

Solvatochromism of β -Naphthol

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Excitation and emission fluorescence spectra of 2-naphthol and 2-methoxynaphthalene were measured in a series of pure solvents. The spectral shifts are correlated by the Kamlet–Taft parameters (π^* , β , and α). As judged from the π^* dependence, both molecules have a negligibly small dipole moment in their ground electronic state, which increases in the excited (S_1) state. However, the majority of the Stokes shift is due to hydrogen-bonding rather than to dipole–dipole interactions. By comparing the shifts for the two compounds, it is demonstrated that the β dependence in 2-naphthol is due exclusively to a hydrogen bond donated from its hydroxylic hydrogen atom to the solvent. This bond becomes stronger upon excitation and hence produces a bathochromic shift. We find α dependence only in the excitation spectrum, indicating that protic solvents stabilize the ground state by donating a hydrogen bond to the hydroxylic oxygen. This bond breaks following excitation to S_1 but re-forms following proton transfer.

1. Introduction

Proton-transfer reactions are a common example of acid–base reactions, one of the most fundamental processes in chemistry and biology. Proton transfer to the solvent (PTTS) is an important class of such reactions. Hydroxyarene molecules (ROH), such as 1-naphthol (1OH) and 2-naphthol (2OH), become strong acids in their first electronically excited state (S_1). Thus light serves as an ultrafast trigger for PTTS. The subject of photoacids was initiated by Förster,¹ who explained the observations of Weber² on the strong pH dependence of the emission spectrum of 1-naphthylamine-4-sulfonate. Weller^{3,4} continued and extended the previous studies and laid the fundamentals of excited-state proton-transfer reactions. The field has been reviewed in refs 3, and 5–9.

Early experiments centered on steady-state absorption and fluorescence measurements.^{3,4,10–13} By use of the Förster cycle, these spectroscopic data successfully predicted the excited-state acidity constant

$$pK_a^* = pK_a + (E_{RO^-} - E_{ROH})/2.3RT \quad (1)$$

from the ground-state pK_a value and the excited-state energy difference, $E_{RO^-} - E_{ROH}$, between the unprotonated and protonated forms of the photoacid. Hence the more blue-shifted (red-shifted) the acid (anion) fluorescence, the stronger the excited-state acidity. For 2OH, such estimates give $pK_a^* \approx 2.8$, lower by nearly 7 pK units as compared with the ground state, $pK_a = 9.5$. These conclusions were later confirmed by numerous time-resolved measurements.^{14–18} In view of the clear relationship between the pK_a changes and absorption and

emission spectra, a study of substituent and solvent effects upon such spectra has direct bearing upon the field of acid–base properties in the excited state.

With a few exceptions,^{4,11,19} not much attention has been paid to the quantitative investigation of the solvatochromism of hydroxyaromatic compounds in neat solvents. It is commonly acknowledged that solvent-dependent spectral shifts can arise from either general or specific solvent effects.²⁰ The first effect results from interactions of the dipole moment of the fluorophore with the reactive field induced in the surrounding solvent. Specific effects result from the short-range interactions between the fluorophore with one or more solvent molecules in its first solvation shell, an important example being the hydrogen bond (HB).²¹ It is thus of interest to quantify the relative contribution from these two effects.

The Stokes shift of the “ideal” chromophore is supposedly determined only by nonspecific solvation.^{22,23} HBs are known to lead to deviations from ideal polarity correlations.^{24,25} Excited-state PTTS is often used as a probe of the microenvironment surrounding the chromophore.^{26,27} More often the reactivity of the naphthol, rather than its solvatochromism, is utilized.^{28–30} In the cases where its spectral shifts were used as microenvironment probes, they were supposed to reflect mainly polarity effects.^{31,32}

On the other hand, the formation of bimolecular HBed complexes between naphthols and various proton acceptors in nonpolar solvents is well documented.^{4,6,10,13,33–35} In the presence of ethers and esters, both absorption and emission bands of naphthols shift to the red.¹⁰ Addition of amines to solutions of naphthols in low-polarity solvents leads to the appearance of a new, low-energy fluorescence band.^{4,34,35} A similar band appears also for intramolecular proton transfer between the hydroxyl and amine substituents of aminoalkyl-naphthol.³⁶ It was suggested that excited-state proton transfer

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TABLE 1: Excitation and Emission Frequencies of β -Naphthol and Its Methoxy Derivative in Different Solvents, and Some Characteristic Solvent Parameters

	solvent ^a	Kamlet–Taft parameters			$\Delta G_s(\text{H}^+)^d$ (kJ/mol)	ν , excitation ^e		ν , emission ^f	
		$\pi^*{}^b$	β^c	α^c		2OH	2OMe	2OH	2OMe
1	hexane	-0.11	0	0		30.28	30.38	29.24	29.09
2	c-hexane	0	0	0		30.27	30.34	29.12	28.90
3	Et ₂ O	0.24	0.47	0		29.94	30.34	28.80	28.88
4	EtOAc	0.45	0.45	0		30.01	30.38	28.60	28.80
5	EtOH	0.54	0.77	0.83	11	30.03	30.36		
6	MeOH	0.60	0.62	0.93	10	30.12	30.38	28.47	28.84
7	ACN	0.66	0.31	0.19	46	30.08	30.36	28.69	28.70
8	CH ₂ Cl ₂	0.73	0	0.3		30.23	30.28	28.92	28.72
9	C ₂ H ₄ Cl ₂	0.73	0	0	2 ^h			28.82	28.73
10	TFE	0.73	0	1.51		30.53	30.64	28.84	28.83
11	DMFA	0.88	0.69	0	-18	29.83	30.27	28.17	28.58
12	DMSO	1	0.76	0	-19	29.74	30.23	28.06	28.57
13	“water”	1.09	0.4 ^g	1.17	0.0	30.41	30.53	28.49	28.73

^a Acronyms: diethyl ether (Et₂O), ethyl acetate (EtOAc), ethanol (EtOH), methanol (MeOH), acetonitrile (ACN), trifluoroethanol (TFE), dimethylformamide (DMFA), and dimethyl sulfoxide (DMSO); “water” is 0.1 M HCl. ^b From ref 41. ^c From ref 40. ^d Proton free energy of transfer, from ref 62. ^e Frequency of the red edge excitation peak (0.2 nm resolution), in 1000 cm⁻¹. ^f Peak frequency of the emission spectrum, in 1000 cm⁻¹, as obtained from a fit to the log-normal distribution (ref 46). ^g From ref 39. ^h Inaccurate value.

to the more basic amines takes place, but the low dielectric constant of the solvent prevents the contact ion pair from separating. Recently, spectral information on HBed complexes of various molecules with 2OH in the gas phase has been collected,^{37,38} and it can be compared with the solution-phase data.

To differentiate between the two effects, quantitative measures for polarity and HBed should be used. Several solvent polarity scales exist.³⁹ The more fundamental approaches, such as that of Lippert and Mataga,³³ define a polarity function using the solvent dielectric constant (ϵ) and refractive index (n). Unfortunately, these do not measure specific solvent–solute interactions such as HBed. We have chosen the empirical solvatochromic scale of Kamlet and Taft.^{40,41} This scale seems to be well tested and provides explicit measures for dipolarity interactions (π^*) and of the HB accepting (β) and donating (α) power of the solvent. Other empirical scales exist, and these have been applied in a recent study of the solvatochromism of 8-hydroxy-1,3,6-pyrenetrisulfonate.⁴²

In the present work, we will attempt to analyze quantitatively the nature of solvatochromism of 2OH and 2-methoxynaphthalene (2OMe), focusing on the separation of general and specific solvent effects. A somewhat surprising finding from the present work is that the solvatochromism of 2OH [and also of 5-cyano-2-naphthol (5CN2OH)]⁴³ is dominated by HBed rather than polarity effects. A comparative study of 2OH and 2OMe fluorescence allows us to identify HBed to the hydroxyl hydrogen. The formation and breaking of HBs are probably the preliminary steps in excited-state proton transfer. Hence the information obtained by the solvatochromic analysis of absorption and fluorescence spectra can be used to establish the reactivity of naphthols.

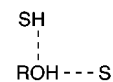
2. Experimental Section

2OH and its methoxy derivative, 2OMe, were purchased from Merck and used without further purification. Solvents were analytical grade and did not contain fluorescent impurities. Sample concentrations were adjusted to optical densities of 0.05–0.1 at the excitation wavelength. Fluorescence spectra of nondeoxygenated, 2OH and 2OMe solutions were recorded on a SLM-Aminco Bowman 2 luminescence spectrometer and corrected according to manufacturer specifications. All experiments were performed at room temperature (ca. 22 °C). Excitation spectra were independent of the emission wavelength and roughly the same as the absorption spectra in the $S_0 \rightarrow S_1$

spectral region. They were collected at an emission wavelength 10 nm to the red of the excitation red edge, with 0.2 nm resolution. Likewise, emission spectra were independent of the excitation wavelength. They were collected following excitation at 290 nm, corresponding to the $S_0 \rightarrow S_2$ transition, chosen (to avoid scattering) outside the spectral window in which the emission was monitored. The fluorescence spectra of 2OH in water were measured in 0.1 M hydrochloric acid, to suppress its protolytic dissociation. We have checked that only the intensity of the R*O⁻ band depends on acid concentration, but not the frequency of the R*OH band. To allow comparison with other work reporting peak wavelengths, fluorescence spectra as a function of λ (in nanometers) were converted to wavenumber, ν (in reciprocal centimeters), without applying any ν^n correction.

3. Basic Assumptions

We wish to understand the solvent effects on the excitation and emission frequencies and, in particular, differentiate between polarity and HBed effects. The latter may involve the bonds to the hydroxyl group



where S and SH stand for general and protic solvents, respectively. Thus an additional goal is to distinguish the individual contributions from these two HBs. To quantify these solvent properties, we will use the empirical Kamlet–Taft parameters,^{40,41} π^* , α , and β , which are collected in Table 1. The π^* parameter is a measure of solvent polarity/polarizability effects, whereas the “acidity” and “basicity” parameters, α and β , measure its HB donating and accepting properties, respectively. In the most general case, the spectral shift is correlated with these parameters by

$$\nu(2\text{OH}) = \nu_0 + p\pi^* + b\beta + a\alpha \quad (2)$$

The coefficients p , b , and a are interpreted as *solute* properties. p is related to the solute dipole moment; b measures its propensity to *donate* a HB to the solvent; a describes its tendency to *accept* a HB from the solvent. The challenge is to relate the values of these parameters to microscopic interactions, such as specific HBs.

To achieve this goal, we set out to compare 2OH with its methoxy analogue, 2OMe. The difference between them is, evidently, in the replacement of the hydroxyl hydrogen by a methyl group. If only the OH group contributes to b , we expect $b = 0$ for 2OMe; namely

$$\nu(2\text{OMe}) = \nu_0 + p\pi^* + a\alpha \quad (3)$$

Thus in nonprotic or other solvents with $\alpha = 0$, the methoxy shifts are governed exclusively by polarity effects.

If the substitution on the oxygen does not affect drastically the electron density on the naphthalenic ring, the dipole moments of the two compounds should be similar. Literature values are 1.28 and 1.54 D for the ground state of 2OMe and 2OH, respectively (Table 43 of ref 44). These increase about 0.5 D for the excited states (Table 8.1 of ref 33). Thus p should be similar for 2OH and 2OMe (perhaps slightly smaller for the latter). If, in addition, their a parameters are similar, the excess shift, $\Delta\nu \equiv \nu(2\text{OMe}) - \nu(2\text{OH})$, would be a function of β alone:

$$\Delta\nu = \Delta\nu_0 - b\beta \quad (4)$$

(Normally, we might expect also $\Delta\nu_0 = 0$.) Otherwise the equation holds only for solvents with $\alpha = 0$.

The above assumptions will be tested by the solvatochromic shifts of the two compounds. A similar value of p from both eqs 2 and 3 will indicate that 2OMe is indeed a good model compound for the polarity effects on 2OH. More important, if $\nu(2\text{OMe})$ proves to be independent of β , whereas eqs 2 and 4 produce a similar value of b , we might conclude that the effect of β arises exclusively from the ROH \cdots S bond donated from the hydroxyl group to the solvent, S.

4. Photoacid Excitation Spectra

Figure 1 shows the excitation spectra, in the $S_0 \rightarrow S_1$ transition region, of 2OMe and 2OH in 12 different solvents. The frequencies, ν , of the red-edge maxima in all solvents are collected in Table 1, which also defines the acronyms for the various solvents. First we note that, for solvents with $\alpha = 0$, the 2OMe spectra are nearly solvent-independent. Figure 2a depicts their peak frequencies as circles. The line is a fit to eq 3, with $\nu_0 = 30\,370\text{ cm}^{-1}$ and $p = -100\text{ cm}^{-1}$ (and $a = 0$). The correlation coefficient is $r = 0.77$. Therefore the ground-state dipole moment must be very small. (We wonder whether the value of 1.28 D for the dipole moment of ground-state 2OMe, Table 43 in ref 44, is not an overestimation.) The squares designate the frequencies in protic solvents. TFE and water, with the largest α values, show a pronounced blue shift. A two-parameter regression, eq 3, of *all* the data in Figure 2a gives $\nu_0 = 30\,350\text{ cm}^{-1}$, $p = -90\text{ cm}^{-1}$, and $a = 190\text{ cm}^{-1}$ (see Table 2). The correlation coefficient is $r = 0.86$. Hence, in ground-state 2OMe, a HB is donated by the protic solvent, SH, to the hydroxylic oxygen. This bond is stronger in the *ground state*, where the charge on the oxygen is more negative than in the excited state; hence the blue shift ($a > 0$).

Consider next the 2OH frequencies, summarized in Table 1 in order of increasing π^* . In Figure 1, the excess red-shift of 2OH (bold lines) as compared with 2OMe (dashed lines) increases along the columns, which are ordered by increasing β . Figure 2b further quantifies this correlation. It shows $\Delta\nu \equiv \nu(2\text{OMe}) - \nu(2\text{OH})$ as a function of β . The numbers identifying the solvents follow the polarity order of Table 1. It is thus clear that the shifts are *not* ordered by polarity. For example, the polar haloaliphatics (solvents 8–10) produce no shift. For nonprotic solvents (circles), we find a very good

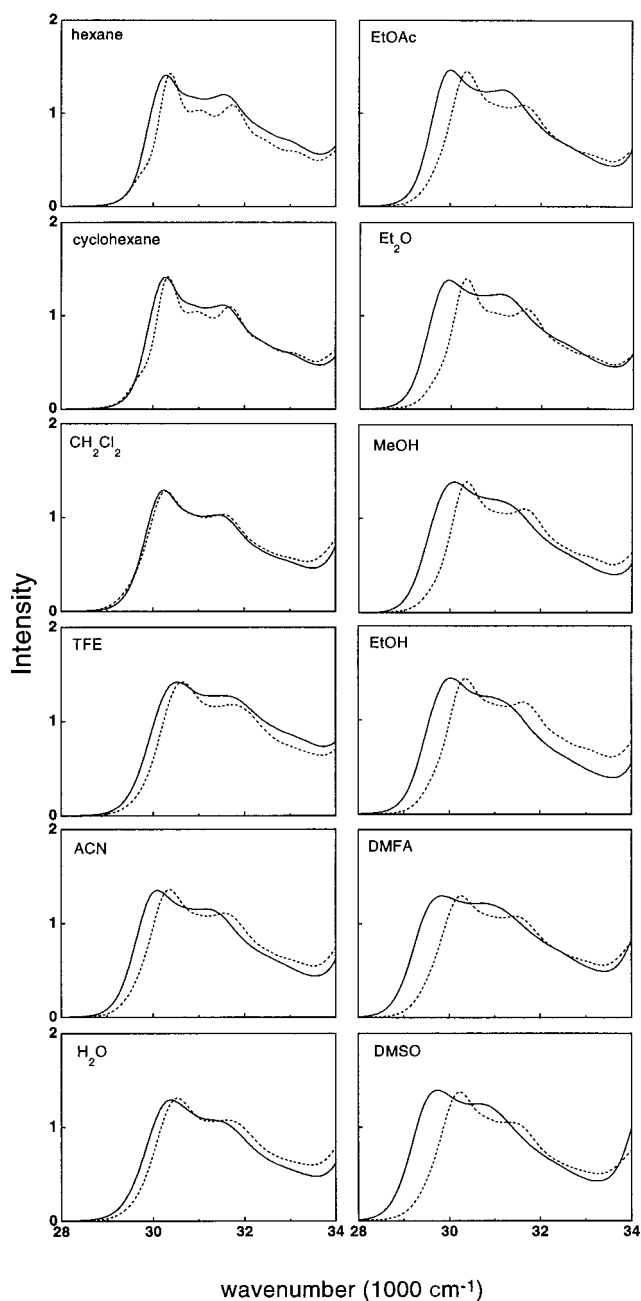


Figure 1. Fluorescence excitation spectra of 2-naphthol (bold lines) and 2-methoxynaphthalene (dashed lines) in the indicated solvents. The columns are ordered by increasing β .

correlation with the solvent HBing *accepting* power, β . A fit to eq 4 gives $\Delta\nu_0 = 90\text{ cm}^{-1}$, $b = -550\text{ cm}^{-1}$ (see Table 2), and $r = 0.985$. The protic solvents (squares) are, again, blue shifted from the correlation line. This indicates that the a parameter is somewhat larger for 2OH than for 2OMe.

A three parameter regression of $\nu(2\text{OH})$ to eq 2 gives $\nu_0 = 30\,240\text{ cm}^{-1}$, $p = -70\text{ cm}^{-1}$, $b = -510\text{ cm}^{-1}$, and $a = 270\text{ cm}^{-1}$, with $r = 0.975$. Comparison of the a values obtained for 2OMe and 2OH (Table 2) indicates that the latter is indeed somewhat larger, as suggested by the deviations of the protic solvents from the correlation line in Figure 2b. This may (or may not) reflect cooperativity of HBs,⁴⁵ which can occur in 2OH but not in 2OMe. The agreement between the values of b found by the two procedures confirms the assignment of the β effect to the ROH \cdots S bond, which is the most pronounced interaction for ground-state 2OH.

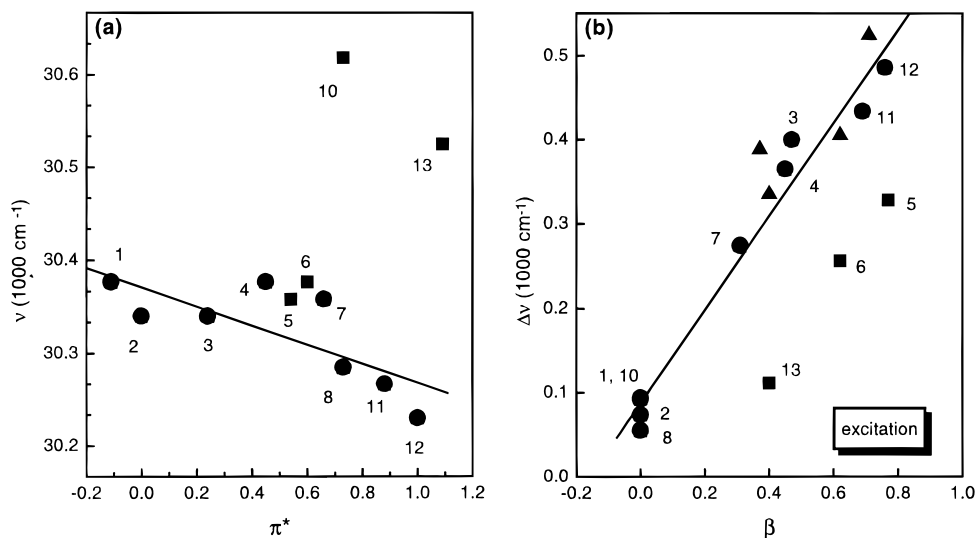


Figure 2. Solvatochromism of the red-edge excitation spectra: (a) 2OMe frequencies and (b) frequency difference between 2OMe and 2OH for the solvents of Table 1. Squares represent protic solvents. Line is a linear fit to the circles; see text and Table 2. Triangles in panel b are from excitation spectra of gas-phase complexes between *cis*-2OH with dioxane, water, methanol, and triethylamine.³⁷

TABLE 2: Comparison of the Kamlet–Taft Coefficients for Two Dye Molecules^a

molecule	S_0			S_1		
	$-p$ (cm^{-1})	$-b$ (cm^{-1})	a (cm^{-1})	$-p$ (cm^{-1})	$-b$ (cm^{-1})	a (cm^{-1})
2OH	70	510	270	450	800	0
	90	550	190	350	850	0
5CN2OH	50	650	170	1600	1950	0
	170	590	210	1600	1820	0

^a 2OH = 2-naphthol; 5CN2OH = 5-cyano-2-naphthol. Upper entries: three-parameter regression, eq 2. Lower entries: Using the corresponding methoxy derivative as a reference; p and a characterize the methoxy shifts, whereas b is from the difference, eq 4.

TABLE 3: Qualitative Summary of the Different Types of Hydrogen Bonds

bond	type	strength	stronger in ^a	shift ^b
ROH \cdots S	β	strong	ES	red
H ₂ OH ⁺ \cdots S	β	very strong		
RHO \cdots HS	α	weak	GS	blue
RO ⁻ \cdots HS	α	very strong	GS	blue

^a ES = excited state; GS = ground state. ^b Induced by increasing HB strength.

It is interesting to compare the shifts observed in solution with those found in gas-phase complexes. Fluorescence excitation spectra of 2OH have been measured in supersonic jets, where ROH \cdots S complexes were observed.³⁷ The spectral shifts due to HBing between *cis*-2OH and water, dioxane, methanol, and triethylamine (Table 3, ref 37) are shown in Figure 2b as triangles. (2OH \cdots NH₃ gives a similar shift to 2OH \cdots triethylamine,³⁸ but the value of β for ammonia is unknown to us.) It is remarkable that the gas-phase data fall on the liquid-phase correlation line. Assuming this is not a coincidence, it supports our conclusion that the β -dependent shift is due to one specific HB. The 1:1 complexes with protic solvent molecules do not deviate from the line as our solution-phase data do, because the additional bond to the oxygen does not exist there.

5. Photoacid Emission Spectra

A more extensive analysis is possible for the emission spectra. Figure 3 compares the emission spectra of the two compounds

in 10 of the solvents. Spectra in three additional solvents (cyclohexane, ethanol, and dichloroethane) are very similar to those in solvents already in the figure (hexane, methanol, and methylene chloride, respectively) and are hence not displayed. The 2OH and 2OMe spectra (bold and dashed lines, respectively) were fitted to a log-normal distribution (dashed–dotted lines).⁴⁶ This serves to average over vibrational structure and produce unbiased estimates for peak frequencies, ν , which were extracted by using previously detailed procedures.⁴⁷ These frequencies are also collected in Table 1. A similar red shift in basic solvents such as tetrahydrofuran (THF), Et₂O, and ACN has been previously observed¹³ and attributed to HBing.

To separate out the polarity and HB effects, we first plot the 2OMe emission frequencies (circles) as a function of π^* , Figure 4a. The line represents a fit to eq 3 with $a = 0$, $p = -350 \text{ cm}^{-1}$ (see Table 2) and a correlation coefficient $r = 0.86$. The parameter p reflects the solute dipole moment that interacts with the solvent via dipole–dipole interactions. As it was smaller for the excitation frequencies ($p = -70 \text{ cm}^{-1}$), the small ground-state dipole moment must increase upon excitation.

However, the enhanced excited-state polarity is not sufficient to explain the bathochromic shifts for 2OH (plus signs in Figure 4a), which tend to be larger than for 2OMe. In Figure 3, like Figure 1, the excess shift increases along the columns, which are ordered by the Taft β parameter. To see the effect more quantitatively, we plot in Figure 4b the excess shift, $\Delta\nu \equiv \nu(2\text{OMe}) - \nu(2\text{OH})$, as a function of β . The line is a fit to eq 4 with $b = -850 \text{ cm}^{-1}$ (see Table 2) and a correlation coefficient $r = 0.97$. The solvents are labeled by their numbers in Table 1, which follow the π^* order. It is thus clear that $\Delta\nu$ does not correlate with polarity. For example, polar solvents such as chlorinated and fluorinated alkanes show no shift, whereas mildly polar solvents such as Et₂O and EtOAc exhibit a shift as large as water. Neither does $\Delta\nu$ correlate with α . For example, TFE with its large α value shows no shift.

To verify the above conclusions, we have performed a multiparameter linear regression to the 2OH peak frequency using eq 2. Within the error bars ($\pm 50 \text{ cm}^{-1}$), this gave $p = -450 \text{ cm}^{-1}$, $b = -800 \text{ cm}^{-1}$, and $a = 0 \text{ cm}^{-1}$, with a correlation coefficient $r = 0.98$. In comparison, the separate correlations using 2OMe as a reference molecule gave $p = -350 \text{ cm}^{-1}$, eq

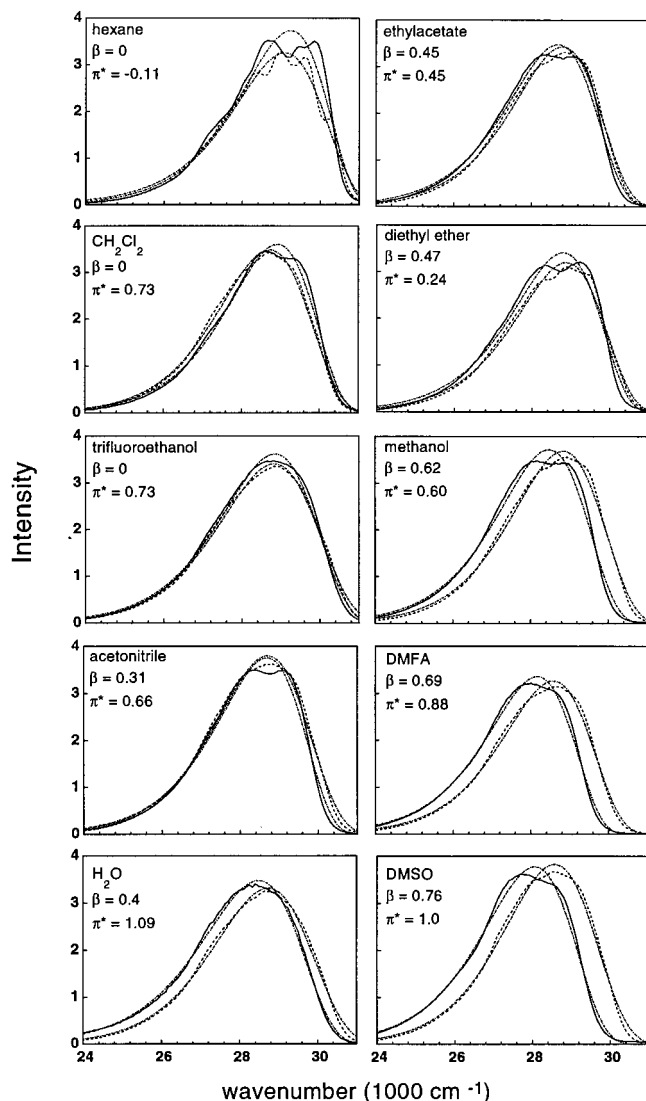


Figure 3. Fluorescence emission spectra of 2-naphthol (bold lines) and 2-methoxynaphthalene (dashed lines) in the indicated solvents. Dashed-dotted curves are fits to the log-normal distribution, from which the peak frequencies reported in Table 1 were extracted. The columns are ordered by increasing β .

3, and $b = -850 \text{ cm}^{-1}$, eq 4. These parameters are summarized in Table 2. The fact that 2OMe and 2OH have similar p values confirms our assumption that 2OMe is a reasonable model for polarity effects on 2OH. Consequently, the excess 2OH shifts are due to HBing *donated* from the OH group to the solvent. This is corroborated by the fact that b for 2OH is the same as that obtained from the frequency difference $\Delta\nu$.

6. Anion Fluorescence

Excited 2-naphthol dissociates only in water (and mixed aqueous solvents). Although there is evidence for PTTS also when amines are used as solvents, their low dielectric constant prevents ion separation.⁴ Therefore, to monitor the anion fluorescence, one has to work under basic conditions when the naphtholate is the dominant species already in the ground state. A recent work reported an extensive investigation of β -naphtholate,¹⁹ with emphasis on ion pairing that occurs in low dielectric solvents. We are interested in the solvation of the isolated naphtholate anion and hence consider its fluorescence only in solvents of relatively high dielectric constants. There the naphtholate spectrum is independent of the counter-

ion,¹⁹ so apparently the two ions have separated. Figure 5 shows the excitation and emission frequencies of 2-naphtholate in the five indicated solvents. These data were taken from Table 1 of Soumillion et al.¹⁹ (measurements not repeated here). The anion shifts correlate exclusively with the Kamlet-Taft α parameter:

$$\nu(\text{RO}^-) = \nu_0 + a\alpha \quad (5)$$

For the excitation spectra we find $\nu_0 = 25\,480 \text{ cm}^{-1}$ and $a = 3100 \text{ cm}^{-1}$, with a correlation coefficient $r = 0.99$. For the emission spectra we find $\nu_0 = 21\,920 \text{ cm}^{-1}$ and $a = 1770 \text{ cm}^{-1}$, with a correlation coefficient $r = 0.98$. The most striking observation is that the (difference in) anion stabilization does not depend at all on polarity, as measured by either π^* or ϵ . In fact, the Born model suggests that the free energy of solvation for an ion of charge z and radius R is given by

$$G_s = z^2/2\epsilon R \quad (6)$$

This model is supposedly very successful in explaining ion hydration.⁴⁸ For the solvents in question, the dielectric constants are MeOH (32.7), DMFA (36.7), ACN (37.5), DMSO (46.7), and water (78.4). This order is completely different from that of the solvatochromic shifts in Figure 5. For example, MeOH, which has the lowest ϵ , induces a shift almost as large as in water. In DMSO and DMFA, which have different values of ϵ , naphtholate fluoresces at identical frequencies. Thus, either the Born solvation energy is somehow identical in the ground and excited states or else the model is inapplicable when comparing protic with aprotic solvents.

The exclusive dependence on α indicates that the anion is solvated predominantly by $\text{RO}^- \cdots \text{HS}$ interactions (HS denotes a protic solvent). It is known⁴⁹ that small anions are strongly solvated by HBs; hence the solvent here is specifically bonded to the negative oxygen center rather than solvating the molecule as a whole. This represents a considerably stronger version of the $\text{RHO} \cdots \text{HS}$ bond observed for ground-state ROH. Indeed, the a parameter there was tiny (270 cm^{-1} , Table 2) as compared with its values for the anion (3100 cm^{-1}), in accord with the full negative charge on the naphtholate oxygen. The partial delocalization of this charge on the aromatic ring in the excited state explains the weaker α dependence of the emission frequencies ($a = 1770 \text{ cm}^{-1}$). For the ROH acid we could detect no α dependence in the emission spectra at all.

We have found a similar trend in the naphtholate emission from 5CN2OH,⁴³ which, in the excited state, does transfer its proton to all the above solvents except ACN. The dependence on α there was somewhat weaker, $a = 1100 \text{ cm}^{-1}$, in accord with the further delocalization of the negative charge by the electron-withdrawing cyano group. Interestingly, a similar order of solvatochromic shifts has also been observed in the emission spectra of 1-[(dimethylamino)methyl]-2-naphthol.³⁶ In both these cases the naphtholate is formed by excited-state PTTS.

7. Discussion

The present work reported standard fluorescence results on standard chromophores, β -naphthol and its methoxy analogue, in a series of neat solvents. It is remarkable that the solvatochromic shifts of 2OH fluorescence have not been analyzed in detail before. By use of the empirical Kamlet-Taft approach, it was possible to separate polarity from HBing effects. In contrast to the situation usually reported for polar solvation of dye molecules,^{20,23} "nonspecific" dipolarity interactions, between the probe molecule and the full ensemble of solvent molecules,

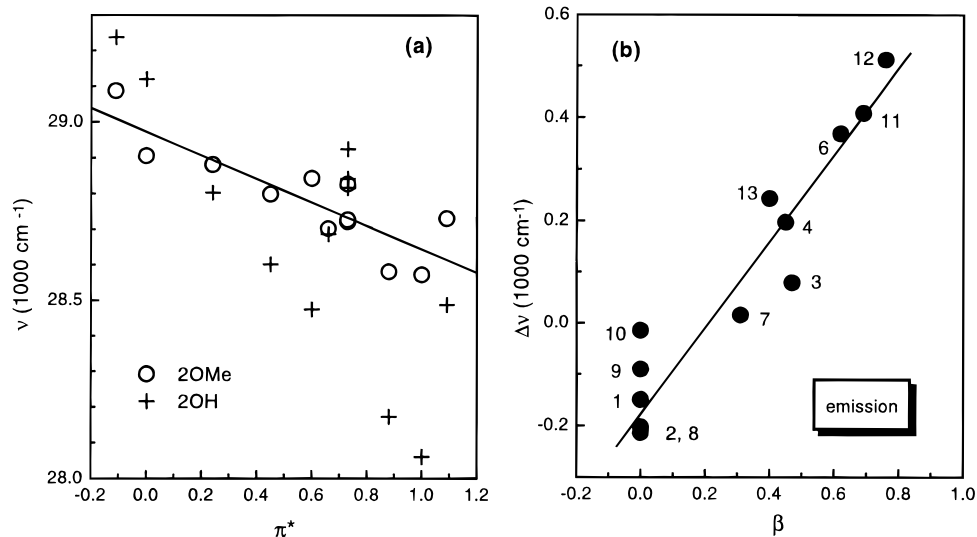


Figure 4. Solvatochromism of the peak emission peak of (a) 2OMe and 2OH and (b) their frequency difference. Line in panel a is a linear fit to the methoxy data (circles). Solvents are detailed in Table 1.

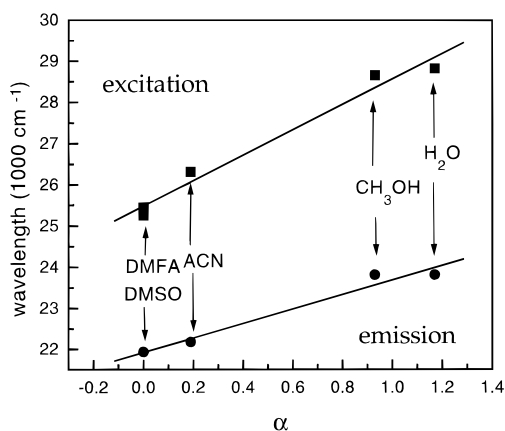


Figure 5. Dependence of the excitation and emission frequencies¹⁹ of β -naphtholate in basic solutions on the Kamlet–Taft hydrogen-bond donation parameter α .

account for a rather modest part of the overall Stokes shift of β -naphthol. Most of the shift appears to be due to the few strong HBs in the first solvation layer.

Our correlations suggest that only two such bonds are important in the solvatochromism of β -naphthol; namely, those to the hydroxyl hydrogen or oxygen atoms. The bond to the hydrogen atom is favored by excess positive charge (or low pK_a). It is thus stronger in the excited state than in the ground electronic state, leading to bathochromic (red) shifts in both excitation and emission spectra with increasing β . This is corroborated by the observation that, for the methoxy derivative, the β -dependent shift is abolished. In contrast, the bond to the oxygen is favored by excess negative charge (or high pK_a). It is thus stronger in the ground state, leading to hypsochromic (blue) shifts with increasing α . The characteristics of the different kinds of HBs are summarized in Table 3.

As a consequence, the situation upon photoexcitation may be envisioned as follows. In protic solvents, both HBs exist in the ground state. This is manifested in the biparametric (α and β) dependence of the excitation spectral shifts. Following excitation to S_1 , the bond to the oxygen breaks, whereas that to the hydrogen is considerably strengthened, leading to an enhanced, uniparametric dependence of the emission spectra on β alone.

For the “super”photoacid, 5CN2OH,⁵⁰ we have found⁴³ a slightly weaker α dependence on the excitation spectra and a considerably larger β dependence for emission (see Table 2). This is understood from the enhanced positive charge on the OH group, as reflected by the values of the equilibrium constants for deprotonation, which vary more for the excited than the ground state. For 2OH, $pK_a = 9.5$ in the ground state and 2.8 in the excited state. In 5CN2OH, these values decrease to 8.8 and ≈ -1 , respectively.⁵⁰

Our results do not implicate the precise geometric change leading to the enhancement in the ROH \cdots S bond strength upon excitation. Gas-phase data^{51,52} shows that photoexcited complexes of 2OH with ammonia shorten their R*OH \cdots NH₃ bond by as much as 0.2 Å. A similar change might occur in solution. Consequently, a time-resolved study of the HB dynamics accompanying proton transfer to solvent is desired.^{53,54} One might expect to see two ultrafast solvation phases:^{25,55} A fast one due to HB shortening and a slower one from nonspecific solvent reorganization.

In contrast to ROH solvation, anion solvation in protic solvents is dominated by the HB donated to the more negative oxygen site. As a result, anion fluorescence is appreciably blue-shifted in protic solvents, water and methanol, as compared with DMFA or DMSO. This shift correlates predominantly with α and not with ϵ . In contrast to the ROH \cdots S bond, which is stronger in the excited state and produces enhanced red shifts in the emission spectra, the opposite holds for the RHO $^- \cdots$ HS bond. It is stronger in the ground state, producing blue shifts that are larger in the excitation than the emission spectrum.

Finally, we consider the relation between the spectral shifts and the propensity for acid photodissociation. For 2OH, water is the only solvent that promotes appreciable dissociation with subsequent ion separation. It was suggested that proton transfer to solvent depends crucially on the availability of “water cluster” proton acceptors.^{56–59} The dominance of the acceptor properties of water has been questioned before.^{60,61} Indeed, water is *not* the best solvent for proton solvation. Proton free energies of transfer from water to various solvents, $\Delta G_f(H^+)$, have been compiled in ref 62 (see Table 1). The more negative $\Delta G_f(H^+)$, the better the proton is solvated by the given solvent. Figure 6 correlates the available literature values with β , for those solvents where both parameters are known. It is seen that the more basic DMFA and DMSO stabilize the proton nearly 20

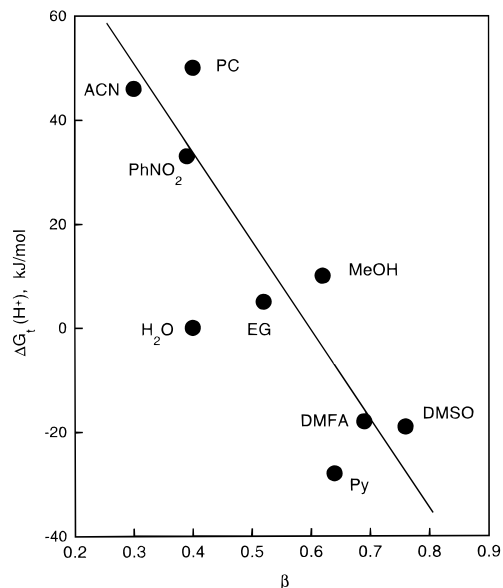


Figure 6. Dependence of proton free energy of transfer⁶² on the basicity parameter β . The line is a fit to $\Delta G^\ddagger(\text{H}^+) = 102 - 171\beta$ (kJ/mol), with a correlation coefficient $r = 0.91$. Additional marked solvents are PC = 1,2-propylene carbonate; PhNO₂ = nitrobenzene; EG = ethylene glycol (1,2-ethanediol); Py = pyridine. Other acronyms as in Table 1.

kJ/mol better than water. These are also the solvents in which the ROH band is most red-shifted, due to their large β value. The shift thus correlates with the degree of proton solvation: The ROH...S bond solvates a "partial" proton. Consequently, the sensitivity to β in Figures 2b and 4b is considerably smaller than that in Figure 6. Basic solvents stabilize the hydronium ion much better than they stabilize the acid.

Solvatochromic shifts in *both* excited acid and base emission are thus intimately related to HB formation and contribute to the $\text{p}K_a^*$. It is interesting to compare this conclusion with the Förster cycle for excited-state acidity. According to eq 1, the $\text{p}K_a^*$ diminishes when the anion fluorescence is red-shifted or the acid fluorescence is blue-shifted. HBing contributes a shift in the opposite direction: The more the anion fluorescence is blue-shifted and the acid fluorescence is red-shifted, the better the anion and proton are solvated and hence the stronger the acid. It would be interesting to turn this understanding into a quantitative procedure for correcting the Förster photoacidity scale. Water is a good solvent for promoting acid dissociation due to its ability to act as both HB acceptor and donor. However, alkylamines are also good HB acceptors, while protonated alkylamines are good donors. Indeed, PTTS is observed in these solvents,⁴ but due to their low dielectric constant the ion pair does not appear to separate. Water is unique for promoting acid dissociation because, in addition to its HBing properties, its high dielectric constant encourages ion separation.

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