Nuclear Quadrupole Hyperfine Structure in the Rotational $^{a}Q_1$-Subbranch of Deuteroisothiocyanic Acid, DNCS

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The two-nuclei quadrupole hyperfine structure of four $^{a}Q_1$-subbranch transitions of deuteroisothiocyanic acid, DNCS, has been resolved and analyzed by use of a waveguide microwave Fourier transform spectrometer. The analysis yielded one previously unknown quadrupole coupling constant ($\chi_- \equiv \chi_{bb} - \chi_{cc}$) for both nitrogen ($\chi_-^N = +27.6(11)$ kHz) and deuterium $\chi_-^D = +175.8(11)$ kHz).

Taking into account the results from earlier work on HNCS, DNCS, HNCO, and DNCO, the orientations of the principal axis systems of the two quadrupole coupling tensors could be calculated. It appears that while the deuterium tensor is aligned to the D−N internuclear axis as expected, the nitrogen tensor is tilted away from the bisector of the DNC angle by 13° towards the NCS chain.

Introduction

Although the rotational spectrum of isothiocyanic acid, HNCS, and its isotopomers have been investigated in a number of publications, only one rather recent work by Rodler et al. [1] seems to have dealt primarily with the nuclear quadrupole hyperfine structure. In that work, the coupling constants χ_{aa} of both HNCS and DNCS were determined with high precision, using a molecular beam microwave Fourier transform (MB-MWFT) spectrometer of the Balle-Flygare type. In addition, a value for the coupling constant $\chi_-^N \equiv \chi_{bb} - \chi_{cc}$ was obtained for HNCS, using a waveguide microwave Fourier transform (MWFT) spectrometer.

In order to characterize the electronic surrounding of the quadrupolar nuclei, properly, values for the constants χ_-^N and χ_-^D for DNCS are necessary. These can best be obtained from a low-frequency microwave study of the $^{a}Q_1$-subbranch of the rotational spectrum of this molecule. However, because of the small size of the effects, ultimate resolving power is required. We have successfully undertaken such a study with our J-band (5–8 GHz) waveguide MWFT spectrometer [2].

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Experiments and Analysis

DNCS was prepared as described in [1] for their cavity spectrometer studies. Decomposition of the substance upon contact with the brass waveguide was significant but not prohibitively fast, and hence a flow system was not necessary. Recordings were performed at about −50 °C, and using total gas pressures of below 0.1 Pa (0.75 mTorr).

The transition frequencies were predicted using the rotational and centrifugal distortion constants given in [3].

We could detect all four $^{a}Q_1$-subbranch transitions expected within the frequency range of the spectrometer; their hyperfine structures were all similar, but only partially resolvable. They all consisted of close doublets (intensity ratio approx. 2:1, with the weaker component to low frequencies), with both doublet components having "shoulders", again to the low frequency sides. Interpreting these as extra, though unresolved, splittings, we observd quartets of the approximate intensity ratio 4:2:2:1. Given the high J quantum numbers (13 to 16) of the transitions, these patterns may be taken as characteristic of a molcule with two spin-1 nuclei, and with the relevant coupling constants having the same sign. The frequencies given in Table 1 are those derived from least-squares fits to the time domain signals [4].

Our analysis was based on a program written in the coupling scheme $\mathbf{I}_N + \mathbf{I}_D = \mathbf{I}$, $\mathbf{I} + \mathbf{J} = \mathbf{F}$, where $\mathbf{I}_N$ and $\mathbf{I}_D$ are the nuclear spin operators of nitrogen and deu-

Table 1. Observed frequencies of hyperfine structure components of $^aQ_1$-subbranch $(J_{1,(J-1)} - J_{1,J})$ transitions of deuteroisothiocyanic acid, DNCS. ν_0 hyperfine free frequency, ν_{hfs} quadrupole offset, $\delta\nu$ observed – calculated offset (in kHz).

J		13		14		15		16	
ν_0 [MHz]		5022.1891		5794.4272		6621.7031		7503.9935	
$F-J$	I	ν_{hfs}	$\delta\nu$	ν_{hfs}	$\delta\nu$	ν_{hfs}	$\delta\nu$	ν_{hfs}	$\delta\nu$
0	2	−51	−1	−50	0	−50	0	−49	+2
−1	2	−40	−1	−41	−1	−40	−1	−39	+1
+1	1	−40	0	−41	0	−40	0	−39	+2
−1	1	+15	−3	+15	−2	+15	−2	+14	−3
+1	2	+15	+2	+15	+3	+15	+2	+14	+1
−2	2	+25	−3	+25	−3	+25	−3	+25	−3
0	0	+25	−2	+25	−2	+25	−2	+25	−1
0	1	+25	+2	+25	+2	+25	+2	+25	+2
+2	2	+25	+3	+25	+2	+25	+2	+25	+2

terium, respectively, **I** is the composite spin operator, **J** the spatial angular momentum operator, and **F** the overall angular momentum operator. Matrix elements off-diagonal in I, but not J, were included. The implicit assumption of small quadrupole energies relative to the differences in rotational energies is well justified for nitrogen and deuterium coupling, and is reflected by the quality of the fit (see Table 1).

Results and Discussion

In addition to one rotational constant, one quartic, and one sextic centrifugal distortion constant (the latter is barely determined, and the former two are not as precise as those given by Yamada et al. [3]; we shall therefore not discuss these three constants), the analysis of the data in Table 1 resulted in two coupling constants $\chi_- \equiv \chi_{bb} - \chi_{cc}$, namely $\chi_-(1) = +175.8(11)$ kHz and $\chi_-(2) = +27.6(11)$ kHz (see Table 2). While one might be tempted to assign the former, larger value to nitrogen, and the latter value to deuterium, a comparison with the observed value for χ_-^D in DNCO [5] (+227.4(22) kHz, see Table 3) and also an *ab initio* calculation for χ_-^D in DNCS by Huber [6] (+184 kHz) shows that the only reasonable assignment is the opposite. Then, $\chi_-^D = +175.8(11)$ kHz, in accordance with the above calculated value, while χ_-^N is only +27.6(11) kHz. Rodler et al. [1] give a value of $\chi_-^N = \chi_{bb}^N - \chi_{cc}^N = -528.4(17)$ kHz + 636.7(16) kHz = +108.3(25) kHz for HNCS. On the other hand, Huber [6] also gives values for χ_-^N for HNCS and

Table 2. Spectroscopic constants (in kHz) of deuteroisothiocyanic acid, DNCS, as determined from its $^aQ_1$-subbranch spectrum, and comparison with the data from [3] (2nd row).

$B-C$	d_1	h_1
55 213.97(12)	0.03432(26)	−0.0000014(11)
55 123.90(?)	0.034551(14)	0.0 fixed

$\chi_-(1)$	$\chi_-(2)$	
+175.8(11)	+27.6(11)	

Table 3. Compilation of quadrupole coupling constants (in kHz) of isothiocyanic acid and isocyanic acid.

| | HNCS | DNCS | |
	N	N	D
χ_{aa}	+1165.1(23) [a]	+1213.5(15) [a]	+94.8(26) [a]
$\chi_{bb} - \chi_{cc}$	+108.3(25)	+27.6(11) [b]	+175.8(11) [b]
χ_{bb}	−528.4(17) [a]	−593.0(9)	+40.5(14)
$\chi_{bb} = \chi_{yy}$	−636.7(16) [a]	−620.6(9)	−135.3(14)
$\chi_{aa} - \chi_{bb}$	+1693.5(37)	+1806.5(23)	+54.3(39)
$\chi_{zz} - \chi_{xx}$	+3819.(120)		+406.(4)
χ_{zz}	+2228.(60)	+2220.(60)	+270.6(28)
χ_{xx}	−1591.(60)	−1599.(60)	−135.3(14)
φ	31.8(16)°	30.9(16)°	41.2(15)°

| | HNC^{17}O | DNCO | |
	N	N	D
χ_{aa}	+2051.(13) [c]	+2123.7(15) [d]	+57.6(54) [d]
$\chi_{bb} - \chi_{cc}$	+1006.(19)	+1018.2(21) [d]	+227.4(22) [d]
χ_{bb}	−472.5(68) [c]	−552.8(13)	+84.9(29)
$\chi_{cc} = \chi_{yy}$	−1578.5(68)	−1571.0(13)	−142.5(29)
$\chi_{aa} - \chi_{bb}$	+2523.5(20)	+2676.5(23)	−27.3(81)
$\chi_{zz} - \chi_{xx}$	not determined		+428.(9)
χ_{zz}	not determined		+285.(6)
χ_{xx}	not determined		−142.5(29)
φ	24.7(24)°	23.2(24)°	46.9(7)°

[a] [1]; [b] this work; [c] [8]; [d] [5].

DNCS. While these values are themselves not sufficiently reliable to serve as a comparison, their difference, $\Delta\chi_-^N \equiv \chi_-^N(\text{DNCS}) - \chi_-^N(\text{HNCS})$, should be, because any errors are likely to cancel largely. However, Huber's value of $\Delta\chi_-^N = -36$ kHz does not make it possible to discriminate between the two possible assignments, $\Delta\chi_-^N = +67.5(13)$ kHz or $\Delta\chi_-^N = -80.7(13)$ kHz, the latter corresponding to $\chi_-(1) = \chi_-^D$ and $\chi_-(2) = \chi_-^N$.

Together with Rodler's value of $\chi_{aa}^N = 1213.5(15)$ kHz for DNCS [1], and using $\chi_-^N = +27.6$ kHz one finds $\chi_{cc}^N = -620.6(14)$ kHz, as compared to $\chi_{cc}^N = -636.7(16)$

kHz in HNCS [1]. The rather large discrepancy between these two values cannot readily be explained. It is quite unlikely that either Rodler's or our measurements are that much in error, given the experimental uncertainties of both frequencies and coupling constants of less than 2 kHz. Rather, one has to assume a molecular effect, possibly associated with the low-lying, large amplitude bending vibration.

Keeping this unexpected discrepancy of 16 kHz in mind, one can proceed to use the linear combinations

$$(\chi_{aa}^N - \chi_{bb}^N) = \frac{1}{2}(3\chi_{aa}^N - \chi_-^N) \qquad (1)$$

of both isotopomers to calculate the angle between the principal inertia and principal coupling axis systems. Taking this angle to be φ' for HNCS, and $\varphi'' = \varphi' - \Delta\varphi$ for DNCS, the derivation is as follows:

$$(\chi_{aa} - \chi_{bb})' = (\chi_{zz} - \chi_{xx}) \cdot \cos 2\varphi', \qquad (2a)$$

$$(\chi_{aa} - \chi_{bb})'' = (\chi_{zz} - \chi_{xx}) \cdot \cos 2\varphi''. \qquad (2b)$$

With $(\chi_{aa} - \chi_{bb})'/{''} \equiv \Delta\chi'/{''}$ and $(\chi_{zz} - \chi_{xx}) \equiv \Delta\chi$, the quotient of these equations is

$$\Delta\chi''/\Delta\chi' \qquad (3)$$

$$= [\cos 2\varphi' \cdot \cos 2\Delta\varphi + \sin 2\varphi' \cdot \sin 2\Delta\varphi]/\cos 2\varphi'.$$

Here it is assumed that $\Delta\chi$ dose *not* change upon isotopic substitution, unlike χ_{cc}; obviously, the following results may therefore be somewhat in error!

Substituting $\tan(x)$ for $\sin(x)/\cos(x)$, (3) transforms to

$$\Delta\chi''/\Delta\chi' = \cos 2\Delta\varphi + \tan 2\varphi' \cdot \sin 2\Delta\varphi,$$

or

$$\tan 2\varphi' = [\Delta\chi''/\Delta\chi' - \cos 2\Delta\varphi]/\sin 2\Delta\varphi. \qquad (4)$$

Since $\Delta\varphi$ can easily and accurately be obtained from the rotational constants of the two isotopomers [7], evaluation of φ', and therefore also φ'', is straightforward. However, since $\Delta\varphi$ is small (only 0.9537°), the uncertainty of the expression in square brackets in (4) (which is approximately the sum of the relative uncertainties of $\Delta\chi''$ and $\Delta\chi'$) is magnified to give the uncertainty in $\tan 2\varphi'$. According to Rodler et al. [1], $\Delta\chi' = (\chi_{aa}^N - \chi_{bb}^N)' = +1693.5(37)$ kHz, while $\Delta\chi''$ can be obtained from their value for $\chi_{aa}^N = +1213.5(15)$ kHz for DNCS and our value $\chi_-^N = +27.6(11)$ kHz to be 1806.5(39) kHz. With the value for $\Delta\varphi$ given above, and neglecting the experimental uncertainty in $\Delta\varphi$, which is probably well justified, the value of $\tan 2\varphi'$ is 2.02, while the resulting uncertainty is 0.11. With error propagation, the angle itself comes out as $\varphi' = 31.8(16)°$, giving $\varphi'' = 30.9(16)°$.

It is again unexpected that the value for φ' is *larger* than that calculated in the same manner for HNCO/DNCO ($\varphi' = 24.7(24)°$, based on the constants given in [5] and [8], and $\Delta\varphi = 1.5178°$ from the data in [9]); considering the bond angle opening upon substitution of O with S, this angle should *decrease!* The angle between the a-axis and the bisector of the HNC angle is 19.1° (taking Yamada's structure [3]), so that the nitrogen coupling tensor x-axis in HNCS is inclined by about 13(2)° with respect to the DNC angle bisector towards the NCS chain; HNCO does not show this feature (there, the angle between the a-axis and the HNC bisector [9] is about 22.6°, which is rather close to the tensor angle of $\varphi' = 24.7°$).

The principal coupling constant differences $(\chi_{zz} - \chi_{xx})$ can be evaluated from a bilinear expression, which can in turn be derived from (2) by adding the squared equations and subtracting their product, the latter multiplied by $2\cos 2\Delta\varphi$, followed by simplifying and reversing the resultant equation:

$$(\chi_{zz} - \chi_{xx})^2 \cdot \sin^2 2\Delta\varphi$$
$$= (\Delta\chi')^2 + (\Delta\chi'')^2 - 2\cos 2\Delta\varphi \cdot \Delta\chi' \cdot \Delta\chi'', \qquad (5)$$

while $(\chi_{zz} + \chi_{xx}) = -\chi_{yy} (= -\chi_{cc}$ in the case of an ab symmetry plane). With the experimental results, this yields

$$\chi_{xx}^N = -1591 \text{ kHz}, \quad \chi_{yy}^N = -637 \text{ kHz}, \quad \text{and}$$

$$\chi_{zz}^N = +2228 \text{ kHz (for HNCS)}, \quad \text{or}$$

$$\chi_{xx}^N = -1599 \text{ kHz}, \quad \chi_{yy}^N = -621 \text{ kHz}, \quad \text{and}$$

$$\chi_{zz}^N = +2220 \text{ kHz (for DNCS)}.$$

(Because $\chi_{yy}^N(\text{HNCS}) \neq \chi_{yy}^N(\text{DNCS})$, we get two sets of principal coupling constants; ideally, they should be identical.)

Here, the x-axis is close to the bisector, and the y-axis is perpendicular to the molecular plane. The uncertainty in $\Delta\chi^N$ is about 120 kHz; therefore the uncertainty in χ_{xx}^N and χ_{zz}^N is bout 60 kHz. Systematic errors, such as vibrational effects on $\Delta\chi'$ and $\Delta\chi''$, or on $\Delta\varphi$, are not accounted for and may be considerably larger.

The coupling constants of deuterium can be interpreted by first assuming that the coupling tensor is cylindrical (the same assumption had been made in [5]). Then, since $\chi_{cc}^D = -\frac{1}{2}(\chi_{aa}^D + \chi_-^D) = -\frac{1}{2}(94.8(26)$ kHz [1] + 175.8(11) kHz) = $-135.3(14)$ kHz is a principal value of this tensor $(=\chi_{yy}^D)$, a second principal value (χ_{xx}^D) is also $-135.3(14)$ kHz, and the remaining

principal value is $\chi_{zz}^D = +270.6(28)$ kHz. This is rather close to the value found in DNCO ($\chi_{zz}^D = +285(6)$ kHz [5]), and is thus reasonable. Comparing again the in-plane constants ($\chi_{aa}^D - \chi_{bb}^D$) and ($\chi_{zz}^D - \chi_{xx}^D$), whose ratio is just $\cos 2\varphi$ (see (2b); φ is the angle between the a- and z-axes), one finds $\varphi = 41.2°$, in good agreement with the angle of $43.3°$ between the a-axis and the DN internuclear axis [3]. Thus, the tensor is aligned with the bond, as one would expect, and as had been found in the case of DNCO, where the corresponding angles are $46.9(7)°$ from the coupling tensor and $49.2(17)°$ from the structure.

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