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Electron transfer in pendant-group and molecularly doped polymers

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Utilizing the molecular-ion model previously constructed to describe photoemission and ultraviolet absorption in pendant-group polymers, we derive an expression for the probability of electron transfer between a molecular ion and a neutral molecular species embedded in a frequency-dependent dielectric medium described by the (nonlocal) longitudinal dielectric response function $\epsilon(\vec{q},\omega)$. The medium is taken to exhibit three branches of its longitudinal polarization excitation spectrum defined by $\epsilon(\vec{q},\omega(\vec{q}))=0$: a low-frequency branch corresponding to intermolecular motions, an infrared branch corresponding to molecular vibrational modes, and a high-frequency branch corresponding to valence-electron excitations. In addition, the linear coupling of the electron to the intramolecular modes of the initial and final molecular ions is incorporated into the model. The electron-transfer probability is evaluated as a function of the spacing, R, between the molecular-ion sites and the energy difference between the intitial and final molecular-ion states. Utilizing parameters in $\epsilon(\vec{q},\omega)$ typical of pendant-group polymers (e.g., polystyrene, polyvinylpyridine) or the matrices utilized in molecularly doped polymers films (e.g., polycarbonates), we find that the electron-transfer process is activated and that the low-frequency dielectric relaxations characteristic of these polymers create this activation. Explicit expressions for the activation energies are derived and evaluated numerically for poly(2-vinylpyridine): a material for which a model of $\epsilon(\vec{q},\omega)$ is available in the literature. The valence-electron excitations do not influence the electron-transfer activation energies, but both the intramolecular and longitudinal-polarization vibrational modes increase these activation energies above the values predicted using the low-frequency relaxations alone. The energies, $\hbar\omega_n$, of many of these vibrational modes are, however, larger than thermal energies, kT. Consequently, the predicted electron-transfer activation energies are smaller than those given by traditional semiclassical models of electron transfer. Moreover, these activation energies also depend explicitly on the spacing, R, between the two sites. This R dependence is evaluated for both classical and quantum-mechanical models of the change densities on the molecular ions. Our analysis predicts, therefore, the complete spacing and temperature dependence of the electron-transfer probabilities as functions of the intramolecular molecular-ion vibrational frequencies and electron-vibration coupling constants, and of the frequency and spatial dependence of the dielectric response of the medium in which these ions are embedded. This prediction permits the identification of scaling laws relating both the activation energies and electron-transfer prefactors to molecular and dielectric observables: an identification which provides valuable guidance in the molecular design of efficient electronic transport media.

I. INTRODUCTION

In recent years the increased use of organic polymers in electronic, electrophotographic, and optical device applications has led to a renewal of interest in the electrical properties of these materials.[1] Two particularly important classes of such substances are pendant-group and molecularly doped polymers which consist of electrically active molecular species in an otherwise inert polymeric matrix. Examples include the use of polystyrene, poly(2-vinylpyridine) and poly(methylmethacrylate) as contact-charge-exchange materials[2] and the consideration of poylcarbonate doped with 2,4,7-trinitro-9-fluorenone (TNF)[3] and triphenylamine (TPA)[4–6] for use in composite photoreceptors. In such polymers charge transport occurs via electron transfer between charged and neutral molecular species present as pendant groups or molecular dopants.

Our purpose in this paper is the provision of a microscopic description of the intermolecular electron-transfer process in terms of parameters which are directly accessible via *independent* experiments. Thus, we predict the probabiltiy of electron transfer between two molecular entities, one charged and the other neutral, a distance R apart, in terms of parameters which may be evaluated either via gas-phase molecular spectroscopy of the species involved or via measurements of the dielectric properties of the polymeric host. These electron-transfer probabilities are the input data used in multiple-hopping models of measured transport properties, e.g., drift mobility[5,7] and photoconductivity.[8] They constitute, therefore, the link between observed transport coefficients and the microscopic electronic structure of the polymer. Hence, the model developed herein provides valuable clues for the design of custom materials with desirable electrical properties.

The model which we utilize to evaluate the electron-transfer probabilities, called the molecular-ion model, has been proposed and described elsewhere.[9] It is based on the concepts that site-to-site variations in the relaxation energies of molecular ions in pendant-group and molecularly doped polymers localize injected charges in these materials as molecular anions or cations, and that, consequently, these relaxation energies can be evaluated as those associated with localized molecular ions in a dielectric medium. This model was tested critically by analysis of photoemission and uv absorption in poly(2-vinylpyridine)[9] and polystyrene.[9,10] It also led to the successful *a priori* prediction of the temperature dependence of photoemission lines from molecular films.[11] Consequently, we believe the applicability of the model to describe individual molecular ion (and exciton) states in polymers has been established. Herein we extend the model to encompass charge transfer between two different molecular ion states. The mathematical formalism utilized to accomplish this extension has been developed in a variety of solid-state, chemical and biological contexts involving electron and exciton transfer reactions between localized states, as may be ascertained from inspection of a recent review of this topic.[12] Therefore we confine our presentation to the recapitulation of the requisite general formulas for the electron-transfer probabilities in Sec. II, and to the evaluation using the molecular-ion model of the expressions involved in these formulas in Sec. III. In Sec. IV we present numerical results for poly(2-vinylpyridine) and indicate the consequences of our results for the design of polymeric films which exhibit efficient transport of injected charges. We conclude with a synopsis.

II. ELECTRON-TRANSFER PROBABILITY

In this section we evaluate the intersite electron-transfer probability resulting from a Hamiltonian describing an excess electron which can reside on one of two molecular ion sites and which interacts both with local intramolecular vibrations at each of the two sites and with longitudinal polarization fluctuations characteristic of the dielectric medium in which the sites are embedded. A schematic diagram of such a model system is given in Fig. 1. In the absence of any direct interaction between electrons on each of the two sites, the model Hamiltonian describing linear interactions between these electrons and the molecular vibrations, of energy $\hbar\omega_{in}$, and longitudinal polarization fluctuations of the dielectric medium, of energy $\hbar\omega_\alpha(\vec{q})$, is given by

$$\begin{aligned}H_0=&\left\{\epsilon_1+\sum_n g_{1n}\hbar\omega_{1n}(b_{1n}^\dagger+b_{1n})\right\}c_1^\dagger c_1\\&+\left\{\epsilon_2+\sum_m g_{2m}\hbar\omega_{2m}(b_{2m}^\dagger+b_{2m})\right\}c_2^\dagger c_2\\&+\sum_{\alpha,\vec{q}} g_\alpha(\vec{q})\hbar\omega_\alpha(\vec{q})[b_\alpha^\dagger(\vec{q})\rho(-\vec{q})+b_\alpha(\vec{q})\rho(\vec{q})]\\&+\sum_n\hbar\omega_{1n}(b_{1n}^\dagger b_{1n}+\tfrac{1}{2})\\&+\sum_m\hbar\omega_{2m}(b_{2m}^\dagger b_{2m}+\tfrac{1}{2})\\&+\sum_{\alpha,\vec{q}}\hbar\omega_\alpha(\vec{q})[b_\alpha^\dagger(\vec{q})b_\alpha(\vec{q})+\tfrac{1}{2}]\ ,\end{aligned}\tag{1a}$$

$$\rho(\vec{q})=M_1(\vec{q})c_1^\dagger c_1+M_2(\vec{q})c_2^\dagger c_2\ ,\tag{1b}$$

$$M_i(\vec{q})=\int d^3r\,|\phi_i(\vec{r})|^2\exp(-i\vec{q}\cdot\vec{r})\ ,\tag{1c}$$

$$g_\alpha(\vec{q})=[2\pi e^2\omega_{p\alpha}^2/q^2\hbar\omega_\alpha^3(\vec{q})]^{1/2}\ .\tag{1d}$$

In Eqs. (1) the ϵ_i are the molecular-ion eigenvalues for the site labeled by i associated with the eigenfunctions $\phi_i(\vec{r})$; the $\{g_{in}\}$ and $\{g_\alpha(\vec{q})\}$ are dimensionless linear coupling constants describing the interaction of these molecular-ion states with intramolecular vibrational modes and medium longitudinal polarization fluctuations, resepctively; the energies, $\hbar\omega_\alpha(\vec{q})$, of the longitudinal polarization fluctuations of wave vector $\vec{q}$ are determined by zeros of the longitudinal dielectric function

$$\epsilon(\vec{q},\omega_\alpha(\vec{q}))=0\ ,\tag{2}$$

and the $\omega_{p\alpha}$ are the plasma frequencies associated with various branches of the polarization fluctuation spectrum, which we define herein by use of the expansion for ϵ^{-1}, i.e.,

$$\epsilon^{-1}(\vec{q},\omega)=1-\sum_\alpha\frac{\omega_{p\alpha}^2}{[\omega_\alpha^2(\vec{q})-\omega^2]}\ .\tag{3}$$

The $\omega_{p\alpha}$ and functional form of the $\omega_\alpha(\vec{q})$ are evaluated from experimental dielectric response data as described by Duke *et al.*[9] in their original proposal of the model defined by Eqs. (1)–(3). Further, the dimensionless linear coupling constants for the intramolecular vibrational modes are nonzero only for the totally-symmetric modes of the molecular ions.[13] They may be evaluated either via analyses of high-resolution gas-phase photoemission spectra (in the case of molecular cations) or via the use of a combination of a molecular orbital model for the electronic structure of the ion and a valence-force-field model to describe its vibrational normal modes. A review of the literature on the evaluation of these quantities for various molecular ions has been given recently by Duke.[14] Finally, Eqs. (1) are written in second-quantized form in which the c_i designate the fermion annihilation operators for the added electron in the molecular-ion orbital at site i, the b_{in} are the boson annihilation operators for the totally-symmetric normal modes of the vibration, labeled by the index n, of the molecular ion at site i, and the $b_\alpha(\vec{q})$ are the corresponding boson annihilation operators of the longitudinal polarization fluctuations of wave vector $\vec{q}$ associated with the branch of the excitation spectrum designated by α.

Two features of the Hamiltonian defined by Eqs. (1)–(3) are important. First, it is defined entirely in terms of independently measurable or calculable quantities. The molecular parameters, ϵ_i, $\phi_i(\vec{r})$, ω_{in}, and g_{in}, are obtained via the analysis of gas-phase molecular spectra as interpreted using molecular-orbital models.[9,10,14] The medium parameters, $\omega_{p\alpha}$ and $\omega_\alpha(\vec{q})$, are evaluated by fitting observed dielectric response data by a phenomenological model of the longitudinal dielectric function. Thus, although in this paper the model will be utilized to describe transport measurements, it contains no parameters that are not obtained independently via other experiments. Second, Eq. (1) can be diagonalized by canonical transform.[15,16] Thus, if we impose a perturbation which mixes the two molecular-ion states directly, i.e.,

$$H_T = U_{12}(c_1^\dagger c_2 + c_2^\dagger c_1) \quad , \tag{4}$$

the electron-transfer probability per unit time, $P_{e,12}$ due to this perturbation can be evaluated in closed form by linear response theory. The result is[12,16]

$$P_{e,12}(T) = (U_{12}/\hbar)^2 F(T,\omega) \quad , \tag{5a}$$

$$F(T,\omega) = \int_{-\infty}^{\infty} dt \exp(i\omega t) \exp[\phi(T,t) - \phi(T,0)] \quad , \tag{5b}$$

$$\hbar\omega = \epsilon_1 - E_{p1} - \epsilon_2 + E_{p2} \equiv E_{12} \quad , \tag{6a}$$

$$E_{p1} = \sum_n g_{1n}^2 \hbar\omega_{1n} + \sum_{\alpha,\vec{q}} g_\alpha^2(\vec{q}) |M_1(\vec{q})|^2 \hbar\omega_\alpha(\vec{q}) \quad , \tag{6b}$$

$$E_{p2} = \sum_m g_{2m}^2 \hbar\omega_{2m} + \sum_{\alpha,\vec{q}} g_\alpha^2(\vec{q}) |M_2(\vec{q})|^2 \hbar\omega_\alpha(\vec{q}) \quad , \tag{6c}$$

$$\phi(T,t) = \phi_1(T,t) + \phi_2(T,t) + \phi_{12}(T,t) \quad , \tag{7a}$$

$$\phi_1(T,t) = \sum_n g_{1n}^2 P_{1n}(T,t) \quad , \tag{7b}$$

$$\phi_2(T,t) = \sum_m g_{2m}^2 P_{2m}(T,t) \quad , \tag{7c}$$

$$\phi_{12}(T,t) = \sum_{\alpha,\vec{q}} g_\alpha^2(\vec{q}) |M_1(\vec{q}) - M_2(\vec{q})|^2 P_\alpha(\vec{q},T,t) \quad , \tag{7d}$$

$$P_{in}(T,t) = N(\omega_{in}) \exp(i\omega_{in}t) + [N(\omega_{in}) + 1] \exp(-i\omega_{in}t) \quad , \tag{8}$$

$$N(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1} \quad , \tag{9}$$

$$P_\alpha(\vec{q},T,t) = N[\omega_\alpha(\vec{q})] \exp[i\omega_\alpha(\vec{q})t] + \{N[\omega_\alpha(\vec{q})] + 1\} \exp[-i\omega_\alpha(\vec{q})t] \quad . \tag{10}$$

In Eqs. (5)–(10) we have assumed that $\omega_\alpha(\vec{q})$ is symmetric as a function of $\vec{q}$, i.e., $\omega_\alpha(\vec{q}) = \omega_\alpha(-\vec{q})$, and that U_{12} is real. Typically, U_{12} is proportional to the overlap of the two molecular ion states, i.e.,

$$U_{12}(\vec{R}) = U \int \phi_1(\vec{r}) \phi_2(\vec{r} - \vec{R}) \, d^3r \tag{11}$$

which scales exponentially as a function of $\vec{R}$, i.e., $U_{12}(R) \sim U \exp(-\gamma R)$, in which γ is a decay constant, typically $\gamma \sim 1$ Å^{-1}. Finally, in Eq. (9) k is Boltzmann's constant and T is the temperature in degress Kelvin.

The model defined by Eqs. (1)–(4) and (11) may not seem appropriate to describe the hopping between molecular ion sites in a polymer because an adequate description of this process must incorporate the fact that the molecular ion energies form broad ($\Delta E \sim 1$ eV) distributions[9,10,17] and that the distances between two sites also form a distribution.

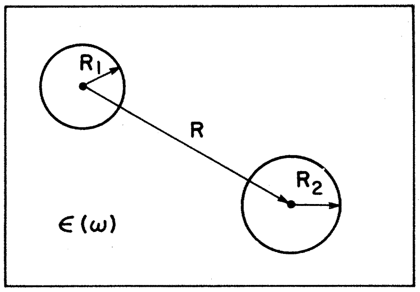

FIG. 1. Schematic diagram of two spherical molecular ions, of radii R_1 and R_2, respectively, separated by a vector $\vec{R}$ and embedded in a local dielectric medium of dielectric function $\epsilon(\omega)$.

Both effects enter the two-site problem by virtue of the fact that $P_{e,12}(T)$ in Eq. (5a) depends on the energy separation between the relaxed molecular-ion eigenvalues on the two sites, i.e., E_{12} defined in Eq. (6a), and on their relative separation, $\vec{R}$, via $|M_1 - M_2|^2$ in Eq. (7d) and $U_{12}(\vec{R})$ in Eqs. (11). Given the continuous distribution of molecular-ion energies and relative positions induced by the (static) disorder in the polymer, and electron (or hole) intial state localized on a given site exhibits a probability $P(\vec{R},\hbar\omega)$ of experiencing a corresponding localized final state of relative energy $\hbar\omega$ on a site a distance $\vec{R}$ away. Because of this fact, the final states for the electron-(hole)-transfer process form a continuum as a function of $\hbar\omega$, so that the probability of back transfer is negligible, and the first-order linear-response theory expression, Eq. (5a), provides the correct formulation of the intersite hopping probability.[12] In other closely related problems, for example the calculation of optical absorption lineshapes in dimers,[18–20] the final states do not form a continuum. Hence, periodic electronic motion results that can make important modifications of the vibrational modes to which the electronic subsystem (in that case an exciton) is coupled. Therefore the statistical, multisite character of the electron hopping motion in pendant-group or molecularly-doped polymers exerts a decisive influence on the mathematical formulation of the appropriate boundary conditions for the corresponding two-site problem. In addition, moreover, we expect $U_{12} < 0.01$ eV (Refs. 11, 12, and 21) for such polymers whereas for typical aromatic pendant groups or molecular dopants $E_{pi} > 0.1$ eV. Consequently, the individual two-site electron-transfer processes occur in the "weak-coupling" limit,[16,18,19] i.e., $U_{ij} << E_{pi}, E_{pj}$. In this limit, even in the absence of static disorder the modulation of the energies of the initial and final electronic states by a continuum of vibrational modes suffices to provide a continuum of electronic final states adequate to render Eqs. (5) a suitable description of the time dependence of the probability that an electron initially localized at one site will make a transition ("hop") to the other [during a time shorter than or comparable to $P_{e,12}^{-1}(T)$]. Thus, the parameters of the individual two-site problems as well as the statistical character of hopping among sites whose energies form a distribution lead us to the linear-response formulation [Eqs. (5)–(11)] of the electron-transfer probabilities. Finally, both aspects of the problem also suggest that corrections to this multiple-independent-hop model, e.g., caused by incomplete vibrational relaxation following one hop before another occurs,[22] are unimportant for carrier transport in molecularly doped and pendant-group polymers: a suggestion which is cleary compatible with the observations[3–6] that in such materials the carrier mobilities, μ, satisfy $\mu < 10^{-5}$ cm^2/V sec and exhibit a thermally activated temperature dependence.

An important limiting case of Eqs. (1)–(11) is the limit in which either the inhomogeneous line broadening due to static disorder[23] or the coupling of the electronic motion to continuum vibrational modes[16] is sufficiently strong that only the short-time behavior of $\exp[\phi(T,t)]$ is important in evaluating the integral in Eq. (5b). In this situation we can expand $\phi(T,t)$ through terms quadratic in t, and perform the integral analytically to obtain[12,16]

$$P_{e,12}^{Q}(T) = (1/\hbar)\,U_{12}^2\,(\pi/\sigma_{12}^2)^{1/2}\exp[-(\hbar\omega - E_{p,12})^2/4\sigma_{12}^2] \; , \tag{12a}$$

$$E_{p,12} = \sum_n g_{1n}^2\hbar\omega_{1n} + \sum_m g_{2m}^2\hbar\omega_{2m} + \sum_{\alpha,\vec{q}} g_\alpha^2(\vec{q})\,|M_1(\vec{q}) - M_2(\vec{q})|^2\hbar\omega_\alpha(\vec{q}) \; , \tag{12b}$$

$$\begin{aligned} 2\sigma_{12}^2 = {} & \sum_n (g_{1n}\hbar\omega_{1n})^2\coth(\hbar\omega_{1n}/2kT) + \sum_m (g_{2m}\hbar\omega_{2m})^2\coth(\hbar\omega_{2m}/2kT) \\ & + \sum_{\alpha,\vec{q}} [g_\alpha(\vec{q})\hbar\omega_\alpha(\vec{q})]^2\,|M_1(\vec{q}) - M_2(\vec{q})|^2\coth[\hbar\omega_\alpha(\vec{q})/2kT] \; . \end{aligned} \tag{12c}$$

The semiclassical limit is obtained with an additional proviso, i.e.,

$$\hbar\omega_{in}, \;\; \hbar\omega_\alpha(\vec{q}) < kT \; . \tag{13}$$

In this limit Eq. (12c) yields

$$\sigma_{12,sc}^2 = (kT)E_{p,12} \; , \tag{14}$$

and hence the electron-transfer probability becomes

$$P_{e,12}^{sc}(T) = \hbar^{-1}U_{12}^2\,(\pi/E_{p,12}kT)^{1/2}\exp(-E^*/kT) \; , \tag{15a}$$

$$E^* = E_{p,12}[1 - (\hbar\omega/E_{p,12})]^2/4 \; . \tag{15b}$$

Thus, in the semiclassical limit the electron-transfer probability is activated with an activation energy, E^*, explicitly related to intramolecular spectral parameters [i.e., the g_{in}, $\hbar\omega_{in}$, and $M_i(\vec{q})$], and intermolecular dielectric parameters [i.e., the $g_\alpha(\vec{q})$, $\hbar\omega_\alpha(\vec{q})$], via Eq. (15b). The intramolecular contributions to E^*, described by $E_{12}(\text{intra})$ in

$$E_{p,12} = E_{12}(\text{intra}) + E_{12}(\text{inter}) \; , \tag{16a}$$

$$E_{12}(\text{intra}) = E_1(\text{intra}) + E_2(\text{intra}) \; , \tag{16b}$$

$$E_i(\text{intra}) = \sum_n g_{in}^2\hbar\omega_{in} \; , \tag{16c}$$

$$E_{12}(\text{inter}) = \sum_{\alpha,\vec{q}} g_\alpha^2(\vec{q})\hbar\omega_\alpha(\vec{q})\,|M_1(\vec{q}) - M_2(\vec{q})|^2 \; , \tag{16d}$$

correspond to the "inner-shell" contributions in conventional models[24–26] of electron transfer in solution. The intermolecular contributions, described by $E_{12}(\text{inter})$ in Eqs. (16a) and (16d) correspond to the contributions of the "outer shells" or the "medium" in these models. For example, formulations of electron-transfer reaction probabilities analogous to Eqs. (15) and (16) in which classical electrostatic models are utilized to obtain $E_{12}(\text{inter})$ have been given by Hush[27] and by Kestner, Logan, and Jortner.[36]

Another limit of particular historical interest in molecular solids corresponds to the "molecular crystal model" initially proposed by Holstein[28] and subsequently studied and extended by others, especially Emin.[29] In this model only the intramolecular electron-vibration coupling is considered, and it is approximated by linear coupling of electrons situated at identical sites to a single intramolecular mode which, however, is allowed to exhibit dispersion. In our analysis this model implies utilizing a single intramolecular mode of energy $\hbar\omega_n$ and setting

$$E_{12}=0 \ , \tag{17a}$$

$$E_{p1}=E_{p2}=g^2\hbar\omega_n=E_p \ , \tag{17b}$$

in Eqs. (6) or

$$E_{12}(\text{intra})=2E_p=2g^2\hbar\omega_n \ , \tag{17c}$$

$$E_{12}(\text{inter})=0 \ , \tag{17d}$$

in Eqs. (16). In either case we obtain

$$E^*=E_{p,12}/4=E_p/2 \tag{17e}$$

in Eq. (15b), recovering the well-known[30] semiclassical result that for identical sites the molecular crystal model predicts a two-site activation energy, E^*, equal to one half the "polaron binding energy," E_p at each site. In fact Eqs. (15) indicate that this conclusion applies to any linear electron interactions with intramolecular vibrations at identical sites. More generally, Eqs. (5)–(11) reveal[12,16] that any model in which the electron coupling to intermolecular modes is neglected leads to the electron analog of the Förster-Dexter model of exciton transfer, a result utilized explicitly by Hopfield[31] to construct models of electron-transfer in photosynthetic membranes.

This consideration of limiting cases of Eqs. (5)–(11) indicates that they reproduce correctly known results[24–31] for electron-transfer probabilities when suitable approximations are introduced. Unfortunately, for conditions typical of room-temperature hopping in pendant-group and molecularly doped polymers neither the quadratic-time expansion [resulting in Eqs. (12)] nor the semiclassical approximation [inequality (13) resulting in Eqs. (15)] is valid for either all of the intramolecular vibrational modes or all of the longitudinal polarization fluctuations with which an excess electron (hole) interacts. Thus, we turn in the next section to the derivation of more suitable evaluations of Eqs. (5)–(11) for parameters typical of these materials.

III. MOLECULAR-ION MODEL

In this section we first indicate the parameters utilized to describe the molecular-ion states and medium dielectric response in the molecular-ion model of localized electronic states in pendant-group and molecularly doped polymers. Then, using representative parameters we evaluate the single-electron-(hole) density of states associated with an injected charge in the otherwise neutral system. Finally, using these parameters we evaluate the electron-transfer probability, given formally by Eqs. (5)–(11), that this injected charge will hop from one site to another a distance $\vec{R}$ away.

A. Model parameters

In order to render our calculations of electron transfer directly comparable to our earlier analyses[9,10,23] of photoemission and uv absorption in poly(2-vinylpyridine) and polystyrene, we adopt a schematic molecular-ion model with parameters typical of these materials. Molecular-ion wave functions, based on the use of the *CNDO*/S3 molecular orbital model,[32] are available for both the phenyl and the pyridyl moieties in these materials on the basis of analyses of the gas-phase photoemission specta of methyl, ethyl, and isopropyl substituted benzene and pyridine.[9–11,33] These wave functions are too detailed, however, to be useful for our present purposes of establishing the order of magnitude of various contributions to relaxation energies, linewidths, and electron-transfer activation energies. A model which premits us to establish the connection between our analysis and classical electrostatic treatments of electron transfer is one in which the molecular ions are represented by point charges each in a sphere of radius R_0 within the dielectric described by $\epsilon(\vec{q},\omega)$. If we treat this charge classically we obtain from Eqs. (1) (Ref. 9)

$$g_\alpha^2(\vec{q})|M_i(\vec{q})|^2\hbar\omega_\alpha(\vec{q})=(2\pi e^2/q^2)|M_i(\vec{q})|^2[\omega_{p\alpha}/\omega_\alpha(\vec{q})]^2=(2\pi e^2/q^2)[\sin(qR_0)/qR_0]^2[\omega_{p\alpha}/\omega_\alpha(\vec{q})]^2 \ . \tag{18a}$$

For such a classical charge density, the intermolecular contributions to the single site polaron binding energy are obtained from Eqs. (6). Substituting Eq. (18a) into Eq. (6b) and further assuming local dielectric response in performing the final sum over $\vec{q}$, we obtain:

$$E_{pi}(\text{inter}) = \sum_{\alpha,\vec{q}} g_\alpha^2(\vec{q})|M_i(\vec{q})|^2\hbar\omega_\alpha(\vec{q}) = \sum_{\vec{q}}(2\pi e^2/q^2)[\sin(qR_0)/qR_0]^2\{1-[1/\epsilon(\vec{q},\omega=0)]\}$$

$$\to (e^2/2R_0)\{1-[1/\epsilon(\omega=0)]\} \tag{18b}$$

in which we utilized Eq. (3) to evaluate the sum over α, and the arrow indicates the results for a *local* dielectric. Since the final form of Eq. (18b) is just the Born formula for the free energy of solvation, it establishes the relationship between the molecular-ion model and the classical theory of solvation in a local dielectric medium.[9] The extension of the Born model to static but nonlocal dielectric response also has been given by Dogonadze and Kornyshev[34] in a form which is equivalent to using a particular parametrized version of $\epsilon(\vec{q},0)$ in evaluating the integral over $\vec{q}$ in Eq. (18b). Extending our analysis to the treatment of electron transfer, when we evaluate Eq. (16d) using this point-charge-in-a-spherical-cavity model, we obtain

$$E_{12}(\text{inter}) = e^2(R_0^{-1}-R^{-1})\{1-[1/\epsilon(\omega=0)]\}\ , \quad R \geqslant 2R_0 \tag{18c}$$

for the intermolecular contributions to the activation energy in the semiclassical limit for a local dielectric medium. As expected from the fact that for identical sites $M_2(\vec{q}) = M_1(\vec{q})\exp(-i\,\vec{q}\cdot\vec{R})$, we see that when $\vec{R}\to\infty$, $E_{12}(\text{inter})$ becomes twice $E_{p1}(\text{inter}) = E_{p2}(\text{inter})$. Hence, in this limit the intermolecular electrostatic contributions to the semiclassical activation energy [given by the $\hbar\omega\to 0$ limit of Eq. (15b)] alone lead to $E^* = E_{pi}(\text{inter})/2$, analogous to the prediction of the molecular crystal model which was discussed in connection with Eqs. (17).

Although the point-ion model is useful for establishing contact with classical electrostatics, it does not permit an internally consistent evaluation of the dependence of the electron-transfer probability on the separation $\vec{R}$ between the initial and final molecular-ion sites. For this purpose we represent the molecular-ion wave functions as an s-wave bound state of decay constant γ, so that the evaluation of $P_{12}(T)$ via Eqs. (5)–(10) is compatible with the expressions for $U_{12}(\vec{R})$ given by Eq. (11). This model predicts

$$\phi_i(\vec{r}-\vec{R}_i) = (\gamma^3/\pi)^{1/2}\exp(-\gamma|\vec{r}-\mathrm{R}_i|)\ , \tag{19a}$$

$$M_i(\vec{q}) = \exp(-i\vec{q}\cdot\vec{R}_i)[1+(q/2\gamma)]^{-2}\ . \tag{19b}$$

For a local dielectric we obtain from Eqs. (6) for the intermolecular contribution to the polaron binding energy the result that

$$E_{pi}(\text{inter}) = \sum_{\vec{q}}(2\pi e^2/q^2)[1+(q/2\gamma)]^{-4}$$

$$\times\{1-[1/\epsilon(\vec{q},\omega=0)]\}$$

$$\to(5e^2\gamma/16)\{1-[1/\epsilon(\omega=0)]\}\ . \tag{19c}$$

In Eq. (19c) the arrow indicates the results for a *local* dielectric, just as in Eq. (18b). Evidently the $(2R_0)^{-1}$ factor characteristic of the point-charge model [i.e., in Eq. (18b)] has been replaced by $5\gamma/16$. Otherwise, the two results are entirely comparable. Similarly, the intermolecular contributions to the semiclassical activation energy [see, e.g., Eq. (16d)] are given by

$$E_{12}(\text{inter}) = \sum_{\vec{q}}(4\pi e^2/q^2)[1+(q/2\gamma)^2]^{-4}[1-\cos(\vec{q}\cdot\vec{R})][1-1/\epsilon(\vec{q},\omega=0)]$$

$$\to((5e^2\gamma/8)-e^2R^{-1}\{1-[\exp(-2\gamma R)/48][8(\gamma R)^3+36(\gamma R)^2+66\gamma R+48]\})\{1-[1/\epsilon(\omega=0)]\}\ . \tag{19d}$$

Equation (19d) also is completely analogous to the point-charge result, Eq. (18c), with the addition of a quantum correction proportional to $\exp(-2\gamma R)$ which reduces the image-charge contribution $-e^2/R$ at short distances, $R<(2\gamma)^{-1}$, where the hopping integrals $U_{12}(\vec{R})$ given by Eq. (11) are large. It is noteworthy that the local dielectric approximation was used only at the final step of the computation in performing the integral over $\vec{q}$ in Eqs. (19c) and (19d). Thus, these equations specify the general form of the intermolecular contributions to the semiclassical polaron binding energy and electron-transfer activation energy (for identical sites), respectively, for isotropic molecular-ion wave functions even in nonlocal dielectric media. Finally, an important feature of Eqs. (18) and (19) is their revelation that the semiclassical activation energy depends explicitly on the site separation, R, increasing as the sites become further separated. Both the hopping integrals, $U_{12}\propto\exp(-\gamma R)$, and the activation energies ($E^* = E_{12}/2$ for identical sites) favor short hops (small R). We examine the consequences of this effect in Sec. IV.

The final molecular-ion parameters which we must specify are the frequencies $\{\omega_{in}\}$ and coupling constants $\{g_{in}\}$ associated with the totally-symmetric molecular-ion vibrations (at least for nondegenerate radical ion states; for degenerate states we must also consider some nonsymmetric modes,[13] but we neglect this refinement here). For substituted benzene and pyridine these modes occur in the energy region[9, 13, 14] $0.05 \leq \hbar\omega_{in} \leq 0.5$ eV. The relevant coupling constants, g_{in}, range from nearly zero to a little over unity depending upon the mode and the orbital.[14] Thus, a representative set of model parameters for our identical sites is a single totally symmetric mode characterized by

$$\hbar\omega_0 = 0.1 \text{ eV} \ , \tag{20a}$$

$$g_0 = 1 \ , \tag{20b}$$

$$E_0(\text{intra}) = g_0^2\hbar\omega_0 = 0.1 \text{ eV} \ , \tag{20c}$$

$$\begin{aligned} 2\sigma_0^2(\text{intra}) &= (g_0\hbar\omega_0)^2\coth(\hbar\omega_0/2kT) \\ &= (0.1 \text{ eV})^2\coth(0.1 \text{ eV}/2kT) \ . \end{aligned} \tag{20d}$$

Since at room temperature $2kT = 0.05$ eV, the electron coupling to the model symmetric intramolecular mode does not lie within the semiclassical limit [inequality (13)]. This situation is the expected one in actual cases which also are characterized by the occurrence of multiple intermolecular modes [e.g., approximately 6 for polystyrene and poly(2-vinylpyridine)]. In these cases we anticipate that at most a few of the lowest-energy modes would satisfy the semiclassical limit at room temperature, so that Eqs. (15) do not describe quantitatively the influence of intramolecular vibrations on the room-temperature electron-transfer probabilities for typical pendant-group and molecularly-doped polymers.

The dielectric response of the polymer matrix is specified by Eq. (3) for the reciprocal of the longitudinal dielectric function. In this model the nonlocality of the dielectric response is described by the dispersion of the longitudinal polarization fluctuations, i.e., the $\vec{q}$ dependence of the $\omega_\alpha(\vec{q})$ For the purpose of our numerical calculations in this paper we utilize a local model of the dielectric response of the polymeric medium so that the $\omega_\alpha(\vec{q})$ are taken to be constants, independent of the wave vector $\vec{q}$. We further utilize a model of the dielectric response of a polar medium in which three branches of longitudinal polarization fluctuations are considered:

$$\alpha = 1, \ \omega_1 \sim 10^3 \text{ sec}^{-1} \text{ (torsional or backbone modes)} \ , \tag{21a}$$

$$\alpha = 2, \ \omega_2 \sim 10^{13} \text{ sec}^{-1} \text{ (vibrational modes)} \ , \tag{21b}$$

$$\alpha = 3, \ \omega_3 \sim 10^{15} \text{ sec}^{-1} \text{ (valence-electron excitations)} \ . \tag{21c}$$

TABLE I. Values of the energies $\hbar\omega_\alpha$ of the three branches of the longitudinal polarization fluctuation spectrum in poly(2-vinylpyridine) and their contributions to the electronic polaron binding energy, $E_{p\alpha}(R_0)$, and effective coupling constants, $g_\alpha(R_0)$, specified by Eq. (22b) in the text for a point charge in a dielectric cavity of radius $R_0 = 1.67$ Å. The evaluation of these parameters is described by Duke *et al.* (Ref. 9).

Type of fluctuation	$\hbar\omega_\alpha$ (eV)	$E_{p\alpha}(R_0)$ (eV)	$g_\alpha^2(R_0)$
Torsional ($\alpha = 1$)	5.36×10^{-11}	2.53	4.72×10^{10}
Vibrational ($\alpha = 2$)	9.4×10^{-2}	0.65	6.91
Valence electron ($\alpha = 3$)	19.2	1.31	6.83×10^{-2}

Once the values of the ω_α have been selected, those of the $\omega_{p\alpha}$ in Eq. (3) are obtained from measured dielectric response data. Moreover, values for "effective" coupling constants, $g_{i\alpha}$, for each branch of longitudinal polarization fluctuation spectrum may be defined by using the point-charge model Eq. (18b) to note that in the absence of dispersion

$$E_{pi}(\text{inter}, R_0) = \sum_\alpha E_{pi\alpha}(R_0) \ , \tag{22a}$$

$$\begin{aligned} E_{pi\alpha}(R_0) &= (\omega_{p\alpha}/\omega_\alpha)^2 \sum_{\vec{q}} (2\pi e^2/q^2)\,[\sin(qR_0)/qR_0]^2 \\ &\to (e^2/2R_0)(\omega_{p\alpha}/\omega_\alpha)^2 \\ &\equiv g_{i\alpha}^2\hbar\omega_\alpha \ . \end{aligned} \tag{22b}$$

Therefore given a value of R_0, the effective coupling constants, $g_{i\alpha}$, for electron coupling to longitudinal polarization fluctuations may be evaluated from the magnitudes of $\omega_{p\alpha}$ and ω_α as determined from the dielectric response data. The values of $\hbar\omega_\alpha$, $E_{i\alpha}(\vec{R}_0)$, and $g_{i\alpha}^2$ obtained using $R_0 = 1.67$ Å for the pyridine moieties in poly(2-vinylpyridine) are given in Table I. It is evident from this table that at room temperature the semiclassical limit [inequality (13)] is applicable for the torsional modes ($\alpha = 1$), at best marginally applicable for the vibrational modes ($\alpha = 2$), and definitely not applicable for the electronic modes ($\alpha = 3$). These results lead to the important consequences, documented below, that the electronic modes are essentially totally responsible for the relaxation energy observed in photoemission in going from gaseous 2-ethylpyridine to (solid) poly(2-vinylpyridine) whereas the torsional modes are primarily responsible for the temperature dependence of the widths of the valence-electron photoemission lines and the electron-transfer activation energies.

B. Electron density of states

A useful quantity for comparison with the electron-transfer probability is the one-electron density of states, $\rho_e(E)$, defined by

$$\rho_e(E) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt \exp(iEt/\hbar) \times \langle c_i(t) c_i^{\dagger}(0) \rangle \ , \tag{23a}$$

in which the brackets indicate a thermal average over the boson states characterizing the intramolecular vibrations and longitudinal polarization fluctuations, and a spatial average over sites in the sample. The hole density of states, essentially $\rho_e(-E)$, can be measured directly by photoemission spectroscopy as discussed earlier.[9–11] Evaluation of Eq. (23a) for identical molecular ion sites gives

$$\rho_e(E,\epsilon) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt \exp[i(E-\epsilon+E_p)t/\hbar] \times \prod_{\alpha} F_\alpha(T,t) \ , \tag{23b}$$

$$F_\alpha(T,t) = \exp[\phi_\alpha(T,t) - \phi_\alpha(T,0)] \ , \tag{23c}$$

$$\phi_0(T,t) = \sum_n g_n^2 P_n(T,t), \quad \alpha = 0 \ , \tag{23d}$$

$$\phi_\alpha(T,t) = \sum_{\vec{q}} g_\alpha^2(\vec{q}) |M(\vec{q})|^2 P_\alpha(\vec{q},T,t) \ , \quad \alpha = 1,2,3 \ , \tag{23e}$$

in which $P_n(T,t)$ is given by Eq. (8), $P_\alpha(\vec{q},T,t)$ by Eq. (10), and $M(\vec{q})$ by Eq. (1c). We have suppressed the site index i on ϵ_i, g_{in}, E_{pi}, and $M_i(\vec{q})$ because we are considering an average in Eq. (23a) over nominally identical molecular ion sites. Noting that

$$E_p = \sum_{\alpha=0}^{3} E_{p\alpha} \ , \tag{24a}$$

$$E_{p0} = \sum_n g_n^2 \hbar\omega_n \ , \tag{24b}$$

$$E_{p\alpha} = \sum_{\vec{q}} g_\alpha^2(\vec{q}) |M(\vec{q})|^2 \hbar\omega_\alpha(\vec{q}), \quad \alpha = 1,2,3 \ , \tag{24c}$$

we can write Eq. (23b) as

$$\rho_e(E,\epsilon) = \rho_0(E-\epsilon) * \rho_1 * \rho_2 * \rho_3 \ , \tag{25a}$$

$$\rho_\alpha(E) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt \exp[i(E+E_{p\alpha})t/\hbar]\, F_\alpha(T,t) \ , \tag{25b}$$

$$\rho_0(E) \prod_{\gamma} * \rho_\gamma \equiv \int_{-\infty}^{\infty} \rho_0 \left(E - \sum_\gamma x_\gamma \right) \prod_\gamma dx_\gamma \rho_\gamma(x_\gamma) \ . \tag{25c}$$

Therefore the total electronic density of states $\rho_e(E)$ is expressed as a convolution product of the partial densities of states, $\rho_\alpha(E)$, associated with the electron interactions with the intramolecular vibrations ($\alpha = 0$) and with each branch of the longitudinal polarization fluctuation spectrum ($\alpha = 1,2,3$). It is these partial densities of states on which we focus our attention for most of the remainder of this section.

The spatial and compositional disorder in the polymer sample is incorporated into the model by taking the molecular-ion eigenvalues to exhibit a Gaussian distribution, so that the probability of finding an eigenvalue ϵ is

$$P(\epsilon) = (\pi\sigma_{in}^2)^{-1/2} \exp[-(\epsilon-\epsilon_0)^2/\sigma_{in}^2] \ , \tag{26}$$

in which ϵ_0 is the mean value of ϵ and the subscript "*in*" designates the *in*homogeneous contribution to the density of states. The total density of states is, therefore, given in terms of Eqs. (23)–(26) as

$$\rho_e(E) = \int_{-\infty}^{\infty} d\epsilon\, P(\epsilon) \rho_e(E,\epsilon) = \rho_0(E) * P \prod_\alpha * \rho_\alpha \ . \tag{27}$$

The corresponding quantity for holes, $\rho_h(E)$, is probed by valence-electron photoemission spectroscopy,[9] so that, in principle, the density of states given by Eq. (27) is a measurable property of pendant-group or molecularly-doped polymers.

We see from Eqs. (20) and Table I that the low-frequency intermolcular ("torsional") longitudinal polarization fluctuations ($\alpha = 1$) lie the semiclassical limit specified by Eqs. (14) and (15). Therefore the partial density of states associated with the electrons interactions with these fluctuations are given by

$$\rho_1(E) = (4\pi E_{p1} kT)^{-1/2} \exp(-E^2/4E_{p1}kT) \ , \tag{28a}$$

in which E_{p1} is given by Eq. (24c) for $\alpha = 1$. For the point-ion model

$$E_{p1} = (e^2/2R_0)(\omega_{p1}^2/\omega_1^2) = (e^2/2R_0)[\epsilon^{-1}(\omega=0) - \epsilon^{-1}(\omega_1 << \omega << \omega_2)] \ , \tag{28b}$$

whereas for the *s*-wave ion model

$$E_{p1} = (5e^2\gamma/16)[\epsilon^{-1}(\omega=0) - \epsilon^{-1}(\omega_1 << \omega << \omega_2)] \ . \tag{28c}$$

From Table I we see that $E_{p1} = g_1^2 \hbar\omega_1 = 2.53$ eV for point ions in poly(2-vinylpyridine).

For the intermolecular vibrations and the vibrational and electronic longitudinal polarization fluctuations we must utilize the exact form for $\rho_\alpha(E)$, i.e.,[15]

$$\rho_\alpha(E) = \exp[-g_\alpha^2(2n_\alpha+1)] \times \sum_{m=-\infty}^{\infty} [(n_\alpha+1)/n_\alpha]^{|m|/2} \times I_m\{2g_\alpha^2[n_\alpha(n_\alpha+1)]^{1/2}\} \times \delta(E + E_{p\alpha} - m\hbar\omega_\alpha) \ , \tag{29a}$$

$$n_\alpha = [\exp(\hbar\omega_\alpha/kT) - 1]^{-1} \ , \tag{29b}$$

in which the I_m are the modified Bessel functions,[35] the g_α are defined by Eqs. (20) and (22), and their magnitudes for $\alpha=2$ and 3 are given in Table I for point ions in poly(2-vinylpyridine). Using the asymptotic form of Eq. (29) in the limits that $g_\alpha < 1$ and $n_\alpha << 1$ (i.e., $\hbar\omega_\alpha >> kT$) we obtain

$$\rho_\alpha(E) \rightarrow \exp(-g_\alpha^2) \sum_{m=0}^{\infty} (g_\alpha^{2m}/m!) \times \delta(E+E_{p\alpha}-m\hbar\omega_\alpha) \quad . \tag{29c}$$

From Table I we see that Eq. (29c) is the suitable limit for describing the interaction of the extra electron with the valence-electron longitudinal polarization fluctuations ($\alpha=3$). Equations (25)–(29) specify our model of the density of states associated with an extra electron (hole) injected into a pendant-group or molecularly doped polymer containing only a single type of site with mean energy ϵ_0.

C. Electron-transfer probabilities

The site-to-site electron-transfer probability per unit time, $P_{e,12}$, is given in closed form by Eqs. (5)–(11). The form of $P_{e,12}$ given in Eq. (5) is identical to that for the electron density of states given in Eq. (23) with minor changes of variables. Thus, the formulas presented in the previous subsection for the electron density of states have direct analogs for electron-transfer probabilities. Examples of such analogs can be found in the Gaussian forms of Eqs. (13)–(15) and Eq. (28a) for the strong-coupling semiclassical limits of the electron-transfer probability and the electron density of states, respectively.

The formula for the partial electron-transfer density associated with the modes labeled by α is [in analogy to Eq. (29)]:

$$P_{\alpha,12}(T,\hbar\omega) = \exp[-E_{p,12}(\alpha,R)(2n_\alpha+1)/\hbar\omega_\alpha] \times \sum_{m=-\infty}^{\infty} [(n_\alpha+1)/n_\alpha]^{|m|/2} I_m\{2E_{p,12}(\alpha,R)[n_\alpha(n_\alpha+1)]^{1/2}/\hbar\omega_\alpha\}\delta(\hbar\omega-m\hbar\omega_\alpha) \quad , \tag{30a}$$

in which the I_m are the modified Bessel functions, the n_α are given by Eq. (29b), and the $E_{p,12}(\alpha,R)$ are obtained from Eqs. (16). For the *intra*molecular contributions we obtain

$$E_{p,12}(0,R) = E_{p,12}(0) = E_1 + E_2 \quad , \tag{30b}$$

independent of R. The *inter*molecular contributions i.e., $E_{p,12}(\alpha,R)$, $\alpha=1,2,3$, are given by

$$E_{p,12}(\alpha,R) = e^2(R_0^{-1}-R^{-1})[(1/\epsilon_\alpha)-(1/\epsilon_{\alpha-1})] \tag{30c}$$

in the point-ion model, and by

$$E_{p,12}(\alpha,R) = ((5e^2\gamma/8) - e^2R^{-1}\{1-[\exp(-2\gamma R)/48][8(\gamma R)^3+36(\gamma R)^2+66\gamma R+48]\})[(1/\epsilon_\alpha)-(1/\epsilon_{\alpha-1})] \tag{30d}$$

in the s-wave model. The dielectric constants are given by $\epsilon_0=4.81$, $\epsilon_1=2.81$, $\epsilon_2=2.56$, and $\epsilon_3=1.00$ for poly(2-vinylpyridine).[9] The magnitudes of the $E_{p,12}(\alpha,R)$ can be estimated from Table I for the interaction of point ions with longitudinal polarization fluctuations in poly(2-vinylpyridine). The intramolecular contributions are obtained from Eq. (20) (i.e., $E_1=E_2=g_0^2\hbar\omega_0$). The asymptotic form of Eq. (30a) in the limits that $n_\alpha << 1$ (i.e., $\hbar\omega_\alpha >> kT$) and $E_{p,12}(R)/\hbar\omega_\alpha < 1$ is given by

$$P_{\alpha,12}(T,\hbar\omega) = \exp[-E_{p,12}(\alpha,R)/\hbar\omega_\alpha] \times \sum_{m=0}^{\infty} (1/m!)[E_{p,12}(\alpha,R)/\hbar\omega_\alpha]^m \times \delta(\hbar\omega-m\hbar\omega_\alpha) \quad . \tag{31}$$

Estimating the magnitude of $E_{p,12}(\alpha,R)$ via Eqs. (17c)–(17e) and Table I we see (as in the previous section) that Eq. (31) is the suitable limit for describing the interaction of the extra electron with the valence-electron longitudinal polarization fluctuations ($\alpha=3$). Similarly, Eqs. (13)–(15) are the appropriate limit for approximating the interaction of an extra electron with the low-frequency longitudinal polarization fluctuations ($\alpha=1$). In the case of the vibrational modes (i.e., $\alpha=0,2$) the general formula, Eq. (30a), must be used to obtain the partial electron-transfer densities.

When the electron interacts with multiple excitations, as in the case of the electronic density of states given by Eqs. (25), the total electron-transfer probability $P_{e,12}(T,\hbar\omega)$, is expressed as a convolution product of the partial transfer densities, $P_{\alpha,12}(T,\hbar\omega)$ associated with the electron interactions with the intramolecular vibrations ($\alpha=0$) and with each branch of the longitudinal polarization fluctuation spectrum

($\alpha = 1, 2, 3$). Thus, Eq. (5a) can be written as

$$P_{e,12}(T,\hbar\omega) = (2\pi/\hbar)\,U_{12}^2(R)\,P_{0,12}(T,\hbar\omega) * P_{1,12} * P_{2,12} * P_{3,12} \ , \tag{32a}$$

$$P_{\alpha,12}(T,\hbar\omega) = (2\pi\hbar)^{-1}\int_{-\infty}^{\infty} dt\, \exp(i\omega t)\exp\left[\sum_{\vec{q}} g_\alpha^2(\vec{q})\,|M_1(\vec{q}) - M_2(\vec{q})|^2[P_\alpha(\vec{q},T,t) - P_\alpha(\vec{q},T,0)]\right] \ , \quad \alpha = 1, 2, 3 \ , \tag{32b}$$

$$P_{0,12}(T,\hbar\omega) \prod_\alpha{}^{*} P_{\alpha,12} \equiv \int_{-\infty}^{\infty} P_{0,12}\left(T,\hbar\omega - \sum_\alpha x_\alpha\right) \prod_\alpha dx_\alpha P_{\alpha,12}(T,x_\alpha) \ , \tag{32c}$$

in which $P_\alpha(\vec{q},T,t)$ is defined by Eq. (10), and $P_{0,12}(T,\hbar\omega)$ is obtained by inserting Eq. (30b) into (30a).

When the convolutions indicated in Eqs. (27) and (32) are performed, using the appropriate limits discussed above, the total electron density of states is given by

$$\begin{aligned}\rho_e(E) = {} & \exp[-g_0^2(2n_0+1) - g_2^2(2n_2+1) - g_3^2] \\ & \times \sum_{p=0}^{\infty} [(g_3)^{2p}/p!] \sum_{l,m=-\infty}^{\infty} [(n_0+1)/n_0]^{|l|/2}[(n_2+1)n_2]^{|m|/2} I_l\{2g_0^2[n_0(n_0+1)]^{1/2}\} I_m\{2g_2^2[n_2(n_2+1)]^{1/2}\} \\ & \times (4\pi E_{p1}kT)^{-1/2}\exp[-(E - l\hbar\omega_0 - m\hbar\omega_2 - p\hbar\omega_3)^2/4E_{p1}kT] \ ,\end{aligned} \tag{33}$$

where the disorder term, Eq. (26), has been omitted. Similarly, the total electron-transfer probability, using the appropriate limiting forms for $P_{\alpha,12}(T,\hbar\omega)$ is

$$\begin{aligned}P_{e,12}(T,\hbar\omega,R) = {} & (2\pi/\hbar)\,U_{12}^2(R)\exp\{-[(E_1+E_2)(2n_0+1)/\hbar\omega_0] - [E_{p,12}(2,R)(2n_2+1)/\hbar\omega_2]\}\exp[-E_{p,12}(3,R)/\hbar\omega_3] \\ & \times \sum_{p=0}^{\infty} [(E_{p,12}(3,R)/\hbar\omega_3]^p/p! \sum_{q,l,m=-\infty}^{\infty} [(n_0+1)/n_0]^{|q|/2}[(n_0+1)/n_0]^{|l|/2}[(n_2+1)/n_2]^{|m|/2} \\ & \times I_q\{2E_1[n_0(n_0+1)]^{1/2}/\hbar\omega_0\} I_l\{2E_2[n_0(n_0+1)]^{1/2}/\hbar\omega_0\} \\ & \times I_m\{2E_{p,12}(2,R)[n_2(n_2+1)]^{1/2}/\hbar\omega_2\} \\ & \times [4\pi E_{p,12}(1,R)kT]^{-1/2}\exp[-E^{*}_{q,l,m,p}(R)/kT] \ ,\end{aligned} \tag{34}$$

where

$$E^{*}_{q,l,m,p}(R) = E_{p,12}(1,R)\{1 - [(\hbar\omega - (l+q)\hbar\omega_0 - m\hbar\omega_2 - p\hbar\omega_3)/E_{p,12}(1,R)]\}^2/4 \ . \tag{35}$$

Separate expansions for the consequences of intramolecular electron-molecular-vibration coupling in the initial ($E_{1,q}$sum) and final ($E_{2,l}$sum) have been retained in Eqs. (34) and (35) for illustrative purposes even though we have taken the initial and final states to be identical (i.e., $E_i/\hbar\omega = g_0^2$). Only a single sum (roughly corresponding to an index $s = l + q$) was utilized in the numerical calculations reported in the following section.

It is noteworthy that expressions similar to Eqs. (34) and (35) have been derived earlier within the context of incorporating the consequences of both inner coordination shell and "medium" vibrational modes in theories of electron transfer in solution.[36–38] Ours differ from these earlier formulas both via their incorporation of a complete (experimentally determined) three-branch longitudinal polarization fluctuation spectrum of the "medium" and via our utilization of Eqs. (8)–(10) and Eq. (29) in which all of the effects of thermal averaging over the initial vibrational states have been incorporated into the single sum over modified Bessel functions given by Eqs. (29).[15] The compact form for $\rho_\alpha(E)$ given by Eqs. (29) and its analog for $P_{\alpha,12}(T,\hbar\omega)$ given by Eqs. (30) render the detailed form of l and q sums in Eq. (34) a little different from earlier formulas for $P_{e,12}$ in which either the thermal averaging was incomplete[38] or less compact expressions than Eqs. (29) and (34) were used to describe the influence of electron coupling to intramolecular modes prior to the derivation of limiting cases of the electron-transfer probability.[36, 37] Although the technical differences between Eq. (34)

and its predecessors[36–38] in electron-transfer theory are minor, the effects of incorporating the influence of the infrared and electronic longitudinal polarization fluctuations are not. Both $E_{p,12}(2,R)$ and $E_{p,12}(3,R)$ exhibit strong dependences on R by virtue of Eqs. (30b) and (30c). Therefore both the spatial and temperature dependence of the electron-transfer probability given by Eqs. (34) and (35) differ significantly from those derived earlier for electron transfer in solution.[24,25,27,36–38]

While Eqs. (33) and (34) may appear complicated, it is not difficult to discover the physical effect of the various excitations ($\alpha = 0, 1, 2, 3$) on the electron density of states and electron-transfer probability. In both the density of states, Eq. (33), and the transfer probability, Eq. (34), the Gaussian term is due to the large coupling of the electronic motion to the low-frequency "torsional" ($\alpha = 1$) modes of the polymeric pendant groups. This Gaussian form leads to the temperature-dependent linewidths found in the photoemission density of states,[11] as expressed in Eqs. (28a) and (33), and also leads to the activated form for the electron-transfer probability, as expressed via Eq. (34). The ir mode ($\alpha = 2$) coupling constant, $g_2^2 = 6.91$, can be viewed as intermediate coupling (see below) so this mode contributes to the photoemission linewidths and transport activation energy. The valence electron excitations ($\alpha = 3$), exhibit weak coupling to the electron motion and a small thermal population. Hence, they make no contribution to the activation energy (only the $p = 0$ or "zero-phonon" term is appreciable), but rather contribute a distance-dependent prefactor to the electron-transfer probability. In the photoemission density of states, however, the valence electron $p = 0$ "zero-phonon" term is shifted to lower energy by amount $E_{3p} = g_3^2 \hbar\omega_3$, accounting for the dominant contribution to the relaxation energy.[9] Due to the intermediate size of both the intramolecular ($\alpha = 0$) and intermolecular ($\alpha = 2$) vibrational interactions with the electron motion, it is necessary to investigate numerically their importance for linewidths, relaxation energies, and activation energies.

In summary, in Sec. III we have indicated the form of the parameters used to describe the coupling of electron motion to intramolecular vibrations and to intermolecular polarization fluctuations in two models: the point-ion model and the *s*-wave model. Using these models, the magnitude of the coupling constants have been shown to lie in three regions: a strong-coupling region ($g_1^2 >> 1$), a weak-coupling region ($g_3^2 << 1$), and an intermediate-coupling region ($g_0^2 \sim g_2^2 \sim 1$). The valence-electron modes have been shown to be responsible for photoemission relaxation energies, while linewidths and the electron-transfer activation energies are caused by coupling to low frequency and possibly ir modes. In the next section we illustrate these results by considering numerical calculations for "typical" values of the model parameters.

IV. NUMERICAL RESULTS

In our numerical analysis we wish to examine three issues: (i) the dependence of the density of states and electron-transfer densities on the magnitude of the "coupling constants" g_α^2 and $E_{p,12}(\alpha,R)/\hbar\omega_\alpha$, and the region of applicability of the semiclassical [Eqs. (12) and (28)] and weak-coupling [Eqs. (29c) and (31)] limits, (ii) the temperature dependence of the electron-transfer probability, and (iii) the dependence of the electron-transfer activation energy on the distance R between the sites as predicted by the point-ion and *s*-wave models, respectively.

In discussing the region of applicability of the semiclassical and weak-coupling limits, we confine our discussion to the electron density of states determined by the coupling constants g_α^2 [Eq. (33)], although we could equally well discuss the electron-transfer probability [Eq. (34a)] with the analogous coupling constants $E_{p,12}(\alpha,R)/\hbar\omega_\alpha$. The exact form of the partial density of states is given by Eq. (29a). In order to ascertain whether the semiclassical [Eq. (28a)] or "weak-coupling" limit [Eq. (29c)] applies, we examine the magnitude of the argument of the modified Bessel function, i.e., $2g_\alpha^2[n_\alpha(n_\alpha+1)]^{1/2}$. For the values of g_α^2 and $\hbar\omega_\alpha$ quoted in the previous section, at room temperature the Bessel function argument assumes the value 0.28 for intramolecular vibrations ($\alpha = 0$), 4.72×10^{19} for low-frequency ("torsional") modes ($\alpha = 1$), 2.16 for ir modes ($\alpha = 2$), and 0.00 for valence-electron excitations ($\alpha = 3$). Hence we see that the strong-coupling Gaussian form (Eq. 28a) is valid for the low-frequency modes ($\alpha = 1$), while the valence-electron modes ($\alpha = 3$) lie in the weak-coupling limit of Eq. (29c). The intramolecular modes ($\alpha = 0$ and ir modes ($\alpha = 2$) are, however, in an intermediate region which must be investigated numerically. The results of numerical evaluation of Eq. (29a) for the intramolecular vibrational contribution to the density of states are shown in Fig. 2(a) by the discrete line spectra. The semiclassical Gaussian approximation (dashed curve) also is shown for comparison. These calculations reveal that the intramolecular partial density of states $\rho_{\alpha=0}(E)$ is well described the asymptotic form of Eq. (29c). The ir partial density of states is shown in Fig. 2(b) by the discrete spectrum representing the exact formula [Eq. (29a)], the dashed line indicating the Gaussian strong-coupling approximation. We see that although the position of the envelope of the discrete spectrum is well represented by the Gaussian envelope with a maximum at $m = g_{\alpha=2}^2$ (a general result), the width of the Gaussian is not. Indeed, numerical studies reveal that the Gaussian width is

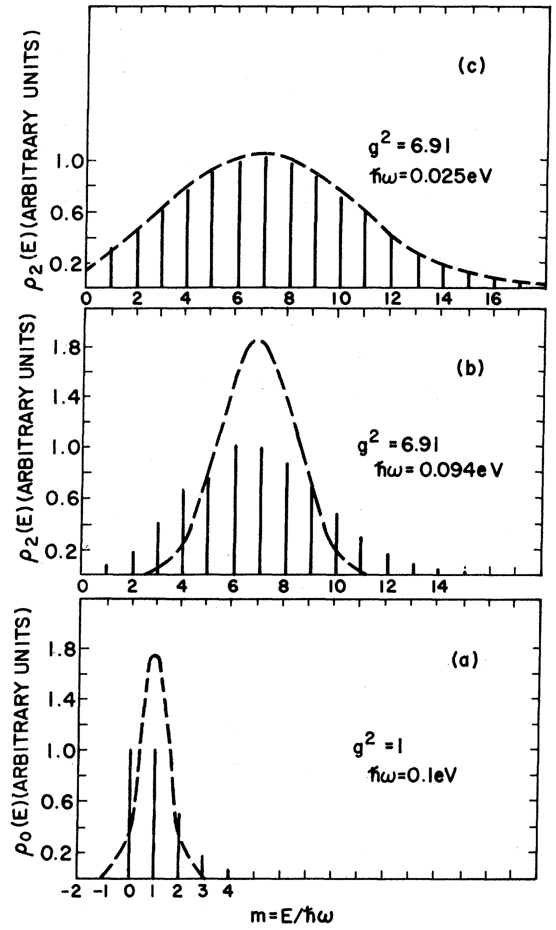

FIG. 2. Partial densities of states for a molecular cation of radius $R_0=1.67$ Å, temperature $T=300$ K calculated using Table I and Eqs. (20a)–(20d), via Eqs. (29). Panel (a): the calculated density of states for the intramolecular ($\alpha=0$) mode, yielding $2g_0^2[n_0(n_0+1)]^{1/2}=0.28$ (small-argument limit). Panel (b): the calculated density of states for the ir ($\alpha=2$) mode, yielding $2g_\alpha^2[n_2(n_2+1)]^{1/2}=2.16$ (intermediate-argument limit). Panel (c): the calculated density of states for a mode with $g_\alpha^2=6.91(\alpha=2)$, but with $\hbar\omega_\alpha=0.025$ eV, yielding $2g_\alpha^2[n_\alpha(n_\alpha(n_\alpha+1))]^{1/2}=13.26$ (large-argument limit). In each case the semiclassical Gaussian approximation is shown as a dotted line for comparison with the discret densities of states shown by solid vertical bars.

poorly approximated by Eq. (12c) unless, in addition to the requirement that the argument of the Bessel function

$$2g_\alpha^2[n_\alpha(n_\alpha+1)]^{1/2}>>1 ,$$

we also impose the condition that $\hbar\omega_\alpha/2kT>1$. In the case of poly(2-vinylpyridine) at room temperature, only the torsional oscillations satisfy these two conditions. This additional requirement that $\hbar\omega/2kT>1$ for the correct prediction of the Gaussian width, σ, by Eq. (12c) is due to the $\exp(-i\omega t)$ term in Eq. (8), which cannot be neglected in the derivation of the strong-coupling limit when $2N(\omega)\cos(\omega t)$ is small. When $\hbar\omega_\alpha/2kT\gtrsim 1$, however, an increased Bessel function argument of 13.26 results and the exact discrete line spectrum agrees well the Gaussian approximation in both width and position as shown in Fig. 2(c).

From the above analysis we determine that the semiclassical expressions are not generally adequate to describe photoemission line broadening. In addition, since the electron-transfer activation energy is a result of the Gaussian form of Eq. (12a), it is unclear whether an activated transport of the form of Eq. (15a) occurs in poly(2-vinylpyridine) when ir modes are considered in the calculation. In an effort to clarify this question, in Fig. 3 we plot $\ln P_{e,12}$, determined from Eq. (34), in the $R\rightarrow\infty$ limit as a function of $1/kT$ for identical sites (i.e., $\hbar\omega=0$). We expect, for an activated transport of the form of Eq. (15a), to find

$$d(-\ln P_{e,12})/d(1/kT)=-(kT/2)+E^* . \quad (36)$$

Using Eq. (36) to analyze the numerical evaluations of Eq. (34) we find $E^*=1.50$ eV over the wide temperature range shown in Fig. 3. This is less than but comparable to the $R=\infty$ result of $E^*=1.71$ eV predicted semiclassically by Eqs. (15b) and (18c), using $R_0=1.67$ Å and $\epsilon(\omega=0)=4.81$.[9] If only the $l=m=p=q=0$ term is retained we find $E^*=[E_{p,12}(1,\infty)/4]=1.27$ eV, i.e., only the low-frequency longitudinal polarization fluctuations contribute to the activation energy. As expected, therefore, the calculated effective value of $E^*=1.5$ eV exceeds the low-frequency-mode contribution alone, but is less than the semiclassical result in which all three branches of the longitudinal polarization spectrum contribute to E^* as described by Eqs. (12)–(15). The slight curvature of the plot of $\log_e(P_{e,12})$ vs T^{-1} shown in Fig. 3 is a consequence of the anticipated increase in the effective value of E^* as the temperature increases.[36]

In evaluating the electron-transfer probability from Eq. (34) it is necessary to keep several terms in the l, m, and q sums in order for the result to converge. Although the zero phonon term (i.e., $l=m=q=0$) is the largest, it typically contributes from 10% to 50% of the total. Thus, in order to obtain accurate activation energies and transfer rates, it is necessary to utilize Eq. (34), rather than a simple single-term formula like Eq. (12a).

Thus far we have discussed the dependence of the density of states and asymptotic electron-transfer probability on (i) strength of coupling to elementary excitations of the polymer and (ii) the temperature. In doing so we assumed $E_{p,12}(\alpha,R)=2E_{p\alpha}$. Since this is

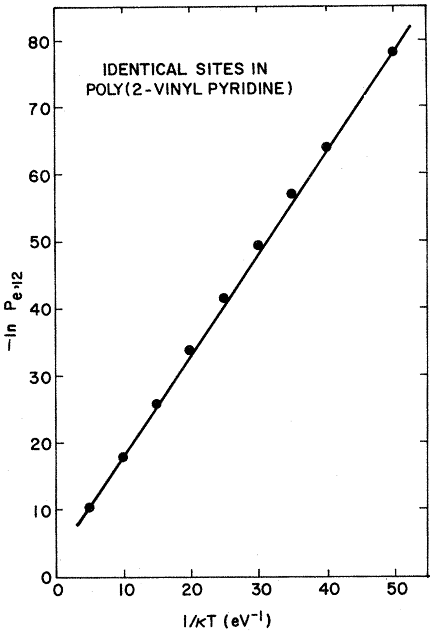

FIG. 3. Variation of the total electron-transfer probability, given by Eq. (34), as a function of $1/kT$ for $\hbar\omega=0$ in poly(2-vinylpyridine). The values of $E_{p,12}(\alpha,R)$ utilized corresponded to the Förster-Dexter (or $R=\infty$) limit of $2g_\alpha^2\hbar\omega_\alpha$. From this plot the value of the effective activation energy may be obtained via Eq. (36).

actually only a limiting result true as $R\rightarrow\infty$, we now investigate the behavior of E_{12}(inter) as a function of R. In previous sections we developed two models for the coupling constants. The point-ion model, based on classical electrostatic arguments, leads to Eq. (18c) for E_{12}(inter) in the semiclassical limit. The s-wave model, based on direct evaluation of Eq. (7d) for s-like molecular orbitals, yields Eq. (19d) for E_{12}(inter) in the semiclassical limit. Each model has one adjustable parameter: R_0 in the point-ion model, and γ in the s-wave model. In Fig. 4 we compare the semiclassical predictions of these two models for E_{12}(inter), using the value $\epsilon(\omega=0)=4.81$ (Ref. 9) and assuming $R_0=1.67$ Å and

$$\gamma=8/5R_0\ . \tag{37}$$

From Fig. 4 we see that the s-wave model and the point-ion model are in excellent agreement in the range $R\geq 2R_0$ where the point-ion model is valid. For smaller separations, i.e., $R<3.5$ Å, it is necessary to use the quantum mechanical s-wave model.

Finally, using the exact form for the electron-transfer probability, Eq. (34), with $E_{p,12}(\alpha,R)$ given by Eq. (30c) and γ by Eq. (37), we evaluated the total electron-transfer probability as a function of site separation R and temperature T. The results are shown in Fig. 5 normalized to reveal the conse-

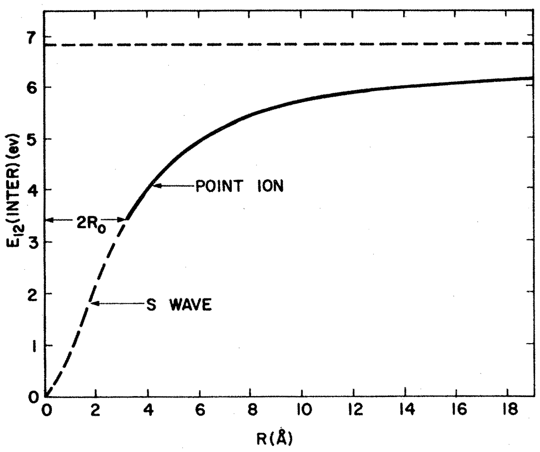

FIG. 4. Variation of E_{12}(inter) calculated via Eq. (18c) in the semiclassical limit for the point-ion model, and via Eq. (19d) in the semiclassical limit for the s-wave model. The dashed line indicates the asymptotic Förster-Dexter limit. Parameters are taken from Eqs. (20a)–(20d) and Table I for poly(2-vinylpyridine).

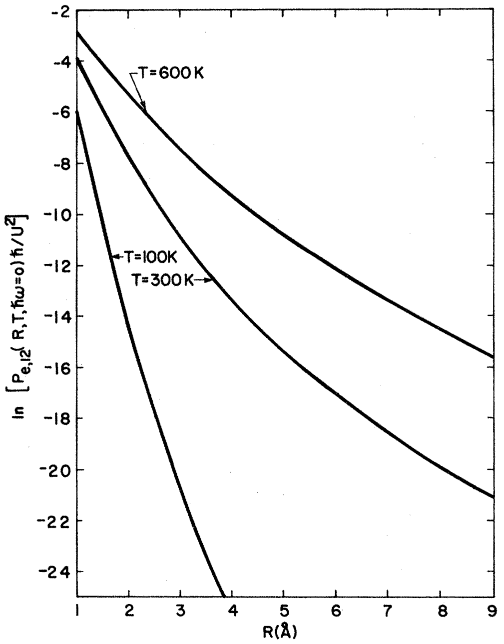

FIG. 5. Variation of the total electron-transfer probability, given by Eq. (34), as a function of R for $\hbar\omega=0$, utilizing parameters for poly(2-vinylpyridne) taken from Eqs. (20a)–(20d) and Table I. The s-wave form [Eq. (30c)] for $E_{p,12}(\alpha,R)$ is utilized, assuming $\gamma=0.96$ Å and the values of the dielectric constants are those given in the text.

quences of the increasing activation energy with increasing R. The plot is not a straight line because the rate of decay becomes smaller as R increases. This phenomenon is incorporated in models of electron transfer is solution by using a suitably chosen "most probable" distance of approach between the charge exchanging ion pairs in the expression for the solute contributions to $E_{p,12}(R)$.[23,25,36] It is neglected, however, in modern models of electron transfer following radiolysis is glassy media.[39,40] In particular, the R^{-1} dependence of $E_{p,12}(R)$ predicted by Eqs. (30c) and (30d) recently has been verified experimentally in studies of electron transfer between Ru complexes separated by $7 < R < 14$ Å and in polar solutions.[41] Consequently, comparable effects of the R dependence of $E_{p,12}(R)$ should be observable in the solid state, even though they are superimposed on the exponential R dependence of $U_{12}^2(R)$.

Due to the rapid decay of the electron (or hole) transfer rate with increasing distance, virtually all hops are expected to occur between nearest-neighbor locations in the solid state. As we have seen previously, the activation energies for this hopping process are largely caused by $E_{p,12}(1,R)$, which is determined by (i) the size of the pendant group, as expressed through γ (s-wave model) or R_0 (the point-ion model), and (ii) the dielectric response of the material as expressed via the $(1/\epsilon_\alpha - 1/\epsilon_{\alpha-1})$ terms in Eqs. (30b) or (30c). It is evident therefore that good electron-(hole) transport is achieved via utilizing large molecular ions and either rigid or nonpolar polymer matrices. In particular, a trade-off exists between the flexibility of the polymer matrix, which implies low-frequency mechanical relaxation processes, and the value of the electron-(hole) transport activation energy. Efficient electron hopping is achieved either by suppressing the low-frequency relaxations, or by rendering such relaxations dielectrically inactive by proper choice of polymer composition. The important point is that the suppression of dielectrically active relaxations with $\hbar\omega < kT$ should result directly in increased electron-transfer rates *ceteris paribus.*

V. SYNOPSIS

In this paper we have specified a model Hamiltonian, Eqs. (1) and (3) which describes the influence on electron transfer in a dielectric medium of the interaction of that electron both with the intramolecular vibrations of the molecule on which it resides (*à la* the Förster-Dexter model,[12,16] Holstein's molecular-crystal model,[28–30] and Hopfield's biological tunneling model[31]) and with the longitudinal polarization fluctuations characteristic of the dielectric medium in which the molecules are embedded (*à la* Fröhlich,[42] Levich,[25] Dogonadze and Kornyshev,[34] and Duke and co-workers[9,15,16]). The major new feature of this model relative to its predecessors is its incorporation of a description of the interaction of the electrons with a complete, experimentally-determined, spectrum of longitudinal polarization fluctuations with frequencies ranging from Hz through the vacuum ultraviolet.[9]

Applying standard techniques, the one-electron density of states and the intersite electron-transfer probability were evaluated using this model. The formal expressions for the intersite transfer probability, $P_{e,12}$, and the density of molecular ion states, ρ_e, are given by Eqs. (5)–(11) and Eqs. (23)–(27), respectively. Manipulation of these expressions for our specific model of polymer dielectric response led to Eqs. (34) and (35) for $P_{e,12}$ and to Eq. (33) for ρ_e. These formulas were evaluated numerically for parameters characteristic of poly(2-vinylpyridine), a "typical" polar polymeric dielectric. The results of this evaluation were presented and discussed in Sec. IV. Specifically we showed that each branch of the intramolecular and of the longitudinal-polarization fluctuation spectrum exerts a characteristic influence on the observable electronic properties of the molecularly doped composite medium. The high-frequency ($\hbar\omega \sim 10$ eV) valence-electron fluctuations cause shifts (relative to the gas phase) in photoemission and uv absorption lines[9] and spatially varying, temperature-independent prefactors in the electron-transfer probabilities. The low-frequency ($\omega \sim 10^3$–10^6 Hz) macromolecular relaxations cause temperature-dependent linewidths in photoemission and uv absorption spectra[9–11,23] and spatially-dependent activation energies for electron transfer. The ir longitudinal polarization fluctuations cause (nearly-temperature-independent) contributions to photoemission and uv absorption linewidths,[9,23] increase the effective activation energies for electron transfer, and produce spatial variations both in these activation energies and in the prefactors for electron transfer. The intramolecular ir modes produce the same type of phenomena as the ir longitudinal polarization fluctuations without inducing any spatial dependence thereof.

These calculations permit, therefore, a comprehensive assessment of the consequences of both intramolecular and nonlocal "medium" dielectric relaxations on the electronic (i.e., photoemission, optical, and transport) properties of molecularly doped dielectric media. Scaling laws relating both the local properties of the molecules and the dielectric response of the media to the electronic properties of the molecularly doped composites are embedded in the formulas presented above and are suitable for use in the molecular engineering of such media to yield prescribed optical and transport properties. Consequently, in this paper together with Refs. 9 and 23 we have presented a complete microscopic model of the electronic properties of molecularly doped dielectric media based on the supposition of the disorder-induced localized electron (exciton) states and the Hamiltonian specified by Eqs. (1) and (3). A number of the model's predictions already have been confirmed in a variety of photoemission and uv absorption experiments.[9–11,33] A critical test of the predictions of electron-transfer probabilities requires, however, the systematic acquisition of transport data for several active molecules in varying host polymers. Suitable data for this purpose are, unfortunately, not yet available, although these predictions are consistent with existing measurements.[3–6]

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[1] C. B. Duke and L. B. Schein, Phys. Today 33 (No. 2), 42 (1980).
[2] C. B. Duke and T. J. Fabish, J. Appl. Phys. 49, 315 (1978).
[3] W. D. Gill, in *Photoconductivity and Related Phenomena,* edited by J. Mort and D. Pai (Elsevier, Amsterdam, 1976), pp. 301–334.
[4] G. Pfister, S. Grammatica, and M. Mort, Phys. Rev. Lett. 37, 1360 (1976).
[5] G. Pfister, Phys. Rev. B 16, 3676 (1977).
[6] P. M. Borsenberger, W. Mey, and A. Chowdry, J. Appl. Phys. 49, 273 (1978).
[7] H. Scher and E. W. Montroll, Phys. Rev. B 12, 2455 (1975).
[8] H. Scher, in *Photoconductivity and Related Phenomena,* edited by J. Mort and D. Pai (Elsevier, Amsterdam, 1976), pp. 71–115.
[9] C. B. Duke, W. R. Salaneck, T. J. Fabish, J. J. Ritsko, and A. Paton, Phys. Rev. B 18, 5717 (1978).
[10] C. B. Duke, Mol. Cryst. Liq. Cryst. 50, 63 (1979).
[11] W. R. Salaneck, C. B. Duke, W. Eberhardt, E. W. Plummer, and H. J. Freund, Phys. Rev. Lett. 45, 280 (1980).
[12] C. B. Duke, in *Tunneling in Biological Systems,* edited by B. Chance, D. C. DeVault, H. Frauenfelder, R. A. Marcus, J. R. Schrieffer, and N. Sutin (Academic, New York, 1979), pp. 31–66.
[13] C. B. Duke, N. O. Lipari, and L. Pietronero, Chem. Phys. Lett. 30, 415 (1975); J. Chem. Phys. 65, 1165 (1976).
[14] C. B. Duke, Ann. N. Y. Acad. Sci. 313, 166 (1978).
[15] C. B. Duke and G. D. Mahan, Phys. Rev. 139, A1965 (1965).
[16] T. F. Soules and C. B. Duke, Phys. Rev. B 3, 262 (1971).
[17] C. B. Duke, T. J. Fabish, and A. Paton, Chem. Phys. Lett. 49, 133 (1977).
[18] A. Witkowski and W. Moffitt, J. Chem. Phys. 33, 872 (1960).
[19] R. L. Fulton and M. Gouterman, J. Chem. Phys. 35, 1059 (1961); 41, 2280 (1964).
[20] A. R. Gregory, W. H. Henneker, W. Siebrand, and M. Z. Zgierski, J. Chem. Phys. 65, 2071 (1976); 67, 3175 (1977).
[21] C. B. Duke, Surf. Sci. 70, 674 (1978).
[22] D. Emin, Phys. Rev. Lett. 25, 1751 (1970); Phys. Rev. B 4, 3639 (1971).
[23] C. B. Duke, in *Extended Linear Chain Conductors,* edited by J. S. Miller (Plenum, New York, in press).
[24] R. A. Marcus, J. Chem. Phys. 43, 679 (1965).
[25] V. G. Levich, Adv. Electrochem. 4, 249 (1966).
[26] J. Jortner, J. Chem. Phys. 64, 4860 (1976).
[27] N. S. Hush, Electrochimica Acta 13, 1005 (1968).
[28] T. D. Holstein, Ann. Phys. (N.Y.) 8, 325, 343 (1959).
[29] D. Emin, Adv. Phys. 22, 57 (1973); 24, 305 (1975).
[30] I. G. Austin and N. F. Mott, Adv. Phys. 18, 41 (1969).
[31] J. J. Hopfield, Proc. Nat. Acad. Sci. U.S.A. 71, 3640 (1974).
[32] C. B. Duke, Int. Jour. Quant. Chem Symp. 13, 267 (1979).
[33] N. O. Lipari and C. B. Duke, J. Chem. Phys. 63, 1748 (1975).
[34] R. R. Dogonadze and A. A. Kornyshev, J. Chem. Soc. Faraday Trans. II 70, 1121 (1974).
[35] *Higher Transcendental Functions* edited by A. Erdelyi (McGraw-Hill, New York, 1953), p. 85.
[36] N. R. Kestner, J. Logan, and J. Jortner, J. Phys. Chem. 78, 2148 (1974).
[37] J. Ulstrup and J. Jortner, J. Phys. Chem. 63, 4358 (1975).
[38] S. Efrima and M. Bixon, Chem. Phys. 13, 447 (1976).
[39] S. Brocklehurst, in *Tunneling in Biological Systems,* edited by B. Chance, D. C. Devault, H. Frauenfelder, R. A. Marcus, J. R. Schrieffer, and N. Sutin (Academic, New York, 1979), pp. 243–268.
[40] J. V. Beitz and J. R. Miller, in *Tunneling in Biological Systems,* edited by B. Chance, D. C. Devault, H. Frauenfelder, R. A. Marcus, J. R. Schrieffer, and N. Sutin (Academic, New York, 1979), pp. 269–280.
[41] G. M. Brown and N. Sutin, J. Am. Chem. Soc. 101, 883 (1979).
[42] H. Fröhlich, Adv. Phys. 3, 325 (1954).