

## LETTERS TO THE EDITORS

## PHYSICS

Absorption Spectrum of  $\gamma$ -Irradiated Lead Silicate Glass

In an earlier communication<sup>1</sup> it was stated that the absorption spectrum of  $\gamma$ -irradiated lead silicate glass showed three absorption bands at 1.7 eV., 2.3 eV. and 3.3 eV. respectively. The separation of the spectral curve into these bands was obtained by assuming that the peak at 3.3 eV. was uninfluenced by the presence of any other bands. The points in the vicinity of this peak were used to estimate the first Gaussian and the other bands were obtained by successive subtraction.

As the amount of available data increased, further work employing different methods has been done in order to confirm this separation, making only the assumption that the spectral absorption curve consists of a small number of Gaussian-shaped components.

This problem is well suited to solution by means of an electronic digital computer and a programme was written using the equation:

$$y = \sum A_i \exp B_i (x - c_i)^2$$

where  $A_i$  corresponds to the peak height of the absorption band at a wave-length of  $1/c_i$ ,  $B_i$  is a function of the half-peak width of this band, and  $x$  is the reciprocal of the wave-length at the point considered. By a process of successive iteration it was found that the full spectral absorption curve in the region 350–1,000 m $\mu$  could be accurately represented as the sum of two Gaussian absorption bands with maxima at 2.54 eV. and 3.36 eV.

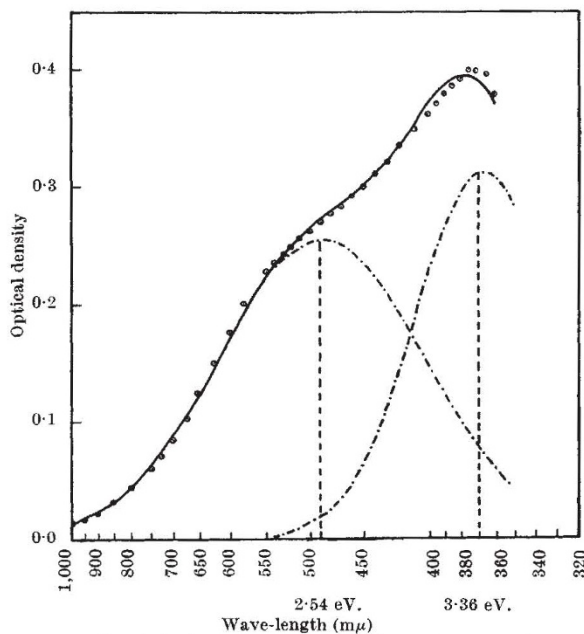


Fig. 1. Spectral absorption curve for  $\gamma$ -irradiated lead silicate glass. Dose,  $3.2 \times 10^4$  rads after 455 min.

The result shown in Fig. 1 is typical of many results so obtained, and it can be seen that there is now no evidence for an absorption band at 1.7 eV., but that there is considerable interaction between the two bands at their peak wave-lengths. The encircled points are the measured values and the full-line is the sum of the two Gaussian bands obtained by computation.

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<sup>1</sup> *Nature*, 187, 135 (1960).

## Rotational Analysis of Absorption Bands of Lead Monoxide

THE low-lying states of  $N_2$  and of CO arise from electron configurations<sup>1</sup> which may be written:

$$\pi^4\sigma^2, X^1\Sigma^+ \quad (1)$$

$$\pi^4\sigma\pi, {}^3\Pi_r, {}^1\Pi \quad (2)$$

$$\pi^3\sigma^2\pi, {}^1\Sigma^+, {}^1\Sigma^-, {}^3\Sigma^+, {}^3\Sigma^-, {}^1\Delta, {}^3\Delta \quad (3)$$

In the group of molecules from CO to PbTe, the allowed absorption bands of longest wave-length may then be expected to be  ${}^1\Sigma^+, {}^1\Pi - X^1\Sigma^+$ . This is found to be the case, for example, in SiS, where the systems  $D^1\Pi - X^1\Sigma^+$  and  $E^1\Sigma^+ - X^1\Sigma^+$  appear readily in absorption<sup>2,3</sup>. In addition, evidence about some other predicted states, notably  $e^2\Sigma^-$ ,  $I^1\Sigma^-$  and (?) ${}^1\Delta$ , has been obtained from work<sup>4,5</sup> on the perturbations in  $D^1\Pi$ . In SiO, GeO and SnO there is no further strong absorption<sup>6</sup> until wave-lengths considerably shorter than those corresponding to the  $E - X$  systems, indicating that more highly excited orbitals than (2) or (3) are here involved.

This comparatively simple situation, which obtains for the lighter molecules of the group, is in strong contrast with that for the heavier molecules, particularly for SnSe, SnTe and the lead compounds. In PbO, for example, the absorption region of longer wave-length ( $\lambda > 2500 \text{ \AA}$ ) shows at least six band systems<sup>7</sup>. The characters of the upper states of these systems have now been determined by rotational analysis of several bands of each system from plates taken on a 6.5-m. grating spectrograph. A summary of the results is given in Table 1. The results for the  $A - X$  system agree with those from the less-extensive analysis of Christy and Bloomenthal<sup>8</sup>; however, their analysis of the  $D - X$  system, which indicated that state  $D$  was  ${}^1\Sigma^+(O^+)$  is incorrect.

In interpreting these results, two possibilities arise: either (i) new low-lying electron configurations other than (2) and (3) become of importance in the heavier molecules, or (ii) the coupling shifts to Hund's case- $c$ . The latter is perhaps the more attractive suggestion. The case- $c$  states of (2) and (3) are as follows:

$$\pi^4\sigma\pi^* \rightarrow 2,1,1,0^+,0^- \quad (2)$$

$$\pi^3\sigma^2\pi^* \rightarrow 3,2,2,1,1,0^+,0^-,0^-,0^- \quad (3)$$