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DISTANCE DEPENDENCE OF ELECTRON TRANSFER RATES

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ABSTRACT

Electron exchange processes between complex ions or aromatic radical ions in solution are typically close to electronically adiabatic. This will generally not be the case for electron transfers over large distances, particularly those in biological (e.g. photosynthetic) systems. The factors governing variation of rate constant with distance are discussed. An important result is that, in favourable cases, 'through-σ-bond' interaction can result in decrease of the electron coupling integral J according to a relatively low inverse power law, rather than the exponential fall-off with distance expected for 'through-space' interaction.[1,2]

INTRODUCTION

The nature and extent of dependence of rates of electron transfer on the distance between donor and acceptor sites has long been a central concern of theories of electron transfer dynamics. It is also of central concern to interpretation of the corresponding radiative (intervalence transfer) processes. Comparison with experiment is, however, often difficult. For outer-sphere transfer between ions in solution (or between ions in solution and an electrode), only an average k_{av} over rates $k(r)$ for separations r can be measured, i.e.

$$k_{\mathrm{av}} = \int u(r)k(r)4\pi r^2 \, dr \ ,$$

where spherical symmetry of the species in solution can be assumed. The problem is alleviated when radiationless or radiative intramolecular electron transfer between sites linked by a bridging ligand is considered. Furthermore, if the bridging ligand is *rigid*, then the electron transfer distance is uniquely defined. It is on systems of this kind that we shall focus attention here.

Our particular concern is with the dependence of transfer rates on donor-acceptor separation, and on the nature of the interaction between them. There is much current interest in interpretation of electron transfer rates in biological systems (including photosynthetic systems).

Typically, these involve quite large donor-acceptor separations, and we ask how the basic parameters in terms of which rates can be expressed vary with

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distance. It turns out that while other factors are important, the critical term is the electron transfer integral J separating reactant and product hypersurfaces. It has been usually assumed that the transfer (coupling) integral always obeys an exponential law of decay with distance as would be anticipated for direct 'through-space' interaction. As we shall see, however, there is good experimental evidence in some systems for transfer integrals of order 1 millivolt for distances of 15Å, even when the bridging ligand is entirely non-conjugated. The likelihood of much less rapid decay of transfer integral with increasing distance which would accompany *through-bond*[3] interaction must be recognized. In favourable cases, this will result in an inverse power law rather than exponential fall-off. Theoretical and experimental evidence for this is discussed below.

RATE CONSTANT FOR ELECTRON TRANSFER

Experimental electron transfer rate constants measured at ordinary temperatures are generally analyzed in terms of transition state formalism. The rate constant k for transfer between donor and acceptor in specified geometry is then expressed as:

$$k = \frac{k_B T}{h} \kappa \Gamma \exp - \Delta G^{\ddagger}/k_B T \ , \tag{1}$$

where $\Delta G^{\ddagger}$ is the free energy of activation, and κ and Γ are the electronic and nuclear non-adiabaticity factors (transmission coefficients) respectively.

Assumptions underlying nuclear transmission coefficient/transition state approach to processes such as atom or electron transfer have recently been discussed in some detail by Cribb, Hush and Nordholm,[4] and comparison with other methods, which consider the internal quantum dynamics in less detail, made. For the present purpose, however, it will be assumed that final-state densities of states are sufficiently high for the Fermi Golden Rule to be applicable; the rate constant, which can be cast in the form of eq. (1), can then be derived by time-dependent perturbation theory. We shall also here not distinguish between high-frequency and low-frequency vibronic coupling modes and emphasize that we are concerned here, for simplicity, with processes for which coupling frequencies ω_k are assumed to obey the relationship $\hbar\omega_k \leq 2kT_B$. [For references to the extensive literature on this subject, see (44).] The rate equation is then essentially that derived by Marcus[5] and by Hush.[6]

In order to discuss the distance dependence of transfer rates, and to provide a specified procedure for interpretation of experimental data, a brief account of the interpretation of eq. (1) to be used here will be sketched.

The process considered is electron transfer from donor $a(e)$ to acceptor b,

$$a(e) + b \rightarrow a + b(e) \tag{2}$$

which may involve either ground-state or electronically excited systems. The coupling of electronic motion to vibrational and phonon modes gives rise to a vibronic coupling energy ('reorganization energy') χ, as illustrated in Fig. 1,

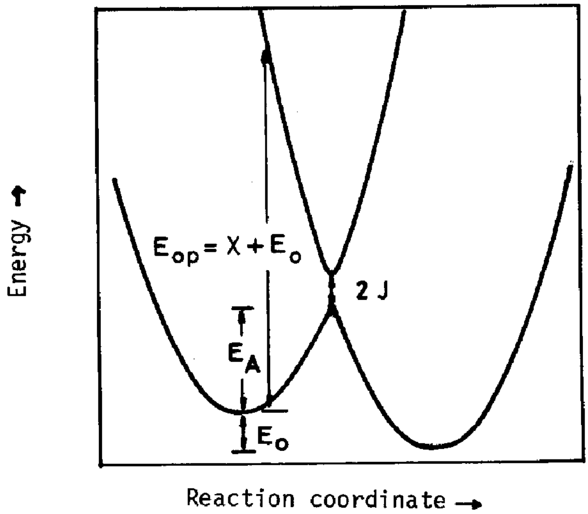


Fig. 1.

which shows a section through the energy hypersurface. The overall energy change is E_0. The upper and lower hypersurfaces are assumed to be separated by the quantity $2J$, where J is the electron coupling (transfer) integral:

$$J_{12} = (H_{12} - S_{12}H_{11})\ (1 - S_{12}^2)\ . \tag{3}$$

In this expression, the initial and final states of the system (corresponding to left- and right-hand sides of eq. (2)) are represented by 1 and 2; $\langle 1|H_{el}|2\rangle = H_{12}$; $\langle 1|H_{el}|1\rangle = H_{11}$, where H_{el} is the electronic (Born-Oppenheimer) Hamiltonian of the system, and $S_{12} = \langle 1|2\rangle$. This is a critical quantity, and much of the succeeding discussion will be concerned with its dependence on microscopic parameters.

We are primarily interested here in processes for which J is very small in comparison with χ; when this is the case, on the further assumption that the intersecting hypersurfaces are harmonic, the potential energy of activation E_A for transfer in intersecting region is clearly $(\chi+E_0)^2/4\chi$.

The electronic transmission coefficient κ is expressed as

$$\kappa = \frac{2P_{12}^0}{1 + P_{12}}\ , \tag{4}$$

where P_{12}^0 is the probability of the system's remaining on the lower surface. This can be calculated by the Landau-Zener approach,[8,9] which yields:[7]

$$p^0_{12} = 1 - \exp\left[-\frac{J^2}{\hbar\bar{\omega}}\left(\frac{\pi^3}{\chi k_B T}\right)^{\frac{1}{2}}\right] \tag{5}$$

where $\bar{\omega}$ is an average vibrational frequency for the coupling modes. Since we are concerned here with non-electronically adiabatic systems, we assume $J << \hbar\bar{\omega}$ and thus set:

$$\kappa = 2p^0_{12} = \frac{2J^2}{\hbar\bar{\omega}}\left(\frac{\pi^3}{\chi k_B T}\right)^{\frac{1}{2}} . \tag{6}$$

For a symmetrical transfer ($E_0 = 0$), and at temperatures sufficiently high that $\hbar\bar{\omega} < 2k_BT$, we will write the free energy $\Delta G^{\ddagger}$ as:

$$\Delta G^{\ddagger} = \frac{\chi}{4} - kT\ \ell n(\hbar\bar{\omega}/k_BT) , \tag{7}$$

where the last term allows for the loss of one degree of vibrational freedom in formation of the transition state. Thus, from eqs. (1,4,6,7), the transfer rate constant k for a symmetrical process can be expressed as:

$$k = \frac{2\pi}{\hbar} J^2 \left(\frac{1}{4\pi k_B T\chi}\right)^{\frac{1}{2}} \exp - \left(\frac{\chi}{4k_BT}\right) . \tag{8}$$

To a good approximation, the experimental rate constant for the unsymmetrical case ($E_0 \neq 0$) can correspondingly be expressed as:

$$k = \frac{2\pi}{\hbar} J^2 \left(\frac{1}{4\pi k_B T\chi}\right)^{\frac{1}{2}} \exp - \frac{(\chi+E_0)^2}{4k_BT\chi} . \tag{9}$$

There is a close connection between the rates of thermal transfer and the corresponding optical transfer probability in the intervalence band,[7,10-12] for which the absorption maximum occurs at $h\nu_{\max} = \chi+E_0$ and the second moment of the band envelope is proportional to χk_BT. These relationships have been used extensively in interpreting the dynamics of electron transfer in mixed-valence systems, particularly by Taube and coworkers,[13] and by Meyer and coworkers.[14] The above expressions relate to the high-temperature limit. The relation of thermal to optical transfer has also been discussed more recently by Hopfield.[15]

The nuclear tunnelling factor Γ can be calculated for symmetrical electron exchange assuming that the vibrational/phonon modes of frequency ω_k coupled to the transferring electronic motion are harmonic and that non-diagonal elements of the vibronic coupling matrix can be neglected. At temperatures such that $\hbar\omega_k < 2k_BT$, the nuclear tunnelling coefficient Γ_k for mode k can be expressed as:[7,16]

$$\Gamma_k(T) = \left[\frac{\hbar\omega_k}{2k_BT}\operatorname{csch}\left(\frac{\hbar\omega_k}{2k_BT}\right)\right]^{-\frac{1}{2}} \exp\left[S_k\left\{\frac{\hbar\omega_k}{4k_BT} - \tanh\frac{\hbar\omega_k}{4k_BT}\right\}\right] , \tag{10}$$

where

$$\chi = \sum_k S_k \hbar\omega_k \ . \tag{11}$$

Thus

$$\Gamma = \prod_k \Gamma_k \ . \tag{12}$$

[Other related formalisms have been proposed - see, e.g., refs. 17, 18.]

In the absence of detailed information about the relative contributions of individual coupling modes, we may consider the coupling to involve an average $\bar{S}$ quanta of a mode of effective frequency $\bar{\omega}$, and write $\Gamma(T) \simeq \Gamma(\bar{\omega},T)$, with $\chi = \bar{S}\hbar\bar{\omega}$.

In this case, the electron transfer rate for a symmetrical exchange becomes

$$k = \frac{2\pi}{\hbar} J^2 \left[\frac{1}{2\pi\hbar\bar{\omega}\chi \ \mathrm{csch}(\hbar\bar{\omega}/2k_BT)}\right]^{\frac{1}{2}} \exp\left[-\frac{\chi}{\hbar\bar{\omega}} \tanh(\hbar\bar{\omega}/4k_BT)\right] \ . \tag{13}$$

The influence of nuclear tunnelling on the overall rate will be smallest, at ordinary temperatures, when the coupling energies are small and frequencies are not very high. Studies of the temperature-dependence of intervalence transfer bands[12] indicate that effective coupling frequencies probably do not usually much exceed ~300 cm^{-1} for systems involving linked metal ions. For coupling energies χ of 0.5, 1 and 2 eV, the values of the tunnelling coefficient Γ_k (eq. (10)) for $\bar{\omega}$ = 300 cm^{-1} at 298 K are 1.22, 1.43 and 2.15 respectively. While nuclear tunnelling is clearly not negligible in these circumstances, its effect on transfer rates is considerably less than an order of magnitude. For the purpose of discussing general trends in transfer rates, including systems for which information about coupling frequencies is absent, we shall henceforth use the high-temperature limiting eqs. (8) and (9). Uncertainties both in measurement and in the calculation of other quantities entering into the expressions are such that this is not a serious oversimplification.

In the high-temperature limit, the Marcus-Hush exchange rate constant is a function of three variables. The first is the overall energy change E_0 ('driving force'). The second and third are respectively the electronic splitting energy J and the vibronic coupling energy χ. Thus the question of distance-dependence of electron transfer dynamics reduces to those of the dependence of J and χ respectively on donor-acceptor separation. At this point it is worth emphasizing that, owing to the close connection[7,10-12] between radiationless and radiative transfers, the values of J, χ and E_0 (together with an estimate of mean coupling frequency $\bar{\omega}$) can be obtained from analysis of the zeroth, first and second moments of the intervalence absorption band. This provides a powerful method for investigating distance-dependence of electronic and vibronic coupling terms.

It is useful to note the quantitative implications of the basic rate equations. In Figs. 2-4, the calculated transfer rate constant is shown for a range of values of the vibronic coupling energy χ, the overall energy E_0 and the electronic coupling energy J. For an electronic splitting of 1 millivolt, rates in the range 10^8-10^{11} sec^{-1} are predicted for systems with low electron vibrational coupling energies ($\chi = 0.5$ eV) and driving force in the range 0 to -0.5 eV. For electronic splitting as small as one microvolt, the corresponding rates lie in the range 10^2-10^5 sec^{-1}.

It will be noted that these comparisons are restricted to transfers for which $E_0 \leq \chi/2$; for larger driving forces, the quadratic relationship of eq. (9) may cease to be obeyed.

DISTANCE-DEPENDENCE OF VIBRONIC COUPLING ENERGY

For outer sphere electron transfer between complex ions or intramolecular transfer in a dynamically valence-trapped mixed-valence complex it is customary to distinguish between the vibrational modes of the complexes (local or inner modes) on the one hand, and those of the medium (outer, collective modes) on the other. The total vibronic coupling energy χ is then written as $\chi = \chi_{\text{inner}} + \chi_{\text{outer}}$. The effect of internuclear separation should then be manifest almost entirely in distance-dependence of the energy χ_{outer} of coupling to medium modes. This will be expected to influence both electron transfer rates and the corresponding intervalence absorption process. If a continuum dielectric model is used for the medium, the coupling integral χ_{outer} can be expressed for a one-electron exchange as:[5] [6]

$$\chi_{\text{outer}} = e^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_{\text{s}}}\right) , \tag{14}$$

where a_1 and a_2 are the radii of the reactant ions whose centre-to-centre separation is r, and ε_{op} and ε_{s} are the optical and static dielectric constants respectively of the medium. Where eq. (14) is appropriate, it is evident that the vibronic coupling energy depends inversely on the transfer distance:

$$\frac{d\chi}{dr^{-1}} = - e^2\left(\frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_{\text{s}}}\right) . \tag{15}$$

For a symmetrical exchange, we thus expect the activation energy to vary as:

$$\frac{dE_A}{dr^{-1}} = - \frac{e^2}{4}\left(\frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_{\text{s}}}\right) \tag{16}$$

and the energy of the maximum $h\nu_{\text{max}} = \chi$ of the corresponding intervalence

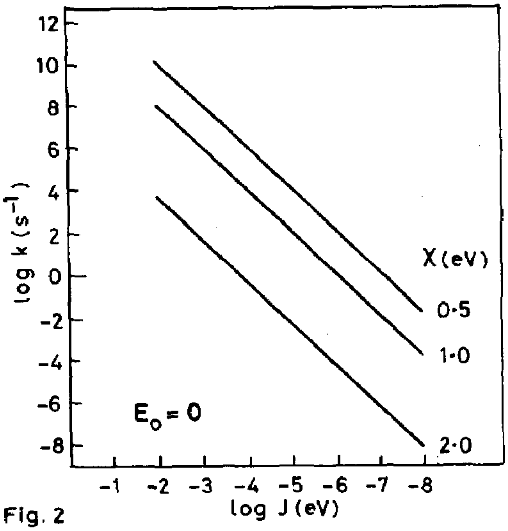


Fig. 2

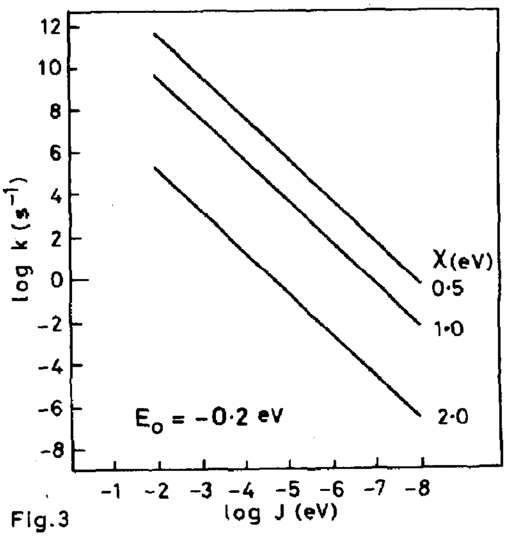


Fig.3

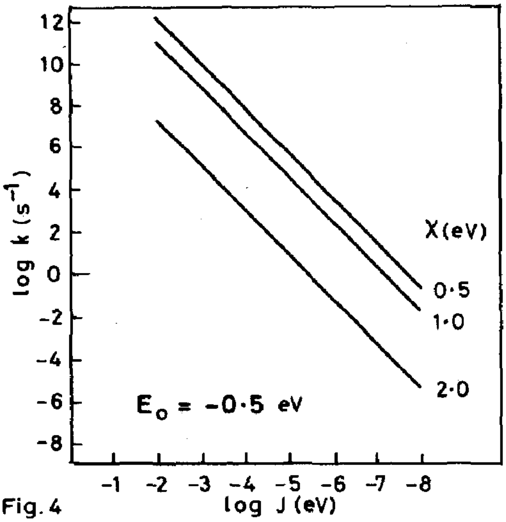
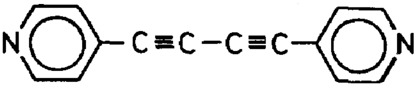


Fig. 4

Dependence of electron transfer rate constant k on electron coupling integral J for a range of values of electron - phonon coupling energy and driving force E_0.
Fig 2: E_0=0 . Fig 3:E_0= -0.2
Fig.4: E_0=-0.5 eV.

absorption band to vary as in eq. (15) with donor-acceptor distance. A decrease in rate constant and hypsochromic absorption frequency shift should accompany increasing distance, as a result of decrease of nuclear screening. Extensive work by Meyer and co-workers has established that an equation of the form (15) holds well for intervalence band maximum in a range of solvents of several series of binuclear mixed-valence complexes: both dependence on distance and on dielectric properties have been examined. There has been rather less investigation of the dependence of activation energy of transfer rates on donor-acceptor separation. Recent work by Haim et al.,[19] however, on exchange rates in H_2O of complexes of ligands of the type



has shown that a linear inverse relation holds between activation energy and internuclear distance, as predicted by eq. (16). The slope is somewhat less than predicted from the dielectric constants of H_2O.

It is evident that retardation of transfer rates through increase of energy of coupling to medium modes increases quite slowly at larger distances. Thus, for transfer in H_2O, the effect is predicted to cause decrease of a symmetrical transfer rate by a factor of 2.6 for an increase of intersite distance from 10 to 20Å.

ELECTRONIC COUPLING ENERGY: DIRECT COUPLING

The electronic interaction J may possibly result from direct overlap of orbitals located on sites which are not bonded to each other. This was proposed for the outer-sphere transfer between hydrated Cr II and Cr III ions.[7] The centre-to-centre metal ion separation is r; the shorter distance between the coordinated oxygen atoms is r' [Fig. 5]. Since this is a dγ-dγ type transfer σ-bonding

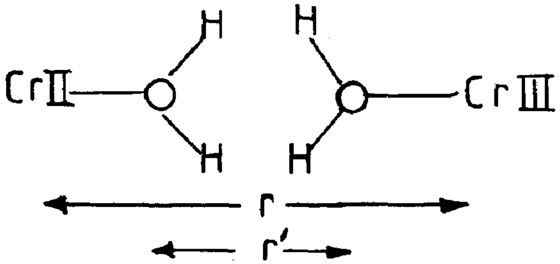


Fig. 5. Nearest-neighbour water molecule configuration at close-contact separation.

between metal $3d_\pi$ orbitals and oxygen p_σ will result in appreciable amplitude of $3d_\pi$ function in the M-O bond. Assuming that the electronic splitting arises from through-space overlap of oxygen p_σ functions at distance r', J can be evaluated by directly calculating the O-O interaction energy and using experimental e.s.r. data to estimate the amplitude of $3d_\pi$ in the M-O bond. This yielded a value of $J \simeq .023$eV at the close contact separation $r' = 2.8$Å, the electronic energy was found to be an exponential function of distance, with $J \propto 10^{-1.6r'}$ in the range $3 \leq r' \leq 5$Å.

Recent, considerably more detailed calculations have been made by Newton[20] for the analogous Fe II/Fe III hexaquo outer-sphere transfer. In this case, the transfer is of d_ε-d_ε type, so that the ligands are involved through weaker π-type interaction. Here also for through-space interaction of the aquo complexes an exponential decrease of J with distance is found; for apex-apex geometry the dependence was found to be $\sim 10^{-1.0r}$. Although the functions used in the calculation do not lend themselves to a simple separation of direct metal-metal interaction and interaction mediated by ligand bonding, it appears from the reasonable correspondence with earlier calculations in which the water molecules were represented by assemblies of point charges that in this case the interaction can be approximately described as d_π-d_π through-space metal-metal overlap.

There have been some discussions of through-space interaction for electron transfer process. For example, calculations employing one-dimensional potential wells of various shapes have led to a proposal that a typical through-space distance dependence of J is $\sim\exp(-.72r)$ (r in Å).[21] It is informative to consider a very simple case, namely the through-space interaction energy of two ethylene molecules in an eclipsed D_{2h} 'sandwich' configuration. We are thus essentially concerned with carbon $2p_{\pi\sigma}$-$2p_{\pi\sigma}$ interaction, with the molecules oriented for maximum σ-type overlap of the $2p_\pi$ functions. Results of ab initio calculations over a range of separations r using an STO3G basis are shown in Table 1. The canonical eigenvalue difference for bonding and antibonding orbitals, which is our approximation to $2J$, falls from 7.3eV at $r = 2$Å to .003eV at $r = 6$Å. This can be compared with the fall-off in first ionization potential I_1 for the dimeric system, which decreases by a similar amount; this is 4.6eV, which is fairly close to half the $2J$ defined above.

At the larger distances (> 3.0Å), broken-symmetry solutions for the $(C_2H_2)_2^+$ ion are closer approximations to the energy than those obtained with D_{2h} symmetry restriction. Calculations for ground and excited states of $(C_2H_2)_2^+$ at $r = 2.5$Å show that the relaxation energy is almost identical in each state (-.026655 and -.023213 a.u. respectively); this adds weight to the use of the simpler canonical eigenvalue difference as a measure of $2J$. At that separation, the calculated ionization potentials I_1 and I_2 are nearly symmetrically

TABLE 1

The dimer radical ion energies in the last three columns were obtained respectively by application of Koopmans' theorem, using dimer eigenvalues (a); SCF calculation with D_{2h} symmetry (b); symmetry-relaxed ("localized") SCF calculation (c). [(b) and (c) are identical for R ≤ 2.0Å.]

R	$E(C_2H_4)_2$	ΔE†	$E(C_2H_4)_2^+$ (a.u.)		
(Å)	(a.u.)	(e.V.)	(a) Koopmans'	(b) Delocalized	(c) Localized
∞	-155.367674	0	-154.900546	-	-154.934607
6	-155.367591	.003	-154.901683	-154.919347	-154.935793
3.8	-155.366288	.599	-154.914361	-154.934253	-154.940215
3.4	-155.364213	1.076	-154.922506	-154.943705	-154.945055
3.0	-155.357325	2.906	-154.933755	-154.956885	-
2.5	-155.326325	3.823	-154.801217 -154,941705	-154.824430 -154.968360	$(E_{relax}=-.023213)$ $(E_{relax}=-.026655)$
2.2	-155.258047	5.680	-154.916847	-154.946534	-
2.0	-155.157678	7.340	-154.861123	-154.893492	-

†canonical eigenvalue difference for bonding and antibonding π-levels.

displaced around I_∞; these are I_∞ - 2.043 eV, I_∞ + 1.873 eV respectively; the difference, 3.916 eV, is numerically close to ΔE (3.823 eV).

The dependence of J on distance for the p_π-p_π interaction in C_2H_4 dimer can be represented reasonably well as (a) $J \approx 30r^{5.68}10^{-1.458r}$ eV or alternatively with similar accuracy as (b) $J \simeq 16r^{1.63}\,S$ eV†, where S is the carbon 2pπσ-2pπσ overlap integral. In either case, the dependence is not simply exponential, although at very large distance the exponential term will dominate. The fall-off with distance in this case is, however, more rapid than the exp(-.72r) dependence discussed in ref. (21), and is more in line with the distance-dependence discussed above for outer-sphere metal-metal transfers.

We shall return to through-space interaction later when discussing transfers at very large distances.

ELECTRONIC COUPLING INTEGRAL: ESTIMATES FROM INTERVALENCE ABSORPTION INTENSITIES

A useful source of information about the magnitude of the electronic splitting J is provided by intervalence transfer absorption spectra. It will be useful to briefly discuss assumptions underlying this and to list the explicit expressions to be used in analyzing experimental data. This is necessary, as somewhat different approximations are made by different authors; while improvements to the theory are to be welcomed, it is important at this stage to have a

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† $S_{2p\pi\sigma 2p\pi\sigma} = [1 + \rho + \frac{2}{5}\rho^2 + \frac{1}{15}\rho^3]e^{-\rho}$; $\rho = 1.625r(a_0)$.

common framework for comparing experimental data. This has to be kept as simple as possible owing to the usual lack of ancillary data (e.g., detailed information about contribution of individual modes to overall vibronic coupling).

The process considered is optical transfer (intervalence transfer) between electron donor (a) and acceptor (b) species at specified geometry:

$$a(e) + b \xrightarrow{h\nu} a + b(e) \ . \tag{17}$$

The donor and acceptor may be complex ions, with the probability density of the transferring electron either strongly localized or delocalized.

Assuming, as before, for the two-site case, coupling of this electronic matrix leads to separation into an upper and a lower harmonic hypersurface [Fig. 1] we can distinguish two transition moments. The first refers to transition from lower to upper surface at zero-displacement of the effective coordinate. The electronic transition dipole moment - i.e., for absorption by the transition state complex - we refer to as $\underline{M}_t$. For absorption from the minimum of either well to the upper surface, the transition moment is $\underline{M}_0$. Writing for the one-dimensional electronic wave function

$$\psi_\pm = c_a^\pm \phi_a + c_b^\pm \phi_b \tag{18}$$

we have

$$\underline{M} = c_a^+ c_a^- \langle a|\underline{r}|a\rangle + c_b^+ c_b^- \langle b|r|b\rangle \tag{19}$$

where the coefficients are expressible in terms of the overall energy E_α and the effective coupling frequency.

For weak interaction ($2J < \chi$), it is sufficient to write

$$\underline{M}_0 = 2\left(\frac{J}{\chi}\right)\underline{M}_t \tag{20}$$

where $\underline{M}_0$ is the transition moment for the transition-state configuration, in which, for a symmetrical transfer,

$$\psi_\pm^\pm = \frac{1}{\sqrt{2}}(\phi_a \pm \phi_b) \tag{21}$$

How is the moment $\underline{M}_t$ to be obtained? On the effective two-site model, for a non-degenerate symmetrical transfer ($E_\alpha = 0$) we write:

$$\underline{M}_t = \alpha\underline{R} \ . \tag{22}$$

On the simplest interpretation, using the dipole length operator for the transition matrix element, $\alpha = 0.5$. However, it is known that the molecular orbital length formula can lead either to overestimation or underestimation of intensities of $\pi \rightarrow \pi^*$ transitions.[‡] Pending a more detailed discussion, we shall assume in what follows that $\alpha = 1$.

The oscillator strength f_{ab} for the transition is related to M^0_{ab} by:

$$f_{ab} = 1.085\times10^{-5}\ h\nu_M[M^0_{ab}/e]^2 \qquad (23)$$

where M^0_{ab}/e is in Å, and $h\nu_M$ is the absorption band maximum in cm^{-1}. For a Gaussian spectral envelope, the extinction coefficient $\varepsilon_{\mathrm{max}}$ at maximum absorption is related to the oscillator strength by:

$$\varepsilon_{\mathrm{max}} = 10^9\ f_{ab}/4.6\ \nu_{\frac{1}{2}} \qquad (24)$$

where $\nu_{\frac{1}{2}}$ is the full width at half maximum intensity. Thus (with eq. (20)) the coupling integral J is obtained from:

$$J = \frac{2.06\times10^{-2}(\varepsilon_{\mathrm{max}}\nu_{\frac{1}{2}}h\nu_{\mathrm{max}})^{\frac{1}{2}}}{\alpha r}\ . \qquad (25)$$

It is not uncommon to encounter difficulties in determining band half-widths with precision. The theoretical expression for $\nu_{\frac{1}{2}}$ may then lead to a more accurate estimate of J. Where in a dynamically-trapped system, vibronic coupling can be assumed to involve a single effective frequency $\tilde{\omega}$, we can write:

$$\nu_{\frac{1}{2}} = \left[\frac{\hbar\tilde{\omega}}{2k_BT}\coth\frac{\hbar\tilde{\omega}}{2K_BT}\right]^{\frac{1}{2}}\nu_{\frac{1}{2}}(\mathrm{HTL}) \qquad (26)$$

$$= g(\tilde{\omega},T)\nu_{\frac{1}{2}}(\mathrm{HTL})$$

where $\nu_{\frac{1}{2}}(\mathrm{HTL})$ is the high-temperature ($2k_BT \gg \hbar\tilde{\omega}$) limiting expression:

$$\nu_{\frac{1}{2}}(\mathrm{HTL}) = [(16\ \ell n\ 2k_BT)\chi]^{\frac{1}{2}}\ . \qquad (27)$$

At T = 298K, this is:

$$\nu_{\frac{1}{2}}(\mathrm{HTL}) = 47.9\chi^{\frac{1}{2}}\ .$$

[‡] For detailed calculations of length and velocity formalisms for transitions in large aromatic molecules, see ref. (22).

In such cases, use of the theoretical expression for the band half-width leads to the alternative expression:

$$J = \frac{0.143\ \varepsilon_{\max}^{\frac{1}{2}}(h\nu_{\max})^{\frac{3}{4}} g(\tilde{\omega},T)^{\frac{1}{2}}}{\alpha r}\ \mathrm{cm}^{-1}. \tag{28}$$

The following table illustrates the dependence of $g(298)^7$ on coupling frequency.

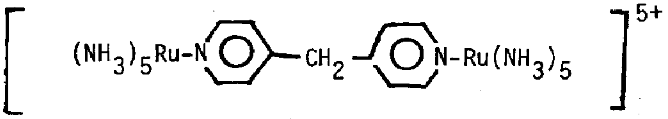
TABLE 2

Ratio (g,T) of intervalence vibronic half-width to high temperature limiting expression at T = 298.

$\tilde{\omega}$(cm^{-1})	g(298)
400	1.14
350	1.11
300	1.08
150	1.06

For effective frequencies in the range 300-400 cm^{-1}, the vibronic half-width will be ~10% larger than the high-temperature limiting value. For a coupling frequency of 300 cm^{-1}, departure from the high-temperature limiting expression in eq. (25) leads to an error in the estimate of J of only 4%. Thus, in view of other approximations involved, and of the desirability of maintaining a uniform approach to evaluation of this phemonological constant, we shall set $g(\tilde{\omega},T) = 1$ in calculations reported here.

Estimates of J, based on interpretation of intervalence transfer intensities, have been made for systems in which the bridging ligand is a conjugated molecule; where $Ru^{II} \rightarrow Ru^{III}$ transfer is involved, Ru(d$_\pi$)-ligand(p$_\pi$) electronic interaction is possible.[23-25] There have been fewer systematic studies for ligands which either exhibit an interrupted conjugated pathway or are saturated molecules. An example of a complex of the former type is the mixed valence ion:



for which J has been estimated from the intervalence intensity to be 1.1×10^{-1} eV for a metal-metal separation of 12.3Å.[26] A set of experiments by Stein and Taube[27] and Stein, Lewis and Seitz[28] using dithiaspiro compounds as bifunctional ligands, gives useful insight into both the order of magnitude and distance dependence of the electron coupling integral for a set of fully saturated ligands. Intervalence absorption was studied in the mixed-valence ions

$[(NH_3)_5Ru - L_n - Ru(NH_3)_5]^{5+}$, where L_{1-3} are 2, 3 and 4-ring dithiaspiro molecules:

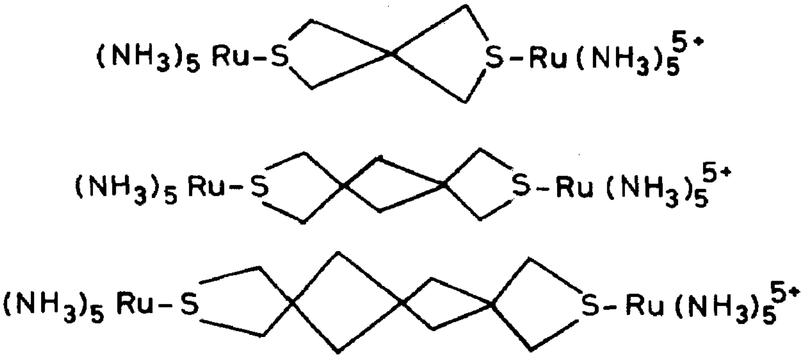


Fig. 6. Complexes of dithiaspiro bifunctional ligands.

The probable d_σ-ring bonding pattern is schematically as shown below for n = 1; each successive ligand ring is rotated by $\pi/2$:

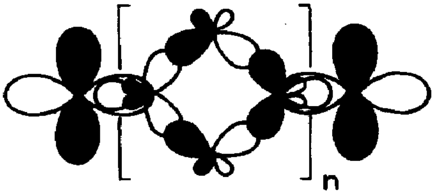


Fig. 7. Metal d_σ-ring σ bonding in model bis-Ru dithiaspiro systems.

A very crude idea of the distance-dependence of through-bond electronic coupling for these systems is obtained from a simple Hückel-type calculation, in which all diagonal elements are set arbitrarily to zero, all off-diagonal elements are equal $[H_{12}]$, and all bond lengths are equal. One d_σ orbital on Ru, three σ orbitals on each $\mathcal{S}$, and two σ orbitals on each c, are included. This yields an $R^{-5.7}$ dependence of J, as shown in Fig. 8:

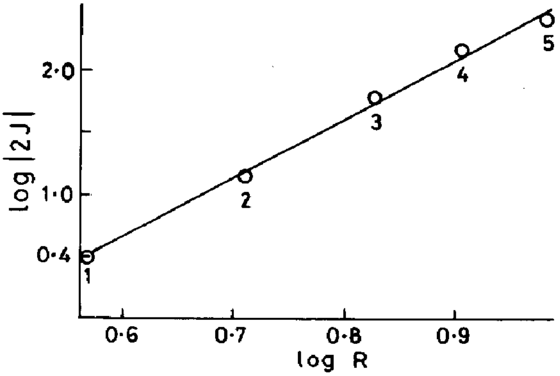


Fig. 8. Dependence of J on metal-metal distance in model calculation for dithiaspiro compounds.

This points to the possibility, mentioned in Introduction, of an inverse power, rather than an exponential, distance dependence of J in these systems.

The experimental spectroscopic contants and values of J derived from the intervalence band intensities using eq. (28) with $\alpha = g(\tilde{\omega},T) = 1$ are shown in Table 3. [Stein et al.[28] calculated values of J approximately 12% higher than these, using a somewhat different approach.]

TABLE 3

Electronic coupling integral in bis (Ru pentammine)$^{5+}$ mixed-valence complexes of dithiaspiro ligands from intensity of intervalence band:

$$J = \frac{1.428\times10^{-1}\ \varepsilon_M^{\frac{1}{2}}(\hbar\omega_M)^{\frac{3}{4}}g(\tilde{\omega},T)^{\frac{1}{2}}}{\alpha R}\ \mathrm{cm}^{-1}.$$

No. rings	$\hbar\omega_M$ (cm^{-1})	ε_M	R (Å)	J (eV)	$90R^{-4}$
2	11,000	43	9	1.4×10^{-2}	1.4×10^{-2}
3	12,400	9	11.2	5.6×10^{-3}	5.7×10^{-3}
4	14,500	2.3	13.4	2.7×10^{-3}	2.8×10^{-3}

We have estimated the direct Ru-Ru distances in these systems, and at present use this,rather than the path length R' defined by the sum of bond lengths, to facilitate comparison with data to be discussed below. In fact, $R' \simeq 1.3R$.

As also indicated in Table 3, the values of J over the available range of R can be expressed with good accuracy as $J = 90R^{-4}$ eV [R in Å] - i.e. with an inverse power dependence similar to but smaller than that of the crude model calculation. The comparatively large magnitude of the non-conjugated through-bond coupling [2.7 millivolt at R = 13.4Å or 'bond path length' R' = 17.6Å] is also noteworthy: together with the bandwidth data, these lead to a prediction of thermal intramolecular self-exchange rates in these systems of 10^6-10^3 s^{-1}

[300K] over the range 9-13.4Å of direct Ru-Ru separation.

ESTIMATES OF ELECTRONIC COUPLING FROM PHOTOELECTRON SPECTROSCOPY

A further, independent and direct experimental method of estimating electron interaction through long saturated linkages is provided by photoelectron spectroscopy of systems in which two ethylene units are linked through norbornadienylog-type bridges. An important feature of these is that they are rigid, so that the donor-acceptor distance can be precisely defined.

In a symmetrical molecule of this type, the relevant quantity is the splitting ΔE between the levels originating from pure bonding $2p_\pi$ orbitals on the separate ethylene groups. An example is the splitting observed in the molecule shown below:

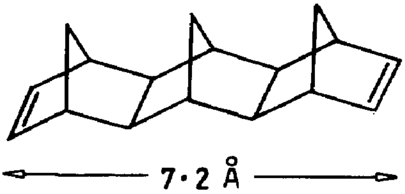
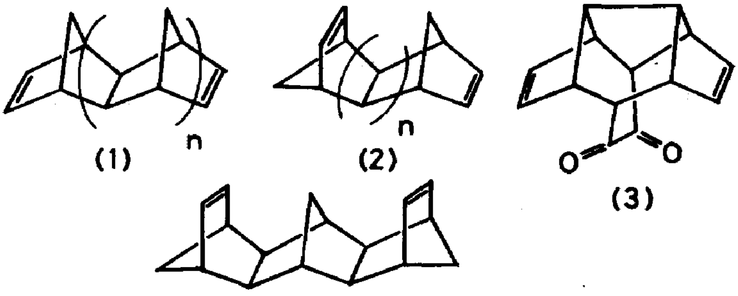


Fig. 9. Bisethylene molecule in which ethylene units are separated by a six-bond norbornadienylog-type rigid bridge.

The observed ΔE, with an inter-ethylene direct separation of 7.2Å, is 0.32 eV;[29] thus the J is 0.16 eV at this distance. This agrees exactly with an STO-3G ab initio calculation.[29] It is evident that this is far too high to be interpreted in terms of the through-space exponential interaction discussed earlier in the section on Electronic Coupling Energy.

Insight into the nature of the distance-dependence of J for compounds of this type is obtained from experimental measurements of the splittings ΔE over the series shown below:



(1) (2) (3) (4)

Fig. 10. Bridged bisethylene molecules.

The inter-ethylene separation R ranges from 2.4 to 9.6Å. The experimental ΔE values are shown in Table 4.

TABLE 4

Splitting ΔE ($\equiv 2J$) of lowest band in photoelectron spectra of bis-ethylene molecules of Fig. 10.

	DIENE	R (Å)	ΔE (eV)	Ref	$100R^{-3}$
Group 1	1(0)	2.4	0.85	30	[7.0]
	2(0)	4.5	0.44	31	[1.1]
Group 2	1(1)	4.8	0.87	32	0.90
	4	6.0	0.53	34	0.46
	3	4.8	0.85	33	0.90
	2(1)	6.6	0.38	31	0.35
	1(2)	7.2	0.32	34	0.27
	1(3)	9.6	[0.1][a]		0.11

[a] SCF calculation.

The molecules are grouped into two sets: the first, in which R is 4.5Å or less, and the larger group in which $R > 4.5$Å. In the second group, the observed splitting decreases according to a low inverse power of R; the value of ΔE ($\equiv 2J$) is given to acceptable accuracy by $\Delta E \cong 100R^{-3}$ eV (R in Å), as shown in the last column of Table 4. At distances ≤4.5Å, it is clear that through-space effects are also important, and we shall not further consider such small separations.

The electron coupling integral J is calculated to be of the quite large order of 0.05 eV at 9.6Å [the photoelectron spectroscopic resolution is too low for a splitting of 0.1 eV to be measured exactly]. In Table 5, a very approximate

TABLE 5

Electron coupling energy J between two ethylene units, extrapolated from interpolating formulae of Table 1 and Table 4 respectively.

R (Å)	J (eV)	
	Direct[a] (through-space)	σ-mediated[b] (through-bond)
10	0.74×10^{-7}	0.5×10^{-1}
15	1.0×10^{-13}	1.5×10^{-2}
20	2.0×10^{-20}	6.0×10^{-3}
25	4.5×10^{-26}	3.2×10^{-3}
30	2.2×10^{-34}	1.8×10^{-3}

[a] D_{2h} configuration.

[b] Norbonyl-type framework as in Fig. 10.

estimate is made of the value of J at very large separations (up to 30 eV), assuming that the R^{-3} dependence observed up to ~10Å is maintained. This is compared with an estimate of non-mediated through-space interaction of two ethylene units in D_{2h} configuration, using the expression [Table 1] $2J = 100R^{-3}$. While one must not put too much reliance on the absolute values, it is reasonably clear that above about 12Å any observable interaction will be of the through-bond type.

Through-bond interaction of the above type has a ready qualitatative interpretation in terms of orbital overlap, which is borne out by ab initio calculation. It is also possible to predict geometries for which σ-mediated interaction of π-bonded systems will be very small owing to near-zero overlap. This is predicted, for example, for inter-ring coupling of π-levels of two ethylene or benzene molecules linked by a σ-framework as in Figs. 11(a) and (b). The prediction is borne out by photoelectron spectroscopy.[35,36] However, when the mid-bridge H atoms are replaced by CH_2, as in Figs. 11(c) and (d), the pseudo-π orbital of the methylene is of the correct symmetry to interact with the end-group π-systems, consistently with the appreciable ΔE splittings observed in the photoelectronic spectra of the latter compounds.[35,36]

ESTIMATION OF ELECTRON COUPLING ENERGY FROM GROUND STATE AND PHOTOINDUCED EXCHANGE RATES AT LARGE DISTANCES

Quite recently, evidence has become available from several groups of measurable electron transfer rates with large, essentially fixed donor-acceptor separations. A selection of the more important of them will be briefly mentioned, and an estimate of the relevant coupling integrals made. The observed timescales range from second to nanosecond at ordinary temperatures.

Second-Millisecond Timescale

Measurements of electron transfer rate between Fe^{III} of the haem c group of horse heart cytochrome c and $Ru^{II}(NH_3)_5$ linked to histidine 33 of the protein have been made independently by Winkler, Nocera, Yocom, Bordignon and Gray,[37] using flash photolysis and by Isied,Worosila and Atherton[38] using a pulse radiolysis technique. At 25°C, the experimental rate constants for the transfer $PFe^{III} - Ru^{II} \rightarrow PFe^{II} - Ru^{III}$ were respectively 20 and 53 s^{-1}; this can be considered remarkably good agreement for two totally different techniques, and a system which is difficult to reproduce exactly.

Electrochemical measurements[37] yield E_0 = - 0.11 eV. A value of χ = 0.5 eV yields an approximate average of reported activation energies. With these parameters, the Fe/Ru coupling integral J for this system is obtained from eq. (9) as $J = 1.3\times10^{-7}$ eV. The direct metal-metal separation is 15Å, although the bond-path length separation through the protein is very much larger.

Similarly for $Cu^{II} - Ru^{II} \rightarrow Cu^{I} - Ru^{III}$ transfer in azurin substituted at histidine 83 with $Ru(II)(NH_3)_5$, a rate constant $k = 1.8\ s^{-1}$ (7 - 43°C) has been obtained.[39] Here, $E_0 = -0.29$ eV, and assuming $\chi \approx 0.5$ eV, a value of $J \sim 10^{-8}$ eV is calculated using eq. (9). [The assumed value of χ would formally lead to an activation energy of 0.024 eV. Experimentally, no dependence of rate on temperature was observed over 7 - 43°C: however, it is probable that a value of E_A of the order of 0.024 eV would probably be within the limits of accuracy.] The metal-metal direct spacing here is 11.8Å, so that a somewhat smaller coupling integral is found here than for the Fe/Ru system with direct spacing 20% larger. This is presumably due both to the difference in detailed nature and geometry of the σ-pathway and to the difference between Cu and Fe metal/ligand overlap integrals.

Hoffman et al.[40] have reported measurements on a hybrid hemoglobin in which Fe(III) in the β chain is substituted by Zn(II). Laser excitation leads to reduction of Fe(III) in the α chain to Fe(II) and oxidation at the Zn site of porphyrin to porphyrin radical cation P^+.

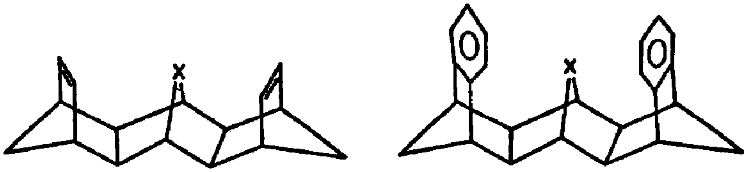
The rate constant for electron transfer from $Zn(II)P_\beta$ to $Fe(III)P_\alpha$ is $60 \pm 20\ s^{-1}$ at 25°C. The interesting features of this exchange are that the centre-to-centre distance is large (24.7Å) and driving force is very high, although not precisely known. A more recent measurement showing an apparent low-temperature tunnelling regime may make possible a reasonably detailed analysis.[41]

Microsecond-Millisecond Timescale

McLendon et al. have reported rates of photoinduced transfer between ruthenium trisbipyridine^{2+*} homologues and methylviologen (MV^{2+}) in rigid glycerol solutions.[42] The estimated distances for most probable transfer are ~11Å centre-to-centre and ~3Å edge-to-edge. For the transfer $(RuL_3)^{2+*} + MV^{2+} \rightarrow MV^{\cdot +} + [RuL_3]^{3+}$, a value of $1 \times 10^6\ s^{-1}$ was found at 250K for L = bipyridine. The driving force E_0 is -0.42 eV and the interpolated value of χ is 0.7 eV. From eq. (9) we obtain $J = 1.3 \times 10^{-5}$.

Nanosecond-Microsecond Timescale

Very fast transfer rates have been obtained using pulse radiolysis techniques by Calcaterra, Closs and Miller[43] for electron transfer from biphenyl negative ion (Ph_2^-) to 2-vinylnaphthalence rigidly linked through a (non-conjugated) steroid framework. For the system shown in Fig. 12, the rate constant for the transfer Ph_2^- - steroid - 2 vinyl Np → Ph_2 - steroid - 2 vinyl Np^- is $4 \times 10^7\ s^{-1}$ at 276K. The driving force E_0 is -0.32 eV. If we interpret this result as before, using eq. (9), the observed E_A of 0.1 eV is consistent with $\chi \approx 1.0$ eV; this leads to a value of $J = 0.6 \times 10^{-3}$ for the centre-to-centre separation of 15Å. This is



(a): X= H_2 (c): X=CH_2 (b): X=H_2 (d): X=CH_2

Fig. 11. Molecules exhibiting either through-space (a) and (b) or through-bond (c) and (d) coupling.

remarkably close to the estimate of inter-group through (σ) bond coupling constants in the structurally similar norbornyl systems in Table 4 and 5.

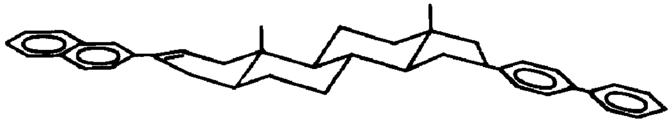


Fig. 12 Steroid bridged electron transfer system (ref. 43)

SYSTEMATIC STUDY OF DISTANCE-DEPENDENCE OF TRANSFER RATES

It is evident that what is now urgently needed is systematic study of the influence of distance on transfer rates for well-defined systems, in which donor-acceptor distance can be systematically varied while the driving force is held constant. Experiments are now in progress in which (a) ground-state electron transfer and (b) excited-state electron transfer are being studied in a series of molecules in which the σ-backbone is an n-bond norbornylog.[45,46]

Typical systems currently under examination are shown in Fig. 13. In (a), the donor/acceptor pair is separated by six single bonds - a '6-bond' system. Fig. 13b shows a 10-bond system. The more electron-attracting group is the keto group in (a) and dicyanovinyl group in (b). The n-bond systems have been synthesized so far for n = 2,4,6,8,10; this range is being extended. Systematic variation of distance with this rigid framework (and with donor/acceptor groups other than those shown) is expected to provide useful information about electron transfer rate distance dependence.

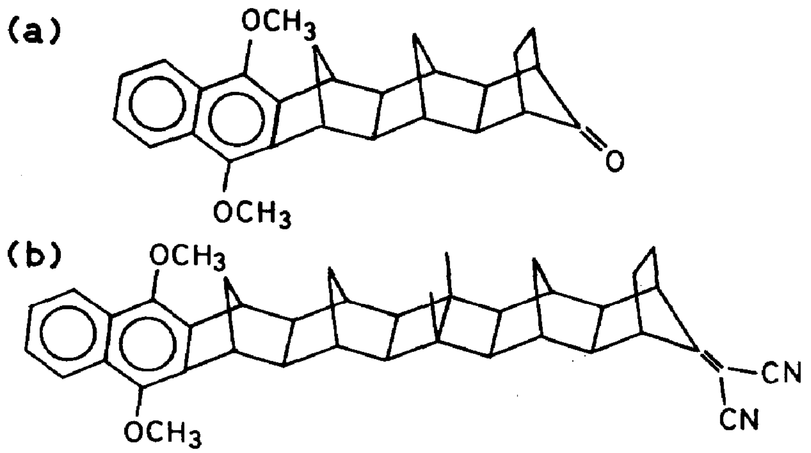


Fig. 13 Examples of rigid norbornylog-bridged donor-acceptor systems.[45,46]

Some preliminary results will be briefly mentioned. Pulse radiolysis experiments[45] under conditions similar to those in ref. (43) for molecules of the type shown in Fig. 13b have yielded lower limits for the rate of transfer of an electron from 1:4 dimethoxy naphthalene to the dicyanovinyl group. For n = 4,6 and 8, the lower limit is of order $10^9 sec^{-1}$, showing that transfer is very rapid through the long saturated bridges. For the negative ion of the molecule in Fig. 13a, intervalence transfer absorption has been observed on a microsecond time scale[45].

Studies of the fluorescence quenching in 8-bond analogue of Fig. 13b in solvents such as diethylether and acetonitrile [46] leads to an estimated photoinduced intramolecular electron transfer of the order of $10^9 sec^{-1}$, showing that very rapid transfer can occur also in the excited neutral molecule. It should be noted that there is here a very large driving force with E_0 probably more negative than -2.5eV.

In the brief space at our disposal it is not possible to discuss further developments of the basic equation (9) discussed, inter alia, in refs (4, 16, 17, 18 and at length in 44). Nor is it possible to consider in any detail the nature of σ-π interaction responsible for the through-bond interactions we have cited: reference to the important and extensive work of Heilbronner, Verhoeven and Paddon-Row and others will be found in ref. 29. It should also be noted that interesting semi-empirical calculations amplifying such approaches and considering their specific application to non-conjugated bonds have been reported; these give useful insight into the bonding patterns.[47] While our emphasis has been on interaction through non-conjugated pathways, it should be mentioned that much is known about the conjugated-ligand dependence of electron transfer (mainly by intervalence absorption studies), particularly through the work of Taube[13,23] and of Meyer[14] and coworkers. and of Haim and co-workers[19].

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