(28) As described in note 25, the measurements depend on the electron transfer reactions with iron(III) complexes which are unfortunately insoluble *in* nonpolar media.

(29) The effects of solvation on ΔG_r° decrease in the less polar solvents.

(30) (a) It is noteworthy that the α values for the best fit to the experimental data are $\alpha(CH_3CN) = 0.55$ and $\alpha(CH_2Cl_2) = 0.66$, which compare well with the independently determined values of $\alpha(CH_3CN) = 0.60$ in eq 17 and $\alpha(CH_2Cl_2) = 0.71$ in Figure 5a. (b) The deviations of the calculated lines for *n*-Bu$_4$Sn and *sec*-Bu$_4$Sn from the experimental points are due to errors in the determinations of either I_D or $h\nu_{CT}$, or both, since they occur by the same amounts in the same direction and considerable scatter is also found for these alkyltins in Figure 4. Indeed, a change of ΔE by only 0.03 and 0.08 eV for *n*-Bu$_4$Sn and *sec*-Bu$_4$Sn, respectively, is required to fit the experimental data like other R$_4$Sn in the figure. (c) Essentially the same analysis can be employed to account for the solvent effect on the *brominolysis* of these alkylmetals studied earlier.[16a] For Et$_4$Sn and *n*-Pr$_4$Sn, the values of $\Delta E(Br_2)$ are 10.2 and 11.9 kcal mol^{-1}, which compare with 10.8 and 12.7 kcal mol^{-1}, respectively, for iodinolysis [Fukuzumi, S., unpublished results].

(31) (a) The change $\Delta E = \omega - \omega_0$ is considered to be largely a steric effect since it consists mainly of Coulombic terms,[9] inversely proportional to the mean separation. The other terms in the interaction energy also probably depend on the mean separation, either directly or indirectly. (b) Solvents have relatively minor effects on ΔE (additional studies in progress).

(32) For a general theory of solvent polarities, see: Abboud, J.-L. M.; Taft, R. W. *J. Phys. Chem.* **1979**, *83*, 412.

(33) (a) The change in solvation energy is defined as $\Delta E_{solv} = RT \ln k/k_r$ where k refers to the rate constants in Table V for *n*-BuSnMe$_3$, and k_r is that in methylene chloride, chosen as a reference solvent. The rate constant in CCl$_4$ was estimated from the selectivity in Table III using eq 36. (b) The dipole moment is $\mu^\ddagger = -\alpha e r^\ddagger$ where α is the degree of charge separation in the transition state. From the slope in Figure 7, $\alpha = [(\text{slope})a^3/(er^\ddagger)^2]^{1/2}$. The value of $r^\ddagger$ is taken as 3.7 Å from $\bar{r}_{mn}$ (as described in note 40) and $e^2 = 14.4$ eV Å. When $a = 1.1\bar{r}_{mn}$, $\alpha = [3.0(1.1)^3(3.75)/14.4]^{1/2} = 1$. The lower limit is obtained when $a = \bar{r}_{mn}$, and then $\alpha = 0.8$.

(34) Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 1855.

(35) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 16.

(36) (a) The diffusion of radicals from the cage is a competing process in eq 28. It accords with the complex interplay of electrophilic and radical-chain reactions often observed in halogenolysis, as described in ref 5 and 16b. (b) Klingler, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626. (c) Compare also Tsou, T. T.; Kochi, J. K. *Ibid.* **1979**, *101*, 6319.

(37) *S*(R/Me) for hexachloroiridate(IV) cleavages of R$_4$Sn are listed in the Experimental Section.

(38) Deduced principally by Gielen, M., Nasielski, J., and coworkers, as reviewed in "Organotin Compounds", Sawyer, A. K., Ed.; Marcel Dekker: New York, 1972; Vol. 3, p 652 ff.

(39) Compare Martino, G.; Jungers, J.-C. *Bull. Soc. Chim. Fr.* **1970**, 3392. Reference 3, p 172 ff.

(40) Since the slope is $(r_m r_n RT)^{-1}$, the mean value of r_m and r_n is $\bar{r}_{mn} = (r_m r_n)^{1/2} = a_H(RT\cdot\text{slope})^{-1/2}$, where a_H is the Bohr radius taken as 0.5292 Å and RT is in atomic units.

(41) For Et$_2$SnMe$_2$ and *t*-Bu$_2$SnMe$_2$, $\Delta E = -\Delta I_D + \Delta h\nu_{CT} = (9.01 - 8.22) - (4.49 - 4.10) = 0.40$ eV from eq 15 and Table I, and $\Delta e^2/r_{mn} = e^2(1/3.7 - 1/4.1) = 0.37$ eV. (b) It is noteworthy that the solvent effect on the iodinolysis of an alkylmetal as described in eq 23 and 36 derives from two independent approaches. (The detailed implications merit further consideration.) Both of these treatments dealing with the *absolute* reactivities of alkylmetals are to be compared with the treatment in eq 21 (Figure 6) which accounts for the solvent effects on the *relative* reactivities. Together, they should allow a general description of solvents effects (studies in progress).

(42) Such a comparison also focuses on the ion-pairing energies since the electrostatic potential in the ion pair in eq 42 is repulsive whereas it is clearly attractive in eq 43.

(43) See, for example, Trotter, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 5721.

(44) (a) In organic chemistry, charge-transfer complexes between halogens and alkenes have been observed and a CT mechanism has been proposed for the addition reaction. See: Dubois, J. E.; Garnier, F. *Spectrochim. Acta, Part A* **1967**, *23*, 2279. Dubois, J. E.; Mouvier, G. *Bull. Soc. Chim. Fr.* **1968**, 1426. Dubois, J. E.; Garnier, F. *Chem. Commun.* **1968**, 241. Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 4285. (b) See also: Sergeev, G. B.; Serguchev, Yu. A.; Smirnov, V. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1973**, *42*, 697. Beletskaya, I. P.; Artamkina, G. A.; Reutov, O. A. *Ibid.* **1976**, 45, 330. Kosower, E. M.; *Prog. Phys. Org. Chem.* **1965**, *3*, 81. Freeman, F. *Chem. Rev.* **1975**, *75*, 439.

(45) The subtle balance between retention, inversion, and racemization in the stereochemical course of iodinolysis is affected by solvents, additives, substrate structures and concentrations.[46,47] The CT formulation can readily accommodate these observations, but we will reserve discussion until further studies directly related to the stereochemistry are developed.

(46) (a) Jensen, F. R.; Davis, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 4048. (b) Chambers, R. L.; Jensen, F. R. In "Aspects of Mechanism and Organometallic Chemistry", Brewster, J., Ed.; Plenum Press: New York, 1978. (c) Sayre, L. M.; Jensen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 1900. (d) McGahey, L. F.; Jensen, F. R. *Ibid.* **1979**, *101*, 4397.

(47) Rahm, A.; Pereyre, M. *J. Am. Chem. Soc.* **1977**, *99*, 1672.

(48) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Elmsford, N.Y., 1966.

(49) Savitskii, A. V.; Syrkin, Ya. K. *Dokl. Phys. Chem.* **1962**, *146*, 700.

(50) See: Ratcliff, M. A., Jr.; Kochi, J. K. *J. Org. Chem.* **1971**, *36*, 100.

Vertical and "Nonvertical" Energy Transfer Processes. A General Classical Treatment

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Abstract: A classical treatment of exchange energy transfer processes in fluid solution is given, which parallels that already used for electron transfer quenching processes. This treatment is based on a model which does not require violation of the Franck–Condon principle, nor the use of ill-defined concepts such as "nonvertical" energy transfer or "phantom" excited states. Making use of absolute reaction rate theory and of recently proposed relationships between free-energy change and free activation energy, a general equation is obtained for the experimental quenching constant. Unlike the well-known Sandros equation, the equation derived in this paper provides a unified view of the so-called vertical and nonvertical energy transfer behavior, and it can also account for the lower than diffusion rates of energy-transfer processes in the exoergonic region. The meaning and limitations of such a classical treatment are critically examined and the relationships between spectroscopic and thermodynamic parameters are discussed. The validity of the proposed treatment is tested on the literature data for energy transfer from aromatic triplets to *cis*- and *trans*-stilbene, ferrocene and ruthenocene, biacetyl and *o*-anisil, and β-diketonatoiron(III) complexes.

I. Introduction

In fluid solution, energy-transfer processes

$$^*D + A \xrightarrow{k^{en}_q} D + {}^*A \tag{1}$$

involving exchange interaction occur with a maximum rate that is equal to the rate of encounters between excited donors and acceptors.[2a] When the donor has insufficient excitation energy to promote the acceptor to its excited state (endothermic en-

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ergy transfer), the energy deficiency has to be made up by vibrational excitation.[2,3] On this basis, the general expression for the experimental rate constant of an energy-transfer process is considered to be given by

$$k^{\mathrm{en}}_{\mathrm{q}} = \frac{k_{\mathrm{d}}}{1 + \exp[-[E(^*\mathrm{D,D}) - E(^*\mathrm{A,A})]]/RT} \qquad (2)$$

where k_{d} is the diffusion rate constant and $E(^*\mathrm{D,D})$ and $E(^*\mathrm{A,A})$ are the energies of the donor and acceptor excited state, respectively.[2] Equation 2 has been obtained by Sandros from simple Boltzmann distribution arguments within the encounter.[2b] When eq 2 is obeyed, the system is said to behave classically.[2-5] For a number of systems,[6-15] however, the rate constants for endothermic energy transfer were found to be much higher than those obtained by introducing the "available spectroscopic data" in eq 2. Common to all these "nonclassical" systems is that the donor and/or acceptor have significantly different equilibrium geometries in their ground and excited states.

Hammond and his colleagues[6,7] introduced the terms "nonvertical excitation" and "phantom triplet" to describe the "nonclassical" behavior of *cis*-stilbene as a triplet energy acceptor.[16] As initially proposed, the nonvertical excitation transfer process was envisioned as proceeding with simultaneous change in the geometry of the acceptor, to reach a distorted, "phantom", nonspectroscopic state. Such a "nonvertical" mechanism has become very popular, but the concepts associated with it have been rather variable and often not clearly understood.[2a,10,11,17] Bylina[18] questioned the validity of Hammond's mechanism, showing that in the case of triplet-triplet transfer to stilbene the so-called nonvertical excitation follows closely the Franck-Condon probabilities of the spectra in the region in which the extinction coefficients are large enough to be measured.[11] A qualitative correspondence between Franck-Condon factors, which are reflected in the spectral distribution, and energy transfer rates has later been discussed by Yamauchi and Azumi.[17] Saltiel et al.,[19] however, have recently questioned Bylina's mechanism on the basis of results obtained on the temperature dependence of the energy transfer rate constant. The role played in the nonvertical excitation transfer by ground-state acceptor molecules which are excited along a favorable distortion coordinate according to the Boltzmann distribution law ("hot-band" mechanism) has been discussed by several authors.[2a,4,6,12,17,20] In particular, Wagner and Scheve[20] concluded that the "hot-band" mechanism is sufficient to explain nonvertical energy transfer, "but far more results and better potential energy diagrams are required before the original concept of nonvertical energy transfer need be replaced completely by the hot-band model." Nonvertical behavior has also been discussed by Farmilo and Wilkinson,[12] who have used eq 2 for nonvertical energy transfer to ferrocene, but they had to introduce an empirical fractional coefficient in the second term of the denominator in order to account for the experimental results. Finally, nonvertical energy transfer has been discussed by Turro[10,15] on the basis of an exciplex mechanism. In conclusion, Farmilo and Wilkinson's statement[12] that "the best conceptual picture of energy transfer involving distorted excited states has not yet been established" seems to be fully justified.

Another puzzling aspect of energy-transfer processes is their maximum rate constant. Although it is commonly stated[2a] that energy-transfer rates of spin-allowed processes are diffusion controlled when they are exothermic by a few kilocalories per mole, Wagner[21] has pointed out several years ago that this is apparently not true for solvents of low viscosity. Clear evidence that intrinsic molecular factors can limit the energy transfer rate to lower than diffusional values has been reported for some sterically hindered organic molecules[2a] and for several transition-metal complexes,[22] where even stepwise plots of log $k^{\mathrm{en}}_{\mathrm{q}}$ vs. $E(^*\mathrm{D,D})$ have been obtained in some cases.[23]

Although usually discussed separately and treated using different formalisms, the quenching of an excited state by exchange energy transfer (eq 1)[2a,15] and outer-sphere electron transfer[24-27]

$$^*\mathrm{D} + \mathrm{A} \xrightarrow{k^{\mathrm{el}}_{\mathrm{q}}} \mathrm{D}^+ + \mathrm{A}^- \qquad (3)$$

are conceptually related processes. In both cases spatial overlap of donor and acceptor orbitals is required, no bond breaking or making processes take place, and Franck-Condon restrictions have to be obeyed because the electronic rearrangement with (eq 3) or without (eq 1) the net transfer of an electron between donor and acceptor occurs in a time short compared to that required for nuclear motions. For a polyatomic molecule in a fluid solution the electronic relaxation times (at least for the lowest excited states) are usually several orders of magnitude longer than the time for thermal equilibration in all other degrees of freedom.[28-30] Thus, the electronically excited states involved in the bimolecular quenching processes (eq 1 and 3) are thermally equilibrated species that can be considered as new chemical entities with respect to the ground-state molecule. Hence the use of thermodynamics is appropriate in dealing with the reactions of these excited states and reactions 1 and 3 can be treated in the same way as the "thermal" (ground state) electron-transfer reactions. For this last class of chemical processes, a quite satisfactory theory has been developed several years ago (Marcus-Hush theory).[31-35] More recently, the formalism of this theory has been successfully applied to the electron transfer quenching processes (section II).[24-27,36-39] In this paper, we will extend the same formalism to energy transfer quenching processes (section III) and we will show that it is possible to develop a general treatment which provides a unified view of the so-called vertical and nonvertical energy transfer processes.[40] Such a treatment does not require violation of the Franck-Condon principle and avoids the use of misleading terms and concepts. Moreover, it can also account for both diffusion-controlled and lower than diffusion rates for highly exoergonic processes.

The approach proposed in this paper is a classical one which makes use of the absolute rate theory expression for the energy transfer rate constant. The meaning and limitations of this kind of treatment are dealt with in section IV. In section V we will examine the literature results of important classes of energy-transfer processes in the light of the treatment formulated in the preceding sections.

II. Quenching by Electron Transfer

For an electron transfer quenching process (eq 3), the following kinetic scheme can be used:[42]

$$\begin{tikzcd} \mathrm{D} + \mathrm{A} + h\nu \arrow[r] & {}^*\mathrm{D} + \mathrm{A} \arrow[r, shift left, "k_{\mathrm{d}}"] \arrow[d, "1/\tau^0_{^*\mathrm{D}}"] & {}^*\mathrm{D} \cdots \mathrm{A} \arrow[l, shift left, "k_{-\mathrm{d}}"] \arrow[r, shift left, "k_{\mathrm{el}}"] & \mathrm{D}^+ \cdots \mathrm{A}^- \arrow[l, shift left, "k_{-\mathrm{el}}"] \arrow[d, "k_{\mathrm{s}}"] \\ & {} & & {} \end{tikzcd} \qquad (4)$$

where k_{s} comprises all possible modes (except $k_{-\mathrm{el}}$) by which the $\mathrm{D}^+ \cdots \mathrm{A}^-$ ion pair can disappear. Using steady-state approximations, this scheme leads to the following equation for the experimental quenching constant:

$$k^{\mathrm{el}}_{\mathrm{q}} = \frac{k_{\mathrm{d}}}{1 + \dfrac{k_{-\mathrm{d}}}{k_{\mathrm{el}}}\left(1 + \dfrac{k_{-\mathrm{el}}}{k_{\mathrm{s}}}\right)} \qquad (5)$$

For the electron-transfer steps of eq 4, the following relationships can be written according to the classical model of the absolute rate theory:[43]

$$k_{\mathrm{el}} = k^0_{\mathrm{el}} e^{-\Delta G^{\ddagger}/RT} \qquad (6)$$

$$k_{-\mathrm{el}}/k_{\mathrm{el}} = e^{\Delta G/RT} \qquad (7)$$

where $k^0{}_{el}$, $\Delta G^{\ddagger}$, and ΔG are the preexponential factor, the standard free activation energy, and the standard free energy change of the forward electron-transfer step. The preexponential factor $k^0{}_{el}$ can be expressed, as usual, by $\mathbf{k}_{el}(kT/h)$, where $\mathbf{k}_{el}$ is the so-called transmission coefficient.[43] The free-energy change ΔG is related to the overall free-energy change from $^*D + A$ to $D^+ + A^-$ by the following relationship:

$$\Delta G = \Delta G_t - W_r + W_p \qquad (8)$$

where W_r and W_p are the so-called work terms, i.e., the energy required to bring the reactants or products together from an infinite distance apart to their separation distance in the activated complex. Assuming an outer-sphere mechanism, W_r and W_p are practically zero when at least one of the two reaction partners is an uncharged species. Using eq 6 and 7, eq 5 can be transformed into

$$k^{el}{}_q = \frac{k_d}{1 + \dfrac{k_{-d}}{k_s} e^{\Delta G/RT} + \dfrac{k_{-d}}{k^0{}_{el}} e^{\Delta G^{\ddagger}/RT}} \qquad (9)$$

The meaning of the free-energy change in excited state electron transfer processes has been discussed elsewhere[24,30] and thus it will not be dealt with here. As is usual for ground-state reactions, the free activation energy can be related to the free-energy change of the process. At least three different relationships proposed by Marcus[31] (eq 10), Rehm and Weller[24,25] (eq 11), and Agmon and Levine[44-46] (eq 12) can be used:[39]

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}(0) \left(1 + \frac{\Delta G}{4\Delta G^{\ddagger}(0)}\right)^2 \qquad (10)$$

$$\Delta G^{\ddagger} = \frac{\Delta G}{2} + \left[\left(\frac{\Delta G}{2}\right)^2 + \left(\Delta G^{\ddagger}(0)\right)^2\right]^{1/2} \qquad (11)$$

$$\Delta G^{\ddagger} = \Delta G + \frac{\Delta G^{\ddagger}(0)}{\ln 2} \ln \left[1 + \exp\left(-\frac{\Delta G \ln 2}{\Delta G^{\ddagger}(0)}\right)\right] \qquad (12)$$

where $\Delta G^{\ddagger}(0)$ is the so-called reorganizational intrinsic barrier (i.e., the free activation energy for $\Delta G = 0$), which is related to the changes in the nuclear positions that have to occur prior to electron transfer, as is required by the Franck–Condon principle.[47] The meaning of $\Delta G^{\ddagger}(0)$ will be discussed in detail later. As previously discussed,[39] the Agmon–Levine relationship[44-46] should be preferred. A general equation for the electron transfer quenching rate constant can thus be obtained by substituting eq 12 into eq 9.

Let us define a homogeneous series of reactions as one in which k_d, k_{-d}, k_s, $k^0{}_{el}$, and $\Delta G^{\ddagger}(0)$ are constant. This may happen when an excited state is quenched by a family of structurally related molecules (or when a family of structurally related excited states are quenched by the same molecule). In such a case, it follows that $k^{el}{}_q$ is only a function of ΔG, i.e., of the redox potential of the quenchers (or of the excited states). Several experimental results have been reported which agree with this expectation.[26,39]

It is now worthwhile recalling the meaning of the intrinsic barrier $\Delta G^{\ddagger}(0)$, which is the key point of this treatment.[31-35] For a generic electron transfer reaction

$$D + A \rightarrow D^+ + A^- \qquad (13)$$

the intrinsic barrier is given by

$$\Delta G^{\ddagger}{}_{DA}(0) = \frac{1}{2}(\Delta G^{\ddagger}{}_D + \Delta G^{\ddagger}{}_A) \qquad (14)$$

where $\Delta G^{\ddagger}{}_D$ and $\Delta G^{\ddagger}{}_A$ are the free energy of activation of the so-called "self-exchange" electron transfer reactions:

$$D + D^+ \rightarrow D^+ + D \qquad (15)$$

$$A + A^- \rightarrow A^- + A \qquad (16)$$

In other words, the intrinsic barrier $\Delta G^{\ddagger}(0)$ of the cross reaction (eq 13) can be written as the sum of two terms (intrinsic barriers), one depending only on the properties of species D in its initial and final states, and the other depending only on the properties of species A in its initial and final states. For each species, the intrinsic barrier receives contributions from changes in the internal nuclear coordinates of the molecule ("inner-sphere" reorganizational energy, $\Delta G^{\ddagger}{}_i$) and from changes in the solvent arrangement around the molecule ("outer-sphere" reorganizational energy, $\Delta G^{\ddagger}{}_o$):[48]

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}{}_i + \Delta G^{\ddagger}{}_o \qquad (17)$$

In principle, both $\Delta G^{\ddagger}{}_i$ and $\Delta G^{\ddagger}{}_o$ can be calculated if appropriate quantities of the system are known.[35] As the electron transfer causes a change in the electric charge of the reactants, $\Delta G^{\ddagger}{}_o$ is always an important term. $\Delta G^{\ddagger}{}_i$ may be negligible when the transferred electron lies in a very delocalized orbital (e.g., aromatic molecules) but it may even be higher than $\Delta G^{\ddagger}{}_o$ when σ antibonding orbitals are involved (e.g., $Fe(H_2O)_6{}^{3+/2+}$). Recently, $\Delta G^{\ddagger}$ values have also been obtained for self-exchange electron-transfer reactions involving excited states.[25,36,49]

III. Quenching by Energy Transfer

For the quenching via energy transfer by a collisional (exchange) mechanism, a kinetic scheme

$$\begin{array}{llllll}
D + A + h\nu \longrightarrow & {}^*D + A & \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} & {}^*D\cdots A & & \\
 & \Big\downarrow 1/\tau^0{}_{*D} & & & & \\
 & & & \underset{k_{-en}}{\overset{k_{en}}{\rightleftharpoons}} D\cdots {}^*A & \underset{k_d}{\overset{k_{-d}}{\rightleftharpoons}} & D + {}^*A \\
 & & & & & \Big\downarrow 1/\tau^0{}_{*A}
\end{array} \qquad (18)$$

analogous to that given before (eq 4) for electron-transfer quenching can be used. In eq 18, k_d and k_{-d} are the rate constants for the formation and dissociation of the encounter, which are taken to be the same for reactants and products as we are considering purely physical encounters between the species involved. Assuming that $1/\tau^0{}_{*A} \gg k_d[D]$ and using steady-state approximations, the experimental quenching constant $k^{en}{}_q$ (eq 1) is given by

$$k^{en}{}_q = \frac{k_d}{1 + \dfrac{k_{-d}}{k_{en}}\left(1 + \dfrac{k_{-en}}{k_{-d}}\right)} \qquad (19)$$

As we are dealing with thermally equilibrated excited states, the following relationships can be written for the energy-transfer step of eq 18 in the frame of the absolute rate theory:[43]

$$k_{en} = k^0{}_{en} e^{-\Delta G^{\ddagger}/RT} \qquad (20)$$

$$k_{-en}/k_{en} = e^{\Delta G/RT} \qquad (21)$$

where $k^0{}_{en}$ is the preexponential factor and $\Delta G^{\ddagger}$ and ΔG are the free energy of activation and the standard free energy change of the forward energy-transfer step. As usual, the preexponential factor is given by $\mathbf{k}_{en}(kT/h)$, where $\mathbf{k}_{en}$ is the transmission coefficient to be discussed later. The standard free energy change of the energy-transfer step is related to the measured free energy change from $^*D + A$ to $D + {}^*A$ by a relationship involving the work terms (see eq 8). In the very common case in which at least one of the two reactants is uncharged (e.g., eq 18), the work terms are negligible as we are considering only processes involving purely physical encoun-

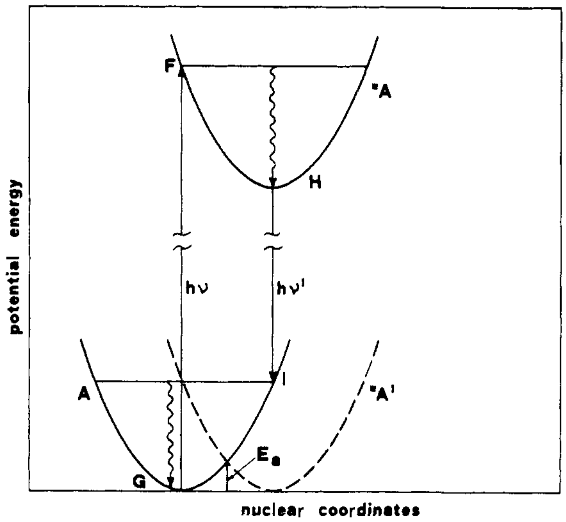

Figure 1. Schematic representation of the relationship between spectroscopic Stokes shift and intrinsic barrier of a "self-exchange" energy transfer reaction (eq 27). The displacement from the ground-state geometry may occur along internal and/or external (solvent) nuclear coordinates.

ters. Using eq 20 and 21, eq 19 can be transformed as follows:

$$k^{\mathrm{en}}_{\mathrm{q}} = \frac{k_{\mathrm{d}}}{1 + e^{\Delta G/RT} + \frac{k_{-\mathrm{d}}}{k^{0}_{\mathrm{en}}} e^{\Delta G^{\ddagger}/RT}} \qquad (22)$$

The standard free energy change in eq 22 is given by

$$\begin{aligned} \Delta G = \Delta H - T\Delta S &= -\Delta G(^{*}\mathrm{D,D}) + \Delta G(^{*}\mathrm{A,A}) \\ &= -\Delta H(^{*}\mathrm{D,D}) + T\Delta S(^{*}\mathrm{D,D}) \\ &\quad + \Delta H(^{*}\mathrm{A,A}) - T\Delta S(^{*}\mathrm{A,A}) \qquad (23) \end{aligned}$$

In condensed phase, at 1 atm and 0 K, the enthalpy difference between excited and ground state of the same molecule is practically equal to the zero-zero spectroscopic energy (E^{00}) of the excited state.[50] Thus, if the vibrational partition functions of the two states are not very different, the enthalpy difference between ground and excited states at room temperature is also equal to the zero-zero spectroscopic energy.[30] The entropy difference between ground and excited state of the same molecule may be due to three different contributions: (1) change in dipole moment with consequent changes in solvation, (2) changes in the internal degrees of freedom, and (3) changes in orbital and spin degeneracy. This last contribution can be straightforwardly calculated, but it is small and in most cases it can be neglected. The two other contributions are generally difficult to evaluate. However, sample calculations[30a,51] show that contributions (1) and (2) are also negligible in most practical cases. Thus, the free-energy difference between excited state and ground state can usually be considered as equal to the zero-zero spectroscopic energy of the excited state:

$$\Delta G \simeq -E^{00}(^{*}\mathrm{D,D}) + E^{00}(^{*}\mathrm{A,A}) \qquad (24)$$

In order to understand the meaning of $\Delta G^{\ddagger}$ in eq 22, consider a "self-exchange" energy transfer reaction, e.g.

$$^{*}\mathrm{A} + \mathrm{A} \rightarrow \mathrm{A} + {}^{*}\mathrm{A} \qquad (25)$$

between an excited state and the ground state of the same molecule having minima at different values of the nuclear coordinates. For the sake of simplicity, suppose that both states can be described by the same harmonic function and that the zero-point energy can be neglected (Figure 1). A collision between *A and A when both are in their zero vibrational levels cannot result in energy transfer because of Franck-Condon restrictions. The "vertical" energy available in the excited state (HI in Figure 1) is in fact much smaller than that needed for the vertical excitation of the ground state (FG). The energy difference FG − HI is equal to the spectroscopic Stokes shift (S). This energy deficiency can be made up by vibrational excitation of *A and/or A. As was pointed out by Lamola[2a] and Sandros,[4] the extra energy needed is actually much less than that corresponding to the Stokes shift because population of higher vibrational levels of the distorted mode in either the excited state or the ground state is effective in reducing the energy required for vertical excitation. In particular, in a case like that of Figure 1 the energy needed for the energy-transfer reaction (eq 27) is $S/2$ if only the donor or the acceptor is vibrationally excited. An even more convenient path is that involving the excitation of *both* *A *and* A to a vibrational level which corresponds to the crossing point between curves A and *A' in Figure 1. In such a case, the activation energy is E_{a} for both A and *A. That is, the total activation energy needed for reaction 25 is $2E_{\mathrm{a}}$, which is equal to $S/4$.[41] It can easily be shown that, for a general case in which the ground and excited states are represented by different harmonic functions, the activation energy has to be lower than $S/4$. When the ground and excited states are represented by sinusoidal potential energy curves (a case which applies to energy transfer involving twisted excited states, section V), analogous arguments show that the activation energy is lower than $S/2$.

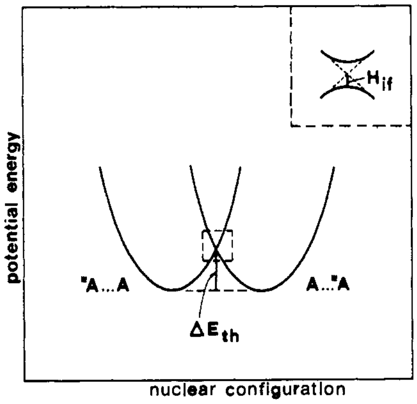

Figure 2. Profile of the potential-energy surfaces as a function of the nuclear configuration for a self-exchange energy transfer reaction. The insert shows in greater detail the "intersection" region.

The above kind of reasoning is completely analogous to that usually adopted in discussing electron-transfer reactions involving ground or excited states within the frame of the Marcus-Hush theory.[31-35] For the simple parabolic case (Figure 1), the profile of the potential energy as a function of the nuclear configuration for a self-exchange energy-transfer reaction (eq 25) can thus be represented as in Figure 2. In this figure, ΔE_{th} is the activation energy needed to transform *A ··· A into A ··· *A, and H_{if} is the interaction energy to be discussed later.

From the above discussion it follows that for each molecule involved in an energy-transfer process we can define a quantity, E_{a}, which is related to the distortion between ground and excited state and which determines the intrinsic barrier to energy transfer. In terms of free energies, the free activation energy of the self-exchange energy-transfer reaction (eq 25) is given by

$$\Delta G^{\ddagger}_{\mathrm{A}} = 2(E_{\mathrm{a}} + C^{\ddagger}) \qquad (26)$$

where E_{a} has the meaning discussed above and $C^{\ddagger}$ accounts for the differences in partition functions between reactants (in the encounter) and transition state. When the donor-acceptor interaction is sufficiently weak, the internal and solvent degrees of freedom are unperturbed in the transition state, so that $C^{\ddagger}$

can be neglected.[33] As in the case of electron-transfer reactions, $\Delta G^{\ddagger}$ receives contributions from changes in the inner nuclear coordinates of the molecule ("inner-sphere" reorganizational energy, $\Delta G^{\ddagger}_{\mathrm{i}}$) and from changes in the solvent arrangement around the molecule ("outer-sphere" reorganizational energy, $\Delta G^{\ddagger}_{\mathrm{o}}$):

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}_{\mathrm{i}} + \Delta G^{\ddagger}_{\mathrm{o}} \tag{27}$$

Contrary to what happens in electron-transfer processes, $\Delta G^{\ddagger}_{\mathrm{o}}$ is usually very small because in energy-transfer processes the electric charges of the reactants do not change. At most, there are changes in dipole moment and polarizability, which usually do not cause a drastic rearrangement of the solvation sphere.

By analogy with the electron-transfer processes, for a "cross" energy-transfer process (eq 1 and 18) the reorganizational energy, $\Delta G^{\ddagger}(0)$, can be defined as

$$\Delta G^{\ddagger}_{\mathrm{DA}}(0) = \frac{1}{2}\left(\Delta G^{\ddagger}_{\mathrm{D}} + \Delta G^{\ddagger}_{\mathrm{A}}\right) \tag{28}$$

where $\Delta G^{\ddagger}_{\mathrm{D}}$ and $\Delta G^{\ddagger}_{\mathrm{A}}$ are intrinsic parameters (see eq 26) of molecules D and A.

Now, let us go back to eq 22. As we have seen before, energy transfer and electron transfer quenching are analogous in that the free energy of activation is only related to the adjustment of the inner and outer nuclear coordinates prior to the electron rearrangements. Thus, the same relationships (eq 10, 11, or 12) used to express the dependence of $\Delta G^{\ddagger}$ on ΔG for electron-transfer processes can be used here. If eq 12 is preferred, as in the electron-transfer case,[39] eq 22 can be transformed as follows:

$$k^{\mathrm{en}}_{\mathrm{q}} = \frac{k_{\mathrm{d}}}{1 + \exp\left(\dfrac{\Delta G}{RT}\right) + \dfrac{k_{-\mathrm{d}}}{k^{0}_{\mathrm{en}}}\exp\left\{\dfrac{\Delta G + \dfrac{\Delta G^{\ddagger}(0)}{\ln 2}\ln\left[1 + \exp\left(-\dfrac{\Delta G \ln 2}{\Delta G^{\ddagger}(0)}\right)\right]}{RT}\right\}} \tag{29}$$

In this equation, ΔG and $\Delta G^{\ddagger}(0)$ represent the free-energy change and the intrinsic barrier of the forward energy transfer reaction. It is interesting to compare eq 29 to eq 2. The dissociation rate constant $k_{-\mathrm{d}}$ which is present in eq 29 can be calculated by means of the Eigen equation.[53] For an energy-transfer process with high preexponential factors (for a discussion, see later), the ratio $k_{-\mathrm{d}}/k^{0}_{\mathrm{en}}$ is much lower than unity. It follows that, when $\Delta G^{\ddagger}(0)$ is equal to zero or very small (i.e., when the excited states involved in the energy-transfer process are not distorted or only slightly distorted), the third term in the denominator of eq 29 can be neglected. On the other hand, ΔG is given by eq 24, so that under such conditions eq 29 reduces to the Sandros equation (eq 2). However, when distorted excited states are involved ($\Delta G^{\ddagger}(0) \neq 0$) and/or the preexponential factor is low ($k^{0}_{\mathrm{en}} \leqslant k_{-\mathrm{d}}$), the third term in the denominator of eq 29 is not negligible. Moreover, for distorted excited states $E^{00}(^*\mathrm{D,D})$ and $E^{00}(^*\mathrm{A,A})$ are generally unknown because the available spectroscopic data usually correspond to vertical transitions. For these reasons, eq 2 often proves to be inadequate to fit the experimental data[2a,3,4,10–15] and the more general eq 29 has to be used. The fact that for distorted excited states the experimental quenching constants have been generally found to be *higher* than the expected (on the basis of eq 2) rates[2a,3,4,10–15] is at first sight surprising because it seems obvious that distortion, introducing an intrinsic barrier, should always cause a decrease in the rate constant. The reason for these apparently contradictory results is that the "expected" rates were calculated using the vertical absorption energies of the distorted excited states of the acceptors,[54] which are of course higher than the zero-zero spectroscopic energies that should have been used in a more correct analysis.

The treatment given above, which has led to the formulation of eq 29, provides a unified view of the so-called vertical and nonvertical energy-transfer behavior. The discussion of energy-transfer processes using eq 29 as a basis facilitates the understanding of the experimental results and can also lead to the evaluation of unknown quantities, such as the zero-zero spectroscopic energy and the (lower limiting) value of the Stokes shift of a distorted excited state (section V). In order to make these points clearer, consider the energy-transfer quenching of a homogeneous family of undistorted excited states having variable excited state energies by a single quencher which is promoted to a distorted excited state. In such a case, k_{d}, $k_{-\mathrm{d}}$, k^{0}_{en}, and $\Delta G^{\ddagger}(0)$ in eq 29 are constant, while ΔG is given by eq 24. Thus, according to eq 29, plots of log $k^{\mathrm{en}}_{\mathrm{q}}$ vs. $E^{00}(^*\mathrm{D,D})$ look like those of Figure 3. That is, for very high $E^{00}(^*\mathrm{D,D})$ values there is a plateau region with $k^{\mathrm{en}}_{\mathrm{q}} = k_{\mathrm{d}}$ for $k^{0}_{\mathrm{en}} \gg k_{-\mathrm{d}}$ and $k^{\mathrm{en}}_{\mathrm{q}} = (k_{\mathrm{d}}/k_{-\mathrm{d}})\,k^{0}_{\mathrm{en}}$ for $k^{0}_{\mathrm{en}} \ll k_{-\mathrm{d}}$. On the other hand, for very low $E^{00}(^*\mathrm{D,D})$ values, log $k^{\mathrm{en}}_{\mathrm{q}}$ is expected to increase linearly with slope $1/(2.3RT)$ as $E^{00}(^*\mathrm{D,D})$ increases. These two linear regions are connected by a region in which log $k^{\mathrm{en}}_{\mathrm{q}}$ increases in a complex but monotonous way as $E^{00}(^*\mathrm{D,D})$ increases. The nonlinear region covers a $E^{00}(^*\mathrm{D,D})$ range which, for a given k^{0}_{en} value, is broader and broader as $\Delta G^{\ddagger}(0)$ increases. A similar kind of plot is expected, of course, for the energy-transfer quenching of a distorted excited state by a homogeneous family of undistorted quenchers having variable excited state energy.

Figures 4–6 show the relationship, for some typical cases, between the spectroscopic parameters of a single molecule A acting as a donor or acceptor and the curves representing log $k^{\mathrm{en}}_{\mathrm{q}}$ vs. the $E^{00}(^*\mathrm{D,D})$ energy of a homogeneous family of undistorted molecules. Figure 4 refers to a molecule having almost identical geometry in the ground and excited state (small Stokes shift, small $\Delta G^{\ddagger}(0)$, "vertical" behavior as both acceptor and donor). Figure 5 refers to a molecule having different geometries and sufficiently large and similar force constants in the ground and excited state (large Stokes shift, large $\Delta G^{\ddagger}(0)$, "nonvertical" behavior as both donor and acceptor). Figure 6 refers to a molecule having different geometries and force constants in the ground and excited state (moderately large Stokes shift, small $\Delta G^{\ddagger}(0)$, "vertical" behavior as acceptor but not as donor (case 6a), and "vertical" behavior as donor but not as acceptor (case 6b)). The available results obtained by several workers from systematic studies of energy-transfer experiments agree with the above expectations (section V).

After having considered in some detail the role played by the exponential factor of the energy transfer rate constant (eq 20), let us briefly discuss the meaning of the preexponential factor. As mentioned above, according to the absolute reaction rate theory

$$k^{0}_{\mathrm{en}} = \mathbf{k}_{\mathrm{en}}\frac{kT}{h} \tag{30}$$

where $\mathbf{k}_{\mathrm{en}}$ is the transmission coefficient and kT/h is a universal frequency. The transmission coefficient can be considered as the product of a nuclear and an electronic factor.[55] The nuclear factor accounts for the possibility that nuclear tunneling may occur, leading from reactants to products without activation

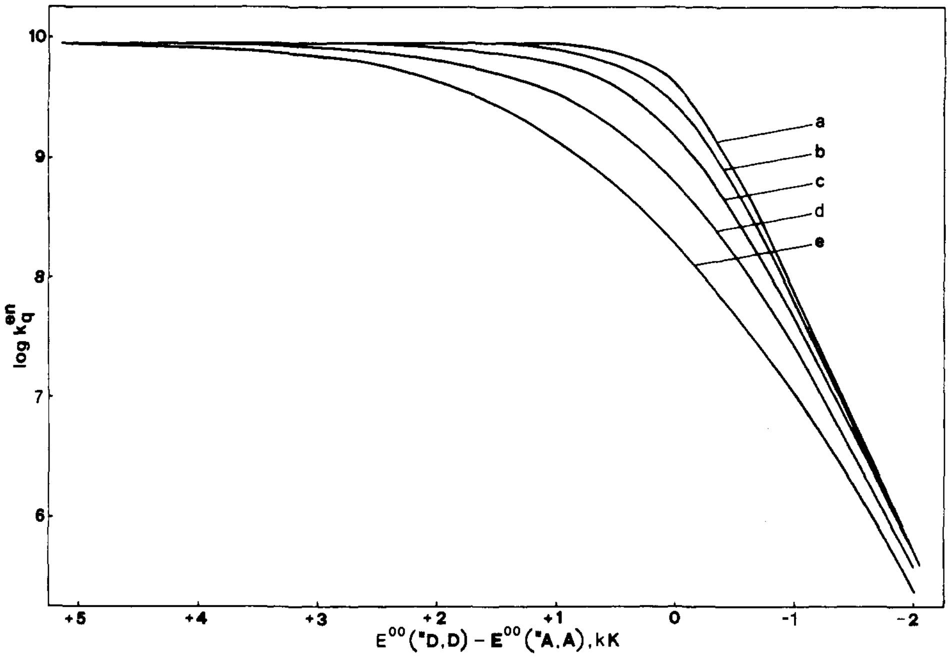

Figure 3. Influence of the intrinsic reorganizational energy on the shape of log k^{en}_q vs. E^{00} (*D,D) curves. The curves have been obtained using eq 31 with the following values: $k_d = 10^{10}$ M^{-1} s^{-1}, $k_{-d} = 1.2 \times 10^{10}$ s^{-1}, $k^0_{en} = 1 \times 10^{11}$ s^{-1}, $T = 293$ K, $\Delta G^{\ddagger}(0)$ = 250 (a), 500 (b), 750 (c), 1000 (d), 1250 cm^{-1} (e).

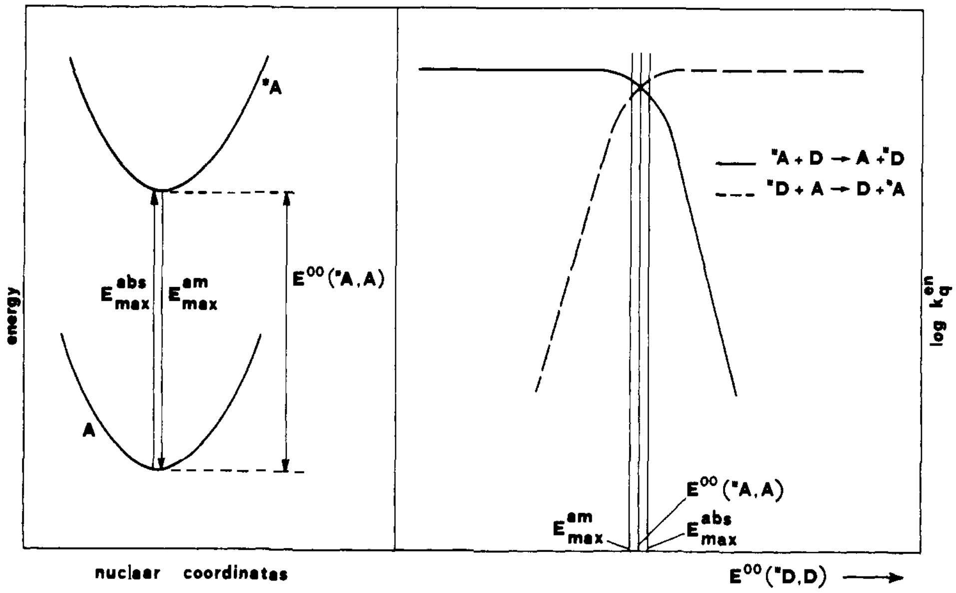

Figure 4. Relationships between the log k^{en}_q vs. E^{00}(*D,D) curves and the spectroscopic parameters of a molecule A having almost identical geometry in the ground and excited state. For details, see text.

to the transition state. The electronic factor is related to the interaction energy H_{if} (Figure 2) between the initial and final states. As is well known, the electronic factor can be very small for spin-forbidden processes.[2a] Less care is usually reserved to the fact that the electronic factor may also be small because of unfavorable spatial overlap between the initial and final electronic wave functions. For exchange energy transfer processes, the overlap criterion is quite stringent[15] because favorable and simultaneous overlap of two orbital pairs (HOMO-HOMO and LUMO-LUMO of the donor-acceptor couple) is required.[56] When the electronic factor is small, the probability of reactants being converted into products in the transition state (i.e., the transmission coefficient) is small and the system can be said to exhibit a "nonadiabatic" behavior.[43]

IV. Meaning and Limitations of the Proposed Treatment

The treatment proposed here is based on a classical model and makes use of the absolute rate theory. Thus, this treatment is subject to all limitations which are encountered when a quantum problem is dealt with in a classical way.

The criterion of applicability of the classical approach is

$$h\nu_i < kT \qquad (31)$$

where the ν_i's are the frequencies of the nuclear vibrations. In any energy-transfer process there is at least one classical component, the solvent, whose frequency of orientation around the molecule is certainly sufficiently low to satisfy the above condition. However, as was mentioned in section III, the free activation energy connected with solvent reorientation ($\Delta G^{\ddagger}_0$ in eq 27) is very small for most energy-transfer processes. In-

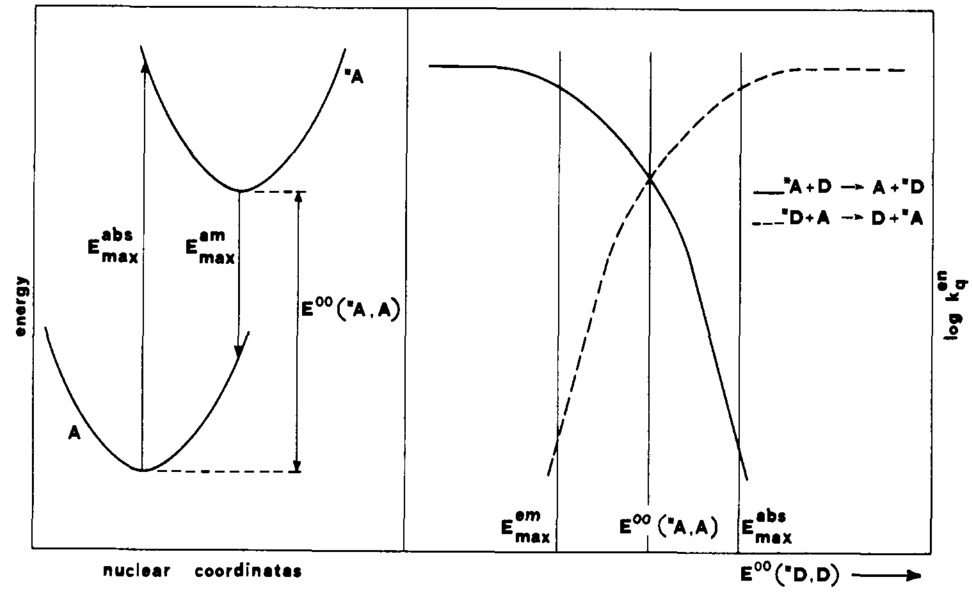

Figure 5. Relationships between the log k^{en}_q vs. E^{00}(*D,D) curves and the spectroscopic parameters of a molecule A having different geometry and sufficiently large and similar force constant in the ground and excited state. For details, see text.

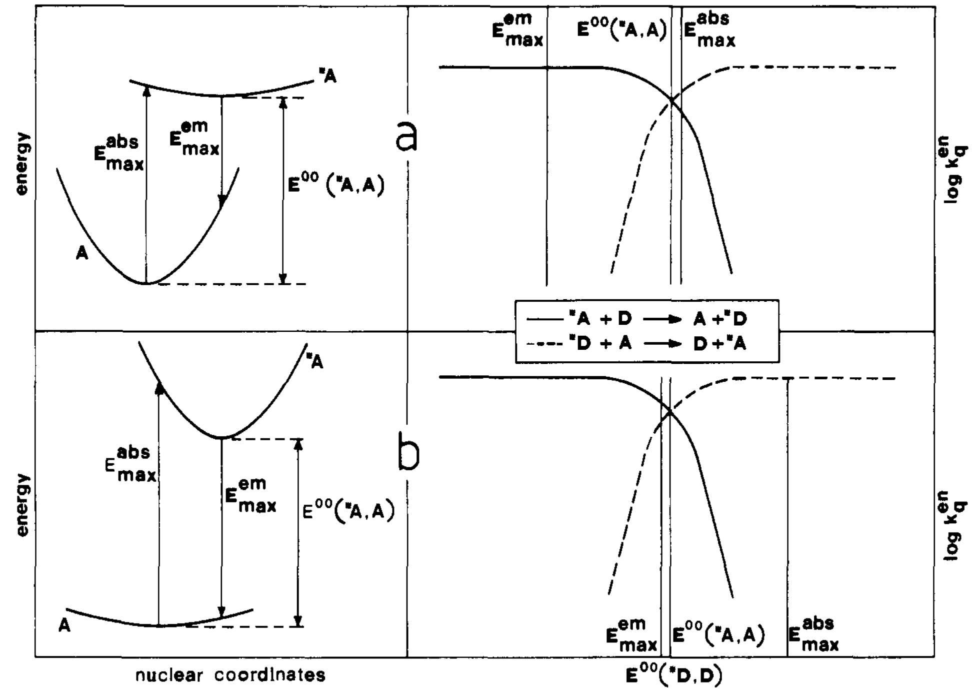

Figure 6. Relationship between the log k^{en}_q vs. E^{00}(*D,D) curves for a molecule A having different geometries and force constants in the ground and excited state. For details, see text.

ternal distortions of the molecule along a low-frequency coordinate (such as, for example, the twisting around the central C=C bond of stilbenes, section V) can also be treated classically to a first approximation. For some molecules the distortion along such low-energy coordinates is very strong and the correspondent $\Delta G^{\ddagger}{}_i$ (eq 27) is so large that, as we have seen in section III, the use of the Sandros equation (eq 2) becomes meaningless. By contrast, energy-transfer processes involving distorted excited states along such low-frequency coordinates can be correctly discussed on the basis of our classical treatment (eq 22).[57]

When, as is usually the case, distortion also occurs along high-frequency vibrational modes ($\hbar\nu_i > kT$), the absolute reaction rate model cannot be strictly applied. A general quantum mechanical approach has been formulated for electron-transfer processes in solution in terms of radiationless transition between electronic states of a "supermolecule" consisting of donor, acceptor, and solvent.[58-60] Considering the similarity of electron and energy-transfer processes, the main features of the electron-transfer treatment can be extended to energy transfer.[61] In this view, the rate constant can be expressed as the product of an electronic and a nuclear term, both of which depend on temperature. The nuclear term is a thermally averaged summation over all the individual vibronic transitions of the system, each having a weight proportional to its Franck–Condon factor. It is impossible to recast the quantum-mechanical expressions of the rate constant in a classical-like (eq 20) form. On the other hand, the application of quantum-mechanical expressions to practical cases is presently prevented by the lack of knowledge of most of the relevant molecular parameters.[62] However, sample calculations[59-61] on model systems indicate that the general behavior

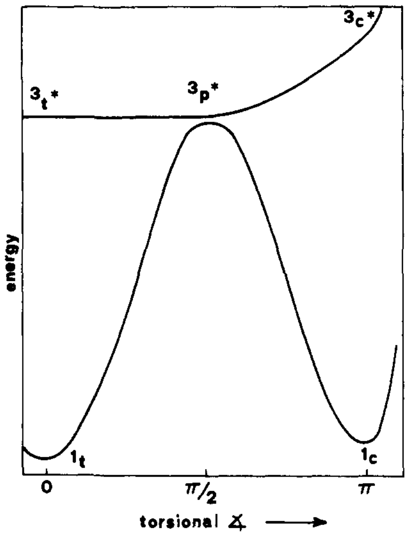

Figure 7. Common representation[1,11] of the potential-energy curves of ground and lowest excited triplet states of stilbene along the C═C torsional coordinate.

of log k^{en}_q vs. ΔG tends to be analogous to that predicted by the simple classical model given by eq 20 and 12. In particular, the following features emerge from the quantum-mechanical treatment: (1) for very endoergonic processes, log k^{en}_q is expected to increase linearly (slope $1/2.3RT$) as ΔG decreases; (2) for slightly endo- or exoergonic reactions, the rate at a fixed ΔG value decreases with increasing distortion; (3) for highly exoergonic reactions, the rate constant is expected to level up to an almost constant value if a sufficient number of distorted vibrations is taken into consideration. Thus, although the classical model is theoretically inadequate for a general treatment of energy-transfer processes, the use of eq 20 and 12 may be formally justified provided that an operational meaning is attributed to the various parameters. A number of examples in which eq 29 (which derives from eq 20 and 12) accounts for the experimental results will be discussed in section V.

Having recognized these limitations, we suggest that eq 29 be used as a yardstick for the following practical purposes:

(1) The experimental quenching constants of energy-transfer processes between a homogeneous series of donors (or acceptors) and a single acceptor (or donor) have to satisfy eq 29; the departure of an experimental point from the best fitting curve is a measure of the nonhomogeneity of that donor (or acceptor) with respect to the other donors (or acceptors) of the series.

(2) The value of $\Delta G^{\ddagger}(0)$ for which the best fit is obtained is taken as a measure of the "overall" distortion of the excited states involved; if two structurally related acceptors (or donors) are equally distorted in the excited state along all but one coordinate, the difference in their $\Delta G^{\ddagger}(0)$ values is a direct measure of the difference in distortion along that coordinate.

(3) The value of ΔG_A (or ΔG_D) for which ΔG in eq 29 is equal to zero is a measure of the zero-zero spectroscopic energy of the donor (or acceptor) (eq 24).

(4) The value of $\mathbf{k}_{en}$ for which the best fit is obtained allows an evaluation of the orbital, spin, and (to a minor extent) Franck-Condon restrictions to energy transfer.

V. Examination of Some Experimental Results

Stilbenes. The photochemistry and photophysics of stilbene are of considerable interest from both a theoretical and a practical point of view because stilbene is the prototype of molecules which play an important role in photobiology. The direct and sensitized cis-trans photoisomerization of stilbene has been thoroughly investigated;[63] as far as the triplet-triplet energy transfer is concerned, *trans*- and *cis*-stilbenes are reported as typical examples of molecules which behave as "vertical" and "nonvertical" acceptors, respectively.[2a,3,6,7,11,15,64] Such behavior is usually discussed on the basis of potential-energy curves like those of Figure 7. The twisting frequency around the ethylenic C═C bond is low,[65] so that the distortion along such a torsional coordinate can be treated classically. The experimental data obtained by Herkstroeter and Hammond[3] for the energy transfer from aromatic triplets to *trans*- and *cis*-stilbene in benzene are shown in Figure 8. It is clear that the nonlinear region of the plot covers a much broader $E^{00}(^*D,D)$ range for the cis than for the trans isomer, as expected on the basis of a different excited-state distortion along the torsional coordinate. It has long been recognized[3] that the Sandros equation (eq 2) is not able to account for the behavior of the cis isomer. In contrast, eq 29 can fit the experimental data of both isomers.[66] Using eq 24 and 29 with $k_d = 1 \times 10^{10}\ M^{-1}\ s^{-1}$, $k_{-d} = k_d(3000)/(Nr^3 4\pi)$,[53] and $r = 0.7$ nm, a graphical procedure[67] has shown that the best fitting curves are obtained for $k^0_{en} = 1 \times 10^{10}\ s^{-1}$, $\Delta G^{\ddagger}(0) = 500\ cm^{-1}$, and $E^{00}(^*A,A) = 17\ 000\ cm^{-1}$ for the trans isomer, and $k^0_{en} = 1 \times 10^{10}\ s^{-1}$, $\Delta G^{\ddagger}(0) = 1000\ cm^{-1}$, and $E^{00}(^*A,A) = 16\ 900\ cm^{-1}$ for the cis isomer. The $E^{00}(^*A,A)$ value obtained in this way for the trans isomer is practically the same as that of the onset of the singlet-triplet absorption (17 100 cm^{-1}),[11] while that obtained for the cis isomer is much lower than the onset of the corresponding absorption band (~19 900 cm^{-1}),[11] but close to that expected for the triplet state in the "perpendicular" configuration.[11] Considering that the enthalpy difference between cis and trans ground-state molecules is 2.3 kcal/mol[19] and assuming that the entropy content is the same for both isomers, the minimum of the free-energy curve of the triplet cis isomer (which corresponds to the "perpendicular" configuration) seems to be slightly higher (17 700 cm^{-1}) than that of the triplet trans isomer.[68] According to the discussion given in section IV, the difference between the values of $\Delta G^{\ddagger}(0)$ for energy transfer to the cis and trans isomers can be taken as a measure of the different excited-state distortion

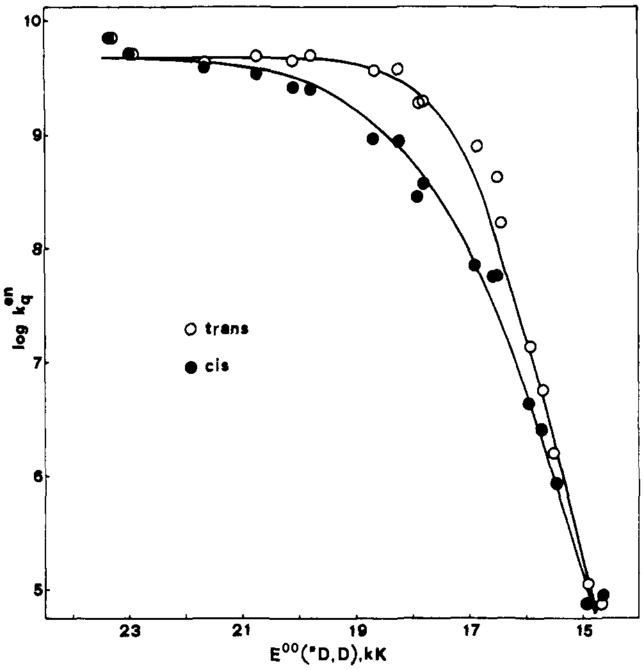

Figure 8. Plot of log k^{en}_q vs. $E^{00}(^*D,D)$ for the energy-transfer quenching of aromatic triplets by *cis*- and *trans*-stilbene in benzene solution. The points represent the experimental data reported in ref 3. The solid lines are the best fitting curves according to eq 29 (see text).

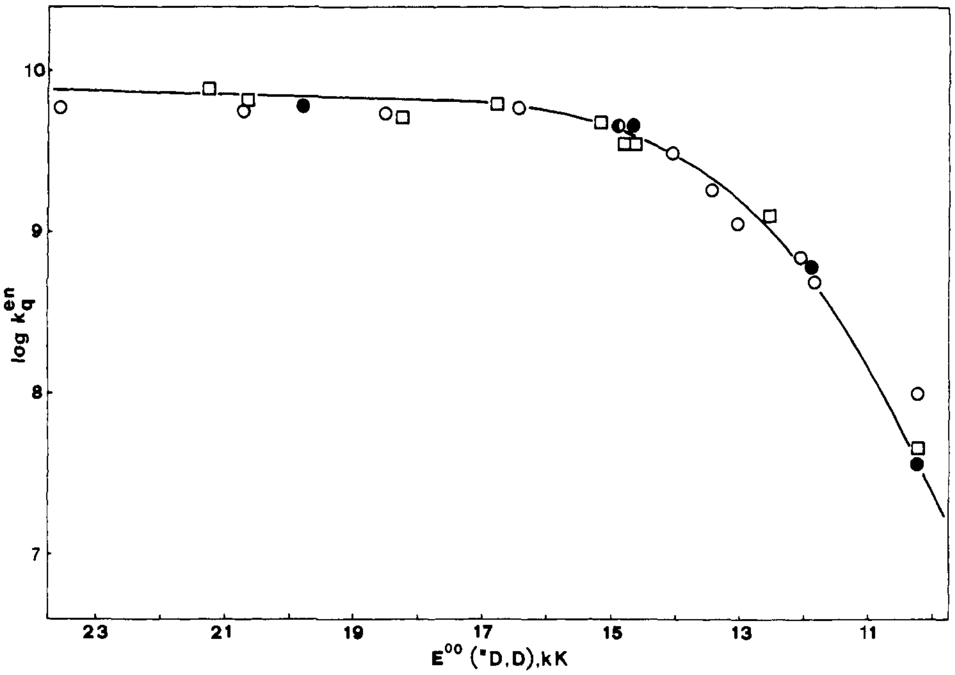

Figure 9. Plot of log k^{en}_q vs. E^{00}(*D,D) for energy-transfer quenching of aromatic triplets by ferrocene. The points represent the experimental data reported in ref 12 (●) and 13 (○) for benzene solutions, and in ref 73 (□) for ethanol solution. The data obtained with quenchers having E^{00}(*D,D) <10 000 cm^{-1} are not considered because for low quenching constants the experimental errors are large and quenching mechanisms other than energy transfer may prevail. The solid line is the best fitting curve according to eq 29 (see text).

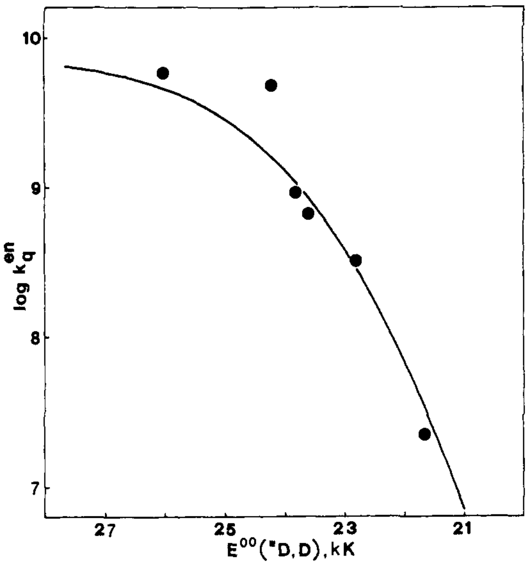

Figure 10. Plot of log k^{en}_q vs. E^{00}(*D,D) for energy-transfer quenching of aromatic triplets by ruthenocene in benzene solution. The points represent the experimental data reported in ref 14. The solid line is the best fitting curve according to eq 29 (see text).

along the twisting around the C=C ethylenic bond (Figure 7). Using eq 28 and assuming that the intrinsic parameters are the same for the aromatic triplet donors and for the trans isomer, $\Delta G^{\ddagger}(0)_{trans}$ results to be ~500 cm^{-1} and $\Delta G^{\ddagger}(0)_{cis}$ ~ 1500 cm^{-1}.

We would also like to note that the value of k^0_{en} for both isomers is more than two orders of magnitude lower than the fully adiabatic kT/h value. A similar conclusion was reached by Wagner and Kochevar[21] by studying the viscosity dependence of energy transfer from ketones to dienes. As these processes are spin allowed, the reasons for such a behavior are to be found in orbital overlap and/or Franck-Condon restrictions.

Metallocenes. Ferrocene has long been known as an efficient quencher of organic triplets. The effective energy position of its lowest excited state,[70] however, is still unknown, and whether or not the quenching is due to electronic energy transfer has been the object of many discussions.[12,13,72-74] Several workers have pointed out that for ferrocene a plot of log k_q vs. the energy of triplet donors is typical of a "nonvertical" acceptor.[12,13,73] Such a plot, in fact, is nonlinear (Figure 9) for a very extended E^{00}(*D,D) range. One of the most detailed investigations on the triplet-state quenching by ferrocene was carried out by Farmilo and Wilkinson,[12] who concluded that the quenching is due to energy transfer and that an empirical coefficient $m = 2.9$ should be introduced in the denominator of the exponential term of the Sandros equation (eq 2) in order to fit it to the experimental results.

In a subsequent investigation Wilkinson et al.[14] found that ruthenocene also behaves as a "nonvertical" acceptor (Figure 10). For this molecule, the situation of the lowest excited state is fairly well known. The low-temperature luminescence with maximum at ~16 500 cm^{-1} observed by Wrighton et al.[74] and by Crosby et al.[75] is assigned by both groups to the phosphorescence emission of the lowest excited state, $^3E_{1g}$. The corresponding lowest absorption maximum is reported[76] to be at 26 000 cm^{-1}, showing that this excited state is strongly distorted with respect to the ground-state geometry.[74,75] An analysis of the phosphorescence emission has indicated that the distortion is due to a symmetrical expansion of the molecule along the a_{1g} ring-metal stretching vibration, whose frequency is 330 cm^{-1} in the ground state.[74,75] As is shown in Figures 9 and 10, eq 29 can fit the experimental data for both ferrocene and ruthenocene.[77] Using eq 24 and 29 with $k_d = 1 \times 10^{10}$ M^{-1} s^{-1}, $k_{-d} = k_d(3000)/(Nr^3 4\pi)$,[53] and $r = 0.7$ nm, a graphical procedure[78] has shown that the best fitting curves are obtained for $k^0_{en} = 5 \times 10^{10}$ s^{-1}, $\Delta G^{\ddagger}(0) = 2000$ cm^{-1}, and E^{00}(*A,A) = 9000 cm^{-1} for ferrocene, and for $k^0_{en} = 5 \times 10^{10}$ s^{-1}, $\Delta G^{\ddagger}(0) = 1300$ cm^{-1}, and E^{00}(*A,A) $\simeq$ 22 000 cm^{-1} for ruthenocene. Once again, the experimental frequency factor is definitely lower than the fully adiabatic kT/h value. For ruthenocene, if we assume harmonic functions for both the ground and excited state, the E^{00}(*A,A) value obtained above

($\sim$22 000 cm^{-1}), taken together with the vertical emission ($\sim$16 500 cm^{-1}) and absorption ($\sim$26 000 cm^{-1}) energies and the vibrational frequency of the ground state (330 cm^{-1}), yields the values of $\sim$280 cm^{-1} for the vibrational frequency of the excited state and $\sim$0.17 Å for the increase of the Ru-ring distance in the excited state. These values, which are obtained in such a simple way, are to be compared with those obtained by Crosby et al.[75] ($\sim$225 cm^{-1} and $\sim$0.15 Å) from a computer Franck-Condon analysis of the structured phosphorescence observed at 4.2 K. As far as ferrocene is concerned, our results provide the first evaluation of the zero-zero spectroscopic energy of the lower triplet state (9000 cm^{-1}). Moreover, the experimental $\Delta G^{\ddagger}(0)$ value (2000 cm^{-1}) taken together with the intrinsic parameter of the aromatic donors ($\sim$500 cm^{-1}; see above), yields (eq 28) an intrinsic parameter of $\sim$3500 cm^{-1} for ferrocene, which sets a lower limiting value of $\sim$14 000 cm^{-1} for the Stokes shift. If the Stokes shift to intrinsic parameter ratio is similar to that of ruthenocene, the lowest "vertical" absorption of ferrocene is more likely to be around 14 000–15 000 cm^{-1} as indicated by Rohmer et al.[79] than at about 19 000 cm^{-1} as suggested by Sohn et al.[76]

α-Diketones. Biacetyl is reported in the literature as a typical example of a molecule which behaves vertically in triplet-triplet energy-transfer processes,[2,4] whereas *o*-anisil (as well as benzil and *p*-anisil) is known to exhibit a typical "nonvertical" behavior.[4] The spectroscopic situation of these molecules is quite interesting. Both the lowest excited singlet and triplet states have $n\pi^*$ orbital character.[80] The comparison between the shapes of the absorption spectra[4] suggests that the equilibrium geometry in the ground state and in the first excited singlet is the same for biacetyl but very different for *o*-anisil. This is confirmed by the Stokes shift between absorption and emission, which is small ($\sim$1200 cm^{-1}) for biacetyl[81] and much larger ($\sim$7000 cm^{-1}) for *o*-anisil.[82] Since in these molecules the lowest triplet behaves as the lowest excited singlet,[80] one expects that the lowest triplet has the same equilibrium geometry as the ground state for biacetyl, but a very different geometry in the case of *o*-anisil. At first sight this expectation seems to be contradicted by the fact that both molecules exhibit a well-structured phosphorescence emission in fluid solutions,[83,84] with the main peak corresponding to the zero-zero transition of a progression along a high-fequency (C=O stretching) coordinate. This spectroscopic behavior, however, shows the the distortion of both molecules is almost the same along such a high-frequency coordinate, but it does not exclude that the situation may be quite different along other (e.g., torsional) coordinates. As it happens for all α-dicarbonyls,[80,81,85] the relaxed geometries of the lowest excited singlet and triplet states correspond to coplanar dicarbonyl groups because the π^* orbital has a bonding character in the region between the two carbon atoms. In the ground state, however, while biacetyl is trans planar,[86] *o*-anisil is most likely skewed.[87] Therefore, *o*-anisil is expected to exhibit a large Stokes shift between absorption to and emission from the lowest triplet, owing to its distortion along the torsional OC-CO coordinate. The fact that such a distortion does not affect the structure of the phosphorescence spectrum may simply be due to the fact that the ground-state curve is nearly flat in correspondence to the minimum of the excited-state curve.

The experimental results obtained by Sandros for the energy transfer from aromatic triplets to biacetyl[2b] and *o*-anisil[4] show that the nonlinear region of the plot of log k^{en}_q vs. E^{00} (*D,D) covers a much broader E^{00}(*D,D) range for *o*-anisil than for biacetyl (see also Figure 2 of ref 41). Sandros[4] was the first to realize that his equation (eq 2) cannot account for the behavior of *o*-anisil. As was shown in our preliminary communication,[41] eq 29 can fit the experimental data of both molecules.[89] Using eq 24 and 29, with $k_d = 1 \times 10^{10}$ M^{-1} s^{-1}, $k_{-d} = k_d(3000)/(Nr^3 4\pi)$,[53] and $r = 0.7$ nm, a graphical procedure[90] has shown that the best fitting curves are obtained for $k^0_{en} = 5 \times 10^{10}$ s^{-1}, $\Delta G^{\ddagger}(0) = 500$ cm^{-1}, and E^{00}(*A,A) = 19 600 cm^{-1} for biacetyl, and $k^0_{en} = 5 \times 10^{10}$ s^{-1}, $\Delta G^{\ddagger}(0) = 1250$ cm^{-1}, and E^{00}(*A,A) = 21 100 cm^{-1} for *o*-anisil. Assuming that $\Delta G^{\ddagger}(0)$ for the self-exchange of the aromatic donors is $\sim$500 cm^{-1} (see also above), the intrinsic parameters are $\sim$500 cm^{-1} for biacetyl and $\sim$2000 cm^{-1} for *o*-anisil (eq 28). As we have seen in section IV, the difference in these values is a measure of the different distortion along the torsional coordinate. As expected for an "undistorted" case (Figure 4), the E^{00}(*A,A) value obtained in this way for biacetyl is only slightly higher than the maximum of the emission spectrum. As far as *o*-anisil is concerned, the difference between E^{00}(*A,A) and $E^{em}{}_{max}$ ($\sim$3000 cm^{-1}) indicates that the Stokes shift ($\sim$7000 cm^{-1}) is almost equally divided into ground and excited state.

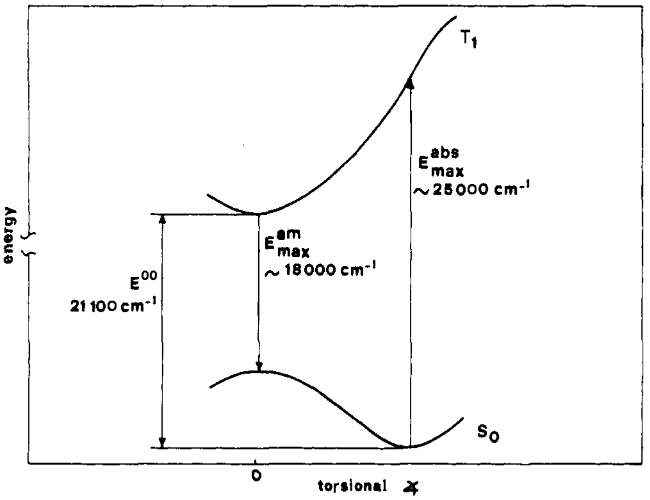

Figure 11. Schematic potential energy curves of ground and lowest triplet state of *o*-anisil as obtained from spectroscopic and energy-transfer results.

The spectroscopic data and the energy-transfer results considered together allow us to define some important features of the potential energy curves of *o*-anisil, which are summarized in Figure 11. It can be noted that this picture is quite similar to that of biphenyl, that has been thoroughly discussed by Wagner.[9,20]

Finally, we would like to note that also for α-diketones the frequency factor is definitely smaller than the fully adiabatic kT/h value.

Metal β-Diketonate Complexes. Very interesting results on the quenching of aromatic triplets by metal acetylacetonates have been obtained by several workers.[23,91,92] For the sake of space we shall only discuss the results reported by Wilkinson and Farmilo[23] for Fe(acac)$_3$ and Fe(dpm)$_3$, where acac is the acetylacetonate ion and dpm is the more bulky dipivaloylmethanate ion (Figure 12). As is indicated in the figure, these complexes have metal-centered (MC) excited states in the range 10 000–14 000 cm^{-1}, a ligand-to-metal charge transfer (CT) excited state at about 23 000 cm^{-1}, and a ligand-centered (LC) triplet state at about 26 000 cm^{-1}.[23] It is clear from the figure that the stepwise increase of k^{en}_q is related to the fact that energy transfer to higher excited states becomes energetically possible as the donor energy increases. Since none of the excited states is expected to be very distorted, the $\Delta G^{\ddagger}(0)$ values should be small in all cases; anyway, they cannot be responsible for the observed behavior. The fact that k^{en}_q reaches different plateau values in the various energy regions is to be ascribed to different transmission coefficients for the energy transfer to the different excited states. In other words, the experimental data indicate that energy transfer from aromatic triplets to these complexes is nonadiabatic (very small interaction energy) when the orbitals involved are metal cen-

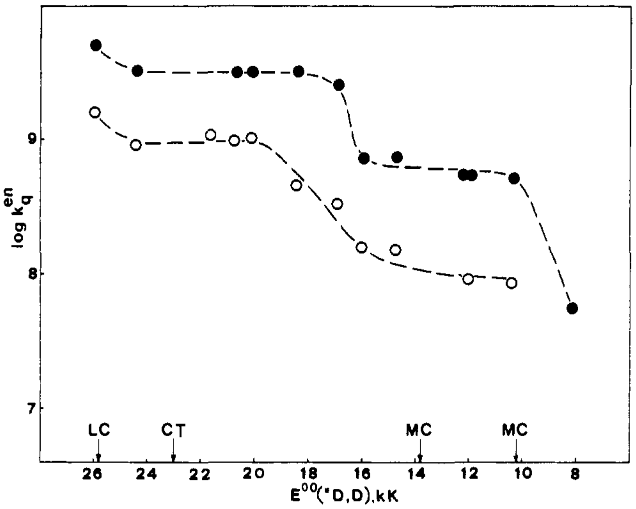

Figure 12. Plot of log $k^{en}{}_q$ vs. E^{00}(*D,D) for energy-transfer quenching of aromatic triplets by Fe(acac)$_3$ (full points) and Fe(dpm)$_3$ (empty points) (from ref 23). The arrows indicate the energy of the absorption maxima of metal-centered (MC) and charge-transfer (CT) bands and the supposed energy in absorption of the spectroscopically unobservable triplet ligand centered (LC) excited state. For details, see ref 23.

tered, and that the degree of adiabaticity increases when ligand orbitals are involved. As we have seen in section IV, the transmission coefficient depends on the electronic interaction energy and the Franck-Condon factors. It does not seem likely that the Franck-Condon factors play an important role in these complexes; moreover, there is no obvious correlation between Franck-Condon factors and orbital nature of the excited states. Thus, the reasons for the observed behavior have to be found in the electronic interaction energy. Since the energy transfer from the triplet donors to the various excited states of the complexes is spin allowed in all cases (although with slightly different spin-statistical factors),[23] the only reason for the noticeable increase of $\mathbf{k}_{\mathrm{en}}$ in passing from MC to CT (or LC) excited states has to reside in the different degree of orbital overlap. This is just what is expected because of the shielding effect of the ligands toward the interaction between the donor and the metal orbitals. The lower values of $k^{en}{}_q$ obtained for Fe(dpm)$_3$, where the metal orbitals are obviously more shielded than in Fe(acac)$_3$, are in agreement with the above hypothesis. Low rates for exoergonic energy transfer to MC excited states of Werner-type transition-metal complexes are common for complexes in which there is a poor mixing between metal and ligand orbitals.[22] The degree of adiabaticity for energy transfer to the MC excited states of such complexes has been found to be related to the nature of the ligands,[93] the geometry of the complex,[93,94] the coordination number,[93] and the nature of the solvent.[95] A more detailed discussion of these problems will be reported elsehwere.[96]

VI. Conclusions

A classical approach to exchange energy transfer processes in fluid solution has been developed which parallels that used for electron transfer quenching processes. This treatment is based on a model which does not require violation of the Franck-Condon principle, nor the use of ill-defined concepts such as "nonvertical" excitation transfer or "phantom" excited states. A general equation (eq 29) has been obtained using the absolute reaction rate theory and the free-energy relationship recently proposed by Agmon and Levine.[44] Such an equation (1) includes as a limiting case the Sandros equation, which was known to hold for processes involving undistorted excited states, (2) accounts for energy-transfer processes to and/or from distorted excited states, and (3) accounts for the possibility of lower than diffusion rates in the exoergonic region. In spite of its classical limitations, eq 29 can be generally used to rationalize the experimental results of exchange energy transfer processes in fluid solution. In particular, eq 29 can be used to identify the nonhomogeneity of a donor or an acceptor within a series, to evaluate the amount of distortion along a coordinate, to obtain the zero-zero spectroscopic energies of distorted excited states, to evaluate lower limiting values for the Stokes shift, and to infer the degree of adiabaticity of the process.

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