Nuclear Shielding and Magnetic Hyperfine Structure of Hydrogen Cyanide [1]

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A millimeter-wave molecular beam maser has been used to resolve the magnetic hyperfine structure of hydrogen cyanide. The spin–rotation interaction constants have been measured for the three nuclei ^{14}N, ^{13}C, and H. The paramagnetic nuclear shielding factors have been calculated for the three nuclear sites. The spin–rotation constants for ^{14}N in $H^{12}C^{14}N$, for H in $H^{12}C^{14}N$ and for ^{13}C in $D^{13}C^{14}N$ are $+10.4$ kHz, -3.7 kHz, and $+15.0$ kHz, respectively. The respective paramagnetic shielding factors are -408.98×10^{-6}, -73.40×10^{-6}, and -249.52×10^{-6}.

I. INTRODUCTION

A millimeter-wave molecular beam maser has been used to resolve the magnetic hyperfine structure of hydrogen cyanide. The small splitting due to the interaction of the hydrogen nucleus with the molecular magnetic field has been resolved and the interaction due to ^{13}C has been observed in $D^{13}C^{14}N$. The interaction due to the ^{14}N nucleus has been reported previously. These measurements make possible the calculation of the hyperfine constants for all isotopic forms of hydrogen cyanide containing H, D, ^{13}C, and ^{14}N. A knowledge of the spin–rotation constants which result from the analysis of this spectra allows evaluation of both the diamagnetic and paramagnetic contributions to the nuclear shielding.

II. HYPERFINE THEORY

The theory of hyperfine interactions in molecules containing two or more interacting nuclei has been discussed by several authors (1, 2). The hyperfine Hamiltonian of $H^{12}C^{14}N$ may be written

$$\mathcal{H} = \bar{V}(N) \cdot \bar{Q}(N) + \bar{m}(N) \cdot \underline{\mu}(N) + \bar{m}(H) \cdot \underline{\mu}(H). \qquad (1)$$

The spin–spin interaction between the hydrogen and nitrogen nuclei is negligibly small due to the $1/r^3$ dependence of the interaction and the large hydrogen–nitrogen separation. Since the nitrogen interaction is much larger than the hydrogen interaction, the coupling scheme

$$\mathbf{J} + \mathbf{I}_N = \mathbf{F}_N$$

$$\mathbf{F}_N + \mathbf{I}_H = \mathbf{F}_H = \mathbf{F}$$

is the most convenient. The matrix elements are

$$\langle \tau' J I_N F_N | \bar{\mathbf{V}}(N) \cdot \bar{\mathbf{Q}}(N) | \tau J I_N F_N \rangle = (-1)^{J+I_N+F_N}(eQq_J)_{^{14}N} f(J) f(I_N)$$

$$\times \begin{Bmatrix} F_N & I_N & J \\ 2 & J & I_N \end{Bmatrix}, \quad (2)$$

$$\langle \tau' J I_N F_N | \bar{\mathbf{m}}(N) \cdot \bar{\mathbf{\mu}}(N) | \tau J I_N F_N \rangle = (-1)^{J+I_N+F_N}(C)_{^{14}N} h(J) h(I_N)$$

$$\times \begin{Bmatrix} F_N & I_N & J \\ 1 & J & I_N \end{Bmatrix}, \quad (3)$$

$$\langle \tau' J I_N F'_N I_H F_H | \bar{\mathbf{m}}(H) \cdot \bar{\mathbf{\mu}}(H) | \tau J I_N F_N I_H F_H \rangle = (-1)^{J+I_N+I_H+2F_N+F_H+1}(C)_H h(J) h(I_H)$$

$$\times [(2F_N + 1)(2F'_N + 1)]^{\frac{1}{2}} \begin{Bmatrix} J & F'_N & I_N \\ F_N & J & 1 \end{Bmatrix} \begin{Bmatrix} F_H & I_H & F'_N \\ 1 & F_N & I_H \end{Bmatrix}, \quad (4)$$

where

$$f(J) = \left[\frac{(2J + 1)(2J + 2)(2J + 3)}{8J(2J - 1)} \right]^{\frac{1}{2}},$$

$$h(I) = [I(I + 1)(2I + 1)]^{\frac{1}{2}},$$

$$(eQq_J) = -(eQq)\frac{J}{2J + 3}.$$

Analysis of the spectrum of this isotopic species yields values for the hydrogen and nitrogen spin–rotation constants.

The ^{13}C spin–rotation interaction was studied in $D^{13}C^{14}N$ rather than in $H^{13}C^{14}N$ because it was felt that the wide (~ 40 kHz) deuterium quadrupole splitting would aid in separating the ^{13}C spin–rotation interaction from the rest of the spectra. The hyperfine Hamiltonian for $D^{13}C^{14}N$ may be written

$$\mathcal{H} = \bar{\mathbf{V}}(N) \cdot \bar{\mathbf{Q}}(N) + \bar{\mathbf{m}}(N) \cdot \bar{\mathbf{\mu}}(N) + \bar{\mathbf{V}}(D) \cdot \bar{\mathbf{Q}}(D) + \bar{\mathbf{m}}(D) \cdot \bar{\mathbf{\mu}}(D)$$
$$+ \bar{\mathbf{m}}(C) \cdot \bar{\mathbf{\mu}}(C) + \mathbf{I}_D \cdot \bar{\mathbf{D}} \cdot \mathbf{I}_C + \mathbf{I}_N \cdot \bar{\mathbf{D}} \cdot \mathbf{I}_C. \quad (5)$$

In the coupling scheme

$$\mathbf{J} + \mathbf{I}_N = \mathbf{F}_N,$$

$$\mathbf{F}_N + \mathbf{I}_D = \mathbf{F}_D,$$

$$\mathbf{F}_D + \mathbf{I}_C = \mathbf{F}_C = \mathbf{F},$$

both nitrogen matrix elements are identical to those for $H^{12}C^{14}N$ above. The remaining matrix elements are

$$\langle \tau' J I_N F'_N I_D F_D | \bar{\mathbf{V}}(D) \cdot \bar{\mathbf{Q}}(D) | \tau J I_N F_N I_D F_D \rangle$$

$$= (-1)^{J+I_N+I_D+2F_N+F_D}(eQq_J)_D f(J) f(I_D)[(2F_N + 1)(2F'_N + 1)]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} J & F'_N & I_N \\ F_N & J & 2 \end{Bmatrix} \begin{Bmatrix} F_D & I_D & F'_N \\ 2 & F_N & I_D \end{Bmatrix}, \quad (6)$$

$$\langle \tau' J I_N F'_N I_D F_D | \bar{\mathbf{m}}(D) \cdot \bar{\mathbf{u}}(D) | \tau J I_N F_N I_D F_D \rangle$$

$$= (-1)^{J+I_N+I_D+2F_N+F_D+1}(C)_D h(J) h(I_D)[(2F_N + 1)(2F'_N + 1)]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} J & F'_N & I_N \\ F_N & J & 1 \end{Bmatrix} \begin{Bmatrix} F_D & I_D & F'_N \\ 1 & F_N & I_D \end{Bmatrix}, \quad (7)$$

$$\langle \tau' J I_N F'_N I_D F'_D I_C F_C | \bar{\mathbf{m}}(C) \cdot \bar{\mathbf{u}}(C) | \tau J I_N F_N I_D F_D I_C F_C \rangle$$

$$= (-1)^{J+I_N+I_D+I_C+F_N+F'_N+2F_D+F_C}(C)_{^{13}C} h(J) h(I_C)[(2F_N + 1)(2F'_N + 1)$$

$$\times (2F_D + 1)(2F'_D + 1)]^{\frac{1}{2}} \begin{Bmatrix} J & F'_N & I_N \\ F_N & J & 1 \end{Bmatrix} \begin{Bmatrix} F'_N & F'_D & I_D \\ F_D & F_N & 1 \end{Bmatrix} \begin{Bmatrix} F_C & I_C & F'_D \\ 1 & F_D & I_C \end{Bmatrix}, \quad (8)$$

$$\langle \tau' J I_N F_N' I_D F'_D I_C F_C | \mathbf{I}_D \cdot \mathbf{D} \cdot \mathbf{I}_C | \tau J I_N F_N I_D F_D I_C F_C \rangle$$

$$= (-1)^{F_D+I_C+F_C+J+I_N+F_N+1}[(15/2)(2F_D + 1)(2F'_D + 1)(2F_N + 1)(2F'_N + 1)]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} F_C & I_C & F'_D \\ 1 & F_D & I_C \end{Bmatrix} \begin{Bmatrix} J & F'_N & I_N \\ F_N & J & 2 \end{Bmatrix} \begin{Bmatrix} F'_N & F_N & 2 \\ I_D & I_D & 1 \\ F'_D & F_D & 1 \end{Bmatrix}$$

$$\times \langle J \| D^{(2)} \| J \rangle \langle I_C \| I_C \| I_C \rangle \langle I_D \| I_D \| I_D \rangle \quad (9)$$

where

$$\langle J \| D^{(2)} \| J \rangle = \langle J J | D_0^{(2)} | J J \rangle \left[\frac{(2J + 1)(2J + 2)(2J + 3)}{(2J)(2J - 1)} \right]^{\frac{1}{2}}$$

and

$$\langle I_\alpha \| I_\alpha \| I_\alpha \rangle = [(I_\alpha + 1)(2I_\alpha + 1)]^{\frac{1}{2}},$$

$$\langle \tau' J I_N F'_N I_D F_D' | \mathbf{I}_N \cdot \bar{\mathbf{D}} \cdot \mathbf{I}_C | \tau J I_N F_N I_D F_D \rangle$$

$$= (-1)^{F_D+I_C+F_C+F'_N+I_D+F_D}[(15/2)(2F'_D + 1)(2F_D + 1)(2F_N + 1)(2F'_N + 1)]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} F_C & I_C & F'_D \\ 1 & F'_D & I_C \end{Bmatrix} \begin{Bmatrix} F'_N & F'_D & I_D \\ F_D & F_N & 1 \end{Bmatrix} \begin{Bmatrix} J & J & 2 \\ I_N & I_N & 1 \\ F'_N & F_N & 1 \end{Bmatrix}$$

$$\times \langle J \| D^{(2)} \| J \rangle \langle I_N \| I_N \| I_N \rangle \langle I_C \| I_C \| I_C \rangle. \quad (10)$$

EXPERIMENTAL

The $J = 1 \rightarrow 0$ rotational transition, which falls in the 3 mm region, is particularly well suited for this investigation. Since the $J = 0$ state has no hyperfine splitting, the beam maser spectrum is an energy level diagram of the $J = 1$ state and is simply related to the spectral constants. The millimeter-wave molecular beam maser used in this experiment is a modification of one described previously (3). The molecular beam is formed in a multiple beam nozzle source and is state selected by stacked quadrupole fields. These beams then interact with the microwave field in a tunable Fabry-Perot cavity. The resolution of a molecular beam maser is ultimately limited by the time of
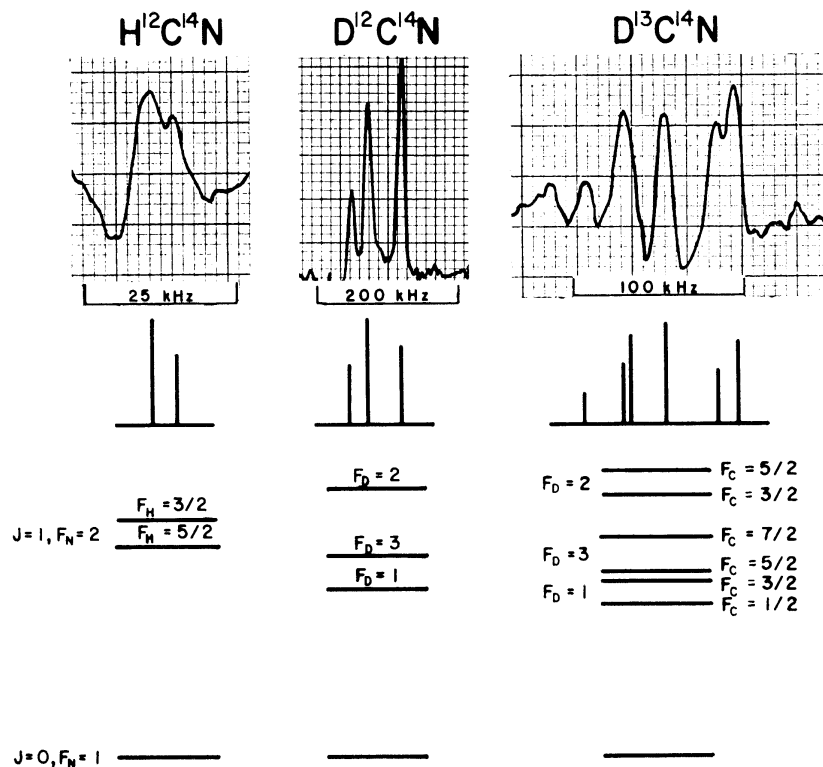
FIG. 1. Effects of isotopic substitution upon the hyperfine spectra of hydrogen cyanide.

flight of the molecules in the microwave field. The diameter of the microwave cavity mode was increased to about 10 cm by increasing the radius of curvature of one cavity plate and by increasing the length of the cavity. The interaction between the molecules and the microwave field is observed by means of a one-klystron superheterodyne system, frequency modulated at 1 kHz. The signal is recovered by a phase sensitive amplifier operating at 2 kHz.

Table I. Hyperfine Structure of $J=1 \to 0$, $F_N = 2 \to 1$ Transition

Upper State	Observed (kHz)	Calculated (kHz)	Difference (kHz)
F_H	$H^{12}C^{14}N$		
5/2	-1.84	-1.84	--
3/2	2.78	2.78	--
F_D, F_{13_C}	$D^{13}C^{14}N$		
1, 3/2 ⎱ 3, 5/2 ⎰	-34.36	-33.24	-1.12
3, 7/2	-11.46	-10.58	-0.88
2, 3/2	19.52	18.20	1.32
2, 5/2	32.57	31.89	0.68

Table II. Hyperfine Constants

$$H^{12}C^{14}N$$

$$C_N \quad = \quad 10.4 \pm 0.3 \text{ kHz}^{a}$$

$$C_H \quad = \quad -3.7 \pm 0.3 \text{ kHz}^{b}$$

$$D^{13}C^{14}N$$

$$(eQq_{J})_D \quad = \quad -38.8 \pm 0.4 \text{ kHz}^{c}$$

$$C_D \quad = \quad -0.6 \pm 0.3 \text{ kHz}^{c}$$

$$C_{13_C} \quad = \quad 15.0 \pm 1.0 \text{ kHz}$$

[a] Ref. 3.

[b] Ramsey has obtained a value of

±4.6 ± 1.0, Ref. 5.

[c] Calculated from data of Ref. 3.

In practice it is possible to detect $D^{13}C^{14}N$ in natural abundance (^{13}C) and to resolve the hydrogen splitting in $H^{12}C^{14}N$ of 4.6 kHz.

RESULTS

The coupling scheme for both $H^{12}C^{14}N$ and $D^{13}C^{14}N$ is well defined and the intermediate quantum numbers F_i, are approximately good quantum numbers. While di-

Table III. Contributions to Hydrogen Nuclear Shielding

$$\sigma_{AV} \quad = \quad 28.32 \times 10^{-6}\ ^{a}$$

$$\sigma_{AV}^{p} \quad = \quad -73.40 \times 10^{-6}\ ^{b}$$

$$\sigma_{AV}^{d} \quad = \quad 101.72 \times 10^{-6}\ ^{c}$$

$$\sigma_{AV}^{d} \quad = \quad 101.64 \times 10^{-6}\ ^{d}$$

$$\sigma_{AV}^{d} \quad = \quad 100.27 \times 10^{-6}\ ^{e}$$

$$\sigma_{AV}^{d} \quad = \quad 97 \quad \times 10^{-6}\ ^{f}$$

$$\sigma_{AV}^{d} \quad = \quad 95.13 \times 10^{-6}\ ^{g}$$

[a] From chemical shift data, Ref. 8.

[b] Calculated from molecular geometry and spin-rotation constant by use of Eq. (13).

[c] Experimental value calculated from Eq. (11) and the values of σ_{AV} and σ_{AV}^{p} above.

[d] Ref. 10.

[e] Ref. 11.

[f] Ref. 12.

[g] Ref. 13.

agonalization of the Hamiltonian is still required, the effect of each interaction is clearly identifiable and relatively independent of other interactions. The ^{14}N electric quadrupole interaction is by far the largest hyperfine interaction and results in a triplet pattern which is observable in an ordinary gas absorption spectrometer. Figure 1 shows the effects of the various isotopic substitutions when the $F_N = 2 \rightarrow 1$ component is investigated under high resolution interaction.

Table I shows the observed hyperfine splittings for $H^{12}C^{14}N$ and $D^{13}C^{14}N$. The hydrogen spin–rotation constant was determined by simply adjusting its value such that the calculated splitting in the $H^{12}C^{14}N$ spectrum equaled the experimental value. For $D^{13}C^{14}N$ the values of $(eQq_J)_D$ and C_D from Ref. (3) were used while the contributions of the spin–spin interactions were calculated from the molecular geometry. Variation of the value of C_{13_C} allowed all observable hyperfine components to be fit with an rms deviation of 1.0 kHz. The corresponding spectral constants are shown in Table II.

DISCUSSION

Nuclear shielding theory as developed by Ramsey (4, 5) involves two effects, a simple diamagnetic term which may be calculated from a knowledge of the ground state molecular wavefunctions and a more complex paramagnetic term which may be related to the spin–rotation interaction.

$$\sigma_{av} = \sigma_{av}{}^d + \sigma_{av}{}^p, \tag{11}$$

$$\sigma_{av}{}^d = (e^2/3mc^2)\langle \psi^0 | \sum_i r_i^{-1} | \psi^0 \rangle, \tag{12}$$

$$\sigma_{av}{}^p = - (e^2/3mc^2)\left(\sum_\alpha \frac{Z_\alpha}{r_\alpha} + \frac{h}{4\mu_N^2 g_I M_p} \sum_{\alpha=1}^{3} \frac{I_\alpha C_{\alpha\alpha}}{2} \right). \tag{13}$$

Table IV. Contributions to Carbon and Nitrogen

Nuclear Shielding (X 10^6)

	$\sigma_{AV}{}^p$	$\sigma_{AV}{}^d$	σ_{AV}
Carbon	-249.52[a]	326.75[b]	77.23[c]
		322.29[d]	72.77[c]
Nitrogen	-408.98[a]	377.62[b]	-31.36[c]
		375.22[d]	-33.76[c]
		381[e]	-28[c]

[a]Calculated from molecular geometry and spin-rota-

tion constant by use of Eq. (13).

[b]Ref. 10. Very similar values are obtained by use of

the simple relations of Ref. 11.

[c]Calculated from Eq. (11) and the values of $\sigma_{AV}{}^p$

and $\sigma_{AV}{}^d$ above.

[d]Ref. 13.

[e]Ref. 12.

Sign convention consistent with Ref. (6) has been used and for linear molecules $C_{11} = C_{22}$ $=C$. It should be remarked that the above theory neglects vibrational effects (as discussed by Hinderman and Cornwall (7)). The total shielding σ_{av} may be obtained directly from chemical shift measurements. Such a measurement for H in HCN has been made and the resulting value for σ_{av} appears in Table III (8). Calculation of the paramagnetic term requires a knowledge of the molecular excited state wavefunctions or a knowledge of the spin rotation constants $C_{\alpha\alpha}$. Chan and Das (9) have performed a calculation for H in HCN using the former method to obtain $\sigma_{av}{}^p = -101 \times 10^{-6}$. Results of calculations based upon Eq. (13) and our measured values of the spin-rotation constants for HCN appear in Tables III and IV.

The diamagnetic shielding is calculable from molecular ground state wavefunctions. It is also possible to deduce a value for $\sigma_{av}{}^d$ from the experimentally determined values of σ_{av} and $\sigma_{av}{}^p$ by use of Eq. (11). Results of these two approaches for the hydrogen shielding appear in Table III. The variation among the several values may result directly from approximations in the calculations of the several values of $\sigma_{av}{}^d$, from uncertainties in the values of $\sigma_{av}{}^p$ and σ_{av}, or from a combination of both. It should be pointed out that since the contribution of the spin rotation constant to $\sigma_{av}{}^p$ is quite small in the case of hydrogen, this constant would have to vary significantly from any of the reported values in order for the $\sigma_{av}{}^d$ calculated from $\sigma_{av}{}^p$ and σ_{av} to be as low as 95 ppm. It should also be pointed out that a change in σ_{av} would affect this value. In order to make a similar comparison in Table IV for the ^{13}C and ^{14}N nuclei, the value of σ_{av} from chemical shift data would be required.

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