Spectroscopy of binary solutions. The benzene–iodine charge-transfer spectrum

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The theoretical formalism introduced in an earlier publication to treat the spectroscopy of excess electrons in condensed media is generalized to the case of a mixed solvent. With a simple redefinition of the reference state, the theory is shown to be equally applicable to the spectroscopy of neutral species, and is employed to calculate the familiar benzene–iodine charge-transfer spectrum. The zeroth order contribution to the intensity spectrum is seen to involve a direct dipole transition from the donor (benzene) to the acceptor (iodine), whereas the first and second order contributions involve dipole transitions modified by the effects of intermolecular electron "hopping" and its fluctuations, respectively. Using the so-called hopping (or resonance) and fluctuation integrals as adjustable parameters, the theory is shown to be capable of reproducing the main features of the experimental spectrum.

I. INTRODUCTION

We have recently developed[1] a quite general model for treating the electronic spectroscopy of excess electrons in one-component liquids. This theory can, rather straightforwardly, be extended to treat mixed solvents of neutral as well as charged species, as is shown in this paper. An experimentally well-characterized charge-transfer spectrum can therefore be used as a critical test for the working machinery of our theory. A charge-transfer (CT) optical spectrum[2] involves an electronic transition of an electron donor–acceptor complex. The CT absorption is characteristic of neither the isolated donor nor acceptor; it is instead a transition in which an electron is transferred from one molecule in the complex to the other to form an ionized donor–acceptor pair. Charge-transfer absorptions are found in the visible and ultraviolet region of the spectrum, are usually quite intense ($\epsilon_{max} \sim 10^6$ dm^3 mol^{-1} m^{-1}), and in both the gas phase and in liquid solution are typically very broad and structureless. The ground state CT complex is usually rather weakly bound ($-\Delta H_f^0 < 10$ kcal/mol), but a CT absorption is also possible when no stable complex is formed, as for example in the case of the so-called "contact" CT absorption of I_2 dimers.[3]

The benzene–iodine (Bz : I_2) complex provides a classic and well-studied example.[4] If iodine is dissolved in benzene, a broad and intense absorption approximately 2900 Å is observed, in a region of the spectrum in which the individual components do not absorb intensely. The shape and position of the spectrum are fairly insensitive to the presence of an inert solvent (e.g., *n*-heptane), and the extinction coefficient (intensity) is only weakly dependent on the solvent.[5,6] The Bz : I_2 absorption has also been observed in the gas phase[7] and in a low-temperature matrix.[8] Relative to the room temperature solution-phase spectra, the vapor phase spectra are blue shifted by several tenths of an eV, indicating a stabilization of the ionic excited state in solution. The low temperature spectra may be shifted, relative to the solu-

tion spectra, either to the blue or to the red, depending on the medium (solid argon, organic glass, etc.). The short-wavelength region of the Bz : I_2 spectrum is overlapped by the strongly-allowed $^1A_{1g} \rightarrow {}^1B_{1u}$ transition of uncomplexed benzene, but if the equilibrium constant of the Bz : I_2 complex is known, the contribution of free benzene to the spectrum can be subtracted, as Ham *et al.* have done,[6] to give the absorption due to the complex alone. Some interesting aspects of the low temperature Bz : I_2 work include the discovery of a new lower energy transition in certain organic glasses,[8(b)] and the discernment of vibrational structure in the noble gas matrix-isolated complex.[8(a)]

The wealth of experimental data on the Bz : I_2 absorption allows for ample opportunity to compare theoretical predictions with observed facts. The motivation for such a comparison goes beyond the need to test our theory. Although present theoretical models of CT spectra are fairly capable of explaining the observed energies and, to some extent, intensities of the transition, an important goal of the present work is the development of a more powerful model which permits the interpretation of more detailed line shape information. Another longer term aim of our study of solvated electron and anion spectra is to obtain reliable estimates of the so-called resonance and fluctuation integrals which appear in our expression for the optical absorption line shape. By extracting these quantities from the experimentally observed spectrum, one can proceed to generalize to the problem of excess electron migration in related systems, as discussed in Ref. 9. This aspect of the problem shall not be addressed in the present work, since we are dealing here with the spectroscopy of a neutral species, namely, the Bz : I_2 CT complex.

In Sec. II some aspects of the well-established Mulliken theory of CT complexes are presented. Section III contains the development of our two-component spectroscopy theory and the generalization to charge-transfer systems. Some comparisons between the previous theoretical treatment and that of this work are made. Section IV contains a discussion of the application of our theory to the Bz : I_2 system, and Sec. V summarizes the results and points to future research problems.

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II. MULLIKEN THEORY

It is necessary and important to refer to and make comparisons with certain features of the presently accepted theoretical descriptions of CT complexes. Therefore a brief review of the Mulliken theory[10] is in order at this point. In this valence-bond picture, the ground electronic state of the complex, ψ_N, is described in terms of a resonance between the hypothetical "no-bond" state, $\psi_0(D, A)$, and the "dative" state, $\psi_1(D^+A^-)$:

$$\psi_N = a\psi_0(D, A) + b\psi_1(D^+A^-) . \tag{1a}$$

The excited state of the complex, ψ_E, is the final state of the CT transition, and is written

$$\psi_E = a^*\psi_1(D^+A^-) - b^*\psi_0(D, A) . \tag{1b}$$

Typical weak complexes such as $Bz : I_2$ have $a \gg b$ and $a^* \gg b^*$, so that absorption of light at the CT wavelength takes the system from a weakly bound ground state to a highly ionic excited state. A straightforward application of second order perturbation theory results in the following expressions for the ground state energy W_N and the excited state energy W_E:

$$W_N = W_0 - \frac{(W_{01} - S_{01}W_0)^2}{(W_1 - W_0)} + \cdots , \tag{2a}$$

$$W_E = W_1 + \frac{(W_{01} - S_{01}W_1)^2}{(W_1 - W_0)} + \cdots , \tag{2b}$$

where $W_0 = \langle \psi_0 | \mathcal{K} | \psi_0 \rangle$, $W_1 = \langle \psi_1 | \mathcal{K} | \psi_1 \rangle$, $W_{01} = \langle \psi_0 | \mathcal{K} | \psi_1 \rangle$, and $S_{01} = \langle \psi_0 | \psi_1 \rangle$. The absorption maximum, in the Mulliken Theory, occurs at a frequency ν_{CT} given by

$$h\nu_{CT} = W_E - W_N . \tag{3}$$

For most weak complexes the overlap S_{01} is quite small, and the ratio of the coefficients is given to a good approximation by

$$b/a = \frac{W_0 S_{01} - W_{01}}{W_1 - W_0} , \tag{4a}$$

$$b^*/a^* = \frac{W_1 S_{01} - W_{01}}{W_1 - W_0} . \tag{4b}$$

To simplify the picture further, the charge-transfer process is conceived of as the transfer of a single electron from a donor molecular orbital, ϕ_D, to a previously unoccupied acceptor orbital, ϕ_A. Note that for initially uncharged molecules, ϕ_D is characteristic of a neutral donor molecule, whereas ϕ_A is to be considered as characteristic of the negatively charged acceptor. Mulliken has shown that the CT transition dipole, which determines the intensity of the absorption, can be expressed approximately as

$$\mu_{EN} = a^*be(\mathbf{r}_D - \mathbf{r}_A) + (a^*a - b^*b)eS_{AD}(\mathbf{r}_D - \mathbf{r}_{DA}) , \tag{5}$$

where $\mathbf{r}_A = \langle \phi_A | \mathbf{r} | \phi_A \rangle$, $\mathbf{r}_D = \langle \phi_D | \mathbf{r} | \phi_D \rangle$, $S_{AD} = \langle \phi_A | \phi_D \rangle$ and $S_{AD}\mathbf{r}_{AD} = \langle \phi_A | \mathbf{r} | \phi_D \rangle$. With reasonable estimates of the sizes of the orbitals and the expansion coefficients, Mulliken obtains $\mu_{EN} = 3.45$ D for the $Bz : I_2$ complex, which corresponds to an oscillator strength of $f = 0.19$. Experimentally obtained oscillator strengths are somewhat higher ($f \sim 0.30$).[11]

While the simple two-term wavefunction described

above has been successfully employed to predict and interpret the spectroscopy of many of the stronger CT complexes, it has not proven adequate to describe the features of CT absorption of the weak $Bz : I$ complex.[12] This is undoubtedly due to the need to include more than just two separated-molecule states in the description of ψ_N and ψ_E. Moreover, the Mulliken model is not designed to include vibrational excitation or fluctuations in the solvent molecules' coordinates. As demonstrated below, these aspects of the problem are essential ingredients in a model which addresses the detailed shape of the absorption spectrum. It should become clear that the theory presented in this paper is potentially much more flexible than the two-term resonance hybrid description, and can, in addition, reproduce the main features of the CT line shape. This latter feature is, of course, a very important attribute of our model.

III. SPECTRAL THEORY OF BINARY SOLUTIONS

In an earlier publication[1] we developed a theoretical foundation for analyzing the optical spectra of solvated electrons in pure liquids. In this approach, one calculates a dynamic property, the electric dipole correlation function, of a molecule in equilibrium with an external medium by incorporating the effects of the medium into a time-dependent effective potential which contains the average molecule–medium interaction and effects of fluctuations in the medium's coordinates. Thus the problem of studying dynamical properties of the molecule reduces to one of studying the behavior of a molecule in a time-dependent external field which no longer depends explicitly on the coordinates of the medium.

The development of the spectral theory for the case of binary mixtures can be carried out in parallel to the pure solvent case. For the sake of completeness we give a brief sketch of this development. From the physical interpretation standpoint, the spectroscopy of binary solutions is quite interesting and involved. Depending upon the concentrations and intermolecular interactions of the species in solution, as well as the distribution (availability) of the electronic states of the solution molecules, a solvated electron sees a varied environment which in turn affects its spectrum.

As has been shown by Gordon,[13] the electronic absorption band shape $I(\omega)$ can be written as the Fourier transform of the time-correlation function of the electronic dipole moment operator, $\langle F(t)F(0) \rangle$:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle F(t)F(0) \rangle . \tag{6}$$

The time evolution of the electric dipole operator $F(t)$ is governed by the combined electron–solvent Hamiltonian, $H = H_N + H_e$, consisting of the part H_N describing the motion of the solvent molecules and the part H_e describing the motion of a single excess electron. H_e consists of the excess electron's kinetic energy and the electron–solvent interaction energies, and is represented within a basis of vacant molecular orbitals of the solvent $\{\phi^I_{R\alpha}\}$, where $I = A$, B refers to the two solvent species present, and R_α labels the position (R) and number (α) of the orbital.

Because the formation of a solvated electron produces appreciable solvent structural changes, the electron–solvent interaction must be treated in a relatively exact manner; the rest of the interactions can then be treated as a perturbation. To facilitate this development, a canonical transformation is performed which expresses H in terms of the motion of a "dressed" electron, the excess electron or anion in the presence of its polarized and distorted molecular environment. The explicit expression for the transformed Hamiltonian is given in terms of the Fermion creation operators $A_{\mathbf{R}_I\alpha}^{+}$ associated with the solvent molecular orbitals $\phi_{\mathbf{R}\alpha}^{I}$ as follows:

$$\tilde{H} = \tilde{H}_N + \tilde{H}_e , \tag{7a}$$

$$\tilde{H}_e = \sum_{I,J} \sum_{m\alpha,n\beta} h_{m_I\alpha,n_J\beta} A_{m_I\alpha}^{+} A_{n_J\beta} , \tag{7b}$$

$$\tilde{H}_N = \sum_{I \neq J} \sum_{m\alpha} \left\{ (A_{m_I\alpha}^{+} A_{m_I\alpha} + 1 - N_e) \sum_i \left[\frac{P_{I_i}^2}{2M_I} + U_I(Q_{I_i}') + \frac{1}{2} \sum_{j \neq i}^{N_I} V_I(\mathbf{X}_{I_i}'(m_I\alpha), \mathbf{X}_{I_j}'(m_I\alpha)) + \frac{1}{2} \sum_j^{N_J} V_{IJ}(\mathbf{X}_{I_i}'(m_I\alpha), \mathbf{X}_{J_j}'(m_J\alpha)) \right] \right\} , \tag{7c}$$

where $\mathbf{X}_{B_i}'(m_A\alpha) \equiv \mathbf{R}_{B_i}'(m_A\alpha)$, $\mathbf{\Omega}_{B_i}'(m_A\alpha)$, $\mathbf{Q}_{B_i}'(m_A\alpha)$ represents collectively the center of mass positions, orientations, and vibrational displacements, respectively, of the ith molecule of species B adjusted to feel the dressed electron in the orbital α of the mth molecule of type A. $\mathbf{P}_{A_i}$ is the total (translational, rotational, vibrational) momentum of the ith molecule of species A. $U(\mathbf{Q}_{I_i}')$ is the internal vibrational energy function of the ith molecule of type I, and V is the intermolecular potential energy. As the solvated electron migrates in time via the resonance (hopping) term, $h_{m_I\alpha, n_J\beta} A_{m_I\alpha}^{+} A_{n_J\beta}$, where

$$h_{m_I\alpha, n_J\beta} = \langle \phi_{m_I\alpha} | -\tfrac{1}{2}\nabla_r^2 + \sum_{K=A,B} \sum_i u(\mathbf{r}, \mathbf{X}_{K_i}'(m_I\alpha)) | \phi_{n_J\beta} \rangle , \tag{8}$$

the solvent molecules' Hamiltonian adjusts (through $A_{m_I\alpha}^{+} A_{m_I\alpha} + 1 - N_e$) to follow the moving electron, causing the geometrical characteristics of a solvent molecule (or cavity) to change from those of an anion to those of a neutral or vice versa.

Similarly, a canonical transformation of the correlation function in terms of dressed electron and solvent molecule coordinates results in

$$\langle F(t)F(0) \rangle = Z^{-1} \sum_{V\tilde{V}} \int\int d\mathbf{X}\, d\mathbf{P} \sum_{k\mu,l\nu} \sum_{I,J} \sum_{p\gamma,q\lambda} \sum_{K,L} \langle 0 | \langle V | e^{-\beta\tilde{H}} \langle \phi_{k_I\mu} | \boldsymbol{\epsilon}\cdot\mathbf{r} | \phi_{I_J\nu} \rangle_t \langle \phi_{p_K\gamma} | \boldsymbol{\epsilon}\cdot\mathbf{r} | \phi_{q_L\lambda} \rangle$$

$$A_{00}e^{i\tilde{H}t} A_{k_I\mu}^{+} A_{l_J\nu} \bar{e}^{i\tilde{H}t} | \overline{V}_{pK\gamma} \rangle \langle \overline{V}_{pK\gamma} | A_{p_K\gamma}^{+} A_{q_L\lambda} A_{00}^{+} | V \rangle | 0 \rangle . \tag{9}$$

In the above expression, $\mathbf{X}$ and $\mathbf{P}$ are used to represent collectively the coordinates and momenta, respectively, of all the solvent molecules. $\boldsymbol{\epsilon}$ is the electric field vector of the incident photon, Z is the total partition function, and $\mathbf{r}$ is the position vector of the excess electron. The reference state, $|V\rangle |0\rangle$, consists of the neutral solvent molecules in their initial states. The operator A_{00}^{+} creates, at time $t=0$, an excess electron in orbital 0 of an A-type molecule at the origin.

As discussed in detail in Ref. 1, the expression in Eq. (9) for the correlation function incorporates all of the relevant physical aspects of the problem. It is now useful to list the important physically motivated approximations which are introduced to permit a more computationally tractable expression for the band shape. These approximations, which were introduced in Ref. 1, are as follows:

(i) We decompose the Hamiltonian as $\tilde{H} = \tilde{H}^0 + \tilde{V}$. The zeroth order part $\tilde{H}^0$ contains the solvent molecules' Hamiltonian $\tilde{H}_N$ plus the equilibrium average of the diagonal part of the dressed electron's kinetic and potential energies ($\langle h_{\mathbf{R}_I\alpha, \mathbf{R}_I\alpha} \rangle = E_{\mathbf{R}_I\alpha}^0$). The perturbation $\tilde{V}$ then contains the off-diagonal elements ($h_{\mathbf{R}_I\alpha, \mathbf{R}_J'\beta}$) as well as the fluctuations in the diagonal elements,

$$\delta h_{\mathbf{R}_I\alpha, \mathbf{R}_I\alpha} \equiv h_{\mathbf{R}_I\alpha, \mathbf{R}_I\alpha} - E_{\mathbf{R}_I\alpha}^0 . \tag{10}$$

(ii) The perturbation decomposition of the Hamiltonian is combined with the Franck–Condon (F–C) approximation, where it is assumed that the time variation of the mixed solvent's coordinates $\mathbf{X}_{J_i}'(R_I\alpha)$ is slow compared to that of the electronic coordinate, $\mathbf{r}$. This allows us to recognize the main (zeroth order) part of the electronic band shape as arising from a sequence of electronic–vibrational transitions at energies ($\Delta E_{e,K} + \Delta E_{v,K}$) whose intensities are governed by the relevant F–C factors. Here

$$\Delta E_{e,K} = E_{s_K\gamma}^0 - E_{00}^0 \tag{11}$$

is the difference between the average electronic energies of the excess electron at the origin in the ground state and the excited electronic state of a molecule of species K at site S. Site S is where the electron is located after photon absorption, $\phi_{00} \xrightarrow{h\nu} \phi_{s_K\gamma}$.

$$\Delta E_{v,K} = \sum_{\lambda_0, \lambda_s} \{\epsilon_{\bar{v}_2, \lambda_s}^{S_K\gamma, A} - \epsilon_{v_2, \lambda_s}^{S_K 0, M} + \epsilon_{\bar{v}_1, \lambda_0}^{00, M} - \epsilon_{v_1, \lambda_0}^{00, A}\} \tag{12}$$

is the vibrational energy difference associated with the process $00 \to S_K\gamma$, in which the anion (of species A) at the origin becomes a distorted molecule whereas the molecule at S (of species $K = A$ or B) becomes a distorted excited anion. λ_0 and λ_s correspond to the vibrational modes of the species at the origin and at S, respectively. The corresponding F–C factors are given in terms of the overlap of vibrational wavefunctions:

$$F_{\lambda_{0_A}}^{A-M}(v_1, \bar{v}_1) = {}^A\langle v_1^{00}\lambda_{0_A} | \bar{v}^{S_K\gamma}\lambda_{0_A}\rangle^M , \tag{13a}$$

$$F_{\lambda_{s_K}}^{M-A^*}(v_2, \bar{v}_2) = {}^M\langle v_2^{00}\lambda_{s_K} | \bar{v}_2^{S_K\gamma}\lambda_{s_K}\rangle^A . \tag{13b}$$

(iii) At this stage we employ Kubo's[14] cumulant expansion technique to carry out the equilibrium average over the rotational and translational degrees of freedom of the solvent molecules. The Kubo technique, as discussed in more detail in Ref. 1, allows us to express the equilibrium average of an exponential operator (e.g., essentially e^{iHt}) in terms of the exponentials of the equilibrium average of the operator, its fluctuations away from the average, plus higher order fluctuations [$\exp(\sum_n K_n(t)$, where $K_n(t)$ is the nth cumulant operator]. When the solvent is not in the neighborhood of a phase transition, or critical point, it is a reasonable approximation to truncate the cumulant expansion at $K_2(t)$ (i.e., correlations among three and more solvent molecules are neglected).

(iv) Since the time scale for electronic transitions is very fast ($\sim 10^{-14}$ to 10^{-16} s) compared to the time variation of the solvent's vibrational, rotational, and translational coordinates, a short time expansion of the cumulant operators reduces the cumulant exponential operator to the form $\exp(i\bar{K}_1 t + \bar{K}_2 t^2)$, where

$$\bar{K}_1 = \sum_{I,J} \sum_{m\alpha \ne n\beta} \langle h_{m_I\alpha, n_J\beta}\rangle [A_{m_I\alpha}^+ A_{n_J\beta},] \tag{14a}$$

$$\bar{K}_2 = -\sum_{I,J,K,L} \sum_{\substack{m\alpha, n\beta \\ r\lambda, s\sigma}} \langle \delta h_{m_I\alpha, n_J\beta} \delta h_{r_K\lambda s_L\sigma}\rangle [A_{m_I\alpha}^+ A_{n_J\beta}, [A_{r_K\lambda}^+ A_{s_L\sigma},]] . \tag{14b}$$

The equilibrium average over the orientational and translational coordinates of the instantaneous fluctuation in the electronic energy of an excess electron in orbital $\phi_{R_I\mu}$ gives rise to an inhomogeneous broadening of width σ_{IJ} to each vibrational transition in the band,

$$\sigma_{IJ}^2 = \langle \delta h_{R_I\mu, R_I\mu}^2\rangle + \langle \delta h_{R_J'\nu, R_J'\nu}^2\rangle - 2\langle \delta h_{R_I\mu, R_I\mu} \delta h_{R_J'\nu R_J'\nu}\rangle . \tag{15}$$

(v) The Fourier transform of the correlation function then leads to the final band shape expression $I(\omega)$, in which the $\exp[i(\Delta E_e + \Delta E_v)t]$ part leads to our zeroth order spectrum $I^{(0)}(\omega)$. The part depending upon $\exp[i K_1 t + K_2 t^2]$, which contains the equilibrium averages of the resonance integrals (coupling orbitals of one molecule to its neighbors) and their fluctuations, modifies the shape and intensity of $I^{(0)}(\omega)$. The details of carrying out these steps are given in Ref. 1 for the case of a one-component liquid. The resultant general expression for the bandshape in a binary solvent is

$$I(\omega) = I^{(0)}(\omega) + I^{(1)}(\omega) + I^{(2)}(\omega) , \tag{16a}$$

$$I^{(0)}(\omega) = Z_v^{-1} \sum_{K=A,B} \int d\mathbf{S}\, \rho_{AK}(\mathbf{S}, 0)$$
$$\times \sum_\gamma \sum_{v_1\bar{v}_1 v_2\bar{v}_2} \prod_{\lambda_0\lambda_s} \exp[-\beta\epsilon_{\lambda_0, \lambda_s}^{0, S_K}(v_1, v_2)] [F_{\lambda_{0A}}^{A-M}(v_{1A}, \bar{v}_{1A}) F_{\lambda_s K}^{M-A^*}(v_{2K}, \bar{v}_{2K})]^2 \, r_{00, s_K\gamma}^2 \, G[\omega, (\Delta E_{e,K} + \Delta E_{V,K}), \sigma_{AK}] , \tag{16b}$$

$$I^{(1)}(\omega) = Z_v^{-1} \sum_{I,K} \int d\mathbf{R}\, d\mathbf{S}\, \rho_{AI}(\mathbf{R}, 0)\rho_{AK}(\mathbf{S}, 0) \sum_{\mu\nu} \sum_{v_1\bar{v}_1 v_2\bar{v}_2} \prod_{\lambda_0\lambda_s} \exp[-\beta\epsilon_{\lambda_0, \lambda_s}^{0, s_K}(v_1, v_2)] [F_{\lambda_{0A}}^{A-M}(v_{1A}, \bar{v}_{1A}) F_{\lambda_s K}^{M-A^*}(v_{2K}, \bar{v}_{2K})]^2$$
$$\times r_{00, s_K\gamma}\{r_{R_I\mu, S_K\gamma}\langle h_{00, R_I\mu}\rangle - r_{00, R_I\mu}\langle h_{R_I\mu, S_K\gamma}\rangle\} \frac{-1}{\sigma_{AK}^2} [\omega - (\Delta E_{e,K} + \Delta E_{v,K})] G[\omega, (\Delta E_{e,K} + \Delta E_{v,K}), \sigma_{AK}] , \tag{16c}$$

$$I^{(2)}(\omega) = Z_v^{-1} \sum_{IJK} \int d\mathbf{R}\, d\mathbf{R}'\, d\mathbf{S}\, \rho_{AI}(\mathbf{R}, 0)\rho_{AJ}(\mathbf{R}', 0)\rho_{AK}(\mathbf{S}, 0)$$
$$\times \sum_{\mu\nu\gamma} \sum_{\substack{v_1 v_2 \\ \bar{v}_1\bar{v}_2}} \sum_{\lambda_0\lambda_s} \exp[-\beta\epsilon_{\lambda_0, \lambda_s}^{0, S_K}(v_1, v_2)] [F_{\lambda_{0A}}^{A-M}(v_{1A}, \bar{v}_{1A}) F_{\lambda_s K}^{M-A^*}(v_{2K}, \bar{v}_{2K})]^2$$
$$\times r_{00, s_K\gamma}\{r_{R_I\mu, S_K\gamma}\langle \delta h_{00, R_J'\nu} \delta h_{R_J'\nu, R_I\mu}\rangle + r_{00, R_I\mu}\langle \delta h_{R_I\mu, R_J'\nu} \delta h_{R_J'\nu, S_K\gamma}\rangle - 2r_{R_I\mu, R_J'\nu}\langle \delta h_{00, R_I\mu} \delta h_{R_J'\nu, S_K\gamma}\rangle\}$$
$$\times \left[\left(\frac{1}{\sigma_{AK}}\right)^4 \{\omega - (\Delta E_{e,K} + \Delta E_{v,K})\}^2 - \left(\frac{1}{\sigma_{AK}}\right)^2\right] G[\omega, (\Delta E_{e,K} + \Delta E_{v,K}), \sigma_{AK}] . \tag{16d}$$

In Eqs. (16), $\exp[-\beta\epsilon_{\lambda_0,\lambda_s}^{0,SK}(v_1, v_2)]$ gives the Boltzmann population of the v_1-th level of the λ_0-th vibrational mode of the anion (or cavity) at the origin times the population of the v_2-th level of the molecule of type K at S. The electric dipole integrals $r_{00,0\gamma}$ and $r_{00,s_{\gamma'}}$ $(\equiv\langle\phi_{00}|\boldsymbol{\epsilon}\cdot\mathbf{r}| \times\phi_{s_{\gamma'}}\rangle)$ have to do with transitions in which the excess electron remains localized or is transferred to a neighboring site, respectively. The localized terms are characterized by single-molecule (or cavity) F–C factors $F_{\lambda_0A}^{A,-A*}(v_1, \bar{v}_1)$ and vibrational excitation energies

$$E_{v,K}^0 = \sum_{\lambda_0}\{\epsilon_{\bar{v}_1,\lambda_0}^{0A\gamma,A} - \epsilon_{v_1,\lambda_0}^{00,A}\} .\tag{17}$$

On the other hand the charge transfer terms, in which the electron is transferred from the anion at the origin to the molecule at S, are characterized by F–C factors $F_{\lambda_0A}^{A,-M}(v_1, \bar{v}_1)$ and $F_{\lambda_sK}^{M,-A*}(v_2, \bar{v}_2)$ and the accompanying vibrational excitation energy, $\Delta E_v(v_1, \bar{v}_1, v_2, \bar{v}_2)$ for the normal modes λ_0 and λ_s of the two species involved. $G[\omega, (\Delta E_e +\Delta E_v), \sigma]$ is a Gaussian function centered at $(\Delta E_e +\Delta E_v)$ having width σ. The solvent pair distribution function [e.g., $\rho_{AB}(R, 0)$] entered into the equation by way of replacing the instantaneous "point-wise" solvent structure information by average liquid structure data.

The equilibrium averaged resonance integrals $\langle h\rangle$ and their fluctuations $\langle\delta h\delta h\rangle$ contribute both to the localized and charge transfer components of $I(\omega)$ by modifying the electronic transition dipole integrals as well as the Gaussian shape of the individual lines. For example, the first (localized) terms in $I^{(1)}(\omega)$ and $I^{(2)}(\omega)$ contain $r_{00,0\gamma}r_{R_I\mu,0\gamma}\langle h_{00,R_I\mu}\rangle$ and $r_{00,0\gamma}r_{R_I\mu,0\gamma}\langle\delta h_{00,R_I'\nu}\delta h_{R_I'\nu,R_I\mu}\rangle$ respectively, which modify the intensity factors; whereas $(-1/\sigma_{AK}^2)(\omega-\omega_0)G(\omega,\omega_0,\sigma_{AK})$ and $[(1/\sigma_{AK}^4)(\omega-\omega_0)^2 -(1/\sigma_{AK}^2)]\,G(\omega,\omega_0,\sigma_{AK})$, respectively, alter the individual line shapes.

It is to be noted that the above results are equally applicable to the optical spectroscopy of neutral binary solvents, and the remainder of this section deals with the adaptation of Eqs. (16) to the calculation of a charge-transfer spectrum. Of course the electronic energy levels E_α^0, the nature of the orbitals $\phi_{R_I\alpha}$, and hence the intermolecular electronic couplings $\langle h\rangle$ and $\langle\delta h\delta h\rangle$ may be qualitatively different for neutral molecules. However the formalism presented above is entirely applicable to the case of the electronic spectra of binary mixtures involving neutral species.

The dipole correlation function of Eq. (9) is easily modified to include only charge-transfer transitions of

(initially) neutral species. One important conceptual difference in the CT case is the definition of the reference state, $A_{00}^*|0\rangle$. This is to be interpreted as a vibronic wavefunction for N_D neutral donor molecules and N_A neutral acceptor molecules in their ground electronic states. Since at time $t=0$ the single "excess electron" resides in an orbital of a D-type molecule (at the origin), the sum over K and L in Eq. (9) is restricted to terms in which $L=D$ and $K=A$. In our system the effect of the operator $A_{p_A\alpha}^+ A_{q_D\delta}$ is to transfer the electron from an occupied benzene orbital at site q to a previously unoccupied acceptor orbital of an iodine molecule at site p. (Henceforth the index δ will be used to indicate a donor molecular orbital and the index α will be reserved for acceptor molecular orbitals. Other Greek letters indicate orbitals which may belong to either the donor or the acceptor).

In the charge-transfer case, the F–C factors are expressed in terms of individual vibrational wavefunctions of donor molecules, donor cations, acceptor molecules, and acceptor anions:

$$F_{\lambda_D}^{M-C}(v_D, \bar{v}_D) = {}^M\langle v_D\lambda_D|\bar{v}_D^\delta\lambda_D\rangle^C ,\tag{18a}$$

$$F_{\lambda_A}^{M-A}(v_A, \bar{v}_A) = {}^M\langle v_A\lambda_A|\bar{v}_A^\alpha\lambda_A\rangle^A ,\tag{18b}$$

$$\mathcal{F}_{\delta-\alpha}(v_A, \bar{v}_A, v_D, \bar{v}_D) \equiv F_{\lambda_D}^{M-C}(v_D, \bar{v}_D)F_{\lambda_A}^{M-A}(v_A, \bar{v}_A) .\tag{18c}$$

In the above expressions $|v_D\lambda_D\rangle^M(|v_A\lambda_A\rangle^M)$ is the vibrational wavefunction for the λ_D-th (λ_A-th) mode of a donor (acceptor) molecule having vibrational quantum number $v_D(v_A)$. $|\bar{v}_D^\delta\lambda_D\rangle^C$ is the analogous wavefunction for a donor cation which is derived from the parent molecule by removing an electron from molecular orbital δ. Similarly $|\bar{v}_A^\alpha\lambda_A\rangle^A$ is the vibrational wavefunction for an acceptor anion with an "extra" electron in orbital α. The vibrational energy change ΔE_v accompanying the CT electronic transition is expressed in terms of the fundamental frequencies of donor molecules (ω_{λ_D}), donor cations $(\omega_{\lambda_D}^\delta)$, acceptor molecules (ω_{λ_A}) and acceptor anions $(\omega_{\lambda_A}^\alpha)$:

$$\Delta E_v \equiv \epsilon_v^{\gamma,\alpha\delta} - \epsilon_v^{00} = (\bar{v}_D\omega_{\lambda_D}^\delta + \bar{v}_A\omega_{\lambda_A}^\alpha - v_D\omega_{\lambda_D} - v_A\omega_{\lambda_A}) .\tag{19}$$

The zero-point energy difference is absorbed into ΔE_e. All of the previously made approximations in the derivation of the two-component intensity (e.g., the insertion of solvent distribution functions, the short-time approximation, the truncation of the cumulant average, etc.) are, of course, equally applicable to the CT case. The resulting expressions for the zeroth, first, and second order contributions to the intensity are:

$$I^{(0)}(\omega) = \frac{N_D}{Z_v}\int dS\,\rho_{DA}(S, 0)\sum_{v_Av_Av_Dv_D}\sum_{\delta,\alpha}e^{-\beta\epsilon_v^{00}}\mathcal{F}_{\delta-\alpha}^2(v_A, \bar{v}_A, v_D, \bar{v}_D)\,r_{0D\delta,S_A\alpha}^2\,G[\omega, \Delta E_{\delta-\alpha}(S) + \Delta E_v, \sigma_{DA}] ,\tag{20a}$$

$$I^{(1)}(\omega) = \frac{N_D}{Z_v}\sum_I\sum_{\delta\alpha\mu}\sum_{\substack{v_Av_A\\v_Dv_D}}\iint dR_I\,dS\,\rho_{DI}(R, 0)\rho_{DA}(S, 0)\,e^{-\beta\epsilon_v^{00}}\mathcal{F}_{\delta-\alpha}^2(v_A, \bar{v}_A, v_D, \bar{v}_D)r_{0D\delta,S_A\alpha}$$

$$\times\{r_{R_I\mu,S_A\alpha}\langle h_{0D\delta,R_I\mu}\rangle - r_{R_I\mu,0D\delta}\langle h_{R_I\mu,S_A\alpha}\rangle\}\left(\frac{-1}{\sigma_{DA}^2}\right)[\omega - \Delta E_{\delta-\alpha}(S) - \Delta E_v]\,G[\omega, \Delta E_{\delta-\alpha}(S) + \Delta E_v, \sigma_{DA}] ,\tag{20b}$$

$$I^{(2)}(\omega) = \frac{N_D}{Z_v} \sum_{IJ} \sum_{\substack{\delta\alpha \\ \mu\nu}} \sum_{\substack{v_A \bar{v}_A \\ v_D \bar{v}_D}} \iint d\mathbf{R}'_J \, d\mathbf{R}_I \, dS \, \rho_{DI}(R,0)\rho_{DJ}(R',0) \, \rho_{DA}(S,0)e^{-\beta\epsilon\hat{\mathcal{I}}^0}\mathfrak{F}^2_{\delta-\alpha}(v_A, \bar{v}_A, v_D, \bar{v}_D)r_{0D\delta, S_A\alpha}$$

$$\times \{ r_{R_I\mu, S_A\alpha}\langle \delta h_{0D\delta, R'_J\nu}\delta h_{R'_J\nu, R_I\mu}\rangle + r_{R_I\mu, 0D\delta}\langle \delta h_{R'_J\nu, S_A\alpha}\delta h_{R_I\mu, R'_J\nu}\rangle - 2r_{R_I\mu, R'_J\nu}\langle \delta h_{R'_J\nu, S_A\alpha}\delta h_{0D\delta, R_I\mu}\rangle \}$$

$$\times \left\{ \left(\frac{1}{\sigma_{DA}}\right)^4 [\omega - \Delta E_{\delta-\alpha}(S) - \Delta E_v]^2 - \left(\frac{1}{\sigma_{DA}}\right)^2 \right\} G[\omega, \Delta E_{\delta-\alpha}(S) + \Delta E_v, \sigma_{DA}] \right\} . \tag{20c}$$

Note that the CT transition dipole $r_{0D\delta, S_A\alpha}$, and the electronic energy change, $\Delta E_{\delta-\alpha}(S)$, depend explicitly on the separation S of the donor–acceptor pair. The product over normal modes has been omitted for simplicity. I_2, of course, has just one vibrational mode, and only those vibrational modes of benzene which are excited upon ionization need to be considered.

It is interesting and informative to consider how Eqs. (20) are related to the Mulliken picture. To address this, consider for simplicity, a purely "no-bond" ground state $\psi_N (b = 0)$ and a purely dative excited state ψ_E (b^* = 0). ψ_0 and ψ_1 would be, to a good approximation, single Slater determinant wavefunctions composed of the donor and acceptor molecular orbitals which are occupied in the respective no-bond and dative states. In this approximation the transition dipole would reduce to

$$\mu_{EN} = e\langle \psi_0 | \mathbf{r} | \psi_1 \rangle = e\langle \phi_D | \mathbf{r} | \phi_A \rangle \equiv e\mathbf{r}_{DA} . \tag{21}$$

ψ_0 and ψ_1 differ in that ϕ_D is occupied and ϕ_A unoccupied in the former, and ϕ_A is occupied and ϕ_D unoccupied in the latter. The above "zeroth order" transition dipole is the same as that which appears in Eq. (20a). Suppose now that b and b^* are not zero, i.e., that the unnormalized ground and excited state wavefunctions are, respectively,

$$\psi_N = \psi_0 + b/a\psi_1 ,$$
$$\psi_E = \psi_1 - b^*/a^*\psi_0 . \tag{22}$$

The transition dipole for the CT absorption is now expressed as

$$\mu_{EN} = \left(1 - \frac{b^*b}{a^*a}\right) e\mathbf{r}_{DA} + b/a \, e\mathbf{r}_1 - b^*/a^* \, e\mathbf{r}_0 . \tag{23}$$

The absorption intensity $I(\omega)$ is of course proportional to μ^2_{EN}. Inspection of Eq. (20b) reveals that the terms involving, for example, $I = D$ give contributions of the form

$$r^2_{DA}\langle h_{DD}\rangle - r_{DD}r_{DA}\langle h_{DA}\rangle . \tag{24}$$

(Orbital and site indices have been omitted here for simplicity). Similarly the $I = A$ term of Eq. (20b) contributes

$$r_{DA}r_{AA}\langle h_{DA}\rangle - r^2_{DA}\langle h_{AA}\rangle . \tag{25}$$

Thus it is clear that the quantity $\langle h_{DD}\rangle - \langle h_{AA}\rangle$ is related to the product of the coefficients b^*b/a^*a, and there also exists a relationship between $\langle h_{DA}\rangle$ and b/a and b^*/a^*. Hence the aptly named "resonance integrals" $\langle h_{IJ}\rangle$ play the same sort of role in our theory as the mixing coefficients a and b play in the Mulliken theory. An important distinction to make is that Eqs. (20) involve a *sum* over all donor and acceptor molecular orbitals, including, in principle, those belonging to mole-

cules not directly involved in the electron transfer process. The result of a calculation using Eqs. (20) would therefore be entirely equivalent to calculating the transition dipole using highly correlated (even intermolecularly) ground and excited electronic states. Of course, Eq. (20c) contains higher order corrections, and along with Eqs. (20b) and (20a) contains information about the actual shape of the spectrum, not just the oscillator strength.

IV. APPLICATION OF THE THEORY

In this section the problem of applying Eqs. (20) to the benzene–iodine (Bz:I_2) complex is dealt with. Since the assumed geometry and energetics of the Bz:I_2 complex determine the manner in which the quantities in the intensity expression (e.g., $\Delta E_{\delta-\alpha}$, $\langle h\rangle$, σ, etc.) are chosen or modeled, a discussion of the various interpretations of the existing experimental data is in order here. An examination of Eq. (2a) reveals that, at least in the two-term resonance picture, the existence of nonzero interaction of the donor and acceptor orbitals is necessary to explain the formation of a stable complex. In addition, the smaller the energy difference between the pure resonance states ψ_0 and ψ_1, the larger the charge-transfer stabilization. In light of these facts, the most widely accepted model for the geometry of the Bz:I_2 complex was for a long time the so-called "resting model,"[10] in which the internuclear I_2 axis is parallel to the plane of the benzene ring. In this configuration the overlap between the degenerate benzene $e_{1g}(\pi)$ highest occupied molecular orbital (HOMO) and the accepting I_2 σ_u lowest unoccupied molecular orbital (LUMO) is nonzero. An alternate proposal for the geometry is the "axial model," a C_{6v} symmetry species in which the I_2 axis is perpendicular to the plane of the benzene ring. This model was originally rejected by some workers because it would require transfer of the electron from a lower lying $a_{1u}(\pi)$ benzene molecular orbital in order to satisfy the nonzero interaction criterion, and the correspondingly larger value of $W_1 - W_0$ might result in less ground state stabilization of the complex. There is, however, some evidence that the larger value of the overlap integral in the axial model is enough to outweigh the effects of the unfavorable energy denominator,[15] and that the various electrostatic interactions (for example, the benzene quadrapole–iodine induced dipole interaction) are more favorable in this geometry.[16] In addition, CNDO molecular orbital calculations on the related Bz:Cl_2 complex predict a bound complex for the axial geometry, and a repulsive state in the resting configuration.[17] X-ray studies[18] of crystalline Bz:Br_2 and Bz:Cl_2 indicate axial geometries for these solid state complexes. All in all, the most recent evidence is in

favor of the axial configuration, and the resting model is now generally considered less probable. [For more discussion on the geometry of Bz : I_2, see Ch. 5 of Ref. 2(a), as well as Ref. 19]. Indeed, in the present investigation it is found that better agreement between the experimental and theoretical spectrum is obtained with the axial model than with the resting model. The most important difference between the two, as far as applying our theory is concerned, is the difference in the energies of the respective benzene donor orbitals, the e_{1g} and a_{1u} π orbitals.

With the axial geometry of the complex in mind, the selection of the experimental quantities which are necessary for implementation of our theory can now be discussed. The electronic energy difference $\Delta E_{\delta-\alpha}$ is, following Mulliken and Person, [2(e)] approximated as follows:

$$\Delta E_{\delta-\alpha} = IP_\delta - EA_\alpha - e^2/R_{DA} , \qquad (26)$$

where IP_δ and EA_α are, respectively, the experimental adiabatic second ionization potential of benzene (a_{1u}) and first electron affinity of iodine (σ_u). R_{DA} represents the separation of the positive and negative charge centers in the dative state, which, for the axial model, is expected to be somewhat less than the donor–acceptor center-of-mass distance, due to charge polarization. Equation (26) is an approximation in that all other contributions to the energy difference are ignored (e.g., the quadrapole-induced dipole interactions, quadrapole–quadrapole interactions, solvent effects, etc. Reference 16 contains a discussion of the importance of some of these terms.) The experimental ionization potential (I. P.) of the lower energy benzene π orbital is obtainable, in principle, from the photoelectron spectrum, [20] but is subject to some uncertainty because the band due to this ionization is strongly overlapped by one due to a sigma-orbital ionization. *Ab initio* calculations have indicated that the adiabatic I. P. of the a_{1u} (π) electron is approximately 11.9 eV, [21] based on a comparison of the calculated and observed vibrational structure of the photoelectron spectrum. Even if the assignments of the workers of Ref. 21 are in error, the actual second π-electron I. P. is probably within a few tenths of an eV of this value. The adiabatic electron affinity of I_2 has not been experimentally determined. A potential surface for I_2^- has, however, been constructed by Person[22] on the basis of semiquantitative arguments. He estimates the adiabatic electron affinity as 2.4 ± 0.3 eV. Indeed, one common method of obtaining vertical electron affinities for otherwise difficult-to-form anion species is to plot the CT absorption energy vs the donor ionization potential for a series of complexes with the same acceptor. Person has also constructed potential surfaces for Br_2, Cl_2, and ICl, and the electron affinities he obtains for these halogens agree well with those obtained from the charge-transfer frequencies, a fact which supports the validity of the result obtained for I_2. Calculation of the third term in Eq. (26) entails knowing the charge separation in the dative state, R_{DA}. Reasonable estimates of the size of this quantity can be made with the help of experimentally determined dipole moments[23] of ground state Bz : I_2. Assuming that the induced dipole moment of the

pure no-bond state is zero, the observed dipole moment μ_N, as Mulliken has shown, is related to that of the pure dative state μ_1, according to

$$\mu_N = (b^2 + ab\, S_{01})\mu_1 , \qquad (27)$$

where $\mu_1 = eR_{DA}$. With Mulliken's estimates of $a = 0.97$, $b = 0.17$, $S = 0.1$; and experimental values of μ_N in the range $0.6-0.7$ D, the equilibrium value of R_{DA} is determined to be in the range $2.8-3.3$ Å. It is important to note that both the experimental dipole moment and the quantity $(b^2 + ab S_{01})$ are subject to great uncertainty, so that the actual values of R_{DA} may very well lie outside of this estimated range.

The vibrational energies and F–C factors which appear in Eqs. (20) are also experimentally unavailable quantities. Von Niessen *et al.* in Ref. 21 determined in their theoretical calculation that only the ν_2 vibrational mode of benzene, with $\omega = 990$ cm^{-1}, is excited upon ionization of the benzene $a_{1u}(\pi)$ orbital. The required benzene–benzene cation F–C factors in this work are taken from the calculated vibrational progression of the $a_{1u}(\pi)$ band in Ref. 21. With Person's[22] estimates of the bond length and vibrational frequency of $I_2^-(r_e = 3.02$ Å, $\omega_e = 128$ cm^{-1}), along with those of the parent molecule[24] $(r_e = 2.67$ Å, $\omega_e = 215$ cm^{-1}), the I_2/I_2^- F–C factors can be calculated from the overlap of the corresponding simple harmonic oscillator wavefunctions. Besides the approximations inherent in the harmonic oscillator model, additional uncertainty is introduced by the uncertainty in the bond length and vibrational frequency of the ionized acceptor. However, it was found that only the first few vibrational states of the molecule and the anion contribute to the F–C intensity. Because the vibrational energies are quite small relative to the entire CT linewidth, small changes in r_e and ω_e would not grossly alter the shape of the predicted spectrum.

While the vibrational frequencies, the F–C factors, the ionization potential, and the electron affinity can be chosen with some confidence, the remaining quantities in the intensity expression are not so easily handled, and we are forced to postulate convenient models. The necessary solvent structure information, in the form of the pair distribution function $\rho_{IJ}(R, 0)$, is not experimentally available. Physically, $\rho_{IJ}(R, 0)$ is the number density of J-type molecules at point R, given that there is an I-type molecule at 0. For a pure solvent ρ_{II} would be zero at $R = 0$, have a maximum at some value of R corresponding to the near-neighbor distance in the liquid, and would tend to a constant value (equal to the number density of the solvent) as R goes to infinity. It should be noted however, in the first and second order intensity expressions of Eqs. (20), that the pair distribution functions are multiplied by quantities which are expected to be rapidly decaying functions of the intermolecular distance, namely $\langle h \rangle$ and $\langle \delta h \delta h \rangle$, respectively. Therefore, in the absence of more exact information, a convenient (and, as we shall see, temporary) approximation to ρ_{IJ} is a simple delta function centered on the appropriate near-neighbor distance:

$$\rho_{DA}(S, 0) = N_A\, \delta(S_{DA} - S) , \quad \rho_{DD}(S, 0) = N_D \delta(S_{DD} - S) . \qquad (28)$$

S_{DA} and S_{DD} are the equilibrium donor–acceptor and donor–donor center-of-mass separation, respectively. (Recall that there is a donor molecule at the origin). For dilute solutions of the donor and acceptor species in an inert solvent, the delta function model is probably not too unreasonable. The real justification for the approximation, however, depends on the fact that the resonance and fluctuation integrals, being dependent upon the overlap of charge densities of different molecules, are expected to decrease rapidly with increasing intermolecular distance.

The transition dipoles, resonance and fluctuation integrals, and σ are potential adjustable parameters which can be used to fit the theory to the experimental results. Many of the possible terms can, however, be rigorously neglected on the basis of symmetry considerations. For example, there exist certain nonzero transition dipoles $r_{DD}*$, corresponding to strongly allowed intramolecular benzene electronic transitions, which could, in principle, contribute to the intensity in the first and second order expressions of Eqs. (20). These are found, however, to be multiplied by resonance (or fluctuation) integrals which would be zero on the basis of symmetry considerations. To be specific, the allowed benzene excitations which might be considered arise from a configuration in which a π electron is promoted from the e_{1g} HOMO to the e_{2u} LUMO. Since the benzene e_{2u} orbital and the iodine σ_u orbital belong to different irreducible representations of the C_{6v} symmetry group, the resonance integral h_{D*_A} which would multiply the intradonor transition dipole $r_{DD}*$ in the first order expression of Eq. (20a) is rigorously zero. Of course, when all of the molecular orbitals of the donor and acceptor are considered, there may be found terms in which the contribution of intradonor transition dipoles is not symmetry forbidden. We have, however, restricted our atten-

tion to those transitions which would contribute to the intensity in the same energy region as the experimental spectrum. This means that the sums over δ and α in Eqs. (20) are to be restricted to include only those terms in which δ is a benzene $a_{1u}(\pi)$ orbital and α is an iodine σ_u orbital. It is also possible to show, on the basis of energetic considerations and symmetry arguments, that intra-acceptor transition dipoles $r_{AA}*$ do not contribute ($r_{AA}*$ is interpreted here as the transition dipole for electronic absorption of the I_2^- ion).

The second order contribution to the absorption intensity, Eq. (20c), can be greatly simplified by using statistical arguments. The approximation to be used here is

$$\langle \delta h_{R_I R'_J} \delta h_{S_K S'_L} \rangle = 0 , \tag{29}$$

unless either $R_I = S_K$ and $R'_J = S'_L$ or $R_I = S'_L$ and $R'_J = S_K$. In other words, correlations of the motion of three or four different molecules are small compared to those of two different molecules. The terms involving only one molecule have been absorbed into the inhomogeneous broadening factor, σ_{IJ}. With this approximation and the previously discussed symmetry considerations, the complicated expression in Eq. (20c) is greatly simplified. The quantity σ_{IJ}, which represents the magnitude of the inhomogeneous broadening, is essentially an adjustable parameter used to smooth the theoretical spectrum to conform to the experimentally observed room-temperature line shape, which is structureless. Intuitively, since vibrational structure has been observed in some low temperature work, we expect σ_{IJ} to have a certain temperature dependence.

With the simplifications discussed above the intensity expressions reduce to

$$I^{(0)}(\omega) = \frac{N_D N_A}{Z_v} r_{\delta-\alpha}^2 \sum_{\bar{v}_D v_A \bar{v}_A} e^{-\beta v_A \omega_A} \mathcal{F}_{\delta-\alpha}^2(0, \bar{v}_D, v_A, \bar{v}_A) G[\omega, (\Delta E_{\delta-\alpha} + \Delta E_v), \sigma_{DA}] , \tag{30a}$$

$$I^{(1)}(\omega) = \frac{N_D^2 N_A}{Z_v} r_{\delta-\alpha} \sum_{\bar{v}_D v_A \bar{v}_A} e^{-\beta v_A \omega_A} \mathcal{F}_{\delta-\alpha}^2(0, \bar{v}_D, v_A, \bar{v}_A) r'_{\delta-\alpha} h_{DD} \left(\frac{-1}{\sigma_{DA}^2}\right) (\omega - \Delta E_{\delta-\alpha} - \Delta E_v) G[\omega, (\Delta E_{\delta-\alpha} + \Delta E_v, \sigma_{DA}] , \tag{30b}$$

$$I^{(2)}(\omega) = \frac{N_D^2 N_A^2}{Z_v} r_{\delta-\alpha}^2 \sum_{\bar{v}_D v_A \bar{v}_A} e^{-\beta v_A \omega_A} \mathcal{F}_{\delta-\alpha}^2(0, \bar{v}_D, v_A, \bar{v}_A) \delta h_{DA}^2 \left[\left(\frac{1}{\sigma_{DA}}\right)^4 (\omega - \Delta E_{\delta-\alpha} - \Delta E_v)^2 - \left(\frac{1}{\sigma_{DA}}\right)^2\right] G[\omega, (\Delta E_{\delta-\alpha} + \Delta E_v), \sigma_{DA}] . \tag{30c}$$

In these expressions $r_{\delta-\alpha}$ is the transition dipole for charge transfer from the benzene $a_{1u}(\pi)$ orbital to the iodine σ_u orbital, evaluated at the equilibrium donor–acceptor distance, S_{DA}, whereas $r'_{\delta-\alpha}$ is the same quantity evaluated at a donor–acceptor distance equal to $S_{DD} - S_{DA}$. h_{DD} is the resonance integral $\langle h_{0_D\delta}, s_{DD\delta} \rangle$ evaluated at the equilibrium donor–donor distance, S_{DD}. The need to consider a second transition dipole, $r'_{\delta-\alpha}$, arises from the possibility of the electron first undergoing a "hop," via h_{DD}, to a near neighbor benzene molecule, and then undergoing dipole absorption to the iodine molecule at S_{DA}. The symbol δh_{DA}^2 is used to represent $\langle \delta h_{S_{DA}\alpha, S_{DD}\delta}^2 \rangle$, again evaluated at the appropriate intermolecular separations. The sum is over vibrational quantum numbers of the benzene cation, iodine molecule, and iodine anion; and it has been assumed that the benzene molecule is initially in its ground vibrational state. The sum of the three contributions to the intensity can be rewritten in a manner which emphasizes the adjustable parameters in the theory:

$$I(\omega) = I^{(0)}(\omega) + I^{(1)}(\omega) + I^{(2)}(\omega) , \tag{31a}$$

$$I(\omega) = K \sum_{\bar{v}_D v_A \bar{v}_A} e^{-\beta v_A \omega_A} \mathcal{F}_{\delta-\alpha}^2(0, \bar{v}_D, v_A, \bar{v}_A) G[\omega, (\Delta E_{\delta-\alpha} + \Delta E_v), \sigma_{DA}]$$

$$\times \left\{ 1 - C_1(\omega - \Delta E_{\delta-\alpha} - \Delta E_v) + C_2 \left[\left(\frac{1}{\sigma_{DA}}\right)^2 (\omega - \Delta E_{\delta-\alpha} - \Delta E_v)^2 - 1\right] \right\} , \tag{31b}$$

where the adjustable parameters are

$$K = \frac{N_D N_A}{Z_v}\, r^2_{b-\alpha} ,\qquad (32a)$$

$$C_1 = N_D \left(\frac{\kappa h_{DD}}{\sigma^2_{DA}} \right) ,\qquad (32b)$$

$$C_2 = N_D N_A \left(\frac{\delta h^2_{DA}}{\sigma^2_{DA}} \right) ,\qquad (32c)$$

$$\kappa = \frac{r'_{b-\alpha}}{r_{b-\alpha}} .\qquad (32d)$$

The multiplicative constant K is to be used as a scaling factor for the purpose of comparing the intensities of the experimental and theoretical spectra, so that the only remaining adjustable parameters are then C_1, C_2, and σ_{DA}. The parameter κ is absorbed into C_1. However, the distance between the donor and acceptor molecules are similar in $r'_{b-\alpha}$ and $r_{b-\alpha}$, so κ is probably close to unity.

It was found, however, at this stage of the calculation that Eq. (31b) could not be made to fit the experimental results with any reasonable combination of the above three adjustable parameters, the defect being that the predicted line shape was much too narrow. This deficiency was found to be due primarily to our nearest neighbor delta-function approach to modeling the benzene–iodine pair distribution function. Physically one important reason for the very broad nature of typical CT spectra has to do with the difference in the shapes of the ground and excited state intermolecular potential energy surfaces. As mentioned above, the resultant Franck–Condon envelope is not broad enough to explain the observed line shape. There must, therefore, be some other effect which contributes to the width of the spectrum. From heats of formation measurements $(-\Delta H_f \simeq 0.06\ \mathrm{eV})$[25] and a consideration of the largely "no-bond" nature of ψ_N, it is clear that the ground state potential energy surface of Bz:I_2 should have a rather shallow potential minimum. On the other hand, the excited state of the complex, being mostly ionic, is expected to be more tightly bound. On the basis of an empirical relation of McConnell et al.[26] the dissociation energy of the excited state of Bz:I_2 is predicted to be about 3.1 eV. This large difference in the depths of the two potential wells, coupled with the reasonable assumption that the minimum in the ground state potential surface occurs at a larger intermolecular separation than does the minimum in the excited state potential surface, accounts for the large half-widths observed for CT spectra.

A modification of the original method of calculation is introduced at this point. This modification is based on experimental observation, and is designed to improve upon our crude model of the solution structure. This improvement necessitates a more explicit consideration of the intermolecular Bz:I_2 degrees of freedom. By considering the change in the number of rotational, translational, and vibrational degrees of freedom upon complex formation, it is easy to show that there are five intermolecular vibrational modes for the Bz:I_2 species. Because the complex is rather weakly bound, the fundamental frequencies of the "donor–acceptor" vibrations

are expected to be quite small compared to the stretching and bending frequencies of ordinary chemical bonds. Indeed, very low energy (~ 50–$200\ \mathrm{cm^{-1}}$) infrared absorption has been reported for many CT complexes,[27] including Bz:I_2,[28,23(a)] and has been attributed to a so-called "donor–acceptor stretch." The workers of Ref. 23(a), however, have explained the broad absorption of Bz:I_2, in the spectral region 50–100 $\mathrm{cm^{-1}}$, in terms of collisionally-induced dipole moments arising from contact complexes. They contend that the absorption can be completely accounted for without postulating the existence of any stable complex. Perhaps the most convincing argument in favor of this interpretation is the fact that, on the time scale of a far infrared absorption experiment, the CT complex is probably too short-lived for the vibrations of the stable species to be observed. (Relaxation studies of weak π complexes indicate lifetimes of the order of $10^{-12}\ \mathrm{s}$.[29]) However, vibrational structure has been reported in the (shorter time scale) electronic CT bands of some complexes of hydrocarbons with substituted benzoquinones,[31(a)] and of aromatic nitrocompounds with aromatic amines.[31(b)] The vibrational spacing of these solution phase, room temperature spectra was 150–200 $\mathrm{cm^{-1}}$, and has been attributed by the authors of Refs. 30 to a donor–acceptor stretching mode. It should be noted, furthermore, that Brownson and Yarwood[31] found (by subtraction of the pure benzene spectrum) that absorption due to Bz:I_2 "collisions" occurs at higher frequency than that of Bz:Bz "collisions." A binary collision mechanism would predict the opposite ordering, since the absorption frequency should vary as the reciprocal square root of the reduced mass. The existence of an attractive interaction between the benzene molecule and the iodine molecule would account for this apparent anomaly. For a more complete discussion of alternative interpretations of the experimental results, see Chaps. 3 and 7 of Ref. 2(b).

We emphasize here that, even if the low frequency absorption band of Bz:I_2 is explainable without assuming the existence of a stable complex, a low frequency ir-active vibrational mode in which the donor–acceptor distance changes is *required* by a normal mode analysis of the complex, regardless of whether the complex is sufficiently long-lived for this vibration to give rise to observable spectroscopic structure. In a sense then, the modification of Eq. (31b) is based on the postulate of a donor–acceptor stretching mode in the frequency range 50–100 $\mathrm{cm^{-1}}$. To provide some guidance in estimating the frequency of this mode, a force constant k based upon a Lennard-Jones 6–12 potential was calculated. In this approximation k is given by 57 ϵ/σ^2, where ϵ is the potential energy at the minimum and σ is related to the size of the complex. The experimentally measured heat of formation of the complex was used to estimate the well depth ϵ, and the assumed values of the Lennard-Jones parameter σ were based on the van der Waal's radii of benzene and I_2 appropriate to the axial geometry of the complex. By using $\sigma_{Bz} = 3.40\ \text{Å}$ (the interplanar separation in graphite) and $\sigma_{I_2} = 4.98\ \text{Å}$, the Bz:$I_2$ stretching frequency was estimated to be about 40 $\mathrm{cm^{-1}}$. The average of σ_{Bz} and σ_{I_2} compares well with the center of mass separation of 4.80 Å which is obtained by ex-
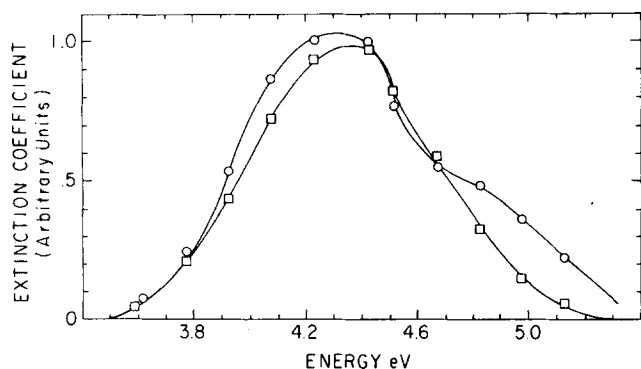
FIG. 1. Calculated (□) and experimental (○) benzene–iodine charge-transfer spectrum.

trapolating the crystal structure data of $Bz:Br_2$ and $Bz:Cl_2$.[16(a)] Similar calculations were also performed for the more stable CT complexes of pyridine and trimethylamine with iodine, and it was found that the resultant Lennard-Jones force constants compare well with those calculated from the experimentally[32,27] determined stretching frequencies. The Lennard-Jones force constants for the pyridine and trimethylamine complexes are approximately 3×10^4 dyn/cm and 5×10^4 dyn/cm, respectively, compared to the corresponding experimental force constants of 3.5×10^4 dyn/cm and 24×10^4 dyn/cm.[27,32] The experimental force constants here are calculated from $k = 4\pi^2 \nu^2 \mu$, where μ is the reduced mass computed as if the complex were a diatomic molecule, and ν is the donor–acceptor stretching frequency in s^{-1}. In summary, then, the force constant used to introduce a thermally distributed range of donor–acceptor intermolecular distances into the line shape calculation is a parameter whose exact value is not known, but which can be estimated with some confidence.

The procedure of averaging over the $Bz:I_2$ intermolecular distance consists of first calculating the intensity spectrum $I_s(\omega)$ as a function of donor–acceptor distance and then averaging this profile over a distribution function governing this intermolecular distance. We let S and S_{eq} represent the instantaneous and equilibrium values, respectively, of the distance between the centers of mass of the donor and acceptor in the ground electronic state, while R and R_{eq} are the corresponding distances between the charge centers in the hypothetical pure "dative" state. In view of the large polarizability of the iodine molecule anion, it is most likely, in the axial configuration, that R_{eq} is less than S_{eq}. Because of the small overlap of the donor and acceptor orbitals, the transition dipole $r_{b-\alpha}$ which multiplies the entire intensity expression of Eq. (31b) is approximately proportional to the charge separation R [see Eq. (5) and Ref. 33]. This is the same charge separation which enters into the electronic energy difference, $\Delta E_{b-\alpha}$, in Eq. (26). With the assumption that the difference between R and S remains constant as the complex vibrates, the averaged intensity $\langle I(\omega) \rangle$ is given by

$$\langle I(\omega) \rangle \propto \int \exp[-\beta(1/2k)(R - R_{eq})^2] R^2 I_R(\omega) \, dR \qquad (33)$$

In this expression $\beta = 1/k_B T$, where k_B is the Boltzmann constant and $T \sim 300$ K, and $k = 4\pi^2\nu^2\mu$ is the force con-

stant. The force constant was computed using a "diatomic" molecule reduced mass μ of 10^{-22} g, and frequencies $\nu = \omega c$ corresponding to $\omega = 30$–100 cm^{-1}. The averaging procedure consists of calculating a spectrum $I_R(\omega)$ at a particular value of R according to Eq. (31b), weighting it by the square of the transition dipole and the classical harmonic oscillator intermolecular distribution function, and then summing up the contributions from all the values of R. It should be mentioned that Eq. (33) is entirely equivalent to taking the pair distribution function ρ_{DA} to be a Gaussian of width $(\beta k)^{-1/2}$, instead of making the (rather severe) delta function approximation. The final expression, Eq. (33), represents a much more realistic description of the solvent structure, and indeed was found to be capable of predicting the broad experimentally observed line shapes.

V. RESULTS AND DISCUSSION

The results of our calculation are shown in Fig. (1). The experimental spectrum is from Ref. 6, and presumably contains no contributions from intramolecular electronic transitions. The optimal values of the adjustable parameters were $C_1 = 1$ eV^{-1}, $C_2 = 5$, and $\sigma_{DA} = 0.05$ eV. The force constant which seemed to yield the best agreement with the experimental spectrum was that pertaining to a stretching frequency of about 40 cm^{-1}, and the temperature was taken from experiment to be 300 K ($k_B T \approx 0.025$ eV). Let us turn now to a discussion of the magnitude of the adjustable parameters and the sensitivity of the calculated results to them.

The parameter C_1 has in it information concerning the resonance integral h_{DD}, whereas C_2 contains the off-diagonal fluctuation integral δh_{DA}. The results of the calculations were found to be quite insensitive to the value of C_1 employed. In fact, C_1 could be set equal to zero without any noticeable effect on the spectrum; hence the resultant value of C_1 is very much uncertain. The reason for this insensitivity is easy to see from Eq. (31b). The effect of the second term in the braces is to increase the intensity on one side of the Gaussian centered at a particular value of $\{\bar{v}_D, v_A, \bar{v}_A\}$ and to subtract intensity from the other side. This effect is then cancelled by the intensities from Gaussians centered at neighboring values of $\{\bar{v}_D, v_A, \bar{v}_A\}$, thus leading to very little influence of C_1. The effect of δh_{DA}^2 was found to be more important. If C_2 is made an order of magnitude smaller than the optimal value, the calculated spectrum becomes too narrow; if it is increased by an order of magnitude the spectrum becomes very broad and exhibits a series of "interference peaks," or oscillations. The value of the inhomogeneous broadening parameter σ_{DA} was adjusted to yield a sufficiently broad and structureless spectrum. The primary role of σ_{DA} is to smooth out the vibrational structure which would be present in the absence of any inhomogeneous broadening. For two Gaussians of width σ separated by frequency ω (the vibrational frequency), it can be shown that the value of σ necessary to entirely smooth out the structure in the region between the two peaks is given by $\sigma = \omega/(8 \ln 2)^{1/2}$. Other workers have estimated the contribution of coordinate fluctuations to the linewidth to be on the order of $k_B T \ln 2$,[34] or about 0.02 eV. Our

value of 0.05 eV is somewhat higher, but includes of course other contributions to the linewidth, for example, the instrumental broadening (the workers of Ref. 6 report a resolution of about 0.02 eV in the spectral region of interest). In the earlier work of Ref. 1, a value of $\sigma = 0.026$ eV was found to yield an optimal fit of the spectra of excess electrons both in low temperature (77 K) anthracene and in ethanol glasses. The larger value of σ_{DA} found in this work is reasonable in view of the higher temperature and the fact that we are dealing here with liquid phase spectra. The earlier mentioned fact that vibrational structure has been observed in some low temperature spectra of $Bz:I_2$ is consistent with this qualitative interpretation of the temperature dependence of σ_{DA}. By assuming one donor molecule and one acceptor molecule surrounded by an inert solvent, Eq. (32c) is used to obtain $\delta \hbar_{DA}^2 = 0.0125$ eV^2. This value is two orders of magnitude larger than the one used in Ref. 1 to fit either the anthracene or ethanol excess-electron spectra, but again this is reasonable in view of the fact that fluctuations in the solvent molecules' coordinates, which give rise to fluctuations in the matrix elements of H_e, become more important in the higher temperature solution phase work.

In addition to the parameters of Eqs. (31), it was necessary to assume some value of the force constant k and the equilibrium charge separation R_{eq} which appear in Eq. (32). The calculated line shape was found to be rather insensitive to changes in the force constant corresponding to donor–acceptor stretching frequencies in the range 30–100 cm^{-1}. The final value used, $k = 5.7 \times 10^4$ dyn/cm, corresponds to a vibrational frequency of 40 cm^{-1}, and a benzene–I_2 center of mass separation of roughly 4.6 Å. (A consideration of the center of mass separation enters into the calculation through Lennard-Jones parameter which occurs in the force constant.) It was found that the exact value of the assumed force constant was not critical to our computations. On the other hand, both the width and the position of the calculated spectrum were highly sensitive to the value of the charge separation R_{eq}. The equilibrium charge separation which gave the best fit was $R_{eq} = 2.6$ Å. The fact that R_{eq} is estimated to be very much less than S_{eq} is not suprising, since a crude calculation based on the polarizability of I_2 molecule (that of I_2^- would be even higher) indicates a very large charge polarization. The value of $R_{eq} = 2.6$ Å is somewhat shorter than the range of values estimated from dipole moment measurements, as discussed in Sec. IV. However, if the second I.P. of benzene happened to be overestimated by as little as 0.4 eV (or if the E.A. of I_2 were underestimated by the same amount) this would cause the optimal value of R_{eq} to be about 0.3 Å too small. Our ability to estimate R_{eq} from the fitting procedure is therefore limited by the uncertainties in the ionization potential and electron affinity. The slight difference in the experimental and theoretical absorption maxima, as seen in Fig. 1, could be accounted for by an error in the I.P. or E.A. as small as 0.05 eV, and is not indicative of any essential inadequacy of our model.

As seen in Fig. 1 the calculated spectrum differs from the experimental one primarily in the short wavelength region, where the theory fails to predict the existence of a shoulder at about 4.8 eV or 2600 Å. It is important to note that this is a region in which uncomplexed benzene absorbs strongly, and most workers have not subtracted the benzene absorption so that absorption due to the CT complex in this region could be seen. Ham, Platt, and McConnell[6] have performed such a subtraction, and in their paper, speculate on the nature of the transition which occurs at 2600 Å. They consider the possibility that the shoulder is due to the $^1A_{1g} - ^1B_{2u}$ or $^1A_{1g} - ^3E_{1u}$ electronic transition of benzene. The former is orbitally forbidden and the latter is spin forbidden. Ham et al. postulate that complex formation could break down the symmetry selection rules to allow the singlet–singlet transition to take place, or, alternatively, the presence of the external heavy atom (the halogen) could cause the singlet–triplet absorption to be allowed. As McGlynn mentions in his review, [2(f)] the interpretation in terms of a singlet–triplet excitation is not very plausible, since these types of transitions are invariably much less diffuse than CT bands, and, even in the presence of an intramolecular heavy atom, are considerably less intense. The workers of Ref. 6 admit the possibility of experimental errors (in spectral measurements as well as in the equilibrium constant used to calculate the concentration of free benzene) affecting the 2600 Å region of the reported spectrum, but conclude that the shoulder is probably not an artifact, but a real transition of the $Bz:I_2$ complex.

It is useful then to speculate on the reasons for the failure of our calculation to reproduce the 2600 Å shoulder. The lower intensity peak which comprises the shoulder occurs at an energy approximately 0.5 eV higher than the principal maximum in the spectrum. It seems possible to explain the second peak in terms of a different combination of the donor ionization potential and acceptor electron affinity. Although gas phase electronic spectra of I_2^- have apparently not been obtained, absorption spectra of I_2^- defects in alkali halide crystals, [35] as well as valence bond calculations, [36] indicate the existence of an excited state of I_2^-, of symmetry $^2\Sigma_g^+$, which lies about 3.1–3.2 eV above the $^2\Sigma_u^+$ ground state of the anion. The transfer of an electron from an $e_{1g}(\pi)$ orbital of benzene (I.P. = 9.2 eV) to the iodine molecule to form the $^2\Sigma_g^+$ excited state of the anion would indeed give rise to a peak about 0.4–0.5 eV higher in energy than the principle absorption maximum. The major weakness of this explanation is the fact that the I_2^- excited state belongs to the "shake-up" configuration $(\sigma_g)^1(\pi_g)^4 \times (\pi_g)^4(\sigma_u)^2$, so that this charge-transfer process would not be very probable. Indeed, all of the low lying excited states of I_2^- are shake-up states, so that explanation of the 2600 Å shoulder in terms of another electron affinity of I_2 is not probable. Charge transfer from the benzene e_{2g} sigma orbital whose I.P. occurs near that of the $a_{1u}(\pi)$ orbital seems like an attractive possibility. Unfortunately the transition dipole r_{DA} for such a process is zero by symmetry. (In addition, if the workers of Ref. 21 are correct, the sigma electron I.P. is *lower* than the $a_{1u}(\pi)$ I.P. by a few tenths of an eV and the Franck–Condon profile of the sigma electron ionization

is quite narrow. Thus it would be difficult to account for both the width and the position of the shoulder in terms of a sigma electron ionization.) It seems unlikely that we can explain the second peak at 4.8 eV by postulating some other combination of donor and acceptor orbitals.

In view of the uncertainties in the work of Ref. 6 and the lack of experimental corroboration, the inability of the theory to reproduce the shoulder observed in the spectrum of Ham, et al. is probably not indicative of any major flaws in the theoretical approach. The important part of the line shape is seen to be reproduced quite well with reasonable values of the parameters. Unfortunately the calculation was found to be rather insensitive to the values assumed for the resonance integral $\langle h \rangle$. It is encouraging to note, however, that calculations involving exciton migration,[37] using quantities similar to our so-called resonance and fluctuation integrals have shown that at room temperature the fluctuations $\langle \delta h^2 \rangle$ are much more important than $\langle h \rangle$. In conclusion then, this work provides further support for the validity of the theoretical approach of Refs. 1 and 9.

ACKNOWLEDGMENTS

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