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Infrared Absorption Spectrum of Hydrogen Cyanide

By Kyu Nam Choi and E. F. Barker
University of Michigan

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The absorption spectrum of HCN in the gas phase has been investigated by a grating spectrometer with high resolution in the region $3\mu-15\mu$. Five of the infrared bands were studied, and of these the very intense fundamental at 14μ has been resolved into individual lines forming P, R and Q branches. The first harmonic of the band at 7μ has two maxima, very nearly symmetrical and equal in intensity, and no Q branch. Although fine structure is indicated, it is not possible to determine the position of successive individual lines. Three other maxima, less intense and unsymmetrical are found at 4.728μ, 4.760μ, and 4.794μ forming the second harmonic of the same vibration. There is a sharp single maximum at 3.57μ with another very strong double band at 3.04μ.

Form of the HCN molecule. The HCN molecule is linear with fundamental frequencies $\nu_2=712$ cm^{-1}, $\nu_3=3289$ cm^{-1} and ν_1 approximately 2100 cm^{-1}. The latter has not been observed directly since the band associated with it is of extremely low intensity, but the combination $\nu_1+\nu_2$ explains the band at 3.57μ. The moment of inertia determined from the fine structure of the 14μ band is 18.68×10^{-40} g cm^2.

Introduction

RECENT improvements in the apparatus available for measuring infrared absorption have made possible the detailed study of spectra of much greater complexity than could be observed only a few years ago. As a consequence, the infrared absorption spectra have furnished decisive information for determining the molecular configurations of a number of molecules, especially when the fine structure of the bands is observable. The purpose of the present investigation is to examine both the fundamental and harmonic bands of HCN; especially to determine the fine structure of the low-frequency bands which have never been studied before with high resolution.

In 1912, Burmeister[1] investigated the absorption spectrum of gaseous HCN in the region from 3μ to 14μ, finding four bands. Of these, the one having the shortest wave-length 3.04μ is very narrow and intense, apparently corresponding to the fundamental of one of the characteristic vibrations of the molecule. The two bands of greatest wave-length near 7μ and 14μ, are also intense, but appear as broad double maxima. The absorption at the two intermediate-maxima, 4.77μ and 3.57μ, is relatively weak and Burmeister was in doubt as to whether these bands should be attributed to HCN.

In 1923, Barker[2] investigated some of the absorption bands of HCN with special gratings ruled by himself, giving higher dispersion than was previously employed. He found two maxima, very nearly symmetrical and of equal

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[1] Burmeister, D. Ges. Verh. **15**, 589 (1913).

[2] Barker, Phys. Rev. **23**, 200 (1924).

intensity, appearing at 6.94μ and 7.32μ. Three others, less intense and unsymmetrical, were observed at 4.756μ, 4.723μ and 4.79μ. Observation at that time did not extend beyond 12μ. From the envelope of the 7μ band he estimated the moment of inertia to be about 13.2×10^{-40}g cm^2.

In 1930, Badger and Binder[3] investigated photographically the absorption spectrum in the region λλ7000–9200 using HCN gas in a 280 cm absorption cell. They observed two weak bands of very simple structure occurring at λ8563 and λ7912 which are interpreted as $3\nu_3+\nu_1$ and $4\nu_3$ respectively. In these bands they have been able to resolve the rotational structure, and compute the moment of inertia as 18.79×10^{-40} g cm^2.

Very recently, Brackett and Liddel[4] examined the absorption spectrum of HCN both in liquid and vapor phase mostly in the region from 1μ to 2μ. The instrument used in their investigation was an automatic recording apparatus yielding high resolution. Three bands were observed at 1.5μ, 1.1μ and 1.0μ in the gas absorption. They were interpreted as second and third harmonics of 3.04μ (ν_3) and the combination $2\nu_3+\nu_1$. All these bands are doublets but the rotational structure was not resolved. The moment of inertia as computed from the envelope of the third harmonic band was $18\pm2\times10^{-40}$ g cm^2.

APPARATUS

The grating spectrometer used in this work is of a type similar to that employed by Barker and Meyer[5] and therefore will not be described here in detail. Modifications of an important nature, however, lead to a high degree of sensitivity of the recording apparatus and hence allow investigation with a grating to a greater wave-length than has been previously reached. As a further consequence of the increased sensitivity, it has been possible to reduce the slit widths considerably and thus obtain improved definition. A grating ruled with 1200 lines per inch was found to be most effective for the region between 7μ and 15μ. From 3μ to the neighborhood of 5μ, the best results were obtained with a grating having 4800 lines per inch. The detecting system consists of a vacuum thermocouple, a Moll thermal relay with a Kipp and Sons high-sensitivity galvanometer of the D'Arsonval type. The calibration is in terms of the mercury line at 1.014μ.

The absorption cells have potassium bromide (K Br) windows and can be used effectively throughout the entire spectral region from 3μ to 15μ. Two absorption cells were used whose lengths are 25 cm and 2.5 cm respectively.

The HCN gas was generated by introducing below the surface of H_2SO_4 a nearly saturated solution of NaCN in water. The gas was frozen in a liquid air trap provided with two stopcocks, and each sample to be examined was distilled over to the absorption cell by warming the trap to 30°C. In order to eliminate the water vapor in the gas, two U tubes were used, the first containing $CaCl_2$ and the second P_2O_5.

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[3] Badger and Binder, Phys. Rev. **37,** 800 (1931).

[4] Brackett and Liddel, Smithsonian Institute **85,** No. 5 (1931).

[5] Barker and Meyer, Trans. Faraday Soc. **25,** 12 (1929).

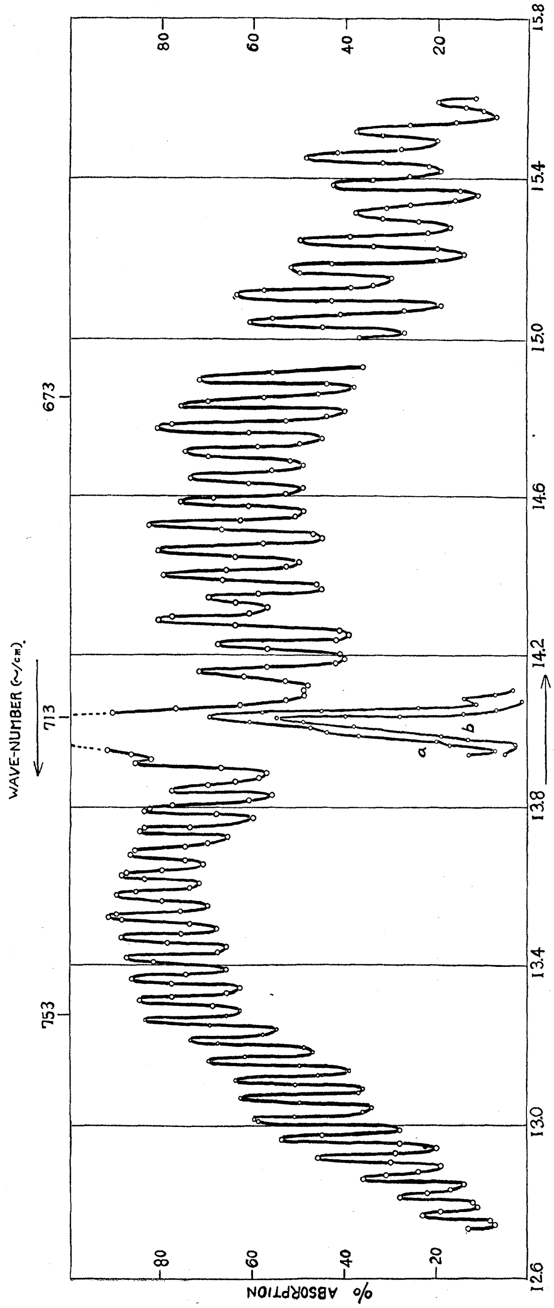

Fig. 1. Fine structure of the 14μ band of HCN.

DISCUSSION OF RESULTS

Region of 14μ

The wide and intense absorption previously observed with two maxima, was resolved into a band consisting of R, Q and P branches as shown in Fig. 1. Repeated observations were taken over this region, using the point by point method, with different pressures of gas and different slits. An extremely small cell, 2.5 cm long with KBr windows, was used, and the figure represents observations made with 35 cm pressure and 0.5 mm slit width. The Q branch is so strong that it was impossible to observe it satisfactorily even with 4 or 5 cm of pressure. In order to locate its maximum, the pressure was considerably reduced. The detached portion of curves a and b shown in Fig. 1 represent observations taken with pressures of 3 mm and 1 mm respectively. The irregularities of the lines which are apparent at the right end of the P branch may be attributed to the CO_2 band at 14.8μ. The energy falls off very rapidly in this region due to absorption by the carbon dioxide of the atmosphere. As shown in Fig. 1 there is a small gap near 14.8μ region where the Q branch of CO_2 falls and observations could not be made. No convergence is apparent in either the R or the P branch, the average spacing of the lines being 2.98 cm^{-1}. The small deviations from this value shown in the Table I are partly due to experimental error but also indicate the effect of superposition of bands due to absorption by excited molecules and disturbances from the CO_2 bands. If the above value of the average spacing is applied to the central portion of the band, it is apparent that there are just

TABLE I. *Rotation lines in the 14 μ band. Q branch at 14.0392 μ or 712.28 cm^{-1}.*

R branch: $\Delta J=+1$			Initial J	P branch: $\Delta J=-1$		
λ	ν	$\Delta\nu$		λ	ν	$\Delta\nu$
13.9780	715.40	3.12	0	—	—	—
13.9200	718.40	3.00	1	—	—	—
13.8544	721.68	3.28	2	14.1554	706.44	—
13.8016	724.55	2.87	3	14.2256	702.95	3.49
13.7489	727.33	2.78	4	14.2841	700.00	2.95
13.6962	730.11	2.78	5	14.3426	697.21	2.79
13.6477	732.72	2.61	6	14.4011	694.39	2.82
13.5909	735.80	3.08	7	14.4654	691.30	3.09
13.5340	738.87	3.07	8	14.5298	688.24	3.06
13.4798	741.85	2.98	9	14.5853	685.62	2.74
13.4299	744.60	2.75	10	14.6438	682.88	2.74
13.3780	747.49	2.89	11	14.7140	679.62	3.26
13.3240	750.72	3.03	12	14.7725	676.92	2.70
13.2711	753.52	3.00	13	14.8310	674.26	2.66
13.2181	756.52	3.00	14	14.8953	671.42	2.84
13.1653	759.57	3.05	15	—	—	—
13.1183	762.27	2.70	16	15.0320	665.24	—
13.0693	765.15	2.88	17	15.1010	662.20	3.04
13.0166	768.24	3.04	18	15.1720	659.10	3.10
12.9640	771.36	3.08	19	15.2410	656.12	2.98
12.9113	774.51	3.15	20	15.3100	653.16	2.96
12.8593	777.65	3.14	21	15.3790	650.23	2.93
12.8203	780.50	1.85	22	15.4480	647.33	2.91
12.7650	783.38	2.88	23	15.5170	644.45	2.88
—	—	—	24	15.5860	641.40	2.85

3 intervals between the innermost lines as would be expected for a linear molecule. The positions of maximum absorption of the *R*, *Q* and *P* branches fall, approximately, at 737.89, 712.29 and 688.00 cm^{-1} respectively. The most probable frequency of rotation $\bar{\nu}_r$ is thus found to be about 24.9 cm^{-1}.

Region of 7μ

This band is unquestionably the first harmonic of the 14μ band, although it has no *Q* branch since ΔL is even. It was examined with the 2.5 cm cell and 35 cm pressure, and with a grating having 1200 lines per inch, using the second order. Observations in this region are rendered difficult by the absorption of atmospheric water vapor which presents many sharp maxima where deflections taken either with or without the absorbing cell are reduced below the limit permissible for precise measurement. Several efforts have been made to resolve the individual lines of this band, but the curve shown

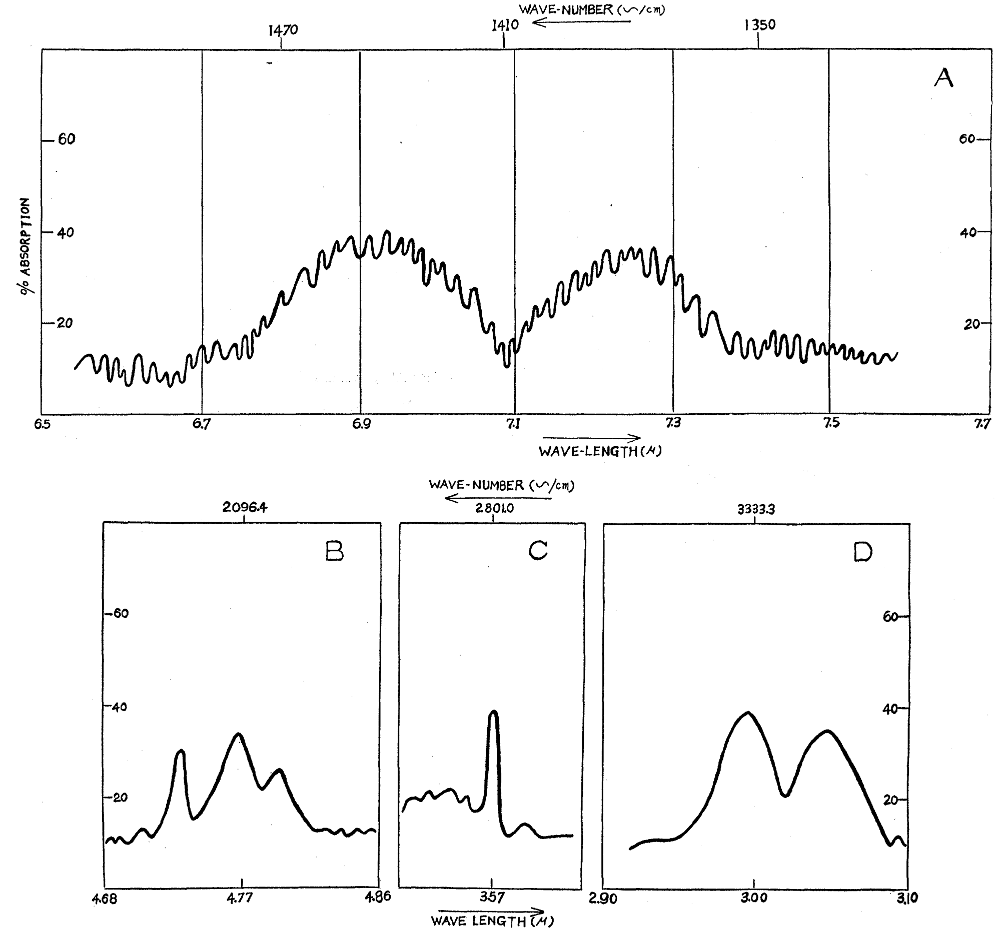

Fig. 2. Near infrared absorption bands of HCN.
$A:2\nu_2$. $B:3\nu_2$. $C:\nu_1+\nu_2$. $D:\nu_3$.

in the Fig. 2A represents the best definition obtained. The irregularities of the rotational lines are to a great extent attributable to the water vapor in the atmosphere but there may also be appreciable absorption here by molecules already excited to the level 1. There are two maxima, very nearly symmetrical, with almost equal intensities, separated by a sharp minimum. The position of the missing line is about 1412.4 cm^{-1}. Measurements have been extended in either direction to the region of very low absorption, with some loss in precision, because on the long wave-length side, the energy of the beam falls off rapidly and on the short wave-length side, the intensity of the water vapor absorption increases. Although fine structure is indicated, it is not possible to determine the positions of successive individual lines.

Region of 4.7μ

This region was examined with a grating having 4800 lines per inch and with 0.3 of mm slit. The absorption was very much less intense and could scarcely be located with the 2.5 cm cell. The third curve Fig. 2B represents the absorption, using the 25 cm cell of saturated vapor at about 25°C and atmospheric pressure. The cell was moved alternately in and out of the beam as before. The principle maximum appears at 4.760μ with a second narrow one at 4.728μ and with a third at 4.794μ. These peaks have the appearance of Q branches. From this curve it would be difficult to make an estimate of the value of the moment of inertia in the usual way, but obviously the wave-number differences are not of the same magnitude as those exhibited at 14μ.

Region of 3.6μ

The absorption band near 3.6μ Fig. 2C is also weak, although it was observed with 2.5 cm cell and with the pressure of 65 cm. A single narrow and fairly intense maximum was found at 3.57μ, with a low background on either side. Some indications of fine structure appear in the R branch but further resolution could not be obtained.

Region of 3μ

The single intense absorption band shown by Burmeister was resolved into a doublet Fig. 2D. It was examined with the 2.5 cm cell and with almost atmospheric pressure. The maxima appear at 2.996μ and 3.045μ. Several unsuccessful efforts have been made to resolve the individual lines with the 7200 line grating and different amounts of absorbing gas. The spacing of the maxima is about 53.7 cm^{-1} which is much greater than that observed at 14μ, but nearly the same as at 7μ. This fact combined with the difficulty in resolving the rotation lines, indicates that the absorption by excited molecules must be appreciable.

MECHANICAL INTERPRETATION OF THE VIBRATION-ROTATION BAND

Assuming that the rotation of this molecule may be represented by the equation for the symmetrical top rotator, the total energy in any stationary state is

$$E = E_p + \frac{h^2}{8\pi^2}\left\{\frac{J(J+1)}{A} + l^2\left(\frac{1}{C} - \frac{1}{A}\right)\right\},$$

where E_p is the potential energy of deformation and C and A are the moments of inertia about the axis of figure and any axis normal to it.

If $C=0$, as in the unexcited molecule, then E will be finite only if $l=0$, and E_p will also vanish, so that the equation passes over into the expression for the energy of a simple rotator,

$$E_r = J(J+1)h^2/8\pi^2 A$$

or $E_r/h = BJ(J+1)$ where $B = h/8\pi^2 A$ and J may assume all integral values.

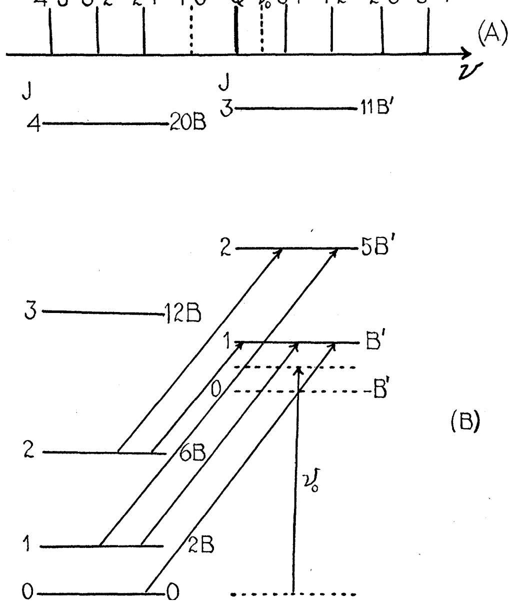

Fig. 3. Band pattern and scheme of energy levels for the transition 0→1 in l.

For the special case of an excited molecule in which $l=1$ the equation becomes

$$E' = E_p' + \frac{h^2}{8\pi^2}\left\{\frac{J(J+1)}{A'} + \left(\frac{1}{C'} - \frac{1}{A'}\right)\right\}$$

or $E'/h = B'\ (J^2+J-1)+\nu_0$ where $\nu_0 = E_p'h + h/8\pi^2 C'$ and $B' = h/8\pi^2 A'$. J may assume all values except 0, since $J \geqq l$.

Fig. 3 shows the energy diagrams for both normal and excited states, with permitted transitions indicated by arrows. Those lines in a band which are due to $\Delta J = 0$ belong to the Q branch, those with $\Delta J = \pm 1$ lead to P and R branches respectively. In other words, the absorption 0→1 corresponds to the first line of the R branch and the absorption 2→1 to the first line of the P branch. There is no transition 1→0 since in the excited state, J cannot be zero. For levels in which $l=0$, J will of course assume all values including 0, while for a level in which $l=2$, J cannot be either 0 or 1.

Fig. 3A represents a system of lines corresponding to a change in l from 0 to 1. ν_0 lies between the Q branch and the first line of the P branch.

THE SCHEME OF VIBRATION LEVELS AND INTERPRETATION OF THE OBSERVED BANDS

Fig. 4 represents the energy levels for the deformation vibration ν_2 following Dennison's analysis. The principal quantum number is the value of v_2 while the subscript is the value of l associated with it. When Δv is odd, Δl is restricted to ± 1 and the change in electric moment is normal to the axis of figure, giving rise to bands with Q branches. When Δv is even, $\Delta l=0$ and there are no Q branches. The most intense absorption bands originate in the level 0_0 but even at room temperature some molecules are excited to higher states. The population of any upper state is determined by the Boltzmann factor and by the statistical weight, the latter being 1 when $l=0$, and 2 when $l\neq 0$. Thus in the state 1_1 there are about 0.06 times as many, in the state 2_0 about 0.0009 times as many, and in 2_2 about 0.0018 times as many as in the state 0_0.

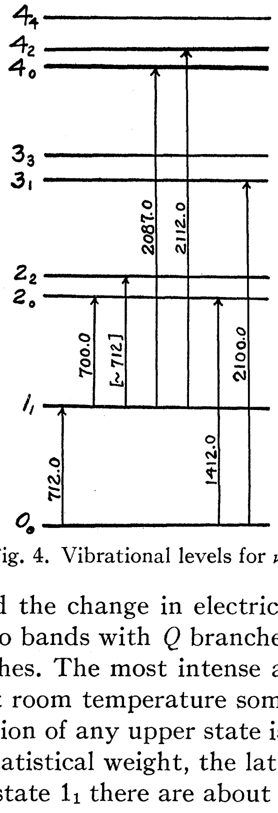

Fig. 4. Vibrational levels for ν_2.

In addition to the three fundamental vibrations and their harmonics, all of which we should expect to be active, combination bands should appear. There is no restriction upon the values of Δv_1, Δv_2 and Δv_3 in combinations. Although ν_1 has not been observed directly, its value is apparently very close to 2100 cm^{-1}. ν_2 and ν_3 have been identified, their values being 712 cm^{-1} and 3289 cm^{-1} respectively. The rest of the observed bands may now be classified. The band at 4.7μ is apparently the second harmonic of ν_2, $\Delta\nu_2=3$, for which zero branches should appear. It cannot be ν_1 since the latter would be a doublet. The three maxima may be interpreted as indicated in the dia-

TABLE II. *Observed band centers and their assigned quantum transitions.*

			Band center		Approximate relative intensity
v_1	v_2	v_3	Wave No. (cm.$^{-1}$)	Wave-length (μ)	
0–1(ν_1)			(2100)	(4.76)	?
	0_0–1_1(ν_2)		712	14.00	1000
	1_1–2_0		700	14.30	12.0
	1_1–2_2		712	14.00	
	0_0–3_1		2100	4.76	0.12
	1_1–4_0		2087	4.79	0.095
	1_1–4_2		2112	4.73	0.105
	0_0–2_0		1412.0	7.00	1.33
		0–1(ν_3)	3289	3.04	4.4
0–1	0_0–1_1		2801	3.57	1.30

gram, $0_0 \rightarrow 3_1$ being the most intense peak at 4.76μ, $1_1 \rightarrow 4_0$, the weakest one at 4.79μ and $1_1 \rightarrow 4_2$ the intermediate one at 4.73μ. Table II shows the observed band centers and their assigned quantum transitions.

The fact that ν_1 has not been observed is somewhat surprising, and must indicate that for this motion the electric moment has a very small amplitude. The resulting weak band might have been observed if the three components of $3\nu_2$ had not been so intense. That ν_1 actually lies in this region is indicated by the Raman spectrum in which it appears as the most intense line. Kastler[6] finds the Raman displacement to be 2089 in the gas and 2098 in the liquid. Bhagavantam[7] gives measurements for liquid HCN only. He finds ν_1 at 2094 for normal molecules, with a weaker line at 2062 doubtless corresponding to absorption by molecules in the excited state 1_1, the intensity ratio being estimated as 24:1. The frequency ν_3 as indicated by his measurements is 3213

ON THE SHAPE OF THE MOLECULE

All of the bands observed, as well as those reported by Badger and by Brackett are consistent with the hypothesis that the molecule is linear. Only for the linear configuration can the simple structure of the 14μ band be understood. From the frequencies given in Table I a value of the moment of inertia may be obtained, since

$$\nu(J' \rightarrow J'') - \nu(J' + 2 \rightarrow J'') = 2B'(2J' + 1)$$

the primes referring to the normal state. Computing in this fashion for each pair of lines, we find an average value $I' = 18.68 \times 10^{-40}$ g cm^2, which compares very well with Badger's value, 18.79×10^{-40} g cm^2. The same order of magnitude is indicated by the frequency interval between the maxima of the P and R branches in the 14μ band, but not in the bands at 7μ and 3μ. For the former with $\Delta\nu = 24.9$ cm^{-1}, the classical formula gives $I = 18.32 \times 10^{-40}$ g cm^2.

It is not possible at present to determine the interatomic distances from the moment of inertia, nor to decide between the two possible configurations designated as hydrogen cyanide HCN or iso-cyanide HNC. However, the simplicity of the rotational structure suggests that probably only one type of molecule is present.

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[6] C. R. Kastler, Comptes Rendus **194,** 858 (1932).

[7] Bhagavantam, Nature **126,** 995 (1930).