

## Solvent effects on intramolecular charge separation

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**Abstract.** Solvent polarity effects on the energetics of charge separation processes, in particular on proton transfer in 1-morpholinomethyl-2-naphthol (M2N), were studied and discussed in the frame of a continuum model. The obtained results were compared to electron transfer (TICT) in *p*-cyano-*N,N*-dimethylaniline (CDMA). Solvatochromic shifts of M2N were explained by an increase of the molecular dipole moment on excitation, but more importantly by a rotation of its direction. A minimum in the excited state lifetime in an intermediate polarity region was attributed to a maximum radiationless transition probability.

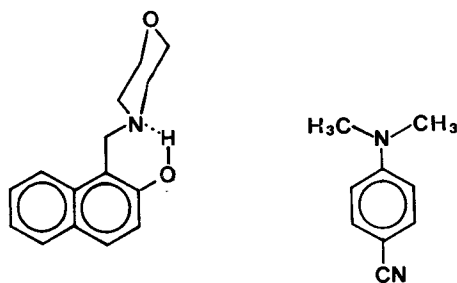
**Keywords.** Solvent effects; intramolecular charge separation; proton transfer; continuum model.

### 1. Introduction

Intramolecular charge separation is a fundamental process in the chemistry of excited states. A charge separation results either from the transfer of an electronic charge from a donor to an acceptor site within a suitable molecule (i.e. an electron charge transfer (ET)) or from a proton transition along an intramolecular hydrogen bond upon excitation (i.e. excited state proton transfer (PT)). As a consequence of such processes a positive and a negative charge are localized in two different and separated functional parts of the molecule and this new charge distribution leads generally to an increase of the molecular dipole moment as well as to structural and electronic rearrangement within the molecules. Additionally, due to the long range of charge–charge interactions in solutions, charge separation requires reorientation of the surrounding solvent. By varying the solvent, both the energetics and the dynamics of charge separation can be influenced and this is usually referred to as “solvent effects”. This demonstrates clearly the many body character of these dynamic processes in solution. Continuum approximation treating the medium around the molecules outside of some cavity as a macroscopic dielectric continuum as well as specific molecular models can be applied to describe solvent effects. Moreover, charge separation is influenced by the solvent dependence of its energetics but also by medium effects on the photophysical properties of the initially excited state, where PT or ET starts from, and of the final charge separated state.

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Scheme 1. M2N and CDMA.

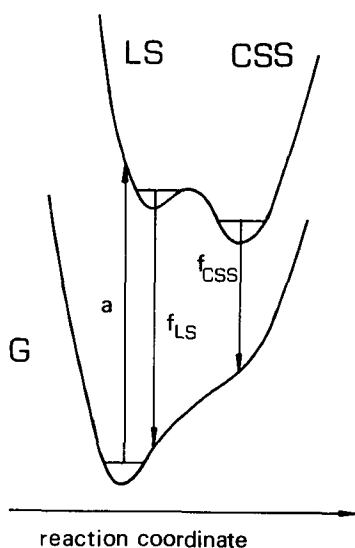
In this paper we will summarize solvent effects on the energetics of intramolecular charge separation within the frame of a continuum model. Such a continuum model was used widely in explaining solvent influences of shift differences and the dynamics of excited states (Nicol 1974; Calef 1988; Suppan 1990). Solvent effects on excited state equilibria are, however, much less considered in the literature. As examples proton transition in 1-morpholinyl-2-naphthol (M2N) (Köhler and Wolschann 1987) and intramolecular electron transfer in the TICT (twisted intramolecular charge transfer) model compound *p*-cyano-*N,N'*-tetramethylaniline (CDMA) (Lippert *et al* 1962; Grabowski *et al* 1979) (scheme 1) are described. Furthermore, solvent effects on the photophysics of the highly dipolar state are compared for both examples.

The understanding of the mechanisms of both PT and ET processes gives an insight into many elementary biological processes (Schuster *et al* 1977; Kosower and Huppert 1986). Most recently these mechanisms gained considerable attention in the technology of converting solar energy to electric energy or in storing solar energy (Vollmer and Rettig 1981).

## 2. Molecular mechanism of charge separation

In order to proceed with the treatment of solvent effects a simple model containing the essential physical processes should be developed. First we assume that both proton transfer in M2N and electron transfer in CDMA are characterized by an equilibrium occupation of two excited states. One is the initially excited state of the molecule (locally excited state LS) and the other is the charge separated state (CSS) emerging from LS by a PT or an ET process, respectively. In the CSS the positive and negative charges are localized on two different molecular subunits and this is characterized by a large dipole moment. Such a two-level model for the excited state reaction is shown in scheme 2. For both processes, mentioned above, the reaction coordinate corresponds to a well defined mode within the molecule and the reaction is supported by rearrangement of the solvent structure.

In the proton transfer reactions the proton is translocated along the hydrogen bond and this motion can be identified with the reaction coordinate, which includes also synchronous solvent relaxation (Köhler and Wolschann 1987). For TICT electron transfer is connected with a relative twist of donor and acceptor subunits about the aryl-amine single bond and therefore the distortion of the dihedral angle characterizes the essential reaction coordinate (Grabowski *et al* 1979). In contrast, there are, however, electron transfer reactions with insignificant changes of the molecular



**Scheme 2.** Model potential energy curves for excited state charge separation ( $G$  ground state,  $LS$  local excited state,  $CSS$  charge separated state).

skeleton and consequently, the structural change of the solvation shell is the only relaxation process (Heitele *et al* 1990).

The ground state potential curve shows a minimum corresponding to the most stable molecular conformation, which relates generally to the neutral form. Along the reaction coordinate the potential increases, and in the case of proton transfer charge separation might be represented by a shoulder or, in some systems, by a second minimum, corresponding to the ground state of the zwitterionic form (Rosetti *et al* 1980).

Absorption emanates generally from the minimum of the potential surface, and thus vertical excitation leads to a molecular excited state of the neutral donor or acceptor moiety respectively. Excited state PT or ET is then enabled by a considerably smaller free energy of reaction ( $\Delta G^*$ ) on the excited state surface compared to the ground state ( $\Delta G$ ). The reason for this emerges from changes in the charge density distribution within the molecule. For proton transfer acid and base properties of the functional groups of many aromatic systems change upon  $S_0 - S_1$  excitation. As an excellent example of this *o*-hydroxybenzoxazole should be mentioned, for which the  $pK$  of the phenolic oxygen decreases by  $-6$  and that of the acceptor nitrogen increases by about 5 units (Van der Donckt and Porter 1968; Mordzinski and Grabowska 1982). Thus in the excited state one can expect effective transition of the proton along the intramolecular hydrogen bond formed between both adjacent groups.

Another example is M2N (Köhler and Wolschann 1987). The  $pK$  of 2-naphthol was shown to decrease by approximately 7 units of excitation (Weller 1952), which enables PT from this center of increasing acidity to the amine moiety of the molecules. M2N resembles a rather exceptional case, as partial charge compensation by electronic redistribution is prevented by the methylene bridge connecting the donor and acceptor subunits. This contrasts with many other systems, where such rearrangement occurs to a

large extent, and in some cases tautomeric, neutral compounds are created (Karelson et al 1990).

The reason for both, the drastic changes of the  $pK$  values as well as for electronic rearrangement lies in a redistribution of charge, leading to an increase of negative charge density on the aromatic moiety (Barltrop and Coyle 1975). This effect accounts also for ET and CDMA. The resulting delocalization of the nitrogen lone pair electron increases also the conjugation between the aromatic  $\pi$  orbitals and the lone pair. Anilines become thus planar in the excited state, whereas they assume a pyramidal geometry in the ground state. Distortion of the dihedral angle of the amino group destroys this conjugation between both orbitals and in a perpendicular conformation their overlap vanishes and only full electron transfer can occur because of symmetry reasons. This reads to a charge separated state, the TICT state, which can become the lowest excited state, because of stabilization by a polar environment.

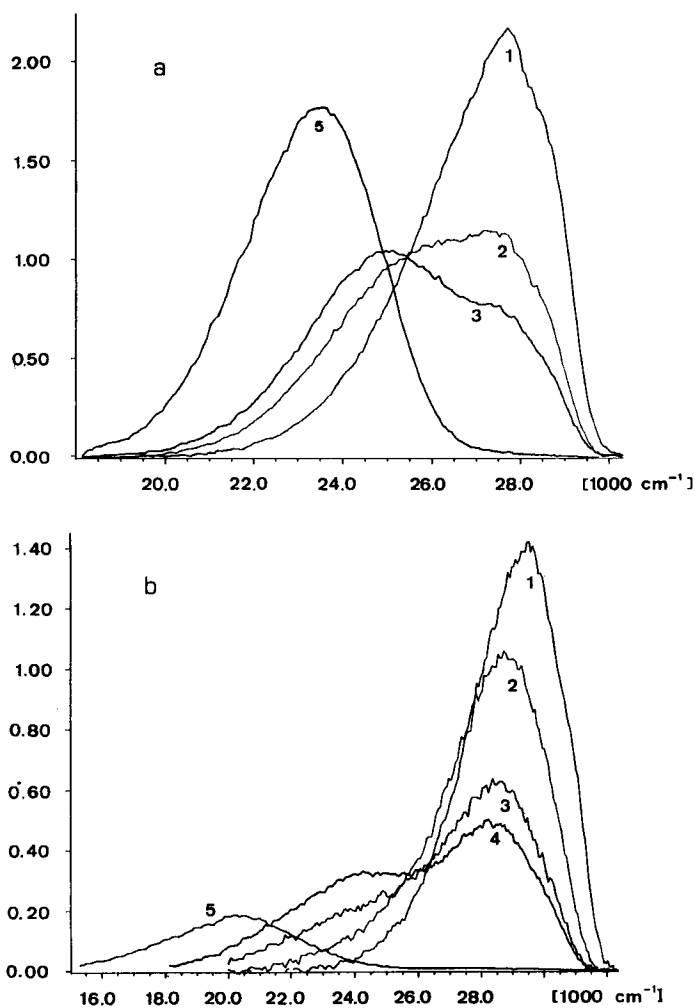


Figure 1. Fluorescence spectra of M2N (a) and CDMA (b) in *n*-hexane (1), dibutylether (2), diethylether (3), butyl chloride (4) and acetonitrile (5).

As a consequence for both examples concerned in this paper, i.e. PT in M2N and ET in CDMA, the existence of two distinct structural minima in the excited state is confirmed by the observation of dual fluorescence emission (see figure 1). The obtained spectra can be described by the superposition of two emissions bands, one emerging from the neutral, the other from the charge separated state. Equilibrium between both structures is established on a picosecond time scale and thus prior to fluorescence emission (Köhler and Wolschann 1987). This excited state equilibrium can be quantitatively described by an equilibrium constant obtained from the relative intensities of the two emissions (Köhler and Wolschann 1987).

In addition to these structural aspects, stabilization of the charged system by solvation is of basic importance. Increasing the solvent polarity causes stronger stabilization of the charge separated state than of the local state (LS). Therefore, the CSS should be preferentially occupied and this is reflected by important changes in the emission spectra (figure 1). The equilibrium constant is thus strongly solvent dependent.

### 3. Properties of equilibrated states

Excited state proton transfer equilibria of M2N were studied recently (Köhler and Wolschann 1987). Contrary to the fluorescence spectra, absorption spectra of M2N show only a slight solvent shift, e.g.  $\lambda_{\max} = 336$  nm in hexane and  $= 335$  nm in acetonitrile (figure 2).

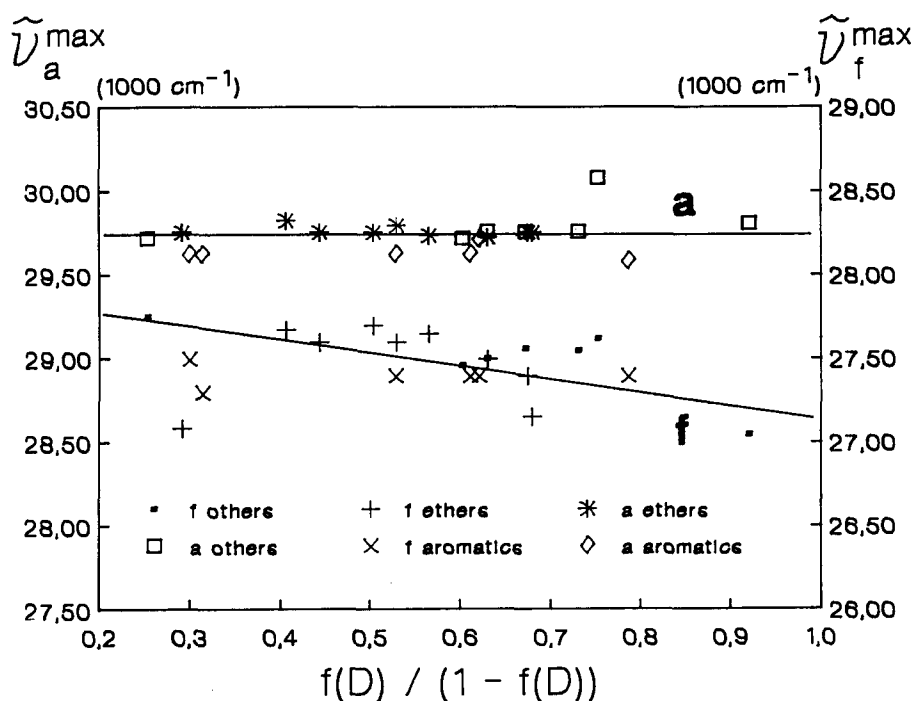


Figure 2. Solvent polarity dependence [ $f'(D) = (D-1)/(2D+1)$ ] of absorption and LS fluorescence maxima of M2N.

**Table 1.** Equilibrium constants  $K$  and fluorescence lifetimes for M2N and CDMA in some solvents of different polarities. For M2N also  $\bar{\nu}_F^{CSS}$ , the wavenumber of the maximum CSS fluorescence is given.

Solvent	$D$	$K$	M2N		CDMA	
			$\bar{\nu}_F^{CSS}(10^3 \text{ cm}^{-1})$	$\tau_F(\text{ns})$	$K$	$\tau_F(\text{ns})$
Hexane	2.02	0	—	5.46	0	3.32
Dibutylether	3.05	0.62	25.0	3.85		2.97
Diethylether	4.38	1.63	24.7	3.40		2.93
Butyl chloride	7.15	1.82	24.7	3.18	2.96 <sup>1</sup>	3.14
Acetonitrile	35.95	24.0	23.3	1.70		3.50

<sup>1</sup>Rotkiewicz and Köhler (1987)

A structureless fluorescence band is observed at 363 nm for M2N in hexane. Increasing the polarity of the solvent causes an increase of a low energy emission, concomitant to a decrease of the 363 nm band. The high energy band corresponds to the fluorescence of the neutral species, whereas that at low energy is attributed to the zwitterionic form. The spectral change represents the adjustment of a chemical equilibrium between both species in the excited state (Köhler and Wolschann 1987).

From these spectra equilibrium constants  $K$  may be calculated, performing a band shape analysis and assuming the radiative rate constants for both states to be nearly independent of solvent (see Köhler and Wolschann 1987). This was supported by measuring solvent dependence of quantum yields and lifetimes. Some data are tabulated in table 1. For such obtained  $K$  values a good correlation to the shift of the CS fluorescence maxima on variation of the solvent was found and this result was interpreted by a modified Förster cycle (Köhler and Wolschann 1987). This depicts the parallel dependence of both, the  $K$  values and the spectral properties, on the molecular environment. As, however, CSS fluorescence is to a CS ground state (correlating to the naphtholate anion), the strong solvent shift and this good correlation does not fully conform to similar dipole moments, expected for the ground and the excited CS state. From this only a small solvatochromic shift of the emission could be expected.

This contrasts partly to the mechanism proposed for TICT formation in CDMA. There are, likewise, two distinct emission bands observed in polar solvents, their distribution depending strongly on the polarity (see figure 1b). There were some attempts to determine equilibrium constants  $K$ , but the assumptions used in the estimation, e.g. that TICT natural lifetimes are constant on variation of the solvent, might not be sufficiently fulfilled (Rotkiewicz and Köhler 1987; Nag *et al* 1989).  $K$  values should be approximately in the same order of magnitude compared to M2N as LS fluorescence quenching is comparable for both solutes in identical solvents. This is in contrast to the large shift of the TICT band from which a high dipole moment was obtained (Suppan 1985; Brittinger *et al* 1990). There is only one ground state surface for CDMA and thus the ground state dipole moment varies only slightly as the amino group is twisted.

In table 1 M2N fluorescence lifetime data in some solvents are compiled. No second lifetime or a risetime was found for this system, which is longer than 100 ps (Köhler and Wolschann 1987). The relaxation time for establishing the equilibrium is thus

much faster than the fluorescence decay. Most importantly, on increasing the polarity of the solvent, the lifetime does not vary uniformly but passes a minimum at intermediate  $K$  values.

This behaviour can be compared to similar data obtained in various binary solvent mixtures (Köhler and Rotkiewicz 1986; Rotkiewicz and Köhler 1987). From these data the conclusion was drawn, that the non-radiative decay rate passes a maximum when the L and CS states are nearly equally populated. Similar conclusions were drawn from studies in isoviscous solvents of different polarity (Nag *et al* 1989).

It is worthwhile to compare these results to electron transfer in CDMA and related compounds. Also in this case a minimum in  $\tau_F$  is found near to  $K \simeq 1$ , but less pronounced (table 1). Studies of CDMA and N,N,*o*,*o'*-tetramethyl-*p*-cyanoaniline in some solvent mixtures led to the same conclusion of a maximum non-radiative decay rate, similar to M2N.

#### 4. Continuum model for solvent effects

A quantitative understanding of solvent dependent excited state charge separation can be achieved by a physical model of the dependence of the excited state free energy function on solvent properties. Variations of state energies with solvent parameters are accounted for by calculating the total energy of the system consisting of the molecule and its environment. This energy might be differently solvent dependent in ground and excited states and, therefore, spectral shifts as well as shifts in chemical equilibrium may be observed upon excitation.

The interaction energy of the solute with its environment is determined by (1) dispersive forces, (2) classical electrostatic interactions and (3) by specific local interactions like hydrogen bonding etc. As local interactions depend specifically on molecular properties they should not be included in a general study. So we concentrate here on long range non-specific interactions of type 1 and 2. Electrostatic interactions can be described by a model, treating the medium outside of some cavity around the reacting molecule as a dielectric continuum. Such approaches are widely used to make detailed comparisons with experiments. The dielectric continuum is hereby characterized by the dielectric constant ( $D$ ) and the refractive index ( $n$ ), interpolated to frequency zero (Böttcher 1952). Such an approximation is justified so far as there is no essential overlap between the electron densities of the considered solute and the surrounding molecules. As we exclude strong interactions explicitly, this condition is sufficiently fulfilled for organic compounds in organic solvents. There are several classical as well as quantum mechanical models, describing energy changes by dispersive and electrostatic forces, reviewed extensively recently (Nicol 1974; Suppan 1990). Following mainly the work of Liptay (1965), the main assumptions appearing in such a treatment are summarized below:

(1) The free molecule has an energy  $E_g$  and  $E_e$ , a permanent dipole moment  $\mu_g$  and  $\mu_e$ , and a polarizability  $\alpha_g$  and  $\alpha_e$  for ground and excited states respectively. The following notations are used for the different states relevant in this model:  $g$  is the index for the relaxed ground state,  $fe$  for the respective Franck–Condon excited state,  $e$  for the relaxed local excited state (LS) and  $fg$  for the respective Franck–Condon ground state. For the charge separated relaxed excited state the index  $s$  is used and  $fs$  for the respective Franck–Condon ground state.

(2) The energy needed to form a cavity in the solvent,  $E^c$ , is accepted to be equal for all states considered, as the molecular volume is assumed not to change upon excitation and charge or proton transfer.  $E^c$  is thus omitted from the further treatment.

(3) When the molecule is introduced into the cavity, the energy of the system is reduced by dispersive forces between solute and solvent, which are generally negligible for polar solutes when compared to electrostatic interactions between the permanent dipoles  $\mu_g$  and  $\mu_e$  with the polarized surrounding dielectricum.

(4) The polarization of the medium results in a reaction field  $F_g^R$  on the place of the molecule, given by:

$$\mathbf{F}_g^R = f(D) \cdot \boldsymbol{\mu}'_g,$$

$$\boldsymbol{\mu}'_g = \boldsymbol{\mu}_g + \alpha_g \cdot \mathbf{F}_g^R.$$

$\boldsymbol{\mu}'_g$  represents the sum of the permanent molecular dipole moment and the moment induced in the molecule by the reaction field. For other states than the ground state the index  $g$  has to be replaced by the respective state index.

$f(D)$  is the Onsager polarity function, which depends on the shape of the cavity and the charge distribution in the molecule. For a spherical cavity (radius  $a$ ) and a point dipole in the center  $f(D)$  appears as (Bottcher 1952)

$$f(D) = \frac{2}{a^3} \cdot \frac{(D-1)}{(2D+1)}.$$

The reaction field is divided into two contributions, one arising from the orientational polarization of the medium  $\mathbf{F}_g^{R^o}$  and a second resulting from the electronic polarization  $\mathbf{F}_g^{R^e}$ . The latter is given by:

$$\mathbf{F}_g^{R^e} = f(n^2) \cdot \boldsymbol{\mu}'_g = \frac{f(n^2)}{(1 - \alpha_g \cdot f(D))} \cdot \boldsymbol{\mu}_g.$$

$f(n^2)$  is obtained from  $f(D)$  replacing  $D$  by  $n^2$ ) and  $\mathbf{F}_g^{R^o}$  is obtained from:

$$\mathbf{F}_g^{R^o} = \mathbf{F}_g^R - \mathbf{F}_g^{R^e} = \frac{(f(D) - f(n^2))}{(1 - \alpha_g \cdot f(D))} \cdot \boldsymbol{\mu}_g.$$

Partitioning of the reaction field is important as in the vertical transition nuclear rearrangement is prevented by the Franck–Condon principle and thus  $\mathbf{F}_g^{R^o}$  is the same for ground and vertical excited states. From this the interaction energy  $F_g^i$  of the reaction field with the permanent and induced dipole moments is obtained:

$$F_g^i = -\boldsymbol{\mu}_g \cdot \mathbf{F}_g^R - \frac{1}{2} \cdot \alpha_g \cdot (\mathbf{F}_g^R)^2.$$

The factor 1/2 for the energy of induced dipoles stems from the work needed in moving apart the positive and negative charge in the molecule against mutual attractive forces. The work reduces the energy, which is obtained by introducing the induced dipole into the reaction field.

For the Franck–Condon excited state the interaction energy becomes

$$F_{fe}^i = -\boldsymbol{\mu}_e \cdot (\mathbf{F}_e^{R^e} + \mathbf{F}_g^{R^o}) - \frac{1}{2} \cdot \alpha_e \cdot (\mathbf{F}_e^{R^e} + \mathbf{F}_g^{R^o})^2,$$



(5) For the polarization of the medium an energy  $P_g(P_e$  or  $P_s)$  is needed. This energy  $P$  can likewise be partitioned into two terms,  $P = p^o + p^e$ , one arising from electronic polarization ( $p^e$ ) and the other from orientational polarization ( $p^o$ ). These quantities are given for spherical cavities around a point dipole in the center by (Böttcher 1952)

$$p_g^o = \frac{1}{2} \cdot \mu'_g \cdot \mathbf{F}_g^{R^o}, \quad p_g^e = \frac{1}{2} \cdot \mu'_g \cdot \mathbf{F}_g^{R^e}.$$

$P$  depends strongly on the shape of the cavity and the charge distribution within. The energy  $p_g^o$  is the same in the ground and Franck–Condon excited states, but the energy arising from electron polarization becomes:

$$p_{fe}^e = \frac{1}{2} \cdot \mu'_g \cdot \mathbf{F}_{fe}^{R^e}.$$

(6) From the treatment given above the dependence of the energies of the various states on  $D$  and  $n^2$  can be calculated. As examples the energy of the ground state becomes:

$$F_g = E_g + F_g^i + P_g,$$

and for the Franck–Condon excited state:

$$F_{fe} = E_e + F_{fe}^i + p_g^o + p_{fe}^e.$$

The shift of absorption with variation of solvent is then given by

$$hc\Delta\nu_a = (F_{fe} - E_e) - (F_g - E_g) = (F_{fe}^i - F_g^i) + (p_{fe}^e - p_g^e).$$

To obtain a practical formula an approximation for the excited state polarizability must be introduced. Generally  $\alpha_e$  is taken as equal to  $\alpha_g$ , i.e.:  $\alpha_e = \alpha_g = \alpha$ . It was argued (Bilot and Kowski 1962) that a good approximation for  $\alpha$  would be:  $\alpha \simeq a^3/2$ , and this was used below.

From this the following equations are obtained (Liptay 1965).

$$hc\Delta\nu_a = -\mu_g \cdot (\mu_e - \mu_g) \cdot \frac{f(D)}{1 - \alpha \cdot f(D)} - \frac{1}{2} \cdot (\mu_e - \mu_g)^2 \cdot \frac{f(n^2)}{1 - \alpha \cdot f(n^2)}, \quad (1)$$

and for the fluorescence emission

$$hc\Delta\nu_e = -\mu_e \cdot (\mu_e - \mu_g) \cdot \frac{f(D)}{1 - \alpha \cdot f(D)} + \frac{1}{2} \cdot (\mu_e - \mu_g)^2 \cdot \frac{f(n^2)}{1 - \alpha \cdot f(n^2)}. \quad (2)$$

Subtracting (2) from (1), one obtains for the Stokes' shift

$$hc(\Delta\nu_e - \Delta\nu_a) = (\mu_e - \mu_g)^2 \cdot \left( \frac{f(D)}{1 - \alpha \cdot f(D)} - \frac{f(n^2)}{1 - \alpha \cdot f(n^2)} \right). \quad (3)$$

In figure 2 absorption and LS fluorescence maxima are plotted for exemplary versus the modified Onsager polarity function. As  $f(n^2)$  is much less solvent dependent than  $f(D)$ , the first terms in (1) and (2) are essential in describing solvent effects in polar solvents. Solvent effect on the absorption is small, as  $\tilde{\nu}_a^{\max}$  stays nearly constant. On the other side  $\tilde{\nu}_{LS}^{\max}$  decreases considerably with increasing  $D$  and consequently the

Stokes' shift increases. According to (1) and (2) this behaviour can be interpreted by the assumption, that  $\mu_e$  and  $\mu_g$  are not parallel and the difference vector  $\mu_e - \mu_g$  is nearly orthogonal to  $\mu_g$ . In this case solvent shifts of the absorption becomes minimal, but not shifts of the fluorescence. In the ground state  $\mu_g$  should be approximately parallel to the naphthol OH-bond. On excitation the negative charge is delocalized on the aromatic moiety and the positive charge on the naphtholic hydrogen increases. Consequently the dipole moment should change its direction upon excitation as was concluded above.

Applying (3), the value of  $|\mu_e - \mu_g|$  can be obtained from a plot of the Stokes' shift versus the polarity function according to (3). Using  $2 \cdot \alpha/a^3 = 1$  and  $a = 5 \text{ \AA}$ ,  $|\mu_e - \mu_g| = 10 \cdot 10^{-30} \text{ Cm}$  results.  $\mu_g = 6 \cdot 10^{-30} \text{ Cm}$  was obtained for 2-naphthol recently (Bilot and Kawski 1962), which should not differ greatly for M2N. Thus the molecular dipole moment increases slightly upon excitation and accounting for a right angle between  $\mu_g$  and  $\mu_e - \mu_g$ ,  $\mu_e = 12 \cdot 10^{-30} \text{ Cm}$  is obtained. The angle between the dipole moments in ground and excited states is then approximately  $60^\circ$ . As CDMA belongs approximately to  $C_{2v}$  symmetry, the direction of the dipole moment should not change significantly, and this causes the solvent dependence of both, absorption and fluorescence (Suppan 1985; Brittinger *et al* 1990).

For CSS only emission data are available, as for the proton transferred ground state no absorption was detected (Köhler and Wolschann 1987). From solvent effects only data on the product  $\mu_s \cdot (\mu_s - \mu_{gs})$  are, therefore, available, a term in which three unknown parameters, the values of both dipole moments and the angle between them, are included. This is different from CDMA, where there is only one ground state, and thus  $\mu_{gs}$  is generally taken equal to  $\mu_g$ . From a plot of the shift of M2N long wavelength emission maxima versus the polarity function (according to (2))  $\mu_s \cdot (\mu_s - \mu_{gs}) = 3,3 \cdot 10^{-58} \text{ C}^2 \text{ m}^2$  is obtained.

The charge-separated ground state of M2N results from a proton translocation by approximately  $0.7 \text{ \AA}$  from the naphtholate OH-group towards the amine (Köhler and Wolschann 1992). Positive charge is then localized on the protonated amine, the negative charge primarily on the oxygen but partly delocalized to the adjoining aromate. As the delocalization of the negative charge should increase after excitation, a rotation of the dipole moment should result, as was already discussed for the neutral species. The value of  $\mu_s$  does, most likely, not increase dramatically.

From a mathematical fit of the measured emission maxima of CS fluorescence for 22 solvents to the polarity function according to (2) both factors including the dipole moments can be obtained. The following values result:  $\mu_s \cdot (\mu_s - \mu_{gs}) = 4 \cdot 10^{-58} \text{ C}^2 \text{ m}^2$  and  $(\mu_s - \mu_{gs})^2 = 6 \cdot 10^{-58} \text{ C}^2 \text{ m}^2$ . Taking  $\mu_{gs} = 2 \cdot 10^{-29} \text{ Cm}$  for the ground state, as was obtained by semiempirical calculations (Köhler and Wolschann 1992),  $\mu_s \cdot \cos \varphi$  becomes equal to  $1,3 \cdot 10^{-18} \text{ Cm}$ .  $\varphi$  is the angle between  $\mu_s$  and  $\mu_{gs}$  and is  $\simeq 50^\circ$  for  $|\mu_s| \simeq |\mu_{gs}|$ . This gives good evidence that the predominant term for the solvatochromic shift of CSS fluorescence is a change in the dipole moment direction, but not a large increase of its value. The latter reason accounts, however, for solvent shifts of TICT fluorescence.

The main promoting force for excited state proton transfer results from a strong decrease of the free energy for this reaction on the excited state surface. In nonpolar solvents the total energy of the CS state is still above that of the local excited state. On increasing the polarity of the environment, the CS state is stabilized much more than the local state, due to its larger dipole moment and the equilibrium is shifted in favour of a population of the CS state. Contrary to CDMA and related compounds, not an increasing dipole moment but a rotation of its direction is responsible for solvent

shifts. The shift originates thus from the non-alignment of the dipole moment and the reaction field vector in a Franck–Condon excited state.

There is, however, no clear cut correlation of the relative intensities of the fluorescence originating from LS and CSS to the solvent polarity functions. Solvent polarity effects on the spectra of M2N and CDMA are of the same order of magnitude, although the change of the dipole moment, caused by charge transfer is much larger for CDMA (Suppan 1985; Brittinger *et al* 1990). These results might be explained by a solvent dependence of the radiative and nonradiative rate constants, which determines fluorescence intensities.

## 5. Experimental

Experimental details were described previously (Köhler and Rotkiewicz 1986; Köhler and Wolschann 1987). The solvents used were of best available quality and further purified by standard methods. The following solvents were used: *n*-hexane, diethylether, diisopropylether, dipropylether, butylmethylether, dibutylether, tetrahydrofuran, dimethoxyethane, tetrahydropyran, dioxane, ethyl acetate, butyl acetate, butyl chloride, 1,2-dichloroethane, dichloromethane, acetonitrile, propylene carbonate, benzene, toluene, anisole, fluorobenzene, chlorobenzene and pyridine. Values for the dielectric constant *D* and the refractive index *n* were taken from Weast (1981).

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