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The Infra-Red Absorption Spectrum of Gaseous Cyanogen, C_2N_2

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A discussion of the thermodynamic functions of cyanogen recently appeared in this journal. We therefore think it of interest to describe our re-examination of the infra-red spectrum. The structure of the bands is critical in arriving at a satisfactory assignment of the fundamental frequencies and we have been able to obtain some additional evidence on this question.

EXPERIMENTAL

1. Apparatus

THE apparatus has been described in previous communications from this laboratory; a Hilger D42 spectrometer is used furnished with quartz, fluorite, rocksalt, sylvine and potassium bromide prisms all of approximately 60° angle. With regard to the dispersion of potassium bromide the early values given by Gundelach[1] are in error; thus calibration curves constructed for the instrument from these data gave an error of some 26 cm^{-1} in the maximum of the CS_2 fundamental at 25.2μ;[2] the latter values obtained by Korth[3] appear to be more accurate.

We have always taken great care to check our calibrations against well-defined bench marks in the infra-red and to observe temperature and setting corrections where necessary. It should be remarked here that a fictitious accuracy is often accorded to measurements obtained in the short wave regions particularly from about 4μ to 1μ. The effective slit width may vary from say 10 to 70 cm^{-1} in this region under the most favorable

conditions, and as a consequence not merely is the determination of the center of a band subject to considerable error, but the experimental contour at this low resolution may be markedly different from that obtained with a grating instrument. The latter effect produces shifts in the apparent maximum of the CO_2 fundamental at 4.25μ with the amount of CO_2 in the air: the shape of envelope is also affected by the presence of foreign gases, slightly different readings being obtained for atmospheric CO_2 compared with a pure sample in the absorption tube.

2. Preparation of the gas

Cyanogen was prepared either by heating mercuric cyanide or from a mixture of potassium cyanide and copper sulphate solutions. The latter method produces spectroscopically large amounts of hydrogen cyanide, a substance which has many very powerful absorption bands. A small proportion was also present in the gas from mercuric cyanide, but a threefold distillation over mercuric oxide was sufficient to remove all traces of the impurity.

EXPERIMENTAL RESULTS

The short wave infra-red spectrum of gaseous cyanogen was previously examined by Bur-

[1] E. Gundelach, Zeits. f. Physik **66**, 775 (1930).
[2] D. M. Dennison and N. Wright, Phys. Rev. **38**, 2077 (1931).
[3] K. Korth, Zeits. f. Physik **84**, 677 (1933).

TABLE I. *The infra-red absorption spectrum of gaseous cyanogen, C_2N_2.*

| BAND | WAVE-LENGTH (μ) | | FREQUENCY (CM^{-1}) B. & C. | RELATIVE INTENSITY | PRISM | SLIT WIDTH (CM^{-1}) |
	B. & C.	BURMEISTER				
A	3.755	3.79	2663	40; w	fluorite	17
B	3.901	3.93	2563	65; m	fluorite	15
C	4.651	4.65	{2156 2143	100; vs	fluorite	9
D	4.778		2093	15; w	fluorite	9
E	13.65	13.50	{739.6 724.1	90; s	rocksalt	3
F	16.18	16.07	617.3	20; w	sylvine	4
G	ca. 50[7]		ca. 200	s		
H	ca. 94[7]		ca. 106	m		

meister[4] and his results are incorporated in Table I. In addition Rubens and von Wartenberg[5] found about two percent absorption near 53μ; later work[6] shows this to be more intense and to extend from about 160 to 330 cm^{-1}, maximum near 200 cm^{-1}, with an additional band near 94μ or 106 cm^{-1}.

In addition to the above there were faint traces of absorption near 3010 and 1090 cm^{-1}, but it is important to note that we found complete transmission between 17μ and 26.5μ. The band contours are given in Fig. 1, and any pertinent remarks on their structure will be found in the discussion.

ASSIGNMENTS

A summary of the many attempts to allocate the observed bands to fundamental modes is given by Woo.[7] The difficulty is to find an arrangement which will simultaneously satisfy the selection rules, accord with the experimental values of the heat capacity[8] and provide reasonable values for the force constants. The molecule has the symmetry $D_{\infty h}$; the vibrational modes are well known, but are given with their characteristics for the sake of easy reference in Fig. 2.

The enumeration is that of Dennison[9] who also gives the selection rules. Since the molecule has a center of symmetry no bands should be active

both in the infra-red and Raman spectra, and a knowledge of the latter is necessary to complete the assignments. The fullest determination of the Raman spectrum is the most recent[10] and was carried out with the liquid; other results are also available for the gas[11] and for the liquid.[12]

The results of the present discussion are embodied in Table II. The valence modes ω_1 and ω_2 will be taken from the strong Raman lines 2330, 848 and 506 cm^{-1}. Calculation supported by experiment[13] shows that the absolute values of ω_1, ω_2, ω_4 and ω_5 remain remarkably constant whether there is a triple bond in the middle of the molecule or a single bond in the middle and a triple at each end, i.e., for either

$$m - M \equiv M - m \qquad (1)$$

or

$$m \equiv M - M \equiv m. \qquad (2)$$
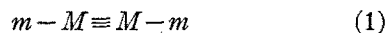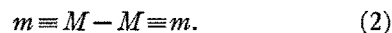
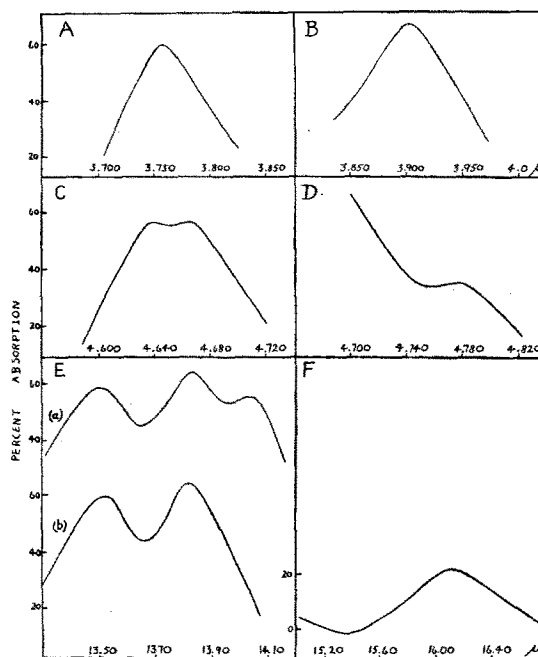It is probable that $\omega_1 = 848$ (liq.) and $\omega_2 = 2330$

FIG. 1. The infra-red bands of cyanogen: E; (a) before removing HCN, (b) after distilling over HgO. A, $p = 70$ cm, B, $p = 70$ cm, C, $p = 3$ cm, D, $p = 70$ cm, E, $p = 6$ cm, F, $p = 40$ cm.

[4] W. Burmeister, Verh. d. deutsch. physikal. Ges. **15**, 589 (1913).
[5] H. Rubens and H. von Wartenberg, Verh. d. deutsch. physikal. Ges. **13**, 796 (1911).
[6] J. Strong and S.-C. Woo, Phys. Rev. **42**, 267 (1932).
[7] S.-C. Woo, Zeits. f. physik. Chemie **B37**, 399 (1937).
[8] D. P. Stevenson, J. Chem. Phys. **7**, 171 (1939).
[9] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[10] A. W. Reitz and R. Sabathy, Wien. Ber. **146**, 577 (1938).
[11] P. Daure and A. Kastler, Comptes rendus **192**, 1721 (1931).
[12] A. Petrikaln and J. Hochberg, Zeits. f. physik. Chemie **B8**, 440 (1930).
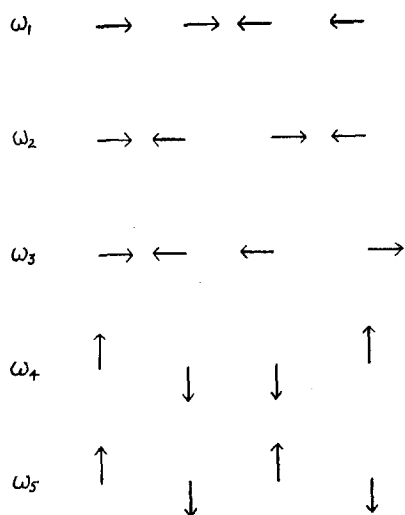[13] F. Trenkler, Physik. Zeits. **36**, 423 (1935).

FIG. 2. Fundamental modes of vibration of the rectilinear molecule $X-Y-Y-X$.

cm^{-1} (gas). Some assignments have given $\omega_1 = 756$; this was found in one case in the liquid[12] although later work[10] does not show it. ω_3 is certainly the powerful infra-red parallel band D at 2150 cm^{-1}, showing only P and R branches ($\Delta\nu \simeq 13$ cm^{-1}). The indications of complexity at E in this band may be due either to $\omega_2 - \omega_4$, which if ω_4 is correctly chosen, may be expected at 2082 cm^{-1}, or to the isotope effect. The shift for a C^{13}—C^{13} molecule is given by the relationship

$$2\omega_3\Delta\omega_3 = \frac{-K\Delta M \times 10^2}{5.863 M},$$

where M is the mass of the C atom and K is the triple bond force constant (*ca.* 17×10^5 dynes/cm) derived from ω_3. This gives $\Delta\omega_3$ as approximately 44 cm^{-1} (the Teller product theorem[14] gives $\Delta\omega_3 = 45$ cm^{-1}) and one might take the shift for a C^{12}—C^{13} molecule as about half this, with a P branch at about 2120 cm^{-1}, so that the first explanation may be more likely. This fundamental is the only affected to any marked extent by the interchange of triple and single bonds mentioned above and in structure (1) with the same masses and force constants would have a value of about 1000 cm^{-1}.

ω_4 is infra-red active and of the perpendicular type. It is this fundamental which has always proved difficult to assign. As Trenkler's models

14 Cf. W. R. Angus, C. R. Bailey and others, J. Chem. Soc. 977 (1936).

show,[13] any oversimplified force field gives calculated frequency values which are lower by some 30 percent than those obtained; one therefore changes Lechner's frequency equation for this mode from

$$n_4{}^2 = d(1/M + 1/m) \quad \text{to} \quad n_4{}^2 = (d+\alpha)(1/M + 1/m),$$

where d and α are, respectively, angular deformation and interaction force constants. The other bending frequency ω_5 is Raman active, and an expression of the type

$$n_5{}^2 = d(9/M + 1/m)$$

gives results which are about six percent too high; if we take ω_5 as the strong Raman line 506 cm^{-1} we may accept d as very close to 0.207×10^5 dynes/cm and $d+\alpha$ as 0.35×10^5 dynes/cm. From this we calculate ω_4 as about 303 cm^{-1}. This result supports reasonably well the assignment of ω_4 to the long wave band located by Rubens and by Strong. We have taken ω_4 as 240 cm^{-1}. The chief difficulty in accepting this allocation is that ω_4 is doubly degenerate and hence the contribution

TABLE II. *Assignments in the spectrum of cyanogen.*

FREQUENCY (CM^{-1})	ACTIVITY	COMBINATION	
2663	IR; $\perp$	$A_u + E_g$;	$= 2656$
		$\omega_3 + \omega_5$	
2563	IR; $\perp$	$A_g + E_u$;	$= 2562$
		$\omega_2 + \omega_4$	
2330	R	A_g; ω_2	
2150	IR; $\parallel$	A_u; ω_3	
2093	IR; $\perp$	$A_g - E_u$;	$= 2082$
		$\omega_2 - \omega_4$	
1026	R	$E_g + E_g$;	$= 1012$
		$2\omega_5$	
848	R	A_g; ω_1	
732	IR; $\parallel$	$E_u + E_g$;	$= 746$
		$\omega_4 + \omega_5$	
618	IR; $\perp$	$A_g - E_u$;	$= 608$
		$\omega_1 - \omega_4$	
506	R	E_g; ω_5	
ca. 240	IR; $\perp$	E_u; ω_4	

from such a low frequency to the specific heat is very large; with the above choice of fundamentals we find C_p at 0°C to be 13.2 cal./mole. Thermal determinations give 10.39 cal. at 0°C[15] and again 10.13 cal. at 6°C.[16] Eucken and others reconcile the thermal and spectroscopic values by taking ω_4 as 732 cm^{-1}: a perpendicular band at this frequency would give satisfactory agreement. It will be remembered that careful purification of the cyanogen was found to be necessary; and the change in appearance of this band as hydrogen cyanide is eliminated may be seen in Fig. 1. E, (a) and (b). The band is of the parallel type and the separation of the P and R branches is 15.5 cm^{-1} corresponding to a moment of inertia of approximately 190×10^{-40} g cm^2: Recent electron diffraction measurements[17] give the interatomic distances as $C \equiv N = 1.16$ and $C - C = 1.37$ A, the corresponding moment of inertia being 180×10^{-40} g cm^2. It may be that the Q branch is very weak; but the analogous vibrations in CO_2 and C_2H_2 do not support this; the doublet structure also forbids its interpretation as $3\omega_4$.

[15] M. A. Masson, Ann. Chim. Phys. 53, 257 (1858).
[16] A. Eucken and A. Bertram, Zeits. f. physik. Chemie B31, 361 (1935).
[17] L. Pauling and H. D. Springall, J. Am. Chem. Soc. 61, 927 (1939).

Further reasons for not accepting 732 cm^{-1} as ω_4 are that anomalous values are obtained for the bending force constants and also that the combination bands B, D, E and F are more reasonably accounted for with $\omega_4 = 240$.

Unless the structure suggested is wrong it is difficult to see how any other allocation is possible, and hence the discrepancy in the specific heat values must await further experimental work before a final decision can be made. The final summary of the assignments is given in Table II.

With regard to the force constants it may be stated that the values $K_{CN} = 16.95$ and $K_{CC} = 5.17$ derived by Reitz and Sabathy[10] accord reasonably well with Pauling's work[17] since the Badger relationship gives 16.8 and 5.6×10^5 dynes/cm. If the electron diffraction results are true then the values obtained by Linnett and Thompson,[18] 17.51 and 6.69×10^5 are too high.

[18] J. W. Linnett and H. W. Thompson, J. Chem. Soc. 1399 (1937).

The Near Infra-Red Absorption Spectra of Pentaerythritol and Diketopiperazine Obtained with Plane Polarized Light

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Pentaerythritol, $C(CH_2OH)_4$, a crystalline alcohol, and diketopiperazine, $(CH_2NHCO)_2$, also crystalline, have been subjected to an infra-red absorption study with plane polarized waves in the region 1–2.5μ. Pronounced pleochroism is observed, and this dependence of absorption upon the plane of vibration of the electric vector, E_0, is used in identifying the bands associated with the normal vibrations of the methylene groups, CH_2, in each crystal. An interesting example of Fermi resonance arises.

In pentaerythritol the appearance of pronounced absorption by perturbed OH groups when E_0 oscillates along the c axis indicates that the feature of the crystalline structure, deduced from an x-ray diffraction study which orients all of the OH groups at right angles to this axis, must be modified.

The absence of the usual NH absorption near 1.50μ supports Corey's assumption of electron resonance in diketopiperazine.

PENTAERYTHRITOL and diketopiperazine are two dissimilar crystalline materials, which, because of the regularity of arrangements of their molecules with respect to the crystal axes, seemed to offer possibilities for obtaining interesting spectroscopic and further structural information if their infra-red absorption were investigated with plane polarized light. The structures of these two crystals have been deduced by means of x-ray diffraction studies