Quadrupole Hyperfine Structure of the Direct *l*-Type Doubling Spectrum of Hydrogen Cyanide by Microwave Fourier Transform Spectroscopy

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The direct *l*-type doublet transitions for $v_2 = 1$ of HCN, DCN and $DC^{15}N$ have been measured between 4 and 16 GHz under very high resolution by microwave Fourier transform spectroscopy. Analysis of the nitrogen-14 hyperfine structure of the transitions of HCN and DCN has required an extension of the Hamiltonian previously used. Accurate values of the *l*-type doublet constants are reported.

Introduction

The direct *l*-type doubling microwave transitions of hydrogen cyanide in the $v_2 = 1$ state have been investigated by several authors [1, 2]. In only two studies has highly resolved fine structure been measured with great precision, both methods employing molecular beam techniques. Radford and Kurtz [3] used an electric resonance maser spectrometer to measure the $J = 1$ transition at 449 MHz giving precise measurement of the hyperfine structure arising from both the nitrogen nucleus and the proton. Tomasevich and Klemperer [4] have obtained equally precise results in the same transition using a conventional molecular beam apparatus. In the present paper we report high resolution studies of a series of direct *l*-type doublet transitions using microwave Fourier transform spectroscopy (MWFT). The nitrogen-14 quadrupole fine structure is reported for $H^{12}C^{14}N$ ($\Delta J = 0$ for J values 4–8) and for $D^{12}C^{14}N$ (J values 5–9, with 8 and 9 partially resolved). In addition the $J = 5–9$ transitions have been measured for $D^{12}C^{15}N$.

Experimental

The spectra were recorded with a microwave Fourier transform spectrometer described elsewhere [5–7]. The hydrogen cyanides were prepared with the isotopes of potassium cyanide and sulphuric acid or perdeutero sulphuric acid. The spectra were recorded at temperatures between −20 and −52 °C and pressures below 0.5 mTorr.

Spectroscopic Analysis

The lowest excited vibrational state for HCN corresponds to the degenerate bending motion $v_2 = 1$ and lies $\sim 712\ \text{cm}^{-1}$ above the ground state. The associated vibration-rotation states ($l = \pm 1$) are sufficiently populated even at dry-ice temperatures and give rise to a strong yet sparse spectrum of lines throughout the radiofrequency and microwave regions. The corresponding R-branch spectra begin at much higher microwave frequencies [1]. For $v_2 = 1$ vibration-rotation interaction gives rise to *l*-type doubling of the energy levels corresponding to symmetric (+) and antisymmetric (−) admixtures of wavefunctions containing those of the $l = \pm 1$ states where the l quantum number governs the vibrational angular momentum $l\hbar$. The separation of the *l*-doublets is given approximately by $q^{(0)} J (J + 1)$, where J is the total rotational angular momentum quantum number and $q^{(0)}$ is the well-known *l*-type doubling constant. The selection rules are: $\Delta J = 0$, $\Delta l = 0$, $+ \leftrightarrow -$. For HCN $q^{(0)}$ is large (~ 224.5 MHz); hence the $\Delta J = 0$ transitions begin at 449 MHz for $J = 1$ and continue from 4488 to 16148 MHz for the $J = 4–8$ transitions studied in the present experiments. Most of the transitions are

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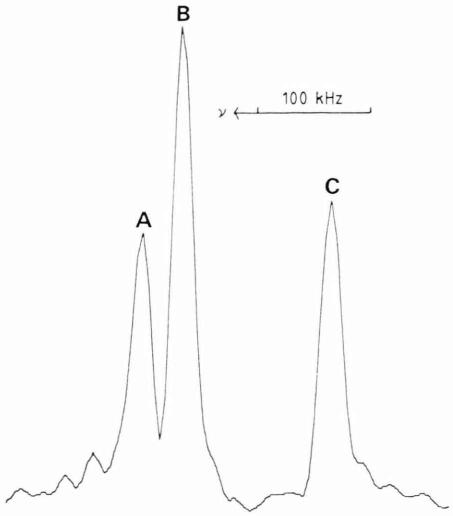

Fig. 1. Direct *l*-type doubling transition, $J = 5$, of HCN in the microwave Fourier transform power spectrum: $A = 6731.982$ MHz, $B = 6731.946$ MHz and $C = 6731.810$ MHz. A range of 400 kHz out of a 10 MHz scan is given. Sampling interval 50 ns, 1280 K cycles, 1024 data points supplemented by 3072 zeros prior to Fourier transformation, microwave signal frequency: $\nu_{\mathrm{MW}} = 6731$ MHz, pressure 0.08 mTorr, temperature −23 °C.

observed as triplets resulting mainly from the ^{14}N quadrupole interaction (see Figure 1). The hyperfine Hamiltonian may be written as [3]:

$$H = H_Q + C_1 \boldsymbol{I}_1 \cdot \boldsymbol{J} + C_2 \boldsymbol{I}_2 \cdot \boldsymbol{J}\,. \tag{1}$$

H_Q is the dominant term and corresponds to the electric quadrupole interaction of the ^{14}N nucleus with the charges of the remainder of the molecule; the terms given via parameters C_1 and C_2 express the spin-rotation magnetic coupling of the nitrogen and hydrogen nuclei, respectively. The appropriate coupling scheme couples $\boldsymbol{I}_1$ to $\boldsymbol{J}$ to give $\boldsymbol{F}_1 = \boldsymbol{I}_1 + \boldsymbol{J}$ and then $\boldsymbol{F} = \boldsymbol{F}_1 + \boldsymbol{I}_2$. $\boldsymbol{F}$ is a good quantum number, whereas $\boldsymbol{F}_1$, $\boldsymbol{J}$, $\boldsymbol{I}_1$ and $\boldsymbol{I}_2$ are assumed to be good quantum numbers. The level scheme for $J = 5$ is schown in Figure 2. The quadrupole energy is given by [3]:

$$W_Q = e\,Q\,q\left[\frac{3 - J(J+1)}{J(J+1)} \pm \frac{\eta}{2}\right] f(I_1, J, F_1)\,, \tag{2}$$

where η is the asymmetry parameter of the electric field gradient at nitrogen and f represents Casimir's function. The ± sign corresponds to the parity of the admixture of *l*-type doublet wavefunctions designated Π_J^+ or Π_J^-. Radford [3] asserts on the basis of vibration-rotation perturbation that for HCN Π_J^- is the upper state in which case η turns out to be positive and therefore $e\,Q\,q\,\eta$ negative, as shown in Figure 2. The first-order magnetic energies are given by

$$\begin{aligned} W_M = \frac{C_1}{2}\,&[F_1(F_1+1) - J(J+1) - I_1(I_1+1)] \\ &+ C_2\,[4F_1(F_1+1)]^{-1} \\ &\cdot [F_1(F_1+1) + J(J+1) - I_1(I_1+1)] \\ &\cdot [F(F+1) - F_1(F_1+1) - I_2(I_2+1)]\,. \end{aligned} \tag{3}$$

The direct spin-spin interaction has been ignored because of the large distance between the H and N nuclei in HCN, as has the electron coupled spin-spin interaction. The C_1 and C_2 constants will not

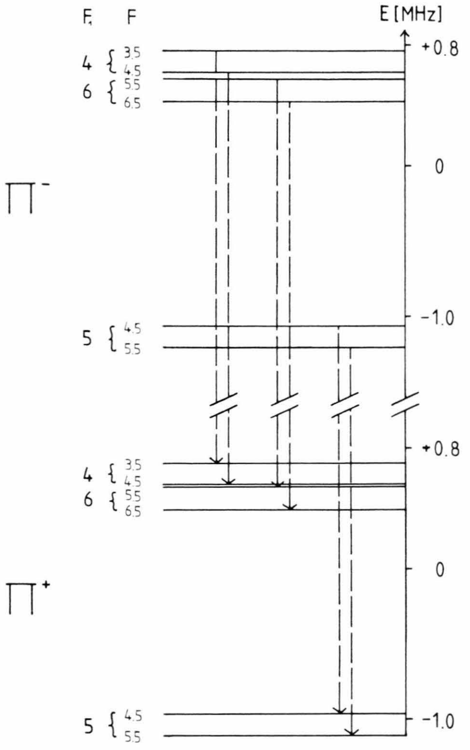

Fig. 2. Hyperfine structure components giving rise to the $J = 5$ *l*-type doubling spectrum shown in Figure 1. Only the strong $\Delta F = 0$ components observed in the power spectrum have been illustrated. The energy level scheme corresponds to a negative value of $e\,Q\,q\,\eta$ for the likely case that Π_J^- is the upper state making η positive. Data used for scheme was taken from [3]: $e\,Q\,q = -4809.2$ kHz, $\eta = 0.08155$, $C_1 = 12.2$ kHz and $C_2 = -27.3$ kHz.

strictly be single parameters because the molecule now has angular momentum about the linear axis; in the symmetric-top approximation C_1 and C_2 would be in the form

$$C = C_\perp - \frac{C_\parallel - C_\perp}{J(J+1)} l^2.$$

If we treat the excited bending state as a slightly asymmetric rotor then the coupling constants C_a, C_b and C_c with respect to the principal inertial axes will be involved and C_1 and C_2 take the form

$$C = \frac{1}{J(J+1)} \sum_{g=a,b,c} C_g \langle \boldsymbol{J}_g^2 \rangle. \tag{4}$$

The magnetic coupling is not expected to show up directly in the observed $\Delta J = 0$ spectra because only $\Delta F = \Delta F_1 = 0$ components are strong enough to be observed in the Fourier transform power spectrum. Nevertheless a small magnetic contribution to the splittings is indicated by the analysis below, and is believed to arise from the dependence of C_1 on the vibration-rotation state $\Pi_J^{\pm}$.

The experimental frequencies are given in Table 1 together with splittings measured from simulated spectra. Splittings close in magnitude to the line width at half height (22 kHz in the present experiment) come out too wide when applying the Fourier transform technique. For this reason carefully simulated splittings rather than the direct measurements have been analysed in this work. The hypothetical centres of the transitions obtained from an analysis of the hyperfine structure with an accuracy of ≦ 2 kHz are given opposite each transition. If we analyse the triplets simply in terms of the quadrupole interaction the close-lying doublets (for example A and B in Fig. 1) are calculated systematically closer by about 4 kHz than the observed splitting. This effect having been carefully confirmed as molecular in origin probably arises from the over-simplified form of the magnetic coupling given in (3). The anomalies in the close splittings have been accounted for by allowing the magnetic coupling coefficient at nitrogen, C_1, to be slightly different in the Π_J^+ and Π_J^- states. Coupling to the proton is unlikely to account for the additional widening of the small splitting. ΔC_1 produces a shift of the N-hfs components. ΔC_2 would lead to a splitting of those components, which has not been observed; these splittings would be expected to be well within the present line widths and not able to cause observable shifts of the quadrupole components. Therefore the term connected to C_2 in (3) has been neglected. The simulated splittings in Table 1 for HCN have therefore been fitted with an average value of $|eQq\eta| = 392(5)$ kHz and ΔC_1

Table 1. Measured and calculated *l*-type doublets of hydrogen cyanide. Simulated Fourier transform splittings have been fitted using values of $|eQq\eta|$ and ΔC_1 given in Table 2. For the centre frequencies of the patterns the residual of the least squares fit (observed-calculated in kHz) is given in brackets; see Table 2 for the constants of the fit.

Molecule	J–J'	F–F'	Experimental ν [MHz]	Simulated $\Delta\nu$ [kHz]	Calculated $\Delta\nu$ [kHz]	Hypothetical centre ν_0 [MHz]
HCN	4–4	4–4	4 488.373	− 97	− 98	4.488.471(−1)
		5–5	4 488.503	33	34	
		3–3	4 488.546	71	72	
	5–5	5–5	6 731.810	− 99	− 98	6 731.911(0)
		6–6	6 731.946	36	36	
		4–4	6 731.982	68	67	
	6–6	6–6	9 423.232	− 98	− 98	9 423.333(−1)
		7–7	9 423.370	38	37	
		5–5	9 423.400	64	65	
	7–7	7–7	12 562.257	−103	− 98	12 562.361(0)
		8–8	12 562.402	42	38	
		6–6	12 562.428	65	63	
	8–8	8–8	16 148.443	−101	− 98	16 148.544(2)
		9–9 7–7	16 148.595	51	47	
DCN	5–5	5–5	5 583.658	− 85	− 85	5 583.745(1)
		6–6	5 583.776	31	32	
		4–4	5 583.806	58	57	
	6–6	6–6	7 816.048	− 85	− 85	7 816.134(−1)
		7–7	7 816.166	34	33	
		5–5	7 816.190	54	55	
	7–7	7–7	10 419.703	− 85	− 85	10 419.789(−1)
		8–8	10 419.825	33	34	
		6–6	10 419.841	53	53	
	8–8	8–8	13 394.253	− 81	− 85	13 394.342(0)
		9–9	13 394.385	38	34	
		7–7		55	52	
	9–9	9–9	16 739.278	− 88	− 85	16 739.370(2)
		10–10	16 739.416	38	35	
		8–8		54	52	

Molecule	J–J'	Experimental ν [MHz]	Calculated ν [MHz]
$DC^{15}N$	5–5	5 280.620	5 280.620
	6–6	7 391.855	7 391.855
	7–7	9 854.231	9 854.231
	8–8	12 667.411	12 667.412
	9–9	15 831.012	15 831.011

Table 2. Molecular parameters for hydrogen cyanide in the $v_2 = 1$ state. The least squares error for the q values is expressed in brackets as one standard deviation in units of the last digit. The errors for the hyperfine parameters indicate the spread of values for the transitions analysed ($J = 4-6$ for HCN and $J = 5-7$ for DCN). The $J = 1$ centre frequency has been included from [3] for the centrifugal distortion fit of HCN.

	$\lvert eQq\,\eta \rvert$ [kHz]	ΔC_1 [kHz]	$q^{(0)}$ [MHz]	$q^{(1)}$ [kHz]
HCN	392(5)	0.35(10)	224.476814(33)	2.65978(75)
DCN	339(2)	0.17(15)	186.190723(34)	2.19716(59)
DC^{15}N	–	–	176.080923(14)	2.00893(22)

(lower-upper) = 0.35 kHz. For DCN the average values $\lvert eQq\,\eta \rvert = 339(2)$ kHz and $\Delta C_1 = 0.17$ kHz have been obtained. There is some evidence from the $J = 7$ and $J = 8$ transitions of HCN that $\lvert eQq\,\eta \rvert$ increases with J, but the scatter is too large to establish the J-dependence.

The hypothetical centres, ν_0 in Table 1, for all three species have been fitted within experimental error ($< \pm 2$ kHz) to the first-order centrifugal distortion expression [2, 9]

$$\nu_0 = q^{(0)} J(J+1) - q^{(1)} J^2 (J+1)^2. \tag{5}$$

This expression is analogous to that for transitions between K-doublet levels of a centrifugally distorted sligthly asymmetric rotor [10] for $K_{-1} = \boldsymbol{l} = 1$ where $q^{(0)} \cong (B - C)/2$ and $q^{(1)} \cong 2\delta_J$. The constants resulting from the fits are given in Table 2. The $q^{(0)}$ values for HCN and DC ^{15}N closely agree with the less accurate values of [2]; the $q^{(1)}$ values also precisely agree although the $q^{(2)} J^3 (J+1)^3$ term, included there, is not justified for the present range of transitions. The agreement is less good for DCN [1, 2].

Discussion

The present Fourier transform measurements on HCN indicate that the simple hyperfine energy expression used by Radford [3] in his analysis at $J = 1$ is not sufficient for the analysis of hyperfine splittings at higher J values. The modification introduced here is to allow a change of the magnetic coupling parameter C_1 with $\Pi_J^{\pm}$ vibration-rotation state. This parameter is expected to depend on the rotational state [8]. In addition it shows a vibrational change from 10.4 → 12.2 kHz in going from the ground state [11] to the $0\,1^1\,0$ state in HCN [3]. The change of 0.4 kHz between Π_J^+ and Π_J^- state seems quite reasonable therefore. The modification suggested here is quite undetectable in the $J = 1$ spectrum because the $F = 0 \rightarrow 0$ transition is forbidden and terms of the type ΔC_1 are totally correlated with terms in $\lvert eQq\,\eta \rvert$. For this reason the precise values of $\lvert eQq\,\eta \rvert = 392.2(16)$ kHz [3] or 395.1(27) kHz [4] obtained in the molecular beam work for $J = 1$ may be subject to a systematic error comparable with the statistical errors quoted in those studies. Similar molecular beam or maser work is desirable at higher J values to establish the additional term in the Hamiltonian and the J dependence of the constants suggested by the present work.

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