

THE ABSORPTION SPECTRUM OF CYANOGEN
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ABSTRACT

The absorption spectrum of cyanogen gas has been investigated in the ultraviolet down to $\lambda 1800$. In the region $\lambda\lambda 2300$ – 1820 more than one hundred bands were found which apparently belong to one system with origin probably at 44900 cm^{-1} . The bands have a pronounced tendency to appear as doublets. The more intense ones are usually broad with edges toward the violet, but many line-like structures appear which are probably Q branches. Some regularities in the spectrum are pointed out and the relation of the ultraviolet spectrum to the infrared absorption and Raman spectrum is briefly discussed.

INTRODUCTION

THE work described in this paper is a part of a program of this laboratory for the investigation of the spectra of the simpler polyatomic molecules. In particular the cyanides have been chosen for study and papers by Badger and Binder¹ on the fine structure of two bands of hydrogen cyanide in the infrared, and by Badger and Woo² on the continuous absorption spectra of the halogen cyanides in the ultraviolet have already appeared. Cyanogen was chosen as the next subject for study since the cyanogen molecule, in its normal state at least, is undoubtedly linear and symmetrical, which permits a simple and quantitative treatment of the normal oscillations. It is further of particular interest to compare the cyanogen molecule with acetylene which is in some respects similar and has been carefully studied in infrared absorption.

EXPERIMENTAL PROCEDURE

A. Middle Ultraviolet Region. The cyanogen gas used in the investigation was prepared by dropping a concentrated solution of potassium cyanide into an all glass generator containing a solution of copper sulfate. The gas generated was dried by passing through a calcium chloride tube, and then passed into the absorption tube. No further purification was made since in previous experiments it was found that cyanogen prepared by the decomposition of mercuric cyanide by heating gave the same absorption spectrum.

The absorption cell was a Pyrex tube 51.5 cm long, one end of which was provided with a plane quartz window, while the other end was separated from the hydrogen discharge tube, used as the light source, by a thin quartz film. All temporary connections were effected with picein, which proved to be least attacked by the cyanogen gas. The gas pressure used was one atmosphere at room temperature.

¹ R. M. Badger and J. L. Binder, *Phys. Rev.* **37**, 800 (1931).

² R. M. Badger and S. C. Woo, *J. Am. Chem. Soc.* **53**, 2572 (1931).

The hydrogen discharge tube was of a type described by Bay and Steiner,³ but all wax joints were avoided by using a quartz window, which was very thin, attached by a quartz-to-Pyrex graded seal. Consequently, after the tube had been cleaned up by running for some time the spectrum remained very pure and continuous. The hydrogen pressure could be regulated by means of a palladium tube which was sealed to the glass.

A Bausch and Lomb quartz spectrograph was used which gives a dispersion of about 5A per mm at $\lambda 2200$. Eastman D-C ortho plates were used, and were sensitized with a light transformer oil which was found to be very effective. The exposures required about two hours. As a comparison spectrum we employed the copper spark lines. Measurements of the bands were made both directly on the plates with a comparator, and on enlarged prints. Any errors will be due principally to the difficulty in deciding exactly what part of a band to measure. The error in measurement we believe to be less than 0.2A.

B. Farther Ultraviolet Region. For this region we employed a small vacuum fluorite spectrograph, with a dispersion of about 12A per mm at $\lambda 1900$. The absorption cell, about 30 cm in length, had at one end no window but was sealed with picein to the spectrograph chamber and communicated with it through the slit opening. At the other end it shared a very thin quartz film window in common with the hydrogen discharge tube used as source. The total absorption path was about 75 cm.

The cyanogen gas was prepared as described above, but was condensed in a liquid air trap and then evaporated into the spectrograph and absorption cell, which had previously been thoroughly evacuated, until a pressure of about 10 mm was attained.

Eastman 40 plates, sensitized with oil, were used, and the exposures usually required two to three hours. As calibration spectrum, the zinc and aluminum spark lines were used. They covered the region $\lambda\lambda 2100-1850$ fairly well.

As before, measurements were made both on the plates and on greatly enlarged prints. The accuracy of measurement was not so great as in the middle ultraviolet region, but in the case of sharp bands the error may not be greater than 0.4A.

EXPERIMENTAL RESULTS

Tables I and II give the wave-lengths and wave numbers of the absorption bands of cyanogen gas in the middle and farther ultraviolet, respectively.

The bands vary considerably in appearance and it is rather uncertain how best to describe some of them until a complete analysis is made of the spectrum. Where a sharp edge appeared this was measured, but in the case of diffuse bands and of the narrow line-like structures the center was measured. The symbols, explained at the foot of the table, indicate in each case the nature of the absorption and what was measured. The general appearance of the spectrum is probably best suggested by the diagram in Fig. 1, in which the types of bands are indicated as far as possible.

³ Z. Bay and W. Steiner, *Zeits. f. Physik* 59, 48 (1929).

The majority of the strong bands are rather broad, with edges toward the violet, but a number of line-like structures are observed, which are probably *Q* branches. In some cases *P* and *R* branches seem to be definitely absent,

TABLE I. *The cyanogen bands in the middle ultraviolet (quartz spectrograph).*

| <i>M</i> | λ (Å) (in air) | ν (cm ⁻¹) | <i>I</i> | <i>D</i> | <i>M</i> | λ (Å) (in air) | ν (cm ⁻¹) | <i>I</i> | <i>D</i> |
|----------|---------------------------|---------------------------|----------|----------|----------|---------------------------|---------------------------|----------|----------|
| VE | 2252.1 | 44389} | 0 | | VE | 2187.3 | 45704} | 00 | |
| CL | 2251.8 | 44395} | | | VE | 2186.9 | 45713} | | |
| CL | 2250.6 | 44419} | 0 | | VE | 2185.7 | 45738} | | |
| CL | 2250.3 | 44425} | | | VE | 2185.3 | 45746} | 0 | |
| RD | 2242.6 | 44577} | | | CL | 2184.4 | 45765} | | |
| CL | 2240.0 | 44629} | | | CL | 2183.3 | 45788} | 0 | |
| VE | 2239.0 | 44649} | | | VE | 2182.6 | 45803} | | |
| VE | 2238.3 | 44663} | | | VE | 2182.0 | 45815} | 1+ | |
| VE | 2237.7 | 44675} | 3 | | CL | 2180.5 | 45847} | | |
| VE | 2231.2? | 44805} | | | CL | 2179.9 | 45859} | 0 | |
| VE | 2230.4 | 44821} | | | VE | 2179.2 | 45874} | | |
| CL | 2228.4 | 44861} | | | CL | 2178.6 | 45887} | 1- | |
| CL | 2227.6 | 44877} | | | CD | 2177.1 | 45918} | | |
| CL | 2227.1 | 44887} | | | CD | 2176.5 | 45931} | 2+ | |
| VE | 2226.7 | 44896} | | | CL | 2173.5 | 45994} | | |
| VE | 2226.4 | 44902} | 5 | A' | CL | 2173.0 | 46005} | 00 | |
| CL | 2225.6 | 44918} | 00 | | CL | 2167.1 | 46130} | | |
| CD | 2223.5 | 44960} | 00 | | CL | 2166.6 | 46141} | | |
| CD | 2219.8 | 45035} | 0 | | CD | 2165.5 | 46164} | | |
| CD | 2217.5 | 45082} | 0 | | CL | 2164.8 | 46179} | | |
| CD | 2215.0 | 45133(d)} | 0 | | VE | 2164.5 | 46186} | 4- | |
| VE | 2213.0 | 45173} | | | VE | 2163.3 | 46211} | 00 | |
| CL | 2212.5 | 45184} | | | CD | 2161.3 | 46254} | 00 | |
| VE | 2212.3 | 45188} | 1 | | CD | 2159.2 | 46299} | | |
| VE | 2209.1 | 45253} | | | VE | 2158.9? | 46305} | 0 | |
| VE | 2208.5 | 45265} | | | VE | 2157.9 | 46327} | | |
| VE | 2207.2 | 45292} | | | CL | 2157.5 | 46335} | 0 | |
| VE | 2205.7 | 45322} | | | VE | 2157.3 | 46340} | | |
| CL | 2205.2 | 45333} | | | CD | 2155.5 | 46378} | 00 | |
| CL | 2204.4 | 45350} | | | CD | 2154.1 | 46409} | 00 | |
| CD | 2203.7 | 45364} | | | CD | 2152.4 | 46445} | 00 | |
| CL | 2203.1? | 45376} | | | CD | 2150.7 | 46482} | 00 | |
| CL | 2202.4 | 45391} | | | VE | 2145.6 | 46592} | 4 | A'' |
| CL | 2200.6? | 45428} | | | VE | 2137.7 | 46764} | 4 | |
| CL | 2200.3 | 45434} | | | CD | 2135.5 | 46813} | 1 | |
| VE | 2200.0 | 45440} | 5 | | VE | 2125.0 | 47044(d)} | 7 | B' |
| CL | 2197.2 | 45498} | | | CD | 2124.0 | 47066} | 0 | |
| CL | 2196.7 | 45509} | | | CD | 2120.9 | 47135} | 0 | |
| CL | 2195.4 | 45536} | | | CD | 2118.9 | 47179} | 0 | |
| CL | 2194.8 | 45548} | | | | | | | |
| VE | 2188.2 | 45685} | 9 | A | | | | | |

EXPLANATION. Columns *M* indicate the part of a band measured, whether a violet or red edge (VE or RE), the apparent red or violet limit of a diffuse structure (RD or VD), the center of a diffuse band (CD), or the center of a narrow line-like structure, probably a *Q* branch (CL). When two parts of the same structure were measured this is indicated by brackets in these columns.

In the frequency columns brackets on the left indicate edges or maxima which apparently belong to one broad structure. Brackets on the right indicate a doublet structure, and (d) a probable doublet structure (incompletely resolved).

The columns *I* and *D* give estimated relative intensities, and designations for a few of the bands.

in others they may be relatively very weak. A pronounced tendency toward doubling will be noticed. In a band progression the doublet separation in-

creases toward the high frequency side. Some of the diffuse bands show indications of being partially resolved doublets. In some cases a number of lines or edges are observed within a broad band. We believe that these are

TABLE II. *The cyanogen bands in the farther ultraviolet (fluorite spectrograph).*

| <i>M</i> | $\lambda(\text{\AA})$ (vacuum) | $\nu(\text{cm}^{-1})$ | <i>I</i> | <i>D</i> | <i>M</i> | $\lambda(\text{\AA})$ (vacuum) | $\nu(\text{cm}^{-1})$ | <i>I</i> | <i>D</i> |
|----------|-----------------------------------|-----------------------|----------|----------|----------|-----------------------------------|-----------------------|----------|----------|
| CL | 2110.6 | 47380 | 0 | | CD | 1969.0 | 50787 | 2 | |
| CL | 2109.4 | 47407 | | | CD | 1963.5? | 50930 | 2 | |
| CL | 2108.1 | 47436 | 7 | | CD | 1959.6? | 51031 | 1 | |
| CL | 2106.6 | 47470 | | | CD | 1958.4? | 51062 | | |
| CL | 2105.0 | 47506 | 1 | | CD | 1953.5 | 51190 | | |
| RD | 2098.4 | 47655 | | | CL | 1952.3 | 51222 | 5 | D' |
| CL | 2097.9 | 47667 | | | CD | 1949.5 | 51295 | 2 | |
| CL | 2096.3 | 47703 | | | CL | 1944.0 | 51440 | 4 | |
| CL | 2095.0 | 47733 | | | CL | 1940.4 | 51536 | 2 | |
| VE | 2094.4 | 47746 | | | CL | 1937.6 | 51610 | | |
| CL or VE | 2093.8 | 47760 | 10 | B | CL | 1936.3 | 51645 | 3 | |
| VE | 2090.4 | 47838 | 4 | | CD | 1931.9 | 51763 | | |
| VD | 2088.2? | 47888 | 2 | | CD | 1929.8 | 51819 | 10 | D |
| VD | 2086.4 | 47929 | 4 | | CD | 1926.5 | 51908 | 7 | |
| CL | 2079.4 | 48091 | 2 | | RE? | 1922.6 | 52013 | | |
| VE | 2075.6 | 48179 | | | CD | 1918.5 | 52124 | 9 | |
| VE | 2074.5 | 48204 | 4 | | VE | 1916.3 | 52184 | | |
| CD | 2069.3 | 48326 | 4 | | VE | 1915.4 | 52208 | 3 | |
| CD | 2065.0 | 48426 | 2 | | CD | 1911.7 | 52310 | 1 | |
| CL | 2058.4 | 48581 | | | CD | 1909.9 | 52359 | 1 | |
| CL | 2057.6 | 48600 | | | VE | 1900.0(d) | 52632 | 9 | |
| CL | 2056.8 | 48619 | | | CL | 1897.5 | 52701 | | |
| CL | 2055.3 | 48655 | 7 | B' | CD | 1894.7 | 52779 | | |
| CD | 2051.2 | 48752 | | | VE | 1893.1 | 52823 | 9 | D'' |
| CD | 2049.3 | 48797 | | | CD | 1885.0 | 53050 | | |
| VE | 2036.0 | 49116 | | | VE | 1884.6 | 53062 | 3 | |
| CL or VE | 2035.2 | 49135 | 7 | C' | CL | 1883.2 | 53101 | 1 | |
| CD | 2023.3 | 49424 | 3 | | CD | 1880.6 | 53175 | 0 | |
| CL | 2021.4 | 49471 | 6 | | CD | 1878.3 | 53240 | 2 | |
| VE | 2018.3 | 49547 | 4 | | CD | 1875.9 | 53308 | 2 | E' |
| CD | 2015.0 | 49628 | | | CL | 1871.1 | 53427 | 1 | |
| CD | 2012.7 | 49685 | | | CL | 1867.3 | 53556 | 1 | |
| CD | 2011.1 | 49724 | | | CD | 1861.8 | 53712 | | |
| CD | 2009.4 | 49766 | | | CD | 1859.6 | 53775 | 5 | E |
| CD | 2007.7 | 49808 | 10 | C | CL | 1857.2 | 53845 | 0 | |
| CD | 2003.4 | 49915 | | | CL | 1855.0 | 53908 | 1 | |
| CD | 2000.7 | 49983 | 8 | | CL | 1850.3 | 54045 | 3 | |
| CD | 1999.3 | 50018 | 3 | | VE | 1846.7 | 54151 | | |
| CL | 1997.5 | 50063 | 3 | | VE | 1844.1 | 54227 | 6 | |
| CL | 1995.4 | 50115 | 3 | | CL | 1834.2 | 54520 | | |
| CL | 1993.8 | 50156 | | | VE | 1827.9 | 54708 | 8 | |
| VE | 1990.8 | 50231 | 8 | | CD | 1826.5 | 54750 | | |
| CL | 1987.0? | 50327 | 0 | | VE | 1825.8 | 54771 | 4 | |
| CL | 1985.9? | 50355 | 0 | | VE | 1823.7 | 54834 | 8 | |
| VE | 1980.3 | 50497(d) | 9 | | CD | 1820.8 | 54921 | 3 | |
| VE | 1978.9? | 50533 | 0 | | | | | | |
| CD | 1975.9 | 50610 | 0 | | | | | | |
| RE | 1975.1 | 50630 | | | | | | | |
| CL | 1972.7 | 50692 | | | | | | | |
| VE | 1971.2 | 50731 | 10 | C'' | | | | | |

due to a vibrational rather than to a rotational structure in the ordinary sense of the word, since the large moment of inertia of the cyanogen molecule makes it improbable that a rotational structure would be resolved with the limited dispersion available.

DISCUSSION OF THE SPECTRUM

The modes of oscillation of the linear symmetrical molecule of the acetylene-cyanogen type have been discussed by Mecke,⁴ but his expression for the deformation frequencies does not seem to be quite right, as has been pointed out by Olson and Kramers.⁵ Unfortunately cyanogen has not been investigated in the infrared with modern technique, but the old measurements of Burmeister,⁶ and the Raman measurements on liquid cyanogen⁷ make it fairly certain that the three longitudinal or valence vibrations have approximately the frequencies 2150 (the active vibration) and 2336 and 860 (the inactive vibrations). It is not expected that these frequencies should appear as differences in the ultraviolet absorption of the gas at room tem-

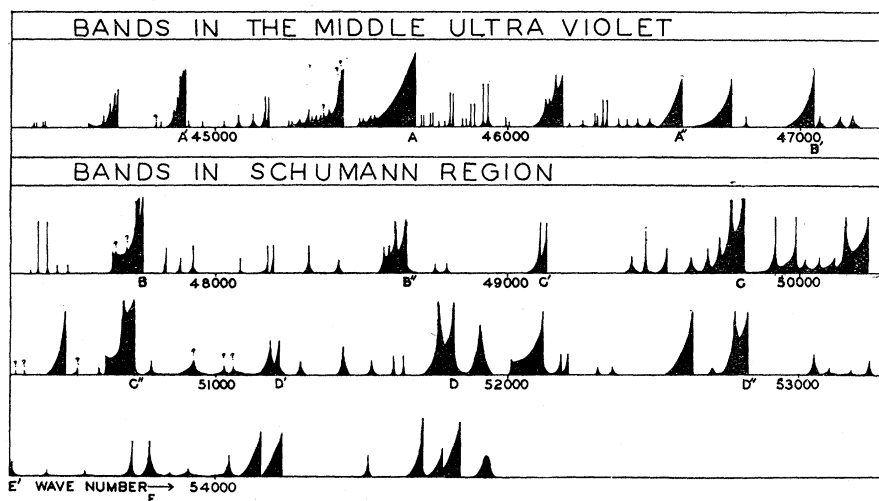


Fig. 1. The ultraviolet absorption bands of cyanogen.

perature. The small deformation frequencies which may appear are more difficult to determine from the existing data. The frequency 512 observed as a Raman shift may be due to the inactive deformation oscillation, and we believe that a weak absorption observed by Rubens⁸ at 52μ indicates that the fundamental band of the active deformation oscillation is not far from this region. It will be noticed that on the red side of a number of bands in the ultraviolet absorption very much weaker bands appear with a frequency difference of about 230. We believe that these latter may be due to absorption of molecules in the first excited state with respect to the deformation oscillation.

⁴ R. Mecke, *Zeits. f. Physik* **64**, 173 (1930).

⁵ A. R. Olson and H. A. Kramers, *J. Am. Chem. Soc.* **54**, 136 (1932).

⁶ W. Burmeister, *Verh. d. D. Phys. Ges.* **15**, 589 (1913).

⁷ A. Petrikaln and J. Hochberg, *Zeits. f. Phys. Chem. (B)* **4**, 299 (1929).

⁸ H. Rubens and H. von Wartenburg, *Phys. Zeits.* **12**, 1080 (1911).

The ultraviolet spectrum of cyanogen is on the whole extremely complex and will require some time for a complete analysis. However, we wish to point out some of the more striking regularities. In particular one notices progressions of doublet bands separated by about 2100 wave number units. Now in room temperature absorption one may expect to find only one strong progression with a given set of frequency differences, though much weaker progressions may be observed displaced to the red, corresponding to absorption from the low lying deformation oscillational levels. However, one may expect to find progressions which are rather similar. If the band system may be very approximately represented by the expression :

$$\nu = \nu_{\text{elect}} + \nu_1' \omega_1' + \nu_2' \omega_2' + \nu_3' \omega_3' + \dots$$

we shall find similar progressions in any one of which one of the vibrational quantum numbers, say ν_1 , takes the values 0, 1, 2, etc., while the other quantum numbers ν_2, ν_3 , etc., remain constant, but change from one progression to another. The frequency differences will not be quite the same for any two such sets of bands, due to the coupling between different kinds of vibration.

In Table III we have given some similar progressions of this sort. It will be noted that the frequency differences are nearly equal to those for the high frequency oscillations in the normal state of the molecule, indicating the persistence of a strong binding in the excited state. The moderate convergence observed shows a rather large dissociation energy for the excited molecule, which evidently must split up into highly activated products, possibly two excited cyanide radicals.

TABLE III. *Some progressions of doublet bands in the cyanogen spectrum.*

| $\nu(\text{cm}^{-1})$ | $\delta\nu$ | $\Delta\nu$ | $\nu(\text{cm}^{-1})$ | $\delta\nu$ | $\Delta\nu$ | $\nu(\text{cm}^{-1})$ | $\delta\nu$ | $\Delta\nu$ |
|-----------------------|--------------------------|-------------|-----------------------|--------------------------|-------------|-----------------------|--------------------------|--------------------------|
| A | 45685(d) | 2075 | A' | 44902 | 2142 | (Doubtful) | | |
| B | 47733 } 47760 } 27 | | (2033) | B' | | 47044(d) | 2091 | A'' |
| | | 2048 | | | | B'' | | 48619 } 48655 } 36 |
| C | 49766 } 49808 } 42 | (1997) | C' | 49116 } 49135 } 19 | (2074) | C'' | 50692 } 50731 } 39 | (2087) |
| | | 2011 | | | 2087 | | | 2092 |
| D | 51763 } 51819 } 56 | (1949) | D' | 51190 } 51222 } 32 | (2050) | D'' | 52779 } 52823 } 44 | |
| | | 1956 | | | 2086 | | | |
| E | 53712 } 53775 } 63 | | E' | 53240 } 53308 } 68 | | | | |