Electronic coupling in inter- and intramolecular donor–acceptor systems as revealed by their solvent-dependent charge-transfer fluorescence

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Abstract.   The solvent dependence of the radiative-rate constant of both inter- and intramolecular donor–acceptor systems reveals the occurrence of significant intensity borrowing from one or more local transitions. This phenomenon appears to be especially pronounced in systems of the type D-3σ-A, where donor and acceptor interact via through-bond interaction over a relay of three σ bonds. Within the context of a three-state model, involving the no-bond state (DA), the charge transfer state (D^+A^-) and a single locally excited state [(DA)*], a simplified method is given to analyse the electronic coupling elements between these states.

1. Introduction

Intramolecular electron transfer in molecules consisting of an electron donor (D) and acceptor (A) connected by a saturated hydrocarbon bridge comprising a relay of n σ bonds (*i.e.* D-$n\sigma$-A) constitutes a continuing subject of investigation[1–13]. As early as 1973, one of us reported[2] that through-bond interaction (TBI) in such compounds may lead to the occurrence of long-range photoinduced electron transfer, charge-transfer (CT) absorption and CT fluorescence with the σ bridge occupying a rigidly extended conformation, which excludes a direct contact between D and A. While the earliest reports[2–4] referred to the observation of these phenomena across three σ bonds (*i.e.* in D-3σ-A), this was soon extended to D-5σ-A[5–7]. Later work[8,9] reported intramolecular charge-transfer absorption (also referred to as intervalence absorption) across as many as six and even eight σ bonds, charge-transfer fluorescence across σ-bond arrays up to 10 bonds[10,11] and photoinduced electron transfer on a nanosecond time scale even in a D-13σ-A system[12,13]. The phenomenon of long-range photoinduced electron transfer in D-$n\sigma$-A systems with a rigidly extended conformation has been given particularly extensive attention[13] and studies in this area have undeniably been instrumental in advancing our knowledge about electron transfer in molecular systems in general.

More limited attention has been given to the CT-absorption and fluorescence phenomena displayed by D-$n\sigma$-A systems. As already realised[14] at an early stage in the development of electron-transfer theory however, these phenomena may in fact reveal important information about the rate and mechanism of long-range non-adiabatic electron transfer. This is because, according to the golden rule, the rate of non-adiabatic electron transfer is proportional to the square of the electronic-coupling-matrix element (V) between the reactant and product states, while the electric transition-dipole moment of a CT transition also depends directly upon such coupling. Applying a "Mulliken type" two-state model[15] in which only interaction between the no-bond DA configuration and the ionic configuration D^+A^- is considered, the latter dependence is particularly straightforward.

Thus within such a model, the well-known[14] *Hush* relation (Eqn. 1) provides a good approximation for the relation between V and the emerging CT absorption with molar extinction ε ($l \cdot mol^{-1} \cdot cm^{-1}$), position ν_{max}, full width at half-height $\Delta\nu_{1/2}$ (both in cm^{-1}), for a DA pair in which charge separation occurs over a (centre to centre) distance R_c (in Å).

$$V = \frac{2.06 \cdot 10^{-2}}{R_c} \sqrt{\varepsilon_{max} \cdot \nu_{max} \cdot \Delta\nu_{1/2}} \ cm^{-1} \tag{1}$$

Within the same model V can also be estimated from the radiative rate constant (k_{RAD} in s^{-1}) of CT fluorescence and its (mean) energy ν (in cm^{-1}) via Eqn. 2 as derived independently by *Verhoeven* et al.[11] and subsequently by *Gould* et al.[16,17]. Here n is the solvent refractive index and $\Delta\mu$ is the change in dipole moment (in Debye) accompanying charge transfer:

$$k_{RAD} = \frac{64 \cdot \pi^4 \cdot n^3}{3 \cdot h} \cdot (V \cdot \Delta\mu)^2 \cdot \nu$$
$$= 3.1 \cdot 10^{-7} \cdot n^3 \cdot (V \cdot \Delta\mu)^2 \cdot \nu \tag{2}$$

However, in an early stage of the investigations of the D-$n\sigma$-A systems it had been noted by *Verhoeven* et al.[7] that the two-state model underlying Eqn. 1 was quite inadequate to describe the CT absorption behaviour of
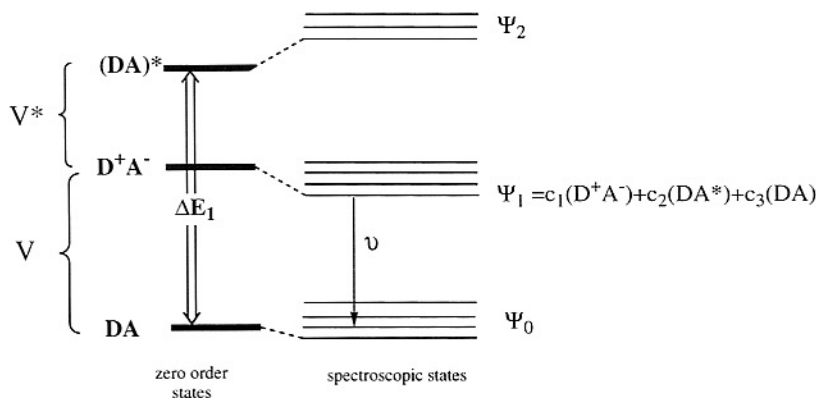
Figure 1. Three-state model for mixing of the charge-transfer state with both the no-bond state and the lowest locally excited state in donor – acceptor (D – A) systems.

such systems. It was shown that the minimum model needed is a three-state model including, in addition to the DA and D^+A^- states, a low-lying locally excited state DA^* of the appropriate symmetry to interact with the D^+A^- state. In such a model, not only the interaction-matrix element between DA and D^+A^- (i.e. V) but also that between D^+A^- and DA^* (i.e. V^*) determines the transition dipole moment of the CT absorption and thus also the radiative rate constant of CT fluorescence. The effect of V^* is that the CT transition "borrows" intensity from the local $DA \leftrightarrow DA^*$ transition by mixing some locally-excited-state character into the spectroscopic CT state (Ψ_1 in Figure 1)

In the absorption spectra of the D-$n\sigma$-A systems for which this model was originally proposed[7], the intensity-borrowing effect was so pronounced that it appeared to be virtually the only source of CT absorption intensity. In some later studies[11] of the CT fluorescence ($\Psi_1 \rightarrow \Psi_0$) of various D-$n\sigma$-A systems, the occurrence of intensity borrowing was also noted but it was assumed that the larger energy gap between the locally excited state and the emissive CT state, resulting from solvent relaxation, should make its contribution relatively unimportant, especially in solvents of medium and high polarity.

A recent quantitative investigation[18] showed this assumption to be unwarranted in many cases, demonstrating the breakdown of Eqn. (2) due to intensity borrowing. Instead it appeared that the solvent dependence of k_{RAD} for a number of D-$n\sigma$-A systems could be satisfactorily described on the assumption that it derives exclusively from intensity borrowing. This would imply that, in Figure 1, $c_2 \gg c_3$ and – depending on the energy gaps involved – also $V^* > V$. The latter result is of direct importance for the understanding the processes of photoinduced charge separation (k_{cs}) and thermal charge recombination (k_{cr}) in such compounds because, under nonadiabatic conditions, these are governed by $(V^*)^2$ and V^2, respectively. In this context it should be noted that the availability of systems in which $V^* \gg V$ is desirable if one wants to prevent rapid loss of photoinduced charge separation by intramolecular recombination without relying only on the differences in Franck–Condon factors for these two processes. This situation of $V^* > V$ may be relevant for the primary electron-transfer processes in photosynthesis.

In order to investigate further the relative importance of admixture of locally excited states in the CT state, we applied the full three-state model derived earlier[18] to a number of D-3σ-A systems that display CT fluorescence over a sufficiently wide range of solvent polarity to separate the effects of V and V^* on k_{RAD} and we compared the results obtained with those reported recently[19,20] from

a similar investigation of intermolecular charge-transfer complexes and exciplexes. From this comparison some interesting conclusions can be drawn regarding the difference in electronic coupling mechanisms between non-bridged and σ-bridged D/A systems.

2. Results and discussion

2.1. The three-state model for weak coupling

As discussed extensively before[18], the radiative rate constant for CT fluorescence in a weakly coupled (i.e. $V \ll \nu$ and $V^* \ll \Delta E_1 - \nu$ in Figure 1) D/A system can be approximated by Eqn. 3.

$$k_{RAD} = \frac{64 \cdot \pi^4 \cdot n^3}{3 \cdot h} \cdot \left\{ (V \cdot \Delta \mu)^2 \cdot \nu \right.$$
$$+ 2 \cdot V \cdot V^* \cdot [\Delta \mu \cdot \mu^* \cdot \cos(\alpha)] \cdot \nu^2 / (\Delta E_1 - \nu)$$
$$\left. + (V^* \cdot \mu^*)^2 \cdot \nu^3 / (\Delta E_1 - \nu)^2 \right\} \quad (3)$$

In Eqn. 3, μ^* is the transition dipole moment of the unperturbed local $DA \rightarrow (DA)^*$ transition, α is the angle between μ^* and $\Delta\mu$, while ΔE_1 designates the energy gap between the locally excited state and the ground state (see Figure 1). In the absence of intensity borrowing (i.e. for $V^* = 0$), Eqn. 3 reduces to Eqn. 2. For dominant intensity borrowing, it can be approximated by the last term, i.e. by Eqn. 4.

$$k_{RAD} = \frac{64 \cdot \pi^4 \cdot n^3}{3 \cdot h} \cdot (V^* \cdot \mu^*)^2 \cdot \nu^3 / (\Delta E_1 - \nu)^2 \quad (4)$$

While fitting procedures based on the simplified Eqns. 2 and 4 are rather straightforward, this is more cumbersome with the 'complete' description given by Eqn. 3. This can, however, be rewritten in the convenient form of Eqn. 5 which shows that the dependence of $k_{RAD}/(n^3 \cdot \nu)$ on $\nu/(\Delta E_1 - \nu)$ should be parabolic and can thus be fitted to a simple second-order polynomial curve. In Eqn. 5, rates are in s^{-1}, energies in cm^{-1} and dipole moments in Debye.

$$\frac{k_{RAD}}{n^3 \cdot \nu} = \frac{64 \cdot \pi^4}{3 \cdot h} \cdot \left\{ (V \cdot \Delta \mu)^2 \right.$$
$$+ 2 \cdot V \cdot V^* \cdot [\Delta \mu \cdot \mu^* \cdot \cos(\alpha)] \cdot \nu / (\Delta E_1 - \nu)$$
$$\left. + (V^* \cdot \mu^*)^2 \cdot \nu^2 / (\Delta E_1 - \nu)^2 \right\}$$
$$= 3.1 \cdot 10^{-7} \cdot \left[(V \cdot \Delta \mu)^2 \right.$$

$$+2 \cdot V \cdot V^{*} \cdot (\Delta\mu \cdot \mu^{*} \cos(\alpha) \cdot \nu/(\Delta E_{1} - \nu)$$
$$+(V^{*} \cdot \mu^{*})^{2} \cdot \nu^{2}/(\Delta E_{1} - \nu)^{2}] \tag{5}$$

From such a fit, the three parameters $V \cdot \Delta\mu$, $V^{*} \cdot \mu^{*}$ and $\cos(\alpha)$ can then, in principle, be obtained directly. The quadratic relation Eqn. 5, and its extension (for the case $V^{*} > \Delta E_{1} - \nu$) were used to fit the experimental data for intermolecular D/A systems[19,20] and for D-3σ-A molecules[21–23]. This numerical fitting procedure resulted in the three parameters with an apparent high accuracy (as expressed in Figures 2, 4, 5, 6). However, in view of physical approximations inherent in the analysis and the experimental uncertainties in the input data, we shall present the parameters within an accuracy of a few per cent.

2.2. Application to intermolecular D/A systems

In order to test the consistency of Eqn. 5 in describing CT fluorescence behaviour, we will first apply it to a series of intermolecular D/A systems that were recently investigated by *Gould* et al.[19,20], applying a more elaborate description of the three-state model including the cases where the weak coupling limit breaks down. The most complete set of data in that study refers to systems consisting of 2,6,9,10-tetracyanoanthracene (TCA) as the acceptor and various polymethylated benzenes as donors in a number of solvents. From a total of 27 D/A/solvent combinations given we have omitted one (*p*-xylene/TCA/cyclohexane), involving ν 19690 cm^{-1} which indicates a rather small energy gap between D^{+}A^{-} and DA* (for TCA a ΔE_{1} of 21600 cm^{-1} is proposed). This leads to stronger mixing than can be adequately described by the first-order perturbation model underlying Eqn. 5. The fit obtained for the remaining 26 data sets is shown in Figure 2A.

From the results the following parameters are derived: $V \cdot \Delta\mu = 5800$ cm$^{-1} \cdot$ D, $V^{*} \cdot \mu^{*} = 2000$ cm$^{-1} \cdot$ D, and $\alpha = 90°$. The latter seems to confirm the validity of the assumption made by *Gould* et al. that in these intermolecular D/A systems the relative orientation is such that $\Delta\mu$ and μ^{*} are virtually perpendicular, which complies with a sandwich-like parallel orientation of the aromatic π-planes of D and A. Also the magnitudes of $V \cdot \Delta\mu$ and $V^{*} \cdot \mu^{*}$ are in reasonable agreement with the data already published[19,20] (9750 and 3780 cm$^{-1} \cdot$ D, respectively). The difference seems to originate from uncertainties in the different fitting procedures employed herein and by *Gould* et al.[19,20].

Although these results support the application of Eqn. 5 for the analysis of CT-fluorescence data within the framework of a three-state model, it should at the same time be noted that the results depend rather critically upon the choice of ΔE_{1}. In Figure 2A we have set this parameter at the value proposed by *Gould* et al. (21600 cm^{-1}) which corresponds to the weighted average fluorescence frequency of TCA. If, however, ΔE_{1} is set equal to the zero–zero energy of TCA (~ 23500 cm^{-1}), which we consider more appropriate, a virtually equally good fit is obtained (see Figure 2B), but now with the parameters $V \cdot \Delta\mu = 8800$ cm$^{-1} \cdot$ D, $V^{*} \cdot \mu^{*} = 4700$ cm$^{-1} \cdot$ D and $\alpha = 130°$. While the former values are still in the same range and their ratio is not changed dramatically, the value now found for α would certainly not allow one to drop the cross term in Eqn. 5, nor to conclude that the complexes have a geometry close to a sandwich with the centres of donor and acceptor superimposed. Taking $\Delta\mu \approx 17$ D and $\mu^{*} \approx 3$ D we infer that $V \approx 520$ cm^{-1} and $V^{*} \approx 1600$ cm^{-1}, whereupon the validity conditions (*i.e.* $V^{*} \ll \Delta E_{1} - \nu$ and $V \ll \nu$) for the applicability of the weak coupling (perturbative) scheme (Eqn. 3), are well satisfied.

It should be pointed out that the insensitivity of the quality of the fit to the choice of ΔE_{1} makes it virtually impossible to base the choice of ΔE_{1} upon such a quality criterion even if a relatively large data set is available. On the other hand, ΔE_{1} values that would make the first or third right-hand term in Eqn. 5 negative or lead to $|\cos(\alpha)| > 1$ are clearly unacceptable. We will come back to this problem more extensively below.

2.3. Analysis of the strongly fluorescent D-3σ-A systems 1–3

We have shown previously[18] that the solvent dependence of k_{RAD} for a number of D-*n*σ-A systems in fact displays a behaviour that cannot be described by Eqn. 2, but fits in quite well with that predicted by Eqn. 4, thus suggesting a dominant role of intensity borrowing. The systems investigated previously[18] displayed relatively weak CT fluorescence that could only be quantified in solvents spanning a limited range of polarity resulting in a limited variation of the fluorescence position ν. Under those conditions, the experimental errors in k_{RAD} prevent the estimation of

fit: y = 10.33 - 0.03x + 1.24x^2   (R^2 = 0.982)
results: VΔμ = 5772 ; V*μ* = 2002

A

krad/v.n^3 vs *v/(21600-v)*

fit : y = 24.28 - 16.48x + 6.73x^2 (R^2 = 0.978)
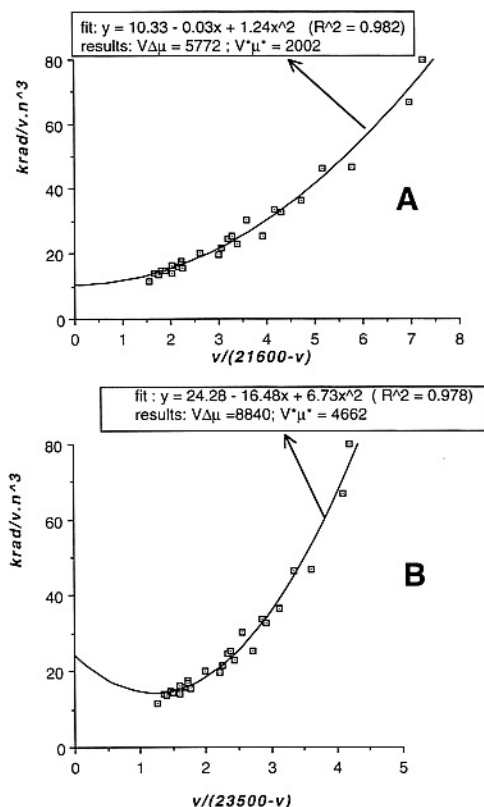results: VΔμ =8840; V*μ* = 4662

B

krad/v.n^3 vs *v/(23500-v)*

Figure 2. Parabolic fit according to Eqn. 5 of literature data[19,20] for the charge-transfer emission of complexes between 2,6,9,10-tetracyanoanthracene (TCA) and (poly)methylated benzenes in various solvents. In A the energy of the locally excited state was set at $\Delta E_{1} = 21600$ cm^{-1} (as proposed by Gould et al.); in B the E_{00} energy of TCA (23500 cm^{-1}) was used instead.
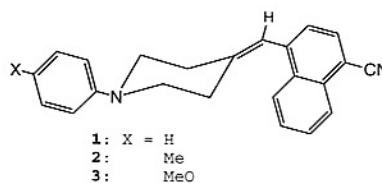

1: X = H
2:     Me
3:     MeO

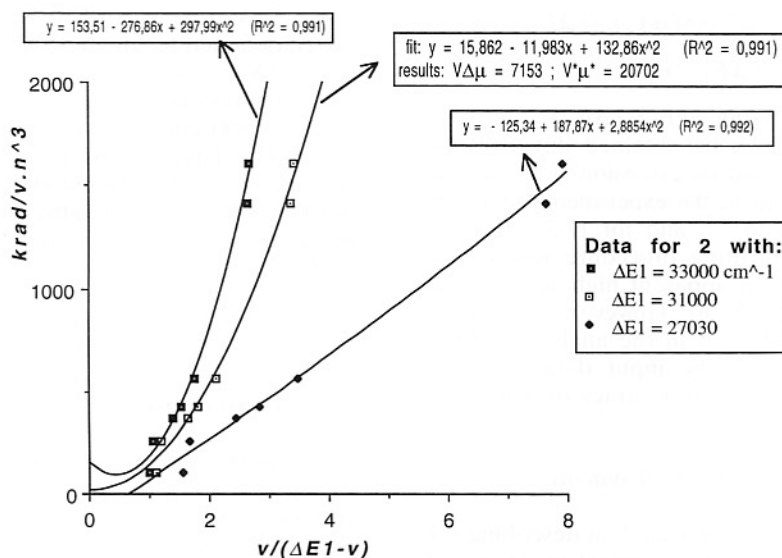*Figure 3. Structure of the D-3σ-A systems investigated.*

Figure 4. Parabolic fit according to Eqn. 5 of the charge-transfer fluorescence data of 2 in various solvents (see Table I) with three different values for the energy of the locally excited state (i.e. $\Delta E_1 = 33000$, 31000 and 27030 cm^{-1})

the other terms in Eqn. 3 with any acceptable degree of accuracy. The D-3σ-A systems 1–3 (see Figure 3), however, are known[21-23] to display quite efficient CT fluorescence over a wide range of solvent polarity. In Table I the relevant photophysical parameters of this fluorescence are compiled as determined previously.

System 2 epitomises the strongly fluorescent D-3σ-A systems 1–3. In this compound, the 1-vinyl-4-cyanonaphthalene acceptor chromophore is the most likely source for a low-lying local excitation from which the CT transition could borrow its intensity. From independent studies[23], E_{00} of this chromophore is known to be located at ~ 31000 cm^{-1}. In Figure 4 we analyse the strong solvent dependence of the fluorescent properties of 2 via Eqn. 5 using ΔE_1 values of 31000, 33000 and 27030 cm^{-1}. The latter values correspond to the absorption maximum and the fluorescence maximum of the acceptor chromophore (solvent n-hexane), respectively. As noted above even such a rather wide variation of ΔE_1 hardly influences the (good) quality of the fit. At the other hand, the value corresponding to the acceptor fluorescence maximum (i.e. 27030 cm^{-1}) is clearly unacceptable because it leads to a

negative value of the first term. Both of the other values are in principle acceptable. For ΔE_1 31000 cm^{-1}, the parameters derived are $V \cdot \Delta\mu = 7200$ cm$^{-1} \cdot$ D, $V^* \cdot \mu^* = 20700$ cm$^{-1} \cdot$ D, $\alpha = 105°$, while for ΔE_1 33000 cm^{-1} these are $V \cdot \Delta\mu = 22300$ cm$^{-1} \cdot$ D, $V^* \cdot \mu^* = 31000$ cm$^{-1} \cdot$ D and $\alpha = 130°$. While we feel that the former choice of ΔE_1 is more realistic it is thus clear that $V^* \cdot \mu^*$ is certainly (much) larger than $V \cdot \Delta\mu$ and since $\Delta\mu > \mu^*$ this implies that $V^* \gg V$ (see below). It is thus evident that the radiative-rate constant is always dominated by the last term (i.e. by intensity borrowing) since, even in the most polar solvents available, $\nu/(\Delta E_1 - \nu) > 1$.

These conclusions are further enhanced by using as a data set all data available (see Table I) for 1, 2, and 3, that share the same acceptor chromophore. As shown in Figure 5 with ΔE_1 31000 cm^{-1}, a quite impressive fit is also obtained for this expanded data set, although the spread is now larger than in Figure 4, probably because the implicit assumption that the three compounds have identical V and V^* values is not fully justified. This also seems the reason that for α a value of 86° is obtained, which is unrealistic because the extended structure of the compounds requires that $\alpha > 90°$. Nevertheless, the average parameters $V \cdot \Delta\mu = 14600$ cm$^{-1} \cdot$ D, and $V^* \cdot \mu^* = 19400$ cm$^{-1} \cdot$ D obtained for this set of data confirm that in all three compounds intensity borrowing is dominant. In view of the high values found for $V \cdot \Delta\mu$ and $V^* \cdot \mu^*$ in

Table I   Fluorescence parameters of 1–3 in various solvents.

Comp.	Solvent	n	ν (cm^{-1})	Φ	τ (ns)	k_{RAD} (10^6 s^{-1})
1[a]	cyclohexane	1.4260	24270	0.13	1.2	108
	benzene	1.5011	20920	0.51	15.0	34.0
	1,4-dioxane	1.4224	19380	0.45	15.0	30.0
	di-n-butyl ether	1.3990	21370	0.60	12.0	50.0
	di-ethyl ether	1.3520	19760	0.24	14.0	17.1
	chloroform	1.4457	18830	0.27	13.0	20.7
	ethyl acetate	1.3724	17450	0.11	6.0	18.3
	tetrahydrofuran	1.4072	17420	0.12	7.0	17.1
	dichloromethane	1.4242	17270	0.13	9.0	14.4
2[b]	n-hexane	1.3750	24000	0.42	4.2	100
	cyclohexane	1.4260	23900	0.47	4.8	97.9
	di-n-butyl ether	1.3990	21000	0.49	15.1	32.5
	diisopropyl ether	1.3680	20000	0.33	15.0	22.0
	diethyl ether	1.3520	19200	0.24	13.7	17.5
	ethyl acetate	1.3724	16900	0.02	1.8	11.1
	dichloromethane	1.4242	16400	0.01	2.0	5.00
3[b]	n-hexane	1.3750	22600	0.42	8.8	47.7
	cyclohexane	1.4260	22500	0.63	10.8	62.0
	di-n-butyl ether	1.3990	19200	0.22	10.6	20.8
	diisopropyl ether	1.3680	18200	0.07	5.1	13.7
	diethyl ether	1.3520	17500	0.02	2.3	8.70

[a] Data taken from Ref. 21.   [b] Data taken from Ref. 23.
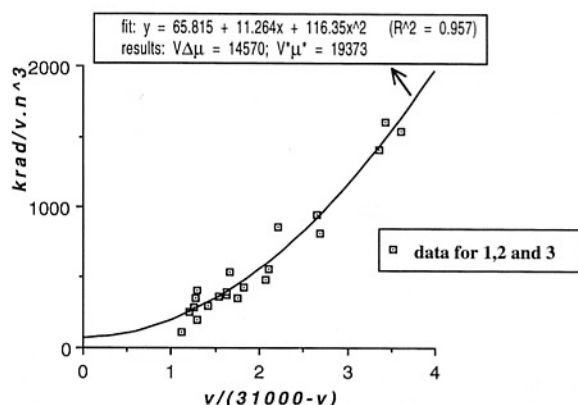

Figure 5. Parabolic fit according to Eqn. 5 of the combined charge-transfer fluorescence data of 1–3 in various solvents (see Table I) with the energy of the locally excited state set at $\Delta E_1 = 31000$ cm^{-1}.

1–3, it is important to check whether the first-order perturbation scheme (i.e. the assumption of weak coupling) underlying the present treatment is in fact applicable. Regarding the coupling between the DA and D^+A^- states this is not a problem. For compounds of type 1–3, the value of $\Delta\mu$ has been investigated extensively, i.e. via fluorescence solvatochromism[21], via time-resolved microwave conductivity[21], and via electrochromism[24]. These measurements consistently led to $\Delta\mu = 23 \pm 2D$ which, together with the results obtained in Figures 4 and 5 for $\Delta E_1 = 31000$ cm^{-1}, implies that V is in the range 300–600 cm^{-1}. This is much smaller than even the most red-shifted CT emission used in the fits (see Table I). More problematic is the situation for the coupling described by V^*. As discussed before[18] a value for μ^* (in Debye) can be derived from the absorption oscillator strength (f^*) of the local transition from which intensity is borrowed via Eqn. 6 in which ν^* and $\Delta\nu^*_{1/2}$ (both in cm^{-1}) give the absorption maximum and FWHM, while ε^* is the molar extinction coefficient.

$$\mu^* = \sqrt{\frac{f^*}{4.7 \cdot 10^{-7} \cdot \nu^*}} \approx \sqrt{\frac{0.0092 \cdot \varepsilon^* \cdot \Delta\nu^*_{1/2}}{\nu^*}} \qquad (6)$$

For the 1-vinyl-4-cyanonaphthalene chromophore, substitution of $\nu^* = 32200$ cm^{-1}, $\Delta\nu^*_{1/2} = 2600$ cm^{-1} and $\varepsilon^* = 11700$ l·mol^{-1}·cm^{-1} gives $\mu^* = 3.0$ D. From the $\mu^* \cdot V^*$ values found, it should thus be concluded that V^* for 1, 2 and 3 is in the range 6500–7000 cm^{-1}. This is in fact in the same range as the energy gap between the locally excited and CT states in nonpolar solvents as measured by $\Delta E_1 - \nu$, which implies that a first-order perturbation approach could be inadequate in such solvents. A rather straightforward investigation of this problem can be achieved by noting that, at the same time, the influence of intensity borrowing becomes completely dominant, so that k_{RAD} can be described by the last term of Eqn. 3 modified to take account of the fact that the condition $V^* \ll \Delta E_1 - \nu$ does not apply. This then leads to Eqn. 7.

$$k_{RAD} = \frac{64 \cdot \pi^4 \cdot n^3}{3 \cdot h} \cdot (V^* \cdot \mu^*)^2 \cdot \nu^3$$

$$/\left[(\Delta E_1 - \nu)^2 + (V^*)^2\right] \qquad (7)$$

This can conveniently be rewritten in the form of Eqn. 8 which implies that a plot of $n^3 \cdot \nu^3 / k_{RAD}$ versus $(\Delta E_1 - \nu)^2$ should be linear and that V^* and μ^* can be calculated from its slope and intercept:

$$\frac{n^3 \cdot \nu^3}{k_{RAD}} = \frac{3 \cdot h}{64 \cdot \pi^4} \cdot \left[\frac{(\Delta E_1 - \nu)^2}{(V^* \cdot \mu^*)^2} + \frac{1}{(\mu^*)^2}\right]$$

$$= 3.22 \cdot 10^6 \cdot \left[\frac{(\Delta E_1 - \nu)^2}{(V^* \cdot \mu^*)^2} + \frac{1}{(\mu^*)^2}\right] \qquad (8)$$

From Figure 6 it is evident that the spread of data is substantial. However, if the two most polar solvents are omitted a good linear fit is obtained and from the ratio of its slope and intercept we find $V^* = 2100$ cm^{-1}. This implies that the fraction (g^*) to which the locally excited state mixes into the CT state in the most nonpolar solvent (i.e., in n-hexane where $\nu = 24000$ cm^{-1}, see Table I) is only $g^* = 0.08$ as calculated via Eqn. 9.

$$g^* = \frac{(V^*)^2}{(\Delta E_1 - \nu)^2 + (V^*)^2} \qquad (9)$$

This is still a small admixture and therefore in line with the experimental results[21,24] that indicated the dipole moment of the emissive state to be essentially solvent-in-
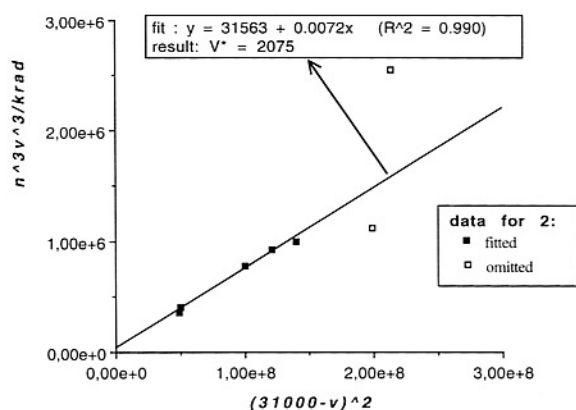

Figure 6. Linear fit of the solvent-dependent fluorescence data for 2 according to Eqn. 8. Note that the data in polar solvents (ethyl acetate and dichloromethane, see Table I) have been omitted in the calculation of the regression.

dependent. It also implies that, in retrospect, our analysis based on Eqn. 5 must have been allowed (note also that the data in polar solvents, where the first and second term cannot be neglected, are well accounted for). In fact from the slope of the regression in Figure 6, $V^* \cdot \mu^* = 21000$ cm^{-1}·D is derived which is almost identical to the result (20700 cm^{-1}·D) derived above (see Figure 4) by application of Eqn. 5. The real problem is thus apparently that the μ^* value we had chosen, based upon the oscillator strength of the first local transition in the absorption spectrum, is too small. Interestingly, application of Eqn. 8, in contrast to Eqn. 5, allows us to determine the effective magnitude of μ^*. From the intercept of the plot in Figure 6, this is found to be $\mu^* = 10$ D, with a considerable uncertainty (i.e. about $\pm 50\%$). In any case, the value of μ^* extracted from the analysis of the radiative rates considerably exceeds the value $\mu^* = 3.0$ D derived from the absorption data.

A possible reason for this discrepancy is that the conformation of the acceptor chromophore in the CT state is changed such that μ^* is significantly enhanced as compared to the ground-state conformation[25]. Another likely reason, however, is that intensity borrowing in fact occurs from more than one local transition so that the V^* and μ^* values found from analyses applying a three-state model do more or less represent a weighted sum of these parameters over all locally excited states that interact with the CT state. This also implies that separating V^* and μ^* is largely an elusive effort and that only their product $V^* \cdot \mu^*$ can be considered as a meaningful parameter to describe the overall contribution of the coupling between the CT state and locally excited states to the radiative transition probability of the former.

Finally, it should be realised that the formalism underlying the present treatment of a three-state system only takes into account electronic coupling while neglecting vibronic effects. If coupling becomes strong – as is the case for 1–3 in less polar solvents – such vibronic coupling may lead to significant deviations from the formalism used above. Efforts are presently being made[26] to incorporate vibronic effects in our model. While the need for such an extension is already suggested by the results described above for 1–3, it is even more important for the description of related systems in which the energy of the CT state encroaches upon that of locally excited states more closely. Thus it was recently found[27] that removing the cyano group from 1 leads to a fluorescent D-3σ-A system for which the CT excited-state dipole moment is diminished in low-polarity solvents indicating admixture

of locally excited states to an extent that probably cannot be treated by the weak coupling (perturbative) model.

3. Conclusions

The results described above provide further demonstration for the major improvement that a three-state model allows in description of the solvent-dependent radiative properties of both inter- and especially intra-molecular donor–acceptor systems as compared to the classical Mulliken-type two-state model. This finding implies that earlier estimates of the electronic coupling V in D–A systems that were based on a two-state model of either CT-absorption intensities[8,9,14] or CT-fluorescence radiative-rate constants[11,17,28] should be subject to reconsideration.

Another important finding of the present study is that the value of $k_{RAD}/(\nu \cdot n^3)$ for CT fluorescence in the intermolecular systems with direct D–A contact compiled in Figure 2 is smaller by one to two orders of magnitude than for D-3σ-A systems such as **1–3** in which direct D–A contact is absent. From the analysis given it appears that this is mainly due to a much enhanced value of $V^* \cdot \mu^*$ in the latter systems, while $V \cdot \Delta\mu$ is comparable in both (the moderate enhancement of $V \cdot \Delta\mu$ in the intramolecular systems can readily be attributed to a larger value of $\Delta\mu$ resulting from the larger D–A separation). Although as discussed above it is not easy to separate V^* and μ^* unequivocally it appears unavoidable to conclude that especially V^* is significantly enhanced in the intramolecular systems. It has been proposed before[7] that a through-bond mechanism of D–A interaction is prone to enhance V^* rather than V and the present results support this view. This may provide an efficient tool to increase the rate of photoinduced charge separation over charge recombination, an issue of considerable importance in the exploration of molecular electronics and photosynthesis.

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