

SMITHSONIAN MISCELLANEOUS COLLECTIONS

VOLUME 85, NUMBER 5

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AND LIQUID

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(PUBLICATION 3123)

CITY OF WASHINGTON

PUBLISHED BY THE SMITHSONIAN INSTITUTION

AUGUST 5, 1931

The Lord Baltimore Press
BALTIMORE, MD., U. S. A.

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INTRODUCTION

The absorption spectrum of hydrogen cyanide in gas phase in the region from 3μ to 15μ was investigated originally by W. Burmeister,¹ and more recently at higher resolution by E. F. Barker.² These investigations have shown the presence of a strong doublet at 14μ , weaker bands at 7μ , 4.7μ , and 3.6μ , with another very strong band at 3.04μ . Whereas the frequency relations supported the view earlier held that the 7μ , 4.7μ , and 3.6μ bands were respectively second, third, and fourth harmonics of a fundamental at 14μ , the intensity of the 4.7μ band led Barker to question this interpretation and to suggest that very likely a new fundamental was present at approximately the same wave-length as the third harmonic. The 3.6μ band is thus more likely to be a combination of the new fundamental at 4.7μ , with the lower frequency vibration.

The band occurring at 3.04μ is recognized as another fundamental. The bands at 14μ and 7μ are clearly of the doublet character. Molecular moments of inertia are readily calculated from these data. From Burmeister's curves for the 14μ band, yielding an apparent separation of maxima of 37.5 cm.^{-1} , one calculates a moment of inertia of $33 \times 10^{-40} \text{ g. cm.}^2$. If, however, the relatively large slit-width at which this work was carried out is taken into account, estimates may be made as to the degree of overlapping, and more probable positions of the two components of the doublets may be plotted from the composite curve. On this basis a larger separation is obtained, of the order of 50 cm.^{-1} . The 7μ band was investigated by Barker at sufficiently high resolution so that no such correction needs to be made.

¹ Verh. Deutsche Phys. Ges., vol. 15, p. 589, 1913.

² Phys. Rev., vol. 23, p. 200, 1924.

Because of some uncertainty as to the exact intensity values, however, the form of the curve introduces some uncertainty in the determination of the separation of the maxima. In view of this, and of the inadequate resolution of Burmeister's apparatus, Barker's calculation of 13.2×10^{-40} g. cm.² for the moment of inertia, based on the separation of 58 cm.⁻¹, is perhaps in as good agreement as could be expected with the corrected value of Burmeister. As the band occurring at 4.7μ is certainly composite, no great significance can be attached to calculations of moments of inertia involving data on this band.

Recently, R. M. Badger and J. L. Binder¹ have carried out a photographic investigation of the absorption spectrum in the near infra-red of hydrogen cyanide vapor in a 280 cm. absorption cell. They have observed two bands in this region occurring at $\lambda 7912$ and $\lambda 8563$, respectively. In these bands they have been able to resolve the fine structure attributed to rotation in the molecules. On the basis of their measurements, they interpret each of the bands as composed of a *P* and *R* branch. From this rotational structure they are able to compute an accurate moment of inertia of 18.79×10^{-40} g. cm.² This calculation is in a reasonable agreement with the values based on doublet separation for the 14μ and 7μ bands. The absence of a *Q* branch is in harmony with the observations of a clearly doublet character of both the latter bands. In regard to the apparent central maxima in the bands occurring at 4.7μ and 3.6μ the question naturally arises as to the possible presence of a *Q* branch. It should be borne in mind, however, that these may readily be explained as due to overlapping.

Assuming three fundamental frequencies corresponding to the bands at 14μ , 4.7μ , and 3.04μ , which have been designated respectively as δ , ν_2 and ν_1 , Badger and Binder have interpreted the near infra-red bands as $3\nu_1 + \nu_2$ for the band at $\lambda 8563$ and as $4\nu_1$ for the band at $\lambda 7912$. Because of the absence of a *Q* branch, they have assumed a linear arrangement of atoms, and on the basis of three fundamental frequencies, offered an interpretation of the three fundamental modes of vibration corresponding to these fundamental frequencies. From an analysis of probable atomic distances of separation, they have come to the conclusion that the molecule must be hydrogen cyanide rather than hydrogen isonitrile (HNC).

¹ Phys. Rev., vol. 37, p. 800, 1931.

EXPERIMENTAL RESULTS

The results to be presented here were obtained with an automatic recording apparatus yielding high resolution and possessing certain novel features. An earlier self-recording instrument of high resolution was set up at the University of California by F. S. Brackett, yielding an effective slit-width of 10 Å. A similar instrument, but one with considerably greater aperture, was constructed by E. D. McAlister at the University of Oregon, yielding an effective slit-width of 6 Å. The instrument used in the present investigation at the Fixed Nitrogen Laboratory is of approximately the same aperture, though of considerably greater focal length, and yields the same effective resolution.

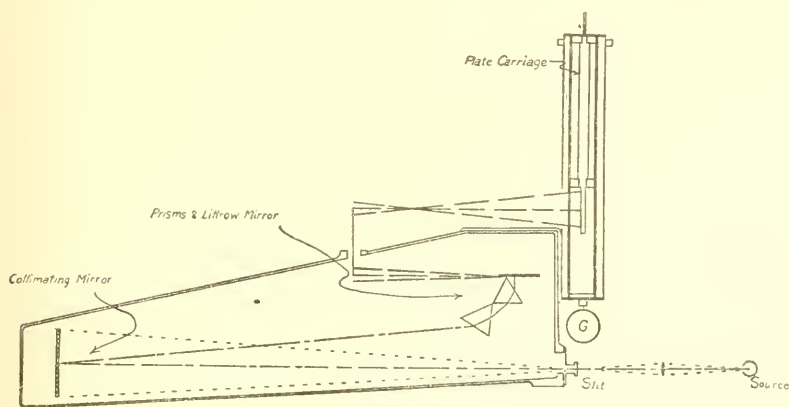


FIG. 1.—Diagrammatic sketch of spectrograph.

The instrument is of the Littrow form, wherein the light twice traverses two 60° prisms. The aperture is limited by the smaller of the two prisms, whose face is 20 cm. high and 15 cm. basal width. The instrument is used at a focal length of 2 meters. The body, a large casting, may be sufficiently evacuated to remove atmospheric absorption. Wave length variation is accomplished by rotation of the plane mirror, which is coupled with the motion of the photographic plate by a lever system. The use of a mechanical lever system with a variable pivot permits a wide range of variation of relative motion of the plate carriage to the angular rotation of the mirror, giving practically any desired spread of spectrum. This improved mechanical system, together with the use of photographic plates instead of film or paper, gives a much greater reproducibility of spectrum and accuracy of wave length than heretofore obtained. The calibration was effected with mercury arc spectra and water vapor bands, the

observed wave lengths being consistent with grating measurements within $\pm 2 \text{ \AA}$.

The thermocouple used is a modification of the type of single junction vacuum thermocouple described by Brackett and McAlister.¹ The source of continuous radiation is a tungsten ribbon filament, using 16 amperes current at 6 volts and working at an approximate temperature of 2900° K .

INVESTIGATION OF LIQUID HYDROGEN CYANIDE

In the present investigation, the absorption spectrum of hydrogen cyanide in liquid phase has been studied with cell thicknesses of 1 mm., 1 cm., 5 cm., and 30 cm.

The liquid hydrogen cyanide was obtained through the courtesy of W. B. Wood of the Plant Quarantine and Control Administration of the Department of Agriculture. This product had quite a perceptible odor of hydrogen sulfide. The original sample containing about 1500 cc. was distilled over P_2O_5 , primarily to remove any water, but a considerable quantity of sulfur was precipitated, as was expected from the presence of hydrogen sulfide. The second 500 cc. fraction was taken as an experimental sample. A drop of it did not affect lead acetate paper. This purification was made possible through the courtesy of Drs. G. E. Hilbert and L. B. Howard of the Fixed Nitrogen Research Laboratory.

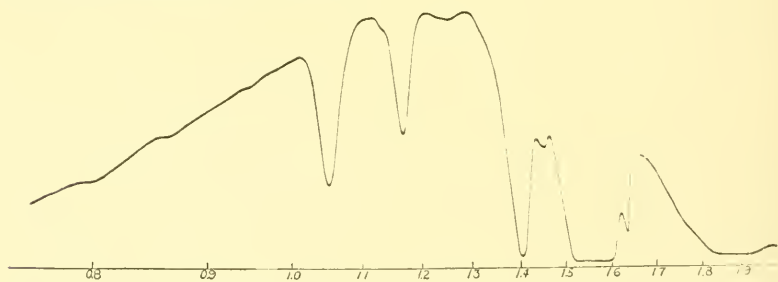


FIG. 2.—Energy transmission curve showing absorption spectrum of 5 cm. cell of liquid HCN at low dispersion. Slit width approx. 40 \AA .

Figure 2 shows the absorption of a 5 cm. cell in the region from 7μ to 2μ . The steadiness of the thermocouple will be apparent from the smoothness of the record. This illustration shows the instrument set for a relatively narrow spread, covering the entire region, and gives a general idea of the relative intensities. Actual observations of wave

¹ Rev. Sci. Instr., vol. 1, p. 181, 1930.

lengths, however, were made mostly on a much wider spread, including simply the region from 1μ to 2μ . A typical plate at this spread of the same cell length is shown in figure 3. Figure 4 shows an



FIG. 3.—Energy transmission curve showing absorption spectrum of 5 cm. cell of liquid HCN at high dispersion. Slit width approx. 9\AA .

analysis of the bands in this region, the frequencies of the maxima being plotted against percentage absorption. Table I gives the summary of the data obtained. The values of the fundamentals in vapor are inserted for comparison since no liquid values have been obtained

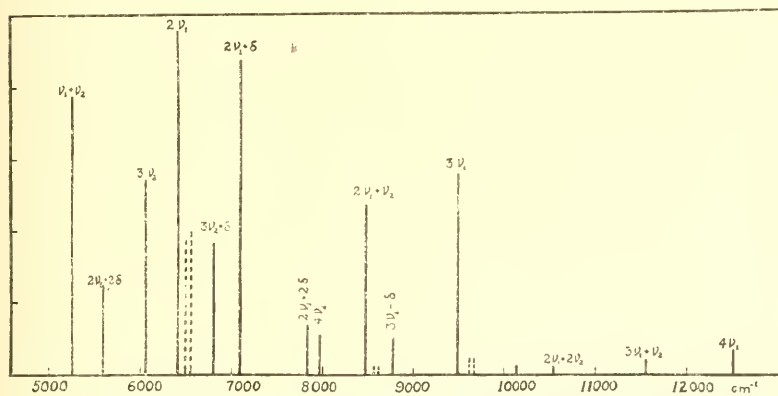


FIG. 4.—Diagrammatic representation of absorption maxima observed with assignments of designations. Broken lines show vapor absorption. Frequency is plotted against per cent absorption.

in that region. Intensity values, both as to percentage absorption and absorption coefficient are only approximate. Generally the estimated uncertainties in the frequency values indicated arise from the difficulty of setting upon broad absorption maxima like those shown in figure 3. Still less favorable are the conditions of the values for $4\nu_1$ and $3\nu_1 + \nu_2$, which were obtained on a low spread plate such as that shown in figure 1. In other cases the larger uncertainties indicated arise from the proximity of strong absorption bands. It will be seen that the observed values of $\Delta\nu$ lie well within the probable values to be expected, taking into account the normal variation to be expected in the successive differences, together with the probable uncertainty of measurement. The agreement certainly excludes any uncertainty as to identification. Not only do the wave lengths lead definitely to

the identification indicated, but the approximate intensities are consistent with such an interpretation. Of the entire 15 bands observed, only one has not been identified. This is almost immeasurably weak, and occurs in a position slightly displaced from the frequency where we should expect $3\nu_1 + \delta$. This excellent agreement throughout leaves little doubt as to the correctness of the choice of fundamentals proposed by Badger and Binder.

TABLE I.—*HCN Bands in Liquid*

Notation	Abs. %	Abs. coeff. k	λ Å	ν cm. ⁻¹	$\Delta\nu$ cm. ⁻¹
$4\nu_1$	6.6	.014	8000	12500 ± 30	3000
$3\nu_1$	57.	.17	10527	9500 ± 10	3090
$2\nu_1$	96.0	.64	15600	6410 ± 10	
(ν_1) vapor				3290	
$2\nu_1 + 2\nu_2$	2.	.004	9500	10527 ± 20	2040
$2\nu_1 + \nu_2$	47.	.13	11787	8487 ± 10	2077
$2\nu_1$				6410 ± 10	
$4\nu_2$	12.	.024	12540	7974 ± 10	1910
$3\nu_2$	(50)	..	16490	6064 ± 10	
($2\nu_2$)					
(ν_2) vapor				2090	
$2\nu_1 + 2\delta$	14.	.020	12760	7837 ± 10	719
$2\nu_1 + \delta$	88.	.42	14050	7118 ± 10	708
$2\nu_1$				6410 ± 10	
(δ) vapor				710	
$3\nu_1 + \nu_2$	3.7	.008	8650	11561 ± 25	2061
$3\nu_1$				9500 ± 10	713
$3\nu_1 - \delta$	10.	.017	11380	8787 ± 10	
$3\nu_2 + \delta$	42.	.11	14690	6804 ± 10	740
$3\nu_2$				6064 ± 10	
$2\nu_2 + 2\delta$	(20)	..	17900	5587 ± 15	
$\nu_1 + \nu_2$	78.	.30	19000	5263 ± 15	

INVESTIGATION OF VAPOR

The absorption spectrum has been obtained of saturated vapor at 22.5°C ., with a 30 cm. length of cell. The three bands observed in the gas absorption, interpreted as $2\nu_1$, $3\nu_1$, and $2\nu_1 + \nu_2$ all show clearly a doublet structure. In the stronger bands, $2\nu_1$ and $3\nu_1$ shown in figure 5, separations of maxima are obtained of $47 \pm 2 \text{ cm.}^{-1}$ and $50 \pm 2 \text{ cm.}^{-1}$, which yield moments of inertia $2I \pm 2 \times 10^{-40} \text{ g. cm.}^2$, and $18 \pm 2 \times 10^{-40} \text{ g. cm.}^2$ respectively. This is consistent, within the order of the accuracy of the work, with the more accurate value obtained by Badger. The combination band is too weak to obtain separation values of significance. On the basis of this conclusive identification of fundamentals, the clearly doublet character of the gas absorption implying the absence of a Q branch, and the approxi-

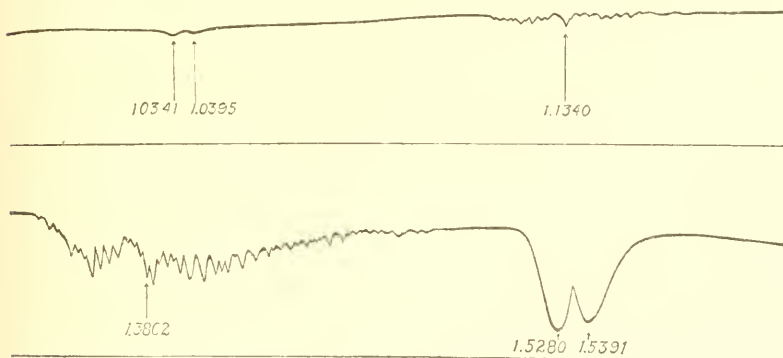


FIG. 5.—Energy curves showing absorption spectrum of 30 cm. Saturated HCN vapor. Slit width approx. 9\AA .

mate values of moments of inertia, we had independently come to the same conclusions regarding the arrangement of atoms, the approximate separations, and the probable modes of vibration before the publication of the work of Badger and Binder.

The position of the $2\nu_1$ and $3\nu_1$ bands, however, is not consistent with the formula

$$\nu_n = 3333.7n - 43.7n^2$$

Assuming the formula

$$r = n\omega_0 - n^2\omega_{0,r}$$

our values indicate a variation in r . This is evident from table 2, where the values of $\Delta\nu_2$ or $2\omega_{0,r}$ have successive values 59, 107, and 133, indicating values of $\omega_{0,r}$ varying from 30 to 67, as against Badger's value of 43.7 based only upon ν_1 and $4\nu_1$. Third differences

suggest that a constant value of $\omega_0 x$ may be approached equal to or slightly greater than 67. On the basis of this value we may compute a heat of dissociation corresponding to an absolute electron voltage of 5.5 volts. This is in much better agreement with the value com-

TABLE 2.—*HCN Bands in Vapor*

Notation	Abs. %	λ μ	ν cm.^{-1}	$\Delta\nu_d$ cm.^{-1}	I 10^{40}	ν (aver.) cm.^{-1}	$\Delta\nu$ cm.^{-1}	$\Delta\nu_2$ cm.^{-1}	ν_L cm.^{-1}	$\nu_1 - \nu_L$ cm.^{-1}
($4\nu_1$)						12636			12500 \pm 30	136
							2991			
	6.6	1.0341	9670 \pm 3							
$3\nu_1$				50 \pm 2	18	9645		133	9500 \pm 10	145
	6.5	1.0395	9620 \pm 3							
							3124			
	80	1.5280	6544 \pm 2							
$2\nu_1$				47 \pm 2	21	6521		107	6410 \pm 10	111
	75	1.5391	6497 \pm 2							
							3231			
(ν_1)		3.04				3290		59		
							3290			
	2	1.1610	8613 \pm 6							
$2\nu_1 + \nu_2$				44 \pm 10		8591			8487 \pm 10	104
	2	1.1670	8569 \pm 6							
							2070			
($2\nu_1$)						6521				
(ν_2)		4.7				2090				

puted from chemical data, 4.2 volts, than would be obtained from Badger's constant value of 43.7.

The displacements to lower frequencies in passing from vapor to liquid show a marked increase for the higher harmonics, with the exception of the $4\nu_1$ value, for which it must be remembered that the liquid value is only approximate.

