

Excess electrons in condensed media: Theory of optical absorption spectrum in molecular solutions

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A theoretical formalism is developed for analyzing the spectra of excess electrons in pure molecular solids and liquids. A perturbation decomposition of the Hamiltonian allows the expression for the band shape $I(\omega)$ to be written as a sum of a zeroth order part, proportional to dipole transition matrix elements and corresponding Franck-Condon factors, and perturbation terms containing effects of electron hopping and their fluctuations. By using several physically motivated approximations (e.g., the temporally localized nature of electronic transitions which allows a short-time expansion of the time dependence of operators), the expression for $I(\omega)$ can be expressed in terms of solvent structure information and the electron-solvent interaction potential. From the general expressions for $I(\omega)$ a simplified model was developed in the special case of systems for which bound-to-bound transitions are dominant. This model has been successfully applied to the spectra of excess electrons in ethanol and anthracene glass, thereby providing some optimism for the potential use of the general formalism derived here.

I. INTRODUCTION

Two of the most important and frequently investigated physical properties of excess electrons¹ in atomic and molecular liquids and solids are optical absorption spectra² and electron mobilities.³ These two processes probe, respectively, the short- and long-time characteristics of the excess electrons. In Ref. 4 (hereafter referred to as I) a formalism was developed to analyze the mobility of one component solutions of excess electrons in terms of the electron-solvent interactions and solvent structure information. In the present work we shall develop, based upon fundamental quantum and statistical mechanical principles, a general formalism for understanding the optical spectrum of excess electrons in molecular solutions for which the electronic states are primarily localized in nature.

Theoretical models⁵⁻¹⁴ developed thus far are adequate to treat, in a semiquantitative fashion, the spectra of polar fluids in which the electron is assumed to be localized in a cavity about some point in space and to have an electronic wavefunction which decreases exponentially with distance away from this point. The potential energy of the cavity is assumed to be due to the orientation of the polar solvent molecules inward toward the trapped electron. The cavity is characterized by a radius R and depth E_0 . Within this class of cavity models the simple cluster type models^{5,6} treat only the first solvation layer around the cavity and therefore include only the short-range interactions. Continuum models,^{7,8} on the other hand, assume a cavity surrounded by a continuum dielectric medium with any one of several forms for the polarization $P(r)$ of the medium. For example, a commonly used form due to Jortner⁹ is

$$P(r) = 0, \quad r < R, \\ = -\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right) \frac{e}{4\pi r^2}, \quad r > R, \quad (1)$$

where ϵ_{op} and ϵ_s are the optical and static dielectric constants of the medium, respectively.

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In the semicontinuum models⁹⁻¹⁴ the above two extremes are modified somewhat by allowing the cluster (cavity surrounded by first solvation layer) to be embedded in a polarizable dielectric continuum. The first solvation layer is then simulated by point dipoles or by *ab initio* self-consistent-field approximations to the solvent species. Calculations of Copeland, Kestner, and Jortner¹⁰ and also of Newton¹³ are some examples of applications of these models. It should be kept in mind that the cluster, continuum, and semicontinuum models are aimed at addressing only one aspect of the solvated electron: its electronic energy levels and transition probabilities. Any consideration of solvent vibrational motion is simply added on at the end of the calculation. The electronic and vibrational motion is not treated in a unified manner.

The optical spectrum of a solvated electron is characterized by the position of the band maximum, the width of the band, and the band shape. Experimentally, almost all solvated electron optical spectra are skewed to the high energy side and display little or no vibrational structure.²⁸ More subtle features, at least from the theoretical point of view, which are seen experimentally are the dependence on temperature, pressure, and density of the absorption line shape. Clearly, any successful theory should be able to explain all of these characteristics of the line shape.

Many electron *ab initio* calculations using cluster models have been performed by Neleway *et al.*⁶ and by Newton⁶ and have also been extended to the semicontinuum model by Newton¹³ and Moskowitz *et al.*¹⁴ using empirical parameters to simulate the dielectric continuum, thus accounting for both long- and short-range interactions. Unfortunately, the results of such model calculations do not account properly for the width and skewness of the spectrum. Using a semicontinuum model, and ascribing the width of the absorption to inhomogeneous broadening of a single bound-to-bound electronic transition, Gaathon and Jortner¹¹ calculate a width which is only ~50% of the experimental value for solvated electrons both in ammonia and water. Equally important is the fact that their calculations failed to describe the

skewed nature of the absorption. The most sophisticated among the semicontinuum model studies is the calculation of Newton,¹³ where parameters such as cavity size, etc. were determined by *ab initio* calculations. The positions of band maxima for e_{aq}^- and e_{am}^- were calculated to lie at only $\sim 70\%$ and $\sim 60\%$ of the experimentally observed values. Moreover, the computed (on the basis of inhomogeneous broadening) widths and shapes were far from correct. Recent experimental evidence provided by Renzepis and Jortner¹⁵ has shown that inhomogeneous broadening cannot account for the very large line widths in e_{aq}^- and e_{am}^- .

Kajiwarra *et al.*¹⁶ proposed a modified cluster model in which (i) one neglects long-range interactions (electron-molecule and molecule-molecule), thereby treating the bound electron as a particle in a box (with R and E_0 as parameters), and (ii) one chooses the cavity such that it has only one bound state. The observed optical spectrum is then assigned to a bound-to-continuum transition. Although these authors had some success in fitting experimental line shapes, a model built on these assumptions can only be justifiable in very specific cases. In particular, it cannot be used to treat transitions which are known to be bound-bound transitions (which are also usually quite broad and skewed). In all of the above models which include only a single cavity the effects of the coupling of the electronic states of one site to those of its neighbors are not accounted for, except to the extent that bound-continuum transitions can be thought of as including neighbors. This kind of coupling is, as we shall see in our development, very important in providing skewedness to the line shape. Therefore, its absence in all previous theories should be viewed as a potentially serious weakness of these theories.

Tsubomura and Sunakawa¹⁷ analyzed the spectra of solvated electrons in aromatic hydrocarbons where many sharp bands are observed at energies above the photodetachment energy of the anion. They emphasize that the excess electron-molecule potential is much more localized than a Coulomb potential. Hence, a simple short-range square-well type cavity model is employed. In addition, they assume that the solvation effect has little influence on the electronic spectra. Thus, the energy levels of the cavity alone, especially in the region $E > E_0$ where they find resonance states to exist, are sufficient to describe the spectra. The lifetime of the resonance states, which they fit to the experimental data, is used to explain the width of the absorption band.

Recently, Bush and Funabashi¹⁸ have proposed a small-polaron model for solvated electrons in alcohols. They assume that only continuum excited states of the anion exist and therefore allow only for electric dipole transitions between a bound ground anion state and a continuum of band states whose near-neighbor amplitudes dominate the electronic transition probability. The width in their line shape then arises from a combination of a vibronic progression (Franck-Condon factor) between the ground (polaron) and excited (band) anion states and electronic broadening due to the dependence of the dipole matrix element on the energy of the

excited continuum state. However, their model, which still neglects coupling of the electronic states of the neighboring sites, is unable to account for proper skewedness of the absorption band.

In developing a more unified and potentially powerful model for solvated electron spectra the approach we follow involves writing the absorption band shape function $I(\omega)$ as the Fourier transform of the time-correlation function¹⁹ of the electronic dipole moment operator $\langle F(t)F(0) \rangle$,

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle F(t)F(0) \rangle. \quad (2)$$

The time dependence appearing in the dipole correlation function is described in terms of both (excess) electronic motion and solvent molecule motion. In this way we simultaneously treat the electronic aspect of the problem (to which all earlier cavity models are directed) as well as the vibrational contribution to $I(\omega)$.

The advantages of this approach are clear. The resulting formulas for $I(\omega)$ are quite general in the sense that they minimize the dependence of calculated results upon the details of any particular model or characteristics of the solvent medium. Even though it is rather difficult to calculate the correlation function exactly, we at least have general expressions which can serve as a convenient and rigorous starting point for the introduction of specific models for the excess electrons' energy levels and the solvent molecules' properties. To make progress toward developing such a systematic framework for approximating $I(\omega)$ let us first turn to a discussion of the Hamiltonian which is to be employed in describing the time dependence appearing in $\langle F(t)F(0) \rangle$.

II. THE HAMILTONIAN AND THE CANONICAL TRANSFORMATION

We are interested in describing the spectroscopy of a solvated excess electron which is already in equilibrium with the solvent. The processes of thermalization and trapping of a nascent free electron are not within the scope of the present work. In this work we consider dilute solutions of excess electrons for which the (excess) electron-electron interactions can be ignored. Because the details of the construction of a proper Hamiltonian and the canonical transformation of this Hamiltonian are given in I, we shall merely quote the final formulas here. The total Hamiltonian $H = H_N + H_e$ consists of a part H_N describing the motion of solvent molecules

$$H_N = \sum_{i=1}^N \left[\frac{P_i^2}{2M_i} + U(Q_i) + \frac{1}{2} \sum_{j \neq i}^N V(\mathbf{X}_i, \mathbf{X}_j) \right], \quad (3)$$

where \mathbf{X}_i represents collectively the center of mass positions of the i th molecule \mathbf{R}_i and the corresponding internal orientations Ω_i and vibrational displacements \mathbf{Q}_i . \mathbf{P}_i is the total (translational, rotation, vibrational) momentum of the i th molecule, $U(Q_i)$ is the internal vibrational potential energy function, and $V(\mathbf{X}_i, \mathbf{X}_j)$ is the intermolecular potential energy. The electronic Hamiltonian H_e describes the motion of a single excess electron in the presence of N solvent molecules, and is written in second quantized notation²⁰ as

$$H_e = \int \psi^*(\mathbf{r}) \left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + \sum_{i=1}^N u(\mathbf{r}, \mathbf{X}_i) \right] \psi(\mathbf{r}) d\mathbf{r}, \quad (4)$$

where \mathbf{r} represents the position of the electron and $u(\mathbf{r}, \mathbf{X}_i)$ is the interaction potential between the electron and the i th solvent molecule.²¹ The field creation operator $\psi^*(\mathbf{r})$ is expressed in terms of the molecular orbitals of the j th solvent molecule (or cavity) $\phi_{\alpha}(\mathbf{r}, \mathbf{X}_j)$ and a set of continuum orbitals²² $\phi_{\mathbf{K}}(\mathbf{r})$:

$$\psi^*(\mathbf{r}) = \sum_{j,\alpha} \phi_{\alpha}^*(\mathbf{r}, \mathbf{X}_j) a_{j\alpha}^{\dagger} + \int d\mathbf{K} \phi_{\mathbf{K}}^*(\mathbf{r}) a_{\mathbf{K}}^{\dagger}. \quad (5)$$

For instance, cavity orbitals would be more appropriate for studying e_{aq}^- or e_{am}^- , whereas molecular orbitals would apply better to studies of anthracene solutions of excess electrons.^{23,31}

The cavity or molecule orbitals ϕ_{α} may include both bound and localized resonance-state orbitals such as Tsubomura and Sunakawa tested. The $a_{j\alpha}^{\dagger}$ and $a_{\mathbf{K}}^{\dagger}$ are fermion creation operators which create an excess electron in the orbitals $\phi_{\alpha}(\mathbf{r}, \mathbf{X}_j)$ and $\phi_{\mathbf{K}}(\mathbf{r})$, respectively. For notational convenience the sets $\{a_{j\alpha}^{\dagger}, a_{\mathbf{K}}^{\dagger}\}$ and $\{\phi_{\alpha}(\mathbf{r}, \mathbf{X}_j), \phi_{\mathbf{K}}(\mathbf{r})\}$ will be denoted by $\{a_{j\alpha}^{\dagger}\}$ and $\{\phi_{\alpha}(\mathbf{r}, \mathbf{X}_j) \equiv \phi_{j\alpha}\}$, respectively. All of the resulting formulas must then be interpreted by remembering that both localized and delocalized continuum orbitals are included. It should also be noted that in writing Eq. (5) we have assumed that $\{\phi_{\alpha}(\mathbf{r}, \mathbf{X}_j)\}$ is an orthonormal complete set.

The electronic Hamiltonian H_e given in Eq. (4) describes an electron in the presence of N solvent molecules. Because the electron-solvent interaction is a strong effect, it is convenient and physically important to treat the major portion of this interaction in an exact manner, then treating the remainder as a perturbation. Toward this end we introduced in I a canonical transformation of the Hamiltonian

$$\tilde{H} = \exp(S) H \exp(-S), \quad (6)$$

where

$$S = \sum_{m\alpha} a_{m\alpha}^{\dagger} a_{m\alpha} \sum_{i=1}^N [\mathbf{X}_i(m\alpha) - \mathbf{X}_i^0] \cdot \nabla_{\mathbf{X}_i}, \quad (7)$$

which has the effect of modifying the center-of-mass coordinates and internal geometries of all solvent molecules to their new "dressed" values $\mathbf{X}'(m\alpha)$:

$$\mathbf{X}'_j(m\alpha) \equiv \mathbf{X}_j + \mathbf{X}_j(m\alpha) - \mathbf{X}_j^0. \quad (8)$$

Here $\mathbf{X}_j(m\alpha)$ designates the coordinates of molecule j which yield minimum potential energy ($U + V + u$) for the solvent in the presence of a single excess electron in $\phi_{m\alpha}$, and \mathbf{X}_j^0 is the value of the coordinates of minimum potential energy in the absence of the excess electron. \mathbf{X}_j is the instantaneous value of the coordinates of the j th molecule which is eventually involved in the equilibrium average appearing in the dipole correlation function.

As shown in detail in I the transformed Hamiltonian \tilde{H} has the form

$$\tilde{H} = \sum_{m\alpha} (A_{m\alpha}^{\dagger} A_{m\alpha} + 1 - n_e)$$

$$\times \sum_{i=1}^N \left\{ \frac{P_i^2}{2M_i} + U[\mathbf{Q}'_i(m\alpha)] + \frac{1}{2} \sum_{j \neq i}^N V[\mathbf{X}'_i(m\alpha), \mathbf{X}'_j(m\alpha)] \right\} \\ + \sum_{m\alpha, n\beta} \langle \phi_{m\alpha} | h_e[\mathbf{X}'_i(m\alpha)] | \phi_{n\beta} \rangle_{\mathbf{X}'(m\alpha)} A_{m\alpha}^{\dagger} A_{n\beta} \equiv \tilde{H}_N + \tilde{H}_e \quad (9)$$

where the dressed electron's Hamiltonian is

$$h_e[\mathbf{X}'_i(m\alpha)] = -\frac{1}{2} \nabla_{\mathbf{r}}^2 + \sum_{i=1}^N u[\mathbf{r}, \mathbf{X}'_i(m\alpha)] \quad (10)$$

and the number-of-excess-electrons operator is

$$n_e = \sum_{p\gamma} A_{p\gamma}^{\dagger} A_{p\gamma}. \quad (11)$$

The operator which creates a dressed electron in $\phi_{m\alpha}$ is

$$A_{m\alpha}^{\dagger} = a_{m\alpha}^{\dagger} \exp \left\{ \sum_{i=1}^N [\mathbf{X}_i(m\alpha) - \mathbf{X}_i^0] \cdot \nabla_{\mathbf{X}_i} \right\}. \quad (12)$$

The results of carrying out the above canonical transformation are clear. The transformed coordinates $\mathbf{X}'_i(m\alpha)$ introduce into \tilde{H}_N characteristics appropriate to a solvent anion, e.g., the m th molecule (or cavity) possesses anion geometries and vibrational frequencies. Also, in $V[\mathbf{X}'_i(m\alpha), \mathbf{X}'_m(m\alpha)]$ one has anion-solvent interactions whereas $V[\mathbf{X}'_i(m\alpha), \mathbf{X}'_j(m\alpha)]$ describes molecule-molecule interactions. Thus, the total Hamiltonian has been expressed in terms of the modified molecular coordinates $\mathbf{X}'(m\alpha)$ thereby allowing it to simulate the ground state anion in equilibrium in solution. As time evolves and the solvated electron (perhaps) migrates, via the off-diagonal electronic matrix elements (resonance integrals) $\langle \phi_{m\alpha} | h_e | \phi_{n\beta} \rangle A_{m\alpha}^{\dagger} A_{n\beta}$, from one site to another the solvent molecules' Hamiltonian adjusts (through the $A_{m\alpha}^{\dagger} A_{m\alpha} + 1 - n_e$) to follow the moving electron, thereby causing the geometrical characteristics of one solvent molecule (or cavity) to change from those of an anion to those of a neutral or *vice versa*. Thus, the concept of a dressed electron, in which the solvent follows the migrating electron, is a useful device in the present work.

Now that the total solvent-plus-electron Hamiltonian has been expressed in a convenient form let us now move on toward developing a physically clear and rigorous treatment of the dipole correlation function of Eq. (2).

III. ELECTRONIC SPECTRAL BAND SHAPE

In this section we derive a general expression for the band shape via a calculation of the electronic dipole correlation function. Our aim is to express the correlation function (or band shape) in terms of the properties of an isolated solvent anion, the anion-solvent interactions, solvent structure information, and electron-solvent interaction data.

A. Calculation of the correlation function

It has been shown, for example by Gordon,¹⁹ that the absorption line shape can be expressed as the Fourier transform of the time correlation function of the transition dipole operator of the system. In the present case this operator is for a single excess electron initially

localized in the 0th orbital of the 0th solvent molecule (or cavity) which defines the laboratory coordinate origin. The electric dipole transition operator, in the Heisenberg representation,²⁰ is

$$F(t) = \exp(iHt) \int \psi^*(\mathbf{r}) \boldsymbol{\epsilon} \cdot \mathbf{r} \psi(\mathbf{r}) d\mathbf{r} \exp(-iHt) \\ = \exp(iHt) \sum_{k\mu, l\nu} \langle \phi_{k\mu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} \rangle a_{k\mu}^* a_{l\nu} \exp(-iHt), \quad (13)$$

where $\boldsymbol{\epsilon}$ is the electric vector of the incident photon. Letting $\langle \rangle_N$ designate the equilibrium average over the initial coordinates \mathbf{X}_i and momenta \mathbf{P}_i of the N solvent molecules according to the equilibrium distribution function $Z^{-1} \exp[-\beta H(\mathbf{X}, \mathbf{P})]$ the desired correlation function is

$$\langle F(t)F(0) \rangle_N = Z^{-1} \int d\mathbf{X} d\mathbf{P} \langle g | \exp[-\beta H(\mathbf{X}, \mathbf{P})] F(t)F(0) | g \rangle, \quad (14)$$

with

$$Z = \int d\mathbf{X} d\mathbf{P} \exp[-\beta H(\mathbf{X}, \mathbf{P})]. \quad (15)$$

As in I, $|g\rangle$ is equal to a product of the ground electronic state of the N solvent molecules represented by $|0(\mathbf{X})\rangle$ and that electronic state which has the excess electron at the origin in the lowest empty orbital $a_{oo}^* |vac\rangle$:

$$|g\rangle = a_{oo}^* |0\rangle = a_{oo}^* |0(\mathbf{X})\rangle |vac\rangle. \quad (16)$$

In writing Eq. (16) we assume that excited electronic states of the solvent are not populated at the temperatures of interest. Using Eq. (13) the correlation function can be written more explicitly as follows:

$$\langle F(t)F(0) \rangle = Z^{-1} \int d\mathbf{X} d\mathbf{P} \langle 0 | a_{oo} \exp[-\beta H(\mathbf{X}, \mathbf{P})] \\ \times \exp(iHt) \sum_{k\mu, l\nu} \langle \phi_{k\mu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} \rangle a_{k\mu}^* a_{l\nu} \exp(-iHt) \\ \times \sum_{p\gamma, q\delta} \langle \phi_{p\gamma} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{q\delta} \rangle a_{p\gamma}^* a_{q\delta} a_{oo}^* | 0 \rangle. \quad (17)$$

To re-express this correlation function in terms of the dressed electron operators we first insert to the left of the a_{oo} in Eq. (17) the identity $\exp(-S) \exp(S)$ with S given in Eq. (6). Then, using the cyclic invariance of the trace, and noting the fact that $|0\rangle$ is a zero-excess-electron state for which $S|0\rangle = 0$:

$$\langle F(t)F(0) \rangle_N = Z^{-1} \sum_{\bar{\gamma}} \int d\mathbf{R} d\mathbf{P} d\mathbf{L} d\mathbf{\Omega} \sum_{k\mu, l\nu} \sum_{p\gamma, q\delta} \langle 0 | V_{oo} | \exp[-\beta(\tilde{H}_{rt} + \tilde{H}_e + \epsilon_{\bar{\gamma}}^{\circ\circ})] \\ \times \langle \phi_{k\mu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} \rangle_t \langle \phi_{p\gamma} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{q\delta} \rangle A_{oo} \exp(i\tilde{H}t) A_{k\mu}^* A_{l\nu} \exp(-i\tilde{H}t) | \bar{V}_{p\gamma} \rangle \langle \bar{V}_{p\gamma} | A_{p\gamma}^* A_{q\delta} A_{oo}^* | V_{oo} \rangle | 0 \rangle, \quad (22)$$

where the subscripts on the vibrational states $|V_{oo}\rangle$ and $|\bar{V}_{p\gamma}\rangle$ refer to the molecule (or cavity) and the orbital which is assumed to contain the electron for that specific vibrational state. The function $|\bar{V}_{p\gamma}\rangle$ satisfies

$$\sum_i \left\{ \frac{P_{vi}^2}{2M_i} + U[\mathbf{Q}_i(p\gamma)] \right\} | \bar{V}_{p\gamma} \rangle = \epsilon_{\bar{\gamma}}^{p\gamma} | \bar{V}_{p\gamma} \rangle \quad (23)$$

$$\langle 0 | \exp(S) = \langle 0 |, \quad (18)$$

Eq. (17) becomes

$$\langle F(t)F(0) \rangle = Z^{-1} \int d\mathbf{X} d\mathbf{P} \sum_{k\mu, l\nu} \sum_{p\gamma, q\delta} \langle 0 | A_{oo} \\ \times \exp[-\beta \tilde{H}(\mathbf{X})] \langle \phi_{k\mu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} \rangle_t \langle \phi_{p\gamma} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{q\delta} \rangle \\ \times \exp(i\tilde{H}t) A_{k\mu}^* A_{l\nu} \exp(-i\tilde{H}t) A_{p\gamma}^* A_{q\delta} A_{oo} | 0 \rangle, \quad (19)$$

where as in I

$$\langle \phi_{k\mu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} \rangle_t \equiv \langle \phi_{k\mu} | [\mathbf{r}, \mathbf{X}'_k(k\mu, t)] | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} | [\mathbf{r}, \mathbf{X}'_l(l\nu, t)] \rangle. \quad (20)$$

In anticipation of the fact that the electronic transition is a temporally localized phenomenon perhaps accompanied by some vibrational excitation the (excess) electronic and vibrational coordinates will be distinguished as "high frequency" (see, for example, Ref. 24) coordinates and the rotational and translational motions of the solvent species, which are essentially free motions within the time scale of the electronic transition, will be distinguished as "low frequency" coordinates. Assuming that only a small coupling exists between the high- and the low-frequency coordinates the equilibrium averaging involving these coordinates, which occurs in Eq. (19), will be performed, respectively, quantum mechanically and classically. To facilitate this separation we recognize the decomposition of H_N as

$$H_N = H_v + H_{rt}, \quad (21a)$$

with

$$H_v = \sum_i \left[\frac{P_{vi}^2}{2M_i} + U(\mathbf{Q}_i) \right], \quad H_{rt} = \sum_i \left[\frac{P_{rti}^2}{2M_i} + \frac{1}{2} \sum_{j \neq i}^N V(\mathbf{X}_i, \mathbf{X}_j) \right], \quad (21b)$$

which implies corresponding expressions for $\tilde{H}_N = \tilde{H}_v + \tilde{H}_{rt}$.

To introduce explicitly the dependence on vibrational function overlap (Franck-Condon factors) we insert a complete set of vibrational states of the solvent for the situation in which the excess electron is on the γ th orbital of the p th molecule $\sum_{\bar{\gamma}} | \bar{V}_{p\gamma} \rangle \langle \bar{V}_{p\gamma} |$ to the left of $A_{p\gamma}^*$ in Eq. (19). This leads, after introducing explicitly the initial vibrational $|V_{oo}\rangle$ states and translation-rotation coordinates and momenta \mathbf{R} , $\mathbf{\Omega}$, \mathbf{P} , and \mathbf{L} as was discussed in the preceding paragraph, to

and is thus a composite vibrational state for the entire N solvent molecule system.

Now we have constructed an expression for the correlation function which incorporates all relevant physical aspects of the problem. The rest of this section will be devoted to simplifying this expression toward the stated objective of expressing it in terms of various interac-

tions of the constituents of the system. To facilitate this we first decompose the Hamiltonian into a zeroth order part \tilde{H}^0 and a perturbation \tilde{V} :

$$\tilde{H} = \tilde{H}^0 + \tilde{V}, \quad (24)$$

where \tilde{H}^0 contains \tilde{H}_N plus the equilibrium average of the diagonal part of \tilde{H}_e :

$$\begin{aligned} \tilde{H}^0 &\equiv \tilde{H}_N + \tilde{H}_e^0 \\ &= \tilde{H}_N + \left\langle \sum_{m\alpha} \langle \phi_{m\alpha} | h_e[\mathbf{X}'_i(m\alpha)] | \phi_{m\alpha} \rangle_{\mathbf{X}'(m\alpha)} A_{m\alpha}^* A_{m\alpha} \right\rangle_N \\ &\equiv \tilde{H}_N + \sum_{m\alpha} E_{m\alpha}^0 A_{m\alpha}^* A_{m\alpha}, \end{aligned} \quad (25)$$

with

$$E_{m\alpha}^0 = \langle \langle \phi_{m\alpha} | h_e[\mathbf{X}'_i(m\alpha)] | \phi_{m\alpha} \rangle_{\mathbf{X}'(m\alpha)} \rangle_N, \quad (26)$$

which represents the average energy of an excess electron residing in orbital $\phi_{m\alpha}$. Clearly, $E_{m\alpha}^0$ has a temperature dependence because of the temperature dependence of $\exp(-\beta\tilde{H})$. This temperature dependence is largely responsible for the red shift in the absorption maximum with increasing temperature. It should be kept in mind that $E_{m\alpha}^0$ can correspond to a bound ($E_{m\alpha}^0 < 0$) or an unbound orbital ($E_{m\alpha}^0 > 0$) and that for the unbound case $E_{m\alpha}^0$ can be complex with the imaginary part corresponding to the width of this resonance state. Because h_e contains the interaction of the excess electron with all N of the solvent molecules, $E_{m\alpha}^0$ consists of the average energy of an electron in the isolated molecule

(or cavity) orbital $\phi_{m\alpha}$ plus the solvation energy of the electron-molecule (or electron-cavity species). The perturbation \tilde{V} consists of the off-diagonal component of \tilde{H}_e plus the deviation of the diagonal component away from its equilibrium average

$$\begin{aligned} \tilde{V} &= \sum_{m\alpha \neq n\beta} \langle \phi_{m\alpha} | h_e[\mathbf{X}'_i(m\alpha)] | \phi_{n\beta} \rangle_{\mathbf{X}'(m\alpha)} A_{m\alpha}^* A_{n\beta} \\ &\quad + \sum_{m\alpha} \{ \langle \phi_{m\alpha} | h_e[\mathbf{X}'_i(m\alpha)] | \phi_{m\alpha} \rangle - E_{m\alpha}^0 \} A_{m\alpha}^* A_{m\alpha}. \end{aligned} \quad (27)$$

The off-diagonal terms occurring in \tilde{V} will be referred to as "hopping" integrals and operators ($A_{m\alpha}^* A_{n\beta}$) because they involve transfer of the dressed (excess) electron from orbital $\phi_{n\beta}$ to orbital $\phi_{m\alpha}$, which, if $m \neq n$, gives rise to a transfer of the excess electron from one molecule to another.

With the decomposition of Hamiltonian given in Eqs. (24)–(27) the $\exp(i\tilde{H}t)$ appearing in Eq. (22) can be written as

$$\exp(i\tilde{H}t) = \exp(i\tilde{H}^0 t) \exp \left[i \int_0^t V(\tau) d\tau \right], \quad (28a)$$

where

$$V(\tau) \equiv \exp(-i\tilde{H}^0 \tau) \tilde{V} \exp(i\tilde{H}^0 \tau). \quad (28b)$$

To consider the effects of these operators let us first rewrite the correlation function of Eq. (22) using Eqs. (24)–(28) as

$$\begin{aligned} \langle F(t)F(0) \rangle_N &= Z^{-1} \sum_{\mathbf{V}} \int d\mathbf{R} d\mathbf{P} d\mathbf{L} d\mathbf{Q} \sum_{k\mu, l\nu} \sum_{p\gamma, q\delta} \langle 0 | \langle V_{oo} | \exp[-\beta(\tilde{H}_{rt} + \epsilon_V^{oo} + \tilde{H}_e)] \\ &\quad \times \langle \phi_{k\mu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} \rangle_t \langle \phi_{p\gamma} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{q\delta} \rangle A_{oo} \exp(i\tilde{H}^0 t) \exp \left[i \int_0^t V(\tau) d\tau \right] A_{k\mu}^* A_{l\nu} \\ &\quad \times \exp \left[-i \int_0^t V(\tau) d\tau \right] \exp(-i\tilde{H}^0 t) | \bar{V}_{p\gamma} \rangle \langle \bar{V}_{p\gamma} | A_{p\gamma}^* A_{q\delta} A_{oo}^* | V_{oo} \rangle | 0 \rangle. \end{aligned} \quad (29)$$

Then it is relatively straightforward to show that

$$\exp(-i\tilde{H}^0 t) | \bar{V}_{p\gamma} \rangle \langle \bar{V}_{p\gamma} | A_{p\gamma}^* A_{q\delta} A_{oo}^* | V_{oo} \rangle | 0 \rangle = \exp[-i(E_{p\gamma}^0 + \epsilon_V^{p\gamma})t] \exp(-i\tilde{H}_{rt} t) | \bar{V}_{p\gamma} \rangle \langle \bar{V}_{p\gamma} | A_{p\gamma}^* | V_{oo} \rangle | 0 \rangle \delta_{q\delta, oo} \quad (30)$$

and

$$\begin{aligned} \langle 0 | \langle V_{oo} | \exp[-\beta(\tilde{H}_{rt} + \epsilon_V^{oo} + \tilde{H}_e)] \langle \phi_{k\mu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} \rangle_t \langle \phi_{p\gamma} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{q\delta} \rangle A_{oo} \exp(i\tilde{H}^0 t) \\ = \langle 0 | \langle V_{oo} | \exp[-\beta(\tilde{H}_{rt} + \epsilon_V^{oo} + E_{oo}^0)] \langle \phi_{k\mu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} \rangle_t \langle \phi_{p\gamma} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{q\delta} \rangle A_{oo} \exp(i\tilde{H}_{rt} t) \exp[i(E_{oo}^0 + \epsilon_V^{oo})t]. \end{aligned} \quad (31)$$

To further simplify the expression in Eq. (22) the first serious (but well-established) physical approximation is introduced. It is assumed that the time variation of the solvent vibrational coordinates \mathbf{Q}'_i compared to the electronic coordinate \mathbf{r} is slow. Thus, electronic processes may be assumed to take place at some average (fixed) vibrational coordinate. This, of course, is nothing but the well-known Franck-Condon (FC) approximation.²⁵ Using this approximation along with Eqs. (30) and (31), Eq. (29) becomes

$$\begin{aligned} \langle F(t)F(0) \rangle_N &= Z^{-1} \int d\mathbf{R} d\mathbf{P} \sum_{\mathbf{V}} \sum_{k\mu, l\nu, p\gamma} \langle \phi_{k\mu} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{l\nu} \rangle_t \langle \phi_{p\gamma} | \boldsymbol{\epsilon} \cdot \mathbf{r} | \phi_{oo} \rangle \langle V_{oo} | \bar{V}_{p\gamma} \rangle^2 \\ &\quad \times \langle 0 | \exp[-\beta(\tilde{H}_{rt} + \epsilon_V^{oo}) A_{oo} \exp(i\tilde{H}_{rt} t) \exp \left[i \int_0^t V(\tau) d\tau \right] A_{k\mu}^* A_{l\nu} \exp \left[-i \int_0^t V(\tau) d\tau \right] \\ &\quad \times \exp(-i\tilde{H}_{rt} t) A_{p\gamma}^* | 0 \rangle \exp[i(E_{oo}^0 + \epsilon_V^{oo} - E_{p\gamma}^0 - \epsilon_V^{p\gamma})t]. \end{aligned} \quad (32)$$

In writing Eq. (32) we have used a shorthand notation in which $d\mathbf{R}d\mathbf{P}d\mathbf{\Omega}d\mathbf{L}$ is written as $d\mathbf{R}d\mathbf{P}$, and the fact that $\bar{H}_{r,t}$ and $\bar{V}(\tau)$ depend on these translational and rotational coordinates \mathbf{R} and $\mathbf{\Omega}$ has been suppressed for convenience. Moreover, $\exp(-\beta E_{oo})$ has been set equal to unity by choosing E_{oo} as our reference point of electronic energy (i. e., $E_{oo} = 0$).

Now we can express the overlaps of the vibrational functions of the solvent-plus-electron system in terms of individual molecular (or cavity) and anion (or cavity anion) vibrational function overlaps. We approximate $|V_{oo}\rangle$ and $|\bar{V}_{pr}\rangle$ as products of individual molecular functions for each vibrational mode as follows:

$$|V_{oo}\rangle = \prod_{\lambda_0 \dots \lambda_N} |v_1^{oo, \lambda_0}\rangle^A |v_2^{oo, \lambda_1}\rangle^M \dots |v_2^{oo, \lambda_p}\rangle^M \dots |v_2^{oo, \lambda_N}\rangle^M \quad (33a)$$

and

$$|\bar{V}_{pr}\rangle = \prod_{\lambda_0 \dots \lambda_N} |\bar{v}_1^{pr, \lambda_0}\rangle^M |\bar{v}_2^{pr, \lambda_1}\rangle^M \dots |\bar{v}_2^{pr, \lambda_p}\rangle^A \dots |\bar{v}_2^{pr, \lambda_N}\rangle^M. \quad (33b)$$

Here, $|\bar{v}_j^{pr, \lambda_j}\rangle^M$ designates the vibrational state corresponding to the λ_j th mode of the molecule on the j th site with excess electron on orbital ϕ_{pr} . In writing Eq. (33) we have assumed that during the electronic transition $\phi_{oo} \rightarrow \phi_{pr}$ the vibrational states of the molecule at the origin (where the electron is initially) and the anion on site p (where the electron exists after the photon absorption) undergo a change, while the rest of the solvent molecules (or cavities) undergo no appreciable change. Using the orthonormality of the vibrational functions of different normal modes, and

$${}^M \langle v^{oo, \lambda_j} | \bar{v}^{pr, \lambda_j} \rangle^M \cong 1$$

for $j \neq 0$ or p , we have

$$\begin{aligned} \langle V_{oo} | V_{pr} \rangle &= \prod_{\lambda_0, \lambda_p}^A \langle v_1^{oo, \lambda_0} | \bar{v}_1^{pr, \lambda_0} \rangle^M \langle v_2^{oo, \lambda_p} | \bar{v}_2^{pr, \lambda_p} \rangle^A \\ &\equiv \prod_{\lambda_0, \lambda_p} F_{\lambda_0}^{A \sim M}(v_1, \bar{v}_1) F_{\lambda_p}^{M \sim A^*}(v_2, \bar{v}_2). \end{aligned} \quad (34)$$

Note that for the special case of the totally localized transitions $\phi_{oo} \rightarrow \phi_{or}$ one has

$$\langle V_{oo} | \bar{V}_{pr} \rangle = \prod_{\lambda_0}^A \langle v_1^{oo, \lambda_0} | \bar{v}_1^{pr, \lambda_0} \rangle^A \equiv \prod_{\lambda_0} F_{\lambda_0}^{A \sim A^*}(v_1, \bar{v}_1). \quad (35)$$

Within the approximation of Eq. (33) for the molecular vibrational functions the corresponding energies will be sums of individual molecular energies. Thus, the difference which occurs in Eq. (32) can be reduced to

$$\epsilon_{\bar{V}}^{pr} - \epsilon_V^{oo} = \sum_{\lambda_0, \lambda_p} (\epsilon_{v_2, \lambda_p}^{pr, A} - \epsilon_{v_2, \lambda_p}^{oo, M} + \epsilon_{\bar{v}_1, \lambda_0}^{pr, M} - \epsilon_{v_1, \lambda_0}^{oo, A}) \equiv \Delta E_v. \quad (36)$$

Again for the totally localized transition $\phi_{oo} \rightarrow \phi_{or}$

$$\epsilon_{\bar{V}}^{or} - \epsilon_V^{oo} = \sum_{\lambda_0} \epsilon_{v_2, \lambda_p}^{or, A} - \epsilon_{v_1, \lambda_0}^{oo, A} \equiv \Delta E_v^0. \quad (37)$$

Having made progress in reducing the FC factors and vibrational energy differences the next step is to perform the equilibrium averaging over the initial (rotational and translational) coordinates appearing in Eq. (32) for the correlation function. One immediately notes some difficulties. For example, one needs to know explicitly the form for the integral $\langle \phi_{k\mu} | \mathbf{e} \cdot \mathbf{r} | \phi_{l\nu} \rangle t$ in terms of initial coordinates $\mathbf{R}'_k, \mathbf{R}'_l$ as well as its time dependence. Similar problems arise for other terms in Eq. (32) involving initial coordinates. Furthermore, for any nontrivial forms for the dependence of such integrals upon initial coordinates (which will inevitably be the case for a theory which realistically mimics the intricacies of the interactions in liquids) it may be prohibitively difficult to perform this equilibrium averaging. However, because the time scale for the electronic transition is very short ($\leq 10^{-14}$ sec) compared to the time scale on which the molecular coordinates $\mathbf{R}'_j, \mathbf{\Omega}'_j$ change, we can simply ignore the time dependence of all terms which arise from time variation of the center-of-mass and orientational coordinates. To proceed toward a more useful final result we follow the ideal developed in I in which we replace the instantaneous "pointwise" liquid structure information by average liquid structure data. In particular, the following types of replacements are made:

$$\begin{aligned} \sum_{k, \mu, pr} \int d\mathbf{R}d\mathbf{P} \phi_{\mu}(\mathbf{r}, \mathbf{R}'_k) \phi_{\gamma}(\mathbf{r}, \mathbf{R}'_p) f[A_{k\mu} A_{pr} \bar{H}(\mathbf{R}', \dots), \dots] \\ \cong \int d\tilde{\mathbf{R}} d\tilde{\mathbf{S}} \rho(\tilde{\mathbf{R}}, 0) \rho(\tilde{\mathbf{S}}, 0) \sum_{\mu\gamma} \phi_{\mu}(\mathbf{r}, \tilde{\mathbf{R}}) \phi_{\gamma}(\mathbf{r}, \tilde{\mathbf{S}}) \int d\mathbf{R}d\mathbf{P} f[A_{\tilde{\mathbf{R}}\mu}, A_{\tilde{\mathbf{S}}\gamma}, \bar{H}(\mathbf{R}', \dots), \dots], \end{aligned} \quad (38)$$

where f represents the remaining terms in Eq. (32) which depend upon the molecular coordinates $\mathbf{R}'_k, \mathbf{R}'_p$. Here $\rho(\tilde{\mathbf{R}}, 0)$ gives the number of solvent molecule (cavity) centers (i. e., \mathbf{R}'_k 's) per unit volume at point $\tilde{\mathbf{R}}$, given that there is a molecule (or cavity) at the origin (where the excess electron was initiated). The purpose of carrying out the above replacement is to render all of the terms in Eq. (32) except $V(\tau)$ independent of the actual initial values of the molecules (or cavity coordinates \mathbf{R}'_k , thereby permitting the equilibrium average over these coordinates to be performed on the $V(\tau)$ -containing terms. A more complete appreciation for the motivations behind this step should develop shortly.

Let us rewrite the expression (32) for the correlation function using Eqs. (34), (36), and (38):

$$\begin{aligned} \langle F(t)F(0) \rangle_N &= Z_v^{-1} \int d\tilde{\mathbf{R}} d\tilde{\mathbf{R}}' d\tilde{\mathbf{S}} \rho(\tilde{\mathbf{R}}, 0) \rho(\tilde{\mathbf{R}}', 0) \rho(\tilde{\mathbf{S}}, 0) \sum_{\mu\gamma} \sum_{v_1, v_2, \bar{v}_1, \bar{v}_2} \prod_{\lambda_0 \lambda_p} \exp \left[-\beta \sum_{\lambda_0 \lambda_p} (\epsilon_{v_1, \lambda_0}^{oo, A} + \epsilon_{v_2, \lambda_p}^{oo, M}) \right] \\ &\times [F_{\lambda_0}^{A \sim M}(v_1, \bar{v}_1) F_{\lambda_p}^{M \sim A^*}(v_2, \bar{v}_2)]^2 \langle \phi_{\tilde{\mathbf{R}}\mu} | \mathbf{e} \cdot \mathbf{r} | \phi_{\tilde{\mathbf{R}}'\nu} \rangle \langle \phi_{\tilde{\mathbf{S}}\gamma} | \mathbf{e} \cdot \mathbf{r} | \phi_{oo} \rangle = Z_v^{-1} \langle 0 | A_{oo} \int d\mathbf{R}d\mathbf{P} \exp(-\beta \bar{H}_{r,t}) \exp(i \bar{H}_{r,t} t) \\ &\times \exp \left[i \int_0^t V(\tau) d\tau \right] A_{\tilde{\mathbf{R}}\mu}^* A_{\tilde{\mathbf{R}}'\nu} \exp \left[-i \int_0^t V(\tau) d\tau \right] \exp(-i \bar{H}_{r,t} t) A_{\tilde{\mathbf{S}}\gamma}^* | 0 \rangle \exp[-i(\Delta E_e + \Delta E_v)t], \end{aligned} \quad (39)$$

where

$$\Delta E_e = E_{sy}^0 - E_{oo}^0, \quad (40a)$$

and for the totally localized transition

$$\Delta E_e^0 = E_{0y}^0 - E_{oo}^0. \quad (40b)$$

In Eq. (39) Z_v and Z_{rt} are the vibrational and rotational-translational partition functions of the solvent, respectively. As pointed out in Eqs. (35) and (37) there are slightly different expressions for the special case of a totally localized transition.

To actually carry out the desired equilibrium average we now use Kubo's cumulant expansion technique,²⁶ which allows us to express the equilibrium average of

an exponential function (or operator) in terms of the exponential of the equilibrium average of the function, plus its fluctuation away from the average, plus higher order fluctuations. Symbolically,

$$\begin{aligned} \langle \exp(f) \rangle_N &= \exp[\langle f \rangle_N + \frac{1}{2} \langle (f - \langle f \rangle_N)^2 \rangle_N + \dots] \\ &\equiv \exp\left(\sum_{l=1}^{\infty} K_l\right). \end{aligned} \quad (41)$$

In implementing this cumulant approximation that part of the expression in Eq. (39) which depends upon initial coordinates and time is extracted from Eq. (39) after which the time invariance of the equilibrium average and the commutation relations $[\tilde{H}_v, \tilde{H}_e^0] = 0$, $[\tilde{H}_{rt}, \tilde{H}_e^0] = 0$, and $[\tilde{H}_v, \tilde{V}] = 0$ are used together with Eq. (40) to write

$$\begin{aligned} &\int Z_{rt}^{-1} \langle 0 | A_{oo} d\mathbf{R} d\mathbf{P} \exp(-\beta \tilde{H}_{rt}) \exp(i \tilde{H}_{rt} t) \exp\left[i \int_0^t V(\tau) d\tau\right] A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} \exp\left[-i \int_0^t V(\tau) d\tau\right] \exp(-i \tilde{H}_{rt} t) A_{sy}^* | 0 \rangle \\ &= \int Z_{rt}^{-1} \langle 0 | A_{oo} d\mathbf{R} d\mathbf{P} \exp(-\beta \tilde{H}_{rt}) \left\{ \exp\left[i \int_0^t \tilde{V}^x(\tau) d\tau\right] A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} \right\} A_{sy}^* | 0 \rangle = \langle \text{vac} | A_{oo} \left\{ \exp\left[\sum_{l=1}^{\infty} K_l(t)\right] A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} \right\} A_{sy}^* | \text{vac} \rangle \\ &\cong \langle \text{vac} | A_{oo} \left\{ \exp[(K_1(t) + K_2(t))] A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} \right\} A_{sy}^* | \text{vac} \rangle, \end{aligned} \quad (42)$$

where the cumulant expansion has been approximated by its first two terms. Here

$$\tilde{V}^x(\tau) \equiv [\exp(-i \tilde{H}_{rt} \tau) \exp(-\tilde{H}_e^0 \tau) \tilde{V}(\mathbf{R}_t') \exp(i \tilde{H}_e^0 \tau) \exp(i \tilde{H}_{rt} \tau)], \quad (43)$$

and the cumulant operators are

$$K_1(t) = i \int_0^t d\tau \langle \tilde{V}^x(\tau) \rangle, \quad (44)$$

$$K_2(t) = - \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \delta \tilde{V}^x(\tau_1) \delta \tilde{V}^x(\tau_2) \rangle, \quad (45)$$

where

$$\delta \tilde{V}^x(\tau) \equiv \tilde{V}^x(\tau) - \langle \tilde{V}^x(\tau) \rangle. \quad (46)$$

Note that $\langle \rangle$ here represents the equilibrium average over rotational and translational coordinates of the solvent molecules. The justification for terminating the cumulant expansion at K_2 is based on the assumption that the equilibrium average dynamics is the dominant contributor to $\langle F(t)F(0) \rangle_N$, and that fluctuations away from the average die away quickly with the order of the fluctuation.²⁷ Following I these expressions for $K_1(t)$ and $K_2(t)$ can be recast in terms of various solvent interactions as

$$K_1(t) = \sum_{m\alpha \neq n\beta} \langle \hat{h}_{m\alpha, n\beta} \rangle \Delta_{m\alpha, n\beta}(t) [A_{m\alpha}^* A_{n\beta}], \quad (47a)$$

where

$$\Delta_{m\alpha, n\beta} = \lim_{\delta \rightarrow 0^+} \{ \exp[i(E_{n\beta}^0 - E_{m\alpha}^0 + \delta)t - 1] / (E_{m\alpha}^0 - E_{n\beta}^0 + \delta) \}. \quad (47b)$$

The (rotational and translational) equilibrium average of the hopping integral is represented by

$$\hat{h}_{m\alpha, n\beta} = \langle \langle \phi_{m\alpha} | \hat{h}_e | \phi_{n\beta} \rangle \rangle \quad (48)$$

and

$$\begin{aligned} K_2(t) &= - \sum_{\substack{m\alpha, n\beta \\ r\lambda, s\sigma}} \int_0^t d\tau_1 \exp[i(E_{n\beta}^0 - E_{m\alpha}^0 + E_{s\sigma}^0 - E_{r\lambda}^0)\tau_1] \\ &\quad \int_0^{\tau_1} d\tau \exp[-i(E_{s\sigma}^0 - E_{r\lambda}^0)\tau] \langle \delta h_{m\alpha, n\beta}(\tau) \\ &\quad \delta h_{r\lambda, s\sigma}(0) \rangle [A_{m\alpha}^* A_{n\beta}, [A_{r\lambda}^* A_{s\sigma}]]. \end{aligned} \quad (49)$$

Further simplifications of $K_1(t)$ and $K_2(t)$ can be accomplished once a specific model has been found for the various equilibrium averaged terms [appearing in Eqs. (47)–(49)] which depend upon properties of solvent molecules or ions, their interactions, and the time evolution of these properties.

As a next step the expression

$$\exp[K_1(t) + K_2(t)] A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} \equiv g(\tilde{R}\mu, \tilde{R}'\nu, t) \quad (50)$$

needs to be cast in a more computationally tractable form. One approach, that is presently under study in this laboratory in connection with the problem of the mobility of the electron in liquids (Ref. 1), is to construct an equation that $g(\tilde{R}\mu, \tilde{R}'\nu, t)$ obeys and to solve this equation as exactly as possible. Such an approach seems to be necessary for the mobility problem since it is a "long-time" phenomenon in which the electron migrates over many molecular distances, which clearly can not be described in terms of low powers of K_1 and K_2 . In our particular case one can get around this problem by invoking the temporally localized nature of the electronic transition. This allows a short-time expansion of $g(\tilde{R}\mu, \tilde{R}'\nu, t)$ to be employed. As we shall see momentarily this approach allows us to further simplify the expression for $I(\omega)$ without having to yet settle for any specific model for the hopping and "fluctuation" integrals and their time variations.

After performing a Taylor's expansion of $K_1(t)$ and

$K_2(t)$ in Eqs. (47) and (49), respectively, around $t=0$ and keeping the first nonzero term in each case one obtains

$$K_1(t) \cong it \sum_{m\alpha \neq n\beta} \hat{h}_{m\alpha, n\beta} [A_{m\alpha}^* A_{n\beta},] \equiv \bar{K}_1 t \quad (51)$$

and

$$K_2(t) \cong -t^2 \sum_{\substack{m\alpha, n\beta \\ r\lambda, s\sigma}} \langle \delta h_{m\alpha, n\beta}(0) \delta h_{r\lambda, s\sigma}(0) \rangle [A_{m\alpha}^* A_{n\beta}, [A_{r\lambda}^* A_{s\sigma},]] \equiv \bar{K}_2 t^2. \quad (52)$$

Note that \bar{K}_1 and \bar{K}_2 are still operators. In \bar{K}_2 there are the off-diagonal terms ($m\alpha \neq n\beta, r\lambda \neq s\sigma$) which correlate the fluctuations of the electron transfer integral terms, as well as the diagonal terms which correlate the fluctuations of the energy of an excess electron $\langle \phi_{m\alpha} | h_e | \phi_{m\alpha} \rangle$. To clearly distinguish these separate phenomena we shall separate these terms

$$\bar{K}_2 = \bar{K}_2^{0d} + \bar{K}_2^d. \quad (53)$$

To understand the meaning of the diagonal term \bar{K}_2^d we look at its effect on the operator $A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu}$ [which is one of the terms in $g(\tilde{R}\mu, \tilde{R}'\nu, t)$]. Making use of the commutation relations for the excess-electron operators $A_{m\alpha}$ we obtain

$$\bar{K}_2^d A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} = -(\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu}^2 \rangle + \langle \delta h_{\tilde{R}'\nu, \tilde{R}'\nu}^2 \rangle - 2\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu} \delta h_{\tilde{R}'\nu, \tilde{R}'\nu} \rangle) A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu}. \quad (54)$$

The first two terms of the type $\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu}^2 \rangle$ represent the average over rotational and translational coordinates of

the instantaneous fluctuation of the (electronic) energy of an excess electron in orbital $\phi_{\tilde{R}\mu}$ (or $\phi_{\tilde{R}'\nu}$), whereas the third term correlates the instantaneous fluctuations in energy of the two electronic energies corresponding to $\phi_{\tilde{R}\mu}$ and $\phi_{\tilde{R}'\nu}$, which is probably smaller than the direct correlation, except for the case of $\tilde{R}\mu = \tilde{R}'\nu$, for which

$$\bar{K}_2^d A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} = 0. \quad (55)$$

For a molecule (or cavity) at \tilde{R} the terms given in Eq. (54) give rise to broadening of each electronic level μ due to fluctuations in the instantaneous center-of-mass positions and orientations of the solvent species. This broadening is usually referred to as inhomogeneous broadening. Clearly, these effects depend upon the magnitude of the fluctuation $\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu}^2 \rangle$ which in turn depends strongly on temperature. As will be seen shortly this broadening has the effect of providing a "width" to each line in a series of vibrational absorption lines. This broadening has the effect of smearing out the vibrational structure as has been universally observed in the experimental spectra²⁸ of solvated electrons in liquids. We note here how the well-known smearing effect arises naturally in the course of the present development of the theory.

Keeping in mind the above interpretation, and anticipating the fact that we will ultimately perform a Fourier transformation of the correlation function to obtain the line shape, we shall treat the two terms $\exp(\bar{K}_1^d t^2)$ and $\exp(\bar{K}_1 t + \bar{K}_2^{0d} t^2)$ in a slightly inequivalent fashion. Using again the characteristics of the time-localized electronic transitions the second term becomes, in the short-time approximation,

$$\exp(\bar{K}_1 t + \bar{K}_2^{0d} t^2) A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} \cong (1 + \bar{K}_1 t + \bar{K}_2^{0d} t^2) A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} = A_{\tilde{R}\mu}^* A_{\tilde{R}'\nu} + it \sum_{m\alpha} (\hat{h}_{m\alpha, \tilde{R}\mu} A_{m\alpha}^* A_{\tilde{R}'\nu} - \hat{h}_{\tilde{R}'\nu, m\alpha} A_{\tilde{R}\mu}^* A_{m\alpha}) - t^2 \sum_{m\alpha, n\beta} (\langle \delta h_{n\beta, m\alpha} \delta h_{m\alpha, \tilde{R}\mu} \rangle A_{n\beta}^* A_{\tilde{R}'\nu} + \langle \delta h_{m\alpha, n\beta} \delta h_{\tilde{R}'\nu, m\alpha} \rangle A_{\tilde{R}\mu}^* A_{n\beta} - \langle \delta h_{\tilde{R}'\nu, n\beta} \delta h_{m\alpha, \tilde{R}\mu} \rangle A_{m\alpha}^* A_{n\beta} - \langle \delta h_{n\beta, \tilde{R}\mu} \delta h_{\tilde{R}'\nu, m\alpha} \rangle A_{n\beta}^* A_{m\alpha}). \quad (56)$$

Then using Eqs. (53), (55), (56), and (50) the final terms in Eq. (42) become

$$\langle \text{vac} | A_{00} g(\tilde{R}\mu, \tilde{R}'\nu, t) A_{\tilde{R}\mu}^* | \text{vac} \rangle = \left\{ \delta_{\tilde{R}\mu, 00} \delta_{\tilde{R}'\nu, \tilde{R}'\nu} + it (\hat{h}_{00, \tilde{R}\mu} \delta_{\tilde{R}'\nu, \tilde{R}'\nu} - \hat{h}_{\tilde{R}'\nu, 00} \delta_{\tilde{R}\mu, \tilde{R}\mu}) - t^2 \left[\sum_{m\alpha} (\langle \delta h_{00, m\alpha} \delta h_{m\alpha, \tilde{R}\mu} \rangle \delta_{\tilde{R}'\nu, \tilde{R}'\nu} + \langle \delta h_{m\alpha, \tilde{R}\mu} \delta h_{\tilde{R}'\nu, m\alpha} \rangle \delta_{00, \tilde{R}\mu}) - 2\langle \delta h_{00, \tilde{R}\mu} \delta h_{\tilde{R}'\nu, \tilde{R}'\nu} \rangle \right] \right\} \exp[-t^2 (\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu}^2 \rangle + \langle \delta h_{\tilde{R}'\nu, \tilde{R}'\nu}^2 \rangle - 2\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu} \delta h_{\tilde{R}'\nu, \tilde{R}'\nu} \rangle)] \equiv g(\tilde{R}\mu, \tilde{R}'\nu, \tilde{\gamma}, t) \exp[-t^2 (\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu}^2 \rangle + \langle \delta h_{\tilde{R}'\nu, \tilde{R}'\nu}^2 \rangle - 2\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu} \delta h_{\tilde{R}'\nu, \tilde{R}'\nu} \rangle)]. \quad (57)$$

Using Eqs. (42) and (57) the expression for the correlation function in Eq. (40) can be written as

$$\langle F(t)F(0) \rangle_N = Z_v^{-1} \int d\tilde{R} d\tilde{R}' d\tilde{\gamma} \rho(\tilde{R}, 0) \rho(\tilde{R}', 0) \rho(\tilde{\gamma}, 0) \sum_{\mu\nu\gamma} \sum_{v_1 v_2 v_1 v_2} \prod_{\lambda_0 \lambda_{\tilde{\gamma}}} \exp[-\beta \epsilon_{\lambda_0, \lambda_{\tilde{\gamma}}}^{00}(v_1, v_2)] \times [F_{\lambda_0}^{A \rightarrow M}(\bar{v}_1, \bar{v}_1) F_{\lambda_{\tilde{\gamma}}}^{M \rightarrow A^*}(v_2, \bar{v}_2)]^2 \langle \phi_{\tilde{\gamma}} | \epsilon \cdot \mathbf{r} | \phi_{00} \rangle \langle \phi_{\tilde{R}'\nu} | \epsilon \cdot \mathbf{r} | \phi_{\tilde{R}\mu} \rangle g(\tilde{R}\mu, \tilde{R}'\nu, \tilde{\gamma}, t) \exp[-i(\Delta E_e + \Delta E_v)t - \frac{1}{2}\sigma^2 t^2], \quad (58)$$

where

$$\sigma^2 = 2(\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu}^2 \rangle + \langle \delta h_{\tilde{R}'\nu, \tilde{R}'\nu}^2 \rangle - 2\langle \delta h_{\tilde{R}\mu, \tilde{R}\mu} \delta h_{\tilde{R}'\nu, \tilde{R}'\nu} \rangle), \quad (59)$$

$$\epsilon_{\lambda_0, \lambda_{\tilde{\gamma}}}^{00}(v_1, v_2) = \sum_{\lambda_0, \lambda_{\tilde{\gamma}}} (\epsilon_{v_1, \lambda_0}^{00, A} + \epsilon_{v_2, \lambda_{\tilde{\gamma}}}^{00, M}), \quad (60a)$$

and for totally localized transitions

$$\epsilon_{\lambda_0}^{00}(v_1) = \sum_{\lambda_0} \epsilon_{v_1, \lambda_0}^{00, A}. \quad (60b)$$

Substituting terms for $g(\tilde{R}\mu, \tilde{R}'\nu, \tilde{\gamma}, t)$ from Eq. (57) into (58), simplifying further by removing the δ functions, and collecting terms with common powers of t [which arise from the zeroth order approximation and the $K_1(t)$ and $K_2(t)$ terms, respectively] we get

$$\langle F(t)F(0) \rangle_N = \langle F(t)F(0) \rangle_N^{(0)} + \langle F(t)F(0) \rangle_N^{(1)} + \langle F(t)F(0) \rangle_N^{(2)}, \quad (61a)$$

where

$$\langle F(t)F(0) \rangle_N^{(0)} = Z_v^{-1} \int d\tilde{s} \rho(\tilde{s}, 0) \sum_{\gamma} \sum_{v_1 v_2 \tilde{v}_1 \tilde{v}_2} \prod_{\lambda_0, \lambda_s} \exp[-\beta \epsilon_{\lambda_0, \lambda_s}^{oo} (v_1, v_2)] [F_{\lambda_0}^{A-M}(v_1, \tilde{v}_1) F_{\lambda_s}^{M-A^*}(v_2, \tilde{v}_2)]^2 r_{oo, \tilde{s}\gamma}^2 \exp\left[-i(\Delta E_e + \Delta E_v)t - \frac{\sigma^2}{2} t^2\right], \quad (61b)$$

$$\begin{aligned} \langle F(t)F(0) \rangle_N^{(1)} = Z_v^{-1} \int d\tilde{R} d\tilde{s} \rho(\tilde{R}, 0) \rho(\tilde{s}, 0) \sum_{\mu\gamma} \sum_{v_1 v_2 \tilde{v}_1 \tilde{v}_2} \prod_{\lambda_0, \lambda_s} \exp[-\beta \epsilon_{\lambda_0, \lambda_s}^{oo} (v_1, v_2)] \\ \times [F_{\lambda_0}^{A-M}(v_1, \tilde{v}_1) F_{\lambda_s}^{M-A^*}(v_2, \tilde{v}_2)]^2 r_{oo, \tilde{s}\gamma} (r_{\tilde{R}\mu, \tilde{s}\gamma} \hat{h}_{oo, \tilde{R}\mu} - r_{oo, \tilde{R}\mu} \hat{h}_{\tilde{R}\mu, \tilde{s}\gamma}) i t \exp\left[-i(\Delta E_e + \Delta E_v)t - \frac{\sigma^2}{2} t^2\right], \end{aligned} \quad (61c)$$

and

$$\begin{aligned} \langle F(t)F(0) \rangle_N^{(2)} = Z_v^{-1} \int d\tilde{R} d\tilde{R}' d\tilde{s} \rho(\tilde{R}, 0) \rho(\tilde{R}', 0) \rho(\tilde{s}, 0) \sum_{\mu\gamma} \sum_{v_1 v_2 \tilde{v}_1 \tilde{v}_2} \prod_{\lambda_0, \lambda_s} \exp[-\beta \epsilon_{\lambda_0, \lambda_s}^{oo} (v_1, v_2)] [F_{\lambda_0}^{A-M}(v_1, \tilde{v}_1) F_{\lambda_s}^{M-A^*}(v_2, \tilde{v}_2)]^2 \\ \times r_{oo, \tilde{s}\gamma} (r_{\tilde{R}\mu, \tilde{s}\gamma} \langle \delta h_{oo, \tilde{R}'\nu} \delta h_{\tilde{R}'\nu, \tilde{R}\mu} \rangle + r_{oo, \tilde{R}\mu} \langle \delta h_{\tilde{R}\mu, \tilde{R}'\nu} \delta h_{\tilde{R}'\nu, \tilde{s}\gamma} \rangle - 2 r_{\tilde{R}\mu, \tilde{R}'\nu} \langle \delta h_{oo, \tilde{R}\mu} \delta h_{\tilde{R}'\nu, \tilde{s}\gamma} \rangle) (-1) t^2 \exp\left[-i(\Delta E_e + \Delta E_v)t - \frac{\sigma^2}{2} t^2\right], \end{aligned} \quad (61d)$$

where

$$r_{\tilde{R}\mu, \tilde{R}'\nu} = \langle \phi_{\tilde{R}\mu} | \mathbf{e} \cdot \mathbf{r} | \phi_{\tilde{R}'\nu} \rangle. \quad (62)$$

Equation (61) is the final form for the desired correlation function. The equilibrium averaging over initial vibrational states can be performed given a specific functional dependence of FC factors and the vibrational energies (in ΔE_v) of these initial vibrational states. Because this step introduces a specific model (for example, a harmonic oscillator model) within the general theoretical framework, discussion of these topics along with possible models for the hopping and fluctuation integrals is deferred to Sec. IV where implementation of the theory is undertaken.

Following the operational development of the correlation function $\langle F(t)F(0) \rangle_N$ up to Eq. (61) one notices that the dipole transition term $r_{oo, \tilde{s}\gamma}$ arises from the electric dipole operator $F(0)$ corresponding to $t=0$. The other terms, inside the parentheses in Eqs. (61c) and (61d) arise from the perturbation expansion around $t=0$. Thus, various terms in Eqs. (61b)–(61d) can be symbolically thought of as resulting from an expansion of the form $\langle F(0)[F^{(0)}(t) + F^{(1)}(t) + F^{(2)}(t)] \rangle_N$. The first product gives the term $r_{oo, \tilde{s}\gamma}^2$ in Eq. (61b) and the other two products give the terms appearing in Eqs. (61c) and (61d) involving rotation–translation averages of various hopping and fluctuations of the excess electron to neighboring molecules (or cavities) followed by an electric dipole transition. Except for charge-transfer spectra it is true that among the transition moment integrals $r_{oo, \tilde{s}\gamma}$ arising from $F(0)$, the “localized” transition $r_{oo, \sigma}$ is probably more important than the “delocalized” transition integral for which $\tilde{s} \neq 0$. Obviously, for charge-transfer transitions²⁹ exactly the opposite is the case. For now we will restrict our attention to optical absorption for which the $\phi_{oo} - \phi_{o\gamma}$ “transition” is the dominant component; the charge-transfer case will be treated in a future publication devoted entirely to this important topic. With this emphasis on localized transitions having been introduced we shall in the next subsection decompose each term arising from the dipole-hopping and dipole-fluctuation pathways into the two cases $\tilde{s}=0$ and $\tilde{s} \neq 0$, respectively. We shall see that such a separation greatly enhances the physical interpretation of our equation as well as facilitating compari-

sons with other theories in the literature. We now turn our attention to a treatment of the spectral band shape.

B. Calculation of band shape

Here we proceed to perform the Fourier transformation, according to Eq. (2), of the correlation function given in Eqs. (61). The time dependences occurring in Eqs. (61) have the form

$$f^{(n)}(t) = (it)^n \exp[-i(\Delta E_e + \Delta E_v)t - \frac{1}{2}\sigma^2 t^2], \quad n=0, 1, 2. \quad (63)$$

Thus, the Fourier transform required by Eq. (2) can be written in terms of the transforms of the terms shown in Eq. (63) which are

$$\begin{aligned} f^{(n)}(\omega) &= \frac{1}{2\pi} \frac{d^n}{d\omega^n} \int_{-\infty}^{\infty} dt \exp\{-[\frac{1}{2}\sigma^2 t^2 + (\Delta E_e + \Delta E_v - \omega)it]\} \\ &\equiv \frac{d^n}{d\omega^n} G[\omega, (\Delta E_e + \Delta E_v), \sigma], \end{aligned} \quad (64)$$

where $G[\omega, \omega', \sigma]$ is a normalized Gaussian³⁰ centered at ω' and of width σ :

$$G[\omega, \omega', \sigma] = \frac{1}{\sigma\sqrt{2\pi}} e^{-(\omega - \omega')^2/2\sigma^2}. \quad (65)$$

Carrying out the differentiations in Eq. (64) one obtains for each of the three terms in Eq. (61) (having different t dependence)

$$f^{(0)}(\omega) = G[\omega, (\Delta E_e + \Delta E_v), \sigma], \quad (66a)$$

$$f^{(1)}(\omega) = \frac{-1}{\sigma^2} [\omega - (\Delta E_e + \Delta E_v)] G[\omega, (\Delta E_e + \Delta E_v), \sigma], \quad (66b)$$

and

$$f^{(2)}(\omega) = \left\{ \frac{1}{\sigma^4} [\omega - (\Delta E_e + \Delta E_v)]^2 - \frac{1}{\sigma^2} \right\} G[\omega, (\Delta E_e + \Delta E_v), \sigma]. \quad (66c)$$

If Eqs. (66) are combined with a separation of each term in the correlation function of Eq. (61) into the special cases $s=0$ and $s \neq 0$ [which correspond to the direct and indirect terms of $F(0)$ and localized and delocalized terms of $F(t)$, respectively], the band shape function of Eq. (2) can be written as

$$I(\omega) = I^{(0)}(\omega) + I^{(1)}(\omega) + I^{(2)}(\omega), \quad (67a)$$

where

$$I^{(0)}(\omega) = Z_v^{-1} \sum_{\gamma} \sum_{v_1, \bar{v}_1} \prod_{\lambda_0} \exp[-\beta \epsilon_{\lambda_0}^{oo}(v_1)] [F_{\lambda_0}^{A-A*}(v_1, \bar{v}_1)]^2 r_{oo, \sigma\gamma}^2 G[\omega, (\Delta E_e^0 + \Delta E_v^0), \sigma] \\ + Z_v^{-1} \int ds \rho(s, 0) \sum_{\gamma} \sum_{v_1, \bar{v}_1} \prod_{\lambda_0, \lambda_s} \exp[-\beta \epsilon_{\lambda_0, \lambda_s}^{oo}(v_1, v_2)] (F_{\lambda_0}^{A-M} F_{\lambda_s}^{M-A*})^2 r_{oo, s\gamma}^2 G[\omega, (\Delta E_e + \Delta E_v), \sigma], \quad (67b)$$

$$I^{(1)}(\omega) = Z_v^{-1} \int dR \rho(R, 0) \sum_{\mu, \gamma} \sum_{v_1, \bar{v}_1} \prod_{\lambda_0} \exp[-\beta \epsilon_{\lambda_0}^{oo}(v_1)] (F_{\lambda_0}^{A-A*})^2 r_{oo, o\gamma} \langle r_{R\mu, o\gamma} \hat{h}_{oo, R\mu} - r_{oo, R\mu} \hat{h}_{R\mu, o\gamma} \rangle \\ \times \frac{(-1)}{\sigma^2} [\omega - (\Delta E_e^0 + \Delta E_v^0)] G[\omega, (\Delta E_e^0 + \Delta E_v^0), \sigma] + Z_v^{-1} \int dR dS \rho(R, 0) \rho(S, 0) \sum_{\mu, \gamma} \sum_{v_1, \bar{v}_1} \prod_{\lambda_0, \lambda_s} \\ \times \exp[-\beta \epsilon_{\lambda_0, \lambda_s}^{oo}(v_1, v_2)] (F_{\lambda_0}^{A-M} F_{\lambda_s}^{M-A*})^2 r_{oo, s\gamma} \langle r_{R\mu, s\gamma} \hat{h}_{oo, R\mu} - r_{oo, R\mu} \hat{h}_{R\mu, s\gamma} \rangle \frac{(-1)}{\sigma^2} [\omega - (\Delta E_e + \Delta E_v)] G[\omega, (\Delta E_e + \Delta E_v), \sigma], \quad (67c)$$

and

$$I^{(2)}(\omega) = Z_v^{-1} \int dR dR' \rho(R, 0) \rho(R', 0) \sum_{\mu, \gamma} \sum_{v_1, \bar{v}_1} \prod_{\lambda_0} \exp[-\beta \epsilon_{\lambda_0}^{oo}(v_1)] (F_{\lambda_0}^{A-A*})^2 r_{oo, o\gamma} \langle \delta h_{oo, R'} \delta h_{R', \nu, R\mu} \rangle \\ + r_{oo, R\mu} \langle \delta h_{R', \nu, o\gamma} \delta h_{R\mu, R' \nu} \rangle - 2r_{R\mu, R' \nu} \langle \delta h_{oo, R\mu} \delta h_{R' \nu, o\gamma} \rangle \left\{ \frac{1}{\sigma^4} [\omega - (\Delta E_e^0 + \Delta E_v^0)]^2 - \frac{1}{\sigma^2} \right\} G[\omega, (\Delta E_e^0 + \Delta E_v^0), \sigma] \\ + Z_v^{-1} \int dR dR' ds \rho(R, 0) \rho(R', 0) \rho(S, 0) \sum_{\mu, \gamma} \sum_{v_1, \bar{v}_1} \prod_{\lambda_0, \lambda_s} \exp[-\beta \epsilon_{\lambda_0, \lambda_s}^{oo}(v_1, v_2)] (F_{\lambda_0}^{A-M} F_{\lambda_s}^{M-A*})^2 r_{oo, s\gamma} \langle r_{R\mu, s\gamma} \delta h_{oo, R'} \delta h_{R' \nu, R\mu} \rangle \\ + r_{oo, R\mu} \langle \delta h_{R', \nu, s\gamma} \delta h_{R\mu, R' \nu} \rangle - 2r_{R\mu, R' \nu} \langle \delta h_{oo, R\mu} \delta h_{R' \nu, s\gamma} \rangle \left\{ \frac{1}{\sigma^4} [\omega - (\Delta E_e + \Delta E_v)]^2 - \frac{1}{\sigma^2} \right\} G[\omega, (\Delta E_e + \Delta E_v), \sigma]. \quad (67d)$$

Note that in writing the localized terms for each order of $I(\omega)$ we have used the appropriate expressions for the FC factors, the energies ΔE_e^0 and ΔE_v^0 , and the equilibrium distribution function exponent $\epsilon_{\lambda_0}^{oo}(v_1)$ from Eqs. (35), (37), (40b), and (60b), respectively. As a further aid toward distinguishing these terms the localized part of Eq. (67b) for $I^{(0)}(\omega)$ where the transition is solely localized on the 0th site will be referred to as a "totally localized" transition. Of course, this term is probably the most important term in determining the line shape; as discussed in Sec. I it has been extensively used in the literature, with small variations (such as, for example, including the effect of the solvent as a polarizable dielectric continuum or treating the case of a continuum orbital γ , etc.) to calculate line shapes. After analyzing the full content our Eqs. (67) one immediately begins to notice sources of potentially serious discrepancies in theories which only treat such totally localized transitions. For example, the delocalized transition term involving $r_{oo, s\gamma}$ for $s \neq 0$, whose amplitude depends on the ratio

$$\chi_2 \equiv r_{oo, s\gamma} / r_{oo, o\gamma}, \quad 0 < \chi_2 < 1,$$

may become relatively important for systems whose excited states extend significantly over neighboring molecules. Clearly, the ratio χ_2 depends upon the nature of the anion-molecule interactions involving sites o and s , the relative position of these sites, the nature of their electronic states ϕ_{oo} , $\phi_{o\gamma}$, $\phi_{s\gamma}$, and the depths of the wells at sites o and s .

Furthermore, since the nonlocalized excitation energy $(\Delta E_e + \Delta E_v)$ is greater than the localized energy $(\Delta E_e^0 + \Delta E_v^0)$ approximately by an amount $\epsilon_{v_1, \lambda_0}^{s\gamma, M} - \epsilon_{v_2, \lambda_s}^{oo, A} \geq 0$ [according to Eqs. (36) and (37)], the nonlocalized terms give contributions to $I(\omega)$ which contribute to relatively

higher ω values than the totally localized terms. Such delocalization components are therefore potential sources of high- ω skewedness of the absorption spectrum.

A clarifying remark is appropriate at this stage of the development. In following our derivation of the first general result for $I(\omega)$ given in Eq. (67) one might wonder whether the treatment and all resulting equations might not be equally applicable to the optical spectroscopy of neutral molecules in solution. The answer is yes. Of course, the electronic energy levels $\{E_{m\alpha}^0\}$ and orbitals $\{\phi_{m\alpha}\}$ of a neutral molecule are qualitatively different from those of a solvated anion molecule (or cavity). These differences are reflected in the experimentally observed facts that molecular ionization potentials are usually larger than negative-ion binding energies and that charge densities of anions are more diffuse than those of neutral molecules. It is our feeling that, because the excess electrons are held less tightly to their binding sites than are the electrons of a neutral molecule, the treatment of intermolecular electronic coupling (through $h_{m\alpha, n\beta} r_{oo, s\gamma}$, and $\langle \delta h_{m\alpha, n\beta} \delta h_{\mu, q\delta} \rangle$) is quite essential in developing a quantitative model for the optical spectra of excess electrons in solution.

Before delving further into the remaining terms of Eq. (67) we shall introduce a simple diagrammatic aid to the interpretation of these terms. In each of the diagrams displayed in Fig. 1 we represent the hopping, the fluctuation, and the electric dipole transition integrals by the following symbols:

- (a) $\hat{h}_{R\mu, s\gamma} \equiv \overline{\overline{R\mu}} \cdots \overline{s\gamma}$;
- (b) $\delta h_{R\mu, s\gamma} \equiv \overline{\overline{R\mu}} \cdots \overline{s\gamma}$;
- (c) $r_{R\mu, s\gamma} \equiv \overline{\overline{R\mu}} \cdots \overline{s\gamma}$;

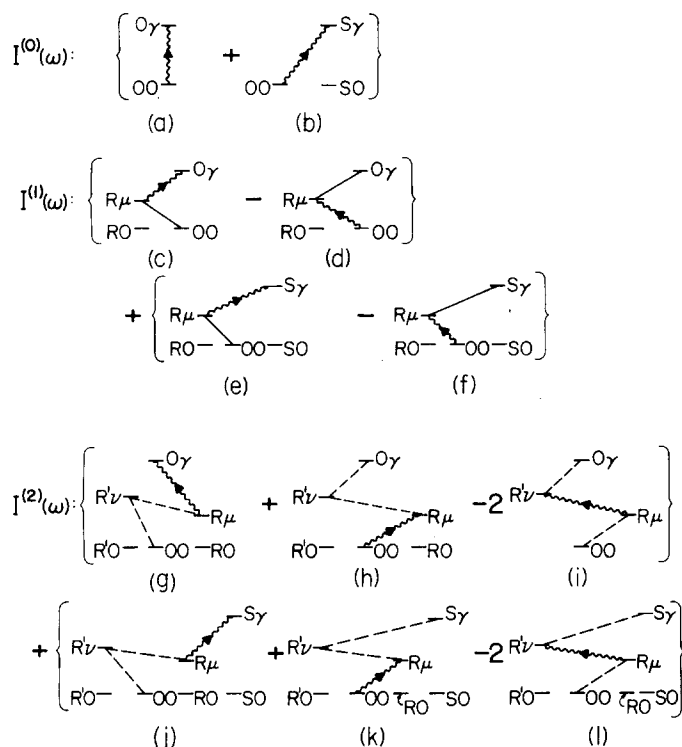


FIG. 1. Diagrammatic representation of the terms for the intensity $I(\omega)$ in Eqs. (67).

(d) for each occurrence of $\sum_{\mu} \int dR \rho(R, 0)$ we assign a vertex $R\mu$, where the line represents one of the three elements given in (a), (b), or (c).

For a given term in Eqs. (67) the associations of proper FC factors and the line shape Gaussian function are made according to the following rules:

(e) For a given diagram of order n ($n = 0, 1, 2$):

(i) for a localized diagram associate

$$Z_v^{-1} \sum_{v_1 \bar{v}_1} \prod_{\lambda_0} \exp[-\beta \epsilon_{\lambda_0}^{oo}(v_1)] [F_{\lambda_0}^{A-A*}(v_1, \bar{v}_1)]^2 \frac{d^n}{d\omega^n} \times G[\omega, (\Delta E_e^0 + \Delta E_v^0), \sigma];$$

(ii) for a nonlocalized diagram associate

$$Z_v^{-1} \sum_{v_1 v_2 \bar{v}_1 \bar{v}_2} \prod_{\lambda_0, \lambda_s} \exp[-\beta \epsilon_{\lambda_0, \lambda_s}^{oo}(v_1, v_2)] \times [F_{\lambda_0}^{A-M}(v_1, \bar{v}_1) F_{\lambda_s}^{M-A*}(v_2, \bar{v}_2)]^2 \frac{d^n}{d\omega^n} G[\omega, (\Delta E_e + \Delta E_v), \sigma],$$

where

$$\frac{d}{d\omega} G(\omega, \omega', \sigma) = -\frac{1}{\sigma^2} (\omega - \omega') G(\omega, \omega', \sigma)$$

and

$$\frac{d^2}{d\omega^2} G(\omega, \omega', \sigma) = \left[\frac{1}{\sigma^4} (\omega - \omega')^2 - \frac{1}{\sigma^2} \right] G(\omega, \omega', \sigma);$$

(f) Attach a multiplicative factor of $r_{oo, o\gamma}$ or $r_{oo, s\gamma}$ for localized and nonlocalized transitions, respectively.

Figure 1 shows all of the diagrams corresponding to Eqs. (67). Each of these diagrams shows a possible

arrangement of the energy levels μ and ν relative to the initial and final levels o and γ , and also a possible arrangement of the sites O , R , R' , and S . Discussions regarding the physical importance of various arrangements of energy levels and sites shall be dealt with shortly. To give an example of how to construct the analytical expression corresponding to a specific diagram we consider the diagram shown in Fig. 1(d). We see it is a first order localized diagram, leading to the localized FC factors and line shape Gaussian function from (i) of rule (e). Then using rules (a)–(d) and (f) one has

$$Z_v^{-1} \int dR \rho(R, 0) \sum_{\mu\gamma} \sum_{v_1 \bar{v}_1} \prod_{\lambda_0} \exp[-\beta \epsilon_{\lambda_0}^{oo}(v_1)] \times [F_{\lambda_0, o}^{A-A*}(v_1, \bar{v}_1)]^2 r_{oo, o\gamma} \hat{h}_{oo, R\mu} r_{R\mu, o\gamma} \frac{(-1)}{\sigma^2} \times [\omega - (\Delta E_e^0 + \Delta E_v^0)] G[\omega, (\Delta E_e^0 + \Delta E_v^0), \sigma].$$

The diagrams of Fig. 1 [or the corresponding terms of Eqs. (67)] represent possible “configurations” of the solvent-plus-electron system which is able to absorb (via dipole transitions) photons of particular frequencies. By configuration we mean the instantaneous vibrational–electronic state of the system which has been fluctuating in character because of the couplings among the $\phi_{m\alpha}$ caused by the resonance or hopping integrals as well as fluctuations in the $E_{m\alpha}^0$ and in the coupling interaction caused by fluctuations in the solvent molecules’ orientations and positions, before the photon hits the system. Of course, these diagrams only represent our description of the “reality” of the electronic transition process in terms of a set of zeroth order states $\phi_{m\alpha}$ and various couplings (\hat{h} and $\langle \delta h \delta h \rangle$) among these functions. It is our belief that the choice of zeroth order states made here is particularly appropriate. It seems natural to attempt to describe the spectral properties of molecular anions in solution in terms of the energy levels and orbitals $\{\phi_{m\alpha}\}$ of the gas-phase anions which can, for example, be probed via electron transmission and photodetachment spectroscopies. The coupling factors $h_{n\beta, m\alpha} A_{n\beta}^{\dagger} A_{m\alpha}$ are then to be viewed as those terms which map the zeroth order states into the proper eigenstates of the solution-phase problem.

Armed with the compact representation of the individual terms of Eq. (67) provided by the diagrams introduced above let us now examine the physical significance of each term in Eq. (67). It should be kept in mind in viewing these terms that the time scale for the electronic transition is so short that no motion of the solvent molecules’ nuclei takes place. The transition which is caused by the incident photon occurs between vibrational–electronic states of the system whose energy (as determined by $E_{m\alpha}^0$, the resonance integrals \hat{h} , and the fluctuations $\langle \delta h \delta h \rangle$) happen to be resonant with the photon. This is the essential content of the Eqs. (67). With this in mind let us consider the localized terms first. For given values of the final electronic level γ the vibrational levels v_1 and \bar{v}_1 of the ground and γ th electronic levels, and the vibrational mode λ_0 , the localized term of $I^{(0)}(\omega)$ gives rise to an absorption line a frequency $\omega_1 \equiv \Delta E_e^0 + \Delta E_v^0$ with a Gaussian line shape of

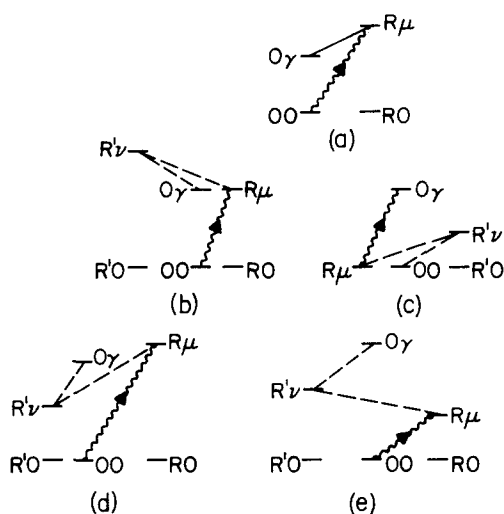


FIG. 2. Special cases of some localized diagrams corresponding to absorption frequencies at and on either side of $\omega_1 = (\Delta E_e^0 + \Delta E_v^0)$.

width σ . The intensity of absorption for such a transition $\phi_{oo} \rightarrow \phi_{or}$ is then the product of the corresponding dipole transition moments and the FC factors $r_{oor}^2 [F_{\lambda_0}^{A-A*} \times (\nu_1, \bar{\nu}_1)]^2$. The localized term in $I^{(1)}(\omega)$, on the other hand, involves one hopping integral. Accordingly, the intensity is modified by a corresponding hopping amplitude. For energy values of the electronic state μ and γ such that $E_{R\mu}^0 > E_{or}^0$ one has a diagram of Fig. 2 leading to an absorption at a frequency $\omega > \omega_1$. Similarly, the situation shown in diagram (d) of Fig. 1 leads to an absorption frequency $\omega < \omega_1$. There is no contribution of $I^{(1)}(\omega)$ to the absorption at the frequency ω_1 . This latter fact is described in the formalism of Eq. (67c) by the fact that the localized first order line shape component $-(\omega - \omega_1)G(\omega, \omega_1, \sigma)$ has a node at $\omega = \omega_1$ and a maximum and a minimum at $\omega = \omega_1 - \sigma$ and $\omega = \omega_1 + \sigma$, respectively. The negative value of the line shape component at $\omega = \omega_1 + \sigma$ corresponds to the situation above in which $E_{R\mu}^0 > E_{or}^0$.

Turning now to the localized term of $I^{(2)}(\omega)$ involving the fluctuation integrals one sees that there now exists the possibility of an absorption contribution at ω_1 . This corresponds to the situations depicted by diagrams (b) and (c) of Fig. 2. On the other hand, the situations shown in diagrams (d) and (e) of Fig. 2 correspond, respectively, to absorptions at $\omega > \omega_1$ and $\omega < \omega_1$. In the formalism of Eq. (67d) the three situations discussed above are described in the line shape component $[(1/\sigma^4)(\omega - \omega_1)^2 - (1/\sigma^2)]G(\omega, \omega_1, \sigma)$ which has extremum values at $\omega = \omega_1$ and $\omega_1 \pm \sqrt{2}\sigma$.

Having covered the localized components of $I(\omega)$ we now deal with the nonlocalized terms of Eq. (67). Interpretations similar to those given for the corresponding localized terms can easily be extended to these cases. The only points of difference to be noticed are (i) that the FC factors now correspond to a product of vibrational overlaps of the initial and final vibrational states (of the corresponding electronic states) of the molecule (or cavity) at site 0 (where the excess elec-

tron was initiated) as well as at site S, where it is located after the absorption, and (ii) that the characteristic frequencies $\omega_{n1} = \Delta E_e + \Delta E_v$ are blue shifted relative to the ω_i 's approximately by an amount $\epsilon_{v_1, \lambda_0}^{P, M} - \epsilon_{v_2, \lambda_s}^{O, A}$ and, as indicated earlier, these nonlocalized terms contribute therefore at relatively higher ω values leading to a high- ω skewedness of the absorption spectrum. Except for these two modifications the interpretations of the nonlocalized components of Eq. (67) can be made in direct analogy to those given above in the localized case.

With the above introduction to the significance of the terms of Eqs. (67) accomplished we shall, in the following section, try to demonstrate how this theory can be implemented for specific cases. For example, it will be noted that for systems in which bound-to-bound transitions are dominant the band shape is determined both by the FC factors (via a vibrational progression) and the electric dipole transition amplitudes. On the other hand, in systems for which bound-to-(resonance)-free transitions are dominant (see Appendix A) the band shape will largely be determined by the decay rates of such states when the lifetime of the state is short. For intermediate lifetimes (10^{-14} – 10^{-15} sec) both the width of the resonance state and the vibrational structure can contribute to the overall electronic transition band shape.

IV. IMPLEMENTATION OF THE THEORY

The final expression of Eq. (67) for the electronic band spectrum gives a closed theory only in the following sense: If information is available on the solvent's molecule (cavity) distribution function, and if reasonable models are introduced for the FC factors, the corresponding vibrational energy differences, the hopping integrals (\hbar), the fluctuation ($\langle \delta h \delta h \rangle$), and the dipole transition integrals r , the expression in Eq. (67) could be used to compute the spectral band shape $I(\omega)$. Presently, this is, within the experimental data resources available to us, still a rather difficult task, especially with respect to formulating reasonable models for the spatial and temperature dependences of \hbar , $\langle \delta h \delta h \rangle$, and the r integrals. However, it is important and useful to enquire as to whether the functional form of $I(\omega)$ given in Eq. (67) has the power to describe (fit), for physically reasonable values of the parameters ($E^0, \hbar, \langle \delta h \delta h \rangle, r$), experimental band shapes for various solvents (at given temperatures). If so, then one would have some initial indication that the present formal theory may prove to be useful for gaining insights into the nature of electric dipole transition amplitudes, electron transfer integrals, and the effects of fluctuations in condensed-phase spectra.

To address this question concerning the potentials of the resultant functional form for $I(\omega)$ we now introduce some physically motivated approximations which serve to reduce Eq. (67) to a more tractable form. Of course, these approximations also reduce the generality of Eq. (67). Therefore, if this less general equation can be shown to be suitable for describing the experimentally observed optical band shape, we shall have encouraging evidence in support of our model, since the more general equation could only give better agreement. The ap-

proximations (or restrictions) to be made, together with some justifying remarks, are as follows:

(1) We assume that the temperatures of interest are low enough so that only the ground vibrational states of the solvent species are initially occupied. This implies that only $v_1 = 0$ and $v_2 = 0$ contribute.

(2) We assume that the transition to be studied is a bound-to-bound transition and we assume that only one bound excited state of the anion is involved. Of course, we will have to return to the consideration of bound-to-resonance transitions for systems where definite evidence of such transitions is present. For the ethanol and anthracene systems studied here there is evidence in favor of a bound-to-bound transition,^{23,31} at least in the low frequency component of $I(\omega)$.

(3) We assume that the integrals $r_{oo,s\gamma}$ and $\hat{h}_{oo,s\gamma}$ are dominated by localized ($s = 0$) and nearest-neighbor ($s = \text{neighbor}$) terms. We further assume that the excited states (γ) on neighboring molecules interact more strongly than do ground states (because the excited states are more loosely bound and hence overlap and interact more). This allows us to say that $\hat{h}_{oo,s0}$ is small compared to $\hat{h}_{o\gamma,s\gamma} \equiv h$:

$$\hat{h}_{oo,s0} = \chi_1 h, \quad 0 < \chi_1 < 1, \quad (68)$$

and that interaction integrals in which the (zeroth order) electronic energy is not conserved are negligible: $\hat{h}_{0\mu,s\nu} \approx 0$ if $\mu \neq \nu$.

(4) We assume that the largest dipole transition amplitude corresponds to transitions between electronic states of the same sites $r_{oo,s\gamma} = r_{R0,R\gamma} \equiv r$, and that transitions between the ground state of one site and excited states of neighboring sites have transition integrals whose magnitudes are a fraction χ_2 of r :

$$r_{oo,s\gamma} = \chi_2 r, \quad 0 < \chi_2 < 1. \quad (69)$$

(5) The fluctuation integrals $\langle \delta h_{R\mu,s\gamma} \delta h_{R'\mu',s'\gamma'} \rangle$, which correlate fluctuations in $h_{R\mu,s\gamma}$ to fluctuations in $h_{R'\mu',s'\gamma'}$, are assumed to be important only if $R\mu = R'\mu'$ and $S\gamma = S'\gamma'$, or $R\mu = S'\gamma'$ and $S\gamma = R'\mu'$, and the largest among such terms are those involving the excited-state orbital $\langle \delta h_{o\gamma,R\gamma}^2 \rangle \equiv \langle \delta h^2 \rangle$, with

$$\langle \delta h_{oo,R0}^2 \rangle = \chi_3 \langle \delta h^2 \rangle, \quad 0 < \chi_3 < 1. \quad (70)$$

This approximation is based upon the assumption that the vibrations and rotations of one molecule are not strongly correlated with those of different molecules and the assumption that the excited (zeroth order) states of neighboring molecules interact more strongly than do the ground states.

(6) In treating the FC factors we assume that the frequencies in the ground and excited electronic states of the anion are the same, but that the excited state potential surface is displaced relative to the ground state surface. Furthermore, we assume that only one vibrational mode is modified in the absorption process. Certainly, these assumptions are quite restrictive and there is no evidence for their general validity. However, Funabashi¹⁸ has shown that they are not far from valid for the specific alcohol system which we are treating here. Moreover, the electron transmission spectrum³² of anthracene gives evidence that it is primarily one carbon-carbon stretching mode which is distorted in forming the anion.

(7) The FC factors and corresponding vibrational energy differences are assumed to be well approximated within a harmonic-oscillator model, and are therefore given as³³

$$F^{A-A^*}(0, v) = \exp(-X_{AA^*}/2) (v!)^{-1/2} (X_{AA^*})^{v/2}, \quad (71)$$

with similar expressions for F^{A-M} and F^{M-A^*} , containing appropriate geometrical displacement parameters³⁴ X_{AA^*} , X_{AM} , and X_{MA^*} , respectively, and

$$\Delta E_v = \omega_0 (\bar{v}_1 + \bar{v}_2), \quad (72a)$$

$$\Delta E_v^0 = \omega_0 (\bar{v}_1), \quad (72b)$$

with ω_0 the vibrational frequency of the one participating mode.

Once these approximations are made Eqs. (67) can be recast into the following form:

$$I(\omega) = I^{(0)}(\omega) + I^{(1)}(\omega) + I^{(2)}(\omega), \quad (73a)$$

where

$$I^{(0)}(\omega) = r^2 \sum_{\bar{v}_1} [F^{A-A^*}(0, \bar{v}_1)]^2 G[\omega, (\Delta E_e^0 + \Delta E_v^0), \sigma] + r^2 n \chi_2^2 \sum_{\bar{v}_1 \bar{v}_2} [F^{A-M}(0, \bar{v}_1) F^{M-A^*}(0, \bar{v}_2)]^2 G[\omega, (\Delta E_e + \Delta E_v), \sigma], \quad (73b)$$

$$I^{(1)}(\omega) = r^2 n \chi_2 h (1 - \chi_1) \sum_{\bar{v}_1} (F^{A-A^*})^2 \frac{1}{\sigma^2} [\omega - (\Delta E_e^0 + \Delta E_v^0)] G[\omega, (\Delta E_e^0 + \Delta E_v^0), \sigma] \\ + r^2 \chi_2 h (1 - \chi_1) [n + \chi_2 n(n-1)] \sum_{\bar{v}_1 \bar{v}_2} (F^{A-M} F^{M-A^*})^2 \frac{1}{\sigma^2} [\omega - (\Delta E_e + \Delta E_v)] G[\omega, (\Delta E_e + \Delta E_v), \sigma], \quad (73c)$$

and

$$I^{(2)}(\omega) = r^2 n \langle \delta h^2 \rangle (1 + \chi_3) \sum_{\bar{v}_1} (F^{A-A^*})^2 \left\{ \frac{1}{\sigma^4} [\omega - (\Delta E_e^0 + \Delta E_v^0)]^2 - \frac{1}{\sigma^2} \right\} G[\omega, (\Delta E_e^0 + \Delta E_v^0), \sigma] \\ + r^2 \chi_2^2 \langle \delta h^2 \rangle (1 + \chi_3) n^2 \sum_{\bar{v}_1 \bar{v}_2} (F^{A-M} F^{M-A^*})^2 \left\{ \frac{1}{\sigma^4} [\omega - (\Delta E_e + \Delta E_v)]^2 - \frac{1}{\sigma^2} \right\} G[\omega, (\Delta E_e + \Delta E_v), \sigma]. \quad (73d)$$

Here, n is the number of near-neighbor solvent molecules (or cavities) surrounding the molecule (or cavity) at the coordinate origin. In writing Eqs. (73) we have also used the fact that transition probabilities depend upon the relative positions of the sites and that the FC factors and energy differences in the near-neighbor approximation are independent of the positions of the solvent species.

This simplified model still contains the essential features of the general expression for the band shape given in Eq. (67) and as discussed earlier is still more sophisticated than most other models in literature. In carrying out the practical application of Eqs. (73) to the two given spectra discussed below we proceed in the following manner: First, we calculate intensities at ω values which are multiples of the fundamental frequency ω_0 [see Eq. (72)], i. e., $\omega = k\omega_0$, $k = 0, 1, 2, \dots$. For these ω values, as was pointed out in earlier discussion of Sec. III. B, the band shape (envelope) is dominated by the zeroth order term $I^{(0)}(k\omega_0)$ given in Eq. (73a). This step allows us to adjust³⁵ the parameters r , X_{AA^*} , X_{AM} , and χ_2 which appear in $I^{(0)}(\omega)$ to generate an optimum fit at these special ω values. For both of the systems studied here the number of nearest neighbors (n) was taken (for lack of further evidence) to be six. The value of r is chosen to match the overall intensity of the absorption while X_{AM} , X_{MA^*} , and χ_2 give the proper high- ω skew to the band. The value of X_{AA^*} is chosen to reproduce the width of the low- ω part of the absorption [or equivalently the position of the maximum of $I(\omega)$], and ΔE_e^0 gives the frequency at which the absorption just begins. Once the parameters within $I^{(0)}(\omega)$ are determined by fitting to the observed intensity of absorption at $\omega = k\omega_0$, the parameters σ , $\langle\delta h^2\rangle$, and \hbar which appear in $I^{(1)}(\omega)$ and $I^{(2)}(\omega)$ can be extracted by fitting to the observed spectrum at values of ω which lie between the above frequencies. The question of uniqueness of the values of the parameters which are determined by such a fitting process can best be answered through the application of our procedure to a large number of systems. Some initial indications concerning the sensitivity of the fitting process are given below in our discussion of the two examples considered here.

In the case of excess electrons in pure anthracene the observed spectrum corresponds to electronic transitions between two bound levels as discussed by Aulich *et al.*²³ The experimental information regarding the ethanol glass system is not yet entirely resolved. According to Perkey *et al.*,³¹ who monitored the appearance of mobile electrons upon optical absorption, the low-frequency portion of $I(\omega)$ corresponds to a bound-to-bound transition, whereas the high frequency component of $I(\omega)$ may include contributions from bound-to-continuum transitions as well. The latter case is rather complicated because the observation of mobile electrons caused by absorption of light with frequency in the high- ω part of the absorption band can be interpreted in several ways. The excited state could lie below the continuum for low vibrational quantum numbers ($\bar{\nu}$) and cross into the continuum for higher vibrational levels. This interpretation would be consistent with the observed absence of mobile electrons for irradiation at low ω (absorption to

low $\bar{\nu}$ values in the excited state) and the presence of mobile electrons for higher ω excitation (absorption to higher $\bar{\nu}$ values which lie in the continuum). Of course, it is also possible that the excited electronic state of the alcohol system is bound and that the appearance of mobile electrons upon irradiation can be ascribed to the photon-induced transition of an electron from one cavity to its neighbor. In the language used in this paper such transitions would correspond to the charge-transfer component of $I^{(0)}(\omega)$, which contains the χ_2^2 factor to account for the electric dipole transition integral $r_{00,R\gamma}$. In the absence of more definitive experimental evidence concerning the nature of the excited state for the electron-ethanol system we proceed under the assumption that this state is bound, at least for its lower vibrational states.

In carrying out the parameter fitting procedure described above the values $\omega_0 = 0.16$ eV, $X_{AA^*} = 7$, and $\Delta E_e^0 = 1.2$ eV for the ethanol system were taken directly from Bush and Funabashi,¹⁸ who argue that these values correspond to geometrical distortions involving primarily the C-O-H bending vibration. As it turned out this was a good choice in that no noticeable improvement in the fit to the experimental data could be made by further adjustment. For anthracene the values of $\omega_0 = 0.059$ eV, $X_{AA^*} = 5$, and $\Delta E_e^0 = 1.39$ eV were obtained by fitting the experimental spectrum of Shida and Iwata³⁶ according to the procedure discussed above. The value of the line shape width σ , which describes the inhomogeneous broadening, was taken to be 0.026 eV for both systems.³⁷

In Figs. 3 and 4 we compare the experimental and the resulting calculated (fitted) spectra for the ethyl alcohol and anthracene systems, within various approximations. The curves (a) corresponding to the localized component of $I^{(0)}(\omega)$ give too small a width and do not show proper skewedness. On the other hand, the spectra generated by including the addition of the nonlocalized contributions to $I^{(0)}(\omega)$, which are shown in Figs. 3(b) and 4(b), give the width and the skewedness quite accurately. The optimum values of the geometrical displacement parameters X_{AM} and X_{MA^*} and the dipole transition ratio χ_2 , which essentially determine the contribution due to non-localized (dipole) electronic transitions, were found to be $X_{AM} = 3$ and $\chi_2 = 0.294$ for ethanol and $X_{AM} = 3$ and $\chi_2 = 0.367$ for anthracene.³⁵ Figure 3(c) is presented to demonstrate the sensitivity of the calculated band shape on the parameter χ_2 [$\chi_2 = 0.365$ for Fig. 3(c)].

After generating spectra for the two systems of interest at the special frequencies ($\omega = k\omega_0$) we next use the full Eqs. (73) to fit the experimental spectrum at "in between" frequencies. For ethanol the values $\hbar = 0.01$ eV and $\langle\delta h^2\rangle = 0.0000965$ eV² (which corresponds to a fluctuation integral of ~ 80 cm⁻¹) were found to be optimum.³⁷ The corresponding curve for the band shape is not greatly discernable from the $I^{(0)}(\omega)$ curve of Fig. 3(b); it is not shown. The fact that the predicted spectral shape is extremely sensitive to $\langle\delta h^2\rangle$ raises problems for applications in which the theory is used as predictive tool, since rather accurate modeling of $\langle\delta h^2\rangle$ would be required. However, from the point of view of

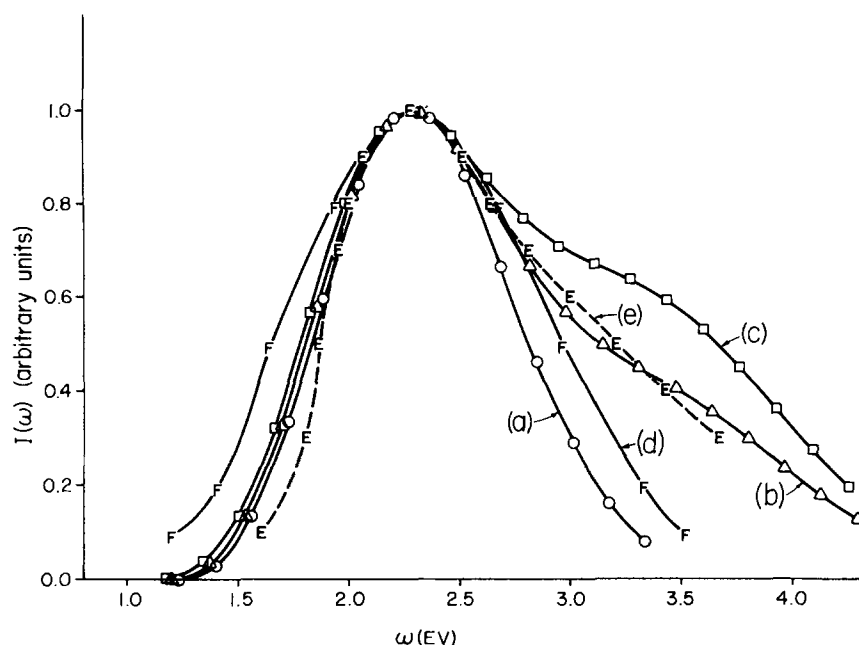


FIG. 3. Absorption spectral band shapes for solvated electron in ethanol, calculated from Eqs. (73). The dotted line (e) shows the experimental spectrum (Ref. 31).

using known experimental spectra to determine the values of $E_{m\alpha}^0$, $\hat{h}_{m\alpha, n\beta}$, $\langle \delta h_{m\alpha, n\beta}^2 \rangle$, etc., which give important insights into the behavior of excess electrons in solvents, one can realistically expect to extract values for these parameters rather accurately using fitting procedures. As can be seen from Figs. 3 and 4 the functional form for $I(\omega)$ given in Eqs. (73) is capable of fitting the two observed spectra for reasonable choices of the parameters. The fact that X_{AA^*} is larger for ethanol than for anthracene implies that the geometrical distortions caused by the presence of the excess electron is larger in the alcohol system. The charge transfer contribution to $I(\omega)$, as contained in the transition dipole ratio χ_2 , seems to be larger for anthracene glass than for

ethanol. This observation could be used to infer that mobile electrons should be formed (via photon-induced charge transfer) in anthracene at least as easily as in ethanol (recall that in Ref. 31 mobile electrons were observed for irradiation in the high- ω part of the band), even though the ground-to-excited state transition in anthracene is known²³ to be bound to bound. An experimental investigation of this question for anthracene now seems to be in order.

For comparison sake the band shape obtained by Bush and Funabashi¹⁸ for ethanol is shown in Fig. 3(d) (after deleting their vibrational structure). The width of their spectra is slightly greater than that obtained by using

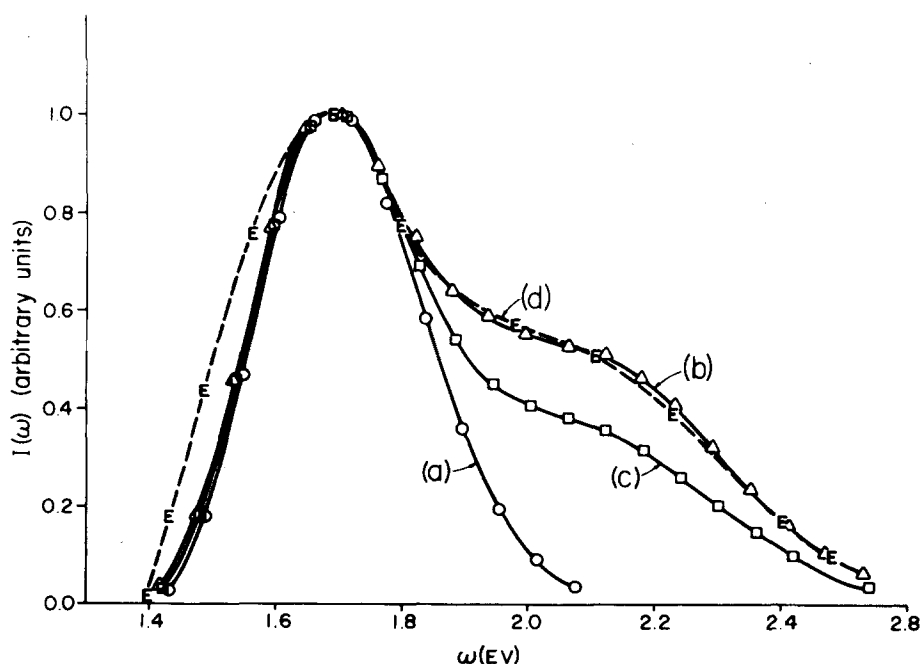


FIG. 4. Absorption spectral band shapes for excess electron in anthracene glass, calculated from Eqs. (73). The dotted line (d) shows the experimental spectrum (Ref. 36).

the localized term of $I^{(0)}(\omega)$, due to their explicit considerations of (assumed) bound-to-continuum transitions. However, their line shape does not have proper skewedness. In addition to comparing to the results of Ref. 18 it should be mentioned here that the use cluster or semi-continuum models (such as the CKJ model¹⁰) would essentially involve finding only the band maximum ω_{max} and $I(\omega_{\text{max}})$ and then assigning a band shape (usually a Gaussian) whose width is ascribed to the effects of symmetric mode (cavity size variations) and dipole orientation fluctuations³⁸ on the energies of the ground and excited electronic states. In our model this inhomogeneous broadening, which is of the order of σ , is assumed to broaden each of the vibrational transition lines in the total electronic transition band. Electronic band shapes whose entire width is obtained from such inhomogeneous broadening mechanisms have been found to be rather inadequate primarily because of the physically unrealistic value of σ needed to fit the observed data.

V. SUMMARY AND CONCLUSION

The basic result of this paper for the absorption spectrum of solvated electrons in condensed media is contained in Eqs. (67). The band shape $I(\omega)$ is expressed as a sum of three contributions, each of which has a localized part corresponding to a dipole transition of the type $\phi_{00} \rightarrow \phi_{0\nu}$ and a nonlocalized part involving $\phi_{00} \rightarrow \phi_{s\nu}$ transitions. In the first contribution to $I(\omega)$ the intensity is expressed as a product of dipole transition matrix elements and corresponding Franck-Condon factors. The intermolecular solvent interactions affect this component only through their influence on the electric dipole matrix elements and the inhomogeneous broadening of each vibronic line. The other two contributions to $I(\omega)$ contain explicitly the effects of rotational-translational motions of the solvent molecules as perturbations giving rise to combinations of electron hopping and fluctuation integrals in the resultant components of the absorption line shape.

Operationally, the expression for the absorption spectrum resulted from a Fourier transformation of the (time) dipole correlation function. By performing a cumulant expansion of the time evolution operators, making a short-time expansion, and assuming a separation of the electronic, vibrational, and rotational-translational motions it was possible to express the correlation function (and, hence, the spectral band shape) in terms of solvent structure information and the electron-solvent interaction potential (through $E_{m\alpha}^0$ and $\hat{h}_{m\alpha, n\beta}$).

In this paper application of the theory was restricted to the analysis of low-temperature experiments in which bound-to-bound transitions are assumed to dominate and the treatment of solvent interactions was confined to near-neighbor sites. This rather simplified model was applied to the two separate cases of solvated electrons in ethyl alcohol and in anthracene glass. The results described in Sec. IV clearly demonstrate that even this simplified model is quite capable of describing (fitting) the solvated electron spectrum, thereby providing optimism concerning the potential of the general formalism to provide quantitative information about the behavior of

solutions of excess electrons in molecular solvents as expressed through the electronic energy levels $E_{m\alpha}^0$ and interaction matrix elements $h_{m\alpha, n\beta}$.

One of the highlights of the present development, in comparison with other treatments which are currently in the literature, has been its generality and its adherence to fundamental principles as opposed to phenomenological developments based on specific models which treat only one aspect of the problem. Specific important points of differences between our theory and others are (i) the introduction of nonlocalized terms which were shown to be responsible for at least part of the high- ω skewedness of $I(\omega)$, (ii) inclusion of the effects of rotational-translational perturbations on the absorption line shape, and (iii) *ab initio* inclusion of inhomogeneous broadening effects which arise naturally due to fluctuations in the instantaneous center-of-mass positions and orientations of the solvent species, as well as broadening due to finite lifetimes of localized resonance states.

As is apparent from our description of the applications given in Sec. IV many important challenging problems still remain before the theory is proven satisfactory. One immediate problem, whose solution may enable one to use the present theory both for quantitative analysis of spectra and as a reliable predictive tool, has to do with developing accurate and physically sound models for the transition dipole, hopping, and fluctuation integrals. It is our opinion that the accumulation of data for a wide range of specific cases and the interpretation of such data in terms of models based on assumptions such as (3), (4), and (5) of Sec. IV will prove to be a very valuable step in learning the strengths, weaknesses, and sensitivities (to parameters) of the present model as well as in testing proposed models for the above integrals. Some ideas regarding possible models for the spatial dependences of these integrals have been put forth in I; the reader is referred to this earlier work for further discussions. One possibility with regard to modeling the temperature dependence of the hopping and fluctuation integrals can be expressed as

$$\hat{h}_{0\mu, 1\mu} = A + B \exp(-E/KT)$$

and

$$\langle \delta \hat{h}_{0\mu, 1\mu} \delta \hat{h}_{1\mu, 0\mu} \rangle = B' \exp(-E/KT),$$

where the "activation energy" E is related to the potential energy barrier between the anion and the neutral geometries, A is a measure of the electron tunneling probability, and B and B' are functions of the spatial extents (and hence overlaps and interactions) of the orbitals at neighboring sites. Clearly, the magnitudes of B and B' are dependent upon the size of the coupling between electronic and nuclear (geometrical) motions. Also, A depends upon the depth ($E_{m\alpha}^0$) and width (intermolecular spacing) of the electron-molecule potential wells. Even though the above model expressions for \hat{h} and $\langle \delta \hat{h} \delta \hat{h} \rangle$ may prove to be useful in fitting experimental data, the modeling process is not complete until more direct connections are made between the parameters E , A , B , and B' and the electron-solvent interaction potential (u) and solvent structure information [$\rho(R, 0)$].

In addition to the above mentioned problems having to

do with developing reasonable models there are other areas in which further development seems especially promising. One application of immediate interest concerns the case of transitions involving localized resonance states in which, as is seen in Appendix A, a main source of linewidth arises from the decay of such states. The application of the present model to cases involving aromatic hydrocarbon solvents which possess resonance states is presently under consideration.

Another problem of major chemical importance is the extension of the basic results presented here to mixed solvents. Here, considerations of interactions among constituent solvent molecules and the numbers of different species in a solvation layer are probably quite important. Such quantities will depend upon both inter- and intramolecular interactions. An especially relevant candidate for spectral line shape studies in mixed solvents is the case of charge-transfer spectra, for which the dominant zeroth order transition corresponds to a nonlocalized event between two unlike molecules $\phi_{A\mu} - \phi_{B\nu}$.

As is clear much important research remains to be done before this preliminary investigation can be put on a more defensible ground and can be straightforwardly and routinely applied to the spectroscopic study of pure and mixed solvents.

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APPENDIX A

In systems for which the bound-to-(resonance) free transitions are also important the resonance state energy is a complex number representing a state which is decaying as $\exp(-\Gamma t)$. For the general case the line shape function of Eq. (64) has the form

$$f^{(n)}(\omega) = \frac{1}{2\pi} \frac{d^n}{d\omega^n} \int_{-\infty}^{\infty} dt \exp \left\{ - \left[\frac{\sigma^2}{2} t^2 + (\Delta E - \omega)it + \Gamma |t| \right] \right\} dt \\ \equiv \frac{d^n}{d\omega^n} f(\omega). \quad (\text{A1})$$

For this case $f(\omega)$ has the following form after integration:

$$f(\omega) = \frac{1}{2\pi\sqrt{a}} \exp\left(\frac{b^2}{4a}\right) \text{erf}(\bar{b}/2\sqrt{a}) \\ + \frac{1}{2\pi\sqrt{a}} \exp\left(\frac{b^2}{4a}\right) \text{erf}(b/2\sqrt{a}), \quad (\text{A2})$$

where $a = \sigma^2/2$, $b = i(\Delta E - \omega) + \Gamma$, $\bar{b} = -i(\Delta E - \omega) + \Gamma$, and $\text{erf}(z) = \int_{-\infty}^z \exp(-x^2) dx$. Further simplification of the expression in Eq. (A2) gives

$$f(\omega) = \frac{1}{\pi\sigma\sqrt{2}} \exp\{[\Gamma^2 - (\Delta E - \omega)^2]/2\sigma^2\} \\ \times 2 \text{Re} \left\{ \exp\left[\frac{i\Gamma(\Delta E - \omega)}{\sigma^2}\right] \text{erf}\left[\frac{i(\Delta E - \omega) + \Gamma}{\sigma\sqrt{2}}\right] \right\}. \quad (\text{A3})$$

This line shape expression is neither simply a Gaussian nor a Lorentzian but is a convolution of both. The limiting values of this expression for the cases of bound-to-bound and bound-to-free transitions are given as follows:

Case 1: In the limit $\Gamma \rightarrow 0$ we have from Eq. (A2)

$$\lim_{\Gamma \rightarrow 0} f(\omega) = \frac{1}{\pi\sigma\sqrt{2}} \exp\left[-\frac{(\Delta E - \omega)^2}{2\sigma^2}\right] \int_{-\infty}^{\infty} \exp(-x^2) dx \\ = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(\Delta E - \omega)^2}{2\sigma^2}\right], \quad (\text{A4})$$

which is a Gaussian function of width σ , as calculated earlier in this paper for bound-to-bound transitions.

Case 2: In the limit $\sigma \rightarrow 0$ we have from Eq. (A2)

$$\lim_{\sigma \rightarrow 0} f(\omega) = \frac{1}{2\pi} \left[\frac{1}{\Gamma + i(\Delta E - \omega)} + \frac{1}{\Gamma - i(\Delta E - \omega)} \right] \\ = \frac{\Gamma}{\pi[\Gamma^2 + (\Delta E - \omega)^2]}, \quad (\text{A5})$$

which is a Lorentzian function of width Γ corresponding to the bound-to-free transition.

The derivatives required for the calculation of higher order line shape can be obtained by using

$$\frac{d^{n+1}}{dZ^{n+1}} \text{erf}(z) = (-1)^{n+1} \frac{2}{\sqrt{\pi}} H_n(z) \exp(-z^2), \quad (\text{A6})$$

where $H_n(Z)$ are Hermite polynomials.

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- ³⁰In case an excited electronic state is a continuum resonance state which decays as $\exp(-\Gamma t)$ corresponding to the width Γ it is shown in Appendix A that the line shape has characteristics due to bound-to-bound transitions (Gaussian inhomogeneous broadening) and bound-to-free transitions (Lorentzian).
- ³¹L. M. Perkey, Farhataziz, and R. R. Hentz, Chem. Phys. Lett. **27**, 531 (1974).
- ³²K. D. Jordan (private communication).
- ³³T. H. Keil, Phys. Rev. A **140**, 601 (1965).
- ³⁴These parameters are given in terms of the actual length displacements (Δq) of the participating vibrational mode as $X = (\Delta q)^2 m \omega / 2\hbar$, where ω is the frequency of the vibration and m is its "reduced mass."
- ³⁵The parameter X_{MA}^* is related to others by $X_{AA}^* + X_{MA}^* = X_{AM}^*$.
- ³⁶T. Shida and S. Iwata, J. Am. Chem. Soc. **95**, 3473 (1973).
- ³⁷This value of σ was chosen according to the discussion due to Kestner [p. 342, Ref. 1(b)], who estimated a maximum possible value of the order of $kT \ln 2$ for the inhomogeneous broadening of the electronic states. As is seen from Eq. (59), σ^2 is of the order of twice the sum of the fluctuations in the ground and excited state energies. Although the diagonal elements $h_{m\alpha, m\alpha}$ are probably larger than the off-diagonal (transfer) integrals $h_{m\alpha, n\alpha}$ ($m \neq n$), the fluctuations in these two integrals might not be much different in magnitude $\langle \delta h_{m\alpha, m\alpha}^2 \rangle \approx O(\langle \delta h_{n\alpha, 1\alpha}^2 \rangle)$. Hence, reasonable values of σ should lie in the range $\sigma^2 \geq 2[\langle \delta h^2 \rangle (1 + \chi_2)]$. The optimum $\langle \delta h^2 \rangle$ values obtained for ethanol and anthracene will be seen to fulfill this criterion if the above choice of σ is made.
- ³⁸N. R. Kestner and J. Jortner, J. Phys. Chem. **77**, 1040 (1973).