ABSORPTION BANDS OF HYDROGEN CYANIDE GAS IN THE NEAR INFRARED

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Abstract

The absorption spectrum of gaseous hydrogen cyanide has been investigated by photographic methods in the region $\lambda 7000$–9200. Two weak bands of very simple structure were found, having P and R branches but no Q branches. The band at $\lambda 7912$ is apparently a harmonic of a fundamental band at 3.04μ, and the very weak band at $\lambda 8563$ is a combination band. The hydrogen cyanide molecule is linear in the normal state, and has a moment of inertia $I = 18.79 \times 10^{-40}$ g·cm². The distance of separation of the carbon and nitrogen atoms is estimated to be 1.15×10^{-8} cm. Hydrogen cyanide is discussed in regard to its three fundamental oscillations which have frequencies 3290, 2090, and 710, respectively, and in regard to its dissociation energy and dissociation products. The evidence requires a molecular structure represented by the formula HCN, and shows that the normal molecule is built from a normal hydrogen atom and a normal CN radical. The absorption of cyanogen gas has also been investigated in the photographic infrared, but no absorption bands could be detected.

Introduction

HYDROGEN cyanide has been the subject of two previous infrared investigations. W. Burmeister[1] observed two double bands with maxima at 14.33μ and 13.60μ, and at 7.22μ and 6.95μ, respectively, a single strong maximum at 3.04μ, and doubtful bands at 4.8μ and 3.6μ. E. F. Barker,[2] working with greater dispersion, confirmed the doubtful bands and found for the one three maxima at 4.79, 4.756, and 4.723μ, and in the case of the other apparently a strong Q branch with maximum at 3.564μ and two weak maxima on either side. Slight evidence of a rotational structure was found in the band at 7μ.

A calculation of the moment of inertia of the hydrogen cyanide molecule from the separation of the maxima of the double band at 14μ, with the use of a classical formula, yielded the improbably large value $I = 33 \times 10^{-40}$.[3] The separation of the maxima in the band at 7μ is much greater and has been interpreted as due to rotation about an axis with moment of inertia $I = 0.907 \times 10^{-40}$.[4]

Experimental Procedure

The hydrogen cyanide gas used in the investigation was prepared by dropping a concentrated solution of sodium cyanide into sulphuric acid. The gas

[1] W. Burmeister, Verh. d. D. Phys. Ges. 15, 589 (1913).

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

[3] R. C. Tolman and R. M. Badger, Jour. Amer. Chem. Soc. 45, 2277 (1923).

[4] Schaefer and Matossi, Das Ultrarote Spektrum, Berlin, 1930.

evolved was dried with calcium chloride and then condensed in a tube immersed in a freezing mixture. This tube was then connected to the evacuated absorption cell until equilibrium between liquid and vapor was established at room temperature. The gas pressure in the cell was consequently usually slightly less than one atmosphere. It seemed undesirable to attempt to increase the pressure by warming the apparatus, since even at atmospheric pressure the absorption lines were rather broad.

The absorption cell was a steel tube 280 cm in length, with a mirror at one end so that the light from the tungsten lamp source traversed it twice. The exposures were taken with the first order of a ten-foot grating in an Eagle mounting, using Eastman Infrared Sensitive Plates hypersensitized in ammonia. As calibration spectrum the iron lines in the second order were used.

Since both absorption bands were very weak it was not possible to make direct measurements on the plates with the use of a comparator. Microphotometer records were consequently made of absorption and comparison spectra, side by side on the same plates, using a linear enlargement of ten times. The tabulated wave-lengths, except for a few weak lines, were calculated from the mean of measurements made on four photometer curves obtained from different parts of two spectral plates.

Experimental Results

A careful examination of spectrograms covering the region $\lambda7000$–9200 resulted in the discovery of two similar absorption bands at $\lambda7912$ and $\lambda8563$, respectively. Both are weak, the latter extremely so, and the lines are broad as is to be expected in a saturated vapor. Each band has a P and an R branch, a missing zero line, and no apparent Q branch. The convergence in the R branches is so large that at first sight the bands appear to have a head. Due to the weakness of the absorption no attempt has been made to estimate relative intensities. The two branches have in each case about equal intensity, and as should be expected there is no indication of alternating intensities.

The wave-lengths and corresponding frequencies on the lines measured are recorded in the accompanying tables. A single question mark indicates low probable accuracy of measurement, and a double question mark, possible doubt as to the reality of the line. The measurements of the lines in the R branches are probably the less reliable due to incomplete resolution of the rather broad lines.

It should be mentioned that cyanogen gas was also studied in the course of this investigation, with pressures up to three atmospheres, but no absorption could be detected.

Discussion of the Results

The rotational energy levels of the upper and lower vibrational states of the molecule were isolated by means of the usual combination relations:

$$\Delta_2 F'(J) = R(J) - P(J) = F'(J + 1) - F'(J - 1) \sim 4B'(J + \tfrac{1}{2})$$
$$\Delta_2 F''(J) = R(J - 1) - P(J + 1) = F''(J + 1) - F''(J - 1) \sim 4B''(J + \tfrac{1}{2}).$$

TABLE I. *The HCN band at λ7912.*

J	R-Branch λ	R-Branch ν	P-Branch λ	P-Branch ν	$\Delta_2 F''(J)$	$\dfrac{\Delta_2 F''(J)}{J+1/2}$	$\Delta_2 F'(J)$	$\dfrac{\Delta_2 F'(J)}{J+1/2}$
0	7910.4	12638.1						
1	08.3	41.5	7913.8	12632.7	8.1	5.39	8.8	5.87
2	06.5	44.4	15.5	30.0	14.6	5.84	14.4	5.76
3	04.9	46.9	17.4	26.9	20.8	5.94	20.0	5.71
4	03.3	49.5	19.5	23.6	27.0	6.00	25.9	5.76
5	01.8	51.9	21.8	19.9	32.8	5.96	32.0	5.82
6	00.4	54.1	23.8	16.7	38.5	5.92	37.4	5.76
7	7898.9	56.5	25.9	13.4	44.0	5.87	43.1	5.74
8	97.7	58.4	28.0	10.1	50.3	5.92	48.3	5.68
9	96.4	60.5	30.4	06.2	55.8	5.87	54.3	5.73
10	95.5	62.0	32.7	02.6	61.9	5.89	59.4	5.65
11	94.0	64.4	35.2	12598.6	67.0	5.82	65.8	5.73
12	92.9	66.1	37.5	95.0	73.6	5.88	71.1	5.69
13	91.9	67.7	40.1	90.8	79.4	5.88	76.9	5.70
14	90.8	69.5	42.7	86.7	85.3	5.88	82.8	5.71
15	90.0	70.8	45.4	82.4	91.2	5.88	88.4	5.70
16	88.8	72.7	48.0	78.3	97.0	5.88	94.4	5.72
17	88.1	73.8	50.8	73.8	103.2	5.90	100.0	5.72
18			53.6	69.5	108.6	5.87		
19			56.3	65.2				
20			59.7	59.8				
21			62.4	55.6				
22			65.4(?)	50.8				
23			68.6(?)	45.8				
24			71.8(?)	40.8				
25			75.2(?)	35.4				
26			78.0(?)	31.0				
27			81.8(?)	25.1				

TABLE II. *The HCN band at λ8563.*

J	R-Branch λ	R-Branch ν	P-Branch λ	P-Branch ν	$\Delta_2 F''(J)$	$\dfrac{\Delta_2 F''(J)}{J+1/2}$	$\Delta_2 F'(J)$	$\dfrac{\Delta_2 F'(J)}{J+1/2}$
0	8561.5(?)	11677.0						
1	59.3	80.0	8565.4(??)	11671.7	8.9	5.92	8.3	5.53
2	57.2	82.8	68.0	68.1	14.7	5.89	14.7	5.88
3	55.4	85.4	70.1	65.3	20.6	5.89	20.1	5.74
4	53.3	88.2	72.3	62.2	26.6	5.94	26.0	5.77
5	51.7	90.4	74.9	58.7	33.0	6.00	31.7	5.76
6	50.1	92.6	77.5	55.2	38.3	5.89	37.4	5.76
7	48.2	95.2	79.8	52.1	44.3	5.91	43.1	5.74
8	46.6	97.3	82.6	48.3	50.3	5.91	49.0	5.76
9	45.1	99.4	85.1	44.9	56.3	5.92	54.5	5.74
10	43.6(?)	11701.6	88.0	41.0	62.0	5.90	60.5	5.77
11	42.1(?)	03.5	90.6	37.4	68.0	5.92	66.1	5.75
12	40.8(?)	05.3	93.5	33.5	73.9	5.92	71.8	5.74
13	39.5(?)	07.1	96.4	29.6	80.3	5.94	77.5	5.74
14			99.8	25.0	86.0	5.94		
15			8602.7	21.1				
16			05.3	17.4				
17			08.8	12.8				
18			11.7	08.9				
19			15.1	04.3				

These differences are presented in the right side of Tables I and II. No effect of the stretching of the molecule as a result of rotation could be detected, and within the accuracy of measurement the rotational energies in all three vibrational states may be represented by simple formulas of the form:

$$E_{\text{rot}} = J(J + 1)B.$$

The best values for the constants for the two bands are given in Table III. The differences in vibrational energies of upper and lower states, and the

TABLE III. *Constants of the HCN bands at λ7912 and λ8563.*

λ	ν_0	B''	$B'-B''$	I''
7911.9	12635.8	1.472	−0.044	18.79×10^{-40}
8563.3	11674.5	1.480	−0.042	18.69×10^{-40}

difference in the rotational energy constants, $B'-B''$, were obtained from a graphical treatment of the combinations:

$$\tfrac{1}{2}[R(J) + P(J + 1)] = \nu_0 + (J + 1)^2(B' - B'').$$

The slight difference in the value of B'', the rotational constant for the ground state, as determined from the two bands, is probably not greater than experimental error as the two bands seem to have a common lower level. The value determined from the data on the band at λ7912 is probably the more accurate.

Structure of the Hydrogen Cyanide Molecule

The simplicity of the two bands here investigated leaves no doubt as to the linearity of the hydrogen cyanide molecule in its normal state, and also in the two other vibrational states concerned. It still remains to be discussed which of the three possible arrangements of the three atoms in a straight line is the correct one. The arrangement with the hydrogen in the center is at once ruled out by the relatively small moment of inertia, ($I = 18.79 \times 10^{-40}$) and need not be discussed on the grounds of chemical improbability. Whether the gas known to chemists should be designated as hydrogen cyanide, HCN, or iso-cyanide, HNC, or whether it may be a mixture of two molecular species has been the subject of numerous discussions, and it seems to be worth while to consider what the spectroscopic evidence has to say in this regard.

We will simply mention at this point that the relation of all the observed infrared bands is such that they are apparently due to only one type of molecule. Further, their intensity is so great that this molecular species must constitute by far the greater part of hydrogen cyanide gas. This particular molecule will be the one with which we shall be concerned, and from now on we shall speak of it as the hydrogen cyanide molecule, and shall examine the data with the purpose of determining its structure. We shall now proceed to discuss three pieces of information which are derived from spectral data, namely the moment of inertia of the molecule, the frequencies of vibration, and the heat of dissociation.

The moment of inertia of the hydrogen cyanide molecule in the normal state, as determined from the data on the band at $\lambda 7912$ is, $I = 18.79 \times 10^{-40}$ g · cm². The fact that this constant is about half as large as that previously estimated from the doublet separation of the band at 14μ may possibly be accounted for by the low resolution used in studying this latter band. It is of course not possible to determine uniquely both interatomic distances in the molecule from the moment of inertia alone. However, the moment of inertia is not very sensitive to the position of the light hydrogen atom, and an estimate of the carbon-nitrogen separation may be made. In Fig. 1 is plotted
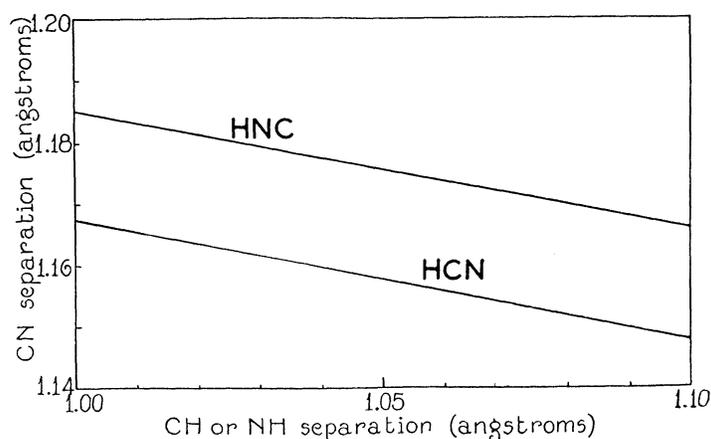
Fig. 1. The C-N separation plotted as a function of the C-H, or N-H separation for HCN and HNC molecular models with $I = 18.79 \times 10^{-40}$.

this distance as a function of the H-C separation, assuming the structure HCN, and of the H-N separation for the HNC structure, with the given moment of inertia. In either case the distance is small and strongly suggests a triple bond linkage between carbon and nitrogen. We may compare with the internuclear separation in the normal state of the CN radical, 1.17×10^{-8} cm.

MODES OF OSCILLATION OF THE HYDROGEN CYANIDE MOLECULE

The observed hydrogen cyanide bands may all be fitted into one simple scheme as given in Table IV, requiring three fundamental frequencies.

TABLE IV. *Designation of the HCN bands.*
$\nu_1 = 3333.7 \, v - 43.7 \, v^2$; $\nu_2 = 2090$; $\delta = 710$

Band	$\nu(\text{cm}^{-1})$	Designation
14μ	710	δ
7μ	1411	2δ
4.7μ	$\begin{cases} 2090 \text{ (approx)} \\ 2112 \end{cases}$	ν_2 3δ
3.6μ	2805	$\nu_2 + \delta$ (and possibly 4δ)
3.04μ	3290	ν_1
0.8563μ	11675	$3\nu_1 + \nu_2$
0.7912μ	12636	$4\nu_1$

The designation of the strong band at 3.04μ as a fundamental, and the band at λ7912 as one of its harmonics seems without objection. These two bands are represented within experimental error by the formula $\nu = 3333.7$ $v - 43.7\ v^2$. That the bands at 14μ and 7μ are fundamental and first harmonic of a "deformation" oscillation is also reasonable, as such an oscillation should be expected to have a low frequency. A deformation oscillation does not necessarily lead to the presence of a strong Q branch as has been shown in the case of acetylene.[5] The choice of the other fundamental frequency, which seems to be comparatively inactive, is more difficult. The form of the unresolved band at 4.7μ suggests the overlapping of two bands, one of which is probably the fundamental in question and the other a harmonic of the 14μ band. The choice of a frequency around 2100 is confirmed by the combination band at λ8563, and seems settled by recent work on the Raman spectrum of liquid hydrogen cyanide.[6]
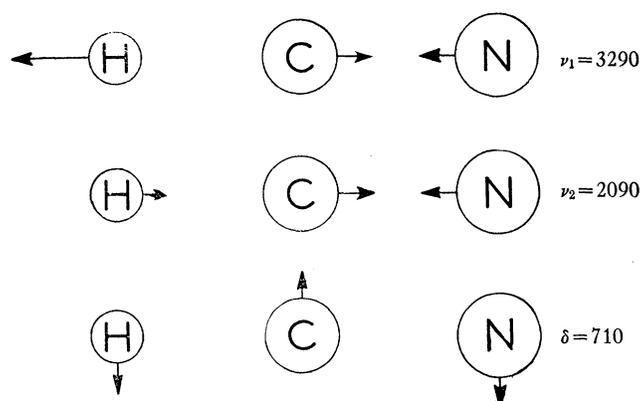

Fig. 2. The fundamental modes of oscillation of the HCN molecular model.

If we represent the hydrogen cyanide molecule by a mechanical model with three masses in the ratio 1.008:12:14, bound by Hooke's law forces, and arranged in a straight line, we find that this model does in fact have three fundamental modes of vibration, all of which will be "active," so to speak. Two of these may be designated as "valence" oscillations, the third as a "deformation" oscillation, as seen in Fig. 2. (Cf. the discussion of molecular oscillation by Mecke.[5]) By the application of normal coordinate methods it is possible to evaluate the ratio of the "valence" force constants which is required to fit the observed frequencies ν_1 and ν_2. That is we may estimate the ratio k_1/k_2 of the constants of the restoring forces which tend to maintain the equilibrium separation between carbon and nitrogen, and between hydrogen and the atom to which it is linked. Since the carbon and nitrogen atoms are of nearly equal mass it does not matter very much which of the two possible

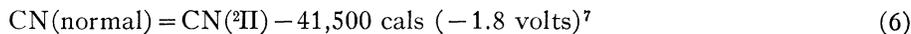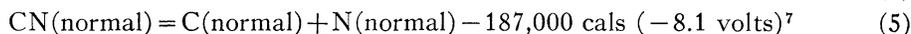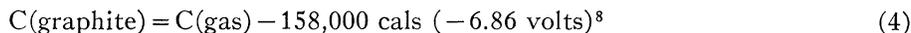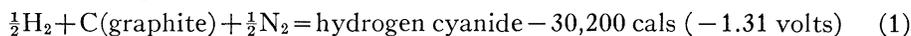[5] R. Mecke, Zeits. f. Physik, **64**, 173 (1930).

[6] Dadieu and Kohlrausch, Berichte **63**, 1657 (1930).

molecular models is considered. For the HCN arrangement we find $k_1/k_2 = 3.2$ and for HNC nearly the same value, 3.1. The former is nearly exactly the ratio of the force constants for CN in the normal state, and for HCl (or CH), and whichever model we choose is strong evidence for a triple bond between carbon and nitrogen. The ratio would be approximately 2 for a double bonded structure, as can for example be seen from a comparison of the binding constants in acetylene and ethylene.[5]
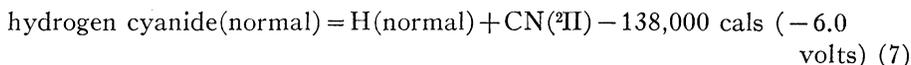
DISSOCATION PRODUCTS AND DISSOCIATION ENERGY OF HYDROGEN CYANIDE MOLECULE

We shall now consider the products of a dissociation process in which the hydrogen atom is removed from a hydrogen cyanide molecule. Three energy states of the CN radical are known. The normal state is a $^2\Sigma$ state formed from a ^4S nitrogen atom and a ^5S carbon atom.[7] A small internuclear separation and high oscillational frequency are evidence of a triple bond. The two excited states are formed from ^4S nitrogen and ^3P carbon. The lower of these, a $^2\Pi$ level with 1.8 volts excitation energy, has a relatively loose binding indicative of a double bond, but the higher, a $^2\Sigma$ state, has surprising rigidity considering its dissociation products and small dissociation energy.

The consideration of the oscillational frequencies rendered it improbable that the normal hydrogen cyanide molecule is formed from the CN radical in the $^2\Pi$ state, and this improbability is confirmed by the following energy considerations. The dissociation energy of normal hydrogen cyanide gas molecules into normal hydrogen atom and CN radical may be calculated from the data embodied in the following equations. These data are partly spectroscopic values, and partly thermal values corrected to the absolute zero by the use of specific heat data.

$$\tfrac{1}{2}H_2 + C(graphite) + \tfrac{1}{2}N_2 = \text{hydrogen cyanide} - 30,200 \text{ cals } (-1.31 \text{ volts}) \quad (1)$$

$$N_2 = 2N - 212,000 \text{ cals } (-9.2 \text{ volts}) \quad (2)$$

$$H_2 = 2H - 100,000 \text{ cals } (-4.34 \text{ volts}) \quad (3)$$

$$C(graphite) = C(gas) - 158,000 \text{ cals } (-6.86 \text{ volts})[8] \quad (4)$$

$$CN(normal) = C(normal) + N(normal) - 187,000 \text{ cals } (-8.1 \text{ volts})[7] \quad (5)$$

$$CN(normal) = CN(^2\Pi) - 41,500 \text{ cals } (-1.8 \text{ volts})[7] \quad (6)$$

From a combination of these data we find:

$$\text{hydrogen cyanide(normal)} = H(normal) + CN(^2\Pi) - 138,000 \text{ cals } (-6.0 \text{ volts}) \quad (7)$$

This is again strong evidence that normal hydrogen cyanide molecule is not directly formed from $^2\Pi$ CN radical, since an abnormally strong binding for the hydrogen would be required by Eq. (7). We should expect a molecule so built to be of the form HNC, and there seems to be no reason to suppose that the binding energy of hydrogen to nitrogen in this case should be much greater than the energy of the H-C linkage. We find for example that the

[7] W. Heitler and G. Herzberg, Zeits. f. Physik 53, 52 (1929).

[8] Brody and Millner, Chem. Zent. I, 237 (1928).

dissociation energy of NH_3 into its atoms is about 4.0 volts per hydrogen atom. A similar argument renders it even less likely that hydrogen cyanide is formed from CN in a state of excitation higher than the $^2\Pi$ state.

We are then left with the one possibility that the dissociation products of normal hydrogen cyanide are a normal hydrogen atom and a normal CN radical. This seems to require the molecular structure HCN, and we may write:

$$HCN(normal) = H(normal) + CN(normal) - 97{,}000 \text{ cals } (-4.2 \text{ volts}) \quad (8)$$

This result is thoroughly reasonable and may be compared with the value $-100{,}000$ cals. (-4.34 volts) which is the dissociation energy of HCl molecule.

It is interesting to consider the possibility of the existence of a hydrogen iso-cyanide molecule formed from hydrogen atom and $^2\Pi$ CN radical. This molecule, as stated above, would probably have the form HNC but would be non-linear. If we may estimate the H-N binding energy at about 4.2 volts, HNC should have about 41,500 cals (1.8 volts) more energy then HCN. We may make a rough estimate of the relative amounts of the two forms in an equilibrium mixture if we assume that the two forms have about the same specific heat and the same entropy. We find

$$K_{298^\circ} = \frac{HCN}{HNC} = 10^{30} \text{ (approx)}.$$

We must then conclude that hydrogen cyanide gas consists almost entirely of linear molecules of the form HCN.

One may be tempted to calculate a dissociation energy for HCN by the use of the vibrational constants in the formula representing the bands with fundamental at 3.04μ. The value so obtained is 6.4 volts, but can not be very significant since only one band of the series has been accurately measured and the constants are consequently inexact. In any case linear extrapolations are found to give uncertain results even in the case of diatomic molecules, and with polyatomic molecules seem to give consistently too high values. This might in some cases be explained by saying that the dissociation leaves a radical in an excited electronic state, but in other cases this is improbable. There seems to the authors to be a certain difficulty in principle in calculating dissociation energies of polyatomic molecules from spectral data. When one of the fundamental oscillations of such a molecule is increased in amplitude until an atom splits off, at the moment of separation the radical remaining may very likely be in a distorted condition, and after the separation will continue to vibrate with considerable energy. This remaining vibrational energy must be subtracted from the value obtained from the band series extrapolation in order to obtain the true dissociation energy. We hope to discuss this question more in detail in a later paper, and have some experiments in progress which may clarify the situation.