1000. *Photo- and Semi-conductance in Organic Crystals. Part V.* Ionized States in Molecular Crystals.*

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The occurrence of ionized states in a molecular crystal such as naphthalene is discussed. Such states are estimated to lie at energy levels accessible with visible and ultraviolet light. The transition probability to the state in which the electron is transferred to the nearest neighbour corresponds to $f \approx 10^{-6}$. The importance of such states to crystal spectroscopy and to photo- and semi-conduction is considered.

PHOTOCONDUCTION in crystals such as anthracene in dry air is predominantly [1] a surface effect, but there has also been observed [2] a small but definite bulk photoconductivity which is possibly an intrinsic property of the crystal. The theory of light absorption by such crystals has been based [3] upon neutral excitation waves, in which the excitation is transferred from molecule to molecule throughout the crystal and has successfully explained many dominant features of the crystal absorption spectrum at the longer wavelengths, *e.g.*, the relation [3] to the single-molecule spectrum, the Davydov splitting, and the intensity of absorption. Since a neutral excitation wave is not associated with conductivity, we must now ask what is the possibility of obtaining ionized excited electronic states as a result of light absorption. Extrinsic, surface, and secondary effects are neglected at present. Certain of the results have been summarized in a preliminary report.[4]

Excited electronic states of a molecular crystal can be described, on the usual

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* Part IV, *J.*, 1957, **3661**.

[1] Part I, Bree, Carswell, and Lyons, *J.*, 1955, 1728.

[2] Part III, Lyons and Morris, *J.*, 1957, **3648**; Compton, Schneider, and Waddington, *J. Chem. Phys.*, 1957, **27**, 160.

[3] Craig, *J.*, 1955, 2302; Craig and Hobbins, *J.*, 1955, 539; Bree and Lyons, *J.*, 1956, 2662.

[4] Lyons, *Austral. J. Chem.*, 1957, **10**, 365.

assumptions, in several ways (N is the number of molecules in the crystal, $\boldsymbol{\rho}_n, \boldsymbol{\rho}_m, \boldsymbol{\rho}_p$ are position vectors of a molecule, and $\mathbf{K}$ is the excitation wave vector):

(*a*) *Neutral excitation wave.*

$$X(\mathbf{K}) = N^{-\frac{1}{2}}\sum_{n=1}^{N}[\exp(i\mathbf{K}.\boldsymbol{\rho}_n)]P_n$$

where, if ϕ_m, ϕ_n' denote unexcited and excited molecule wave functions on sites $\boldsymbol{\rho}_m$, $\boldsymbol{\rho}_n$

$$P_n = \phi_1\phi_2\phi_3 \ldots . \phi_{n-1}\phi_n'\phi_{n+1} \ldots \phi_N$$

(*b*) *Ionized excitation wave.*

$$X(\mathbf{K},\mathbf{r}) = N^{-\frac{1}{2}}\sum_{m=1}^{N}[\exp(i\mathbf{K}.\boldsymbol{\rho}_m)]Q_{m,m+r}$$

where, if ϕ_m^+, ϕ_{m+r}^- denote wave functions of molecules on sites $\boldsymbol{\rho}_m$, $\boldsymbol{\rho}_{m+r}$, which have lost and gained an electron,

$$Q_{m,m+r} = \phi_1\phi_2 \ldots . \phi_{m-1}\phi_m^+\phi_{m+1} \ldots . \phi_{m+r}^-\phi_{m+r+1} \ldots . \phi_N$$

Here site $\boldsymbol{\rho}_{m+r}$ is separated by a distance $\mathbf{r}$ from site $\boldsymbol{\rho}_m$.

(*c*) *Ionized state with free electrons.* Here the motion of the excited electron is independent of the motion of the hole. Bloch functions become more appropriate as the energy of the excited state increases. The excited electron is described by a function of the type

$$b(\boldsymbol{\lambda}) = N^{-\frac{1}{2}}\sum_p[\exp(i\boldsymbol{\lambda}.\mathbf{p})]f_p'$$

where $\boldsymbol{\lambda}$ is the wave vector of the excited electron and f_p' the one-electron function of the excited electron at centre $\mathbf{p}$. For a completely free electron f_p' is a constant; otherwise f_p' may be a highly excited molecular orbital, in which case this ionized state with free electrons may be built of excitation waves having all possible values of $\mathbf{r}$, including $\mathbf{r} = 0$. The wave function of the hole can be written in terms of Bloch orbitals for each electron in the ground state, where in each case the Bloch orbital can be expressed in terms of the individual one-electron molecular orbitals. A wave-vector will be associated with the motion of the hole and will differ according to which electron is excited.

$X(\mathbf{K})[\equiv X(\mathbf{K},0)]$ and $X(\mathbf{K},\mathbf{r})$ can be constructed for each excited molecular function. Since for a given level of the excited molecule each $X(\mathbf{K},\mathbf{r})$ will have a different energy, depending upon both $\mathbf{K}$ and $\mathbf{r}$, there is a great number of possible energy levels in the crystal. In addition there is a near-continuum of levels in which the electron is free. The position is somewhat simplified by considering only optically accessible states, for which $\mathbf{K} \approx 0$.

Exact quantum mechanical calculations being very difficult, however, we now consider the energies of the various ionized levels in anthracene and naphthalene crystals, using approximate classical methods.

(i) *Energies of Free-electron States.*—Compare the energy, I, needed to ionize a ground-state molecule in a crystal with the energy, I_g, of ionization in the gas phase. Ionization in the crystal is regarded as the withdrawal of the electron to a distant point still within the crystal, at which the electron is not specifically attached to any one molecule. A difference between I and I_g arises from the effect of the charges, both positive and negative, which polarize the surrounding region of the crystal. An average polarizability, α, may be attributed to each anthracene molecule. The anisotropic components of α do not appear to be known. For naphthalene estimates have been made [5] and rough values can be deduced for anthracene. The polarization energy, W, arising from a singly-charged positive ion on one site can be calculated from the known crystal structure by summing the contributions from all the surrounding molecules. Since W falls off as $(1/S^4)$, where S is the separation of

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[5] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

the charged and neutral molecule, the sum over all the surrounding region quickly converges. If α is taken as 15 Å^3, the error can be shown not to exceed 30%. Since [6] $W = -[\alpha e^2/2S^4]$ the nearest four neighbours in the (001) plane contribute $-0{\cdot}58$ ev to W, and the nearest 18, $-0{\cdot}88$ev. Molecules in adjacent planes also contribute a little, and so $W = -1{\cdot}0 \pm 0{\cdot}3$ ev. In comparison with the error due to the method itself (which is expected to underestimate W), the error ($<4\%$) due to neglecting the polarizability of the positive ion is negligible. For naphthalene $W = -0{\cdot}8 \pm 0{\cdot}3$ ev. For the polarization due to a free electron it seems best to take the same value as for a positively charged molecule. Using $I = I_g - 2W$, we find $I = 5{\cdot}2 \pm 0{\cdot}6$ ev for anthracene and $6{\cdot}5 \pm 0{\cdot}6$ ev for naphthalene. The energy necessary to liberate an electron from the crystal should be given by $I_g - W$, *i.e.*, 6·2 ev for anthracene and 7·3 ev for naphthalene. Photoemission from anthracene is therefore expected at about 2000 ± 100 Å; the experimental value is 2200 Å. In naphthalene emission is expected at about 1700 Å. Free electrons should be produced within the crystal by radiation of wavelength 2400 ± 200 Å for anthracene and 1900 ± 200 Å for naphthalene.

(ii) *Energies of Bound Levels of Large Orbital Radius.*—The relation between the ionization potentials I' and I_g' of an excited molecule in gas and crystal is given [7] approximately by $I' = I_g'(1/\varepsilon^2)$, where ε is the bulk dielectric constant equal to the square of the refractive index, provided that the excited electron before ionization is in an orbital which is large enough to encompass several neighbouring sites. The change in polarization of the crystals as ionization proceeds is very much smaller than the value calculated for ground-state ionization and may therefore be neglected. For simplicity an average dielectric constant (as for an isotropic crystal) is assumed, but this restriction is easily removed if desired. The orbitals which can be treated in this way are the Rydberg orbitals. The energy range over which they occur is reduced from 2—3 ev in the gas to *ca.* 0·2 ev in the crystal, where they occur just below the ionization limit, I. Rydberg levels with $n = 3$ are irregular in gaseous spectra and of relatively small size so that they should be excepted from the applications of this method. Closely spaced Rydberg levels have not been observed in organic crystals but have been observed [8] both in absorption and fluorescence in some inorganic crystals, where they presumably indicate neutral highly excited waves.

(iii) *Energies of Ionized Exciton States.*—Anthracene and other aromatic molecules, except benzene, have been shown [9] to have a positive electron affinity, A. Consequently a free electron in the crystal may be trapped by a molecule in its path. The existence of positively and negatively charged molecules has already been suggested [2] to explain some features of photoconduction. Let us consider the energy of a state in which the electron has been removed from one molecule in a unit cell to its neighbour. This will be the ionized state of lowest energy. All others in which the separation of positive and negative charge is greater will have energies between this value and I. A cycle, such as was applied [10] to the energies of alkali halide crystals, is given in the Table (M denotes a molecule and M^+, M^- molecule-ions). The polarization energy was calculated on the assumption that M^+M^- constituted a dipole of length equal to the distance between neighbouring sites (5·23 Å, anthracene; 5·10 Å, naphthalene). To produce a pair of ions on neighbouring sites, 2·2 ev are needed for anthracene. To produce a widely separated pair of ions, wherein no coulombic attraction exists but the polarization of the crystal is greater by 1·2 ev than when the ions are neighbours, $2{\cdot}2 + 2{\cdot}8 - 1{\cdot}2 = 3{\cdot}8$ ev are necessary.

Compared with gaseous ionization, relatively little energy is required to ionize a molecule in a crystal or other condensed phase. Such a result must be of importance in the

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[6] Böttcher, " Theory of Electric Polarization," Elsevier, Amsterdam, 1952, p. 143.

[7] Mott and Gurney, " Electronic Processes in Ionic Crystals," Clarendon Press, Oxford, 1940.

[8] Gross and Karryev, *Doklady Akad. Nauk S.S.S.R.*, 1952, **84**, 471; Hayashi and Katsuki, *J. Phys. Soc. Japan*, 1952, **7**, 599; Pesteil and Zmerli, *Compt. rend.*, 1956, **242**, 2822.

[9] Lyons, *Nature*, 1950, **153**, 193.

[10] von Hippel, *Z. Physik*, 1936, **101**, 680.

photochemistry and even the thermochenistry of, for example, large aromatic molecules. The ionization of chlorophyll[11] is an example.

A summary of the results is given in Figs. 1 and 2, which show the energy levels observed and calculated as above. Only the lowest triplet level is shown. Rydberg levels for which $n = 3$ are omitted.

The probability of a transition from the ground state to an ionized level of a unit cell can be estimated as follows. Consider the transition of one electron from the highest occupied molecular orbital f_α of molecule α to the lowest unoccupied orbital f_β' of the neighbouring molecule β. The transition moment $M = \int f_\alpha.\mathbf{r}.f_\beta'\,dv$ (where $\mathbf{r}$ is the co-ordinate of the electron). Since the orbitals are on different sites, $\mathbf{r}$ may be considered approximately constant; $\mathbf{r} \approx 5$ Å. Thus $M \approx 5\int f_\alpha f_\beta'\,dv$ (Å). The integral, being the overlap of $2p\pi$ molecular orbitals, will be less than the overlap of two carbon $2p\pi$ orbitals, the axes of which are parallel when the centres are at the distance of closest approach of two carbon centres, one from each molecule in the crystal (3·5 Å). The overlap of two such atomic orbitals is *ca.* 0·008. Pairs of carbon centres separated by 5 Å or more will contribute almost nothing to the overlap of molecular orbitals, so that $\int f_\alpha f_\beta'\,dv < 10^{-3}$; and $M < 5 \times 10^{-3}$ Å. Hence the oscillator strength $f < 3 \times 10^{-5}$. We therefore conclude that $f \approx 10^{-5}$—10^{-6}, and transitions to ionic states are almost as weak as single–triplet transitions in molecules. A crystal between 1 and 10 mm. thick might therefore reveal absorption which produces ionized states, unless the bands are very diffuse. Such transitions bear an obvious resemblance to charge-transfer[12] spectra which,

FIG. 1. *Anthracene.*

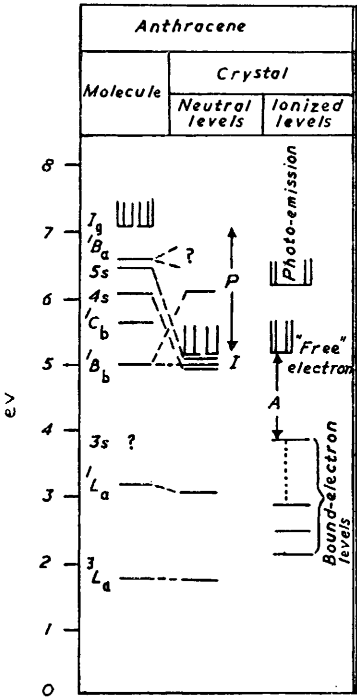
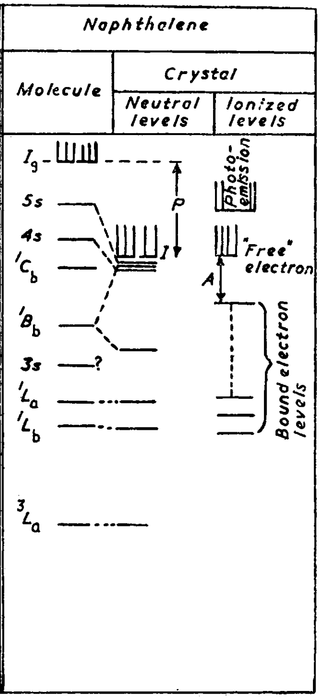


FIG. 2. *Naphthalene.*



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[11] Calvin and Sogo, *Science*, 1957, **125**, 499.

[12] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

however, are generally considered to arise from a partly ionic ground state. The lifetime of an ionized state should be at least 10^{-3} sec. and so fluorescence of this time constant would provide evidence for their existence. Observation of ionized states is therefore feasible. Have they been observed ? In experimental spectroscopy the following observations may be relevant:

(*a*) In naphthalene crystals several mm. thick a band at 29,945 cm.$^{-1}$ has been repeatedly observed in both absorption and fluorescence at 20° K. It must mark an electronic transition. Previously it was suggested that it marks the second triplet level, but although the intensity seems rather high for this there is no certain conclusion possible at present. It could mark an ionized level.

(*b*) In both anthracene and naphthalene a phosphorescence lasting several minutes has been reported, with a maximum in both cases at *ca.* 5200 Å. The similarity of energy in the two cases means that ionised states are of doubtful relevance. The time constant also seems too long for what is being sought, so that ionised states are unlikely here, but not impossible.

Quantum-mechanical " mixing " of electronic states has so far not been considered, yet it certainly must occur. Mixing of the two lowest neutral exciton states has been both discussed and observed.[3] All ionized exciton states of the same crystal symmetry as neutral states must mix with them, with the result that the neutral states become partly ionic and *vice versa.* Ionic states of symmetry species B_u and A_u (in group C_{2h} of the unit cell) certainly exist and can be described in terms of molecular orbitals as $(1/\sqrt{2})(\phi_\alpha{}^+\phi_\beta{}^- \pm \phi_\alpha{}^-\phi_\beta{}^+)(\phi^+,\ \phi^-$ are of symmetries B_{3g}, B_{1u} in $D_{2h})$. The coefficients of mixing of such states with neutral states and with other ionized states can be determined, at least in principle, by use of second-order perturbation theory. Very roughly, the mixing will increase as the overlap increases and decrease with increasing energy separation of the states concerned. Since the overlap of $2p\pi$ neutral and ionized states is certain to be small, a " neutral " state will be only very slightly ionic. Thus the neglect of ionized states in earlier theories is justified. The physical effects of " mixing " will be seen, *e.g.*, in an increased probability of transition to an ionized state, as the result of its becoming partly neutral; if the coefficient were 10^{-4} the oscillator strength would increase in anthracene by 10^{-5}.

The more highly excited Rydberg states will overlap considerably with neighbouring orbitals of neighbouring molecules. The resulting mixing with ionic states would therefore be much greater than in the long-wavelength region of the spectrum. If mixing with a complete set of ionised states, $\sum_r X(\mathbf{K},\mathbf{r})$, occurs then the result can be expressed in an equivalent way for the excited electron in terms of a Bloch delocalized orbital (cf. ref. **13**). Thus free-electron conductivity may arise in the more highly excited exciton states.

Ionized States and Photoconduction.—Free-electron ionized states, such as those above 5·1 ev in anthracene, should be photoconducting, with the greater fraction of the current carried by electrons. This photoconductivity has not yet definitely been observed, but there seems little doubt of its possibility.

Light which is absorbed in a transition to a " neutral " exciton state may give rise to an ionized exciton state in two distinct ways: (*a*) directly, because the " neutral " state has a small probability of being ionized; and (*b*) indirectly, if a transition occurs from the " neutral " state to an ionized state of lower energy. In either case no current can flow under the influence of an electric field, since the positive and negative charges are bound in hydrogenoid orbitals and must move as a pair. Dissociation of the ion pair must occur. This could conceivably occur (i) at a suitable discontinuity in the lattice, (ii) thermally, or (iii) by a sufficiently strong electric field. The thermal energy necessary for dissociation from Figs. 1 and 2 is 0·5 ± 0·6 ev for anthracene and 0·8 ± 0·6 ev for naphthalene. The observed " activation energy " (derived from the temperature coefficient of the photocurrent) of photoconduction is 0·2 ev for anthracene. This mechanism therefore appears

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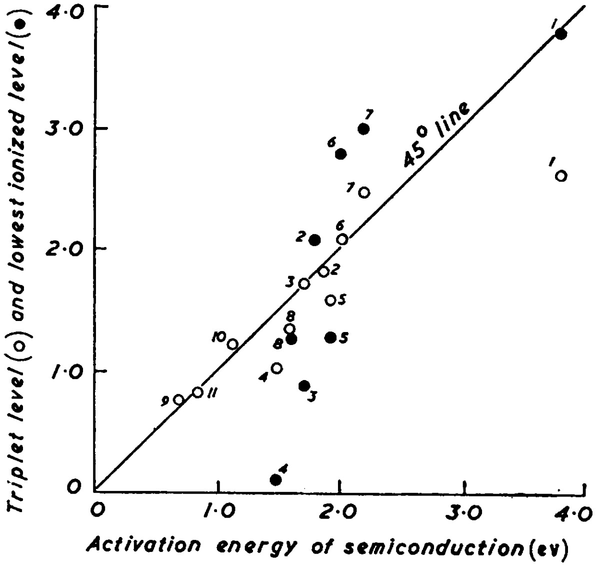
[13] Slater and Shockley, *Phys. Rev.*, 1936, **50**, 705.

to be a real possibility. Strong electric fields must occur in the crystal (apart from the applied voltage) in the double layers on the surface and at the electrodes. (If the effect of oxygen and similar gases at the surface is indeed to form a more pronounced double layer than exists in a vacuum then a possible mechanism is obtained to explain the observed surface effect.) Both electric and thermal dissociation may therefore be expected. Fluorescence and phosphorescence processes of course compete with ionization mechanisms.

Ionised States and Semiconduction.— Fig. 3 shows the energy gap, ΔE, of semiconduction plotted against both the estimated height of the lowest ionized state and also the energy [14] of the molecular triplet level which can be assumed to resemble closely the value in the crystal. There appears to be some correlation, especially between the triplet level and the energy gap [defined by the equation $I = I_0 \exp(-\Delta E/2kT)$]. The experimental and theoretical errors are both appreciable and any interpretation must therefore be cautious. It is not at all clear why a triplet level should need to be formed. The optical levels observed with pyranthrene, ovalene, and violanthrene have been assumed to be

Fig. 3. *Comparison of energy quantities.*



1, Naphthalene; 2, anthracene; 3, tetracene; 4, pentacene; 5, perylene; 6, pyrene; 7, chrysene; 8, anthanthrene; 9, pyranthrene; 10, ovalene; 11, violanthrene.

Energy of formation of ionized states.

	Work needed (ev)	
	Anthracene	Naphthalene
Withdraw 2M from lattice	$2x$	$2y$
$M \longrightarrow M^+ + e^-$	7·2	8·1
$M + e^- \longrightarrow M^-$	−1·4	−0·7
Replace M^+ in lattice	$-x$	$-y$
Replace M^- in lattice, at a point distant from M^+	$-x$	$-y$
Bring M^+ and M^- to neighbouring sites	−2·8	−2·9
Polarize crystal surrounding ion pair	−0·8	−0·6
	2·2	3·9

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[14] See Carswell, Ferguson, and Lyons, *Nature*, 1954, **173**, 736; Inokuchi, *Bull. Chem. Soc. Japan*, 1954, **27**, 22; 1956, **29**, 131; Northrop and Simpson, *Proc. Roy. Soc.*, 1956, *A*, **234**, 124; Mette and Pick, *Z. Physik*, 1953, **134**, 566.

triplets. A direct thermal equilibrium with dissociated ion pairs is expected and appears feasible in cases such as pentacene, perylene, and tetracene, although unlikely with pyrene and chrysene. Where the lowest ionized level lies above the triplet, formation of the latter is not sufficient to produce ions; some auxiliary and presumably non-thermal mechanism must be invoked. If a thermal mechanism operates then there is no reason for the triplet level to be indicated by the energy gap.

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