PHOTO-INDUCED CHARGE TRANSFER

A CRITICAL TEST OF THE MECHANISM AND RANGE OF BIOLOGICAL ELECTRON TRANSFER PROCESSES

J. J. HOPFIELD, *Joseph Henry Laboratories of Physics, Princeton University, Princeton, New Jersey 08540, and Bell Laboratories, Murray Hill, New Jersey 07974*

ABSTRACT The vibronic coupling theory of electron tunneling between biomolecules requires that *all* such tunnelings involve vibronic coupling, finds temperature dependence to tunneling at finite temperatures, and predicts relatively short tunneling distances. This theory might be expected to apply to most electron transfers involved in the membrane-bound electron transfer reactions of photosynthesis and oxidative phosphorylation. This paper calculates the properties of a weak charge-transfer optical absorption band, whose predicted characteristics are a direct and simple consequence of the model that describes vibronically coupled tunneling. The new absorption band provides the basis for a critical experimental test of the constructs and parameters of the tunneling theory. If the tunneling theory is valid, the oscillator strength of such bands will be the most reliable measure of the tunneling matrix element and of the distance between the sites exchanging an electron.

INTRODUCTION

Understanding the physical mechanism by which electrons are transferred between biological molecules is essential to a fundamental understanding of photosynthesis or oxidative phosphorylation. The relative rates of various competing electron transfer reactions are central to understanding how photon or oxidative energy can be converted into useful chemical energy. The distance over which electrons can be transferred and the selectivity of the electron transfer process are dominant elements in the logic of the structure of the photosynthetic apparatus. Electron transfer reactions are the simplest chemical reactions from the standpoint of physics, and thus represent one of the few cases where an important absolute reaction rate might be understood in a complex biological system.

Many of the electron transfer steps in photosynthesis take place between a donor molecule and an acceptor molecule relatively well fixed with respect to each other (at least at the time of transfer). If the distance of separation is "reasonable," tunneling is a possible means of electron transfer, and several important experimental results have been interpreted as suggesting that tunneling, at least at low temperatures (1, 2), is the mechanism for electron transfer to and from bacteriochlorophyll. The electron tunneling problem between two fixed sites, unlike the electron tunneling probblem between two metals usually treated in quantum mechanics texts, necessitates the use of molecular vibrations to conserve energy. As a result, the tunneling transfer rate is in theory temperature-dependent, and will often have a thermally activated form at higher temperatures (3, 4).

While the vibronically coupled tunneling description can quantitatively account for the rate and temperature dependence of some simple biological electron transfers (4, 5), the direct evidence that the description is correct is less than compelling. The theory in its simplest form contains three unknown parameters, fit by using the zero temperature transfer rate, the high temperature activation energy, and the characteristic temperature below which the behavior is temperature-independent. There are no leftover internal checks for quantitative consistency, and no strong qualitative checks on the concepts introduced in the vibronic calculation, nor is the simplest form necessarily quantitatively accurate.

A new charge-transfer optical absorption band has been recently noted as a necessary theoretical consequence of the vibronically assisted tunneling description. This band is the most diagnostic of three independent methods of testing the theory (5). Absorption in this band takes the electron from one molecule to the other. This paper calculates the theoretical properties of the infrared absorption band in terms of the parameters and concepts already part of the tunneling theory. The oscillator strength of this band directly determines the tunneling matrix element. The location and shape of the absorption band are a consequence of the vibronic coupling, and yield the vibronic parameters important to tunneling. The study of this absorption will provide qualitative and quantitative critical examination of vibronically assisted tunneling. The theoretical description of thermally activated (vibronically coupled) tunneling and all the structural and rate implications drawn from this theory (4, 5) must stand or fall on the basis of experiments that check these theoretical ideas.

THE BASIS OF THE VIBRONICALLY ASSISTED TUNNELING DESCRIPTION

An isolated donor molecule d has two electronic states relevant to electron transfer (4). One electronic state describes the ground electronic state of $n_d + 1$ electrons on the donor molecule before it has transferred an electron. There are many vibrational states i of this ground electronic state, and a particular molecular state of this ground electronic configuration will be described by the subscripts $d + 1, i$. The other relevant electronic state is the ground state of a donor molecule having one fewer electron. Again, there will be many vibrational states, and in this case a typical vibronic state will be denoted by the subscripts d, j.

The approximation of factoring the wave function for the electronic and nuclear coordinates is adequate to many problems of molecular and solid state physics (6). In this approximation we can think of the states as, $\phi_{d+1}\psi_{d+1,i}$ and $\phi_d\psi_{d,j}$, where ϕ_{d+1} and ϕ_d are electronic wave functions and $\psi_{d+1,i}$ and $\psi_{d,j}$ are vibrational wave functions. The quantity

$$D_d(E) \equiv \sum_{i,j}\sum P_{d+1,i} \mid < \psi_{d+1,i} \mid \psi_{d,j} > \mid^2 \delta(E_{d+1,i} - E_{d,j} - E) \qquad (1)$$

becomes the analogue of the density of electronic states associated with the occupancy of the donor by an extra electron. $E_{d+1,i}$ is the total energy of the states having $n_d + 1$ electrons and vibrational wave function $d + 1, i$, and $E_{d,j}$ similarly, *mutatis mutandis.* $P_{d+1,i}$ is the thermal probability of the occupation of vibrational state i when the extra electron is present.

$D_d(E)$ has the appropriate normalization associated with a single electron level, namely

$$\int D_d(E)\mathrm{d}E = 1. \qquad (2)$$

Further, if there is no vibronic coupling,

$$D_d(E) = \delta(E_{d+1} - E_d - E), \qquad (3)$$

and is a δ-function at the energy of binding of the $n_d + 1^{st}$ electron. The difference between the electronic states between ϕ_{d+1} and ϕ_d can be thought of by saying that ϕ_{d+1} has an extra electron in a particular orbital. $D_d(E)$ can be thought of as the density of states of this occupied single electronic level, which in some sense no longer has a single sharp energy because of the vibronic interactions. The utility of the point of view is that simple transition calculations of the present type can be made in a one-electron approximation in the presence of vibronic coupling if $D_d(E)$ is used as the density-of-states of the electronc level (3).

Similarly, an acceptor also has two relevant states, one with n_a electrons and the other with $n_a + 1$. For adding an electron to the acceptor, the initial thermal population that must be summed over has only n_a electrons present, so the relevant average is

$$D'_a(E) \equiv \sum_{i,j}\sum P_{a,j} \mid < \psi_{a+1,i} \mid \psi_{a,j} > \mid^2 \delta(E_{a+1,i} - E_{a,j} - E). \qquad (4)$$

This is the effective density of state for adding an electron to the acceptor. In a one-electron description, this extra electron will be put into the first vacant orbital.

The approximations involved in the vibronic wave functions used for calculating the spectral function, $D_d(E)$ and $D'_a(E)$, are the ones conventional in calculating tunneling in other circumstances and in calculating the shape of optical absorption lines. The factored wave function approximation is not exact, particularly in the spatial tails of the electron wave function important to tunneling, but has often proved to contain the essence of the vibronic coupling problem (6).

Let T_{da} be the matrix element of the electronic Hamiltonian H for electron transfer, i.e.

$$T_{da} \equiv \; <\phi_{d+1}\, \phi_a \mid H \mid \phi_d\, \phi_{a+1}>. \qquad (5)$$

In a one-electron description, T_{da} will correspond to the matrix element for taking an electron from the highest occupied donor orbital to the lowest unoccupied acceptor orbital. T_{da} has exactly the same meaning for this two-site problem that the Huckel matrix element β has in molecular orbital calculations (7). For optical absorption, the matrix elements of the electric dipole operator ex are needed. The intuitive forms of these matrix elements are

$$<\phi_{d+1}\,\phi_a\,|\,\mathrm{ex}\;|\,\phi_d\,\phi_{a+1}\;> \;=\; 0, \tag{6}$$

because the overlap is small, and

$$<\phi_{d+1}\,\phi_a\;|\,\mathrm{ex}\;|\,\phi_{d+1}\,\phi_a> \;-\; <\phi_d\,\phi_{a+1}\;|\,\mathrm{ex}\;|\,\phi_d\,\phi_{a+1}> \;=\; ea, \tag{7}$$

where a is the separation between the centers of gravity of the orbitals between which the electron is being transferred. This form can be shown to be correct for calculations of the optical absorption at low energies by using a tunneling formalism (8). Note that Eqs. 6 and 7 are evaluated for electronic states which are not eigenstates of the Hamiltonian (because $T_{da} \neq 0$).

From the "golden rule" for transition rates (9), the rate of transfer of an electron from the donor to the acceptor is

$$W_{da} = (2\pi/\hbar),\,|\,T_{da}\,|^2 \int D_d(E)D'_a(E)\,\mathrm{d}E. \tag{8}$$

The integration on E represents an integration over the initial energy distribution, $D_d(E)$, while the factor $D'_a(E)$ represents the final state density-of-states for the electron at energy E. The rate of the reverse transfer, from acceptor back to donor, is

$$W_{ad} = (2\pi/\hbar),\,|\,T_{da}\,|^2 \int D_a(E)D'_d(E)\,\mathrm{d}E. \tag{9}$$

Notice however, that $D_d(E) \neq D'_d(E)$, and that the difference in rates W_{da} and W_{ad} comes from the important physical difference between the primed and umprimed spectral functions.

We have assumed throughout that $|\,T_{da}\,|$ is small. A much more complete analysis of this problem, including the case of large $|\,T_{da}\,|$, is given in ref. 3 for the analogous problem of excitation transfer.

Relations 8 and 9, evaluated for a particular simple model of the spectral functions, were the basis of the description of thermally activated electron tunneling recently given (4). Jortner (10) has more recently used the same basic description with a slightly improved model of the spectral functions.

If the sites were not fixed but allowed to vary in position, the transfer rate could be calculated by doing an appropriate positional average of Eq. 9. The "non-adiabatic outer sphere transfer" (11, 12) of classical electrochemistry is in some cases closely related to such a calculation, though that theory does not develop the concepts most important to the present problem.

THE CHARGE-TRANSFER ADSORPTION BAND DUE TO T_{da}

When the donor and acceptor weakly overlap, the major optical absorption bands of the system will be those of the isolated donor and acceptor, with minor perturbations of shape and position. In addition, there will be a new absorption band due to the process in which a photon directly transfers an electron from one molecule to the other. We calculate the strength, shape, and location of this charge-transfer absorption band, which can lie in energy regions outside the electronic optical absorption region of both the isolated donor or the isolated acceptor.

For optical absorption, as well as for tunneling, the effect of vibronic coupling on the donor has the effect of replacing the donor level by a statistical distribution of levels, the spectral weight function $D_d(E)$. Similarly, the final state energy level of the electron on the acceptor must be averaged over the distribution $D_a'(E)$. Let $g(E_d', E_a', E_0)$ be the molar extinction coefficient for photons of quantum energy E_0 if the donor electron state had the precise energy E_d' and the acceptor state had the precise energy E_a'. The appropriately averaged molar extinction coefficient $\epsilon(E_0)$ is then

$$\epsilon(E_0) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} D_d(E_d')D_a'(E_a')g(E_d', E_a', E)\mathrm{d}E_d'\mathrm{d}E_a'. \qquad (10)$$

The calculation of the absorption coefficient is thus resolved into two problems, the calculation of the spectral functions already evaluated for tunneling, and the known optical absorption in a problem of two sharp levels.

For the two-level absorption problem, the matrix element of the electric dipole operator between the initial and final electronic egienstates must be calculated. Within the tunneling description, the existence of the matrix elements T_{da} mean that the actual ground eigenstate (correct to first order in overlaps) is

$$\psi_G = \phi_{d+1}\phi_a + T_{da}/(E_d' - E_a')\phi_d\phi_{a+1} \quad E \approx E_d', \qquad (11)$$

and the actual excited state is $E \approx E_a'$

$$\psi_{ex} = \phi_d\phi_{a+1} - T_{da}/(E_d' - E_a')\phi_{d+1}\phi_a; \qquad (12)$$

In the true ground state of the system, the electron is chiefly on the donor, but also has a small amplitude on the acceptor. These small amplitude components (proportional to T_{da}) on the "wrong" site are responsible for the optical matrix element in the present representation.

The matrix element of the electric dipole operator between these eigenstates, from Eqs. 6 and 7, is

$$|<\psi_G|ex|\psi_{ex}>| = eaT_{da}/(E_d' - E_a'), \qquad (13)$$

where a is the separation between the center of the donor and acceptor wave function charge distributions, and e the electronic charge. Eq. 13 has been derived only in the tunneling Hamiltonian approximation, valid when the separation between the centers is large compared to the natural scale of exponential decay of the wave functions. In addition, the relevant energies of transfer must be smaller than the typical electronic excitation frequencies of the molecules if overlap contributions to Eqs. 6 and 7 are to be neglected. In our present application, overlap contributions to Eqs. 6 and 7 are expected to result in 25% corrections to Eq. 13. The suppositions behind Eq. 13 are equivalent to the basis of "microwave-assisted tunneling" descriptions between metals (13).

The optical molar extinction coefficient for a two-level problem with state energies E_d' and E_a' and transition matrix element ea is

$$g(E_d', E_a', E_0) = 2n/(n^2 + 1)\,(N_0/2{,}300)\,(2\pi^2/3)\,(E_0 e^2 a^2/\hbar c) \cdot \\ [\delta(E_d + E_0 - E_a) - \delta(E_a + E_0 - E_d)]. \qquad (14)$$

n is the index of refraction of the material in which the transition is embedded. The factor (Avogadro's number /2,300) is the ubiquitous conversion to the usual base 10 units of molar extinction. The second δ-function represents photon emission, is irrelevant to present discussions, and will be dropped. Substituting Eq. 13 and Eq. 14 into Eq. 10, one finds

$$\epsilon(E_0) = 2n/(n^2 + 1)(2\pi^2/3)(N_0/2{,}300)(\,|\,T_{da}\,|^2 a^2 e^2/E_0\hbar c) \cdot \\ \int_{-\infty}^{\infty} D_d(E)\,D_a'(E + E_0)\mathrm{d}E. \qquad (15)$$

This equation forms the basis of our calculation of the optical absorption to be expected from the electron transfer band due to T_{da}.

ABSORPTION IN THE GAUSSIAN APPROXIMATION

The simplest version of the tunneling theory used a Gaussian approximation to the spectral functions. The spectral functions are then

$$\begin{aligned} D_d(E) &= (1/2\pi\sigma_d^2)^{1/2}\exp - [(E - E_d + \Delta_d)^2/2\sigma_d^2], \\ \sigma_d^2 &= \Delta_d \kappa T \coth T_d/2T, \\ D_a'(E) &= (1/2\pi\sigma_a^2)^{1/2}\exp - [(E - E_a - \Delta_a)^2/2\sigma_a^2], \\ \sigma_a^2 &= \Delta_a \kappa T \coth T_a/2T. \end{aligned} \qquad (16)$$

Here E_d and E_a are the redox energies (the negative of the standard redox potentials) of the donor and acceptor redox couples, Δ_d and Δ_a are the vibronic coupling parameters of donor and acceptor (the Stokes shifts of each) and T_d and T_a are the characteristic vibrational temperatures of the frequencies of the relevant molecular vibrations. Since both spectral functions are Gaussians, the convolution of Eq. 15 is immediately calculable, yielding

$$\epsilon(E_0) = [2n/(n^2 + 1)](2\pi^2/3)(N/2{,}300)\,(T_{da}^2 a^2 e^2/E_0 hc)\,(1/2\pi\sigma^2)^{1/2} \cdot \\ \exp - [(E_0 + E_d - E_a - \Delta)^2/2\sigma^2], \quad \Delta = \Delta_a + \Delta_d, \quad \sigma^2 = \sigma_a^2 + \sigma_d^2. \qquad (17)$$

Fig. 1 shows calculated molar extinction coefficients for reasonable values of anticipated transfer parameters, as judged from biological examples involving chlorophyll and *c*-type cytochromes. T_{da} has been fixed at 0.001 eV, and the separation "*a*" of the center of gravity of the donor and acceptor wave functions is 12 Å. Both of these

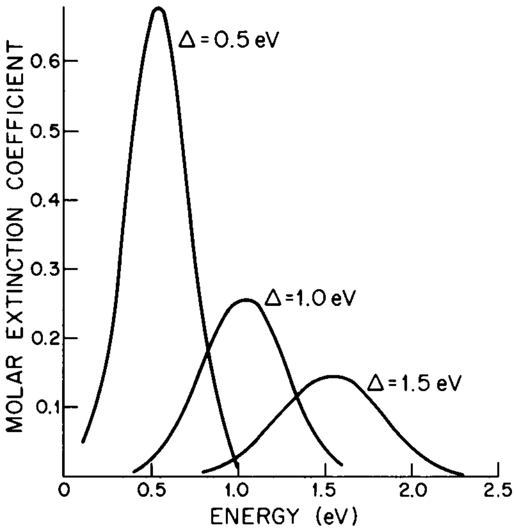

FIGURE 1 The calculated charge transfer band spectrum for $T_{ab} = 0.001$, $E_a - E_d = 0.1$ eV, and the values of Δ indicated. Notice the low peak values of the molar extinction coefficient.

parameters enter only as multiplicative factors. Both characteristic temperatures have been taken as 350°K, and the calculation is made for 300°K. $E_d - E_a$ was taken as 0.1 eV. The parameter Δ is the most critical to the spectral shape, and three values of Δ are shown, covering the expected range (5) for Δ in biological electron transfer. The T_{da} corresponds to a tunneling distance of about 6 Å. In problems with delocalized molecular orbitals, the tunneling distance will represent the separation between the closest aromatic atoms on the donor and acceptor, while "*a*" (the separation between the centers of the orbitals) will be rather larger. The Stokes shift is the dominant contributor to the position of the expected absorption line in this example. The figure defines the experimental problem of searching for such an absorption band, for the typical peak molar absorption coefficient of the charge transfer band is expected to be only a few tenths, compared to strong absorption electronic bands, which have peak molar absorptions 10^6 times larger.

But intrinsic infrared absorption need not be strong—a ferric *c*-type cytochrome has infrared absorption bands only 10–100 times stronger than the bands sought, and ferrous cytochrome absorbs much more weakly in this region—and the expected bands may be studied by measuring difference spectra.

CONCLUSION

The predictions of new charge transfer optical absorption bands, a necessary consequence of the vibronically assisted tunneling description of electron transfer, will allow a detailed experimental examination of that theory. The following are the important theoretical properties of the absorption band. (*a*) The oscillator strength of such a band should correspond to the tunneling matrix element deduced from electron transfer rate experiments (*b*) The band should have a width and shape compatible with that expected from the estimate which the tunneling parameters give for the spectral functions. The optical absorption spectrum is thus a check for the existence and shape of the hypothesized spectral functions of the tunneling description. (*c*) The absorption band should lie at the energy expected from the redox potential difference of the donor and acceptor plus the Stokes shift energy calculable from tunneling experiments and tunneling theory. (*d*) The new absorption band should yield prompt transfer electrons between donor and acceptor with a quantum efficiency of unity. The above are stated with a Gaussian model, and must be modified in obvious ways if the spectral functions are more complicated.

An experimental check of these properties will yield a detailed test of the constructs and parameters of the tunneling description in relevant cases. The experimental study will not be easy, for the typical system is expected to introduce a weak, broad absorption band in the near infrared, having an oscillator strength on the scale of 10^{-6} and a peak molar extinction coefficient less than 1. However, the absorption can be distinguished from other uninteresting absorptions by the fact that it directly produces charge transfer. Experiments that examine transient photo-induced charge transfer using excitation light not normally absorbed by the donor or acceptor have a high rejection of uninteresting absorption events, and should have sufficient sensitivity to search for a charge transfer absorption band as weak as those anticipated.

The charge-transfer absorption band is the most accurate means of measuring the tunneling matrix element. The oscillator strength can be determined at a single temperature, and is therefore not sensitive to a temperature-dependence of the separation between sites, which can confuse the experimental activation energies. In addition, the connection between oscillator strength and the tunneling matrix element is direct, and does not necessitate assumptions about the form of spectral functions.

Thus, the optical study of T_{da} as a function of conditions (ionic strength, temperature, etc.) can potentially yield information about geometry changes, information much less directly inferable from measures of the condition-dependence of the transfer rate alone.

If tunneling theory can be shown to work, it can provide an approximate distance scale for the separation between the donor and acceptor sites through the exponential relation between the tunneling matrix element and site separation. While this relation will never be very precise because of the dependence of the exponential on the material separating the sites, it can provide a semiquantitative guide to distances in electron transfer complexes. The extent to which Förster excitation transfer (in spite of its ambiguities) has proved useful in establishing structured ideas indicates the importance that even imprecise distance scales can have on establishing crucial structural relations. At present, the distances assigned by different descriptions (1, 4) to a particular biological charge transfer can be as discrepant as 7 and 80 Å, with the vibronically assisted tunneling description yielding the shorter distance. This kind of gross divergence of view, with its concomitant divergent structural implications for biology, will be resolvable by experiments on charge transfer bands. Tunneling theory has also been used to give an orderly account of the process of charge separation in photosynthesis and of the effect of redox potential on electron transfer rates. It is time for critical tests to demonstrate whether the understanding arising from the vibronic tunneling theory are real or illusory.

The work at Princeton is supported in part by National Science Foundation Grant DMR 75-14264.

Received for publication 3 December 1976.

APPENDIX

Is the Gaussian Approximation Adequate?

Short of attempting a detailed calculation of vibrational couplings in realistic situations, the only information on the adequacy of Gaussian approximation comes from experiments that measure $D_d(E)$ or related functions.

The electrons emitted by a molecule bombarded by ultraviolet monochromatic light have a kinetic energy distribution which should closely resemble $D_d(E)$. Fig. 2 shows $D_d(E)$ thus obtained for vapor phase benzene (14). The average location of the strength is at about 0.2 eV (with large background correction uncertainties), so Δ_d for vapor phase benzene as a donor would be 0.2 eV. Vibronic structure is pronounced, and the form has little resemblance to a Gaussian centered at 0.2 eV.

Optical absorption spectra also measure close analogues of $D(E)$, while emissions spectra measure the analog of $D'(E)$, with the 0–0 optical transition energy servings as the analogue of the redox potential (4). The strength of the vibronic coupling for π-π^* excitation is expected to be somewhat less than that for electron removal, so Δ_d as determined from optical absorptions will typically be an underestimate. Fig. 3*a* shows the absorption spectrum of benzene (15) in a typical liquid phase environment. Clearly there is still much vibronic structure resolvable, but the overall spectrum is much more nearly a structured Gaussian. Because the emission of benzene comes dominantly from a forbidden transition essentially invisible in absorption, the Stokes shift should not be determined by comparing absorption and emission.

Fig. 3*b* shows the absorption and emission spectra of analine in ethanol (15). In this case, there are no selection rule problems. The absorption and emission spectra are both structureless Gaussians of very similar widths, and the spectra are mirror images of each other about a common energy, just as $D_d(E)$ and $D_d'(E)$ are in the Gaussian description. The separation of the two maxima is $2\Delta_d$.

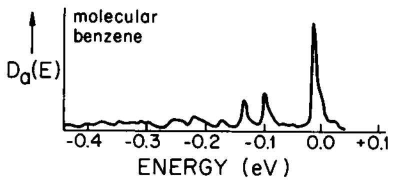

FIGURE 2 $D_d(E)$ for the benzene molecule in the vapor phase. The value of Δ is about 0.2 eV, with considerable uncertainties resulting from the uncertainty in what background subtraction to make from the original experimental data (14).

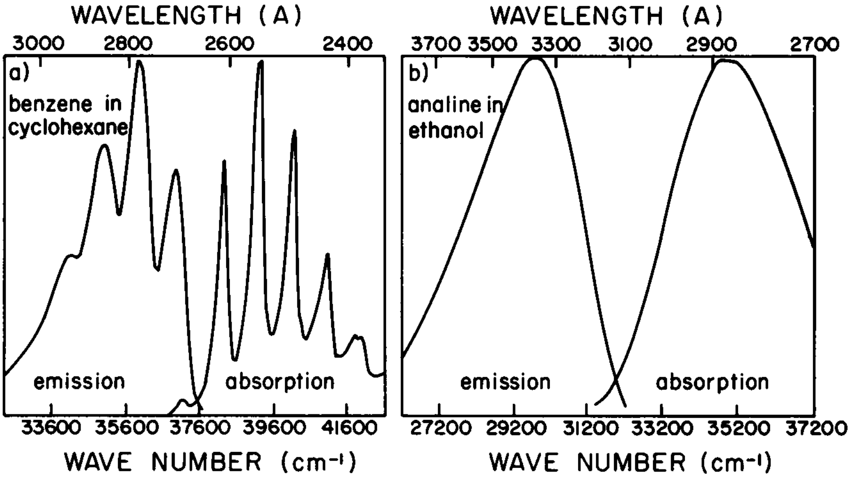

FIGURE 3 Absorption and emission spectra of benzene and analine in solvents (15). The separation of the absorption and emission peaks of analine shows that Δ is 0.4 eV for optical excitation in this case. Selection rules make benzene less simple, but the absorption spectrum alone can be used to conclude that Δ for optical excitation is about 0.15 eV. These values should be somewhat smaller than typical Δ_a or Δ_d for electron removal or insertion in such molecules.

Is the Guassian approximation adequate? Clearly under some circumstance it will be, particularly because stronger vibronic coupling leads to a more Gaussian, broader spectrum, and the broader spectrum will dominate the convolution of Eq. 15. Electrons chiefly localized in a few bonds will tend to strong vibronic coupling, as will the motion of polar groups in the environment of the donor or acceptor. The Gaussian approximation is in general expected to be better near the center of the spectrum than in the tails, and better at high temperature than at low. The approximation is therefore worst for low temperature tunneling between very similar energy levels, where the tail of the spectra can be important, and best for optical absorption studies at room temperature. When the spectral shape is Gaussian, its characterization by a single vibrational frequency may still not be a good approximation. In the last analysis, the Gaussian calculation gives a guide to the energy and scale of the expected absorption spectrum. If such spectra can be found experimentally, their shapes will directly show whether a Gaussian or a more complicated function results from the convolution in Eq. 15. For Eq. 15 the optical absorption (and the general theory of tunneling as well) remains a valid description whatever the form of the spectral functions.

REFERENCES

1. DEVAULT, D., and B. CHANCE. 1966. Studies of photosynthesis using a pulsed laser. *Biophys. J.* **6**:825.
2. MCELROY, J. O., D. G. MAUZERALL, and G. FEHER. 1974. Characterization of primary reactants in photosynthesis. II. *Biochim. Biophys. Acta.* **333**:261.
3. SOULES, T. F., and C. B. DUKE. 1971. Resonant energy transfer between localized electronic states in crystals. *Phys. Rev.* **B3**:262.
4. HOPFIELD, J. J. 1974. Electron transfer between biological molecules by thermally activated tunneling. *Proc. Natl. Acad. Sci. U.S.A.* **71**:3640.
5. HOPFIELD, J. J. 1976. Fundamental aspects of electron transfer in biological membranes: phénomènes electrique au niveau des membrane biologique. Proceedings of the 29th International Congress of the Société de Chimie Physique, Elsivier, U.M., Amsterdam. In press.

6. Hochstrasser, R. M., and P. N. Prasad. 1974. Optical spectra and relaxation in molecular solids. *In* Excited States. E.C. Lim, editor. Academic Press, Inc., New York. 79–84.

7. Salem, L. 1966. The Molecular Theory of Conjugated Systems. W. A. Benjamin, Inc., New York. 109, 138, 143.

8. Cohen, M. H., L. M. Falikov, and J. C. Phillips. 1962. Superconductive Tunneling. *Phys. Rev. Lett.* **8**:316.

9. Merzbacher, E. 1961. Quantum Mechanics. John Wiley & Sons, Inc., New York, 470.

10. Jortner, J. 1976. Temperature dependent activation energy for electron transfer between biological molecules. *J. Chem. Phys.* **64**:4860.

11. Levich, V. G. 1965. Present state of the theory of oxidation-reduction in solution advances. *Electrochem. Electrochem. Eng.* **4**:249.

12. Marcus, R. A. 1964. Chemical and electrochemical electron transfer theory. *Annu. Rev. Phys. Chem.* **15**:155.

13. Tien, P. K., and J. P. Gordon. 1963. Multiphoton process observed in the interaction of microwave fields with the tunneling between superconductor films. *Phys. Rev.* **129**:647.

14. Asbrink, L., E. Lindholm, and O. Edqvist. 1970. Jahn-Teller effect in the vibrational structure of the photoelectron spectrum of benzene. *Chem. Phys. Lett.* **5**:609.

15. Berlman, J. B. 1971. Handbook of fluorescent spectra of aromatic molecules. Academic Press, Inc., New York. 108–144.