

LETTERS TO THE EDITOR

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RAMAN SPECTRUM OF CARBORUNDUM

CARBORUNDUM crystals are known to exist in five different forms,¹ four of which belong to the hexagonal class and the remaining one cubic. Because of the simplicity of its structure this substance offers scope for a detailed study of its vibration spectrum. Consequently, a preliminary study of its Raman spectrum was made by the writer nearly a year ago and it has not been possible since then to pursue this study further. For this investigation a thin transparent plate of carborundum was placed at the disposal of the writer by Prof. C. V. Raman to whom the author's grateful thanks are due. Using the $\lambda 4358$ radiation of a mercury arc as exciter and a Hilger two-prism spectrograph of high light gathering power, its

Raman spectrum was recorded. The spectrogram, though faint, revealed the existence of a fairly sharp Raman line with a frequency shift of 818 cm^{-1} and a few feebler ones in its neighbourhood. The sharp line may be assigned to the fundamental mode in which the carbon atoms oscillate against the silicon atoms. The frequency shift of this line is found to correspond with the strong infra-red reflection maximum at 12μ reported by Schaefer and Thomas² in one of the hexagonal forms of carborundum. An examination of the optical properties of the specimen used by the writer showed that it is also of the hexagonal class. From the known symmetry of carborundum, this coincidence between the infra-red maximum and the Raman line is only to be expected, even if the form of the specimen used

by the author is different from that employed by Schæfer and Thomas.

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1. Ott, H. *Zeits. f. Krist.*, 1925, **61**, 515; **62**, 201; 1926, **63**, 1. 2. Schæfer and Thomas, *Zeits. f. Phys.*, 1923, **12**, 230.

SPECTRAL STUDIES OF OZONISER DISCHARGES IN NITROGEN

THE spectrum of an ozoniser discharge at voltages from 800 to 6,000 in pure stagnant nitrogen at 20 mm. pressure is characterised by the presence of a large number of band systems of the nitrogen molecule. Extended exposures of over 60 hours do not record, even as traces, any one of the NO bands. The following Table contains a complete list of band systems and bands and lines obtained in these experiments. The intensities are visually estimated relative values. In the case of band systems, they represent the intensity of the strongest band of the system recorded.

Bands	r_e in the initial state (cf. Rosen and Herman)	Intensity
<i>Triplet systems :</i>		
2nd positive ..	1.2123	100
4th do ..	1.108 (r_0)	30
1st do ..	1.293	0.5
<i>Singlet systems :</i>		
P system ..	1.12 (r_0)	40
Q do ..	1.32 _s (r_0)	20
8 do ..	(1.27)	20
R do ..	1.20 (r_0)	20
S do ..	1.23 ₂ (r_0)	20
T do ..	1.22 (r_0)	20
θ do	2
2839 and 2980 Å	15
2462.3, 2567.5, 2679.7 and 2810.6 Å	1
2723 and 2852.4 Å	10
Kaplan's 2nd system ..	1.16 (r_0)	15
5th positive or Van der Ziel's ..	1.18	5
<i>N₂⁺ system</i>		
1st negative ..	1.075	60

In addition to the above, the following lines and band heads due to trace impurities have been recorded on long exposure plates, with intensities ranging from 10 to 20 on the above scale: 2883 and 2896 Å due probably to CO₂⁺, 3064 Å due to OH, 2536 Å due to Hg.

Unclassified bands :

2417.9, 2424.0, 2459.6, 2612.0, 2673.0 and 2907.5 Å
 r_e in the ground state, X¹Σ_g⁺, 1.094

The characteristic features of the spectra are :

(a) Among the triplet systems, the second positive is the strongest with the fourth positive as the next best. The first positive system

is extremely weak. While an exposure time of 2 hours brings out all the bands of the second positive system on a small quartz Hilger E₈ spectrograph with the usual slit width of 0.02 mm., only a faint impression of three groups of the first positive system at 5850 Å, 6200 Å and 6600 Å, is obtained in 24 hours with a slit width of 0.22 mm., other factors being strictly the same. No other system is recorded.

(b) Among the singlet systems involving transitions to $a^1\pi_g$, seven out of the eight known systems (Gaydon and Herman, 1946) are excited simultaneously, whereas some of these systems are known to be selectively excited under special conditions of excitation and discharge (Rosen and Herman, 1951) like the luminescence discharges, discharges in the presence of rare gases and through nitrogen at moderate but controlled pressures and mildly condensed hollow cathode discharges through flowing nitrogen at a few mm. pressure. The single progression of bands at 2839 Å and 2980 Å, recorded by Janin (1949), is obtained; in addition, there are two more progressions which also probably involve transitions from new initial electronic levels to the $a^1\pi_g$ state.

Among the electronic levels that are excited, there are many in which the internuclear distance is much different from that in the ground state of the molecule. This indicates that under the present conditions of discharge, excitation of spectra is brought about not only by electron collisions but also appreciably by atomic and ionic collisions. This view is further borne out by observations based on microphotometer traces of the first and second positive bands. These show: (1) Among the groups of bands excited in the first positive system, the group at 5850 Å ($\Delta v = 4$ sequence) is stronger in intensity than that at 6600 Å ($\Delta v = 3$ sequence). The relative intensity distribution is thus similar to the one obtained in the afterglow spectrum (Johnson, 1949) or the positive column discharge through nitrogen (Pearse and Gaydon, 1950) wherein ions and metastable atoms play a significant part in the excitation of spectra. (2) The relative intensity distribution of the (0, 1), (0, 2) and (0, 3) bands of the second positive system resembles more or less the one obtained in the positive column discharge in air (Tawde, 1934).

The abnormally low intensity of the first positive bands in this type of ozoniser discharge is probably due to deactivation of the excited emitters in the electronic level, B³Π_g, by collisions (Gaydon, 1944; Tawde and Patankar, 1944) and by possible radiationless transfer to repulsive states (Kaplan, 1931; Okubo and Hamada, 1932) in the manner suggested by Zener (1933).