# Nitrogen Quadrupole Coupling in Ethyl Isocyanide, $C_2H_5NC$

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In this paper we present a $^{14}$N-quadrupole hyperfine structure analysis for ethyl isocyanide, $CH_3CH_2NC$, by use of microwave Fourier transform spectroscopy. For earlier works as e.g. $CH_3NC$ [1], such narrow splittings as they are met with in the case of the isonitriles had to be measured employing a maser beam spectrometer.

Only few rotational spectra of isocyanides have so far been investigated for their nitrogen nuclear quadrupole hyperfine structure (hfs) [1–3] because of the very narrow splittings.

We continued the series with ethyl isocyanide, $CH_3CH_2NC$, by using microwave Fourier transform (MWFT) spectroscopy [2, 4–6].

The substance was prepared according to [7].

The spectra were recorded at a temperature of − 68 °C and pressures below 1 mTorr. An example is given in Figure 1. As ethyl isocyanide was assigned and first investigated by Anderson and Gwinn [8] and later by Bolton et al. [9], we could easily assign the lines we wanted to measure by MWFT spectroscopy. These lines, which are contained in Table 1 of this paper, were checked for consistency with those of Table I of [8] and those of Table 3 of [9] performing a first order centrifugal distortion analysis. Fitting the three rotational constants $A$, $B$, and $C$ and the five centrifugal distortion parameters $D_J$, $D_{JK}$, $D_K$, $d_1$ and $d_2$ to the experimental line centres, we used the following Hamiltonian operator according to Watson's S-reduction [10, 11]:

$$\begin{aligned} H = {} & ((X' + Y')/2)\, P^2 + (Z' - (X' + Y')/2)\, P_z^2 \\ & + ((X' - Y')/4)\, (P_+^2 + P_-^2) - D_J\, P^4 - D_{JK}\, P^2\, P_z^2 \\ & - D_K\, P_z^4 + d_1\, P^2\, (P_+^2 + P_-^2) + d_2\, (P_+^4 + P_-^4) \qquad (1) \end{aligned}$$

with $P_\pm = P_x \pm i\,P_y$ and $X'$, $Y'$, $Z'$: rotational constants $A$, $B$, $C$ in the order given by the representation used.

The experimental centre frequencies $\nu_0$ and their fitting errors $\delta\nu_{\text{calc-exp}}$ are listed in Table 1, and the results of the centrifugal distortion analysis are

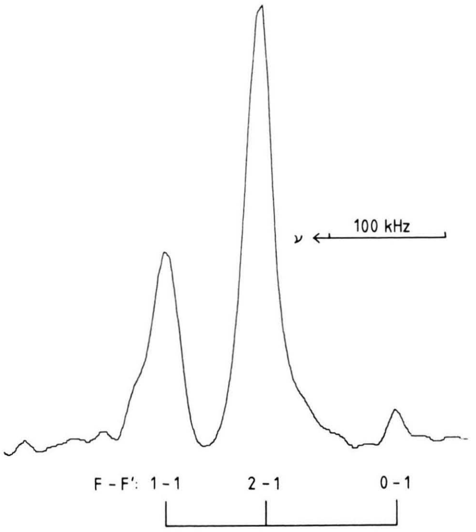

Fig. 1. A range of 400 kHz out of a 10 MHz-scan of the rotational spectrum of ethyl isocyanide. $J_{K_-K_+}\,J'_{K'_-K'_+} = 1_{01} - 0_{00}$; power spectrum, sample interval: 50 ns, 2560 K cycles, 1024 data points supplemented with 3072 zeros, microwave polarizing frequency: $\nu_{\text{MW}} = 9677.5$ MHz; pressure: $p = 0.1$ mTorr, temperature: $T = -68$ °C.

included in Table 2 together with those of the $^{14}$N-nuclear quadrupole hfs analysis which is discussed in the following section.

To reduce frequency errors due to overlapping lines, we simulated the multiplet pattern for each rotational transition and extracted corrected hyperfine structure component frequencies $\nu_{\text{sim}}$ [12].

From the splittings of these components $\nu_{\text{sim}}$ relative to the most intense hfs line for each transition*, we determined with first order theory the quadrupole coupling constants $\chi_+ = \chi_{bb} + \chi_{cc}$ and $\chi_- = \chi_{bb} - \chi_{cc}$ by a least squares fit. No line within

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* In Table 1 we do not give the splittings explicitly.

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Table 1. Measured transitions of ethyl isocyanide, $C_2H_5NC$.

| $J\ K_-K_+ - J'\ K'_-K'_+$ | $F - F'$ | $\nu_{\mathrm{exp}}$ | $\nu_{\mathrm{sim}}$ | $\nu_{\mathrm{sim}} - \nu_0$ | $\delta\nu_{\mathrm{calc\text{-}exp}}$ | $\nu_0$ | $\delta\nu_{\mathrm{calc\text{-}exp}}$ |
|---|---|---|---|---|---|---|---|
| 1 0 1 − 0 0 0 | 2 − 1 | 9679.186 | 9679.187 | −0.013 | 0.000 | 9679.200 | −0.023 |
| | 1 − 1 | 9679.265 | 9679.262 | 0.062 | 0.001 | | |
| | 0 − 1 | 9679.066 | 9679.074 | −0.126 | −0.001 | | |
| 2 0 2 − 1 0 1 | 3 − 2<br>2 − 1 | 19348.217 | 19348.219 | −0.006 | 0.002 | 19348.225 | −0.036 |
| | 1 − 0<br>2 − 2 | 19348.297 | 19348.296 | 0.071 | −0.002 | | |
| 2 1 1 − 1 1 0 | 3 − 2 | 19913.883 | 19913.881 | −0.012 | −0.003 | 19913.893 | 0.048 |
| | 2 − 1 | 19913.958 | 19913.954 | 0.061 | 0.002 | | |
| 2 1 2 − 1 1 1 | 3 − 2 | 18803.190 | 18803.190 | −0.019 | 0.003 | 18803.209 | −0.123 |
| | 2 − 1 | 18803.285 | 18803.275 | 0.066 | −0.003 | | |
| 3 0 3 − 2 1 2 | 4 − 3<br>2 − 1 | 6899.714 | 6899.715 | −0.010 | −0.002 | 6899.725 | 0.177 |
| | 3 − 2 | 6899.750 | 6899.750 | 0.025 | 0.002 | | |
| 4 1 3 − 4 1 4 | | 5552.162 | | | | 5552.162 | 0.241 |
| 5 1 4 − 5 1 5 | | 8325.686 | | | | 8325.686 | −0.406 |
| 6 2 4 − 7 1 7 | 7 − 8<br>5 − 6 | 8507.998 | 8507.997 | 0.009 | 0.001 | 8507.988 | 0.000 |
| | 6 − 7 | 8507.965 | 8507.968 | −0.020 | −0.001 | | |

$\nu_{\mathrm{exp}}$: experimental frequency, $\nu_{\mathrm{sim}}$: by line shape analysis corrected frequency, $\nu_0$: unsplit rotational centre frequency; frequencies, splittings and deviations in MHz.

Table 2. Rotational [MHz], centrifugal distortion [kHz] and nitrogen-14 hfs [kHz] constants of ethyl isocyanide.

| | $CH_3CH_2NC$ | Correlation matrix | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $A$ | 27856.82(18) | 1.00 | | | | | | | |
| $B$ | 5117.334(33) | 0.39 | 1.00 | | | | | | |
| $C$ | 4561.834(31) | 0.65 | 0.80 | 1.00 | | | | | |
| $D_J$ | −2.4(13) | 0.49 | 0.88 | 0.83 | 1.00 | | | | |
| $D_{JK}$ | −25.6(52) | 0.01 | 0.20 | 0.17 | −0.05 | 1.00 | | | |
| $D_K$ | $97.44(15) \cdot 10^3$ | 0.78 | 0.24 | 0.48 | 0.45 | −0.44 | 1.00 | | |
| $d_1$ | −2.26(14) | 0.38 | −0.40 | 0.12 | −0.31 | 0.14 | 0.41 | 1.00 | |
| $d_2$ | −4.81(92) | 0.41 | −0.41 | −0.09 | −0.35 | −0.26 | 0.65 | 0.78 | 1.00 |
| $N$ | 25 | | | | | | | | |
| $\sigma$ | 222 | | | | | | | | |
| $\chi_+$ | −253.2(59) | 1.00 | | | | | | | |
| $\chi_-$ | 42(15) | −0.05 | 1.00 | | | | | | |
| $N$ | 6 | | | | | | | | |
| $\sigma$ | 5 | | | | | | | | |
| $\overline{\Delta\nu_{\mathrm{exp}}}$ | 70 | | | | | | | | |
| $\chi_{aa}$ | 253.2(59) | | | | | | | | |
| $\chi_{bb}$ | −106(11) | | | | | | | | |
| $\chi_{cc}$ | −148(11) | | | | | | | | |

$N$: number of lines, $\sigma$: standard deviation of the fits [kHz], $\overline{\Delta\nu_{\mathrm{exp}}}$: mean experimental hfs splitting [kHz]; standard errors in units of the last digit in brackets.

Table 3. Comparison of the $^{14}$N-quadrupole coupling constants [MHz] of isonitriles and nitriles.

| Molecule | Reference | $\chi_{aa}$ | $\chi_{bb}$ | $\chi_{cc}$ |
|---|---|---|---|---|
| $CH_3NC$ | [1] | 0.4894(4) | $\underline{-0.2447(2)}$ | $\underline{-0.2447(2)}$ |
| $CH_3CH_2NC$ | this work | 0.2532(59) | −0.106(11) | $\underline{-0.148(11)}$ |
| $CH_2{=}CHNC$ | [2] | 0.258(5) | −0.258(6) | $\underline{0.000(6)}$ |
| $C_3H_5NC$ | [3] | 0.331(3) | $\underline{-0.128(9)}$ | −0.204(9)* |
| $CH_3CN$ | [13] | −4.22534(73) | $\underline{2.11267(37)}$ | $\underline{2.11267(37)}$ |
| $CH_3CH_2CN$ | [14] | −3.309(33) | 1.265(13) | $\underline{2.044(20)}$ |
| $CH_2{=}CHCN$ | [15] | −3.7800(21) | 1.6798(55) | $\underline{2.1002(55)}$ |
| $C_3H_5CN$ | [16] | −3.453(11) | $\underline{1.759(16)}$ | 1.694(27) |

Underlined values: $\chi_{gg}$'s with $g$ perpendicular to the symmetry plane of the molecule.
* Misprinted in [3] Table 3.

the range of our spectrometer is sensitive to $\chi_{ab}$. The standard error of the fit in 5 kHz and the mean experimental splitting 70 kHz.

The experimental unsplit line frequencies $\nu_0$ were obtained by calculating the arithmetic mean of the hfs components $\nu_{\text{sim}}$ for each line corrected with the calculated deviation from the rigid rotor frequency. The hfs predicting calculation was based on the analysis described above.

In Table 3 we give a comparison of the isonitriles investigated for $^{14}$N-quadrupole coupling and the analogous nitriles. Unfortunately the structure of most molecules is not known precisely, nor could $\chi_{ab}$ or $\chi_{ac}$ be determined, which would both have opened the possibility to get the coupling constants in a bond system. So only the $\chi_{gg}$'s with $g$ perpendicular to the symmetry plane of the molecule can be compared. These are roughly one tenth in the case of the isonitriles compared to the nitriles, which is due to the charge distribution being nearer to central symmetry for isonitriles. The variation of the $\chi_{gg}$-values within the isonitriles is equal in trend to that within the nitriles with the exception of $CH_2{=}CHX$, X=NC, CN. For the isonitriles the relative variation is slightly larger in magnitude, which reflects the closer neighbourhood of the substituents to the $^{14}$N-nucleus.

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