Migration and Photochemical Action of Excitation Energy in Crystals

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Migration and Photochemical Action of Excitation Energy in Crystals

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A crystal which has absorbed a light quantum can be treated either as an assembly of molecules or else as a giant molecule. If the exchange of excitation energy between crystal cells is slow as compared to the periods of vibration, the first description is preferable; if it is fast, the second picture is better. Both cases are discussed in connection with the following question: To what extent can excitation energy absorbed by an arbitrary cell of the crystal be used photochemically at a specific point which may be far removed from the absorbing cell? The results are applied to the behavior of polymerized pseudoisocyanines, to the hypothetical photosynthetic unit and to the theory of sensitized photographic plates.

PHOTOCHEMICAL processes in crystals and on crystalline surfaces have been subject recently to several discussions. The fact that according to quantum mechanics the excitation energy may be propagated in a crystal seemed to offer possible explanations for some important photochemical processes. For instance it has been proposed that several quanta absorbed by different molecules in a sensitized photographic plate are propagated to one silver ion and cooperate to dissociate it. In a similar way it has been assumed that in the photosynthetic process in plants thousands of chlorophyl molecules combine to form a photosynthetic unit; light-energy absorbed by any one of them is carried to one and the same CO_2 molecule and effects there photoreduction. In fact, the possibility of a collective interaction of molecules in a crystal with light has not only been postulated by theory, but has also been observed directly in experiments of Scheibe and Jelley on pseudo-isocyanine. Here association of molecules into complexes containing a very great number of molecules is accompanied with the appearance of a new narrow absorption band; fluorescence in the wave-length of the incident light and also the phenomenon of quenching have been observed.

Our purpose in the present paper is to discuss the possibilities and limitations of photochemical processes in crystals from a theoretical point of view. The results will be applied to the examples mentioned above.

The interaction of light with crystals and the behavior of crystals in the excited state has been discussed by Peierls[1] and Frenkel.[2] Their results are of fundamental importance in crystal photochemistry. It will be necessary therefore to repeat many points which have been discussed in their papers.

1. PROPAGATION OF EXCITATION. THE EXCITON

A crystal consists of identical elementary cells, which may be atoms, molecules or groups of atoms, molecules or ions. If a crystal is excited, the excitation may be localized in any one of these elementary cells. Such a localized excitation will not represent, however, a stationary state. The coupling between the particles in the crystal and the resonance caused by the identity of the crystal cells has the consequence that the excitation energy will be transferred from one crystal cell to another. A stationary state will be obtained according to Frenkel and Peierls by assuming that any one of the N crystal cells may be excited and that the excitations of the crystal cells shall be superimposed with coefficients which vary with a sine or cosine of the coordinate of the cell measured along any given direction in the crystal. The excitation energy will depend on the wave-length and the direction of the "excitation wave." The lowest excitation energy will be obtained frequently, but not necessarily if the excitation in all the cells is

[1] R. Peierls, Ann. d. Physik **13**, 905 (1932).
[2] J. Frenkel, Phys. Rev. **37**, 1276 (1931); **37**, 17 (1931). Physik. Zeits. Sowjetunion **9**, 158 (1936).

multiplied by the same factor. In the neighborhood of this state, i.e., for "excitation waves" with a wave-length long compared to the lattice distance, the excitation energy will be a quadratic function of the reciprocal wave-length or, more exactly, of the wave number. Choosing the x, y and z coordinate directions in an appropriate way one may write

$$E_{\text{exc}} = E_0 + I_x \bar{\nu}_x{}^2 + I_y \bar{\nu}_y{}^2 + I_z \bar{\nu}_z{}^2. \qquad (1)$$

Here $\bar{\nu}_x$, $\bar{\nu}_y$ and $\bar{\nu}_z$ are the components of the wave number in the x, y and z directions, i.e., half the number of nodes per cm which are found if one proceeds along the x, y and z axis respectively. I_x, I_y and I_z are constants proportional to the rates with which excitation energies are exchanged between cells in the x, y and z directions.

There exists an analogy between the excitation waves with an energy expressed by (1) and the de Broglie waves of a material particle. The energy of a particle can be represented by

$$E = E_0 + E_{\text{kin}} \qquad (2)$$

with

$$\begin{aligned} E_{\text{kin}} &= (p_x{}^2 + p_y{}^2 + p_z{}^2)/2m \\ &= (h^2/2m)(\bar{\nu}_x{}^2 + \bar{\nu}_y{}^2 + \bar{\nu}_z{}^2). \end{aligned} \qquad (3)$$

Here p_x, p_y, p_z are the components of the momentum of the particle and m its mass. In (3) we have used the de Broglie relation

$$p_x = h\bar{\nu}_x \qquad p_y = h\bar{\nu}_y \qquad p_z = h\bar{\nu}_z. \qquad (4)$$

It will be seen that the equations connecting the wave number and the energy will become the same for the excitation waves and the matter waves if we have $I_x = I_y = I_z{}^*$ and if we set

$$I = I_x = I_y = I_z = h^2/2m. \qquad (5)$$

Thus excitation waves will behave as matter waves with a mass defined by (5); in particular the group velocity will be the same in the two cases. Now the group velocity corresponds in the particle picture to the velocity with which the particle represented by the wave picture is moving. Frenkel has proposed to consider the excitation wave as representing a particle, the exciton, having a mass

$$m_e = h^2/2I \qquad (6)$$

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* This will be the case for crystals of cubic symmetry.

and moving along with the group-velocity of the excitation waves.

The mass of the exciton may vary from case to case in wide limits according to the value of I. However, the mass will never be of a smaller order of magnitude than the mass of the electron, since the propagation of excitation waves is essentially due to the motion of electrons in their orbits. On the other hand, there is no upper limit to the mass of the exciton: Any great value of the mass may be obtained for sufficiently small values of I, that is, for slow exchange of the excitation energy. If we want to treat the exciton as a particle, the following complications present themselves.

(1) In noncubic crystals $I_x = I_y = I_z$ will not hold. The exciton must then have a mass depending on the direction in the crystal. Along different axes the factors connecting momentum (or wave number) and velocity will be different.

(2) The simple relation (1) holds only for long waves. If the wave-length becomes comparable to the lattice distance, it must be replaced by a more complicated relation amounting to a variation of the mass of the exciton with its velocity. For some wave-lengths the mass of the exciton will even be negative. A negative mass means that if the exciton loses energy, its velocity (i.e., the group velocity) increases and that if it gains energy it will be slowed down.

(3) The state where the excitation of the crystal cells is superimposed with the same coefficient frequently is not the state of lowest energy. In such cases negative masses may be needed to describe the behavior of long waves.

(4) The number of excitons is not conserved. They can be created and destroyed by absorption and emission of radiation or other processes.

(5) If the excited state of a single cell is degenerate an internal degree of freedom of the exciton must be introduced in order to describe the state of the crystal.

Although Eq. (1) is valid only for long excitation waves, we may apply it, nevertheless, to the shortest waves possible in the crystal and obtain thereby an estimate of the total energy range of which an exciton is capable. The shortest possible wave-length is the lattice distance L multiplied by two. Thus we have

$\bar{\nu}^{(\text{max})} = 1/2L$ and from (1)

$$E^{(\text{max})} = E_0 + I/4L^2. \qquad (7)$$

Using (5) we obtain for the range covered by the exciton energies

$$\Delta E_e = E_{\text{exc}}^{(\text{max})} - E_0 \approx I/4L^2 = h^2/(8L^2 m). \quad (8)$$

The greatest possible range of the exciton energies is obtained if both L and m are small, the minimum value for the latter being of the same order of magnitude as the electronic mass. For the highest possible value of ΔE we therefore obtain a few electron volts, i.e., energies comparable to those of the electrons in the outermost atomic shells. There is, of course, no lower limit for ΔE.

The minimum time, T, required for the excitation to spread to a neighboring lattice point, is closely connected with ΔE. The frequency $\Delta E/h$ will correspond to the fastest possible oscillation of the exciton. T will be one-half times the period of this oscillation

$$T \approx h/(2\Delta E_e) \approx (2hL^2)/I = (4L^2 m)/h. \quad (9)$$

Expressions (6), (8) and (9) offer three different possibilities to interpret the quantity I which we have introduced. According to (6) I is proportional to the reciprocal value of the mass of the exciton. (8), on the other hand, connects I with the breadth of the band of levels in the crystal corresponding to the excited level of a single cell. Finally (9) shows that the greater I is, the shorter will be the time T during which the excitation spreads from one cell to the next.

2. FORMATION OF THE EXCITON BY ABSORPTION OF LIGHT

If we want to follow an exciton from its "creation" to its photochemical action the following questions will have to be discussed:

(1) If light is absorbed and an exciton is created, what can be said about its position and its energy?

(2) In what way can the exciton spread to the point of its photochemical action and how can this propagation be disturbed by the lattice vibrations?

(3) Can the exciton be annihilated by emitting its energy in form of radiation or by converting it into heat before it could cause photochemical action?

(4) What effects will occur on disturbed lattice points and surfaces? Most of the proper photochemical processes will fall under this heading.

We shall consider first the creation of an exciton by absorption of light. The wave-length of the light is in general long compared to the lattice distance. The excitation will take place, therefore, on neighboring lattice points with very similar phases, i.e., the coefficient with which the excitation on a definite lattice point has to be multiplied will vary slowly with the lattice point. In such a case we speak about a long wave exciton. These long excitation waves will frequently correspond to the lowest possible value E_0 of the excitation energy and the exciton will have in such cases no kinetic energy to start with. As has been pointed out, however, in the previous section, the state of equal phases may correspond to a high or the highest kinetic energy of the exciton.

In any case, however, the state of equal phases will possess a group velocity equal to zero and correspondingly the excitons' particle velocity vanishes. But if the state of equal phases has the lowest energy, the only way in which the exciton may gain velocity is that it obtains energy from some source, e.g. from lattice vibrations. If, on the other hand, the state of equal phases is a state of high energy, the exciton may lose energy and still be accelerated at the same time.

If distortions and vibrations of the lattice in the fundamental and in the excited electronic state are absent, only long wave excitons will be obtained. The absorption or resonance spectrum may, therefore, appear sharp even though the breadth of the exciton energy band ΔE is great.

Nevertheless there are reasons why other than long wave excitons may be obtained. In the first place, the absorption of light may be so strong that the light can penetrate into the crystal only by a fraction of its wave-length. This may be the case if the absorption is very sharp and if a relatively great oscillator strength of the absorbing electrons is concentrated into a small spectral region. One can hardly expect, however, that the light does not penetrate at least several

crystal layers and the exciton wave-length remains, therefore, long, compared with the lattice distance. The importance of the phenomenon just discussed may be that in such cases the exciton will be created near the surface, i.e., near the place where many photochemical reactions may occur.

A more general reason which causes the creation of short wave excitons is the irregularity in the crystal brought about by lattice vibrations. If a region of the crystal is distorted, both the excitation energy and the energy corresponding to the exchange or propagation of excitons will be affected. Thus even if the light acts in the same phase at all the distorted lattice points they will not absorb light quite similarly and further changes of phase may result by the time the lattice swings back to its equilibrium position.

According to Peierls, two cases must be distinguished. In the first case the perturbation caused by lattice vibrations is smaller than the greater of the two quantities ΔE and the energy range of vibrational quanta of the lattice. In the second case the perturbation of the vibration is greater than both ΔE and any quantum of the perturbing lattice vibrations. The amplitude of the perturbing lattice vibrations will be determined by the temperature if we are above the Debye θ for the corresponding vibration. Below the Debye θ the zero point amplitude must be taken.

In the first case of Peierls primarily long wave excitons will be obtained. Peierls calls such crystals scatterers. In the second case all kinds of exciton wave-lengths will be created. The name used in this case is "absorber." The significance of these names will appear later.

Even if we deal with scatterers there will be a possibility (decreasing with the perturbation by the lattice vibrations) that excitons of shorter wave-lengths may be created. The most probable process will be, however, the creation of a long wave exciton giving a sharp line in the absorption spectrum. The sharp line will be accompanied by a weaker band corresponding to the creation of various short wave excitons. It is necessary, however, that together with any short wave exciton a vibration may appear. The sum of the wave numbers of exciton and crystal vibration

must be equal to the wave number of the incident light plus or minus any multiple of the number of lattice points per unit of length. That means that though the phases of the exciton are not equal on neighboring lattice points, they become equal if multiplied by the phases of the vibration which has been excited simultaneously.

The statements in the last paragraph can be formulated somewhat simpler if particles—the vibrational quanta or phonons—will be used to represent the lattice vibrations. The mass of the phonon m_p will be connected with the energy range ΔE_p of the corresponding lattice vibrations by

$$\Delta E_p = h^2/8L^2 |m_p|. \tag{8a}$$

The momentum of the phonon will be obtained again from the wave number by multiplication with h. In general several kinds of phonons may exist in a crystal. The number of them is equal to the number of degrees of freedom in a crystal cell. Three of the phonons—corresponding to Debye's acoustical frequencies—will have a rest-energy equal to zero. The absolute value of their average mass will be given, however, by (8a). The other degrees of freedom will correspond in general to phonons with varying rest energies (which we called in case of the exciton E_0). If free rotations are present these will not be described very well by the picture of phonons.

Using the phonon one may express the phase relation discussed above by saying that in the process

$$\text{photon} \rightarrow \text{exciton} + \text{phonon}$$

the momentum must be conserved. This conservation law is, however, only valid modulo the momentum which corresponds to the wave number of the reciprocal lattice.

Using the energies of phonon E_p and the energy range of the exciton ΔE_e, one may subdivide the scatterers of Peierls into phonon scatterers for which $E_p \gg \Delta E_e$ and exciton scatterers for which $\Delta E_e \gg E_p$ and therefore $m_p \gg m_e$. For phonon scatterers several vibrations are completed in a lattice cell before the excitation spreads to the neighboring cell. If in a phonon scatterer an exciton and a phonon are created simultaneously, the energy of the absorbed photon will differ from the energy of a

long wave exciton mainly by the phonon energy. Thus this case corresponds to the application of the spectroscopic principle often called Franck-Condon principle to molecules which have nearly the same equilibrium positions in the excited and fundamental states and which will have mainly $0-0$, $1-1$, $2-2$, $\cdots$ vibrational transitions with relatively weak $0-1$, $1-2$, $\cdots$ and $1-0$, $2-1$, $\cdots$ transitions. There is, however, an essential difference between the case of the molecule and the case of the crystal: In the latter it is possible that the phonon and the exciton created together may separate themselves from each other.

In exciton scatterers the excitation will spread many lattice distances during the time of one vibration. The photon energies for the excitation of long wave and short wave excitons will differ essentially by the kinetic energies of the exciton. In these cases the breadth of the weaker band accompanying the main absorption (which creates a long wave exciton) will be a measure for ΔE_e and m_e, i.e., for the breadth of the region of exciton energies. For phonon scatterers the breadth of adsorption merely measures the energy range of possible E_p values for the disturbing phonons.

Crystals which according to Peierls' definition are absorbers for a certain electronic transition will as a rule produce, together with the exciton, several phonons. Accordingly the absorption will be more uniform lacking the sharp line which corresponds to the strong excitation of a long wave exciton unaccompanied by phonons. Frenkel points out that there will exist in general between the phonons emitted together with the exciton a phase relation of such kind that the lattice will be most strongly distorted around the exciton. Moreover, at least part of the distortion of the lattice will be permanently attached to the exciton. The exciton will be "trapped." This phenomenon has also been discussed by Landau[3] and by v. Hippel.[4]

Absorbers behave as molecules with equilibrium positions differing in the fundamental and excited states. According to the Franck-Condon principle, vibrations will be excited together with the electronic excitation. Since

here the zero-point vibration suffices to cause a great perturbation and since the exciton and part of the lattice distortion may remain permanently bound together, it is no longer possible to distinguish sharply between phonon absorbers and exciton absorbers. One may talk, nevertheless, about phonon absorbers if the exciton velocity in the undisturbed lattice would be small compared to the phonon velocity. If, furthermore, the perturbation and trapping in a phonon absorber is effected by internal degrees of freedom of the cell, the spectrum will be very similar to that of an isolated cell. If it is effected by acoustic vibrations, it is similar to what would be the spectrum of a small group of cells.

3. PROPAGATION OF AN EXCITON

In a crystal undisturbed by irregularities or lattice vibrations, an exciton will be propagated like a particle moving freely. The velocity will be the group velocity of the excitation wave.

If perturbation by lattice-vibrations is taken into account, an exciton may emit or absorb a phonon. It may also, with smaller probability, emit or absorb two phonons or absorb a phonon and emit another; i.e., scatter a phonon. For scatterers in which long wave excitons are created almost exclusively, such emissions, absorptions and scatterings will be relatively rare processes. But as the ratio of long wave to short wave excitons produced by light absorption approaches unity, the propagation of the exciton is disturbed more frequently by the lattice vibrations.

There is, however, no strict relation between the mean free path of · the exciton and the absorption spectrum. Thus the conservation laws for energy and momentum influence the propagation and the creation of excitons in a different way. Here again phonon scatterers and exciton scatterers have to be distinguished.

If we have an exciton scatterer with $m_e \ll m_p$, an exciton of small mass will emit a heavy phonon. In the emission (absorption or scattering) process, the energy of the exciton will not change much, but its direction of propagation may change very greatly.

In considering the phonon scatterers, a further distinction must be made according to whether

[3] Landau, Physik. Zeits. Sowjetunion 3, 664 (1933).
[4] A. v. Hippel, Zeits. f. Physik 93, 86 (1934).

the disturbing lattice vibration—and consequently the emitted phonon—belongs to an acoustic wave or an inner vibration of the lattice cell. If an acoustic wave is emitted for which the rest-energy is equal to zero, $E_p \gg \Delta E_e$ implies $m_p \ll m_e$. Therefore the heavy exciton will emit light phonons and the conservation of energy and momentum requires that the momentum and consequently the energy of the exciton shall not change greatly in an emission process. In such cases the mean free path of the exciton may become short and the exciton will nevertheless be propagated nearly in a straight line.

If the emitted phonon corresponds to an internal vibration the phonon will have in general a rest energy which is greater than its range of kinetic energies. Then it follows from $\Delta E_e \ll E_p$ that the kinetic energy of the exciton does not suffice to emit a phonon of any momentum whatsoever. In such cases the exciton will be propagated in a straight line even though in absorption processes where energy is furnished by the absorbed light a considerable probability exists for creating an exciton and a phonon simultaneously. In the case just mentioned it will be possible that the exciton should be deflected from the straight line by emission of an acoustic phonon. But such emissions might have a small probability. Again a deflection may be caused by the scattering of a phonon which process is never excluded by the conservation laws. But scattering being a double process is improbable and moreover at low temperatures where no phonons are excited initially, scattering becomes impossible. Thus we see that excitons may have a long free path even though in the process of light absorption the creation of short wave excitons is probable.

For absorbers the change in excitation energy produced by zero-point vibration or temperature vibration will be larger than the greater one of the following two quantities: The maximum kinetic energy of the exciton (exciton absorber) and the maximum energy of the phonon (phonon absorber). One may expect in this case that a distortion of the lattice around the position of the exciton will lower the excitation energy and destroy the resonance giving rise to the propagation of exciton or phonon, i.e., the exciton will be trapped.

The position of a trapped exciton may change in two ways. In the first place the thermal vibration of the lattice may bring about an atomic configuration for which resonance is restored. Owing to the irregular nature of temperature motion the exciton will be able to move only to the neighboring cell where it might be trapped again. Thus we are dealing with a diffusion process.

Secondly the temperature may be so low that the energy is not sufficient to excite a phonon. Then the resonance which exists between any two positions in which the exciton may be trapped becomes effective. The trapped exciton may be propagated along a straight line. However, two trapped positions will differ not only in their electronic wave functions but also in the positions of the heavy nuclei. Therefore the transition from one trapped position to a neighboring one will be slow and will correspond to the tunnel effect for the heavy particles which have to slip from one equilibrium position to another. It should be remembered in that connection that a tunnel effect for heavy particles is very improbable; indeed no clean-cut evidence for such a process has been found in physical chemistry.

4. ANNIHILATION OF THE EXCITON IN THE NORMAL LATTICE

An exciton may be annihilated if it emits light. This is the reverse of the process of creation which we have discussed in §2. In a crystal not disturbed by irregularities or vibrations, an exciton can radiate only if its wave-length agrees with that of the photon to be emitted. The state for which the wave-length agrees with that of the photon will radiate with a very high probability. The lifetime in this state will be that of a single cell if radiating by itself, divided by the number of cells in which the interacting photon and exciton can be described by a pure sine wave and for which, therefore, interference of the emitted light can occur. All the other states of the exciton have to be regarded as metastable.

For a "one-dimensional crystal" (an example will be discussed in connection with the chlorophyll problem) the exciton wave-length for which

destructive interference of the emitted light can take place is limited by the wave-length of the light. Only excitons of shorter wave-length will be metastable. Those of longer wave-length may emit light at an angle to the direction of the crystal.

If we consider an ideal crystal and if the perturbations by lattice vibration are not essential, light can be absorbed only into a state of extremely short lifetime. The light will be re-emitted, therefore, at once without causing any permanent change in the crystal. This means that the crystal will interact with the photon by scattering or rather reflecting it. If, on the other hand, the exciton interacts strongly with the phonons, the light, even if it is re-emitted, will cause in general a permanent change in the crystal. That is the reason why Peierls calls the first kind of crystals scatterers and the second kind absorbers.

The difference between scatterers and absorbers is, of course, a gradual one, as even in scatterers permanent changes may occur in the crystal. That will be, in particular, the case whenever the exciton gets into a metastable state either by the direct (though weak) absorption leading to such states or through absorption into the short life state and subsequent emission or absorption of a phonon. In a metastable state an exciton may be "conserved" and, propagated to the part of the crystal where a photochemical action can take place, it may produce the photochemical effect. It is, therefore, of particular interest to see what is the lifetime of an exciton in a metastable state.

If an exciton in any state will emit or absorb a phonon more readily than a photon and if kT is great as compared to ΔE_e and E_p, then— owing to the possibility that the exciton will be thrown into its short life state—the actual lifetime will be that of a cell radiating by itself. If, on the other hand, an exciton scatterer is considered and if $kT < E_e$, the behavior of the exciton will depend on the question whether its long wave states will have the lowest energies or whether they have high kinetic energies (exceeding kT). In the former case the lifetime of the metastable state will be shorter than the lifetime of the excitation in an isolated cell, since the Boltzmann factor favors the transition

of the exciton into the long wave state. In the latter case, however, the Boltzmann factor for the long wave state may become so low that a transition into this state becomes practically impossible. The emission from metastable states will then be due to the fact that during the temperature or zero-point vibrations of the lattice the phases of excitation on the lattice cells are changed. The lifetime of the metastable exciton may then become very long. It can be estimated from the intensity of the weak absorption band which in scatterers accompanies the sharp absorption (or scattering) due to the long wave exciton state.

It might seem possible to assume that these metastable states explain several cases of crystal phosphorescence. However, the lifetime of the metastable states will, in general, not be sufficient for this purpose. For exciton scatterers the lifetime will be that of an excited isolated cell multiplied with $(\Delta E_e/P)^2$ where P is the energy (or more exactly the matrix element) of the perturbation produced by the lattice vibration. The ratio $\Delta E_e/P$ will be of the same order of magnitude as the magnitude of interatomic distances divided by the amplitude of vibration. Thus we have at low temperatures $\Delta E_e/P \approx 10^2$ and $(\Delta E_e/P)^2 \approx 10^4$ and the lifetime of the metastable state will exceed that of an isolated excited cell as a general rule by no more than a factor 10^4.

For phonon scatterers, ΔE_e must be replaced in the above estimate by E_p. A limit for $(E_p/P)^2$ and therefore for the lifetime of metastable states in phonon scatterers can be obtained from the estimate for $(\Delta E_e/P) \approx 10^2$ and from the assumption $\Delta E_e \ll kT$. Thus for room temperature where kT is not much smaller than E_p, the lifetimes of the metastable states in phonon scatterers will not exceed the lifetimes obtained above for exciton scatterers.

For absorbers, if the exciton is trapped, the situation will be entirely different. If the exciton is annihilated by emission of a photon a spherical wave of lattice vibrations will be emitted from the point at which the exciton has been localized. Thus, the final state of the emission process varies with the position of the exciton in the initial state and no interference phenomena are to be expected. An exciton trapped in a certain position will radiate without being disturbed by

the fact that the exciton might have been trapped in another position. The transition probabilities will be comparable to those which one obtains in spectra of polyatomic molecules.

To this general statement a more specific one can be added if in a phonon-absorber the coupling is due to molecular vibrations. In this case the emission will take place from states close to the lowest vibration level in the excited molecule. The fluorescence spectrum may then closely resemble the high pressure fluorescence in the gas or the fluorescence in the solution.

In crystals, as in polyatomic molecules, excitation energy may be converted completely into vibrations and therefore into heat, and the exciton may thus cease to exist without emitting a photon. Such transitions unaccompanied by radiation may occur if potential surfaces cross. If during the trapping processes the nuclei will be displaced strongly from their equilibrium positions, we shall expect these transitions to occur with considerable probability.

It is also possible that instead of the total exciton energy a part of it will be converted into heat or electromagnetic radiation, the remaining energy appearing as a lower excitation energy.

Finally, it will be noticed that in an absorption the exciton energy may be also transformed into chemical energy rather than heat. This must be considered as one type of a photochemical process.

5. Interaction of an Exciton with a Distorted Lattice. The Photochemical Process

If a photochemical process sets in on an atom or molecule differing from the other constituents of the lattice, or if the process proceeds on the surface of the crystal, the photochemical process is essentially an interaction of the exciton with a disturbed lattice point. Such interactions may, of course, also occur without giving rise to photochemical processes.

The case of greatest interest is that of a scatterer. It appears that the exciton may be transported to the point where it can act photochemically with a high velocity and at the point of irregularity it may be trapped giving rise to a photochemical process. We shall investigate the conditions necessary for such a process.

The perturbation of the exciton by lattice vibrations must not be quite negligible otherwise as has been shown in the previous section only long wave excitons of very short life are created. It is best if the long wave excitons have a high kinetic energy so that metastable states may be obtained. By this means the number of excitons lost in fluorescence processes might be reduced.

The photochemical yield will be greatest for phonon scatterers, particularly if the perturbation is due to an internal vibration. The reason is that such interaction may be large and may cause creation of short wave excitons without preventing the exciton from being propagated in a straight line (see §3).

Finally the perturbed lattice point on which the photochemical process will proceed has to fulfill some conditions which we proceed to discuss.

A perturbed lattice point or a perturbed region of the lattice will act on the exciton as a potential acts on a particle. It may attract the particle, it may repel the particle or, finally, the particle may be reflected according to wave mechanics if the potential change occurs too suddenly. In the crystal the first two cases will occur if the excitons on the distorted lattice points are nearly in resonance with excitons on regular points, the difference being smaller than ΔE_e. Reflection will occur, on the other hand, if the distortion has destroyed the resonance. Thus it will be favorable for the photochemical process if on the distorted lattice point the exciton energy is a little lower than on other points. By this mechanism excitons may, for instance, be attracted to the surface of the crystal and if they then emit a phonon they may be left with too little energy to leave the surface. It shall be noted that if a lattice cell is distorted its neighbor will, in general be distorted too. This may act to make the changes of the "potential field" in which the exciton moves less sudden and may make the reflection of an exciton from the "surface" of a distorted region less probable.

It is most favorable for the photochemical process if the time necessary to trap the exciton after it has reached the disturbed lattice point is comparable to the time T given in Eq. (9). If the time necessary for the trapping is much longer than T, the exciton will escape from the disturbed lattice point before it can be trapped. If, on the

other hand, the time of trapping is short compared to T, this short period process will destroy the resonance between the exciton positions on the regular and on the disturbed point. Thus the exciton will be reflected with a great probability before it can reach the distorted lattice point.

Once an exciton reaches a distorted lattice point and is trapped, the photochemical process may occur. If trapping occurs in the undisturbed lattice, the propagation of the trapped exciton to the perturbed lattice cell will be a slow process. In general the exciton will be annihilated by light emission or radiationless transition before it can act photochemically. In addition resonance between the disturbed and undisturbed lattice points is necessary in order that the photochemical process shall occur.

The above discussion shows how many conditions have to be satisfied if we want the absorption of a whole crystal to be used in order to produce photochemical action on a few disturbed lattice points. On the other hand, the photochemical process mentioned at the end of the last section does not require so many conditions. Indeed, it does not differ essentially from a photochemical process in the gaseous state or in solutions.

APPLICATIONS

Pseudoisocyanines

Propagation of excitons in crystals have been frequently used to explain certain features of absorption and emission spectra. Indeed, it is often unavoidable to assume the propagation of excitation energy (e.g. in some cases of excitation of phosphorescence). But it is probable that in nearly all these cases the energy is transported by electrons.[5]

Clearcut evidence for the specific properties of a freely moving exciton is shown by a strong and sharp absorption of the pseudoisocyanines.[6] It has been shown that the pseudoisocyanines when present in a highly polymerized form possess an absorption band which is absent in the molecular solution. The absorption bands of the molecular

solution are separated from this characteristic sharp band by several hundred A units. The sharp band is absent in the dry crystalline form of the pseudoisocyanines but reappears if some water vapor is added. If the polymerized form consists only partly of pseudoisocyanine molecules and partly of a related dyestuff, the new band remains sharp but appears in a shifted position. The band has a half-width of 140–180 cm^{-1} and is, therefore, much sharper than the other absorption bands of these dyes. Fluorescence in the sharp band has been observed both by using the frequency of the band itself and by higher frequencies absorbed by the molecules of the dyestuff. The fluorescence can be weakened by appropriate chemical substitutions. The state of high polymerization and the sharp absorption band can be destroyed in a reversible way by raising the temperature.

Scheibe suggested that the excited state corresponding to the sharp band is a communal electronic state of the polymerized substance. We explain its sharpness by assuming that we are dealing with a scatterer so that light can excite only long wave excitons of a definite energy. The absence of the band in the solution indicates a strong influence of the neighboring molecules in this particular excitation. The behavior of polymerized aggregates consisting of two kinds of molecules is a further proof for the strong coupling. Thus it is very probable that these polymerized dyes are exciton scatterers. For such an exciton scatterer resonance fluorescence is to be expected. Excitation of fluorescence by shorter wave-lengths will be explained by radiationless transitions to the excited state of the sharp band. From the appreciable intensity of this indirectly excited fluorescence and from the absence of afterglow we conclude that long wave excitons have a low energy. The observed breadth of the band may be due to temperature motion of the molecules or to irregularities of the "crystallite." Since the dry macroscopic crystal does not show the new band it is probable that the molecular configuration in the desiccated crystal is not favorable to a fast exchange of excitation energy between the molecules.

The resonance fluorescence seems to have a yield considerably smaller than one. This may be understood in connection with the fact that the

[5] Compare, for instance, results of Riel on luminophores, Ann. d. Physik **29**, 640 (1937).

[6] G. Scheibe and co-workers, Zeits. f. angew. Chem. **49**, 563 (1936); **50**, 51 and 212 (1937); Naturwiss. **25**, 75, 474, 795 (1937); **26**, 412 (1938); Kolloid Zeits. **82**, 1 (1938); E. E. Jelley, Nature **138**, 1009 (1936); **139**, 378, 631 (1937).

polymerized state can be dissociated easily. Though our hypothesis that we are dealing with a scatterer seems to exclude trapping processes, such trappings may occur at points where the "lattice" is strongly distorted. Strong distortions by temperature motion have to be expected in consequence of the ease with which the polymerized state can be destroyed by temperature. As soon as the exciton is trapped its energy may be used for chemical processes, e.g. for the separation of a molecule from the crystallite.

The photosynthetic unit

It has been suggested that in photosynthesis light absorbed by many chlorophyll molecules is utilized for the reduction of a single CO_2. This hypothesis was used to explain certain features of light-saturation and also the apparent absence of a long induction period in weak light. The following detailed picture has been suggested. The chlorophyll molecules are arranged in a one-dimensional crystal to which CO_2 molecules are attached at the ends. Light absorbed in any cell of the crystal must be transported to a CO_2 molecule before being used photochemically. We shall show that it is not easy to reconcile this picture with the behavior of chlorophyll in absorption and fluorescence.

Chlorophyll has two regions of strong absorption in the visible spectrum, namely in the red and in the blue. They appear to correspond to two different electronic transitions. The positions of the absorption maxima vary slightly with the solvent. The variation of the red maximum amounts in molecular solutions to 250 cm^{-1} (6605A–6760A). The maximum in the leaf (6770A) almost coincides with the maximum in methylene iodide solution (6760A). Strong fluorescence has been observed in sufficiently inert solvents. A much weaker fluorescence has been observed in plants. Under stationary conditions during photosynthesis the fluorescence amounts to 0.15 percent of the absorbed radiation. The emitted light is always red independent of the wave-length of the exciting radiation. It follows that the excited state of the absorption in blue will be transformed in that of the red absorption by an internal conversion. Thus the higher excited electronic state has a very short life and we need not consider it in connection with

the photosynthetic unit. The absorption in the red region fades out gradually towards short waves whereas near the red end the absorption coefficient drops much more suddenly. For fluorescence the reverse statements hold. The maxima of absorption and fluorescence coincide within close limits while the spectrum extends for several thousand wave numbers in one case towards the violet, in the other towards the red. These facts can be explained immediately if the maximum of absorption and fluorescence is assumed to correspond to the O−O transition, i.e., to a transition from a nonvibrating excited state to a nonvibrating fundamental state. The shape of the curves shows that the equilibria in the excited and fundamental states correspond to somewhat different configurations of atoms in space. The absorption and emission spectra do not differ essentially in the leaf and in solution except for the slight shift of the spectra and the yield of the fluorescence.

The similarity of optical behavior in solution and in the leaf indicates that, if a photosynthetic unit exists, the excitation of its different cells are not strongly coupled, i.e., the kinetic energy of its excitons is small. Thus we are dealing with a phonon scatterer or a phonon absorber. Indeed an exciton scatterer should show a sharp absorption and emission maximum in the leaf for which there is no evidence. The assumption of an exciton absorber would provide no immediate explanation for the similarity between leaf and solution and leads, moreover, to difficulties which will be mentioned later. The decision between a phonon absorber and phonon scatterer depends on the question whether more or less than one vibrational quantum is excited on the average during the electronic transition. Though the maximum apparently corresponds to the O−O band the total intensity of other transitions seems to predominate. Therefore, taking into account the shape of the curves for absorption and emission, the photosynthetic unit should be classified as a phonon absorber or perhaps as an intermediate case between a phonon absorber and phonon scatterer.

Making, however, the assumption that we are dealing with a phonon absorber it is difficult to understand why the yield of fluorescence is so low in the leaf. The half-life of the excited state of

chlorophyll in solution with regard to radiation is about 2.10^{-7} second. Assuming that the half-life in the photosynthetic unit is the same and remembering that the yield of the fluorescence is only 0.15 percent, it will be necessary to assume that the excitation energy must be used in the photosynthetic unit for some radiationless process within the limit of 3.10^{-10} second. Since, furthermore, the quantum yield for photosynthesis approaches under favorable conditions the theoretical value of four quanta, we must conclude that the photosynthetic process is identical with the radiationless process mentioned above, i.e., the photosynthetic process takes place within 3.10^{-10} second. Now the exciton must traverse 10^3 crystal cells before arriving at the CO_2 and therefore the time for propagation from one cell to the next must not be longer than 3.10^{-13} second. Thus it follows from Eq. (9) $\Delta E_e = h/2T$, with $T = 3.10^{-13}$ sec. must be greater than 50 cm^{-1}.

From the vibrational structure in the spectra of chlorophyll a and b in solutions we obtain $E_p \sim 1000$ cm^{-1}. For a phonon absorber ΔE_e must be smaller that 1000 cm^{-1} for an idealized non-vibrating state in which the atoms of all molecules are held in the same positions. But the propagation in the one-dimensional crystal takes place after the trapping, i.e., after the excited molecule has assumed its Oth vibrational state around the distorted equilibrium position of the excited electronic state. Then the spreading of the excitation energy to a neighboring molecule must be accompanied by a tunnel effect and ΔE_e will be strongly diminished. According to the argument given above it must remain nevertheless greater than 50 cm^{-1} and we are thus left with a limited range for ΔE_e.

In fact our only possibility to avoid an actual contradiction is to assume (as has been done tacitly in the preceding discussion) that the mean free path of an exciton becomes comparable to the dimensions of the photosynthetic unit as soon as it arrives in the Oth vibrational state. If, for instance, we assume that owing to collisions with slower vibrations the mean free path is $1000/n$ crystal cells, the exciton shall perform a "brownian motion" with an n times longer duration than that of the propagation on a straight line. Thus ΔE_e for the trapped exciton will become

n 50 cm^{-1}. For $n \gtrsim 10$ this is incompatible with our assumption of a phonon absorber.

The assumption of an exciton absorber would lead to even greater difficulties. Here we have to assume $n \approx 1000$ and $\Delta E_e > n \cdot 50$ cm$^{-1} = 5.10^4$ cm^{-1}. In an exciton absorber the time of trapping must be shorter than $h/\Delta E_e$ and the breadth of the spectrum must be greater than ΔE_e. Thus we obtain from our assumption a far too diffuse band. Apart from this, however, it is absurd to assume that the coupling of the excited states measured by ΔE_e is 5.10^4 cm^{-1} and the absorption spectrum is nevertheless practically the same as in a molecular solution.

The only remaining assumption, namely that of a phonon absorber, could be tested by the following experiment. The fluorescence should be excited by a wave-length 6700A leading directly to the Oth vibration of the excited state. Thus we obtain through direct absorption the "trapped" state of the exciton and at the same time we shall have an excited state for which the phases are the same for all crystal cells. Such a state should radiate in a much shorter time ($\approx 2.10^{-10}$ sec.). Since moreover the photosynthetic unit will remain in this state for a period $(1000/n)h/2\Delta E_e$ and $n \lesssim 10$, we must obtain a fluorescence of at least several percent. This fluorescence will, moreover, belong to the $O-O$ transition and will, therefore, not extend as far towards long waves as the fluorescence hitherto observed. We conclude that according to whether this new kind of fluorescence appears or fails to appear we shall have to conclude that the photosynthetic unit does or does not exist.*

Even on the present basis it seems to us that the existence of the photosynthetic unit is improbable. We have seen that there is left barely sufficient time for the exciton to be transported to the CO_2. We should have to assume further that photochemical action takes place whenever the exciton arrives at the CO_2. This is, however, only possible if the time for trapping the exciton at the CO_2 is just right, i.e., if it is about 3.10^{-13} sec. This same statement must, moreover, hold for all the intermediate stages of photosynthesis.

The sensitized photographic plate

Finally we shall discuss the sensitization of the

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* It is planned to carry out this experiment.

photographic plate by dyes which have in the infra-red an absorption analogous to the new band observed with the polymers of pseudo-isocyanines. It has been suggested[7] that two or more excitons are propagated to the same point and cooperate there to split off an electron from the halogen ion. This picture has been used to explain that absorption of light with a much longer wave-length than that absorbed by the silver halide crystal itself can produce a latent image. Though it is generally admitted that in the crystal the migration of electrons is of importance for the photographic process a summation of quanta is in disagreement with experimental evidence and moreover, it is unnecessary.

It has been shown that if the intensity of the light is not too small the effect produced by light on the sensitized photographic place depends in the first approximation on the amount of light, i.e., the product of light intensity and time of irradiation. This fact can be easily understood by assuming that one quantum is sufficient to produce a practically permanent change[8] in the plate. If two quanta would be necessary the effect produced should be proportional to the square of the intensity, and even higher powers should be observed if still more quanta would be needed. If, moreover, the weakest possible intensity is used, for which the dependence on the intensity is still practically linear,[8] less than one quantum per minute is absorbed by a grain in the photographic plate and one should obtain therefore for such intensities a very small quantum yield (probably smaller than 10^{-5}) if two (or more) excitons are necessary to produce an effect on the silver halide.

The production of the latent image by temperature has shown that only 15,000 cal. are needed to obtain the latent image.[9] An immediate necessity of summation of quanta would, therefore, only exist if light with a wave-length longer

than 1.9μ would produce the image. The long wave limit of absorption in the crystal does not correspond to the minimum energy necessary to produce a free electron but rather to produce the free electron while keeping the atoms in fixed positions in the lattice.[10] An impact of the second kind such as we may have in a sensitized plate shows similarities to the excitation by temperature. The energy transfer to the crystal can be delayed until the atoms in the crystal get into favorable positions. This will be the case if the dye used for photosensitizing the plate shows fluorescence under suitable conditions.

Another possibility which may be considered is based on the fact that the properties of the ions on the surface are different from the properties of the ions in the interior. Thus the surface ions may absorb light of longer wave-length. This absorption may be weak. But if a strongly absorbing dye is in contact with them, the excitation may be transferred readily from the dye to the crystal surface. The two propositions which we have mentioned certainly do not exhaust the possibilities for explaining the sensitization. They serve only to show that the summation of quanta need not be assumed.

It is possible that some of the photosensitizing dyes, being adsorbed in a monomolecular layer, form a surface crystal which is an exciton scatterer. They would thus be analogous to the pseudoisocyanines. Since, however, the exciton while being propagated would remain in contact with the silver halide crystal, the exciton energies would be available at any time for the photochemical process. An exciton scatterer may be useful for sensitizing the photographic plate for a certain spectral region since it has a particularly strong adsorption in a rather narrow band so that enough light of a suitable wave-length may be absorbed in a monomolecular layer of dye. The adsorption of a phonon scatterer seems to be just as favorable.

[7] G. Scheibe, Naturwiss. 25, 795 (1934).
[8] Photographic Plates for Use in Spectroscopy and Astronomy (Eastman Kodak Co., 1935), p. 12, Fig. 6, plate F.
[9] J. M. Blair and P. A. Leighton, J. Opt. Soc. Am. 24, 1185 (1934).

[10] A. von Hippel, Zeits. f. Physik 93, 86 (1934); 101, 680 (1936).