

IONIZED STATES OF MOLECULAR CRYSTALS*

By L. E. LYONS†

The ionized electronic states (cf. Seitz 1940) expected in molecular crystals are of two types, in which (i) the electron is free within the crystal, and (ii) the electron is bound to an individual molecule.

(i) If the molecular orbital from which the electron is excited is large enough to encompass several neighbouring molecular sites then the ionization takes place in a medium having the bulk dielectric constant ϵ (equal to the square of the refractive index). We assume an isotropic crystal although this restriction is easily removed. Ionization from such orbitals needs energy

$$I_c = I_g / \epsilon^2,$$

where I_g is the gaseous ionization potential (Mott and Gurney 1940). Excitation from such an orbital to a higher orbital is expected to give rise to Rydberg levels over a range calculated as 0.25 eV. Such levels have been reported in Cu_2O and CdS (Gross and Karryev 1952; Hayashi and Katsuki 1952) but have not yet been discovered in organic crystals.

If the original orbital is small compared to the intermolecular spacing, then $I_g - I_c$ is due only to P , the polarization energy of the crystal. For anthracene, P has been calculated as 2 eV. Photoemission has been observed with anthracene (Carswell and Iredale 1953) irradiated with quanta of energy 5.6 eV, which compares with the value calculated as 6.2 eV.

(ii) Levels with the electron bound to a neutral molecule occur at lower energies than those for which the electron is free, provided the molecule has a positive electron affinity A . For anthracene, $A = 1.4$ eV (Lyons 1950). Polarization when the electron is on the nearest neighbour to the positive hole has been calculated as 0.8 eV. The mutual attraction of the opposite charges lowers the ionization energy by 2.8 eV for nearest neighbours. The net energy needed to form the lowest ionized state is accordingly 2.2 eV (cf. von Hippel 1936).

There will be many ionized levels between that of lowest energy and the point $I_c - A$ at which the positive and negative centres are separated to a large distance within the crystal.

Consequently, the energy diagram expected for anthracene will be in outline similar to Figure 1, in which for simplicity excitation transfer is neglected. This neglect is not as serious as might at first seem, provided attention is confined to optically allowed transitions.

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It is seen that the lowest ionized states are comparable in energy to the usual $2p\pi$ excited states. Transitions to the ionized states are expected to be very feeble due to the small overlap of the orbitals of different molecules. Even for nearest neighbours the oscillator strength is estimated as 10^{-5} to 10^{-6} , little greater than that of singlet-triplet transitions.

The observation in both absorption (Prikhotjko 1944 ; McClure and Schnepf 1955) and fluorescence (Obreimov and Shabaldas 1943) of a band in an *c.* 3 mm thick naphthalene crystal at 29945 cm^{-1} is possibly a direct observation of an ionized state.

Photoconduction in molecular crystals is expected if an ionized bound-electron state produced optically is then dissociated (e.g. thermally or electrically). The positive and negative centres would then be free to move through the crystal independently and so contribute to the conductivity. This is indeed what is observed (Putseiko 1949 ; Lyons and Morris 1957).

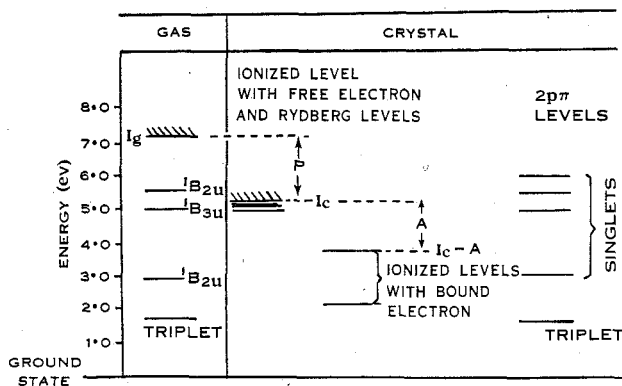


Fig. 1.—Some energy levels in anthracene.

The positive temperature coefficient of photoconduction (Chynoweth and Schneider 1954 ; Bree and Lyons 1956) becomes explicable for this mechanism as due to the energy necessary to dissociate the ion pair.

The existence in these crystals of positive and negative ions has been suggested earlier (Lyons and Morris 1957), to explain the occurrence of observed space charge effects. Details of the present calculations will be published elsewhere. Use of a von Hippel cycle in the case of helium, but without numerical values of the inclusion of polarization terms has been made independently by Dr. J. N. Murrell, with whom, as with Professor William Moffitt, I have had interesting discussions.

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