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The New Absorption System of Cyanogen Gas in the Near Ultraviolet. System I

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A new system of absorption bands has been found in the region $\lambda\lambda 3020\text{--}2400$ with an absorbing path of three meters and a pressure of two atmospheres. The gross structure of the system is comparatively simple. Two main progressions of bands with frequency differences 2050 cm^{-1} and 895 cm^{-1} have been found. The bands in these progressions can be accurately represented by a general formula:

$$\nu = A + \omega_1'v_1' + x_{11}'v_1'^2 + \omega_2'v_2' + x_{22}'v_2'^2 + x_{12}'v_1'v_2'$$

with $A = 33,293.63$, $\omega_1' + x_{11}' = 895.75$, $\omega_2' = 2065.38$, $x_{22}' =$

-15.13 and $x_{12}' = -8.00$. The electronic excitation is mainly at the C—N bond. The structure of the molecule in the excited state, its normal frequencies and symmetry properties are also discussed. The frequency difference 2050 cm^{-1} is considered as due to the totally symmetric longitudinal (C—N) vibration in the excited state and a tentative assignment is suggested as follows: $\nu_1' = 895\text{ cm}^{-1}$, $\nu_2' = 2050\text{ cm}^{-1}$, $\nu_3' = 1770\text{ cm}^{-1}$, $\delta_2'(u) = 210\text{ cm}^{-1}$. Other possible assignment has also been briefly discussed.

ALTHOUGH numerous investigations of the ultraviolet absorption spectra of polyatomic molecules have been made in the past, only in a few fortunate cases have they been completely explained. The most natural attempt toward simplification is to investigate those molecules which possess a structure of high symmetry. This has actually been done in most of the successful cases. In the case of linear polyatomic molecules, great similarity of the spectra with those of diatomic molecules is to be expected. But even here, complications may come in from the increasing possibilities of excitation at different bonds, the overlapping of several electronic systems, the uncertainty concerning the structure of the molecule in the excited state, and the interaction between degenerate electronic state and deformation oscillations.

The structure of the cyanogen molecule is probably of the collinear symmetrical type. Its ultraviolet spectrum has been studied by several

investigators.¹ The complexity probably lies in the overlapping of several electronic systems. With a long absorbing path, we have now found a new weak absorption system which is well separated from other electronic systems. Thus it simplifies the problem greatly. Consequently an analysis of this comparatively simple system may throw some light on the nature of excitation and the structure of the molecule in the excited state, and may facilitate the analysis of the more complicated group of bands found in the shorter wave-length region.

EXPERIMENTAL

The cyanogen gas used in the investigation was prepared in an all-glass apparatus by dropping a concentrated solution of potassium cyanide into a solution of 100 grams of copper sulphate in 200

¹ R. B. Mooney and H. G. Reid, *Proc. Roy. Soc. (Edinburgh)* **52**, 152 (1932); Sho-Chow Woo and Richard M. Badger, *Phys. Rev.* **39**, 932 (1932); T. R. Hogness and Liu-Sheng Ts'ai, *J. Am. Chem. Soc.* **54**, 123 (1932).

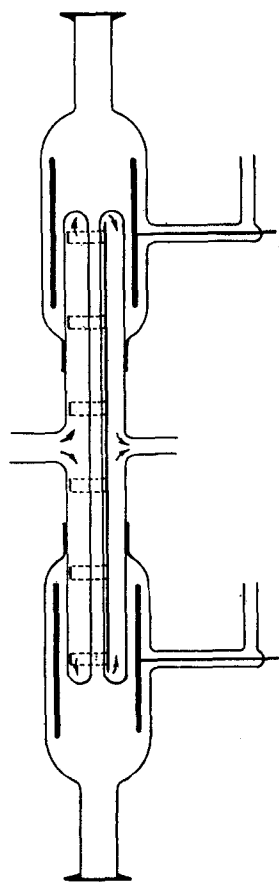


FIG. 1.

cc of water. The gas after being dried with CaCl_2 and P_2O_5 was collected in a trap cooled by a mixture of solid carbon dioxide and ether. The chemicals used for the preparation were of C. P. grade. Before being introduced into the absorption tube, the gas was purified by fractionation under reduced pressure. The middle portion was then collected in a liquid-air trap and subjected to thorough evacuation in order to remove any volatile impurities which might be present. The gas thus obtained could be kept for months without any sign of polymerization. Since the new bands found here began to appear only with a fairly long absorption path, the spectrum might be enormously affected by traces of impurities which might be present in the sample. In order to insure the purity of the cyanogen gas and to verify the real absorber of these bands, preparations from different sources were considered necessary, especially when one notices the fact that potassium cyanide, even of the highest

C. P. grade, does not have a purity higher than 98 percent. Two samples were thus prepared, one by heating C. P. mercuric cyanide and the other by the process described above, using in place of potassium cyanide, a mixture of aqueous potassium hydroxide and hydrogen cyanide which was freshly prepared and purified before use. The samples prepared by these different methods did not show any difference in the spectrum. This may be considered a strong evidence for the purity of the gas. In order to avoid any complication coming in due to the presence of mercury vapor, plates were also taken without using a Hg manometer.

The experimental arrangement was as usual. The hydrogen discharge tube used as the continuous light source had the construction shown in Fig. 1. The whole apparatus was made of Pyrex glass and consisted of two parts, the inner discharge tube and the electrode compartments, joined together with cement which had been proved to have no effect on the purity of the spectrum. The inner tube which had an internal diameter of 5 mm, was silvered and provided with a cooling device. The special advantage of this type of tube lies in its simplicity of construction. Broken parts could be replaced and assembled within one or two hours and moreover it possesses the merit of high intensity which characterizes the types suggested by Bay and Steiner and by Kistiakowsky. The provision of two end windows is recommended for facilitating the line-up with the optical axis of the spectrograph. In the present experiment, the tube was excited with a 1 kva transformer at 3000 v in the secondary.

The spectrum was taken with a Bausch and Lomb large Littrow type spectrograph which has a dispersion of 4.2A/mm at 3000A and 1.2A/mm at 2040A. We are quite satisfied with the instrument except that when it was set for the region $\lambda\lambda 2400\text{--}2000$, the optical system was in such a position that the light of longer wave-lengths dispersed from the system fell upon the wall of the instrument and was reflected directly on to the central portion of the photographic plate. Thus the spectrum was considerably affected by this stray light in a one-hour exposure. This defect was effectively removed by inserting in the instrument a diaphragm which cut off com-

pletely the reflected beam without any effect on the incident light.

Glass tubes of 50 cm and 150 cm long, fitted with quartz windows, and connections to traps, manometer and vacuum pump, were used as absorption cells. For pressures greater than one atmosphere, a 3 m copper tube provided with screwed-on windows was employed. The pressure of the absorbing gas varied from 0.5 mm to about one atmosphere in the case of the shorter tubes, and from one to two atmospheres in the case of the longer tube. It was found that the nature of part of the bands varied greatly with the amount of the absorbing gas. Plates were taken at adjusted pressure intervals in order to develop the systems as completely as possible. Ilford Empress and Eastman 33 and 40 plates were used. Iron arc and copper spark lines were used as comparison spectra.

Measurement of the bands was made with an S.I.P. comparator. The error of measurement for bands above $\lambda 2100$ was less than $\pm 1 \text{ cm}^{-1}$ while for those below $\lambda 2100$ it might be somewhat greater. Microphotometer tracings were also made with a Kipp and Zonen instrument.

RESULTS AND DISCUSSION

With the above described experimental conditions, there were obtained in the region $\lambda\lambda 3020\text{--}2030$ more than 900 bands including

TABLE I. The cyanogen bands in the region $\lambda\lambda 3020\text{--}2480$, system I.

$\lambda(\text{\AA})$ (IN AIR)	$\nu(\text{cm}^{-1})$ (IN VACUUM)	I	DESIGNATION	$\lambda(\text{\AA})$ (IN AIR)	$\nu(\text{cm}^{-1})$ (IN VACUUM)	I	DESIGNATION
3024.6	33053	0		2618.4	38180	0	
3006.9	33247	1		2617.0	38200	1	
3004.7	33272	2		2616.0	38215	0	
3002.7	33294	3	a_0	2614.0	38244	4	b_2
2925.5	34172	0		2555.6	39118	2	
2924.1	34189	1	b_0	2544.4	39290	0	
2853.7	35031	0		2543.9	39299	0	
2852.6	35045	0		2540.3	39354	5	a_3
2851.0	35065	2		(2520.1)	(39669)	1	
2849.1	35088	1		(2519.6)	(39677)	1	
2834.0	35276	2		(2518.7)	(39691)	1	
2831.1	35312	3		(R2510.0)	(39829)	1	
2828.6	35343	5	a_1	(V2509.2)	(39841)	7	
2780.3	35957	0		(R2509.0)	(39844)	7	
2764.3	36165	0		(2508.6)	(39851)	7	
2763.8	36172	0		(V2508.5)	(39853)	7	
2762.4	36190	0		(R2508.4)	(39854)	7	
2762.0	36195	0		(V2507.5)	(39868)	5	
2761.3	36205	2		(2507.1)	(39874)	0	
2760.0	36221	00	b_1	2505.4	39902	0	
2759.2	36232	3		2491.2	40129	0	
2698.5	37047	1		2490.8	40136	0	
2695.6	37087	0		2490.4	40142	0	
2693.4	37116	0		2489.4	40158	0	
2684.2	37244	0		2488.6	40171	0	
2680.8	37291	1		2487.9	40182	0	
2678.5	37323	4	a_2	2485.3	40225	2	b_3
2675.6	37364	6					

those in the region $\lambda\lambda 2300\text{--}2030$ reported by previous authors. However, since we used higher dispersion and finer adjustment of the pressure, the number of bands in the latter region increased considerably and many of them were much better resolved. The bands on the red side of $\lambda 2300$ began to appear and extended already to $\lambda 3020$ when the pressure was one atmosphere with an absorption path of 150 cm. On doubling both the pressure and absorption path, little further extension was observed except the appearance of additional weaker bands in this region.

The possibility of ascribing these high pressure bands to molecules other than cyanogen, present as impurities, appears to be excluded by the careful purification of the sample and also by the fact that the different samples prepared by quite different methods gave the same spectrum. Furthermore they cannot very well be due to the CN molecule which might have been formed by photochemical dissociation for two reasons. First of all, if any CN molecules were formed in a concentration sufficiently high to give these bands, it would certainly be high enough to show the CN red and violet systems, which were certainly absent in our present case. In the second place it is impossible for any diatomic molecule to give

TABLE II. Main progressions in C_2N_2 , system I.

$\nu(\text{cm}^{-1})$	$\Delta\gamma$	$\nu(\text{cm}^{-1})$	$\Delta\gamma$	
33722	22	34172	17	$b_0 - a_0 = 895$
a_0 33294		b_0 34189		
35312	2049	36205	2043	
a_1 35343	31	b_1 36232	27	$b_1 - a_1 = 889$
	28	...	31	
37323	2021	b_2 38244	2012	$b_2 - a_2 = 880$
a_2 37364	41	...	31	
39299?	1990	b_3 40225	1891	$b_3 - a_3 = 871$
a_3 39354	55			

TABLE III.

ν_1'	ν_2'	ν (obs.)	ν (calc.)
0	0	33294	33293.6
	1	34189	34189.5
1	0	35343	35343.9
	1	36232	36231.6
2	0	37364	37363.9
	1	38244	38243.6
3	0	39354	39353.6
	1	40225	40225.4

rise to bands forming regular progressions with two normal frequencies (see below).

In Table I are given only the wave-lengths and wave numbers of those bands in the region $\lambda\lambda 3020-2480$ where most of them constitute a well defined system (which will be designated as C_2N_2 system I) with very little overlapping. They are considered to belong to a separate electronic system for the following reasons. Firstly, they form regular progressions with reasonable intensity distribution and converging intervals, which cannot be extended to bands on the shorter wave-length side. Secondly, the frequency separations between bands in the progressions are definitely smaller than the corresponding ones of the other systems. Only the bands of system I will be discussed here while those in parentheses are of another electronic system and will be reported together with the low pressure bands which are still under investigation.

Most of the bands in system I are rather sharp and narrow. They degrade very slightly toward the red, showing a very slight increase of moment of inertia by the excitation. Some of them, e.g., a_0 , a_1 , a_2 , $a_3(?)$, b_0 and b_1 appear to be doublets with separations increasing toward the high frequency side. Two main progressions of regular intensity distribution are given in Table II. These bands can be fitted into a general formula:

$$\nu = A + \omega_1'v_1' + x_{11}'v_1'^2 + \omega_2'v_2' + x_{22}'v_2'^2 + x_{12}'v_1'v_2' \quad (1)$$

with $A = 33,293.63$

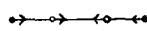
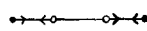
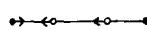


$$\omega_1' + x_{11}' = 895.75, \quad x_{12}' = -8.00 \\ \omega_2' = 2065.38, \quad x_{22}' = -15.13.$$

The calculated and observed wave numbers are given in Table III.

Before any meaning can be ascribed to the frequency differences 2049 cm^{-1} and 895 cm^{-1} , a discussion of the structure of the molecule, the normal frequencies in the ground state and the symmetry properties is necessary. The zero electric moment of the molecule points to a symmetrical structure. From the result of electron diffraction, Wierl² suggested for the structure of the molecule in the ground state a model with the two CN radicals bent in a transposition. The

result can, however, be more plausibly explained by a symmetrical collinear model as shown by Brockway.³ This latter model is also supported by the results of infrared and Raman spectra. Thus the molecule in the ground state should have a symmetry, $D_{\infty h}$. There are two vibrations having the symmetry A_g , and three others having respectively the symmetry A_u , E_g and E_u . Only the two A_g vibrations are totally symmetrical and nondegenerate with respect to all the symmetry elements. If the molecule in the excited state has the same symmetry as that in the normal state, it will be seen that only these two totally symmetrical vibrations can undergo any change of quantum number during the electronic transition, although the unsymmetrical, non-degenerate and the degenerate vibrations may change their quantum numbers with certain restrictions which depend upon the nature of the electronic states taking part in the transition.⁴ This means that from the symmetry considerations alone, only the frequencies of these totally symmetrical vibrations will appear strongly in the spectrum.

We have previously had occasion to discuss the normal frequencies of the cyanogen molecule in the ground state and have assigned the following values:⁵

$\nu_1''(A_g)$		756
$\nu_2''(A_g)$		2336
$\nu_3''(A_u)$		2150
$\delta_1''(E_g)$		512
$\delta_2''(E_u)$		230

From what has been said above, it will be seen that the frequency difference 2049 cm^{-1} found in our main progression must be the frequency ν_2' of the totally symmetrical vibration in the excited state and hence the electronic excitation must have taken place mainly at the C—N bond.

Difficulties have been experienced in assigning the frequency difference 895 cm^{-1} . The most natural assignment is $\nu_1' = 895 \text{ cm}^{-1}$. If this is the case, the electronic excitation must have affected both the C—N and C—C bonds with a

³ L. O. Brockway, Proc. Nat. Acad. **19**, 868 (1933).

⁴ G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

⁵ Sho-Chow Woo, Ta-Kong Liu and T. C. Chu, J. Chinese Chem. Soc. **3**, 301 (1935).

² R. Wierl, Ann. d. Physik **13**, 453 (1932).

TABLE IV. Bands with 1770 cm^{-1} and 1980 cm^{-1} separations.

35045 } 1773	35031 } 1978	38180 } 1985
33272 } 1773	33053 } 1978	36195 } 1985
35065 } 1771	35276 } 1982	38200 } 1979
33294 } 1771	33294 } 1982	36221 } 1979
35957 } 1768	36172 } 1983	38215 } 1983
34189 } 1768	34189 } 1983	36232 } 1983
37047 } 1771	37047 } 1982	40158 } 1978
35276 } 1771	35065 } 1982	38180 } 1978
37087 } 1775	37291 } 1979	40182 } 1982
35312 } 1775	35312 } 1979	38200 } 1982
37116 } 1773	37323 } 1980	
35343 } 1773	35343 } 1980	

result of weakening the former and strengthening the latter simultaneously. A detailed calculation on the variation of ν_2/ν_1 with $\gamma=k_2/k_1$ and $\delta=k_3/k_1$ (where k_1 and k_2 are, respectively, the force constants of the C—C and C—N bonds while k_3 denotes the force constant accounting for their mutual interaction, the interaction between the two C—N bonds being neglected) shows that in order to have $\nu_2'/\nu_2'=2049/895 \div 2.3$, the interaction between the C—C and C—N bonds must have also been increased to a considerable degree.

A physical interpretation of the above results may be found on the basis of Pauling's theory of resonance. This has been done by Brockway³ in interpreting his electron diffraction results, where the molecule of cyanogen in the ground state is regarded as having a structure formed mainly by the resonance of the following two structures with I predominant.



Now if the electronic excitation is such that the molecule in the excited state is brought to a structure with II predominant, our results—the weakening of the C—N bond and the strengthening of the C—C and of the interaction between C—C and C—N can be satisfactorily explained.

Since the electronic excitation has affected the C—N bond, the frequencies ν_3' and $\delta_2'(u)$ (or strictly $2\nu_3'$, $2\delta_2'(u)$ and $\nu_3'+\delta_2'(u)$) may have the possibility of appearing in the spectrum. As a matter of fact, we have found weaker bands with frequency differences 1770 cm^{-1} and 1980

TABLE V. Force constants of the cyanogen molecule.

STATE	k_1 (C—C)	k_2 (C—N)	k_3
Ground state	5.13×10^5	17.48×10^5	0.099×10^5 dyne/cm
Excited state	8.3×10^5	11.8×10^5	0.87×10^5 dyne/cm

cm^{-1} (Table IV). The former may be considered as ν_3' and the latter as the sum of ν_3' and $\delta_2'(u)$, although the selection rules of Herzberg and Teller⁴ are not strictly followed here. The decrease of ν_3 from 2150 cm^{-1} to 1770 cm^{-1} by the electronic excitation is just what should be expected from the above interpretation.

It may be of interest to see how the force constants of the different bonds have been changed by the electronic excitation. Calculation has thus been carried out for both of the normal as well as the excited states. The results are given in Table V.⁶

It will be seen that the above interpretation explains satisfactorily nearly all the experimental results. However, it still leaves some of the weak bands on the red side of the main bands untreated. An alternative interpretation has thus been tried by regarding 895 cm^{-1} as $2\delta_1'(g)$ and setting the selection rule $\Delta v_{\delta_1'} = \text{odd}$, which may be true for a forbidden transition. The bands a_0 and b_0 are considered as due to transitions from the vibrationless level in the ground state to levels in the excited state with $v_{\delta_1'}$ excited by 1 and 3. A combination of this assumption with $\nu_2'=2049$, $\nu_3'=1770$, $\delta_2'(u)=210$ and $\delta_2''(u)=230$ may reproduce all of the bands to within 10 cm^{-1} . However, from the selection rule and intensity considerations, this is quite improbable.

In conclusion the authors want to express their sincere thanks to Professor Richard M. Badger for his kindness in reading the manuscript before publication and to Dr. Ny Tsi-Zé and Mr. S. C. Tsien for the preparation of the microphotometer curves. Our thanks are also due to Mr. T. C. Puan for his assistance in making the preliminary experiments with the Hilger E1 of the Physics Institute.

⁶ It may be admitted that the neglect of the interaction between the two C—N bonds may introduce appreciable error for the case of the excited state. However, not all of the four constants can be evaluated directly from the three frequencies. The calculation may be accurate enough for our present purpose where only the approximate values of the K 's are needed.