previously undetermined coupling constant ($\chi_{bb}-\chi_{cc}$). With the assumption of cylindrical symmetry for the deuterium quadrupole coupling tensor its principal values have been estimated and have been found to be in excellent agreement with a theoretical prediction. Within experimental error the z-principal quadrupole axis and the D–N internuclear axis coincide.

Introduction

Over the years the microwave spectrum of isocyanic acid has received considerable attention [1–4]. This is partly because the molecule has a rather unusual structure, in which all the heavy atoms are very close to the a-inertial axis, making the rotational constant A extremely large. It is also partly because the molecule has been found in interstellar space [5]. Spectroscopic constants for several isotopic species have been reported, and have included the ^{14}N quadrupole coupling constants [1].

Resolution of the hyperfine structure due to D in DNCO is beyond the capability of most Stark modulated microwave spectrometers. With more specialized techniques, notably beam maser spectroscopy and microwave Fourier transform (MWFT) spectroscopy, this structure can be observed. Kukolich et al. [6] have, in fact, measured this splitting in the $J(K_a, K_c) = 1(0, 1)-0(0, 0)$ transition with a beam maser spectrometer, and have used it to evaluate the deuterium quadrupole coupling constant χ_{aa}. Because the remaining constant, $(\chi_{bb}-\chi_{cc})$, is unavailable from this transition, they were forced to make several assumptions in obtaining the chemically interesting principal quadrupole coupling constant χ_{zz}, which they assumed to be along the DN bond. The value they obtained, 345 ± 2 kHz, is inconsistent with that estimated by an *ab initio* calculation [7]; since similar calculations produced many constants consistent with experiment, this value is open to question.

In the present work we have measured the 6(1, 5)–6(1, 6) transition of DNCO. Hyperfine structure due to both D and ^{14}N has been well resolved, and the previously unmeasured deuterium coupling constant has been obtained for the first time. The coupling constant χ_{zz} has been revised.

Experimental Methods

The DNCO sample was prepared by pyrolysis of deuterated cyanuric acid, $(DCNO)_3$, which itself had been obtained by boiling normal cyanuric acid with excess D_2O over a period of about an hour. The transition was observed using the G-band (4.0–6.0 GHz) MWFT spectrometer recently constructed at the University of Kiel [8]. The temperature was $-50\,^{\circ}$C and pressure rather less than 2 millitorr. The transition is illustrated in Figure 1. It was obtained by accumulating the decays of $3.2 \cdot 10^6$ cycles, sampled at 50 ns intervals over 50 μs, and taking the fast Fourier transform after the addition of zeroes at a further 3 K points at the same intervals.

Results and Discussion

The measured frequencies are given in Table 1. They were obtained by a least squares fit in the time domain in order to minimize any effects of line overlap [9]. Since the coupling due to D is very much less than that due to ^{14}N, the coupling scheme $\mathbf{I}_N + \mathbf{J} = \mathbf{F}_1$; $\mathbf{I}_D + \mathbf{F}_1 = \mathbf{F}$ is a good approximation ($\mathbf{I}_N$ and $\mathbf{I}_D$ are the

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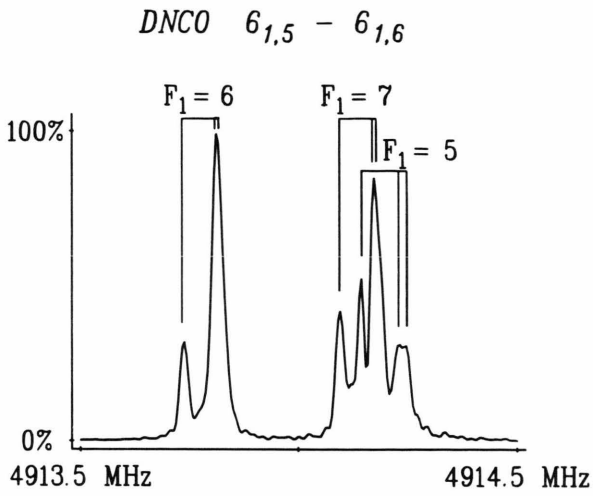

Fig. 1. 1-MHz-section of the rotational spectrum of DNCO showing the transition 6(1, 5)–6(1, 6) split by nuclear quadrupole coupling. F_1 quantum numbers are given. For experimental conditions see text.

nuclear spin operators of ^{14}N and D, respectively). Accordingly, assignments to the quantum numbers F_1 and F are also given.

A least squares fit was made of the combined data of the present work and of [6] to the ^{14}N and D quadrupole coupling constants, using the shifts of the hyperfine components from the unsplit lines. Although the program used was written in the coupling scheme $\mathbf{I}_N + \mathbf{I}_D = \mathbf{I}$, $\mathbf{I} + \mathbf{J} = \mathbf{F}$, terms off-diagonal in the quantum number I were included. Terms off-diagonal in J were not included; this is, however, an excellent approximation for the small interaction energies involved. Although Kukolich et al. [6] reported spin-rotation constants, as well as effects of DN spin–spin coupling, we did not include them in our fits for the following reasons. In the first place all these effects are below 1 kHz in the transitions, and are thus well below our measurement accuracies. In addition, the line assigned in [6] to the upper state quantum number $F' = 3$ (which was used in evaluating the constants) is an overlap of lines with $F' = 3$ and 1, and the constants in their Table 3 do not seem to follow from the coefficients in their Table 2.

The constants obtained in the present analysis are given in Table 2. They are evidently all well determined and reproduce the quadrupole shifts well, as is shown by the deviations given in Table 1. Table 2 also gives a comparison with corresponding values from earlier work. For the ^{14}N constants there is excellent

Table 1. Observed rotational transitions of DNCO showing resolved deuterium hyperfine structure.

Transition[a]	F_1	F	Observed frequency (MHz)	Deviation[b] (MHz)
1(0, 1)–0(0, 0)[c]	0	1	20392.31460	0.000
	2	1	20392.27018	0.008[d]
	2	3		0.001[d]
	2	2	20393.28193	0.001
	1	1	20393.90183	0.001
	1	2	20393.90920	0.000
	1	0	20393.92163	−0.001
6(1, 5)–6(1, 6)	6	6	4913.741	0.000
	6	7	4913.816	0.000
	6	5	4913.827	−0.001
	7	7	4914.096	0.001
	7	8	4914.174	0.001
	7	6	4914.186	0.001
	5	5	4914.155	−0.001
	5	6	4914.231	0.000
	5	4	4914.244	−0.003

[a] The quantum numbers F_1 and F refer to the upper state. The observed transitions of 6(1, 5)–6(1, 6) all had $\Delta F_1 = \Delta F = 0$.
[b] Observed quadrupole shifts minus those calculated from the constants obtained in the least squares fit.
[c] Frequencies of the transition 1(0, 1)–0(0, 0) taken from [6].
[d] Not included in the least squares fit.

Table 2. Experimental nuclear quadrupole coupling constants of D and ^{14}N in DNCO.

Nucleus	Constant	Value (kHz)		
		Present work	Ref. [6]	Ref. [1]
^{14}N	χ_{aa}	2123.7(15)[a]	2123.0(10)	–
	$\chi_{bb} - \chi_{cc}$	1018.2(21)	–	1031(18)
D	χ_{aa}	57.6(54)	53.6(2)[b]	–
	$\chi_{bb} - \chi_{cc}$	227.4(22)	–	–

[a] Numbers in parentheses are one standard deviation in units of the last significant figure.
[b] This is the value quoted in [6], Table 3. A recalculation using the data of their Table 2 gives 51.3 kHz.

agreement, with $(\chi_{bb} - \chi_{cc})$ considerable improved. Although the χ_{aa} constants for both ^{14}N and D are seemingly less well determined than from the beam maser work, they are in agreement, in spite of the problems of [6] mentioned earlier. This is the first determination of $(\chi_{bb} - \chi_{cc})$ for D in this molecule.

An estimate was made of the principal values of the D quadrupole tensor, with the sole assumption that the tensor is cylindrically symmetric. This was one of the assumptions made by Kukolich et al. and is justi-

fied by the theoretical calculation [7], which predicts 1.6% asymmetry. A value for χ_{cc}, the out-of-plane constant, was first obtained; it is -142.5 ± 3 kHz. Since by symmetry of the molecule this is a principal value ($\equiv \chi_{yy}$), the second principle value χ_{xx} is -142.5 ± 3 kHz as well (by symmetry of the coupling tensor). Thus the third principal value becomes $\chi_{zz} = 285 \pm 6$ kHz. This is in remarkable agreement with the value $\chi_{zz} = 286.3$ kHz obtained in the theoretical calculation [7].

With these results we could also obtain the angle θ_{za} between the z-principal quadrupole axis and the a-inertial axis. It came out to be $46.9 \pm 0.7°$. This can be compared with the angle between the DN bond and the a-inertial axis evaluated from the structure of Yamada [4]; this is $49.2 \pm 1.7°$, in good agreement with θ_{za}. We conclude that the DN bond is cylindrically symmetric and a principal axis of the D quadrupole tensor.

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