

# Hydrogen-bonding interactions of photoacids: correlation of optical solvatochromism with IR absorption spectra

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Received 15 November 2002; received in revised form 27 January 2003; accepted 3 February 2003

## Abstract

The effect of specific hydrogen-bonding interactions on the electronic spectra and the infrared (IR) absorption spectra of several naphthol-type photoacids was investigated. A correlation between the  $pK_a^*$  of the photoacid and its optical solvatochromism was observed for  $R^*O-H \cdots B$ -type hydrogen bonds using the Kamlet–Taft (K–T) analysis. In addition, a correlation between the spectral shift in the IR stretching frequency of the  $RO-H \cdots B$  bond and the optical Stokes shift in the fluorescence spectra of the photoacids was found.

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*Keywords:* Hydrogen bonds; Photoacid; Optical solvatochromism; IR absorption spectra

## 1. Introduction

Hydrogen-bonding interactions are extremely important in all fields of chemistry. In particular, proton transfer between Brønsted acids and bases occurs along a hydrogen bond of the type  $A-H \cdots B \leftrightarrow A^- \cdots H-B$ , where the hydrogen-bonding interaction determines the reactive coordinate of the proton [1–3]. Hydrogen-bonding interactions also play central role in biology. In particular, hydrogen bonds are responsible for structure making of macromolecules and take an important role in the function of enzymes [4].

One of the most intriguing questions of acid–base reactions concerns the relation between aqueous acidity and the hydrogen-bonding interactions of Brønsted acids in nonaqueous environments. In this contribution, we report on such a relation found in a class of Brønsted acids known as “photoacids.” Photoacids are weak Brønsted acids in their electronic ground state. Upon optical excitation, photoacids become strong Brønsted acids and readily dissociate in aqueous solutions.

Hydroxyarenes are, arguably, the most well-researched photoacids. Among the hydroxyarenes, 1-naphthol and 2-naphthol have been extensively studied in the past 60 years

[5–13]. Peculiarities in the electronic structure of their excited electronic states [14–17] have made these molecules a target for studies of intermolecular hydrogen-bonding interactions.

The influence of hydrogen bonding on the UV–Vis and the emission spectra of naphthols have been studied by Baba and Suzuki [18] and Tramer and Zaborowska [19]. Switching of the lowest excited states of 1-naphthol, from  ${}^1L_b$  state to  ${}^1L_a$  state (Platt notation), as a result of better stabilization due to hydrogen-bond interactions was suggested. Recently, we have reported on a comparative analysis of the effect of solute–solvent interactions on the stabilization of the excited electronic states of 1-naphthol, 1-methoxynaphthalene, and 2-methoxynaphthalene [20]. Investigation of the effect of hydrogen bonding on photodissociation of 1-naphthol was reported first by Takemura et al. [21]. The ground-state (UV–Vis absorption) and the excited-state (fluorescence) solvatochromism of several naphthalene derivatives was analyzed by Mataga and Kaifu [22] in terms of nonspecific solute–solvent interactions (the dielectric constant and the refraction index) and specific hydrogen-bonding interactions. Empirical scales of solvent polarity developed by Taft et al. [23], Marcus [24], and Reichardt [25] have been very useful in numerous attempts to correlate various empiric manifestations of solute–solvent interactions. The description of the electronic emission spectra of 1-naphthol and 1-methoxynaphthalene by two Pekarian functions has allowed us to distinguish between its

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two overlapping emitting states ( $^1L_a$  and  $^1L_b$ ) and to obtain good correlation between the fluorescence maximum of each emitting band and the Kamlet–Taft (K–T) empiric solvent parameters [20]. In addition, we have reported in a recent publication on the correlation between the fluorescence maxima of pyranine (8-hydroxypyrene, 1,3,6-trisulfonate) with several sets of empirical solvent polarity parameters [26]. Solvatochromic shift of emission and absorption bands maxima of the photoacids 2-naphthol and 5-cyano-2-naphthol has been studied by Solnsev et al. [27] in terms of the Kamlet–Taft solvent polarity  $\pi^*$  and solvent basicity  $\beta$  parameters.

The effect of hydrogen bonding on the stretch vibration frequencies of the –OH moiety of phenol and naphthol derivatives has been studied intensively by infrared (IR) absorption spectroscopy [28]. A correlation between the –OH stretching frequency in substituted phenols and their reactivity was reported [29]. Two absorption bands in the region of 3.6  $\mu\text{m}$  were assigned to the stretching vibrations of the “free” unbonded –OH (blue band) and to the hydrogen-bonded –OH (red band) [28,30,31]. Theoretical studies of the linear correlation between the enthalpy and the IR wavenumber shift for hydrogen-bonded phenols have been undertaken by Purcell and Drago [32]. The formation of specific hydrogen bonds results in deviations from the nonspecific dependence of vibronic transitions on solvent polarity. It was also shown that the frequency shift in the IR vibronic band of the valent bond X–H depends on the strength of the H bonds formed [33–37].

Our present study consists of two parts. We first study the correlation between the excited-state aqueous acidity ( $\text{p}K_a^*$ ) of several common photoacids and the extent of their hydrogen-bonding interactions in various solvents. A general correlation between the magnitude of the effect of hydrogen bonding on the optical transitions of the photoacids and their acidity was established.

Next, we examine, by means of IR absorption spectroscopy, the hydrogen-bond interactions of two of the total sets of photoacids studied in the first part, 1-naphthol and 2-naphthol. This was done in hope of correlating the shifts in the O–H stretching frequency with the optical shifts due to hydrogen bonding observed in the fluorescence spectra of photoacids.

## 2. Experimental

All measurements were performed at room temperature ( $20 \pm 0.5$  °C), if not otherwise specified in the text. 1-Naphthol was from Fluka (>98%) and 2-naphthol was from Kodak (>98%). Both photoacids were recrystallized from water/ethanol (20% vol.) mixtures. All solvents (listed in Table 1) used for the preparation of solutions were of HPLC or spectroscopic grade purity (Sigma-Aldrich) and were stored under nitrogen to prevent water contamination. The excitation wavelengths for both molecules (300 nm for 1-

Table 1  
Set of solvents used in this study

1	<i>n</i> -Hexane
2	$\text{CCl}_4$
3	1,2-Dichloroethane
4	Ethyl acetate
5	Acetonitrile
6	1,4-Dioxane
7	Diethyl ether
8	Isopropyl ether
9	DMF
10	THF
11	DMSO
12	<i>c</i> -Hexane
13	2,2,2-Trifluoroethanol
14	Glacial acetic acid
15	Propylene carbonate
16	1,4-Dioxane
17	Ethanol
18	2-Propanol
19	1-Propanol
20	1-Butanol
21	1-Octanol
22	<i>n</i> -Decanol
23	<i>c</i> -Hexanol
24	Formamide
25	Water

naphthol and 290 nm for 2-naphthol) were chosen from their absorption spectra near an absorption maximum. Concentrations of the measured solutions were about  $10^{-4}$ – $10^{-5}$  M, having optical densities of 0.1–0.2 O.D. at the excitation wavelength.

Steady-state fluorescence measurements were carried out on SLM-AMINCO-Bowman 2 spectrophotometer.

The collected emission spectra having a spectral resolution of 0.25 nm were fitted using Pekarian functions as described below and in Ref. [20].

The emission spectra of 1-naphthol and 2-naphthol in the ternary system *n*-hexane:naphthol:base were also approximated by two Pekarian functions to account for the free and the hydrogen-bonded populations of photoacids.

The IR spectra of 1-naphthol and 2-naphthol were collected on JASCO FT/IR-400 600 spectrophotometer in the region of the stretching vibration of the O–H group from 3000 to 3800  $\text{cm}^{-1}$ . Sodium chloride and calcium fluoride cells with 0.05–1 mm thickness were used. The concentrations of 1-naphthol and 2-naphthol were about 0.02–0.1 M in pure solvents and 0.01–0.02 M in ternary mixtures in *n*-hexane.

## 3. Results and discussion

### 3.1. The Pekarian functions

Emission spectra corresponding to several overlapping electronic–vibronic transitions can be approximated by the Pekarian function  $P(\nu)$  [38]. We have previously used this

functional formalism to describe the fluorescence emission of 1-naphthol and 1-methoxynaphthalene. The intensity of measured emission spectra  $I(\nu)$  can be expressed as:

$$I(\nu) \sim h\nu^3 P(\nu) \quad (1)$$

where  $h\nu$  is the energy of the photon emitted during phototransition (emission), and  $\nu^3 P(\nu)$  is the probability of electronic transition with a frequency  $\nu$  (dipole–dipole transitions). According to Seshadri and Kenkre [39] and Pope and Swenberg [40], the function  $P(\nu)$  describes a system of “elementary” vibronic bands (in our case, in the ground state) relatively displaced by a frequency  $\delta$  (harmonic approximation). The relative contribution of these bands to the total spectra changes according to a Poisson distribution. The fundamental 0–0 transition is approximated by a Gaussian line shape:

$$P_0(\nu) = P_{00} \exp(-(\nu - \nu_0)^2 / 2\sigma^2) \quad (2)$$

Accordingly,

$$P_i(\nu) = P_{00} \frac{s^i}{i!} \exp\left(-\frac{(\nu - (\nu_0 + i\delta))^2}{2\sigma^2}\right) \quad (3)$$

In Eqs. (2) and (3),  $P_{00}$  is  $P_0(\nu_0)$ ,  $\nu_0$  is the frequency of the 0–0 transition;  $i$  is the number of the successive  $i$ th “elementary” transitions, and  $s$  is a fitting parameter that describes the relaxation process within the energy potential well of the final state. The final form of the Pekar function is:

$$P(\nu) = \sum_{i=0}^n P_i(\nu) \quad (4)$$

Typical parameters used in our fits:  $n \leq 6$  for two Pekar fittings;  $0 \leq s \leq 2$ ; and  $1000 \text{ cm}^{-1} \leq \delta \leq 1800 \text{ cm}^{-1}$ .

### 3.2. The $pK_a^*$ —fluorescence Stokes shift correlation

According to Taft et al. [23] and Kamlet et al. [37], there are three basic interaction that determine the solvent effect on solutes. These interactions were designated  $\pi^*$ ,  $\alpha$ , and  $\beta$ , and stand for the total nonspecific polar interactions of the solvent ( $\pi^*$ ), and for the specific hydrogen-bonding interactions between the solvent and the solute ( $\alpha$ ,  $\beta$ ). The solvent may accept or donate the hydrogen bonds that it forms with a solute. In the first case, the solvent behaves as a base (described by the solvent basicity scale,  $\beta$ ) and, in the latter case, the solvent behaves as an acid (described by the  $\alpha$  scale). The extent of solvent basicity and solvent acidity of a given solvent is given by the numeric values of its  $\beta$  and  $\alpha$  parameters, respectively.

The change in the frequency of the optical (electronic) transition of a photoacid as a result of its polar interactions

with a solvent may be correlated with the  $\pi^*$ ,  $\alpha$ , and  $\beta$  values of a given solvent according to:

$$\nu - \nu_0 = s\pi^* + \alpha\alpha + b\beta \quad (5)$$

where  $\nu$  is the measured frequency of the optical transition of the solvated photoacid,  $\nu_0$  is the transition frequency in a reference solvent (cyclohexane), and  $s$ ,  $a$ , and  $b$  depend on photoacid properties and describe its sensitivity to the various polar interactions extended by the solvent. Ideally, the  $\pi^*$ ,  $\alpha$ , and  $\beta$  scales are independent of each other (orthogonal), and  $s$ ,  $a$ , and  $b$  are pure solute properties, independent of the solvent used in the experiment. In reality, these conditions are rarely fully met, so one needs to use a relatively large set of solvents in order to extract a statistically meaningful set of  $s$ ,  $a$ , and  $b$  values for a given solute.

The  $b$  values of several naphthol-type photoacids were extracted by the Kamlet–Taft analysis using a set of 25 common solvents described elsewhere [20,26]. In Fig. 1, the  $b$  values of the photoacids were plotted against their respective  $pK_a^*$  values in aqueous solutions. The two sets of parameters were correlated using the valence bond-order model of hydrogen bonding based on the concept of Pauling [41]. Our analysis follows the one published recently by Lorente et al. [42] for the correlation of  $^{15}\text{N}$

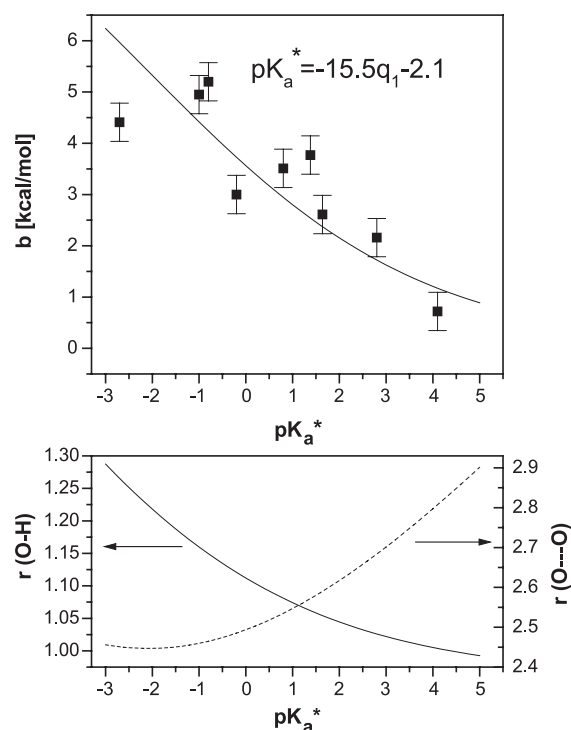


Fig. 1. Top: The  $b$  values of several naphthol-type photoacids found by the Kamlet–Taft analysis plotted as a function of the corresponding  $pK_a^*$  of the photoacids. The solid line was calculated using Eq. (10) with the parameters  $r_{\text{O}\cdots\text{H}}=0.96 \text{ \AA}$  and  $k_{\text{OH}}=0.38$ . Bottom: The relation between the heavy atom distance  $r_{\text{O}\cdots\text{O}}$  and the bond length  $r_{\text{O}\text{---}\text{H}}$  with the  $pK_a^*$  values of the photoacids.

NMR shielding with the  $pK_a^*$  values of a set of carboxylic acids in a series of hydrogen-bonded acid–base complexes of collidine. These measurements were done in the solid state in a nonaqueous environment.

Briefly, we have assumed a correlation between the location of the hydrogen atom in the A–H · · B complex and the spectral shift observed in the fluorescence of the photoacids judged from the shift in energy of the fluorescence maximum. The correlation has the form proposed by Lorente et al. [42] and has linear dependence on the oxygen–hydrogen bond-order of the photoacid  $P_{OH}$ :

$$\delta = \delta^\infty - (\delta^\infty - \delta^0)P_{OH} \quad (6)$$

where  $\delta^0 = 0$ ,  $\delta^\infty$  is the limiting fluorescence shift, and  $P_{OH}$ , according to the valence bond-order concept [41] is:

$$P_{OH} = \exp[-(r_{OH} - r_{OH}^0)/k_{OH}] \quad (7)$$

where  $r_{OH}$  is the O–H bond distance in the O–H · · B complex,  $r_{OH}^0$  is the O–H distance in the free (unbound) photoacid, and  $k_{OH}$  is the decay parameter of the band. It is convenient to define additional coordinates  $q_1$  and  $q_2$  according to:

$$q_1 = \frac{1}{2}(r_{OH} - r_{HB}), \quad q_2 = r_{HB} + r_{OH} \quad (8)$$

where  $r_{HB}$  is the HB distance in the O–H · · B complex.

From Eq. (8), we get that  $r_{OH} = q_2/2 + q_1$ ; hence,

$$\begin{aligned} \delta &= \delta^\infty - \delta^\infty \exp[-(r_{OH} - r_{OH}^0)/k_{OH}] \\ &= \delta^\infty - \delta^\infty \exp\left[-\left(q_1 + \frac{1}{2}q_2 - r_{OH}^0\right)/k_{OH}\right] \end{aligned} \quad (9)$$

Assuming that the total bond order of the hydrogen atom is unity, Lorente et al. [42] have shown that the two bond distances  $r_{OH}$  and  $r_{HB}$ , or, alternatively,  $q_1$  and  $q_2$ , cannot be varied independently:

$$\begin{aligned} q_2 &= r_{O-H} + r_{HB} \\ &= 2r_{OH}^0 + q_1 + 2k_{OH} \ln\left(1 + \exp\left(-\frac{2q_1}{k_{OH}}\right)\right) \end{aligned} \quad (10)$$

In addition, we assumed, as Lorente et al. did [42], a linear correlation between the  $pK_a^*$  and  $q_1$  (the proton transfer coordinate):

$$pK_a^* = c_1 q_1 + c_2 \quad (11)$$

The  $c_1$  and  $c_2$  parameters were found by fitting the experimental data with the theoretical correlation curve.

The solid line in Fig. 1 (top) was calculated using Eq. (10) with the parameters  $r_{O-H}^0 = 0.96 \text{ \AA}$  [2] and

$k_{OH} = 0.38$  for hydrogen bonds of the type O–H · · O. For our calculation, we assumed a linear relation of  $pK_a^*$  with the proton transfer coordinate  $q_1 = 1/2(r_{OH} - r_{HB})$ , given by  $pK_a^* = -15.5 q_1 - 2.1$ . Fig. 1 (bottom) shows the correlations between the O · · O and O–H distances and the  $pK_a^*$ . As the acidity of the photoacid increases, its hydrogen-bonding interaction with the solvent increases and the O–H bond length increases, up to the proton transfer point.

The above analysis suggests, although does not prove, a correlation between the spectral shift of the fluorescence spectra of hydrogen-bonded photoacid and the bond length of the O–H covalent bond of the photoacid, Fig. 1. It is well established that the IR vibration spectra of the O–H bond are red-shifted by hydrogen-bonding interactions, and that the shift is correlated with the strength of the hydrogen-bonding interactions (see below). In addition, Kamlet et al. [37] have found good correlation between the K–T  $\beta$  scale and the red shift in the IR vibration frequency of the O–H moiety of hydrogen-bonded phenol in  $CCl_4$  [37]. Since the  $\beta$  scale was originally constructed using, among other probes, the relative optical shifts in the fluorescence of substituted phenols in various hydrogen-bonding solvents, the correlation found by Kamlet et al. [37] suggests a linear correlation between the effect of hydrogen-bonding on the stretching frequency of the O–H bond and the Stokes shift in the fluorescence spectra of the chromophore due to hydrogen bonding.

We have checked the generality of this observation by carrying out IR absorption and fluorescence studies on, arguably, the two most studied photoacids, the 1-naphthol and 2-naphthol molecules. The location of the maxima of the O–H stretching bands was estimated by calculation of the first moment of the bands. The effect of hydrogen bonding on optical transition was judged from the location of the fluorescence maxima, which was found to be much more sensitive to hydrogen bonding than the corresponding absorption spectra—the effect on the fluorescence spectra being twice to three times larger. We have, thus, preferred to correlate our IR data with the fluorescence spectra of photoacids, where the hydrogen-bonding interaction is enhanced compared to the ground state.

The assignment of the stretching bands in the IR spectra of 1-naphthol and 2-naphthol in the pure solvents (Fig. 2a and b, respectively) was performed by comparison with the IR spectra measured in ternary mixtures (Fig. 2c and d). The IR spectra of 1-naphthol and 2-naphthol in pure solvents consist of two bands (Fig. 2c and d), which correspond to the stretching frequencies of associated O–H groups. The peak of unbonded (“free”) O–H vibration was at  $3609 \text{ cm}^{-1}$  and the 1:1 hydrogen-bond complexes were at lower frequency, down to about  $3200 \text{ cm}^{-1}$  for the strongest hydrogen bonds. The IR absorption of self-associated 1-naphthol and 2-naphthol in *n*-hexane was at  $3469$  and  $3481 \text{ cm}^{-1}$ , respectively.

The stretching frequencies  $\nu^{OH}$  of 1-naphthol and 2-naphthol were correlated with the Kamlet–Taft empirical

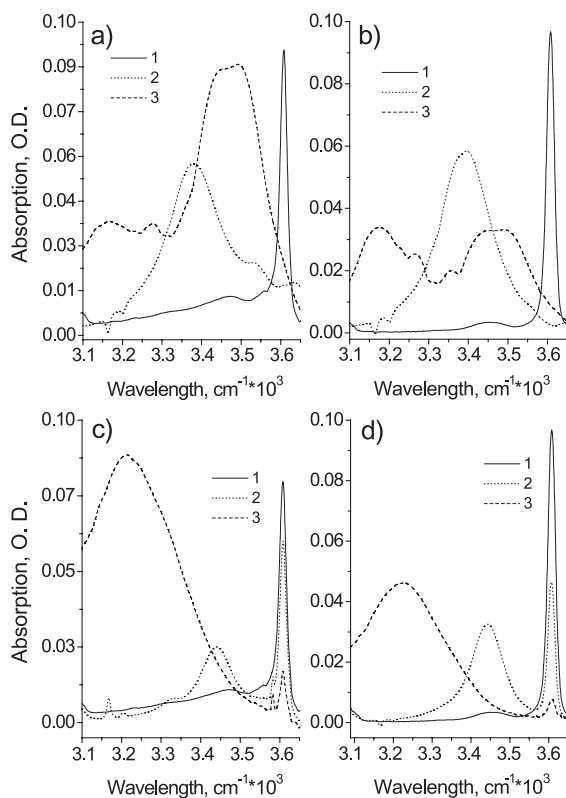


Fig. 2. IR absorption spectra of (a) 1-naphthol and (b) 2-naphthol measured in pure solvents. Solid line: in *n*-hexane; dotted line: in acetonitrile; dashed line: in DMSO. IR absorption spectra of 1-naphthol (c) and 2-naphthol (d) measured in the ternary system *n*-hexane:naphthol:base. Solid line: the spectrum in pure *n*-hexane; dotted line: with addition of acetonitrile; dashed line: with addition of DMSO. The narrow absorption at  $3608\text{ cm}^{-1}$  is the OH bond stretch vibration.

solvent parameters. The empirical relations between the red shift in the vibration frequency of the O–H bond and solvent polarity parameters were found (see Fig. 3). From this correlation, it is clear that most of the solvent effects on the IR absorption spectra of photoacids are due to 1:1 complexes of the type  $\text{R}^*\text{OH} \cdot \text{B}$ , where  $\text{R}^*\text{OH}$  is the photoacid and B is a base or a solvent molecule. The coefficient of  $\beta$  reflects the proton donor ability of the photoacid in the ground state, where 1-naphthol and 2-naphthol have similar acidity ( $\text{p}K_{\text{a}}=9.2$  and  $9.5$  for 1-naphthol and 2-naphthol, respectively) [7]. Contributions from nonspecific solute–solvent interactions  $\pi^*$  are small and negative. They are too small to be analyzed reliably and are in line, assuming that hydrogen bonds become stronger as the polarity of the solvent decreases. Similar  $\beta$ -values were found for the two photoacids in ternary systems, indicating that the O–H  $\cdot \text{B}$  bonds are similar in both environments (Fig. 5). Relatively high hydrogen-bonding acceptor ability ( $\alpha$ ) of 1-naphthol was observed for 1-naphthol in both the IR and the emission spectra [20]. A possible explanation is the slight basicity of the aromatic naphthalene ring of 1-naphthol due to charge migration from the oxygen atom to the ring [6,10,15].

### 3.3. Fluorescence emission spectra of 1-naphthol and 2-naphthol in pure solvents

The existence of hydrogen-bonding interactions is evident from both the absorption and fluorescence spectra of photoacids [18,19]. The first and second excited singlet states of 1-naphthol,  $^1\text{L}_{\text{a}}$  and  $^1\text{L}_{\text{b}}$ , respectively, are spaced very closely [17–20]. A large difference in the dipole moments of these closely spaced excited states in 1-naphthol leads to different stabilization of the two states in solvents of high and low polarity. Two Pekarian functions are needed to simulate the fluorescence spectrum of 1-naphthol. The red-edge Pekarian peak, corresponding to the electronic  $^1\text{L}_{\text{a}}$  state, gives good correlation ( $r=0.95$ ) with the K–T parameters [20]:

$$\nu - \nu_0 = 2.8\pi^* - 1.3\alpha + 3.1\beta \text{ (kcal/mol)} \quad (13)$$

The second, blue-edge, Pekarian, which corresponds to the electronic  $^1\text{L}_{\text{b}}$  state, correlates with the K–T parameters with much smaller  $\pi^*$ ,  $\alpha$ , and  $\beta$  values (correlation coefficient  $r=0.94$ ):

$$\nu - \nu_0 = 1.1\pi^* - 0.1\alpha + 0.8\beta \text{ (kcal/mol)} \quad (14)$$

indicating that the  $^1\text{L}_{\text{b}}$  state is much less polar than the  $^1\text{L}_{\text{a}}$  state [20].

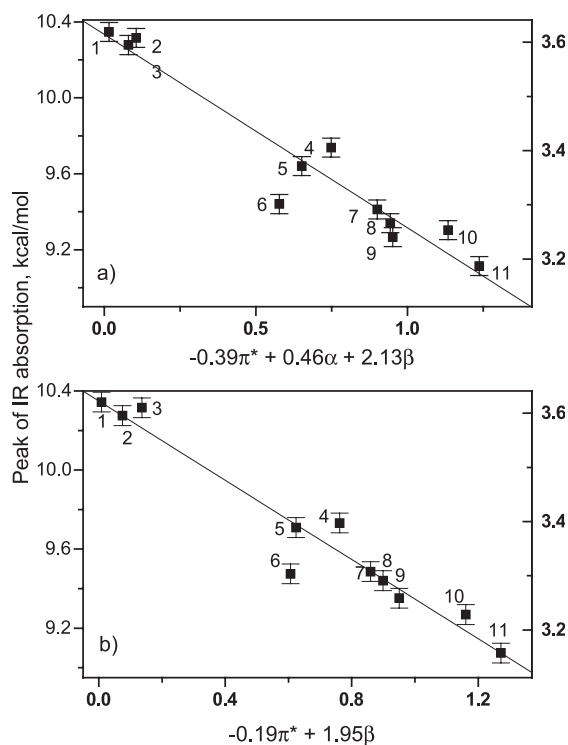


Fig. 3. The peaks of the IR absorption of the OH bond of (a) 1-naphthol ( $r=0.96$ ) and of (b) 2-naphthol ( $r=0.95$ ) measured in pure solvents correlated with Kamlet–Taft parameters.  $\nu^{\text{OH}}$  and other coefficients are expressed in kilocalories per mole.

The fluorescence spectrum of 2-naphthol measured in 22 pure solvents was approximated by one Pekarian function corresponding to the  $^1L_b$  electronic state. The correlation found is shown in Fig. 4. The polarity of the emitting state of 2-naphthol is roughly half of that of 1-naphthol.

### 3.4. Fluorescence emission spectra of 1-naphthol and 2-naphthol measured in ternary systems

The emission spectra of naphthols in ternary systems of *n*-hexane:naphthol:base (Fig. 5) were approximated by two Pekarian functions to account for the spectra of “free” and hydrogen-bonded photoacids. The shift in the peak of the Pekarian function describing the fluorescence of the hydrogen-bonded fraction of the photoacids was correlated with the  $\beta$  parameter of the complexing base. We have found  $b$  coefficients equal to 2.55 kcal/mol ( $892\text{ cm}^{-1}$ ) and 1.82 kcal/mol ( $637\text{ cm}^{-1}$ ) for 1-naphthol and 2-naphthol, respectively (see Fig. 6).

### 3.5. IR absorption spectra of 1-naphthol and 2-naphthol in ternary systems

The IR absorption spectra of 1-naphthol and 2-naphthol measured in the ternary systems in *n*-hexane (Fig. 2c and d) consist of two absorption bands that are assigned to the stretching vibration of the O–H moiety: a “free” (relative to *n*-hexane) band with peak position at  $3608\text{ cm}^{-1}$  and an H-bonded band with peak position in the region  $3212\text{--}3442\text{ cm}^{-1}$ . The position of the “free” absorption band of the O–H depends only on the solvent because changes in the solvent polarity of the ternary systems were practically

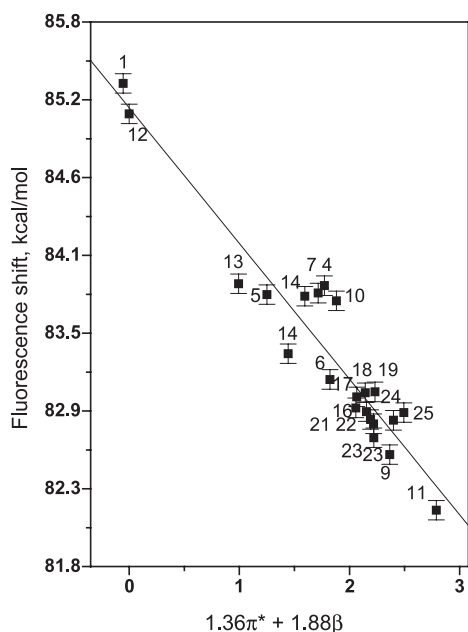


Fig. 4. Correlation of the shift in the fluorescence maximum of 2-naphthol, judged by a fit to one Pekarian function, with the Kamlet–Taft parameters of the pure solvent ( $r=0.95$ ). For numbering of the solvents, refer to Table 1.

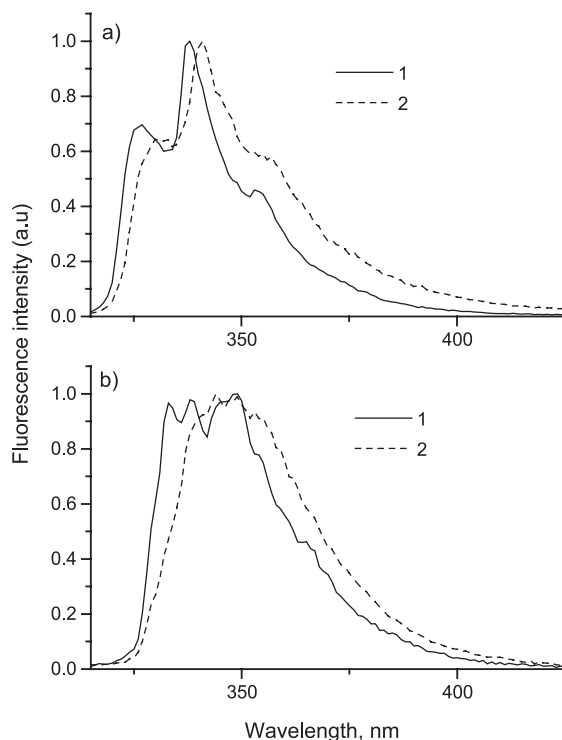


Fig. 5. (a) Fluorescence emission spectra of 1-naphthol measured in pure *n*-hexane (solid line) and after addition of  $10^{-4}$  M DMSO (dashed line). (b) Fluorescence emission spectra of 2-naphthol measured in *n*-hexane (solid line) and after addition of  $2 \times 10^{-4}$  M DMSO (dashed line).

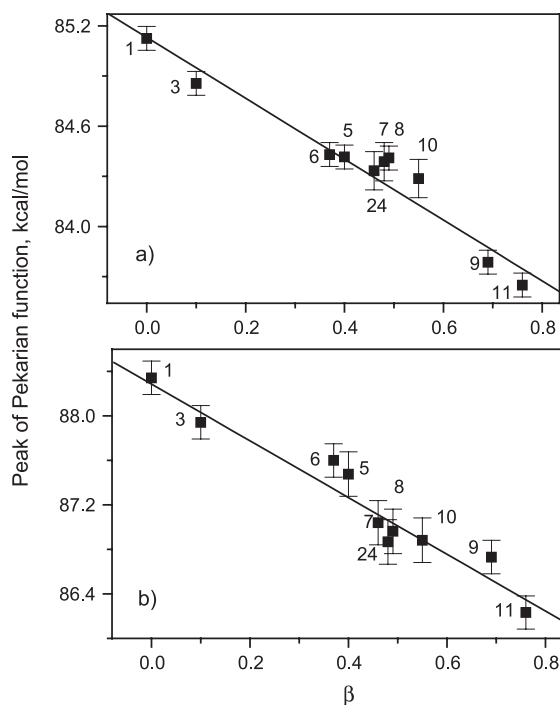


Fig. 6. Correlation of the maxima of the Pekarian functions simulating the fluorescence spectra of (a) 1-naphthol ( $r=0.98$ ) and (b) 2-naphthol ( $r=0.98$ ), measured in the ternary system *n*-hexane:1-naphthol:base with  $\beta$ . For numbering of the bases, refer to Table 1.

negligible. The frequency shifts were, in general, larger for 1-naphthol than for 2-naphthol.

We have found good correlation between the position of IR absorption band of the O–H ···B complex and Kamlet–Taft's  $\beta$  parameter of the base. For *n*-hexane:naphthol:base systems, we obtained *b* coefficients of 1.79 kcal/mol (622 cm<sup>-1</sup>) and 1.68 kcal/mol (586 cm<sup>-1</sup>) for 1-naphthol and 2-naphthol, respectively (see Fig. 7).

### 3.6. Correlation between solvatochromic shifts in the ground state (IR) and excited state (fluorescence) of naphthols

The correlation of the peak position of the IR stretching vibration of the hydrogen-bonded O–H moiety with the peak position of the Pekarian function describing the emission spectrum of the photoacid was attempted. For 1-naphthol, the fluorescence spectrum was decomposed into two subbands, as described in the text. The red-edge band, corresponding to the <sup>1</sup>L<sub>a</sub> transition, correlated with the maximum of the IR absorption (Fig. 8a). In the case of 2-naphthol, good correlation was found between the position of the maximum of the fluorescence emission and the IR absorption spectra (Fig. 8b).

We have found:

$$\nu_{\text{fl}} = A + B\nu_{\text{IR}} \quad (15)$$

with the correlation factor *B* equal to 3.80 and 2.25 for 1-naphthol and 2-naphthol, respectively, indicating the larger

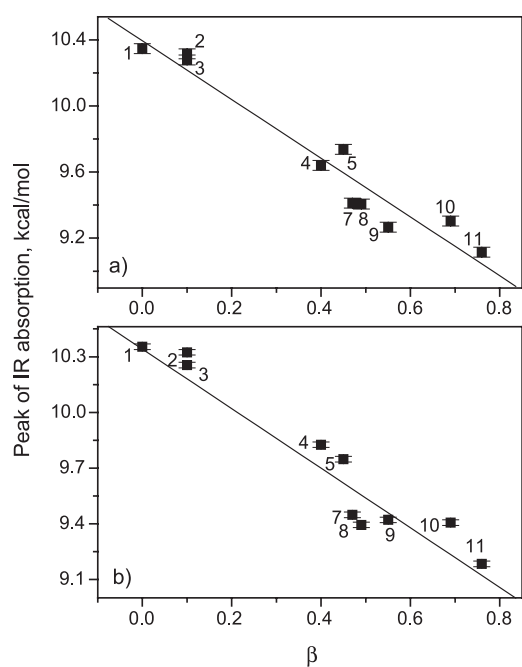


Fig. 7. Correlation of the frequency of the OH bond of (a) 1-naphthol and (b) 2-naphthol measured in the ternary system *n*-hexane:naphthol:base with  $\beta$ . For numbering of the bases, refer to Table 1.

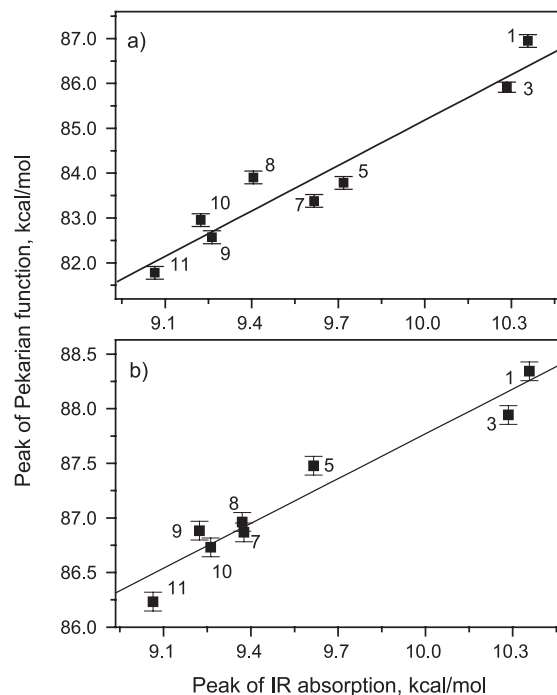


Fig. 8. The correlation between the maxima of the Pekarian functions simulating the fluorescence spectra of 1-naphthol and 2-naphthol in pure solvents and the stretching frequency of the OH bond measured by IR absorption spectroscopy. (a) 1-naphthol (red-edge emission from the <sup>1</sup>L<sub>a</sub> state),  $r=0.95$ ; (b) 2-naphthol,  $r=0.94$ . For numbering of the solvents, refer to Table 1.

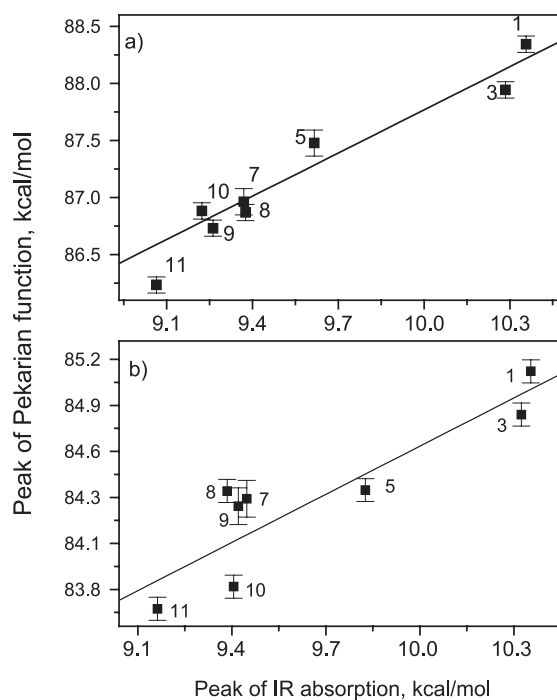


Fig. 9. Correlation of the maxima of the Pekarian functions simulating the fluorescence spectra of 1-naphthol and 2-naphthol with the stretching frequency of the OH bond of the photoacids measured in the ternary system *n*-hexane:naphthol:base. (a) 1-naphthol,  $r=0.95$ ; (b) 2-naphthol,  $r=0.91$ . For numbering of the bases, refer to Table 1.

sensitivity of the fluorescence spectra of 1-naphthol to polar interactions due to 1-naphthol being in the more polar  $^1L_a$  state.

For the ternary systems, a similar correlation between the ground IR absorption and the excited-state solvatochromic shifts was observed (Fig. 9). Here the correlation factor  $B$  (energy–energy) was found to be 2.62 and 1.05 for 1-naphthol and 2-naphthol, respectively, showing an almost three-time-larger Stokes shift in the fluorescence spectra of 1-naphthol compared to 2-naphthol as a result of the single  $R^*O-H \cdots B$  bond.

#### 4. Conclusion

The red Stokes shift in the fluorescence spectra of solvated photoacids due to hydrogen-bonding interactions of the type  $R^*OH \cdots B$  was found to correlate with the  $pK_a^*$  value of the photoacids. IR measurements of the O–H stretching frequency of hydrogen-bonded 1-naphthol and 2-naphthol have shown similar dependence on the solvent basicity parameter  $\beta$ . The effect of hydrogen bonding on optical transition was shown to correlate with a corresponding effect on the IR stretching vibration of the O–H bond. This observation indicates that the spectral shifts in the excited-state (fluorescence) and the ground-state (IR) spectra of photoacids are likely to originate from the same phenomenon, namely, the weakening and lengthening of the O–H bond due to hydrogen-bonding interactions.

#### Acknowledgements

We thank the James Frank German Israel Binational Program in Laser–Matter Interaction for financial support.

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