

absorption spectra of the Ce^{+++} ion in solution. For this purpose we prepared cerium chloride ($CeCl_3$) from chemically pure cerium nitrate. In solution it is known that the Cl^- ion shows absorption for wave-lengths $< 200m\mu$, and therefore the region where the absorption due to the Ce^{+++} ion was expected would not be masked by the presence of the Cl^- ion. As a result of our investigations, we found two regions of selective absorption, which appear fairly narrow in width and of measurable intensities at two different dilutions. In the following table their positions are given, with the dilutions at which they appear most distinct. The wave-lengths of the emission doublet attributed to Ce^{+++} ion is also given.

Dilution.	Absorption wave-length.	Emission wave-length.
1/40 mol.	2960 A.	2779 A.
1/1000 mol.	2550 A.	2457 A.
	$\Delta\nu = 5432 \text{ cm.}^{-1}$	4707 cm.^{-1}

It appears that the agreement between the two sets of values are as good as can be expected under the given conditions. The absorption lines are shifted towards the longer wave-length side. From magnetic measurements made on cerium salts, both in the solid state and in solution, it is known that the Ce^{+++} ion is in the $4^2F_{5/2}$ state corresponding to the following electronic distribution :

$$\begin{array}{ccc} 4f & 5s & 5p \\ 1 & 2 & 6 \end{array}$$

By light absorption the $4f$ electron is raised to the $5d$ level, giving rise to $5^2D_{3/2, 5/2}$ terms. The calculated relative intensities of the doublet lines due to the transitions $4^2F_{5/2} \rightarrow 5^2D_{3/2, 5/2}$ is 14 : 1.

The result of our observation is compatible with the predicted ratio of intensities, if it is assumed that the $^2D_{3/2}$ term represents the higher energy level. The shift of the absorption band towards the longer wave-length side can be explained as due to the work done on the radiating electron by the surrounding dipole water molecules, when it is shifted from the inner $4f$ orbit to the outer $5d$ one, on the periphery of the Ce^{+++} ion.

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¹ *Zeit. für Phys.*, **57**, p. 11; 1929.
² *Phys. Rev.*, **33**, p. 157; 1929.

Band Spectrum of the Green Flame of Phosphorus.

I HAVE made several unsuccessful attempts within the last two years to obtain a satisfactory photograph of the band spectrum of the green flame obtained when hydrogen containing a little phosphorus vapour is burnt in the air. The difficulty has mainly been that photographic plates are very insensitive in the green and the flame is not easily maintained for long periods.

I have recently obtained a good photograph, giving an exposure of 100 hours, using a two prism glass spectrograph giving a dispersion of about 10 A. per mm. in the green. In the most intense bands there is considerable overlapping, but a fainter band at $\lambda 5066$ comes out clearly, and Fig. 1 is a reproduction of a register of the band made for me very kindly by Dr. Baker, of the Royal Observatory, Edinburgh. The appearance is very like that of an infra-red vibration-rotation spectrum, but might be an electronic band in which the moment of inertia of the molecule in the

excited and unexcited condition is very nearly the same.

The separation of the bands is about 14.4 cm.^{-1} on the blue side of the gap and 18 cm.^{-1} on the red side. The frequency differences between the gaps in the strongest two pairs of bands are 1187 cm.^{-1} and

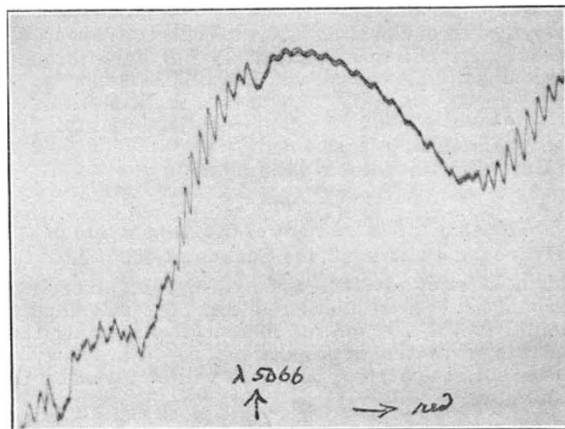


FIG. 1.

1306 m.^{-1} , but these measurements are only rough at present and the analysis of the whole system has not yet been made. The moment of inertia calculated from the value 14.4 cm.^{-1} is 3.95×10^{-40} , which is not conclusive but suggests that the emitting molecule is more likely to be a hydride than the P_2 molecule.

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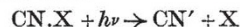
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Ultra-Violet Absorption Spectra of Cyanogen and the Cyanogen Halides.

WE have photographed the absorption spectra of cyanogen chloride, bromide, and iodide, and cyanogen itself in the gaseous state. The light source was a water-cooled quartz hydrogen tube consuming 0.5 amp. at 10,000 volts, from which the emission was perfectly continuous up to the short wave-length limit of the spectrograph (1840 A.).

Cyanogen chloride (pressure, 760 mm.) and cyanogen bromide (pressure, 76 mm.) showed continuous absorption, beginning about 2240 A. and 2540 A. respectively, and extending in each case to 1840 A. Cyanogen iodide at room temperature has a continuous absorption with long wave-length limit about 2150 A. At higher temperatures ($100^\circ - 125^\circ \text{ C.}$) another region of continuous absorption appears with a maximum of 2500 A. and long wave-length limit at 3100 A.

The most probable mechanism for the photo-dissociation seems to be



where CN' has the excitation energy 41 kcal. in all cases except the far ultra-violet absorption of cyanogen iodide, where CN' has 73 kcal. excitation energy. This leads to values 86, 71, and 51-59 kcal. for the heats of dissociation of cyanogen chloride, bromide, and iodide respectively into CN and halogen atom. These values are each about 10 kcal. greater than the mean values given by Eucken for the carbon-halogen linkages in aliphatic compounds.

The absorption spectrum of cyanogen is discontinuous. Between 2380 A. and 1860 A. there are