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Microwave Spectrum and Molecular Constants of Hydrogen Cyanide*

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Precision measurements of the frequencies of the $J=0\rightarrow1$ transition of $HC^{12}N^{14}$, $HC^{13}N^{14}$, $DC^{12}N^{14}$, and $DC^{13}N^{14}$ have been made with multiples of a 10-mc/sec. frequency monitored by Station WWV. The B_0 and I_0 values are, respectively: 44300.83 mc and 18.93_{790} g cm$^2\times10^{-40}$ for $HC^{12}N^{14}$; 43154.83 and 19.44_{080} for $HC^{13}N^{14}$; 36207.40 and 23.17_{108} for $DC^{12}N^{14}$; 35587.57 and 23.57_{465} for $DC^{13}N^{14}$. The interatomic distances determined are $d_{CH}=1.061$A and $d_{CN}=1.157$A. The nuclear quadrupole coupling of N^{14} is determined as 4.58±0.05 mc/sec.

THE light-weight linear molecule, HCN, has been carefully investigated with optical spectroscopy.[1] In fact, among the polyatomic molecules its spectrum is one of those most accurately measured by optical techniques. Nevertheless, the newly developed microwave methods are capable of extending significantly the accuracy of certain of its molecular constants.

Using the instruments and techniques previously developed in this laboratory[2] for the wave-length region below four millimeters, we have measured the frequencies of the first rotational lines ($J=0\rightarrow1$ transition) to seven figures for the different isotopic species $HC^{12}N^{14}$, $DC^{12}N^{14}$, $HC^{13}N^{14}$, and $DC^{13}N^{14}$. Only the first two of these species have been investigated with optical spectroscopy. In the preliminary microwave investigations by Smith, Gordy, Simmons, and Smith,[2(a)] the first rotational line of $HC^{12}N^{14}$ was detected, and an approximate measurement was made with a cavity wave meter. The present work extends the range of precision frequency measurements to the region of 88,000 Mc.

The radiation source used was a crystal multiplier which produced harmonics of energy from a Raytheon klystron. The second harmonic was used for measurements on DCN, and the third harmonic for those on HCN. Coin silver K-band wave guide was used for the cell, with tapered transition sections to couple it to the H-band components. The frequency measurements were made with multiples of a ten-megacycle crystal oscillator continuously monitored by Station WWV, of the Bureau of Standards.[3]

In Table I are listed the measured frequencies of the various lines. The $J=0\rightarrow1$ rotational line of each molecule is split into a triplet hyperfine structure by the nuclear quadrupole coupling of N^{14}. This structure for $DC^{12}N^{14}$ is shown in Fig. 1, where the calculated hyperfine structure is compared with the cathode-ray trace of the observed lines.

The rotational energy of a linear molecule in the ground vibrational state is

$$E_r(\text{cm}^{-1})=B_0J(J+1)-DJ^2(J+1)^2.$$

With the Bohr relation and the selection rule, $\Delta J=1$, this gives the frequency of the first line as

$$\nu(\text{cm}^{-1})=2B_0-4D.$$

The centrifugal stretching constant D cannot be evaluated from the present measurements. Fortunately, since we are dealing with the $J=0\rightarrow1$ line, the centrifugal effects are very small and can be neglected entirely without affecting the accuracy of the molecular structure determination. However, D has been evaluated approximately from the higher rotational lines in the optical region. In determining the B_0 and I_0 values for each of the isotopic forms, the value $D=3.3\times10^{-6}$ cm^{-1} given for HCN by Herzberg[4] was used. The resulting

TABLE I. Observed line frequencies.

Molecule	Transition	ν (mc/sec.)
	$J=0\rightarrow1$	
$HC^{12}N^{14}$	$F\rightarrow F'$	
	$1\rightarrow0$	88603.56±0.30
	$1\rightarrow2$	88601.49
	$1\rightarrow1$	88600.11
$HC^{13}N^{14}$	$1\rightarrow0$	88311.54±0.30
	$1\rightarrow2$	86309.49
	$1\rightarrow1$	86308.12
$DC^{12}N^{14}$	$1\rightarrow0$	72416.68±0.20
	$1\rightarrow2$	72414.62
	$1\rightarrow1$	72413.25
$DC^{13}N^{14}$	$1\rightarrow0$	71177.02±0.20
	$1\rightarrow2$	71174.96
	$1\rightarrow1$	71173.58

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[1] (a) G. Herzberg and J. W. T. Spinks, Zeits. f. Physik **91**, 386 (1934); (b) P. F. Bartunek and E. F. Barker, Phys. Rev. **48**, 516 (1935); (c) Herzberg, Patat, and Verleger, Zeits. f. Physik **102**, 1 (1936); (d) E. Lindholm, Zeits. f. Physik **108**, 454 (1938); (e) G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 391.

[2] (a) Smith, Gordy, Simmons, and Smith, Phys. Rev. **75**, 260 (1949); (b) W. Gordy, Rev. Mod. Phys. **20**, 668 (1948).

[3] The method of monitoring is described in reference 2(b).

[4] G. Herzberg, reference 1(e), p. 393.

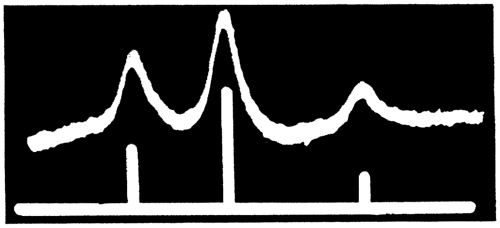

FIG. 1. Calculated and observed hyperfine structure of the $J=0\rightarrow1$ transition of $DC^{12}N^{14}$.

TABLE II. Molecular constants.*

Molecule	ν_0 (mc/sec.)	B_0 (Mc/sec.)	I_0 (g cm$^2\times10^{-40}$)
$HC^{12}N^{14}$	88601.26	44300.83	18.93_{790}
$HC^{13}N^{14}$	86309.26	43154.83	19.44_{080}
$DC^{12}N^{14}$	72414.39	36207.395	23.17_{108}
$DC^{13}N^{14}$	71174.73	35587.565	23.57_{465}

* The ν_0 represents the frequency of the $J=0\rightarrow1$ rotational line corrected for hyperfine splitting. In computing B_0 from ν_0, D was taken as 0.1 mc. The value of h used in computing I_0 is $6.624_2\times10^{-27}$ erg-sec.

TABLE III. Molecular dimensions* of hydrogen cyanide determined from different isotopic combinations.

Molecular pair used	CH or CD distance (10^{-8} cm)	CN distance (10^{-8} cm)
$DC^{12}N^{14}-DC^{13}N^{14}$	1.0817	1.1500
$HC^{12}N^{14}-HC^{13}N^{14}$	1.0665	1.1561
$DC^{12}N^{14}-HC^{13}N^{14}$	1.0610	1.1571
$DC^{12}N^{14}-HC^{12}N^{14}$	1.0605	1.1573
$HC^{13}N^{14}-DC^{13}N^{14}$	1.0593	1.1575
$HC^{12}N^{14}-DC^{13}N^{14}$	1.0586	1.1577
	Av. 1.0647	Av. 1.1560

* The constants used in these calculations are: $M_{\mathrm{H}}=1.00813$, $M_{\mathrm{D}}=2.01473$, $M_{\mathrm{C}^{12}}=12.00386$, $M_{\mathrm{C}^{13}}=13.00761$, $M_{\mathrm{N}^{14}}=14.0075$, all in a.m.u.; $h=6.6242\times10^{-27}$ erg-sec. and the unit atomic mass $M=1.6599\times10^{-24}$ g.

B_0 values are listed in Table II with the frequencies of the hypothetical unsplit rotational lines, ν_0, and the moments of inertia.

The moment of inertia of hydrogen cyanide may be expressed in terms of its structural parameters as

$$I=\frac{1}{M_{\mathrm{H}}+M_{\mathrm{C}}+M_{\mathrm{N}}}\{M_{\mathrm{H}}M_{\mathrm{C}}d_{\mathrm{CH}}^2+M_{\mathrm{C}}M_{\mathrm{N}}d_{\mathrm{CN}}^2+M_{\mathrm{H}}M_{\mathrm{N}}(d_{\mathrm{CH}}+d_{\mathrm{CN}})^2\},$$

where the subscript H refers to H or D and the subscript C to C^{12} or C^{13}. With the available data, four independent equations can be written which can be combined in six different ways to yield values of d_{CH} and d_{CN}. Because of the differences in zero point energies of the different isotopes, the interatomic distances for the ground vibrational state depend somewhat on the mass of the isotope. This unfortunate circumstance prevents the use of microwave data on different isotopic combinations for highly accurate structural determinations, except in rare instances where it is possible to determine equilibrium values of B. From the degree of consistency of the results obtained with different isotopic combinations one can estimate the probable error arising from this effect.

It is apparent from an examination of Table III that the results are reasonably consistent except for the combination $DC^{12}N^{14}-DC^{13}N^{14}$. This pair gives an anomalously large d_{CD} in comparison with the d_{CH} determined from $HC^{12}N^{14}-HC^{13}N^{14}$. The implication is that the d_{CD} in this case is actually longer than the d_{CH} since the pairs are identical except for the difference in D and H. The probable error is greatest for $DC^{12}N-DC^{13}N$ since here the isotope changed is nearest the center of gravity. However, the difference appears too great to be accounted for entirely by experimental error. In choosing the most probable value for the d_{CH} and d_{CN} we omit those for $DC^{12}N-DC^{13}N$ and average those for the remaining five combinations. The resulting values are: $d_{\mathrm{CH}}=1.061_3$A, $d_{\mathrm{CN}}=1.157_1$A. The average deviations are 0.002A and 0.0005A, respectively. The average deviations from these values become 0.005A and 0.0015A, respectively, when the values from $DC^{12}N-DC^{13}N$ are included.

The optical spectroscopy measurements included $DC^{12}N^{14}$ and $HC^{12}N^{14}$ only. The most recent values from optical spectroscopy, $d_{\mathrm{CH}}=1.058_7$ and $d_{\mathrm{CN}}=1.157_4$, are from Herzberg.[5] These are in excellent agreement with the ones determined here from the same pair of isotopes.

The N^{14} nuclear quadrupole coupling constant, $eQ\partial^2V/\partial z^2$ is, within the experimental error, the same for all the different isotopic combinations studied. Table IV lists the values obtained from measurements

TABLE IV. Nuclear quadrupole coupling of N^{14} in HCN.

Molecule	N^{14} nuclear coupling $eQ\partial^2V/\partial z^2$ (mc/sec.)
$HC^{12}N^{14}$	4.58_5
$HC^{13}N^{14}$	4.56_5
$DC^{12}N^{14}$	4.57_5
$DC^{13}N^{14}$	4.59_5
	Av. 4.58_0

TABLE V. Comparison of N^{14} nuclear quadrupole coupling and CN length in HCN with those in the halogen cyanides.

Molecule	CN length (A)	N^{14} nuclear coupling (mc/sec.)
HCN	1.157	4.58[a]
ICN	1.159	3.80[b]
BrCN	1.160	3.83[b]
ClCN	1.163	3.67[b]

[a] Present work.

[b] From Smith, Ring, Smith, and Gordy, Phys. Rev. 74, 370 (1948), and Townes, Holden, and Merritt, Phys. Rev. 74, 1113 (1948).

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[5] G. Herzberg, reference 1(e).

on the different molecules. The average value $4.58_0 \pm 0.050$ is slightly lower than the earlier less accurate value.[2] Table V compares the nuclear coupling in HCN with that in the halogen cyanides. The higher value for HCN reveals a small but definite difference in the electronic structure of the CN bond. A slight difference is also revealed by the shorter CN distance for HCN shown in Table V.

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On the Emission Bands of CCl

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Some new bands of CCl are recorded and these together with those reported by earlier workers are arranged in a vibrational scheme. The electronic transition is $^2\Sigma \rightarrow {}^2\Pi$, the doublet separation for the $^2\Pi$ state being 138 cm^{-1}. By way of comparison it is mentioned that the uncondensed transformer discharge gave CF_2 bands in the case of CF_4, CCl, and Cl_2 bands in the case of CCl_4 and only Br_2 bands in CBr_4. It is pointed out that the supposed CBr bands reported by Durie and Iredale are not due to CBr but due to Br_2.

FLOWING vapor of carbon tetrachloride was excited by an uncondensed transformer discharge and the spectrum obtained was photographed on Medium Hilger quartz and E_1-quartz (Littrow type) spectrographs. Besides the continuous bands of Cl_2 and the CCl bands reported by earlier workers,[1–3] some extra bands of CCl were recorded. The wave-lengths and the wave numbers together with the estimated intensities of the band heads, which are all degraded to shorter wave-lengths, are given in Table I. The intense bands were photographed in the second order of a 21-ft. Wadsworth mounting grating spectrograph, and the rotational structure of the bands could be seen, but the dispersion is not high enough to make any rotational analysis.

All the new bands, marked*, together with those reported by earlier workers can be arranged in the vibrational scheme shown in Table II, which represents an extension of the analysis of Asundi and Karim.[1] The electronic transition, as suggested by Asundi and Karim, appears to be $^2\Sigma \rightarrow {}^2\Pi$, $^2\Pi$ being the ground state. The doublet separation $^2\Pi_{3/2} - {}^2\Pi_{1/2}$ is 138 cm^{-1}. From the analysis the Q heads can be fairly well represented by the following formula.

$$\nu = \left.\begin{matrix} 35834 \\ 35972 \end{matrix}\right\} + (866v' - 1.5v'^2) - (845v'' - 1.0v''^2).$$

Horie[3] gave a vibrational analysis of the CCl bands** which does not appear to be satisfactory for the following reasons: (1) Some of the extra bands obtained in the present experiments, namely 34098, 34169, and 36012 cm^{-1} do not fit in the scheme proposed by Horie. (2) The $\omega_e'x_e'$ value 18.8 cm^{-1} obtained by Horie's analysis appears to be too high and out of proportion with the value 3.5 cm^{-1} obtained by him for $\omega_e''x_e''$.

TABLE I.

Intensity	λ_{air}	ν_{vac}
1	2931.9	34098
1	2927.4	34150
?	2925.8	34169
1	2919.5	34242
1	2916.3	34280
3	2861.5	34936
5	2857.1	34990
4	2855.5	35010
4	2849.2	35087
5	2846.0	35127
?	2844.2	35149
4	2794.2	35778
6	2789.8	35834
10	2788.3	35854
5	2786.7	35874
8	2782.3	35931
7	2778.9	35975
10	2777.6	35992
?	2776.0	36012
1	2724.0	36700
2	2721.5	36734
?	2717.4	36789
2	2713.9	36836
1	2711.5	36869

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* Post Doctoral Research Fellow, Molecular Spectra Research Project.

[1] R. K. Asundi and S. M. Karim, Proc. Ind. Acad. Sci. **6A**, 328 (1937).

[2] Asundi, Singh, and Mishra, Current Science **12**, 204 (1943).

[3] Tadao Horie, Proc. Phys. Math. Soc. Japan **21**, 143 (1939).

** The isotope displacements due to CCl^{35} and CCl^{37}, reported by Horie for three of the bands are, however, not noticed in the present experiments.

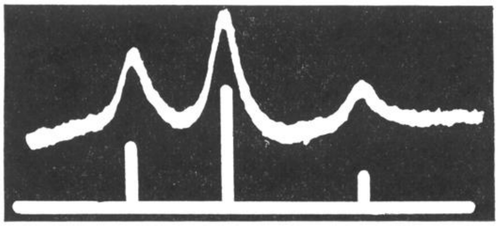

FIG. 1. Calculated and observed hyperfine structure of the $J=0\rightarrow1$ transition of $DC^{12}N^{14}$.