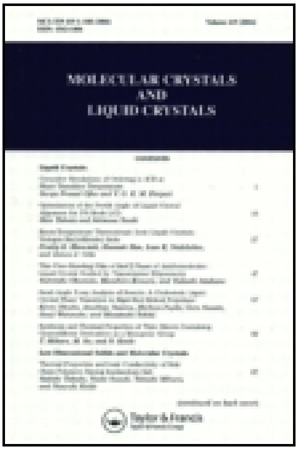

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Lattice Random Walk Theory of Geminate Recombination

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Lattice Random Walk Theory of Geminate Recombination

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We review herein a lattice-random-walk theory of geminate recombination of charge carriers in condensed phases. The results depend on a set of molecular parameters which make it possible to relate geminate recombination to material properties. The relationship of this theory to the Onsager (continuum) theory is discussed.

I. INTRODUCTION

Geminate recombination of photogenerated charges carriers is the most fundamental process governing the efficiency of photoelectronic devices. The problem is simply stated. An electron-hole pair is produced by the absorption of a photon in a condensed phase. An external electric field is applied to the system. The carrier pair is thus subject to two oppositely acting electric fields-the Coulomb attraction between the electron and hole, which favors recombination, and the external field, which tends to separate the carriers. One would like to know the probability that the carrier pair will separate (recombine).

Clearly, the dissociation efficiency η is a function of the molecular properties and geometric structure of the phase in which this process occurs. Excellent fits to experimental data,[1-4] however, have resulted from the use of a continuum-based theory, originally developed by Onsager to treat ionic conductance in solution 5 and geminate ion recombination in insulating liquids.[6] The Onsager theory is formulated in terms of two parameters—r_o, the initial separation of the electron and hole, and ϕ_o, the quantum yield for initial production of the charge-carrier pair. Fits to data give values of r_o and ϕ_o.

It has been recognized for some time[7] that, although data are well fit by the

Onsager theory, the broad assumptions of the continuum approximation are at variance with the conditions obtaining in many of the solids in which data have been collected. Furthermore, it is not easily possible to relate r_o and ϕ_o to molecular properties of the solid. For these reasons, we have undertaken the development of a new theory of geminate recombination, which allows explicit consideration of the molecular and phase structure of the photoconductive solid in which the process occurs. In this approach,[8-12] the hole is regarded as fixed at the origin of a lattice, in the presence of an applied electric field. The electron, initially fixed at a specified site on the lattice, executes a nearest-neighbor random walk on the lattice under the influence of two electric fields—the external field and Coulomb interaction with the fixed hole. In the following section, we outline the framework of this theory.

II. MOLECULAR THEORY

It is necessary to pick a kinetic scheme for the recombination process. We choose to consider a system in which each site on the lattice except that at the origin has one state available for occupation by the electron. The site at the origin, where the hole is localized, has two states—S_0 and S_1. From a nearest neighbor site, only S_1 is directly accessible to the electron. Once the electron is in S_1, it can either transfer to a nearest-neighbor site or undergo a transition to S_0. If this $S_1 \rightarrow S_0$ transition occurs, recombination is complete and the random walk is at an end.

We denote the probability that the electron will be at site 0 in state S_0 at $t = \infty$ (i.e. that recombination will have taken place) as $\tilde{P}_1(0,\infty)$. It can then be shown[9] that

$$\tilde{P}_1(0,\infty) = \psi_{12}(0)R(0,0). \tag{1}$$

Here $\psi_{12}(0)$ is the Laplace transform (LT) of the $S_1 \rightarrow S_0$ transition probability, and $R(0,0)$ is the $\mu = 0, 1 = 0$ limit of the LT of the function $\tilde{R}(1,t)$, which is the probability per unit time that the electron will just arrive at site 1 at time t, having started its random walk at site 1_0 at $t = 0$. It is demonstrated in Reference 9 that a closed set of equations for the R functions can be developed by separating the sites of the lattice into two subsets—one (denoted by L) in which the transition rate for the electron leaving a given site is influenced by the Coulomb potential due to the fixed hole, and its complementary subset in which transitions are not influenced by the Coulomb interaction. [Of course, the suitability of this division is not immediately obvious, because of the long-range nature of the Coulomb potential. However, in Reference 12 methods are presented which enable us to make the set L essentially arbitrarily large, and it is demonstrated that convergence of results for η, particularly at high field, is apparently observed even when the Coulomb potential is truncated at relatively short range.] For sites λ in the set L, these equations are

$$G(\lambda - 1_0) = \sum_{\lambda'} [G(\lambda - \lambda') - f(\lambda; \lambda')]R(\lambda'), \tag{2}$$

where G is the lattice Green's function in the presence of the external electric field, f is defined by

$$f(\lambda;\lambda') = \sum_{1'} G(\lambda - 1')\,\psi(1' - \lambda';\lambda') \tag{3}$$

and $\psi(1' - \lambda';\lambda')$ is the transition probability for the electron to transfer from site λ' to site $1'$, when λ' is in the set L. Equation (2) can be regarded as a matrix equation, and solutions for R obtained by inverting the matrix M with elements.

$$M_{\lambda\lambda'} = G(\lambda'\lambda') - f(\lambda;\lambda'), \tag{4}$$

the size of which is determined by the number of sites in the special set L. Insertion of the resulting solution for R into Equation (1) gives η.

This calculation depends on the availability of two functions—the field-dependent Green's functions G and the transition probabilities ψ. Methods have been developed[12] to calculate the former on several two- and three-dimensional lattices, as a function of applied electric field. The transition probabilities are readily calculated from the relationship

$$\psi(1,1') = \frac{W(1;1')}{\sum_{1''} W(1'';1') + \delta_{1',o}W(S_1 \rightarrow S_0)}. \tag{5}$$

Here $\psi(1,1')$ is the probability of a transition from site $1'$ to site $1' + 1$, and $W(m,n)$ is the rate of a transition from site n to site $n + m$. $W(S_1 \rightarrow S_0)$ is the rate of decay of the excited state S_1 at the origin to S_0. The rate is calculated from

$$W(m,n) = W_0 e^{-\beta(E_{n+m}-E_n)} \tag{6}$$

where $\beta = (k_BT)^{-1}$ and E_i is the energy of the system when the electron is at site i. When calculating $\psi_{12}(0)$ the numerator of Equation (5) is replaced by $W(S_1 \rightarrow S_0)$.

The energies in the exponent of Equation (6) contain three contributions—a field-dependent term, a Coulomb term, and an effective ionization potential for transitions from S_1 to nearest-neighbor sites:

$$\begin{aligned} E_{n+m} - E_n = {} & -e(\mathbf{r}_{n+m} - \mathbf{r}_n)\cdot\mathbf{E} - (1 - \delta_{n+m,o})(1 - \delta_{n,o}) \\ & \times \frac{e^2}{D}\left[\frac{1}{r_{n+m}} - \frac{1}{r_n}\right] + (\delta_{n,o} - \delta_{n+m,o})E_{\text{ex}} \end{aligned} \tag{7}$$

Insertion of Equations (6) and (7) into Equation (5) gives the transition rate in terms of four dimensionless parameters: γ, a dimensionless electric field, χ, a dimensionless Coulomb parameter, ϵ_{ex}, a dimensionless ionization potential, and R, the trapping/hopping branching ratio. For the simple cubic lattice, these are defined by

$$\gamma = \frac{\beta eaE}{2} \tag{8a}$$

$$\chi = \frac{\beta e^2}{2aD} \tag{8b}$$

$$\epsilon_{ex} = \beta E_{ex}/2 \tag{8c}$$

$$R = W(S_1 \rightarrow S_0)/W_0 \tag{8d}$$

where D is the dielectric constant and a is the lattice constant.

III. RESULTS

Application of the theory outlined above enables us to calculate the probability of carrier pair dissociation, η. We present herein results for the case where the set L (defined above) includes sites up to fourth neighbors of the fixed hole. It has been demonstrated in Reference 12 that this choice leads to good convergence. As further confirmation of this observation, we can employ methods outlined in Appendix D of Reference 9 to estimate the range of values of χ for which this approximation should be valid. We find that the approximation should be acceptable for $\chi \leqslant 18.94$. For a system with dielectric constant $D = 3$, this corresponds to requiring a lattice constant a $\gtrsim 0.55$ Å, a constraint which is generally well satisfied.

In Figure 1, we exhibit plots of $\eta(\gamma)$ calculated on the simple cubic lattice for a number of values of the parameters (ϵ_{ex}, χ, R). Comparison with data[1-3] reveals that the calculated curves exhibit the full range of qualitative behavior observed experimentally. It should be noted, however, that the behavior of the system is controlled by the three molecular parameters and the initial distribution of the electron around the hole, which we are free to specify. These factors determine both the low-field behavior of $\eta(\gamma)$ and its high-field saturation value. This is in sharp contrast to the continuum theory, in which the high-field saturation is determined by the "initial quantum yield" ϕ_o, an empirical multiplicative parameter which does not arise from the continuum theory of the dissociation process.

Another important distinction between the molecular and Onsager theories is revealed by a study of the temperature dependence of $\eta(\gamma)$. In Figure 2 we exhibit the temperature dependence of $\eta(\gamma = 0)$, in the large-R regime (corresponding to the Onsager perfect-absorption boundary condition). It will be seen that $\eta(0)$ exhibits Arrhenius behavior (i.e. linearity of ln $\eta(0)$ with $1/T$), a property predicted also by the Onsager theory. However, the Onsager theory predicts a relationship between the activation energy derived from the Arrhenius plot and r_o, the initial separation of the charge carrier pair. When this relationship is applied to experimental data (for which the actual initial separation is never known), an apparent

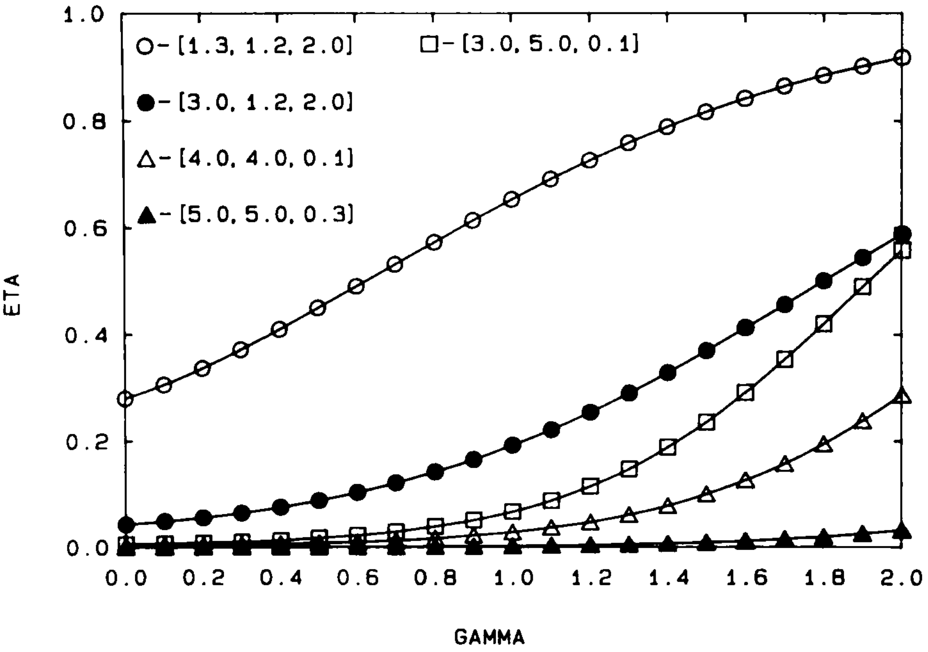

FIGURE 1 Field-dependent dissociation probability,[12] $\eta(\gamma)$, plotted for a variety of values of the dimensionless parameters (ϵ_{ex}, χ, R) (see text). These results arise from the use of an initial distribution in which the electron is at a nearest-neighbor site to the hole with angular distribution Boltzmann-weighted by the electron-external field interaction.

value of r_o can be derived. In the present calculations, however, r_o is known exactly. It is found that the apparent r_o and the actual initial separation are not equal—in fact, the apparent r_o varies as the initial angular distribution of the electron about the hole is varied *even at fixed initial separation*. These results demonstrate that r_o and ϕ_o values derived from experimental data can not generally be regarded as actual physical quantities, but must rather be seen as fitting parameters of somewhat uncertain meaning.

In related work, we have also shown[11] that $\eta(\gamma)$ varies with fixed molecular parameters *and* initial distribution as the structure of the lattice changes. In general, $\eta(\gamma)$ increases as the coordination number of the lattice increases, since this results in a greater number of escape pathways for the electron.

IV. SUMMARY

A theory of geminate recombination of charge-carrier pairs in condensed phases has been developed which takes into account the molecular properties of the system as well as the connectivity of the lattice. We have used the theory to investigate the parameter dependence of the dissociation efficiency, as well as the physical meaning of the model parameters which arise in the Onsager (continuum) for-

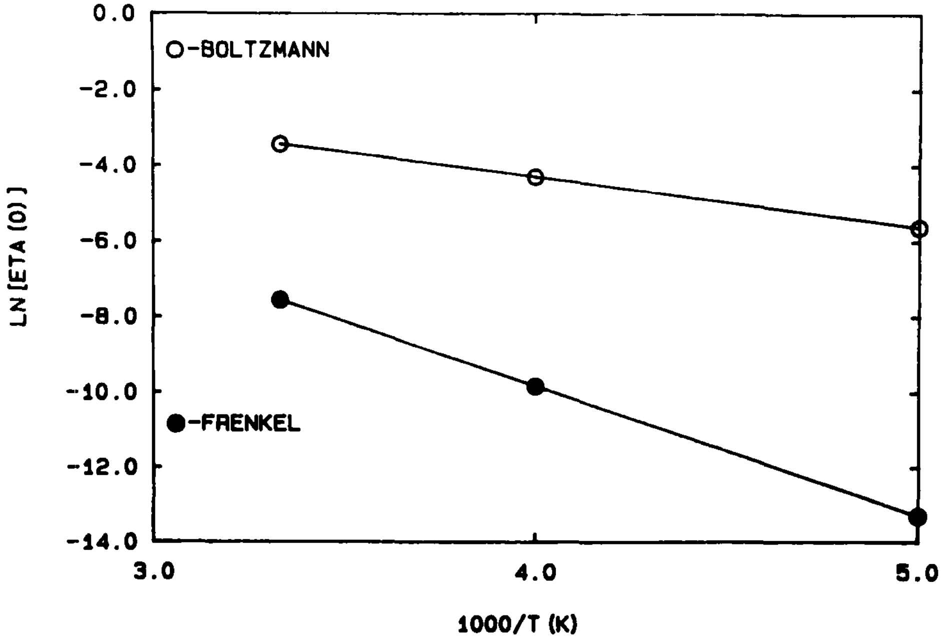

FIGURE 2 Arrhenius plot[12] of $\ln\eta(0)$ vs. $1000/T$, for the parameter set which equals (1.3, 3.4, 100.0) at 300K. The upper line arises from the Boltzmann initial condition (Figure 1), while the lower line arises from the Frenkel initial condition, in which the electron is initially in S_1 at the origin (see text).

mulation of geminate recombination. It is hoped that in future work, this approach can be applied to material design, as well as the study of such fundamental questions as the time-dependence of geminate recombination. We also hope to address the calculation of the slope-to-intercept ratio of $\eta(\gamma)$, an important, experimentally measurable property which is well-predicted by the Onsager theory.

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