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*DELOCALIZED VERSUS LOCALIZED PICTURES IN RESONANCE ENERGY TRANSFER**

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1. *Introduction.*—At the conference on Comparative Effects of Radiation the question was discussed whether in excitation transfer a delocalized (collective) or a localized picture should be accepted.[1] The consensus of participants appears to have been that a delocalized picture is appropriate for strong and medium interac-

tions;[2] but that the weak interaction case must be treated in a localized way, such that ". . . the excitation is temporarily entirely localized in one single molecule."[3] This distinction was based on the presence of coherence in strong and medium interactions, and the absence of coherence in the weak-coupling case.

We are going to show that the criterion to be applied is not the presence or absence of coherence, but the presence or absence of localizing processes in the system.[4] As a consequence of this criterion, we find that for weak interactions in liquid solutions, the prototype of localization in past treatments, the general rule is delocalization.

2. *Localization Criterion.*—In the treatment of energy transfer in a system of N identical molecules by the Schrödinger equation,

$$(H_o + H')\Psi = i\hbar \frac{\partial \Psi}{\partial t}, \tag{1}$$

H_o is the Hamiltonian of the unperturbed system, and H' that of the interaction. We first consider H' to result only from resonance interactions among pigment molecules. The solution is written as a superposition of localized wave functions, ϕ_k, such that

$$\Psi = \sum_{k=1}^{N} a_k(t)\phi_k, \tag{2}$$

where ϕ_k is a product,

$$\phi_k = u_1 \ldots u_k^* \ldots u_N, \tag{3}$$

of the wave functions, u_l, of the individual molecules. The symbol * indicates the wave function of the excited state.

In (2), the a_k's are (continuous) functions of time, and are generally nonzero,[5] even if initially only one of them is different from zero. This expresses the fact that initially *localized* excitations become delocalized in time; localized states are not stationary. Therefore, the extreme localization theory, in which the energy resides in one molecule until the location of the energy changes suddenly to another molecule, does not follow from the above quantum mechanical treatment.

The Hamiltonian should include interactions between pigment and solvent molecules in the case of a solution. Inclusion of these interactions makes the form of (1) very complicated; still, in principle, the a_k's are generally nonzero, and the delocalized picture applies.

On the other hand, one can look for self-contained *measuring* processes which localize the excitation energy. The results of such measuring processes are different values of a parameter q, dependent on the energy of a pigment molecule. If

$$|q(E^*) - q(E)| > \delta q, \tag{4}$$

then the outcome of a particular measurement distinguishes E^* from E in a single molecule. Here, E^* and E are the energies of the excited and ground states, respectively, and δq is the quantum mechanical uncertainty of q under the prevailing circumstances.

As an example, consider the absorption of a blue quantum and subsequent emission of a red quantum. If a radiationless transition of the molecule takes place

from the higher to the lower excited state, energy is given to the surroundings. If this relaxation energy is larger than the energy uncertainty of the surroundings, then the red quantum energy is initially localized to one molecule.

In the following, we examine three processes which previously have been considered causes of localization in weak interaction energy transfer in liquid solutions.

(a) *Elastic collisions between pigment and solvent molecules:* Nonquenching collisions produce random phase changes in the oscillations of dipoles. The resulting lack of coherence has been interpreted as the main cause of, or even equivalent to, localization.[6]

We show that phase-changing collisions in liquids are not, in general, energy measuring processes. The quantity q of (4) is here the momentum of the scattered particles. The prototype of such energy measurements is the Stern-Gerlach experiment. The scattering then takes place in a well-prepared field of constant gradient into which a properly defined wave packet of the molecule enters. The momentum imparted to the molecule while it travels through the field is $(\partial E^*/\partial x)T$ when the molecule is excited and $(\partial E/\partial x)T$ in the ground state.[7] T is the duration of the experiment. The experiment is successful if

$$\Delta p_x = \left(\frac{\partial E^*}{\partial x} - \frac{\partial E}{\partial x}\right) T > \delta p_x, \tag{5}$$

where δp_x is the uncertainty of the momentum in the previously prepared wave packet; i.e., $\delta p_x \sim h/d = (\lambda/d)p$, where λ is the de Broglie wavelength of the particle and $d = \delta x$ is the width of the beam. The gradient $\partial E/\partial x$ is independent of x in such experiments. Since $\partial E/\partial x$ increases with applied field strength, it is in principle always possible to satisfy condition (5).

While the molecule passes through the field, its oscillation frequency,

$$\nu = h^{-1}[E^*(F) - E(F)], \tag{6}$$

is a function of the field strength F. In the time interval T a phase change

$$\Delta\varphi = 2\pi h^{-1}[E^*(F) - E(F) - h\nu_0]T \tag{7}$$

is produced; ν_0 is the frequency in the absence of the field.

It is important to note that while Δp_x in (5) depends on the gradient of the applied field, $\Delta\varphi$ depends on the field strength itself. Therefore, the change in the momentum (which is utilized for the energy measurement) and the change in phase produced in the experiment are in general uncorrelated quantities.[8] A simple example is a uniform field ($\partial F/\partial x = 0$) which produces $\Delta\varphi$ but no Δp_x. This leads one to suspect that phase changes by collisions (and hence destruction of coherence) do not necessarily effect localization.

The collisions between two molecules (a pigment and a solvent) in a liquid represent quite a departure from the well-prepared conditions of a Stern-Gerlach experiment. In the former, the uncertainties of the position and momentum of *both* colliding partners enter the initial conditions, and the acting forces and their gradients change violently with the distance (impact parameter). If the position uncertainty of the two molecules is larger than the range of the forces, then the wave packets corresponding to E and E^* are not resolved with respect to space coordinates. Therefore, it is impossible to decide between E and E^* in a single experiment.

Estimates given below show that this is the case in a liquid at room temperature.

The average de Broglie wavelength at room temperature for a molecule of molecular weight 100 is $\lambda \sim 10^{-9}$ cm. A mean "free path" of the molecule can be estimated from its thermal velocity and the collision frequency. This latter quantity, ν_c, as determined from the spectral broadening, is $\nu_c \sim 10^{12}$ to 10^{13} sec^{-1}. The ratio of the mean free path, Λ, to the de Broglie wavelength is $\Lambda/\lambda \sim 10$ for $\nu_c = 10^{12}$ and $\Lambda/\lambda \sim 1$ for $\nu_c = 10^{13}$ sec^{-1}. The smallest position uncertainty of the colliding molecules is λ; if this is the case the directions of the momenta are completely uncertain and no knowledge of the energy E^* or E can be gained from the scattering experiment.

On the other hand, if the position uncertainty is as large as its maximum, Λ, then the impact parameter is unknown to within Λ. Since in the collision short-range forces (van der Waals) are certainly also involved, the outcome of the individual experiment can be the same angle of scattering for both E and E^*.

Therefore, phase disturbing collisions do not in general localize the excitation. Very infrequently, a Λ large enough and a λ small enough to distinguish E^* from E may occur, but by no means are such events the rule.

(b) *Exchange of vibrational energy:* If v labels vibrational levels in both ground and excited states of the molecule, then $(E_v - E_{v'})$ may differ from $(E_v^* - E_{v'}^*)$. To distinguish E^* from E when energy exchange with the surroundings occurs,

$$\left|(E_v^* - E_{v'}^*) - (E_v - E_{v'})\right| > \delta\epsilon, \tag{8}$$

must hold; $\delta\epsilon$ is the width of a vibrational level. Pigment molecules in solution at room temperature display little or no vibrational structure in either absorption or emission spectra. Thus, $\delta\epsilon$ is likely to be so large that condition (8) cannot generally be fulfilled.

(c) *Formation of "localized" excitons:* Davydov[9] treats "localized" excitons in molecular crystals. These are associated with local lattice deformations which travel together with the excitation[10] and generally shorten the excitation lifetime. No similar effect appears to have been described in liquid solutions.

Distortions in a molecular crystal are caused by resonance interactions between like molecules. Since there are usually no resonance interactions between pigment and solvent molecules, the formation of "localized" excitons is unlikely in a solution. If present, "localized" excitons should shorten the excitation lifetime. Hence, "localized" excitons are restricted to quenching solvents and cannot be used to argue for localization in weak interactions in general.

3. *Ensemble Averages in the Incoherent Limit.*—As noted earlier, coherence among the amplitudes, a_k, of the localized states, ϕ_k, is interrupted by collisions in the weak-interaction case. In this case the energy transfer involves broad spectra, and in the incoherent limit the perturbation problem may be treated by Fermi's "Golden Rule."[11] Equations (1) and (2) may then be replaced by

$$(d/dt)|a_i|^2 = \sum_k F_{ki}(|a_k|^2 - |a_i|^2), \tag{9}$$

where the F_{ki} are pairwise transfer rates,[12] and we have neglected radiation. Since, in general, all of the $|a_i|^2$ are nonzero, (9) also corresponds to a delocalized picture.

One mayalso consider an ensemble of systems in each member of which (at any

instant of time) one of the $|a_i|^2 = 1$, and all the others are zero. If the relative number of systems in which $|a_j|^2 = 1$ is given by the solution of (9) for $|a_j|^2$, then the ensemble of localized-excitation systems has the same average properties as an ensemble of (identical) delocalized-excitation systems. If one follows the time course of a single member of the ensemble, the energy appears to "jump" around as a particle in Brownian motion. The localized ensemble leads to the random walk problem of mathematics. It has been known for some time[13] that the random walk problem may also be solved by differential equations of the form (9).

If the density of (dye) molecules in the aggregate is high, it is possible to approximate the system of differential equations (9) by a diffusion equation. Such a calculation is applied to the photosynthetic unit in a subsequent paper.[14]

In regard to the use of the localized picture, some errors occurred in the past. If the number of "jumps" to a specific site (considered to be a trap) is known from the solution of the random walk problem, it is incorrect to calculate the trapping time as the product of that number and the pairwise transfer time. If a molecule has several nearest-neighbors, the "jump" into one of them occurs more rapidly because of the others. (A small additional diminishing of the mean "jump" time is produced by the effect of the nonnearest neighbors.) Thus, for example, if two weakly interacting molecules are isolated in solution with separation r and (pairwise) transfer time t_1, then in a cubic lattice of constant r of the same molecules, the actual transfer time is approximately $0.12\ t_1$. The delocalized mathematical treatment takes account of the branchings (many neighbors) automatically.

The delocalized description has a further advantage for ensembles of systems in each of which the probability of initial excitation is equal for all molecules. The differential-equation system of such an ensemble can be solved using the uniform delocalization of the excitation energy as the initial condition.

The localized and delocalized pictures lead to the same ensemble averages in the incoherent limit. On the other hand, it must be emphasized that complete incoherence can never be achieved in the presence of resonance interactions, however weak.[15] Thus, the equations (9) are not completely valid, and hence the delocalized picture (with the possibility of relocalizations) is the only tenable one.

Summary.—(1) In excitation transfer, energy must be considered delocalized unless the presence of specific localizing processes is demonstrated. (2) A criterion for localizing processes is given. On the basis of this criterion, it is found that, for weak interactions, localizing processes in liquid solutions at room temperature are unlikely. (3) Localized and delocalized pictures give equivalent ensemble averages in the incoherent limit. Since this limit cannot be reached in the presence of resonance interactions, the equivalence is only approximate, and only the delocalized picture is generally valid.

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STUDIES ON CYCLOSERINE-CATALYZED REACTIONS

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The reaction of diisopropylphosphofluoridate (DFP) with chymotrypsin and other serine esterases has been well documented in literature[1-4] and the sequence of amino acids of the peptides containing the diisopropyl phosphoryl (DIP) moiety from various DFP-inhibited serine esterases has been established.[5-10] The phosphoryl moiety appears to be located on a serine residue in the enzyme protein. Also, the specific acetylation of chymotrypsin with p-nitrophenyl acetate originally reported by Balls and Aldrich[11] has been shown to result in the acetylation of the serine hydroxyl group which presumably is the same serine residue as that involved in the phosphorylation with DFP.[12] Several mechanisms have been proposed to explain the catalytic action of chymotrypsin and other esterases susceptible to inhibition by DFP.[13-16] However, none of the model systems proposed, e.g. the oxazoline model[15] and the bicyclic intermediate formed from aspartyl serine peptide,[16] was either catalytic or able to react with DFP.

During an investigation on the second phosphorylation site in DIP-trypsin,[17] a new amino acid was observed and on the basis of its chromatographic and electrophoretic behavior and its susceptibility to periodate oxidation, it was tentatively concluded to be hydroxylysine.[18] However, in the course of the isolation of this new amino acid on a large scale, it was found to differ from δ-hydroxylysine in its chemical properties despite its striking resemblance to the latter on the basis of criteria earlier employed. Some properties[18a] of this new amino acid suggested that it could be a derivative of hydroxylamine. Several hydroxylamino acids, ε-N-hydroxylysine[19] and δ-N-hydroxyornithine,[20, 21] and hydroxylamine derivatives of amino acids, cycloserine,[22, 23] have been reported in recent years. A study of the properties of some of these hydroxylamino acids was undertaken with the idea of