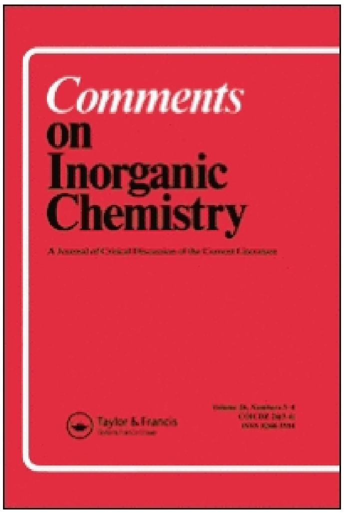

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The Relation Between the Barriers for Thermal and Optical Electron Transfer Reactions in Solution

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The Relation Between the Barriers for Thermal and Optical Electron Transfer Reactions in Solution

The relation between the energy of the intervalence (or metal-to-metal charge-transfer) transition in mixed-valence systems and the magnitude of the barrier to thermally activated electron transfer is described. We note that, contrary to what has frequently been assumed, the relation is in terms of free energies rather than internal energies or enthalpies. It is also shown, from plots of the enthalpies of the reactants and products versus the reaction coordinate, that negative activation enthalpies are a natural consequence when the standard enthalpy change for the reaction is sufficiently negative.

The parameters determining electron transfer rates can be obtained from studies of the electronic absorption spectra of (Class II) mixed-valence systems.[1-3] The reorganization barrier to the electron transfer can be evaluated from the energy of the maximum of the intervalence absorption band, while the integrated intensity of the transition provides a measure of the electronic coupling of the reactants. Here we consider the former aspect, specifically the relation between the energy of the intervalence transition and the magnitude of the barrier to thermally activated electron transfer. We point out that, in terms of a widely used classical model,[4-6] the relation between the energy of the intervalence transition and the barrier to thermal electron transfer is in terms of free energies rather than of energies. This distinction, which has frequently been overlooked, is important when the electron transfer is between oppositely charged reactants or between reactants that interact very differently with the solvent.

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In the weak-interaction limit thermally and optically activated electron transfer are conveniently described in terms of a transition from a reactants' to a products' potential-energy surface. These potential-energy surfaces are functions of the intramolecular bond lengths and angles as well as of the configurations of the surrounding solvent molecules. The intramolecular changes are generally sufficiently small that the bond distortions may be assumed to be harmonic. While motions of individual solvent molecules are generally not harmonic, it can be shown that, provided the dielectric polarization outside the inner-coordination shells of the reactants and products responds linearly to any change in charge, the *free-energy* profile will be harmonic along the reaction coordinate at a given temperature and pressure.[7] This is illustrated at the top of Fig. 1 for the case where the reactants' and products' free-energy profiles have identical "force constants." (The "symmetrized" potential-energy surfaces of Ref. 5(b) are used in calculating the free-energy plots.) The nature of these free-energy profiles is described more fully in the Appendices.

For a light-induced electronic transition, absorption of a photon ($E = h\nu$) leads to an increase in the energy of the system. Prior to the optical transition, the system is characterized by an equilibrium distribution of nuclear coordinates and momenta. In the usual Franck–Condon treatment of light absorption there is no change in the nuclear coordinates or the momenta, i.e., the electronic transition is "vertical." Consequently, the distribution of coordinates and momenta immediately after the optical transition is the same as the distribution just before the transition (i.e., in the ground state). The entropy depends on this distribution and so the entropy of the system just after the optical transition is the same as just before (apart from entropy changes associated with changes in electronic multiplicity). In view of the fact that there is no change in entropy during the transition, the vertical change in free energy (for any value of the reaction coordinate ($-m$), Fig. 1) equals that in enthalpy. There is also no instantaneous volume change during the transition[8] and consequently the instantaneous enthalpy increase equals that in the energy, i.e., $\Delta E = \Delta H = \Delta G$ for a vertical transition.

When $\Delta G^{0\prime} = 0$ (as for the top pair of curves in Fig. 1), $\Delta H^{0\prime} = T\Delta S^{0\prime}$ and $\Delta H^{0\prime}$ is not equal to zero unless $\Delta S^{0\prime}$ also equals

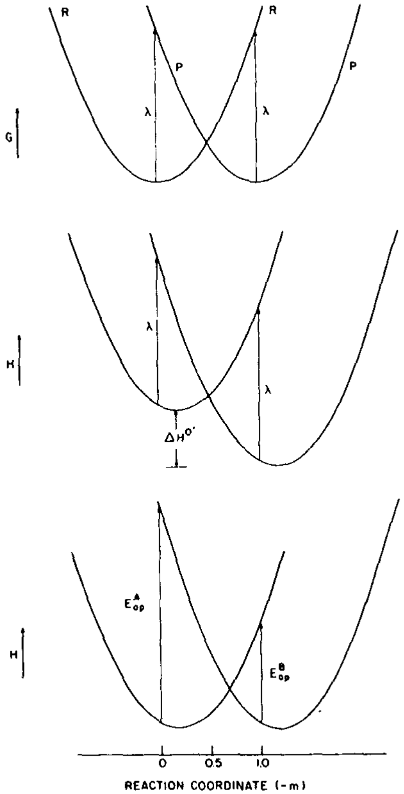

FIGURE 1 Upper curves: plot of the free energy of the reactants (left-hand curve) and products (right-hand curve) as a function of the reaction coordinate ($-m$) for the case that $\Delta G^{0\prime} = 0$ and identical shapes ("force constants") of the two free-energy curves. The minima in the reactants' and products' free-energy curves are at $m = 0$ and $-m = 1$, respectively. The intersection of the two free-energy curves occurs at $-m = 1/2$. λ is the vertical difference between products' and reactants' free-energy curves at the reactants' minimum (or at the products' minimum). Middle curves: plot of the enthalpy of the reactants and products as a function of the reaction coordinate for the same system as for the upper curves ($\Delta G^{0\prime} = 0$) and for the case that $\Delta H^{0\prime} = T\Delta S^{0\prime}$ is negative. Note that at each value of m, the vertical difference between the two enthalpy curves is equal to the vertical difference between the two free-energy curves. In particular, the vertical differences between the two enthalpy curves at $m = 0$ and $-m = 1$ are both equal to λ, as in the upper set of free-energy curves. Lower curves: plot of enthalpy of the reactants and products as a function of the reaction coordinate for the case that $\Delta H^{0\prime} = 0$ and $\Delta G^{0\prime} = -T\Delta S^{0\prime}$ is positive; $E_{\rm op}^{\rm A}$ and $E_{\rm op}^{\rm B}$ are the vertical differences at $m = 0$ and $-m = 1$ Note that $E_{\rm op}^{\rm A} = (\lambda + \Delta G^{0\prime}) = (\lambda - T\Delta S^{0\prime})$ and $E_{\rm op}^{\rm B} = (\lambda - \Delta G^{0\prime}) = (\lambda + T\Delta S^{0\prime})$.

zero. (The primes indicate work-corrected thermodynamic quantities). In Appendix II it is shown that, while the "force constants" for the reactants' and products' enthalpy curves are the same as those for the free-energy curves, when $\Delta S^{0\prime} \neq 0$ the enthalpy curves are displaced (both horizontally and vertically) relative to the free-energy curves. This is illustrated in the middle of Fig. 1. Horizontally (i.e., along the reaction coordinate) the reactants' and products' enthalpy curves are displaced by the same amount, but vertically they are displaced by different amounts (so that $\Delta H^{0\prime} \neq 0$). In order to further emphasize this point the enthalpy curves are drawn at the bottom of Fig. 1 for the case that $\Delta H^{0\prime} = 0$ (i.e., $\Delta G^{0\prime} = -T\Delta S^{0\prime}$ is positive). The equilibrium initial state of the reactants (i.e., the distribution of nuclear coordinates appropriate to the equilibrium set of configurations of the reactants and the surrounding medium) defines the position of the free-energy minimum of the reactants' curve, at a given temperature and pressure, and similarly for the products. The light absorption is by reactants in their equilibrium nuclear configurations and the optical transition thus occurs from the minimum in the reactants' *free-energy* curve.

Provided that the reactants' and products' free-energy surfaces have identical "force constants" (as in Fig. 1) and the electronic coupling (H_{AB}) is not too large, the barrier to thermally activated electron transfer is given by Eq. (1)[4,5]

$$\Delta G^* = \frac{(\lambda + \Delta G^{0\prime})^2}{4\lambda} \qquad (1)$$

where λ, the reorganization parameter, includes inner-shell and solvent contributions, and $\Delta G^{0\prime}$ is the standard free-energy change for the electron transfer when the two redox sites are at the separation distance appropriate to the actual electron transfer; when $\Delta G^{0\prime} = 0$, $\Delta G^* = \lambda/4$ and the vertical separation of the reactants' and products' free-energy curves at the reactant and product minima is equal to $4\Delta G^*$ or λ.

The activation enthalpy and entropy for the electron transfer can be obtained from Eq. (1) by using the Gibbs–Helmholtz equation. If λ is assumed to be temperature independent,[9,10] the following expressions are obtained:

$$\Delta H^* = \frac{(\lambda + \Delta H^{0\prime})^2}{4\lambda} - \frac{(T\Delta S^{0\prime})^2}{4\lambda} \tag{2}$$

$$\Delta S^* = \frac{\Delta S^{0\prime}(\lambda + \Delta G^{0\prime})}{2\lambda} \tag{3}$$

It is evident from Eq. (2) that ΔH^* will be negative when the second term on the right-hand side of the equation is larger than the first term. These two terms have an interesting interpretation. The first term has the same form as the activation free energy (Eq. (1)) and is the vertical difference between the intersection of the enthalpy curves and the minimum of the reactants' enthalpy curve[11] and is, of course, never negative. The second term, which is also always positive, is the enthalpy difference between the reactants at their equilibrium configuration (i.e., their initial enthalpy) and at their enthalpy minimum.[12] Thereby ΔH^* is, as is also evident from the middle pair of curves in Fig. 1, the enthalpy of the reactants at the intersection minus their enthalpy at their equilibrium configuration (the free-energy minimum). Evidently ΔH^* will be negative when the intersection of the enthalpy curves lies below the enthalpy of the reactants in their set of equilibrium configurations. As noted above, this occurs when the second term on the right-hand side of Eq. (2) is larger than the first term. The second term can be quite large for electron-transfer reactions in polar solvents, mainly because of differences in the freedom of the orientational and librational motion of the solvent molecules surrounding the reactants and products.

For an optical transition $\Delta E = \Delta H = \Delta G$ since, as noted above, there is no change in entropy or volume[8] during a vertical transition. In other words, although E_{op}, the energy corresponding to the absorbance maximum of the intervalence band, is really the vertical difference between the enthalpies (energies) of the ground and excited states, it is also equal to the vertical free-energy difference between the states. At $\Delta G^{0\prime} = 0$, E_{op} is equal to λ (top pair of curves in Fig. 1). However, at $\Delta G^{0\prime} = 0$, $\Delta H^{0\prime} = T\Delta S^{0\prime}$ so that E_{op} can be written equivalently as $\lambda - T\Delta S^{0\prime} + \Delta H^{0\prime}$. If, now, the products' potential-energy surface in N-dimensional coordinate space is vertically displaced upward, the distribution of coordinates (and momenta) remains unchanged and so the mean energy (the sum of the average kinetic energy and potential energy) relative to the value of the potential energy at the new position of the minimum in the surface remains unchanged. There is thereby also no entropy or volume change caused by this vertical displacement. Consequently, $\Delta S^{0\prime}$ is unchanged and the change in $\Delta H^{0\prime}$ (and $\Delta G^{0\prime}$) is equal to the amount of the vertical displacement of the products' potential-energy surface. Thus E_{op}, which was equal to $\lambda - T\Delta S^{0\prime} + \Delta H^{0\prime}$ when $\Delta G^{0\prime} = 0$, is now equal to λ plus this (positive) change in $\Delta H^{0\prime}$. Thus when $\Delta G^{0\prime} \neq 0$ we can still write E_{op} as $\lambda - T\Delta S^{0\prime} + \Delta H^{0\prime}$, i.e., as $\lambda + \Delta G^{0\prime}$ (Eqs. (4) and (5)).[13]

$$E_{op} = (\lambda - T\Delta S^{0\prime}) + \Delta H^{0\prime} \tag{4}$$

$$= \lambda + \Delta G^{0\prime} \tag{5}$$

Evidently for a series of related reactants or compounds (constant $T\Delta S^{0\prime}$) a linear dependence of E_{op} on both $\Delta H^{0\prime}$ and $\Delta G^{0\prime}$ is predicted. However, the intercept of the plot in the former case will equal $\lambda - T\Delta S^{0\prime}$ while it will equal λ in the latter case.

The curves in Fig. 1 illustrate several points: (1) The transition corresponding to the charge-transfer absorption maximum always occurs from the minimum of the free-energy curve; it does not occur from the minimum of the enthalpy curve unless $\Delta S^{0\prime} = 0$. (2) The vertical difference between the products' and reactants' enthalpy curves (and also between their free-energy curves) at the minimum in the reactants' enthalpy curve is equal to $\Lambda + \Delta H^{0\prime}$. E_{op} clearly does not equal $\lambda + \Delta H^{0\prime}$ (except in the special case that $\Delta S^{0\prime} = 0$). (3) When, as in the bottom set of curves, $\Delta H^{0\prime}$ is equal to zero the vertical energy difference E_{op} at the equilibrium set of configurations of the reactants is not simply equal to λ; instead it is equal to $\lambda + \Delta G^{0\prime}$. (4) The width of the absorption band arises from fluctuations along the reaction coordinate (cf. Appendix II). (5) The enthalpy at the intersection of the two middle curves can, when $\Delta H^{0\prime}$ is sufficiently negative, occur below the initial enthalpy, i.e., below the enthalpy at $m = 0$. Thereby, the activation enthalpy, which is the enthalpy of the transition state minus that of the initial state, is negative. We make this last point in a somewhat different, but related, way in Ref. 10.

In conclusion, the following additional relations follow from the assumption of identical, harmonic free-energy curves for the reactants and products (with the simplification that λ is temperature independent[9])

$$\Delta G^{*} = \frac{(E_{\mathrm{op}})^{2}}{4(E_{\mathrm{op}} - \Delta G^{0\prime})} \tag{6}$$

$$\Delta H^{*} = \frac{E_{\mathrm{op}}\,(E_{\mathrm{op}} + 2T\Delta S^{0\prime})}{4(E_{\mathrm{op}} - \Delta G^{0\prime})} \tag{7}$$

$$\Delta S^{*} = \frac{E_{\mathrm{op}}\,\Delta S^{0\prime}}{2(E_{\mathrm{op}} - \Delta G^{0\prime})} \tag{8}$$

Application of the above equations may resolve certain inconsistencies found in the literature. For example, it has recently been shown[14] that use of the above relationship between E_{op} and $\Delta G^{0\prime}$ removes some apparent anomalies regarding intervalence transitions in $\mathrm{Ru(NH_3)_5L^{3+}|M(CN)_6^{4-}}$ ion pairs (M = Fe, Ru, Os) that had resulted from the use of $\Delta H^{0\prime}$ rather than $\Delta G^{0\prime}$ in Eq. (5).[15] Further applications should provide a critical test of the assumption of harmonic free-energy surfaces with identical (i.e., "symmetrized") "force constants" that underlies the derived expressions.

APPENDIX I

We give in this Appendix a justification for the use of free-energy plots (Fig. 1) and relate the free energies to the photon energy $h\nu$ absorbed.

By use of the Condon approximation (in which any dependence of the dipole moment operator on the displacements of the nuclear coordinates is neglected) and Fermi's golden rule, it can be shown that the probability of a radiative transition between the set of i vibrational levels of state A to the set of f vibrational levels of state B at the photon energy $h\nu$ is given by[16]

$$\Gamma(h\nu) = \frac{4\pi^{2}}{hQ}\,|\langle\psi_{\mathrm{A}}|\mu|\psi_{\mathrm{B}}\rangle|^{2} \sum_{i,f} e^{-E_i/RT}|\langle\psi_i|\psi_f\rangle|^{2}\delta(E_f - E_i - h\nu)$$

where μ is the electric dipole moment operator, E_f and E_i are the energies of the final and initial states, respectively, and Q is the vibrational-rotational-librational partition function. The electronic factor $|\langle\psi_A|\mu|\psi_B\rangle|^2$ is independent of the nuclear coordinates while the overlap integral $|\langle\psi_i|\psi_f\rangle|^2$ is over the wavefunctions for the nuclear motion (vibrational, rotational, librational) in the upper and lower states for every initial and final state in the sum. When the vibrational-rotational-librational overlap factor is treated semiclassically (use of WKB wavefunctions), as in the analogous electron transfer problem,[17] the sums over the initial and final states are each written as integrals. There are now three integrals, one over the nuclear coordinates q (it occurs twice), one over the initial quantum states i and one over the final quantum states f. Each integral over the coordinates contains the product of the semiclassical wavefunctions for the initial and final states and is evaluated in the stationary phase approximation.[17] This approximation yields at once the Franck–Condon condition that, for each value of the nuclear coordinates, each individual momentum immediately after the transition equals its value just before. As in Ref. 17, the delta function $\delta(E_f - E_i - h\nu)$ in the above expression now becomes $\delta(U_f - U_i - h\nu)$ because of the above equality for the individual momenta and hence for the kinetic energy (U_f and U_i are the potential energy functions for the final and initial electronic states, respectively, and E_f (or E_i) is the sum of U_f (or U_i) and the sum of the kinetic energies). The integral over the final states is transformed into an integral over the coordinates and the integral over the initial quantum states is next transformed to an integral over the momenta, and the integration over the latter is then performed. In this way the transition probability at frequency ν is found to be proportional to

$$\int\cdots\int \exp(-U_i/RT)\,\delta(U_f - U_i - h\nu)\,dq_i\cdots dq_N$$

$$\div \int\cdots\int \exp(-U_i/RT)\,dq_i\cdots dq_N,$$

in an N-coordinate system.[18]

With this result in mind we proceed to a formulation of the free-energy plots such as that in Fig. 1. We first consider the $h\nu$ for the absorption maximum, i.e., $h\nu = h\nu_m$, for which the numerator in the above expression is a maximum. If the upper potential-energy surface U_f is lowered by an amount $h\nu_m$, the two surfaces in N-dimensional coordinate space now intersect at the bottom of the U_i surface, on a surface plotted vs. the $(N - 1)$ coordinates. On this $(N - 1)$-coordinate surface, there is an equilibrium population represented by the Boltzmann factor $\exp(-U_i/RT)$. Associated with this equilibrium population we can now define a configurational free energy for the system constrained to lie on this $(N - 1)$-coordinate intersection surface. A system similarly distributed on the upper surface U_f has, apart from the energy difference $h\nu_m$, the same distribution and hence the same configurational free energy. The momentum distribution for each of these two systems is also the same (since the individual momenta were the same immediately before and after the transition) and so the total free energies only differ by the energy quantity $h\nu_m$.

If we next raise or lower the upper surface by some other amount $h\nu$ there will be a new intersection surface, defining a new set of points in an $(N - 1)$-dimensional subspace. Associated with the equilibrium population on the new surface is a new free energy. The system on the surface U_f has the same new free energy, apart from the additional amount $h\nu$, since it has the same distribution of coordinates and momenta. These $(N - 1)$-dimensional subspaces form a family, each of which can be described by some value of the Nth nuclear coordinate, and which in turn depends only on a single parameter $h\nu$. In this way one can plot the two free-energy curves versus some coordinate, as in Fig. 1.

We see from the above argument that the energy difference $h\nu_m$ for absorption, or indeed any $h\nu$, is exactly equal to a free-energy difference as stated in the text. The potential energy functions U_i and U_f themselves are far from being harmonic oscillator functions when plotted versus most of the $(N - 1)$ coordinates: only along the axes that describe the bond lengths are they approximately quadratic functions. The free-energy functions just described are, on the other hand, quadratic functions of the abscissa, in the linear response region. The calculation of these free-energy functions contains the constraint of being confined to a subspace of $(N - 1)$ coordinates in a total space of N coordinates. To evaluate such constrained functions, which also involve complicated motions of the solvent molecules, it is convenient to introduce the notion of an equivalent equilibrium distribution, i.e., to introduce for each value of the abscissa a distribution centered on the constrained region but not confined to it.[5] In this way, as in the thermal electron-transfer case,[17] one retrieves earlier expressions for the dependence of the free-energy curves on solvent dielectric properties.

The width of the charge-transfer absorption band arises as follows: The free-energy profiles in Fig. 1 refer to a system of $(N - 1)$ coordinates for each value of the reaction coordinate $(-m)$. Different values of the absorbed energy $h\nu$ correspond to different values of the Nth coordinate, i.e., to different values of the reaction coordinate. Fluctuations in this Nth coordinate thereby give rise to the width of the absorption band. A calculation of the polar contribution to the spectral width of charge-transfer absorption bands is given in Eqs. (24)–(28) of the article cited in Ref. 13.

The remarks in this Comment regarding the relation between absorption spectra and free energies apply also to emission spectra. The relation between emission spectra and free energies is discussed in the article cited in Ref. 13 and is made use of in a recent study of chemiluminescent reactions.[19]

APPENDIX II

In order to describe in more concrete terms the plots of the thermodynamic properties along the reaction coordinate it is convenient to use the Lagrangian multiplier $-m$ as abscissa, where m is described in Refs. 4 and 5. The free energy of the reactants and environment G^{r} can be written as[4,5]

$$G^{\mathrm{r}} = G_0^{\mathrm{r}} + m^2\lambda \qquad \text{(A1)}$$

where G_0^{r} is the value of G^{r} at the minimum of the reactants' curve (namely, at $m = 0$). The "force constant" for the G^{r} curve, $\partial^2G^{\mathrm{r}}/\partial m^2$, is 2λ. Similarly for G^{p}, the free energy of the products and environment, we have[4,5]

$$G^{\mathrm{p}} = G_0^{\mathrm{p}} + (m + 1)^2\lambda \qquad \text{(A2)}$$

where G_0^{p} is the value of G^{p} at the minimum of the products' curve (namely, at $m = -1$), and the "force constant" for the G^{p} curve, like that for the G^r curve, is 2λ, a result arising from the use of "symmetrized" potential energy surfaces in Ref. 5(b). The vertical free-energy difference is thus given by

$$G^p(m) - G^r(m) = \Delta G^{0\prime} + (2m + 1)\lambda \tag{A3}$$

where $\Delta G^{0\prime}$ is $G_0^p - G_0^r$ and is the "standard" free energy of reaction (specifically, the free energy of reaction for unit concentration of reactants and products) in the prevailing medium. We note that at the intersection of the two curves, G^p equals G^r and so $-(2m + 1)\lambda = \Delta G^{0\prime}$, an equation obtained previously[4,5] for the value of m ($= m^*$) in the transition state. With this value of m, the value of G^r ($= G^{r*}$) at the intersection is seen from Eq. (A1) to be given by the usual expression

$$G^{r*} = G_0^r + (\Delta G^{0\prime} + \lambda)^2/4\lambda \tag{A4}$$

We turn next to plots of the other thermodynamic properties. The vertical differences for the entropy and enthalpy curves are, as already noted, equal to zero and to $G^p - G^r$, respectively:

$$S^p(m) - S^r(m) = 0 \tag{A5}$$

$$H^p(m) - H^r(m) = \Delta G^{0\prime} + (2m + 1)\lambda \tag{A6}$$

As may perhaps be intuitively guessed from Eqs. (A5) and (A6), one should be able to show that, while H^r and H^p, like G^r and G^p, are quadratic functions of m with the same "force constant" 2λ, S^r and S^p are linear functions of m. This result can be shown as follows.

The entropy at the intersection of the G^r and G^p curves is obtained by differentiating $G^r(m^*)$ in Eq. (A4) with respect to T. Thereby, if λ is assumed to be temperature independent, as also seen previously in Eq. (3),

$$S^{r*} = S_0^r + [(\Delta G^{0\prime} + \lambda)/2\lambda]\Delta S^{0\prime} \tag{A7}$$

where S_0^r is the value of S^r at $m = 0$ (the equilibrium configuration of the reactants). By virtue of the fact that $-(2m^* + 1)\lambda$ equals

$\Delta G^{0\prime}$ we then have

$$S^{r}(m^{*}) = S_{0}^{r} - m^{*}\Delta S^{0\prime} \qquad (A8)$$

Different values of m^{*} are generated by raising or lowering the products' curve, thus varying $\Delta G^{0\prime}$ but not $\Delta S^{0\prime}$. Thereby Eq. (A8) applies for any m

$$S^{r}(m) = S_{0}^{r} - m\Delta S^{0\prime} \qquad (A8')$$

and the linear dependence of S^{r} on m is established. $S^{p}(m)$ is also given by Eq. (A8′) by virtue of Eq. (A5).

From Eqs. (A1) and (A8′) we then have

$$H^{r}(m) = H_{0}^{r} + m^{2}\lambda - mT\Delta S^{0\prime} \qquad (A9)$$

where H_{0}^{r} is the value of H^{r} at $m = 0$. The "force constant" of $H^{r}(m)$, $\partial^{2}H^{r}(m)/\partial m^{2}$, is seen to be 2λ, which is the same as the force constant for $G^{r}(m)$. The minimum of the G^{r} plot occurs at $m = 0$, while the minimum of the H^{r} plot is seen, by setting $\partial H^{r}/\partial m = 0$, to occur at $m = T\Delta S^{0\prime}/2\lambda$. From Eq. (A9) we also have

$$H^{r}(m^{*}) - H_{0}^{r} = (m^{*})^{2}\lambda - m^{*}T\Delta S^{0\prime} \qquad (A9')$$

which gives Eq. (2) upon substitution of $m^{*} = -(\Delta G^{0\prime} + \lambda)/2\lambda$.

Similarly, from Eqs. (A4) and (A9) we have

$$H^{p}(m) = H_{0}^{r} + \Delta G^{0\prime} + (m + 1)^{2}\lambda - mT\Delta S^{0\prime} \qquad (A10)$$

Thereby,

$$H^{p}(m) = H_{0}^{p} + (m + 1)^{2}\lambda - (m + 1)T\Delta S^{0\prime} \qquad (A11)$$

[Equation (A11) could also have been obtained directly from Eq. (A9) by interchanging[5] r and p symbols (whence $\Delta S^{0\prime} \rightarrow -\Delta S^{0\prime}$, for example) and interchanging m and $-(m + 1)$.] We see from Eq. (A11) that the "force constant" of $H^{p}(m)$, namely $\partial^{2}H^{p}/\partial m^{2}$, is 2λ and that the minimum of the $H^{p}(m)$ vs. m curve, which occurs at $\partial H^{p}/\partial m = 0$, occurs at $(m + 1) = T\Delta S^{0\prime}/2\lambda$ instead of at $(m + 1) = 0$.

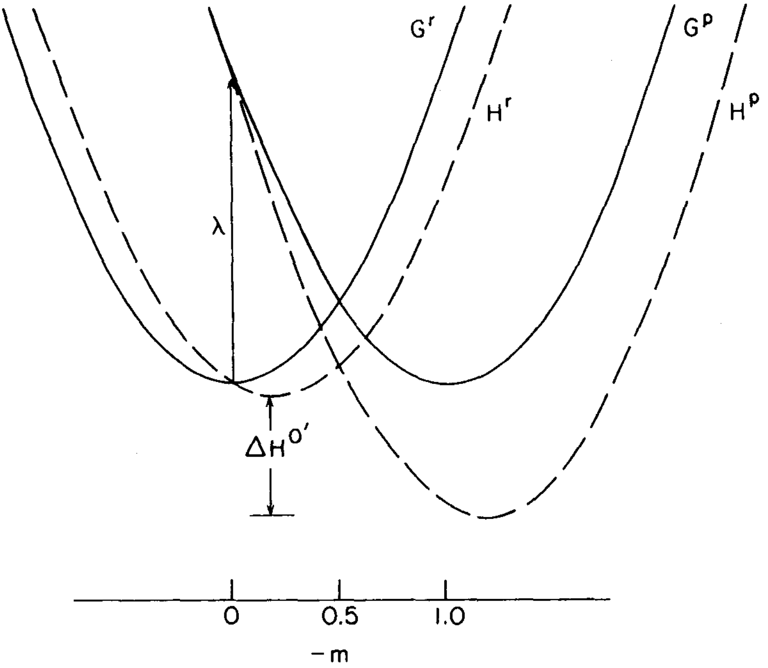

FIGURE 2 Overlay of the upper and middle sets of curves of Fig. 1. The solid curves are the free-energy curves: the minimum in the reactants' free-energy curve is at $m = 0$ while the minimum in the products' free-energy curve is at $-m = 1.0$. The dashed curves are the enthalpy curves: the minimum in the reactants' enthalpy curve is at $m = T\Delta S^{0\prime}/2\lambda$ while that in the products' enthalpy curve is at $m = -1 + T\Delta S^{0\prime}/2\lambda$. The curves have been drawn so that $G^r = H^r$ at $m = 0$ in order to show that the vertical difference between the pair of free-energy curves equals that between the pair of enthalpy curves. This difference equals λ at $m = 0$. The vertical displacement of the minima in G^r and H^r is $(T\Delta S^{0\prime})^2/4\lambda$.

The relationship between the free-energy and enthalpy curves is further illustrated in Fig. 2, in which the upper and middle set of curves in Fig. 1 have been overlayed in order to emphasize the relation between them.

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7. The harmonic (quadratic) behavior of the free-energy profile along the reaction coordinate ($-m$) bears a simple relationship to a harmonic dependence of the free energy on the charge distribution: the charge distribution used to generate the changes in dielectric polarization depends linearly on this quantity m, as shown in Refs. 4 and 5. For a discussion of the quadratic free-energy dependence on a change of charge distribution see, for example, R. A. Marcus, J. Chem. Phys. **24**, 979 (1956); *ibid.* **39**, 1734 (1963). The dielectric continuum discussion refers to a constant temperature and pressure system, while the statistical-mechanical treatment is for a system at constant temperature and volume. However, a related statistical-mechanical treatment can be given for a constant temperature and pressure system.
8. The equality of ΔE and ΔH for a vertical transition arises because there is no time for a volume change during the vertical transition (which occurs at constant nuclear coordinates in the Franck–Condon approximation): any volume change occurs in the relaxation process after the vertical transition. For a process in a condensed phase ΔE and ΔH differ negligibly because the $P\Delta V$ term is very small for a reaction in a condensed phase under normal conditions. Along the

reaction coordinate there are nevertheless volume changes so that, at a given temperature and pressure, the volume of the system at $-m = 1$ will differ from that at $m = 0$ when $\Delta V^{0\prime} \neq 0$.

9. The assumption that λ is temperature independent has been made in order to simplify the resulting expressions. Expressions for thermally activated electron transfer derived without this assumption are presented in Ref. 10.
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11. This result can be obtained using the results in Appendix II. In particular, in terms of the quantities derived there, one uses Eq. (A9), first with m equal to its value at the intersection ($m^* = -(\Delta G^{0\prime} + \lambda)/2\lambda$) and then with m equal to its value at the minimum of the H^r vs. m curve ($m = T\Delta S^{0\prime}/2\lambda$) and subtracting. The difference yields the first term on the right-hand side of Eq. (2). One can also obtain this result by noting that H^r and H^p are quadratic functions of m and for this reason the value of H at the intersection equals, as in the G plots, the square of the vertical difference, $\Delta H^{0\prime} + \lambda$, between the products' and reactants' H curves at the minimum of the reactants H curve, divided by 4λ.
12. This result follows immediately using Eq. (A9) with m equal to its value at the minimum of the H^r vs. m curve, namely $m = T\Delta S^{0\prime}/2\lambda$, as in the preceding footnote.
13. As we noted in Ref. 6, Sec. IIID, this equality of E_{op} and $\lambda + \Delta G^{0\prime}$ was also shown in a previous paper on solvent effects on spectra, R. A. Marcus, J. Chem. Phys. **43**, 1261 (1965): this equality is evident from Eq. (14) of that paper, where $F^{op}_{e-g} - F_{e-g}$ is the polar contribution to λ and $F_e - F_g$ is the polar contribution to ΔF^0 ($\Delta G^{0\prime}$ in the present notation).
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18. In this discussion we have tacitly used, for simplicity, a distribution function for a constant volume system rather than for an isobaric system and, in so doing, we have neglected for these condensed-phase systems the (indeed negligible) difference between enthalpy and energy. The relationship between Helmholtz and Gibbs free energies for this problem is described in the article cited in Ref. 13.
19. D. K. Liu, B. S. Brunschwig, C. Creutz and N. Sutin, J. Am. Chem. Soc. (in press).