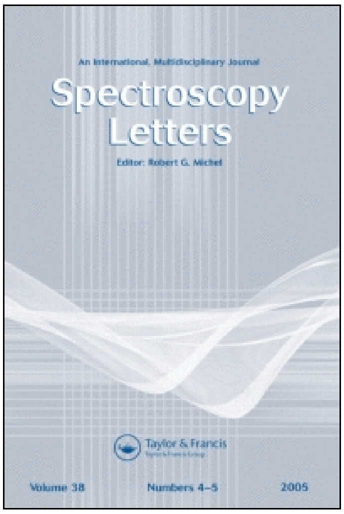

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# Inverted Region in Intermolecular Electronic Energy Transfer

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# INVERTED REGION IN INTERMOLECULAR ELECTRONIC ENERGY TRANSFER

*Key words:* Electron Exchange, Energy Transfer, Inverted Region.

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## ABSTRACT

A critique of some recent publications (concerning the so-called inverted region in exchange-induced electronic energy transfer) is presented. It is first pointed out that the phenomena reported therein have in fact been known for nearly two decades; next, a derivation of the expression (used in the aforementioned communications) for $k_{\mathrm{EnT}}$, the transfer rate constant, is presented; finally, it is stressed that this formula cannot provide reliable quantitative predictions.

## INTRODUCTION

The prediction,[1] and subsequent experimental confirmation,[2] of the inverted region in electron transfer reactions has rekindled interest in the electronic energy transfer analog, where the rate constant of energy transfer, $k_{\mathrm{EnT}}$, falls off rapidly as the energy of the first excited state of the donor, $E_1^{(D)}$, greatly exceeds that of the acceptor, $E_1^{(A)}$.[3-5] However, the inversion may be masked if the energy gap $E_1^{(D)} - E_1^{(A)}$ becomes larger than $E_2^{(A)} - E_1^{(A)}$; for transfer can then take place with much larger efficiency to the *second* excited state of the accepting species.

The purpose of this paper is threefold: to point out that both the inversion and its masking were announced nearly twenty years ago,[6,7] to present an alternative, physically transparent derivation of an expression for $k_{\mathrm{EnT}}$ which has gained much vogue, and to stress the precarious nature of the assumptions implicit in the derivation.

## THEORY

One finds, on adopting the crude adiabatic approximation,[8] which consists in ignoring the variation of the electronic wavefunctions with changes in nuclear coordinates, that the transfer rate constant may be factorized and written as[6]

$$k_{\mathrm{EnT}} = \frac{2\pi}{\hbar} U^2 J, \tag{1}$$

where $U$ is an electronic matrix element which provides a measure of the exchange interaction, and

$$J = \int I_D(E)\, I_A(E)\, dE, \tag{2}$$

$$I_D = \int g'(E'_D)\, \Pi_D^2(E'_D, E'_D - E) dE'_D, \tag{3}$$

$$I_A = \int g(E_A)\, \Pi_A^2(E_A, E_A + E) dE_A, \tag{4}$$

the functions $g'$ and $g$ are Boltzmann factors which make provisions for thermal averaging, and

$$\Pi(E_1, E_2) = \langle\chi(E_1)|\chi(E_2)\rangle \tag{5}$$

is an integral (whose square is known as the Franck-Condon factor) measuring the overlap between vibrational wavefunctions $\chi$. By using the closure relation, one can easily verify that

$$\int I_D\, dE = 1 = \int I_A\, dE. \tag{6}$$

It has become customary to call $J$ the Franck-Condon weighted density of states (FCWD). The quantity of prime interest is the magnitude of $U$, which can be extracted from the measured value of $k_{\mathrm{EnT}}$ only after $J$ has been evaluated. The calculation of $J$ occupies the rest of this paper.

## ESTIMATION OF *FCWD*

Since there is no realistic hope of calculating $J$ from first principles, one must make recourse to some approximations. The two strategies which have so far been used will now be spelled out.

In one approach,[6] which can be traced to Condon's seminal paper,[9] the crude adiabatic approximation is invoked once more; this allows one, with the help of Einstein's relations between the probabilities of radiative transitions, to relate the the emission spectrum, $f(\nu)$, and the absorption spectrum, $\epsilon(\nu)$, of a molecule to the appropriate Boltzmann-weighted Franck-Condon factor:[10]

$$f(\nu) \propto \nu^3 n(\nu) \int g'(E')\,\Pi^2(E', E' - h\nu)dE', \tag{7}$$

$$\epsilon(\nu) \propto \frac{\nu}{n(\nu)} \int g(E)\,\Pi^2(E, E + h\nu)dE. \tag{8}$$

By overlooking the $\nu$-dependence of the refractive index $n$, one can now relate the integrals $I_D$ and $I_A$ to (respectively)

$\hat{f}_D \equiv C_D f_D(\nu)\nu^{-3}$, the reduced emission spectrum of the donor and $\hat{\epsilon}_A \equiv C_A \epsilon(\nu)\nu^{-1}$, the reduced absorption spectrum of the acceptor, where $[C_D]^{-1} \equiv \int f_D(\nu)\nu^{-3}d\nu$ and $[C_A]^{-1} \equiv \int \epsilon_A(\nu)\nu^{-1}d\nu$ are normalization constants. As a result of these definitions, one can now express $J$ in terms of observable quantities:[11,12]

$$J = \int \hat{f}_{\rm D}(\nu)\hat{\epsilon}_{\rm A}(\nu)d\nu \tag{9}$$

The early work on exchange-induced energy transfer[6,7,13] exemplifies the approach outlined above. The choice of the acceptor compounds, viz. azoalkanes[6,7] and ketones,[13] which have weak but easily observable absorption bands, allowed an empirical *estimation*, from the spectral data, of the overlap integral, $J$, appearing in eq 9.

In more recent work,[3–5] which involves transfer to a triplet acceptor, the absorption spectrum of the latter is not as easy to obtain; accordingly, $J$ has been calculated by adopting analytically soluble models. The resulting expression stems from adapting the treatment of Ulstrup and Jortner[14], which was concerned with the inclusion, in electron transfer reactions, of quantized vibrational modes. Here we present a simple direct derivation for the particular case in hand (energy transfer).

The reduced absorption spectrum of the acceptor and the reduced emission spectrum of the donor can each be represented as the superposition of several peaks of different heights (see Figure 1). Since these peaks are not infinitely sharp, one must assign them a normalized distribution of finite width; in common with other workers, a gaussian shape will be chosen here, though other distributions cannot be ruled out *a priori.* With this proviso, each spectrum can be expressed formally as a sum:

$$\hat{\epsilon}_A(\bar{\nu}) = \sqrt{1/2\sigma_A^2\pi} \sum_{j=0}^{\infty} A_j \exp[-(\bar{\nu} - a_j)^2/2\sigma_A^2], \tag{10}$$

$$\hat{f}_D(\bar{\nu}) = \sqrt{1/2\sigma_D^2\pi} \sum_{k=0}^{\infty} D_{-k} \exp[-(\bar{\nu} - d_{-k})^2/2\sigma_D^2]. \tag{11}$$

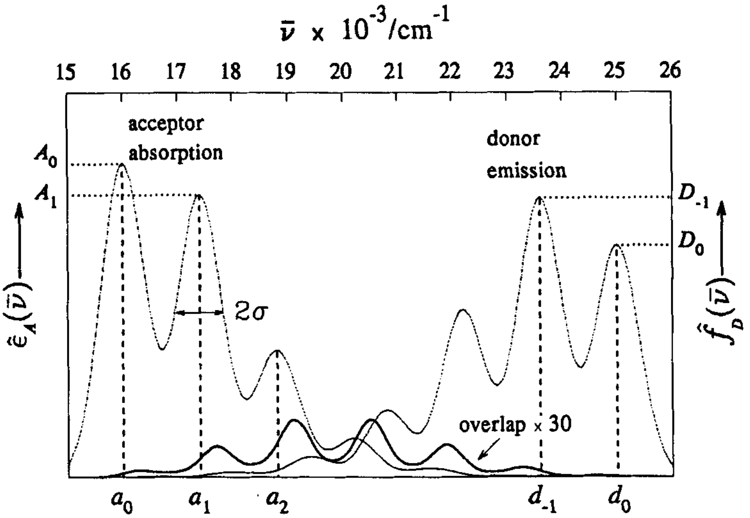

FIG. 1. Estimation of the spectral overlap integral ($J$), defined in eq 9, according to the displaced-oscillator model. Normalized absorption and emission spectra have been plotted using eqs 10 and 11, respectively, with $A_j$ and $D_{-k}$ given by eq 13 and $S_A = 0.9$, $S_D = 1.2$, $\hbar\omega_D = 1400$ cm$^{-1}$ $= \hbar\omega_A$ and $\sigma = 400$ cm$^{-1}$. For clarity the overlap integral has been multiplied by a factor of 30. The difference $(d_0 - a_0)$ equals $E_1^{(D)} - E_1^{(A)}$. It should be noted that though the heights of the peaks at $j = 5 = k$ are negligible, the corrresponding overlap cannot be neglected.

To proceed further, we will make the reasonable assumption that all peaks have the same width, which amounts to setting $\sigma_A^2 = \sigma^2 = \sigma_D^2$. Inserting eqs 10 and 11, into eq 9, and using

$$\int_{-\infty}^{\infty} du \exp(au - bu^2) = \sqrt{(\pi/b)} \exp(a^2/4b),$$

one immediately sees that $J$ comes out to be a double sum:

$$J = \frac{1}{2\sigma\sqrt{\pi}} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} A_j D_{-k} \exp[-(a_j - d_{-k})^2/4\sigma^2]. \qquad (12)$$

# DISCUSSION

Apart from the assumption that all peaks have the same gaussian distribution, the expression for $J$ in eq 12 is perfectly general, but it can be used to calculate $J$ only if $A_j$, $D_{-k}$, $a_j$, and $d_{-k}$ are known. Clearly, if the actual spectra are available, eq 9 is superior to eq 12 for numerical purposes. The problem is to calculate $J$ in the absence of such knowledge; hence the need to appeal to special models (which have severe limitations for quantitative work).

The most popular choice is the displaced-oscillator model,[15] which assumes that each spectrum is governed by a single, totally-symmetric, harmonic, skeletal stretching mode, and neglects the change in force constant that invariably accompanies electronic (de)excitation; in this case one can immediately write down the expressions for the unknown quantities appearing in eqs 10 and 11 (with $X, x, m = A, a, j$ or $D, d, -k$):

$$X_m = \exp(-S_X) S_X^m / m!, \qquad x_m = x_0 + m\hbar\omega_X. \qquad (13)$$

If the above expressions are substituted into eq 12, one immediately gets an expression for FCWD which is equivalent to that used in recent publications,[3-5] where $\lambda_s k_B T$ appears in place of $\sigma^2$, $\lambda_s$ being the solvent reorganization parameter.

If one looks at the comparison[16] between the lowest energy, singlet-singlet absorption spectrum of anthracene and its vibrational analysis according to eq 13, one sees that, after $j \geq 4$, the agreement between calculation and experiment becomes particularly poor. The cases of maximum interest, those when $J$ becomes very small, arise when only the tails of the two spectra overlap;[17] this would correspond to $j \geq 4$ *and* $k \geq 4$, and there is really no reason to place confidence in the outcomes of eq 13 in such cases.

In addition, there is enough evidence[15] to believe that high-energy (ca. 3000 cm$^{-1}$), C–H stretching modes become more effective in accepting energy in excess of ca. 5000 cm$^{-1}$, and that these modes deviate considerably from harmonicity. Since the analytical form of the expression for Franck-Condon factors for such modes does not conform to eq 13, the observed agreement[18] between theory and experiment should be regarded as fortuitous; in a highly exothermic (low overlap) reaction, only a combination of C–C and C–H modes can account satisfactorily for FCWD, and deuteration would exert a noticeable influence.[15,19]

Even when the Franck-Condon factors are determined primarily by the 1400 $\mathrm{cm}^{-1}$ C–C mode, adherence to the above model is an exception rather than the rule. In anthracene, which is regarded as a successful illustration of eq 13, a second totally symmetric mode (ca. 400 $\mathrm{cm}^{-1}$) reveals itself in the form of a progression even in room temperature spectra,[20] and in azulene one *has* to take account of two skeletal modes, 700 $\mathrm{cm}^{-1}$ (bending) and 1400 $\mathrm{cm}^{-1}$ (stretching) for reproducing the essential features of the absorption spectrum;[21] the fluorescence spectrum and the corresponding absorption spectrum of phenanthrene are known to deviate markedly from the Poisson distribution and the mirror symmetry implied by eq 13.[22] These examples show that, even if one does not dispute the the factorization of $k_{\mathrm{EnT}}$ stated in eq 1, the measured values of $k_{\mathrm{EnT}}$ will lead to reliable estimates for $U$ only if $J$ is amenable to experimental evaluation.

Finally, a comment concerning the remark[4] that "electron transfer (ET) and energy transfer, particularly triplet energy transfer (TT), have certain features in common": when the acceptor transition has a low dipole strength or the fluorescence yield of the donor is vanishingly small, coulombic interaction becomes inoperative, and singlet-singlet transfer stands on the *same* footing as triplet-triplet transfer, because $k_{\mathrm{EnT}}$ is then determined in both cases solely by the exchange integral, $U$.[23] Since the longest wavelength singlet-singlet transitions in azo and carbonyl compounds have low molar absorptivities, transfer of singlet energy to these acceptors proceeds primarily via electron exchange; conversely, in photosynthetic systems containing light-harvesting carotenoids,[24–27] which are practically nonfluorescent, electron exchange is necessary for the carotenoid-to-chlorophyll singlet-singlet energy transfer.[24]

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