Nitrogen-14 Quadrupole Coupling Constants in Propanedinitrile, CH$_2$(CN)$_2$, by Microwave Spectroscopy

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Nitrogen-14 quadrupole hyperfine structure has been resolved in the microwave spectrum of propanedinitrile, CH$_2$(CN)$_2$. Measurements between 5 and 30 GHz by Fourier transform and Stark modulation spectroscopy have been analysed. The general matrix elements for nuclear quadrupole interaction in molecules containing two equivalent coupling nuclei have been derived as simple formulae.

The quadrupole coupling constants determined for the inertial axis system of CH$_2$(CN)$_2$ are $\zeta_{aa} = -2.368(28)$ MHz, $\zeta_{bb} = 0.318(20)$ MHz, and $\zeta_{cc} = 2.050(20)$ MHz. These values are used to establish that the electric field gradient tensor at nitrogen is cylindrically symmetric about the C ≡ N bond with a value of $\zeta_{CN} = -4.09(4)$ MHz, close to values found for other organic cyanides.

1. Introduction

Several small molecules containing the C ≡ N group have been studied by microwave spectroscopy [1, 1a]. In these studies the CN bond length shows a remarkably small range close to 1.158 Å [2]. More interestingly in the asymmetric top molecules the CN internuclear axis is found to be bent by a few degrees from the X–CN internuclear axis:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$(CN)$_2$</td>
<td>1.2(5)°</td>
</tr>
<tr>
<td>CH$_3$CH-CN</td>
<td>1.9(2)°</td>
</tr>
<tr>
<td>S(CN)$_2$</td>
<td>0.0(2)°</td>
</tr>
<tr>
<td>NF$_2$CN</td>
<td>6.1(2)°</td>
</tr>
<tr>
<td>PF$_2$CN</td>
<td>8.8(8)°</td>
</tr>
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</table>

The question arises whether the chemical bond strictly coincides with the internuclear axis, i.e. the question: Is a bent bond involved? The quadrupole coupling at the nitrogen nucleus provides a means of examining the triple bond environment in such cases.

The microwave spectrum of propanedinitrile (malononitrile) CH$_2$(CN)$_2$, has been extensively studied in the laboratory [10–13] as well as being detected from interstellar space in the comet Kohoutek [14]. Our structural studies of CH$_2$(CN)$_2$...

2. Experimental

A commercial sample of CH$_2$(CN)$_2$ (Aldrich Chemical Company) was used in the studies. Microwave transitions above 18 GHz were measured at Bristol, using a conventional 100 kHz Stark modulated spectrometer employing klystron and BWO sources (see Figure 1). At a later stage ten transitions below 18 GHz were measured under the very high resolution of microwave Fourier transform spectroscopy [29–31] at Kiel (see for example Figure 2). The Stark modulated measurements were made at room temperature while the Fourier transform work was carried out at –20 °C. The pressures were 10 mTorr and below 1 mTorr respectively.

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3. Theory and Spectroscopic Analysis

Quadrupole fine structure arising from two equivalent nitrogen-14 nuclei has been measured for the transitions given in Table 1. The total Hamiltonian may be written as

\[ H = H_R + H_Q, \tag{1} \]

where \( H_R \) is the rotational energy operator, and \( H_Q \) is the quadrupole interaction Hamiltonian for two nuclei given by

\[ H_Q = H_{Q1} + H_{Q2}. \tag{2} \]

It is convenient for the evaluation of the interaction Hamiltonian to express (2) as the sum of two scalar products of irreducible tensor operators [32–34]*:

\[ H_Q = V^{(2)}_1 \cdot Q^{(2)}_1 + V^{(2)}_2 \cdot Q^{(2)}_2. \tag{3} \]

For two nuclei with identical quadrupole coupling the appropriate vector coupling scheme is \( I_1 + I_2 = I \) and \( I + J = F \). The Hamiltonian of (2) and (3) can then be expressed in terms of the reduced matrix elements using Wigner 6-\( j \) symbols [35].

* The sign of [34] Chapt. 7.2 is used.
Table 1. Observed rotational transitions of CH₂(CN)₂ in the ground vibrational state showing ^14N quadrupole hyperfine structure. Transitions below 18 GHz have been measured with microwave Fourier transform spectroscopy and those above with 100 kHz Stark modulation spectroscopy. The calculated hyperfine structure has been obtained using the constants of Table 2.

<table>
<thead>
<tr>
<th>J</th>
<th>K₋</th>
<th>K₊</th>
<th>J'</th>
<th>K₋</th>
<th>K₊</th>
<th>F</th>
<th>I</th>
<th>F'</th>
<th>I'</th>
<th>Observed/MHz</th>
<th>Obs-calc/MHz</th>
<th>Weight</th>
<th>νq/MHz</th>
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<tbody>
<tr>
<td>4</td>
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<td>4</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>5 045.964</td>
<td>−0.001</td>
<td>1.000</td>
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<tr>
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<td>1</td>
<td>4</td>
<td>7</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>11 176.925</td>
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</tr>
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<td>8</td>
<td>2</td>
<td>7</td>
<td>2</td>
<td>17 413.510</td>
<td>0.012</td>
<td>1.000</td>
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<td>1</td>
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<td>10</td>
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<tr>
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<td>2</td>
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<td>2</td>
<td>17</td>
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<td>3</td>
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<td>18 266.790</td>
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<td>18 266.790</td>
<td>0.102</td>
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<td>18 266.790</td>
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</tbody>
</table>

Note: The table entries include observed transitions, calculated transitions, weight, and quadrupole coupling constants (νq).
We obtain

\[
(F_{M_F}J\tau I I_1 I_2 | Q J) = \mathcal{W} \cdot \{ (J \tau | V^{(2)}_2 | J' \tau') (I I_1 I_2 | Q^{(2)}_1) \} + \{ (J \tau | V^{(2)}_2 | J' \tau') (I I_1 I_2 | Q^{(2)}_2) \}.
\]  

(4)
the interaction Hamiltonian are thus given by
\[
(F M F J \tau I I_1 I_2 | H_{Q_1} + H_{Q_2}, F M F J' \tau' I' I_1 I_2)
= (-1)^{F+I-J} \sqrt{(2 I + 1) (2 J' + 1)}
\begin{pmatrix}
  \frac{1}{4} & \frac{1}{2} & 1 & 1
\end{pmatrix}
\begin{pmatrix}
  I_1 & I_1 & 2 & 1
\end{pmatrix}
\begin{pmatrix}
  I_1 & 1 & 0 & -I_1
\end{pmatrix}
\begin{pmatrix}
  I_2 & 2 & I_2
\end{pmatrix}
\begin{pmatrix}
  I_2 & 2 & I_2
\end{pmatrix}
\]
with
\[
e Q_{J} = \langle I, M_f = I | Q_{J} | I, M_i = I \rangle
= (-1)^{2I} \left( \begin{array}{ccc}
  I_1 & 2 & I_1
\end{array} \right) (I_1 | Q_{J} | I_1)
\]
and
\[
q_{J,2}(i) = \langle J \tau M_J = J | V_{i,0} | J' \tau' M_J = J \rangle
= (-1)^{J' + J} \left( \begin{array}{ccc}
  I' & 2 & J
\end{array} \right) (J_0 | V_{i,0} | J' _2)
\]
\[i = 1, 2.
\]
The round brackets denote Wigner 3-\( j \) symbols [36] and the curved brackets Wigner 6-\( j \) symbols.

If for two equivalent nuclei we substitute
\[
e Q_1 q_{J_1}(1) = e Q_2 q_{J_2}(2) = e Q q_{J,2} \quad \text{and} \quad I_1 = I_2 = I_0 \quad (\equiv I_0)
\]
in (5), the matrix elements are reduced to
\[
\langle F M F J \tau I I_0 I_0 | H_{Q_1} + H_{Q_2}, F M F J \tau I I_0 I_0 \rangle
= W_{Q_0+Q_0}(I_0, I)
\]
\[
= (-1)^{2J} 2 e Q q_{J,2} \left( \frac{1}{2} C (C + 1) - I (I + 1) J (J + 1) \right)
J (2J - 1) (2I - 1) (2I + 3)
\]
\[
= \frac{1}{2} \left( I^2 + I - 1 \right) - I_0 (I_0 + 1)
I_0 (2 I_0 - 1)
\]
\[\text{(6)}\]
and
\[
\langle F M F J \tau I I_0 I_0 | H_{Q_1} + H_{Q_2}, F M F J \tau I + 2 I_0 I_0 \rangle
= (-1)^{2J} \frac{3}{16} e Q q_{J,2} \frac{[F + I + J + 3] (F + I + J + 2) (F - I + J) (F - I + J - 1)]^{1/2}}{(2I + 3) [2I + 5] (2I + 1)]^{1/2}}
\frac{[F + I + J + 2] (F + I + J + 1) (-F + I + J + 2) (-F + I + J + 1)]^{1/2}}{J (2J - 1)}
\frac{[(I + 2 I_0 + 3) (I + 2 I_0 + 2) (2 I_0 - 1) (2 I_0 - I_0)]^{1/2}}{I_0 (2 I_0 - 1)}
\]
\[\text{(7)}\]
where
\[
C = F (F + 1) - I (I + 1) - J (J + 1).
\]

Elements with \( \Delta I = 1 \) are zero.

Equation (6) may be compared with the diagonal matrix element \( W_{Q_0}(I) \) of the quadrupole interaction Hamiltonian for a single coupling nucleus with the spin \( I \):
\[
W_{Q_0+Q_0}(I_0, I)
= (-1)^{2I} 4 \frac{l \frac{1}{2} (I^2 + I - 1) - I_0 (I_0 + 1)}{I_0 (2 I_0 - 1)}
\]
\[\text{(8)}\]
where \( W_{Q_0+Q_0}(I_0, I) \) and \( W_{Q_0}(I) \) are the diagonal elements for two equivalent coupling nuclei with spin \( I_0 \) and total spin \( I \) and a single one with spin \( I \) respectively. For \( CH_2(CN)_2 \) \( I_0 = 1 \) and the expressions derived for the quadrupole energies agree with those given in reference [23].

A computer program has been written to calculate quadrupole splittings based on (6) and (7). Ten highly resolved transitions measured by Fourier transform spectroscopy have been combined with eleven transitions measured by Stark spectroscopy. A total of 94 quadrupole components have been analysed by least squares fitting in terms of \( e Q q_{aa} \) and the asymmetry parameter \( s = (\chi_{bb} - \chi_{cc})/\chi_{aa} \) (see Table 2). As shown in Table 1 the Stark spectrometer measurements have been included in the fit with a small weighting.

| A/MHz | 20 882.7537(8) |
| B/MHz | 2 942.3003(16) |
| C/MHz | 2 616.7225(16) |
| \(\chi_{aa}\)/MHz | -2.368(28) |
| \(\eta\) | 0.7311(83) |
| \(\sigma\)/kHz | 3.4 |
| \(\chi_{aa}/\eta\) | 0.92 |

Table 2. Rotational and quadrupole coupling constants of \( CH_2(CN)_2 \). The rotational constants \( A, B \) and \( C \) are from [12]. \( s \): standard deviation of the fit, \( |\chi_{aa}/\eta| \): correlation between \( \chi_{aa} \) and \( \eta \); least squares errors in brackets as one standard deviation in units of the last digit.
reflecting the lower resolution and precision of that work; nevertheless the inclusion of these transitions gives a significant improvement in the accuracy of the coupling constants derived. The weighting factors adopted are not critical and a very satisfactory fit to the patterns has been obtained, see Table 1 and Figs. 1 and 2.

The fit shows that a first order treatment is sufficient. So off-diagonal elements in J have been neglected. The second-order quadrupole perturbation terms in \( \mathcal{Z}_{ab} \) have been tried but do not improve the fit; these terms are insignificant because no appropriate near-degeneracies occur. Such is the quality of the present fit that it has not been thought worthwhile to include spin-rotation terms in the analysis.

Assignment of the \( F \) components in the patterns was made by comparison of synthesized and observed spectra using a curve plotter. Experimental half-widths were used in the calculations. In calculating relative intensities it was important to consider the nuclear spin statistical weights. CH\(_3\)(CN)\(_2\) has \( C_{2v} \) symmetry with three pairs of equivalent nuclei; one pair of fermions and two pairs of bosons. The total wavefunction has to change sign for the symmetry operation of rotation of 180° about the \( b \)-axis. For the ground vibronic state the ratio of statistical spin weights is 15:21 comparing rotational transitions with \((K_- + K_+)\) even for the upper and lower energy level to transitions with \((K_- + K_+)\) odd. When the nitrogen quadrupole splitting of a single rotational transition is considered, these weights are divided as follows: If \((K_- + K_+)\) is even for both levels, we get a ratio of \( 5:9:1 \) for the \( I = 2, 1 \) and \( 0 \) states respectively; for \((K_- + K_+)\) being odd the ratio is \( 15:3:3 \). Thus the statistical weights have a pronounced effect on the nitrogen-14 patterns. Moreover for the \( (I = 0, 2) \) states for \( J = F \), the mixing of wavefunctions through the \( \Delta I = 2 \) matrix element (Eq. (7)) has to be taken into account to obtain the correct frequencies and relative intensities.

4. Discussion

The analysis yields the quadrupole coupling constants at the nitrogen nuclei in the inertial principal axis system. These values may be used to test the cylindrical symmetry of the electric field gradient tensor along the \( C \equiv N \) bonds. Assuming this cylindrical symmetry to exist, the three \( \mathcal{Z}_{ab} \) values allow three independent values of \( \mathcal{Z}_{CN} \) to be derived from the equation

\[
\mathcal{Z}_{xy} = \frac{1}{2} (3 \Phi_g^2 - 1) \mathcal{Z}_{CN},
\]

where \( \Phi_g \) is the direction cosine relating the \( C \equiv N \) axis with the inertial principal axis \( g = a, b \) and \( c \). \( \mathcal{Z}_{cc} \) leads directly to \( \mathcal{Z}_{CN} = -4.10(4) \) MHz, and taking \( \Phi_b = \cos 58.0° \) from the structure determination \([4]\) \( \mathcal{Z}_{ab} \) and \( \mathcal{Z}_{bb} \) give values of \( \mathcal{Z}_{CN} = -4.09(5) \) and \( -4.04(25) \) MHz respectively. The excellent agreement among these values for \( \mathcal{Z}_{CN} \) firmly establishes that the electric field gradient tensor at nitrogen is cylindrically symmetry about the \( C \equiv N \) bond within the accuracy of the hyperfine measurements. The average value of \( \mathcal{Z}_{CN} \) obtained, \( -4.09(4) \) MHz, is very close to the values found for CH\(_3\)CN \( \left( \mathcal{Z}_{CN} = -4.21(2) \right. \) MHz \([37]\)\), CH\(_2\)CH\(_2\)CN \( \left( \mathcal{Z}_{CN} = -4.14(4) \right. \) MHz \([5, 6, 38]\)\) and other organic cyanides.

The quadrupole coupling results for CH\(_2\)(CN)\(_2\) are very interesting in view of the structural result \([3, 4]\) that the \( C \equiv N \) groups are bent away from each other by 4°. Both the \( C \equiv N \) bond length \( 1.156(2) \) Å \([4]\) and the local bonding symmetry about the nitrogen atom appear to be practically unchanged by the angular distortion. The chemical bonding of the cyano group is relatively unaffected by the hydrocarbon group to which it is attached, strengthening arguments about the localised nature of the bonding in the \( C \equiv N \) linkage. The situation is very different in S(CN)\(_2\) where appreciable asymmetry in the quadrupole coupling about the CN bond is found \([7]\). This finding together with the short SC bond length is taken as an indication for a significant \( \pi \)-back bonding with sulphur.

Acknowledgements

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[35] Ref. [34], Chapter 6.2.

[36] Ref. [34], Chapter 3.7.
