UV-Visible spectra and photoacidity of Phenols, Naphthols and Pyrenols.

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I. INTRODUCTION

Hydroxyarenes become stronger acids upon electronic excitation[1-5]. Such a property of an aromatic molecule is usually described as "photoacidity", and the molecules undergoing such a transition upon electronic excitation are usually named "photoacids". Photoacids are Brønsted acids, and their excited-state acidity may be described in terms used for ground-state acids as were defined by Brönsted some 80 years ago[6,7]. Following Brønsted, one usually associate acidity with a proton-transfer reaction where a proton is transferred from a proton donor (an acid) to a proton acceptor (a base).

$$\mathrm{AH\ (acid) + B\ (base)} \leftrightarrows \mathrm{A^{-}\ (base) + BH^{+}\ (acid)} \qquad (1)$$

The reversible nature of acid-base reactions implies the existence of conjugated acid-base pairs, i.e., A^- is the conjugate base of AH and AH is the conjugate acid of A^-. A more modern observation is that proton-transfer proceeds most often along a hydrogen-bond, formed between the proton donor and the proton acceptor so the reactive coordinate where proton-transfer occurs is usually of the type $A{-}H\cdots B$. The hydrogen-bonding interaction may be viewed as a relatively weak interaction between the proton donor and the proton acceptor through the sharing of a hydrogen atom.

Proton-transfer reactions and hydrogen-bonding interactions may occur within one molecule or between two molecules (intra- and intermolecular proton transfer, respectively). Photoacids such as the phenols or the naphthols readily undergo intermolecular proton transfer reactions in aqueous solutions[1-5]. When the proton is transferred to a solvent molecule the reaction is sometime called a "proton-transfer-to–solvent" reaction (PTTS reaction)[8,9]. In non-aqueous solutions, hydroxyarenes form moderately strong hydrogen bonds of the type: O-H---O which usually do not lead to a full proton transfer reaction either in the ground or the excited-state of the photoacid.

The discovery of photoacidity was made by Förster more then 50 years ago[1-4]. Förster correctly explained the unusual large Stokes shift found in the fluorescence of several classes of aromatic dyes, including 1- and 2-naphthol derivatives as an indication of excited-state proton-transfer reaction which results in the formation of the molecular anion still in the excited-state. Thus, it become clear that excited-state proton-transfer may compete with other radiative and non-radiative decays routs of the photoacid. The main modern-days importance of photoacids lays in their ability to initiate and then to follow acid-base reactions so they may be regarded as optical probes for the study of general proton transfer reactions.

Over the years the field of photoacids (and photobases) has been reviewed many times[10-18]. The most extensive list of photoacids appeared, so far, in a 1976 review by Ireland and Wyatt[12]. The hydroxyarenes are the most widely used photoacids. In polar solutions they may undergo an excited-state proton-transfer reaction according to the following general reaction scheme:

a. Electronic excitation:

$$\mathrm{ROH} \xrightarrow{h\nu} (\mathrm{R^{*}OH})_{LE} \qquad (2)$$

b. Partial intramolecular charge transfer assisted by the solvent:

$$(R^*OH)_{LE} \rightarrow (R^{*-}OH^+)_{S_1} \qquad (3)$$

LE = locally excited singlet state, S_1 = the first singlet state of the photoacid in polar solvents. The S_1 state may be directly accessed from the ground state.

c. Formation of a reactive coordinate along a hydrogen-bond between the photoacid and a base molecule:

$$(R^{*-}OH^+)_{S_1} + B \rightarrow (R^{*-}O - H^+ \cdots B)_{hb} \qquad (4)$$

The base molecule, B, may either be a solvent or a solute molecule and hb is the hydrogen-bonded reaction complex.

This stage may involve some further electronic rearrangement in the photoacid toward the formation of the photobase.

d. Photoacid dissociation and ion-pair recombination:

$$(R^{*-}O - H^+ \cdots B)_{hb} \underset{k_r}{\overset{k_d}{\leftrightarrows}} [R^*O^- \cdots H^+ - B]_{ip} \underset{k_D}{\overset{k_S}{\leftrightarrows}} R^*O^- + {}^+HB \qquad (5)$$

ip is the ion-pair state, which may be either solvent separated or a contact pair, k_d and k_r are the "on-contact" rate constants for the photoacid dissociation and ion pair recombination, respectively.

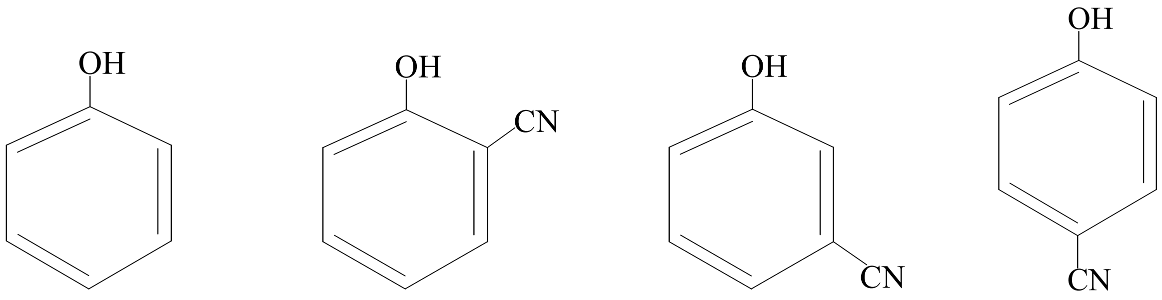
k_S and k_D are the diffusion limited rate constants for ion-pair dissociation to infinite separation and ion-pair formation, respectively[5].

The charge separation stage, *hb→ ip,* may involves considerable electronic rearrangement in the photobase.

Some of the most common hydroxyarenes[5, 8-17]which are used as photoacids are listed in Figs. (1-3). These include the phenols (Fig. 1), the 1- and 2- naphthol derivatives (Fig. 2), and the 1- hydroxypyrene derivatives (Fig. 3).

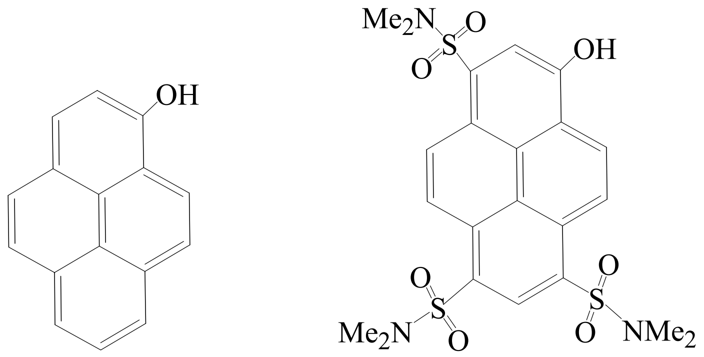
It is the aim of this chapter to describe some of the modern views on the origins of photoacidity of simple hydroxyarenes. Some of these photoacids were extensively studied in the gas-phase in solvent-clusters of various sizes including small to medium size clusters of ammonia[18-23], water[18, 20, 24-27] and methanol[28]. A second branch of research was carried out in solution and has been focusing on the various dynamic aspects of the proton transfer reaction from photoacids observed mainly in aqueous solutions[5,10-17]. The two main branches of the study of photoacids have been carried out mostly in parallel lines. The effort to converge the two methodologies into one coherent view of photoacidity is not always apparent in the literature and is far from being concluded. Indeed, much of the issues described in this chapter are still in debate or are altogether unresolved.

Figures 1-3 list some of the most representative hydroxyarenes photoacids. Phenol and phenol derivatives have been mainly used in gas-phase research due to their relatively small molecular weight and their relatively high vapor pressure[23, 29-30]. Naphthols, having intermediate molecular weights and strong photoacidities, have been studied both in the gas-phase[18-29] and in the liquid[30-51]. The pyrenols have been almost exclusively studied in the liquid due to their low vapor pressure and their excellent properties as dye molecules [5,52-66].



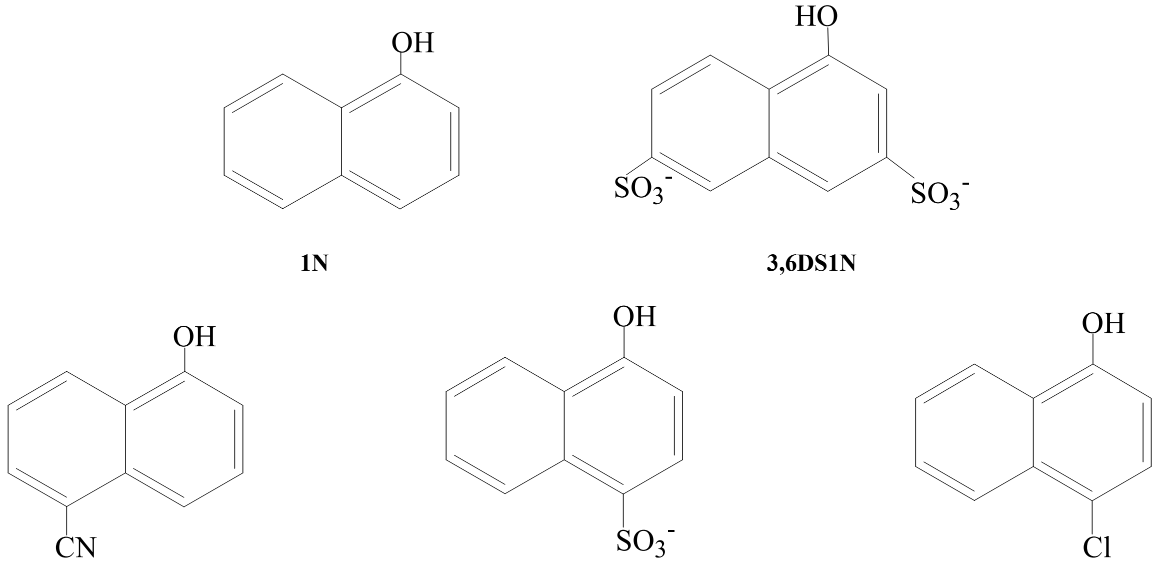
Ph **2CPh** **3CPh** **4CPh**

FIGURE 1. Molecular structure of phenol, 2-cyanophenol (2CPh), 3-cyanophenol (3CPh) and 4-cyanophenol (4CPh).



1HP **HPTA** **HPTS**

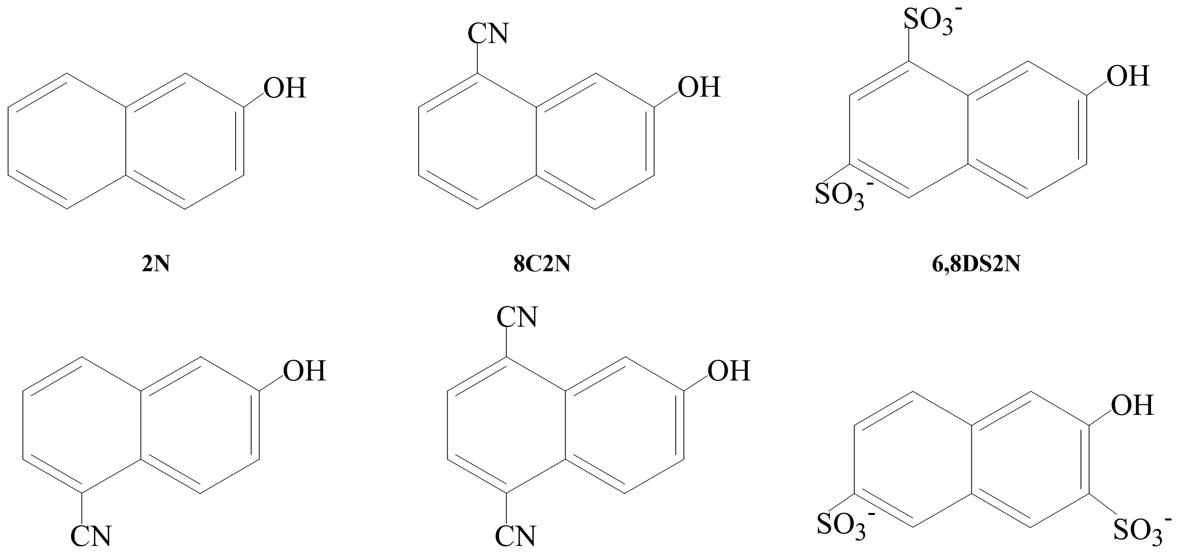
FIGURE 2. Molecular structure of 1-hydroxypyrene (1HP), 8-hydroxypyrene-1,3,6-trisulfonate-dimethylamine (HPTA) and 8-hydroxypyrene 1,3,6-trisulfonate (HPTS).



1N **3,6DS1N**

5C1N **4S1N** **4Cl1N**

FIGURE 3a. Molecular structure of 1-naphthol (1N), 1-naphthol-3,6-disulfonate (3,6S2N), 5-cyano-1-naphthol (5C1N) , 1-naphthol-4-sulfonate (4S1N) and 1-naphthol-4-chlorate (4Cl1N).



2N **8C2N** **6,8DS2N**

5C2N **5,8DC2N** **3,6DS2N**

FIGURE 3b. Molecular structure of 2-naphthol (2N), 8-cyano-2-naphthol (8C2N), 2-naphthol-3,6-disulfonate (3,6S2N), 5-cyano-2-naphthol (5C2N), 5,8-dicyano -2-naphthol (5,8DC2N) and 2-naphthol-6,8-disulfonate (3,6DS2N).

II. THE THERMODYNAMIC ASPECTS OF PHOTOACIDITY.

Photoacidity is most often described by the Förster cycle diagram, Figure 4 [2]. Following Förster, photoacidity is defined in terms of K^*_a, the excited state equilibrium constant for the dissociation reaction of the photoacid,

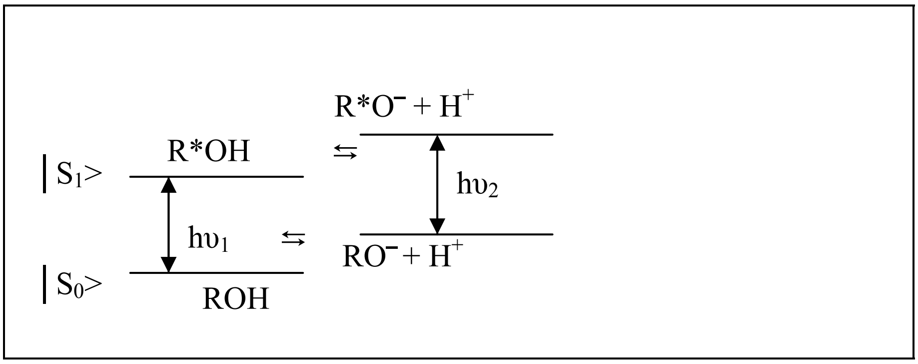


FIGURE 4. Schematic representation of energy levels of a photoacid RO*H and its conjugate base R^*O^-, $\Delta pK_a = pK_a - pK^*_a = Nh\Delta\nu / (\ln(10)RT)$, where N is the Avogadro constant and h is the Planck constant, $\Delta\nu = \nu_1 - \nu_2$, ν_1 is the 0-0 transition of the acid and ν_2 is the 0-0 transition of the anion, $|S_1>$ is the first singlet excited-state and $|S_0>$ is the ground-state.

Photoacidity occurs, per definition, when the excited molecule becomes a stronger acid in the excited state as compared to its ground state acidity, so $pK^*_a < pK_a$, where pK_a is the equilibrium constant for the proton dissociation reaction in the ground state. For phenols naphthols and pyrenols, the enhancement in the acidity constant is between 5 (1HP) and 12 (3,6DC2N) orders of magnitude, which in room temperature translates into a free-energy increase of 7 to 16 kcal/mol in favor of the dissociation reaction in the excited-state of the photoacid. Förster cycle is a thermodynamic cycle. It connects between the optical properties of the photoacid and its conjugate photobase and the thermodynamic properties of the excited-state proton transfer reaction. The main practical use of the Förster cycle is to get a rough estimation (usually, Förster cycle pK^*_a values of hydroxyarenes come within one to two pK_a units of the pK^*_a values found by direct time resolved measurements) of the excited state proton acidity of the photoacid but it does not give much clue for the molecular process(s) which are involved in photoacidity. Nevertheless, Förster cycle makes an excellent starting point for the discussion of photoacidity, as it allows the estimation of the excited-state acidity of many photoacids from simple, readily done optical measurements and establishes the idea that photoacids may be treated from a thermodynamic point of view similar to ordinary ground-state acids. Figure 5 shows the absorption spectra of phenol and the phenolate anion in water. The first 3 electronic transitions are shown for the base form while the same spectral range covers the first 2 electronic transitions of the acid form. The electronic transitions of the acid are blue-shifted compared to the electronic transition of the base. In both cases the oscillator strength of the S_1 transition is much weaker than that of the S_2 transition. The first two electronic transitions of phenol and phenolate are assigned ^1L_b (S_1) and ^1L_a (S_2) transitions according to Platt notations[67,68]. Fluorescence is from S_1 and obeys the Kasha rule, which states that internal-conversion processes are much faster then the S_1 radiative-decay rate back to the ground-state. Thus, ordinary Förster cycle calculations only consider the energies of the S_1 transitions of the photoacid and its conjugate photobase anion. Photoacidity of the first electronic triplet state () is not considered in this review.

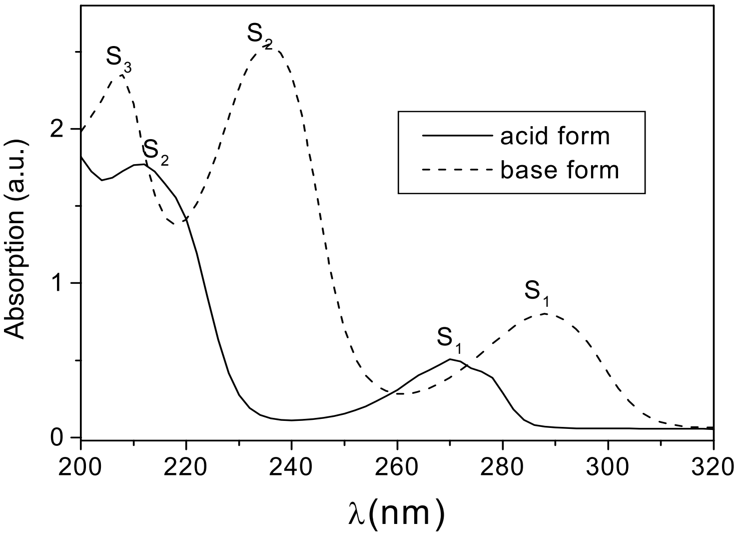


FIGURE 5. Absorption spectra of phenol and phenolate ion in water; acid form pH = 6.0, base form pH = 12. (E. Pines unpublished data).

Figures 6 and 7 shows the spectral behavior of HPTA, which is a much stronger photoacid than phenol having $pK_a^* = {}^{-}0.8$ compared to pK_a^* of about 4 of phenol. The photoacidity of HPTA sufficiently large for HPTA to dissociate in pure methanol, while proton dissociation of excited phenol is not observed even in water.

Weller[5,32,33] have shown that photoacids may be titrated while in the excited state by monitoring their fluorescence intensity as a function of the pH of the solution. The fluorescence titration curves, after lifetime correction, yield similar information to the information gathered by acid-base titrations in the ground-state. Thus, the gradual addition of a strong mineral acid such as HCl to a solution of a photoacid gradually shift the acid-base equilibrium both in the ground- and the excited-state of the photoacid toward the acid form when the titration starts in basic conditions.

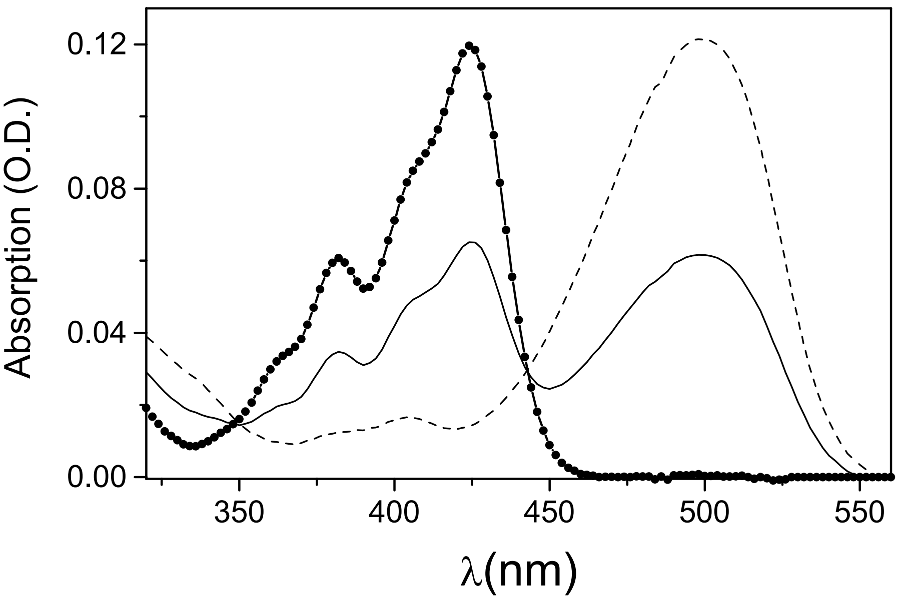


FIGURE 6. Absorption spectra of HPTA in MeOH: the base form at 499 nm was titrated by trifluorosulfonic acid. The acid form is at 425 nm. Full line: intermediate pH at which both acid and base forms are present in the solution. (E. Pines, unpublished data).

In Figure 6 the shift in the ground-state equilibrium populations of the acid and base forms of HPTA was monitored by absorption spectroscopy, while the corresponding shift in the excited-state population as a result of the change in the pH of the solution was monitored by fluorescence spectroscopy and is shown in Figure 7. Only S_1 transitions are depicted.

The pK^*_a found in this way may be directly compared with Förster cycle calculations. However, straight-forward utilization of the fluorescence titration method is usually limited to moderately strong photoacids due to partial deactivation processes of the photoacid occurring in very concentrated mineral acid solutions. The most accurate method of finding the pK^*_a of a photoacid is by direct kinetic measurements of the excited-state proton dissociation and recombination rates [58-60]. However these measurements are not trivial and are limited to relatively small number of photoacids were accurate measurement of the excited-state reversible dynamics of the proton transfer reactions are possible.

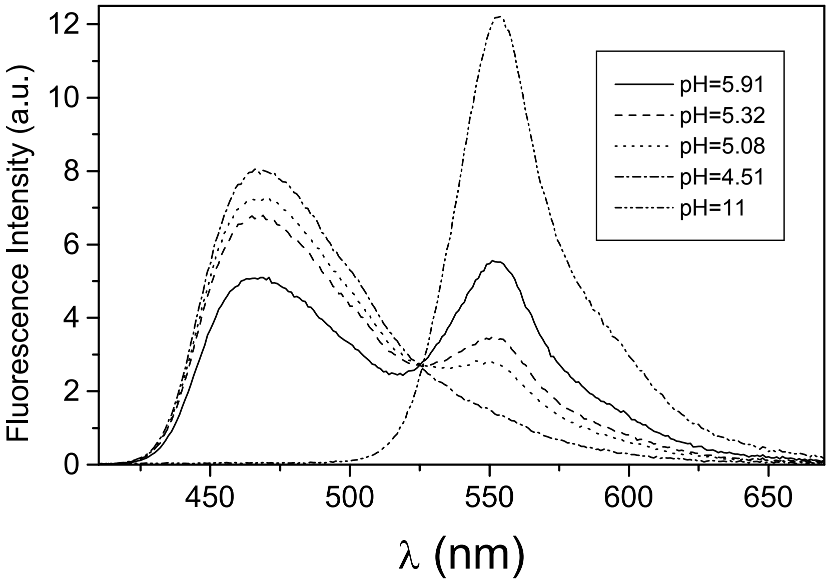


FIGURE 7. Excited-state acid-base equilibrium of HPTA in MeOH followed by the fluorescence titration of the base form. The base was titrated by trifluorosulfonic acid. Acid band is at 466 nm and base band is at 553 nm. Notice the red shift in the fluorescence spectra compared to the absorption spectra shown in Fig. 6. (E. Pines unpublished data)

Förster cycle calculations thus appear to be the most general way for estimating the pK^*_a values of photoacids. There was some confusion in the past regarding the practical method for estimating the 0-0 transitions of the photoacid in solution. Using either the absorption spectra or the fluorescence spectra alone usually introduces considerable errors into the calculation, each set of data producing a different pK^*_a value. Estimating the 0-0 transitions from the crossing points between the absorption and the fluorescence spectra of the photoacid and the photobase is not always possible. Weller [67] suggested to average the transition energies of absorption and fluorescence taken at the peak intensities of the transition bands. The averaging procedure is carried out for the photoacid-side transitions and for the base transitions. Förster cycle calculations with the averaged transition energies values is usually found to fall within one pK^*_a unit of the true pK^*_a value found by direct measurements.

The absorption maxima of the phenol and phenolate anion appear to be in water at 270 nm and 286 nm respectively. Introducing these values into Förster cycle together with the known ground-state pK_a of phenol (9.99) gives a pK^*_a of 5.7 which underestimates the acidity of excited phenol. Introducing the values of the fluorescence maxima of 229 nm (phenol) and 336 nm (phenolate) gives a pK^*_a of 2.3 which overestimates the photoacidity of phenol. Introducing the averaged transition energies gives a pK^*_a of 4.0 which should be a good value for the photoacidity of phenol. The averaging procedure seems even to work in cases were the emitting state is thought to be different than the state directly accessed by absorption. An example for this is 1-naphthol were the averaged Förster cycle value is about -0.5 compared to the directly measured value of -0.2.

Table 1 summarizes the pK_a and pK^*_a values in water of the photoacids shown in Figures (1-3). The pK^*_a values were found from Förster cycle calculations if not otherwise stated. Most of the error in the Förster cycle calculations appears to be instrumental, i.e., the error introduced by uncertainties in the spectroscopic measurements of the absorption and fluorescence maxima. Misreading or uncalibrated instrumental reading of 1nm at 275nm will result in 0.3 pK^*_a units error. The severity of this problem tend to relax by the averaging procedure outlined above which usually results in 'cancellation of errors'. This is especially important when the reading errors are systematic. Even so, deviations of up to one pK^*_a units between the spectroscopic data of different laboratories appear to be common. Large data base of pK^*_a values from various sources was summarized in ref. (12). The pK^*_a values given in Table 1 are judged to be reliable.

Table 1. pK_a and pK_a* values of some common hydroxyarene photoacids.

Photoacid	**pK_a**	**pK_a***
phenol	9.82 [69]	4 [70]
2-cyano-phenol	6.97 [71]	0.66 [71]
3-cyano-phenol	8.34 [71]	1.89 [71]
4-cyano-phenol	7.74 [71(a)]	3.33 [71(a)]
1-hydroxypyrene	8.7 [12]	3.6 [12]
HPTS	8.0 [59]	1.4 [59]
HPTA	5.6 [72]	-0.8 [72]
1-naphthol	9.4 [78]	-0.2 [45]
1-naphthol 3,6-disulfonate	8.56 [73]	1.1 [42]
5-cyano-1-naphthol	8.5 [47]	-2.8 [47]
1-naphthol-4-sulfonate	8.27 [74]	-0.1 [74]
2-naphthol	9.6 [78]	2.8 [9]
5,8-dicyano-2-naphthol	7.8 [9]	-4.5 [9]
5-cyano-2-naphthol	8.75 [9]	-0.3 [9]
8-cyano-2-naphthol	8.35 [9]	-0.4 [9]
2-naphthol-6,8-disulfonate	8.99 [73]	0.7 [71(b)]

III. On the origins of photoacidity

It makes sense to start the discussion on the molecular-level processes which are responsible for photoacidity by first analyzing Brönsted-acidity in general .

The attachment of a proton to a negatively charged molecule or to a neutral molecule is always a very exothermic process in the gas phase, the proton affinity (PA) of most common organic molecules being between 160 and 220 kcal/mole [75,76] where proton affinity the energy gained in the following process in the gas phase:

$$M + p^+ \rightarrow Mp^+ \qquad (6)$$

where M is the isolated molecule in the gas phase and p+ is the proton. When the proton is attached in the gas phase to a negative ion such as the phenolate anion, one may express the proton affinity of the anion using the following ionization route:

$$ROH \rightarrow RO\cdot + H\cdot \qquad (7)$$

$$H\cdot \rightarrow H^+ + e^-$$

$$RO\cdot + e^- \rightarrow RO^-$$

$$ROH = H^+ + RO^-$$

It follows that the proton affinity of RO^- in the gas phase reaction $RO^- + H^+ \rightarrow ROH$ may be broken down to three separate contributions: the formation of the ROH bond D(ROH), the attachment of an electron to the proton I(H) and the ionization of the molecular anion, $E(RO^-)$. The first two processes are exothermic and the third one, endothermic:

$$PA(RO^-) = D(ROH) + I(H) - E(RO^-) \qquad (8)$$

where I(H) is equal to the ionization energy of the hydrogen atom and $E(RO^-)$ is equal to the electron affinity of the molecular radical. The gas phase proton affinity of anions is much larger then the proton affinity of their corresponding neutral molecules. Two examples are:

PA(H_2O) = 167 kcal/mol, PA(OH^-) = 391 kcal/mol; PA(HF) = 117 kcal/mol, PA(F^-) = 371 kcal/mole[75,76]. The difference between the proton affinities of the neutral molecules and the proton affinities of their corresponding anions being usually more then 200 kcal/mole, and is attributed mainly to the neutralization of the charge of the proton by the anion. The proton affinity of the phenolate anion is about 350 kcal/mol, which is significantly less then the typical proton affinities of small anions, the difference between PA(OH^-) and PA(PhO^-) being about 40 kcal/mol, which is partly due to the stabilization energy of the phenolate anion by electronic resonance which shifts some negative charge away from the oxygen atom to the benzene ring and is expected to be larger than the electronic resonance energy of phenol. One may conclude that Brønsted basicity rather than Brønsted acidity is the fundamental property of neutral molecules and negative ions in the gas-phase, and that molecular properties and charge distribution affect the inherent gas-phase basicity of molecular anions. In situations where a second base is present in the gas-phase a proton transfer reaction may occur:

$$ROH + B = RO^- + BH+ \qquad (9)$$

The free energy change, ΔG, of such a reaction in the gas- phase is simply PA(RO^-)-PA (B). When B is OH^- then ΔG_g is PA(RO^-) – PA (OH^-) = - 41 kcal/mole (ROH is phenol), so in this reaction the phenol molecule acts as the Brønsted acid and the OH^- anion as the Brønsted base. Clearly, relative proton affinities values determine the relative acidity scale of molecules in the gas-phase.

Brønsted acidity comes into play in condensed phases, where proton dissociation is stabilized by the solvent or by other solute molecules which act as proton acceptors (bases). The acid dissociation of phenol in solution may be written as:

$$(ROH)_s = (RO^-)_s + (H^+)_s \tag{10}$$

where s denotes fully solvated (equilibrium solvation) species. The overall free-energy change (and hence the proton dissociation constant, see below) following the proton dissociation reaction in a solvent s is given by:

$$\Delta G_s = \Delta G_g + \Delta G_t(RO^-) + \Delta G_t(H^+) - \Delta G_t(ROH) \tag{11}$$

where ΔG_g is the free-energy change upon proton dissociation in the gas-phase and $\Delta G_t(X)$ is the free-energy change upon transferring the reactant X from the gas-phase to solution.

The conventional thermodynamic description of an acid dissociation in solution is by the equilibrium constant of the dissociation reaction:

$$K_a = [RO^-][H^+]/[ROH] \tag{12}$$

where,

$$K_a = \exp[-\Delta G_s/RT] \tag{13}$$

It follows that,

$$pK_a = \Delta G_s /\ln(10)RT = \Delta G_s/2.3\ RT \tag{14}$$

It is usually extremely difficult to calculate ΔG_s of ground-state acids from first principles with uncertainty of less then several kcal/mole which translates into uncertainty of several pK_a units. In the excited–state an additional difficulty involves the accurate electronic description of the excited state, which makes the task of calculating the pK_a* of a photoacid even tougher. A recent attempt [77] to calculate the excited state pK_a* of phenol resulted in a value larger by more then 4 pK_a units then the experimental one (−0.2 compared to the experimental value of about 4). A very recent calculations of the ground-state pK_a of phenol resulted also in over-estimation of the dissociation constant, 7.2 compared to the experimental value of about 10.0 [31].

To have a feeling for the computational difficulties involved in this type of calculation equation (12) may be rewritten as:

$$\Delta G_s = PA\,(RO^-) - \Delta G_t(H^+) + \Delta G_t\,((RO^-) - (ROH)) \qquad (15)$$

For phenol one has, PA (phenolate) = 350 kcal/mole, ΔG_t of the proton is about 260 kcal/mole [76] and $\Delta G_t\,((RO^-) - (ROH))$ may be roughly estimated assuming it is mainly given by the Born free-energy of solvation of charged cavities immersed in a dielectric continuum:

$$\Delta G_{Born} = e^2/2\,(1 - 1/\varepsilon_s)(1/r_B) \qquad (16)$$

where e is the electron charge, ε_s is the static dielectric constant of the solvent and r_B is the radius of the Born cavity around the charge, which may be approximated by the radius of the isolated ion. The solvation energy (Born-energy) is calculated for a transfer from vacuum conditions to the solvent s.

Substituting in eq. (11) the known experimental parameters for phenol dissociation, (ΔG_s = 13.8 kcal/mole calculated from the ground-state equilibrium constant, pK_a =10.0) $\Delta G_t\,((RO^-) - (ROH))$ of the phenolate/phenol system is about -76 kcal/mole which is about 10% less then the accepted value for the electrostatic solvation energy of the chloride anion in water, $\Delta G_e(Cl^-) = -85$ kcal/mole. These simple considerations imply that the ΔG_t ((RO$^-$) – (ROH)) contribution to the overall free energy of solvation is largely electrostatic, and that relatively small differences in the gas-phase proton affinity of the base and in specific solvent-solute interactions of the photoacid and the base determine the relatively narrow (in free-energy units) acidity-scale in aqueous solution. It is clear that the calculation of the absolute pK_a values in solution from first-principles is a formidable task if one insists that the calculated pK_a values should exactly reproduce the experimental ones. A one pK_a unit error in the calculated pK_a translates into a mere 1.3 kcal/mole error in the calculated overall stabilization energies of all species involved in the proton dissociation reaction, each of these stabilization energies being about two orders of magnitude larger then the desired error bars.

This situation considerably improves if one limits himself to the calculation of the relative acidity of the excited-state compared to the acidity in the ground-state. It is clear that photoacidity depends on the difference between ground and excited state free-energies of solvation. Of all the parameters appearing in equation (12), only $\Delta G_t(H^+)$ does not depend on the electronic state of the photoacid:

$$pK_a^* - pK_a = (\Delta G_s^* - \Delta G_s)/2.3RT =$$

$$= (PA(R^*O^-) - PA(RO^-) + \Delta G_t((R^*O^-) - (RO-)) + \Delta G_t((ROH) - (R^*OH)))/2.3RT \qquad (17)$$

Equation (17) may be viewed as an explicit form of the Förster cycle. It depends on both intramolecular and intermolecular factors which determines the extent of the photoacidity. These factors are the difference between the excited-state and the ground-state proton affinities of the photobase. This difference will be equal to the difference in the intramolecular stabilization of the proton upon the electronic excitation of the acid, and will depend, in general, on the quantum mechanic properties of the first excited electronic state of the photoacid. The second factor is the difference in the solvation energies of base and photoacid upon electronic excitation. The magnitude of the solvation energy terms will depend in general both on the solvent and the solutes and will depend on the electronic state of the photoacid and its conjugate base.

The traditional approach has been to define photoacidity as an intramolecular property of the photoacid[10,12,13,79,80]. In terms of equation 17, this approach places the main reason for photoacidity in reduced proton affinity of the molecular anion in the electronic excited state. Alternatively, this means that photoacidity is mainly the result of the reduction in the dissociation energy of the photoacid in the gas-phase upon electronic excitation. What is the reason behind this reduced proton affinity of the photobase?

There are two views regarding this scenario. The traditional view has been to place photoacidity mainly with the increased reactivity of the photoacid in the excited state brought about by charge migration from the non-bonding electrons of the oxygen atom to the aromatic π system of the photoacid (n-π^* transition), thus weakening the O-H bond and making the photoacid a stronger acid in the excited state. The aromatic residue is viewed in this approach as becoming more electronegative in the excited-state shifting some electron density away from the oxygen atom thus making it a weaker base[80,81]. This intramolecular charge redistribution following electronic excitation is stabilized by polar solvents. This view of photoacidity is portrayed in Figure 8. The increased acidity of 2-naphthol in the excited-state is rationalized assuming that a partial positive charge develops on the oxygen atom and a partial negative charge develops on the distal aromatic ring of the naphthol. The oxygen atom, then, becomes partially "repulsive" toward the proton which in turn explains the rapid dissociation of the proton observed in the excited state[80,81].

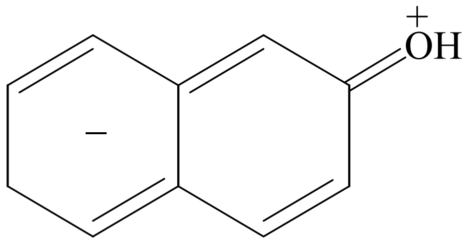


FIGURE 8. A traditional view of the electronic structure of a "classic" photoacid, 2-naphthol in its first electronic excited state. (after Bell[80])

A second, very recent view of photoacidity, places the main electronic rearrangements within the product side of the dissociation reaction (the photobase)[66,77,82]. This view is backed by ab initio and semi-empiric calculations of the electronic distribution of several photoacids and photobases which show the excited-state of the photobase to have a much larger CT character than the corresponding electronic state of the photoacid[66,77]. No significant n-π^* transition was observed in the photoacid side of phenol and pyrenol. According to this recent view of photoacidity, photoacids become stronger acids in the excited state because the photobase become much weaker base in the excited state. It is clear from the foregoing discussion, that both scenarios full within the arguments leading to equation 17 and define acidity in general terms. Rather, the two scenarios differ in the details of the molecular mechanism which is responsible for the proton affinity of the photobase being less in the excited-state in respect to the ground-state: Is it because the excited base is less reactive toward the proton brought about by larger internal stabilization energy of the negative charge, hence the smaller proton affinity (second scenario), or is the proton affinity of the excited anion smaller because the formed photoacid is less stable and more reactive (first scenario)? There is already a debate developing over this second recent scenario [66,82] : Is it or is it not a true revisionist description of photoacidity? Clearly, this question goes back to the basic definition of Brønsted-acidity: Is acidity some inherent property of the acid or is it just reflecting the low reactivity of the base toward the proton? In other words, is it possible to define an acidity scale based entirely on the properties of the acid? And by doing so is it possible to separate between the actual proton transfer act, which clearly depends also on the stabilization energy of the base (both internal (gas phase) and external (solvation) energies) and the property we call "acidity"? Excited-state proton transfer may or may not happen during the lifetime of the excited-state depending on the polarity of the solvent. So should it not be better to concentrate on the intramolecular processes occurring at the acid side regardless if they lead to an observed proton transfer reaction? In other words, is there a better way to define photoacidity than by using Brönsted-type terminology and the pK^*_a scale?

Aside from these fundamental questions, some more questions arise from the practical difficulty in exactly calculating the Förster cycle parameters of a photoacid from first principles (equation 17). From a thermodynamic point of view, in order to justify a product-side-driven reaction it is not sufficient to identify a larger electronic rearrangement in the excited state of the base than the rearrangement found in the excited acid side. One rather has to show that both internal energies and solvation energies of the photobase are larger than in the ground-state and are driving the proton dissociation reaction and so are the main reason behind the enhancement in the acidity of the photoacid. In this stage one can not conclude with certainty from either theoretical or experimental consideration that this is indeed the general situation which account for photoacidity (see the following section) . In contrast, it is rewarding to point out several experimental observations which, although do not prove, point out that both the acid side and the base side are active in determining the extent of photoacidity of hydroxyarenes in solution. The first observation which probably has led to the traditional view of photoacidity, is that most of the enhanced acidity of excited hydroxyarenes may be traced back to the increase in the dissociation rate of the photoacid and to a much lesser extent to the decrease in the rate of the proton recombination to the photobase. Taking HPTS as an example, the dissociation rate of the acid on contact (i.e., excluding the effect of the electrostatic attraction between the proton and the anion) in the excited-state increases by about 5 orders of magnitude, from about 10^5 s^{-1} to about 10^{10} s^{-1}. At the same time, the proton recombination rate to the photobase decreases by about 2 orders of magnitudes, from less then $10^{12}s^{-1}$ to about $3x10^9s^{-1}$. For 1-naphthol the situation is even more extreme. The dissociation rate of the photoacid increases by about 8 orders of magnitude while the recombination rate of the proton to the photobase decreases by less than 2 orders of magnitude. Clearly, the main dynamic effect appears from the photoacid side and not from the photobase side. However, this observation is by no means a general rule of photoacidity. There are good indications that the extreme excited-state acidity of protonated amine photoacids such as the protonated 1-aminopyrene photoacid [15], comes from a very large reduction in the photobase reactivity, while the dissociation rates of the photoacids do not increase dramatically in the excited-state and are typically two orders of magnitudes smaller than the dissociation rates of hydroxyarenes photoacids having similar pK^*_a values [83].

The second observation concerns the increase in the hydrogen-bonding interaction of the O-H moiety of the hydroxyarenes. Several observations of this effect were reported in the past, for phenol, naphthol and pyrenol derivatives. Perhaps the most direct observation concerns the red shift observed in the IR absorption frequency of the complexed O-H bond. A shift of about $250cm^{-1}$ was observed for $O\text{-}H\cdots O$ and $O\text{-}H\cdots N$ type bonds of 1:1 complexes of 1-naphthol with water and ammonia when 1-naphthol was electronically excited. This shift translates to about 0.7 kcal/mole increase in the hydrogen-bonding interaction in the excited-state of the photoacid. A similar effect was observed in solution by Weller for the system 1-hydroxypyrene complexed with pyridine in methylcyclohexane[5]. Other observations include phenol and 1- and 2-naphthol complexed with dioxane in isooctane[34], and HPTA complexed with dioxane and DMSO in dichloromethane and dichloroethane[84]. In all cases the hydrogen-bonding interaction of the photoacid were found to increase upon electronic excitation by 0.5-3 kcal/mole. No proton transfer was observed in these systems.

The increase in the hydrogen-bonding interaction in the electronic excited- state of the photoacid is a very convincing indication for stronger hydrogen bonds as compared to the ground–state situation. According to the widely accepted model of Pimentel[85,86] for the effect of the hydrogen-bonding interaction on the electronic transitions from- and to the ground electronic state of the chromophore, a situation where both the absorption and the fluorescence spectra are red-shifted and the fluorescence shift being the larger one, can only arise from the hydrogen-bond being stronger in the excited-state. This is, indeed the situation for 1- and 2-naphthol and HPTA. Finally, the spectral shift of the photoacid due to polar interactions with the solvent may be correlated with empiric solvent parameters in a procedure suggested by Kamlet and Taft and their co-workers (the K-T analysis[87-89], see below). Such correlations usually result in a much larger effect of solvent basicity (β factor) on the fluorescence spectra of the hydroxyarene than the solvent basicity effect on the absorption spectra, indicating, again, according to Pimentel's model[85,86], stronger hydrogen bonds in the excited-state of the acid. It does appear, then, that the O-H moity of hydroxyarenes forms stronger hydrogen-bonds in the excited-state implying photoacidity emerging, at least partially, from the photoacid side. A correlation between the aqueous pK_a values of various acids and the strength of the hydrogen-bonding interaction of their acidic proton was demonstrated in the solid-state by NMR measurements giving some direct evidence that stronger acids form stronger hydrogen-bonds[90]. The NMR measurements have been mainly carried out in non-polar environments which do not support the ionization process involved in the proton dissociation reaction of hydroxylarenes.

The relative strength of the hydrogen-bonding interactions may also be estimated indirectly by correlating their effect on the optical transition frequencies of the chromophore. In the Kamlet-Taft (K-T) analysis [87-89], any solvent-influenced property of the solute may be correlated using a multi-parameter fit, eq. 18,

$$P_{s\text{-}s} = P^{o}_{s\text{-}s} + s\pi^{*} + a\alpha + b\beta \tag{18}$$

where $P_{s\text{-}s}$ is the measured solvent-influenced property of the solute; $P^{o}_{s\text{-}s}$ is the numeric value of the chosen solute property in cyclohexane; π^* is the normalized solvent polarity scale; α and β are the solvent acidity and the solvent basicity scales respectively. s, a and b are solute dependent and are the specific numeric coefficients, which characterize the solute molecule. The π^*, α and β parameters are assumed to be independent of each other (orthogonal) and additive, i.e., an ideal binary mixture of two solvents, should correlate according to their combined values of π^*, α and β weighted by their relative composition in the solvent mixture.

Figure 9 shows an example of correlating the spectral shift of the peak fluorescence frequency of HPTA photoacid with the K-T parameters of several organic solvents. Most of the investigated solvents did not support proton-dissociation within the lifetime of the excited-state of HPTA which is about 3.7 ns.

The K-T analysis which is backed by direct IR measurements of the absorption of the stretching frequency of the O-H bond, shows that HPTA act as strong hydrogen-bond donor (large beta value) through hydrogen-bonding interaction of the type O–H···s [91]. At the same time, there is no evidence for the oxygen atom accepting hydrogen- bonds of the type

O···H—s (a small α value). This means large sensitivity of the fluorescence spectra to the basicity of the solvent, and much smaller sensitivity to the acidity of the solvent. In addition, the photoacid exhibit large sensitivity to the polarity of the solvent (the π* factor), indicating a relative large dipole moment of the photoacid in the excited-state compared to the ground-state.

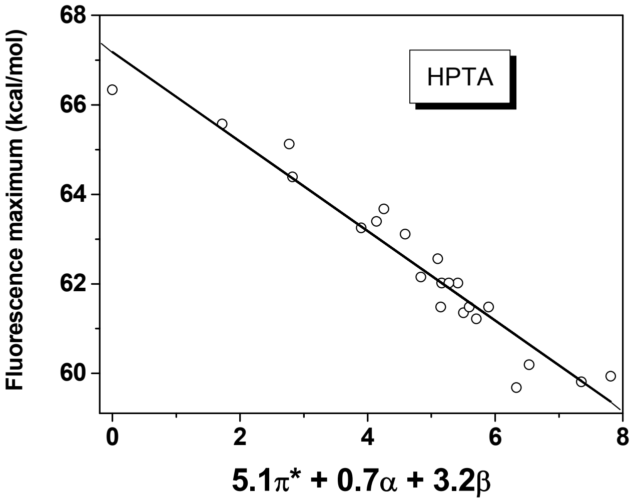


FIGURE 9. Correlation of the fluorescence spectra of HPTA measured in pure solvents with Kamlet-Taft solvent - polarity parameters [91].

In an additional set of similar experiments the methoxy derivatives of HPTA, HPTS [91] and 1- naphthol [91] and 2-naphthol[49] were examined by the K-T procedure. It was found that replacing the proton by the methoxy group almost eliminated the hydrogen-bond interactions of the oxygen atom, so solvent basicity had a much smaller effect on the fluorescence spectra of these methoxy-photoacids (Figure 10). At the same time the shape of the spectra, its location and the π* parameter remained almost unchanged, indicating that the intrinsic electronic structure of the methoxy derivative is analogous to that of the photoacid.

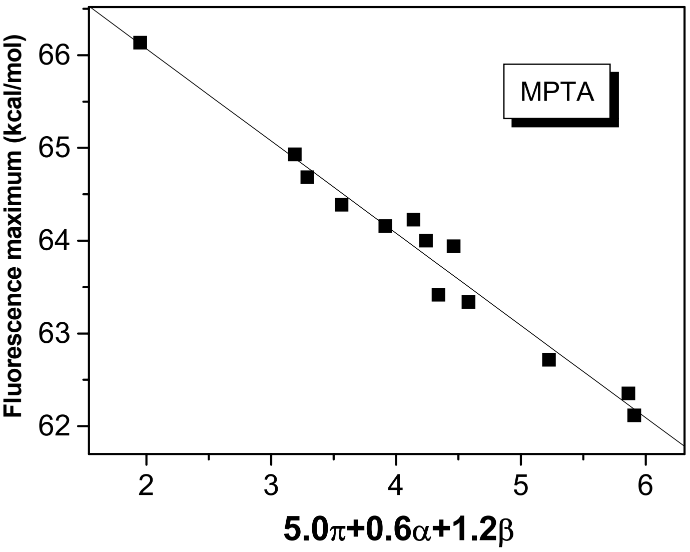


FIGURE 10. Correlation of the fluorescence spectra of MPTA measured in pure solvents with Kamlet-Taft parameters. MPTA has similar electronic structure to HPTA but is much less affected by hydrogen-bonding interactions[91].

In contrast, it was found by a similar K-T analysis that the conjugate photobase acted as a hydrogen-bond acceptor in the ground-state accepting an hydrogen-bond of the type $RO^{-}\cdots s$ [49]. This set of observations supports the idea that both the acid-side and the base-side are generally active in determining the extent of photoacidity of hydroxyarenes. The acid being a stronger acid in the excited-state while the base being a stronger base in the excite-state.

Finally, there appears to be a correlation between the acidity of the photoacid in aqueous solutions and the strength of the hydrogen-bonding interaction, see Figure 11[91]. This observation is in accord with the general observation stated earlier that the stronger is the acid the stronger are the hydrogen-bond interactions that it undergoes with a given base.

Figure 11 shows the hydrogen-bonding free-energy of interaction of a series of hydroxyarenes photoacids plotted against their photoacidity strength scaled in terms of their free-energy of proton-dissociation in aqueous solutions. There is a linear correspondence between the two values indicating that the relative strength of hydroxyarene photoacids in non-polar solvents may be scaled using their relative pK^*_a values in aqueous solutions.

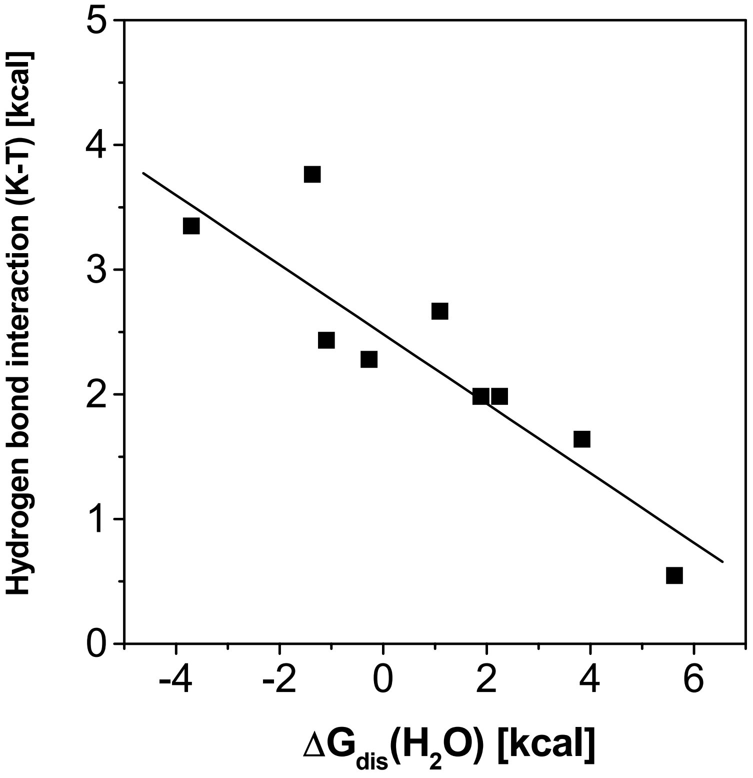


Figure 11. The hydrogen-bond interaction of hydroxyarenes photoacids in a DMSO-like solvent against the dissociation free energy of the photoacids in water [91].

A general rule may be extracted from these observations. For a given hydrogen-bond donor (the photoacid) the strength of the hydrogen-bond that it forms in the excited-state with an hydrogen-bond acceptor (a solvent molecule, or an additional base molecule dissolved in the solvent) will increase with the increase in the β value of the hydrogen-bond acceptor. Similar observation holds for a given hydrogen-bond acceptor. In this case, the hydrogen-bond strength will increase with the α value of the proton donor.

In conclusion, it is the opinion of this review that photoacidity manifest itself both in the photoacid and the photobase sides, the reactant-side becoming a stronger acid and the product-side becoming a weaker base in the excited state. It is still a matter of additional experimental and theoretical studies to establish if general rules can be drawn out concerning the relative importance and generality of these processes. Similarities to ground-state situation should also be pointed out. The following remarks concerning the debate over the traditional description of photoacidity may help clearing this issue. Enhanced-acidity due to the anion side stabilized by electronic resonance has been a text-book explanation for the marked ground-state acidity of hydroxyarenes. Electronic resonance stabilization of the anionic charge by the aromatic ring is traditionally considered the main effect for the increased acidity of hydroxyarenes compared with the acidity of non-aromatic alcohols and the main reason for strong deviation from Hammett's type structure-acidity correlations, See Figures 12 and 13. Figure 12 is adopted from Hammett's book[92] and was used to explain the very large acidity of p-nitrophenol. In this case, the resonance structure of the anion is much more important than the resonance structure of the acid, resulting in a great increase in the acidity of the substituted phenol as compared with the predicted inductive effect of the p-nitro group.

Figure 13 is adopted from a collage text book on organic chemistry[93]. In this case, the resonance structures of the phenolate anion are thought to be more important than the resonance structures of the phenol molecule by several kcal/mole. This was used as an argument for the increased acidity of phenol over non-aromatic alcohols[93].

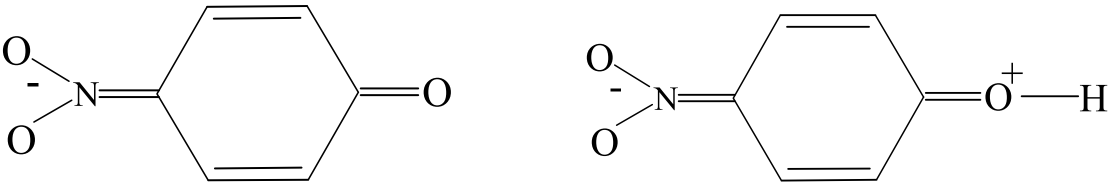


Figure 12. Resonance structures of p-nitrophenol and its conjugate anion in the ground-state (after Hammett [92]).

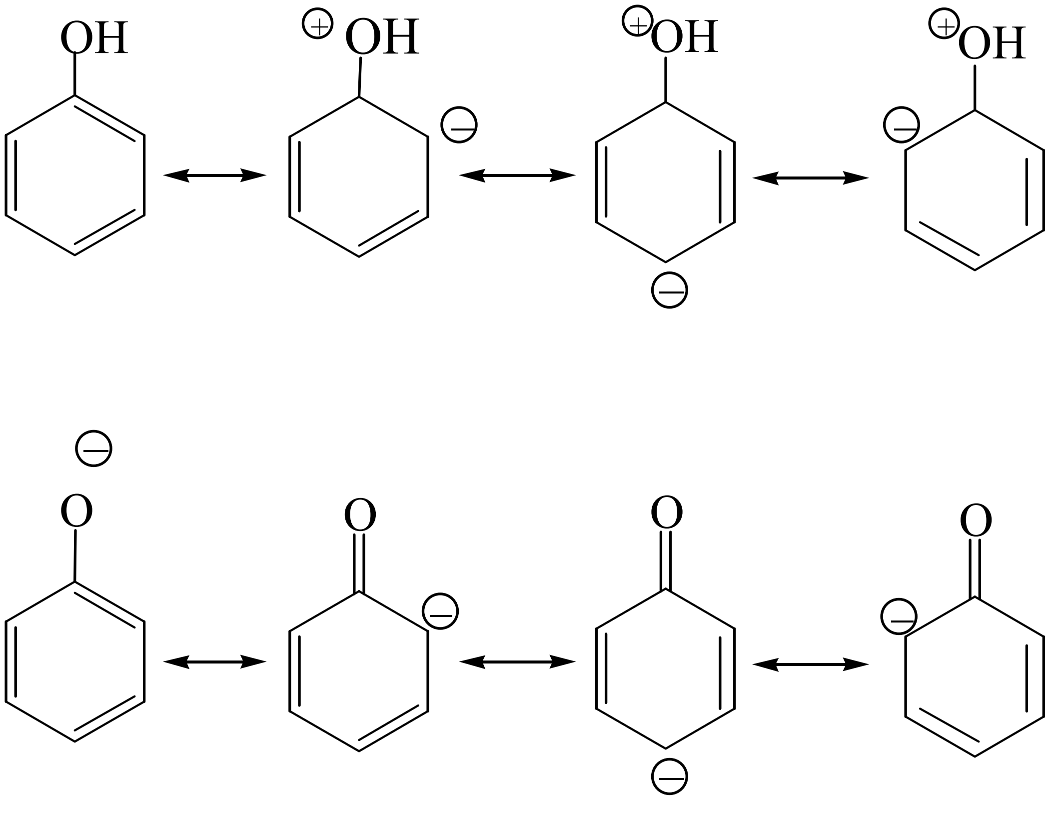


FIGURE 13. Resonance structures of phenol and phenolate anion in the ground-state[93].

However, having saying that, the anion-side scenario was generally overlooked when excited-state photoacidity was considered even in cases where it has become evident that the photobase undergoes an extensive intramolecular charge transfer process. As an example, an extensive charge-transfer process has been assumed in the 1-naphtholate anion where a recent ab initio calculation showed that roughly 2/3 of a unit charge are transferred from the oxygen atom to the naphthalene ring[46,51]. In contrast, the electronic structure of the photoacid did not show such an extensive charge transfer process. This observations have been made without remarking which side is more active in determining the overall photoacidity of 1-naphthol. All said, it is perhaps best to refer to Bell's book "the proton in chemistry" [80], which about 30 years after the publication date of its 2nd edition is still, arguably, the most authoritative contribution on the physical aspects of acid-base reactions. In Bell's book, almost side by side, ground-state and excited-state acidities of hydroxyarenes are discussed. To account for the considerable ground-state acidity of phenol Bell invokes the anion-side electronic- resonance description of the phenolate anion which reduces the reactivity of the base by spreading part of its negative charge over the aromatic residue. In contrast, the large increase in the excited-state acidity of 2–naphthol is attributed, exclusively, to a resonance structure of the photoacid similar to the one shown in Fig 8. In view of many similar arguments appearing all over the literature describing photoacidy in terms of the increased acidity of the acid-side [12], it is only fair to say that the recent paper by Hynes and coworkers[66] was very important and constructive in stressing the importance of the anion-side charge transfer reaction in the excited-state of photoacids, and by doing so, in a somewhat paradoxical way, making photoacids more like ordinary ground-state acids than, perhaps, what has been traditionally thought before.

Finally, we believe that a search for a new, more general, definition of photoacidity is in place perhaps through their ability to form strong hydrogen-bonds in the excited state, regardless if proton dissociation occur within the excited-state lifetime of the photoacid. Thus, it may well be rewarding to describe the photoacidity phenomenon in terms not necessarily connected to proton-transfer and Brønsted-acidity and by doing so making the definition applicable to a larger group of molecules and extending its application to non-polar environments where no proton transfer occurs within the excited-state lifetime. Clearly, much more studies are needed to be carried out before conclusive treatments of these issues may be brought out.

IV. THE ELECTRONIC STRUCTURE OF PHOTOACIDS.

The origins for the enhanced acidity of hydroxyarenes and other photoacids are clearly placed in the differences between the quantum mechanic properties of the first electronic singlet-state (the fluorescence emitting state) and the ground electronic state of the photoacid. Aside from the question which reaction side (acid or base) is more important in determining the pK^*_a of the excited photoacid one faces a more fundamental question in why photoacidity occurs at all. To answer this question one should deal with the electronic structure of the photoacid in the excited-state. Both the electronic structure of the photoacid and the photobase are important in determining the observed increase in the Brønsted-acidity of the photoacid in the excited-state. The elucidation of the electronic structure of hydroxyarenes in the excited-state has become one of the most intriguing and demanding tasks in photoacid research. Although considerable progress has been made, our current understanding of this problem is still far from being conclusive on the underlying questions of photoacidity. Is there a 'special' electronic state which is responsible for photoacidity? Is this 'special' state accessed directly from the ground-state? How long it takes for the electronic-state to relax from the locally-excited (LE) state to this photoacidity-state in case it is not accessed directly from the ground-state? What intra- and intermolecular processes control the rate of this electronic relaxation? Which is the more important electronic rearrangement, the one occurring at the acid side or the one occurring at the anion side?

From experimental and theoretical point of view, these questions should have been approached by first of all undertaking the task of spectroscopic assignment of the first few electronic transitions covering the relevant absorption and fluorescence spectra of the photoacids in question. Unfortunately, the systematic analysis of the electronic spectra of hydroxyarenes has met with great difficulties already in the stage of the spectroscopic assignment. In many cases the electronic spectra of the photoacid is congested and is usually thought to be made of two overlapping transitions, each of them mixed to a various degree with other, higher-lying electronic states.

The discussion of the theoretical aspects of the electronic structure of optically excited hydroxyarenes has been greatly influenced by the work of Platt and his co-workers at the University of Chicago. A source book of the papers of the Chicago group (1949-1964)[68b] summarizes the Chicago group considerable contribution to the interpretation of the electronic spectra of simple aromatic systems. Platt's model utilizes the free-electron molecular-orbital method (when applied to conjugated linear chains of alternating single and double bonds as found in some polyenes this method is sometimes called the "electron in a box" model). Platt applied this model to aromatic molecules which may be viewed as having π electronic system lying on a single closed loop or a '"perimeter". Platt's "Perimeter Model" was developed for "catacondensed" hydrocarbons, whose general formula is $C_{4n}+2H_{2n+4}$ and their carbon atoms form a single periphery. The general results of the model which was backed by experimental findings where the following: There are regularities in spectra of simple aromatic compounds. These regularities are the energies of their lower electronic levels, the ordering of the levels according to one spectroscopic scheme and the distinctive molecular orbital characteristics of each level. The energy of these levels changes smoothly moving from one molecular system to the other.

The lowest four electronic levels common to all catacondensed hydrocarbons are according to Platt's notation, ^1L_b,^1L_a,^1B_b and ^1B_a. The L transitions are generally forbidden having very small oscillator strength, while the B transitions are strongly allowed having typically between one to two order of magnitude larger oscillator strengths than the L transitions. In Platt's notation the 'a' index stands for electronic levels having the electron density of the electrons on the atoms and the nodal points (zero electron density points) on the bonds connecting the atoms. The 'b' index stands for electronic levels having the electron density of the π electrons on the bonds and the nodal points on the atoms. In general, the number of nodal points of the two lowest states, the L states, equal the number of atoms and their dipole moment are expected to be small and similar in magnitude to the ground state dipoles . The dipoles of the ^1L_b and ^1L_a states are generally orthogonal to each other, the dipole of the ^1L_b state being along the short symmetry axis and the dipole of the ^1L_a state being along the long symmetry axis of the molecule. Also the ^1L_b state usually appears to be more vibronically structured then the ^1L_a state. Clearly, the main idea behind Platt's free electron model is its simplicity which allows each electronic level to be described by some characteristic molecular orbitals properties which define its unique physical identity. Experimentally, Platt's approach is strictly valid in a limited number of unsubstituted aromatic systems. The assignment of these levels already become uncertain in the pyrene system which only 14 out of its 16 carbon atoms lie on one peripheral. Substituents and polar interactions with the solvent also affect the simple picture outlined by Platt. However, it is customary to retain the Platt notation in the assignment of the electronic levels of substituted benzene and naphthalene although the distinctive physical character of these levels become blurred in the substituted molecules. Polar substituents are believed to stabilize the ^1L_a state more then the ^1L_b state so they lower the transition energy of the ^1L_a state compared to the transition energy of the ^1L_b state. Polar substituents may also enhance the polarity of the ^1L_a and ^1L_b states and mixed them . Inversion between the two L states may occur in polar environment which further stabilizes the ^1L_a state over the ^1L_b state. The two L states may also be coupled to each other by some vibronic modes of the aromatic ring. This may result in the two L states being in a dynamic equilibrium with each other. Moreover, each of the two L states may be mixed to a different degree with the allowed B levels, thus "borrowing" oscillator strength from these levels and considerably changing their characteristic spectra.

Over the past decade Platt's notations were extensively used to describe the electronic levels of several hydroxyarene photoacids. This was very constructive in bringing to attention, in a qualitative way, the complexity of the electronic structure of some very common photoacids. However, the extent of the quantitative analysis which may be drawn from such considerations is still unclear. Arguably, the most researched and the best example for the complexity of the photoacidity phenomenon from the point of view of the electronic structure of the photoacid is the 1-naphthol molecule. The ground-state acidity of 1-naphthol is almost identical with the ground-state acidity of the 2-naphthol isomer, yet the excited state acidity of 1-naphthol is 3 orders of magnitude larger than the corresponding acidity of 2-naphthol. This observation have puzzled researchers for the past 50 years. The spectroscopic scope of this problem is evident when the absorption spectra of 1-naphthol is compared with that of 2-naphthol, Figure 14.

The absorption spectra of 2-naphthol consist of two excitation bands, assigned as ^1L_b (S_1) and ^1L_a (S_2) transitions. In contrast, the absorption spectra of 1-naphthol taken at the same spectral range contains only one absorption band having roughly the same spectral width as the combined spectral width of the ^1L_b and ^1L_a absorption bands of 2-naphthol.

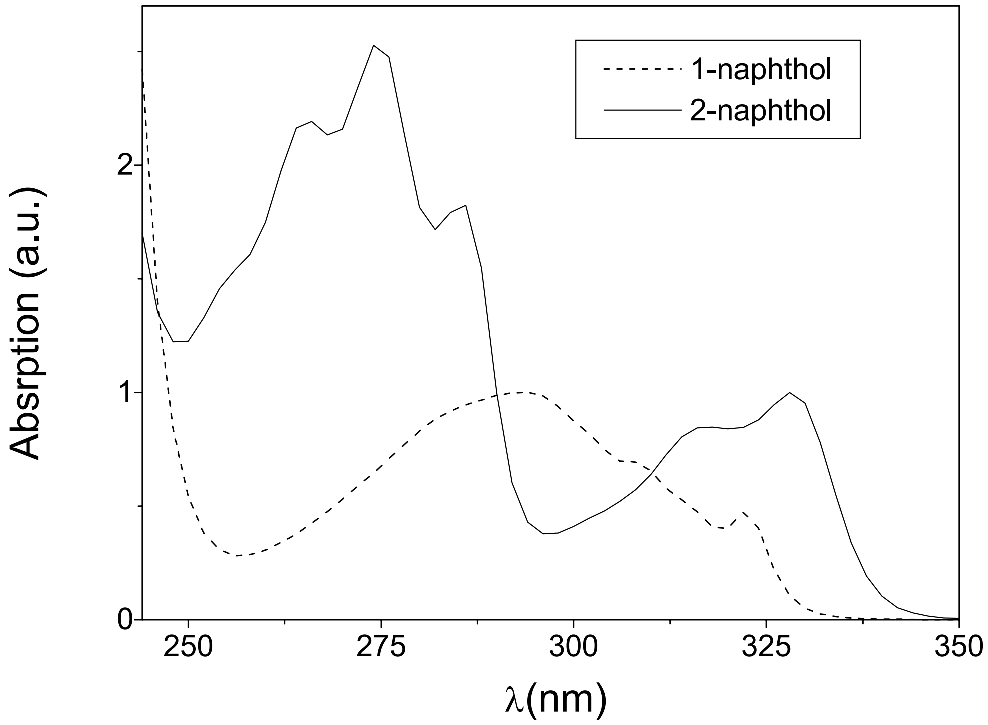


Figure 14. Absorption spectra of 1-naphthol (dots) and 2-naphthol (solid line) in H_2O [51].

The large difference in the appearance of the electronic absorption spectra of 1- and 2-naphthol seems to indicate that photoacidity may be correlated with some spectral features common to all photoacids of a given family. Such common features, if indeed exist, may be used as 'fingerprints' for identifying the extent of inherent photoacidity exhibited by the photoacid, regardless if it may be ionized in the medium or not. Before addressing the various approaches dealing with this issue in connection with the 1- and 2-naphthol dilemma it is worthwhile pointing out that the general situation is most probably more complicated than what it may appear to be from the visual inspection of the spectra of 1- and 2-naphthol. Figure 15 shows the absorption spectra of several 1- and 2-naphthol derivatives:

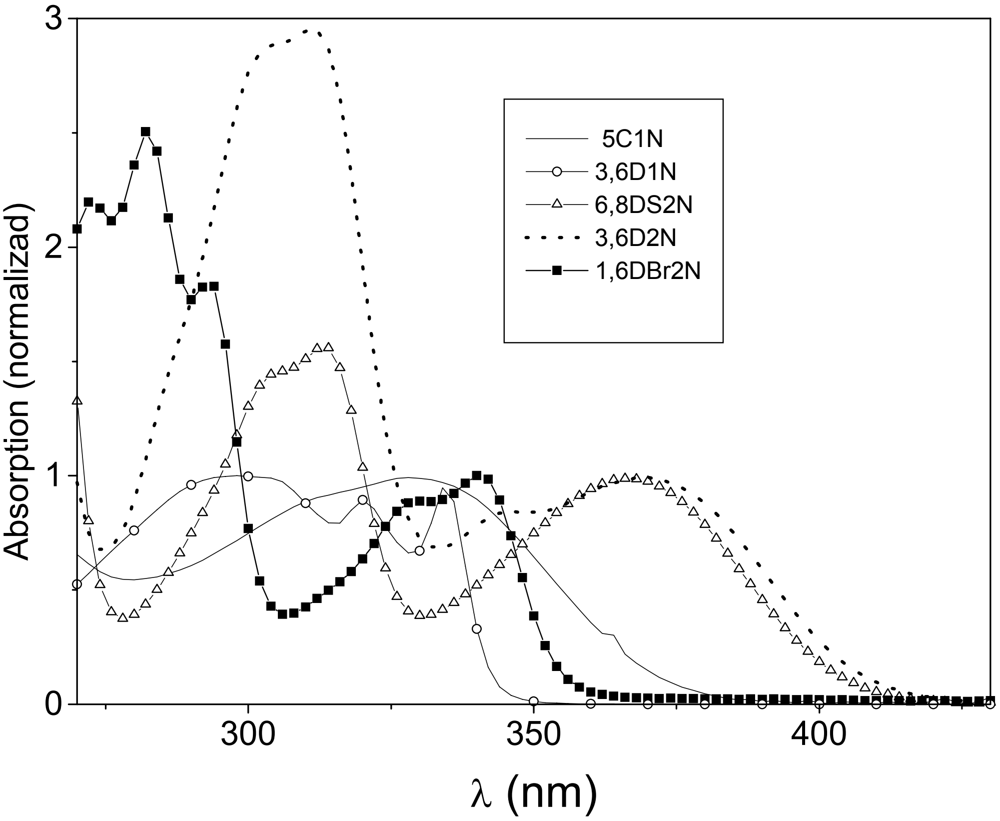


Figure 15. Absorption spectra of 5-cyano-1-naphthol (5C1N), 1-naphthol-3,6-disulhfonic acid sodium salt (3,6DS2N), 2-naphthol-3,6-disulhfonic acid sodium salt (3,6DS2N), 2-naphthol-6,8-disulhfonic acid sodium salt (6,8DS2N), and 1,6-dibromo-2-naphthol (1,6DBr2N) measured in water at different pH (from 4 to 7). All spectra were collected at 20°C [91].

The very broad absorption band of 5-cyano-1-naphthol looks like a red-shifted 1-naphthol spectra where the spectrum of 1,6-dibromo 2-naphthol resembles the two-band absorption spectrum of 2-naphthol shifted to the red by about 20 nm. The broad absorption spectrum of 1-naphthol is retained in the absorption spectra of 3,6-disulfonate-1-naphthol, however the spectrum becomes much more structured. In contrast, the familiar spectral features of 2-naphthol become blurred in the case of 2-naphthol 6,8-sulfonate and 1,6-dibromo-2-naphthol which are considerably red-shifted and appear wider and almost featureless. In fact, the two spectra resemble each other more than they resemble the spectrum of either the 'parent' 2-naphthol molecule or the 1-naphthol isomer. In addition, no clear correlation exist between the shape of the spectra and the pK^*_a of the photoacid, the three 2-naphthol derivatives and 3,6-disulfonate 1-naphthol all having a pK^*_a that fall within 1 pK_a unit of each other, while 5-cyano-1-naphthol is a much stronger photoacid having a pK^*_a value of about -2.8[47]. Evidently, substitutions change the spectra of naphthols not in a simple way, the magnitude of the change depending on the number of the substituents, their ring-position and their chemical nature.

We thus limit ourselves mainly to the discussion of the electronic spectra of the unsubstituted naphthols and phenol. The very important class of pyrenols photoacids are also largely excluded from our discussion, as these molecules do not fulfill Platt's classification of a catocondensate molecule. This by no means consist a statement that, from pure theoretical background, pyrenols should not be analyzed in terms of Platt's notation, a practice that has been extensively undertaken, very recently, by Hynes and coworkers[65,66]. Our opinion is, rather, that regularities concerning the molecular basis for photoacidity should be drawn only in face of clear experimental evidence backed by unambiguous theoretical models. Considering our current state of knowledge this does not appear to be the case when pyrenols are considered, see also Figure 16.

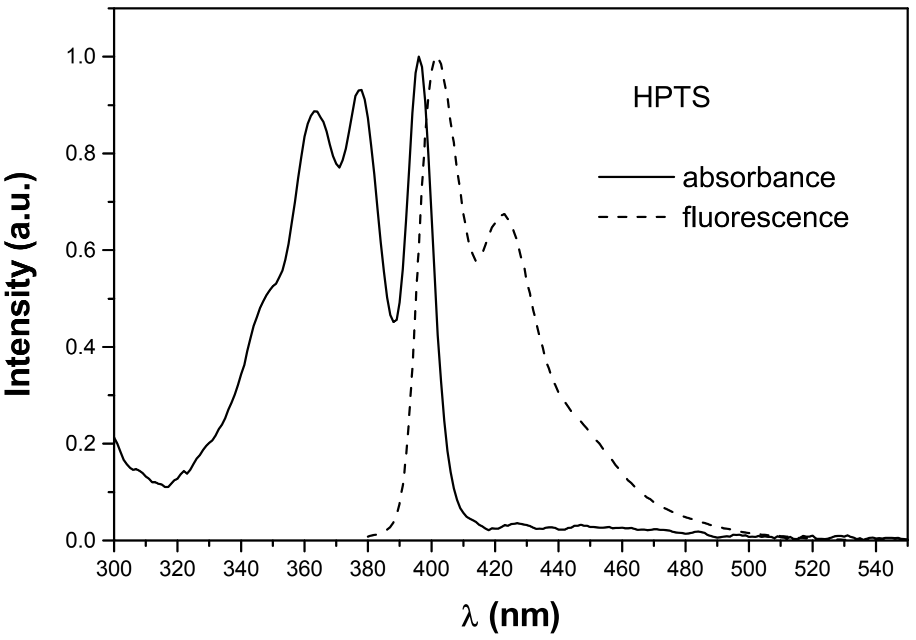


FIGURE 16. Absorption and fluorescence spectra of the HPTA molecule in acetonitrile . The mirror-like symmetry appearing at first sight to exist between the absorption and fluorescence spectra is misleading, the absorption spectra being about 30% wider and more structured. The sharp, vibronic-like spectral features were interpreted as coming from a mixture of ^1L_b and ^1L_a transitions, similar to the 1-naphthol case[65], or alternatively, as originating from strong solvent-solute interactions of a single S_1 state in the case of the methoxy analogue of HPTA, the MPTA molecule [94].

With the above reservations in mind we summarize below the different approaches that attempt to elucidate the excited-state acidity of 1- and 2-naphthol by analyzing the structure of their electronic spectra. As already pointed out, there is a considerable difference between the photoacidity of 1- and 2- naphthol (about 3 pK_a units). In contrast, the two naphthol isomers exhibit almost identical ground-state acidities, the difference between the pK_a of the two isomers being less than 0.2 pK_a units (pK_a = 9.4 and 9.5 for 1- and 2- naphthol, respectively). This simple observation suggests, although does not prove, that the two isomers differ mainly in their electronic structure in the excited-state. The direct comparison between the electronic spectra of the two isomers have provided, arguably, the best known case where enhanced photoacidity was tracked back to some specific electronic rearrangement in the excited photoacid namely, the ^1L_b to ^1L_a level crossing. At least three different scenarios are attached to this proposed electronic transition. In all scenarios the ^1L_b state is assumed the lower singlet state of the molecules in the gas phase (the S_1 state) and the ^1L_a level is assumed to be higher in energy (the S_2 state) and more polar then the ^1L_b state. Level inversion may occur in polar solvents which stabilize the ^1L_a state more than they stabilize the less polar ^1L_b state. Polar substituents may cause level crossing already in the gas phase. An example for such a substituent effect is found in the 1-naphtholate anion where the S_1 state in the gas phase is thought to be the ^1L_a state [Refs (35), (68b) (p.240)] (strictly speaking, Platt's notation describes the unsubstituted naphthalene molecule so the 1-naphtholate anion should be viewed as a naphthalene molecule with O^- substituent at the 1 position). The enhanced photoacidity of 1-naphthol over 2-naphthol is explained then, as the result of level inversion: While the emitting state of 2-naphthol is the directly excited ^1L_b state, level inversion occurs in 1-naphthol where the emitting state is not directly accessed from the ground-state and is identified as the more polar ^1L_a state. The three scenarios which make this mechanism their starting point differ by the way they treat the inversion process.

The origins of the first scenario goes back to the classic studies described in refs.(34,35). In this scenario the ^1L_b and ^1L_a transitions are congested together in the absorbance (absorption spectrum of 1-naphthol in water is shown in Figure 14) and fluorescence spectra of 1-naphthol (Figure 17).

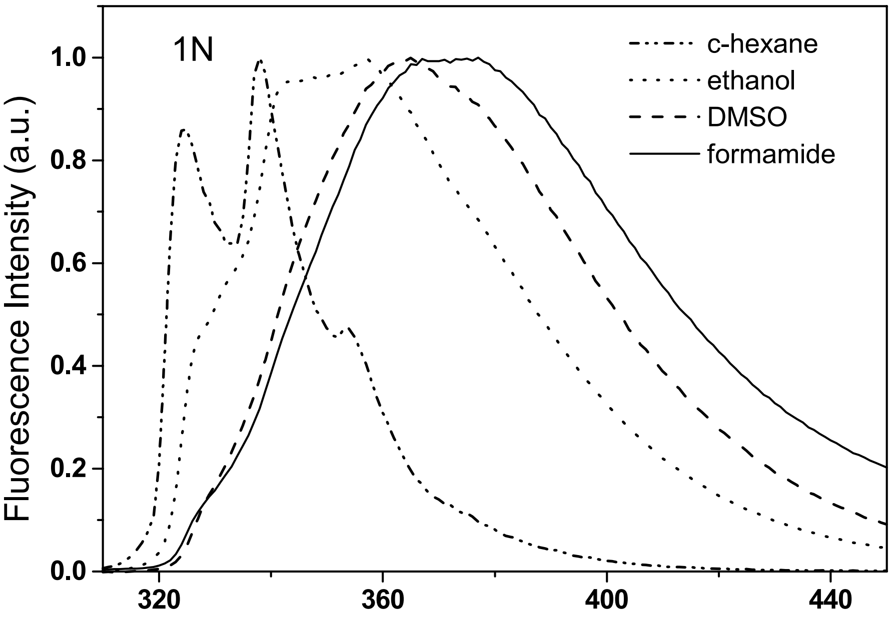


FIGURE 17. Fluorescence spectra of 1-naphthol in different solvents. Moving from formamide to cyclohexane, the fluorescence spectra is considerably shifted to the blue and becomes much narrower and more structured. In formamide and cyclohexane the emitting state of 1-naphthol is thought to be ^1L_a and ^1L_b respectively [51].

In this scenario, the absorption red edge of 1-naphthol is thought to be mainly the ^1L_b state and the blue edge of the absorption spectrum to be mainly the ^1L_a state[34]. This is the suggested reason for the absorbance spectra of 1-naphthol being roughly as wide as the first and second transitions of 2-naphthol combined together. The situation is reversed in the fluorescence spectra of 1-naphthol in polar solutions (see Figure 17). Here, as in the absorption spectra, the width of the fluorescence band is roughly twice as large as the fluorescence band of 2-naphthol. The red edge of the band is assigned to the ^1L_a state and the blue edge is assigned to belong to the ^1L_b state[35, 51]. Moving to less polar solvents, the fluorescence spectrum becomes narrower and more structured than the fluorescence spectrum in water. This progression in the various spectra is explained by the two states being strongly coupled and in rapid equilibrium. The relative "^1L_b" or "^1L_a" character of the fluorescence band is determined by the polarity of the solvent, changing gradually from being mostly ^1L_a type in water and formamide to being mostly ^1L_b type in cyclohexane[51]. Such a gradual change in the structure of the spectrum is not observed in the case of 2-naphthol[51] where much smaller spectral changes are observed as a function of solvent polarity (see Fig. 18).

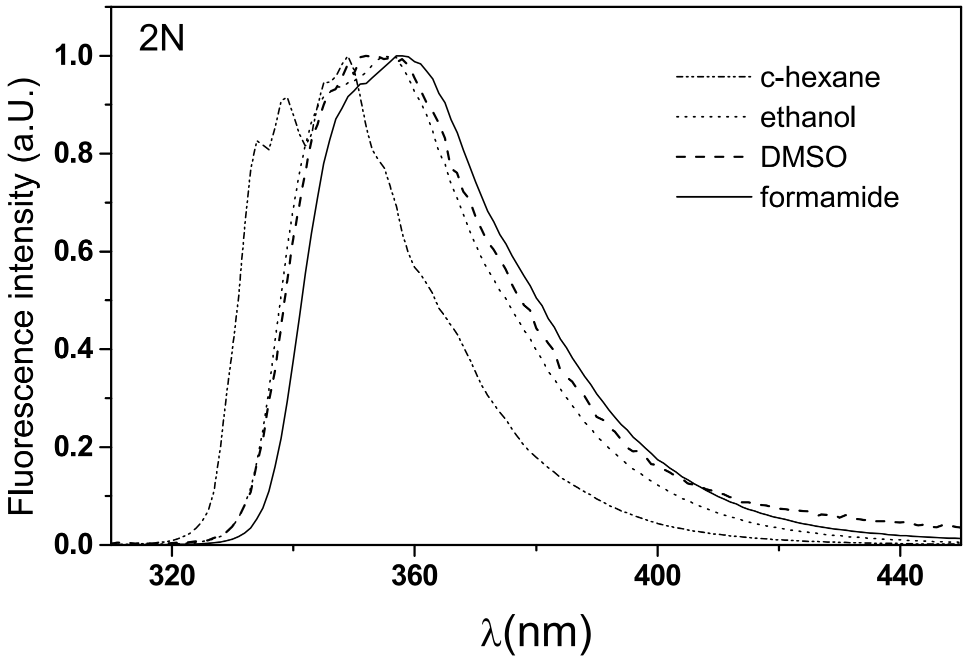


FIGURE 18. Fluorescence spectra of 2-naphthol in several solvents of various polarity. Notice the much smaller solvent effect on the fluorescence spectra of 2-naphthol compared to 1-naphthol in the same solvents, Fig. (17). The emitting level of 2-naphthol is thought to be the ^1L_b state in all solvents, (adopted from[51]).

Similar conclusion about the emitting state of 1- and 2-naphthol was reached from the K-T analysis of the fluorescence spectra of the two isomers [51], see Figures 19 and 20.

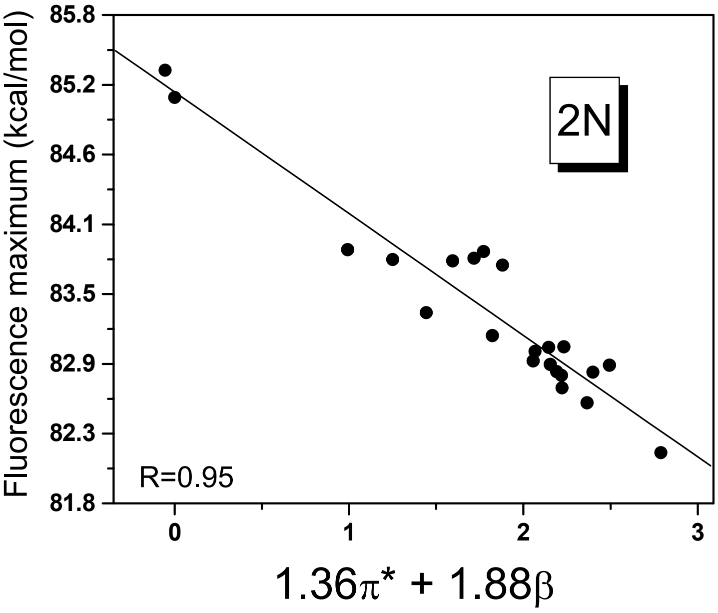


FIGURE 19. The good correlation found between the fluorescence maximum of 2N and solvent polarity using Kamlet-Taft analysis in 15 solvents. In this case no level crossing is evident and the emitting state is assumed to be ^1L_b in all solvents (adopted from [51]).

The K-T analysis showed much better correlation of the 2-naphthol spectra in various solvents than the corresponding 1-naphthol spectra

Good correlation (R=0.94) was found when the fluorescence spectrum of 1-naphthol was divided into two emitting states. For the red edge emitting state (^1L_a) the correlation has yielded a polar state, $2.8\pi^* -1.3\alpha+3.1\beta$, and for the blue edge emitting state (^1L_b) the outcome was a non-polar state, $1.1\pi^* -0.1\alpha +0.8\beta$ (R=0.95) [51]. The poor correlation of the position of the fluorescence maxima shown in Fig (20) was attributed to the fluorescence maximum being the combination of two emitting singlet states of different polarity which partially overlap . This indicates non-trivial changes in the 1-naphthol fluorescence spectrum as a function of the polarity of the solvent, the location and the relative weight of each emitting state having different dependence on solvent polarities. The two overlapping fluorescence transitions were assigned ^1L_b and ^1L_a transitions. In this scenario level dynamics are assumed to be extremely fast and follow the solvation relaxation dynamics of the solvent. The rate determining step of the photoacid dissociation was assumed to be intermolecular, the activated proton transfer to the solvent.

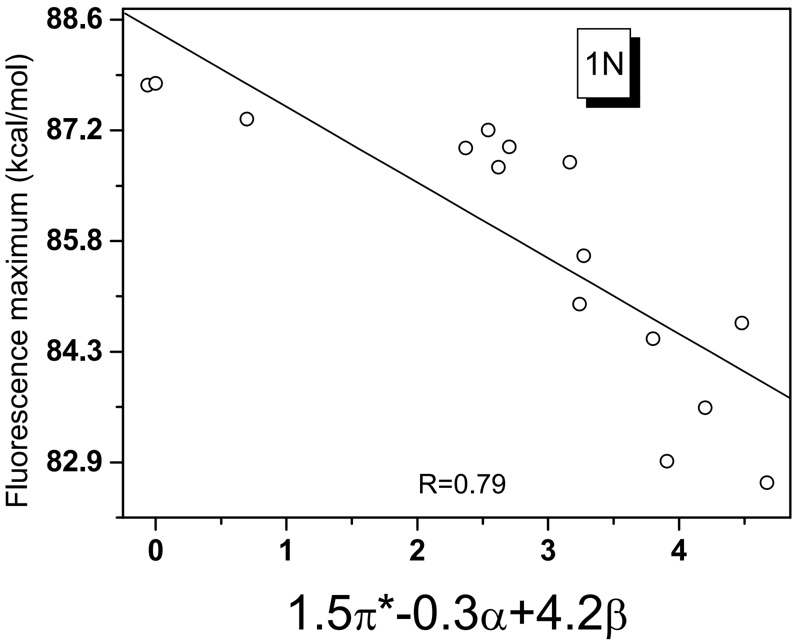


FIGURE 20. The poor correlation found between the fluorescence maximum of 1N and solvent polarity using Kamlet-Taft solvent polarity parameters of 15 common solvents (adopted from[51]).

The second scenario was developed to describe the situation pertaining to 1-naphthol in the gas phase[18,25,27,28]. In the gas phase excitation is assumed to be a pure ^1L_b transition. Following excitation, level crossing to the ^1L_a state may occur in 1-naphthol-base gas-phase clusters and is promoted by some vibrational modes of the naphthalene ring which allow the otherwise symmetry forbidden L_b to L_a transition. Polar interactions in the cluster stabilize the level crossing. Level dynamics was suggested the rate determining step for the onset of the photoacidity of 1-naphthol in gas-phase clusters and aqueous solutions. The characteristic level-crossing time was estimated to be several ps in water clusters.

In the third scenario[66], developed for phenol derivatives on theoretical grounds, enhanced photoacidity was traced to the ^1L_b-^1L_a transition occurring upon proton dissociation. In this intriguing scenario the photoacid is assumed to be in a ^1L_b state which polarity and internal acidity resemble that of the ground state. Level crossing to the polar ^1L_a state occurs in the anion which, for that reason, is a much weaker base then the ground-state anion. In this scenario level crossing does not consist the rate limiting step for the proton transfer although such a possibility was not entirely ruled out. An additional activated charge transfer process was assumed to be the likely rate limiting step for proton dissociation.

It is unclear if any of these scenarios may be considered a general description of photoacidity. More likely, each of these scenarios describes a possible intramolecular route which may contribute to photoacidity under certain experimental conditions but does not exclusively define photoacidity by itself. One should not role out situations where the photoacidity state is directly accessed from the ground-state and no further level 'switching' or crossing occurs either in the photoacid or the photobase side. This seems the case of 2-naphthol and its derivatives, see below. Also, it is unlikely that level dynamics determine the rate of the proton transfer reaction in solution, the latter being usually a much slower process determined by the overall free-energy change upon proton dissociation. In fact, if we consider the arguments brought up in the first part of this review, even the seemingly clear cut assignment of the emitting states of 1- and 2- naphthol must raise questions when their overall photoacidity is examined from Förster cycle considerations. The general rule is that the lowest emitting state of 1-naphthol and 2-naphthol is ^1L_a and ^1L_b respectively. In order to preserve the logic of the forgoing discussion, one must assume that the 1-naphtholate and 2-naphtholate anions are also ^1L_a and ^1L_b respectively since any other situation would not result in 1-naphthol being the strongest photoacid out of the two isomers. This indeed appear the case [95,96]. It means that being in the ^1L_a state rather then in the ^1L_b state roughly adds one third out to the total photoacidity of 1-naphthol. It follows that the increase in the photoacidity due to the photoacid and the base being in the more polar ^1L_a state rather than being in the relatively non- polar ^1L_b is only one half the effect of the photoacid being in the excited-state.

If one adopts the idea that regularities are found in the first two electronic levels of unsubstituted hydroxyarenes then it is clear that the effect of the electronic structure on photoacidity according to the ^1L_b, ^1L_a terminology should increase in the order: ^1L_b to $^1L'_b$: ^1L_a to $^1L'_a$: ^1L_b to $^1L'_a$ and ^1L_a to ^1L_b where ^1L designate the electronic level of the photoacid and $^1L'$ designate the electronic level of the photobase. In the case of 1-naphthol the acid side changes from being ^1L_a - like in water to being ^1L_b - like in non-polar solvents, while the naphtholate anion is probably $^1L'_a$ in all polar and moderately polar solvents. It follows from the above order of photoacidities that the photoacidity of 1-napththol should increase moving from water to less polar solvents were the acid side becomes higher in energy due to electronic rearrangement to form the less polar ^1L_b state. In contrast, 2-naphthol dissociation is either ^1L_b to $^1L'_b$ as usually assumed[95,96] or ^1L_b to $^1L'_a$ where the $^1L'_a$ is of greatly reduced charge-transfer character than the corresponding $^1L'_a$ state of 1-naphthol. It follows, that in the case of 2-naphthol one expects a much smaller solvent effect on the Förster cycle acidity than the corresponding effect on 1-naphthol acidity. This indeed seems to be the case, when the photoacidity of 1-naphthol and 2-napthol was estimated from Förster cycle calculations in water and methanol (Tables 1 and 2).

Table 2. pK_a^*- pK_a values of some common hydroxyarene photoacids from Förster cycle calculations in methanol [91].

Photoacid	**pK_a^*- pK_a methanol**
1-naphthol	10.9
1-naphthol-2-sulfonate	12.3
1-naphthol-3-sulfonate	11.3
1-naphthol-4-sulfonate	9.3
1-naphthol-5-sulfonate	8.8
1-naphthol-4-chlorate	9.8
1-naphthol 3,6-disulfonate	12.2
2-naphthol	6.5
2-naphthol-6,8-disulfonate	7.3
HPTS	7.9, 6.5
HPTT	6.8

Absorption and fluorescence spectra of the acid and base forms of 2N, 3,6DS2N and 3,6DS1N in methanol used for Förster cycle calculations in methanol are shown in Figure 21.

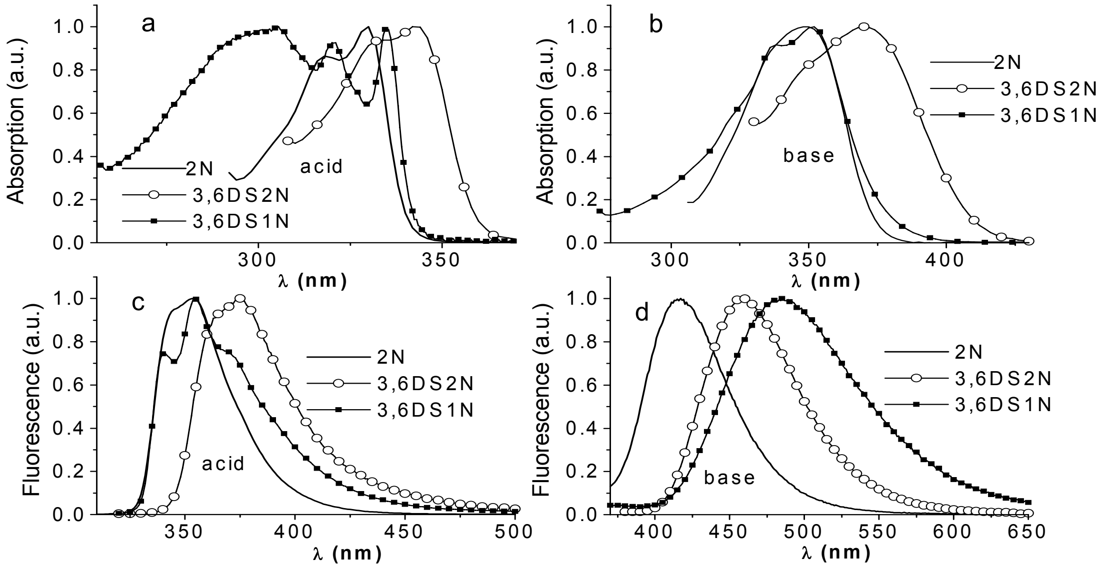


FIGURE 21. Absorption (a,b) and fluorescence spectrum (c,d) of acid form (a,c) and base form (b,d) of 2N and 3,6DS2N and 3,6DS1N in methanol[91].

2-naphthol and its 3-6 sulfonate derivative show consistency in their spectral features both in the photoacid and base sides, while much less consistency is evident in the spectral features of the 1-naphthol derivatives in the acid side, where the fluorescence spectrum appears to be much narrower and more structured than the absorption spectrum (Figure 21). This point to more extensive electronic rearrangements in the acid side of 1-naphthol as a function of the solvent than in the acid side of 2-naphthol, and that both isomers show relatively small changes in the spectral features at the naphtholate side. This indicates the consistency of the emitting state of the naphtholate anion of both isomers. Figures 22 and 23 offer a closer look at the absorption and fluorescence spectra of several 1-naphthol derivatives in methanol. In this case of sulfonate-substituted 1-naphthols, the substituent effect on the absorption spectra is relatively small, while a considerable effect is observed in the corresponding fluorescence spectra of the photoacids.

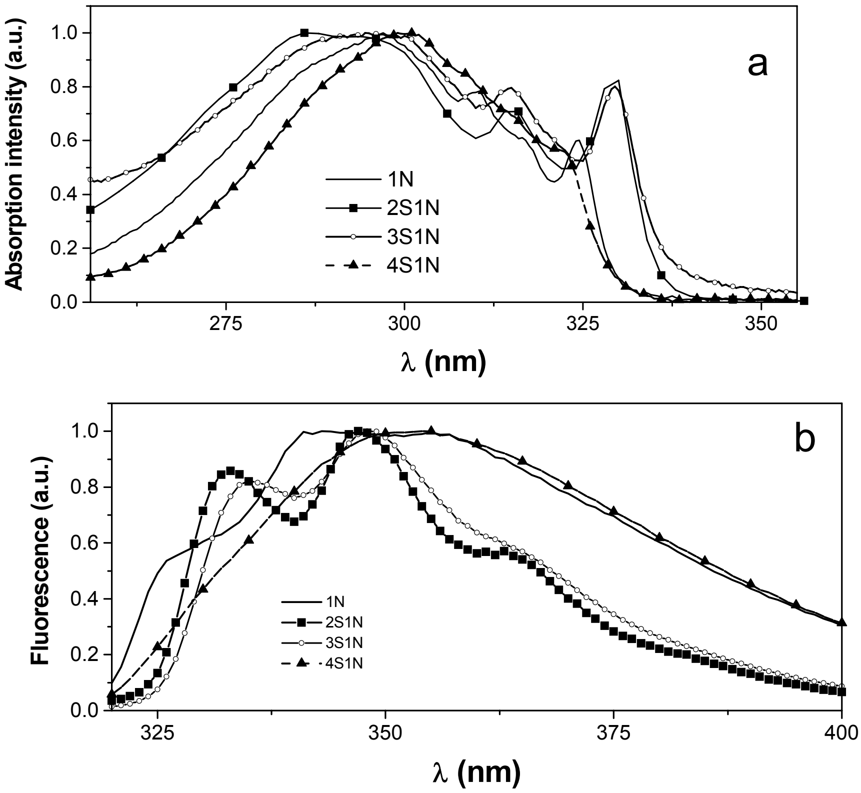


FIGURE 22. (a) Absorption spectra of acid forms of 1N and 2S1N 3S1N and 4S1N in methanol. (b) Fluorescence spectra of acid forms of 1N, 2S1N, 3S1N and 4S1N in methanol[91].

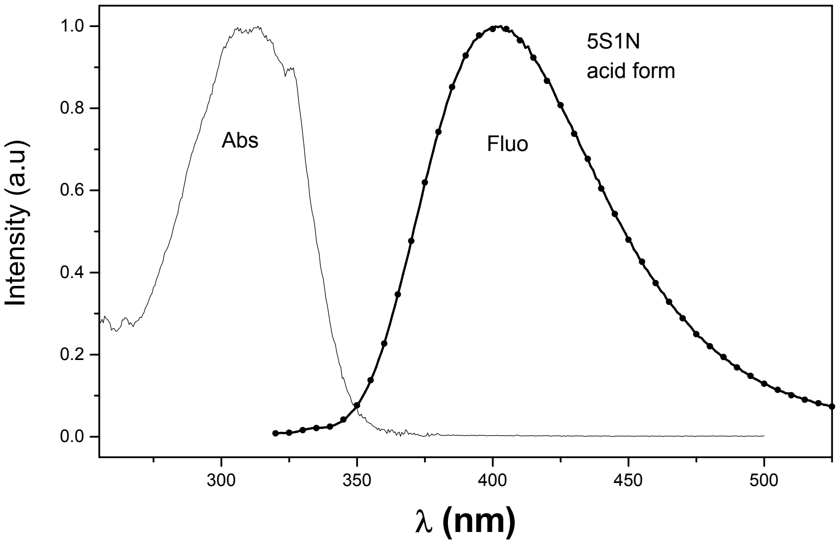


Figure 23. Absorption and fluorescence spectra of acid form of 5S1N in methanol [91].

This effect resemble the solvent effect on the fluorescence spectrum of the parent 1-naphthol molecule. Using the analogy to solvent polarity, the ring position of the sulfonate group seems to appear more 'polar' moving from the 2- to the 4- position of the naphthol ring system. The order of polarity appears to be using the ring position numbering, 4 > 3 > unsubstituted > 2. This means that the further the substituent from the OH group, the larger is its effect on the polarity of the first emitting state of 1-naphthol, probably through better stabilization of the charge-transfer character of the ^1L_a state. A second mechanism which seems to increase the ^1L_b character of the emitting state is direct hydrogen-bonding interactions between the OH and the sulfonate group at the 2 position and to a letter extent at the 3 position.

Interestingly, Förster cycle calculations of the pK*a in methanol (Table 2) seem to confirm the substituent effect on the polarity of the emitting state of the 1-naphthol as discussed above: the less polar is the emitting state of the acid compared to the emitting state of its conjugate base, the larger is the Förster cycle acidity of the photoacid. The calculated Förster-cycle difference between the ground-state and excited-state acidities in methanol was 12.3, 11.3, 10.9, 9.3, 8.8 for the 2 substituted, 3 substituted, unsubstituted 4 and 5 substituted sulfonate photoacids respectively.

These sort of arguments demonstrate the need for defining a photoacidity scale which is independent of the photoacid being able to dissociate within the excited-state lifetime or not. The five photoacids derivatives of 1-naphthol discussed above do not dissociate in methanol and the order of their acidity in methanol extracted from Förster cycle calculations awaits further confirmation by some other method which would provide a direct measure for their photoacidity as judged by the scaling of some chemical property common to all photoacids in questions.

Before such an endeavor is carried out one must rely on circumstantial evidence. Doing so, it does appear like polar substituents affect photoacidity not just by processes identified in ground-state acids, such as the inductive and resonance effects, but in the case of 1-naphthol, also by systematically affecting the character of its electronic excited-state.

It is also encouraging to find out that the effect of polar solvents on the electronic spectra of 1-naphthol appears to be qualitatively similar to the effect of polar substituents. This raises hope that the paradigm of the photoacidity of 1-naphthol could be potentially resolved in a general way.

However, as already indicated before, it is very difficult to find regular patterns in the electronic structure within one family of photoacids which directly correlate all their photoacidity related properties. An example for this difficulty is found in the classic paper of Suzuki and Baba [34] on the hydrogen bonding interactions of phenol and 1- and 2-naphthol.

The two lowest electronic transitions of the three photoacids were assigned in the very non-polar isooctane solvent by analyzing the effect of hydrogen-bonding on their respective absorption spectra. In all cases the level ordering was found to be ^1L_b (S_1) and ^1L_a (S_2). The effect of hydrogen bonding was to shift the absorption spectra to the red. For phenol and 1-naphthol the red-shift of the absorption of the ^1L_a state was much larger than the red-shift of the absorption of the ^1L_b state, observation which seems to be in harmony with the assignment of ^1L_a as the more polar state of the two. However, the situation was found to reverse in 2-naphthol where the red-shift of the ^1L_b state due to hydrogen-bonding was found to be three-time larger than the red-shift of the $1L_a$ state. Apparently, the position of the OH group affects the relative polarities of the two lowest electronic states of naphthols. When the absolute magnitude of the red-shift was considered, the ordering of the red-shift was found to be, ^1L_a (1-naph) >> ^1L_b(2-naph) >> ^1L_b(1-naph) = ^1L_a (2-naph), in accordance with the order of the photoacidity of the lowest emitting state of the two photoacids in polar solvents, 1-naphthol >> 2-naphthol. Similar situation is found when the red-shift of the single absorption band of 1-naphthol is compared with the relative red-shift of the two absorbing bands of 2-naphthol measured in the same solvents. Figure 24 shows the red-shift of the absorption spectra of 1-naphthol to be the largest, in agreement with its greater sensitivity to solvent polarity, but the S_1 state of 2-naphthol was found to shift, as in the Suzuki and Baba experiment, more than its S_2 state, an observation which seems to contrast the assumption that in this case the S_1 transition is to the less polar ^1L_b state. Evidently, even in this seemingly simple case, the molecular orbital character of the ^1L_b and ^1L_a states are not directly transferable moving from 1-naphthol to 2-naphthol.

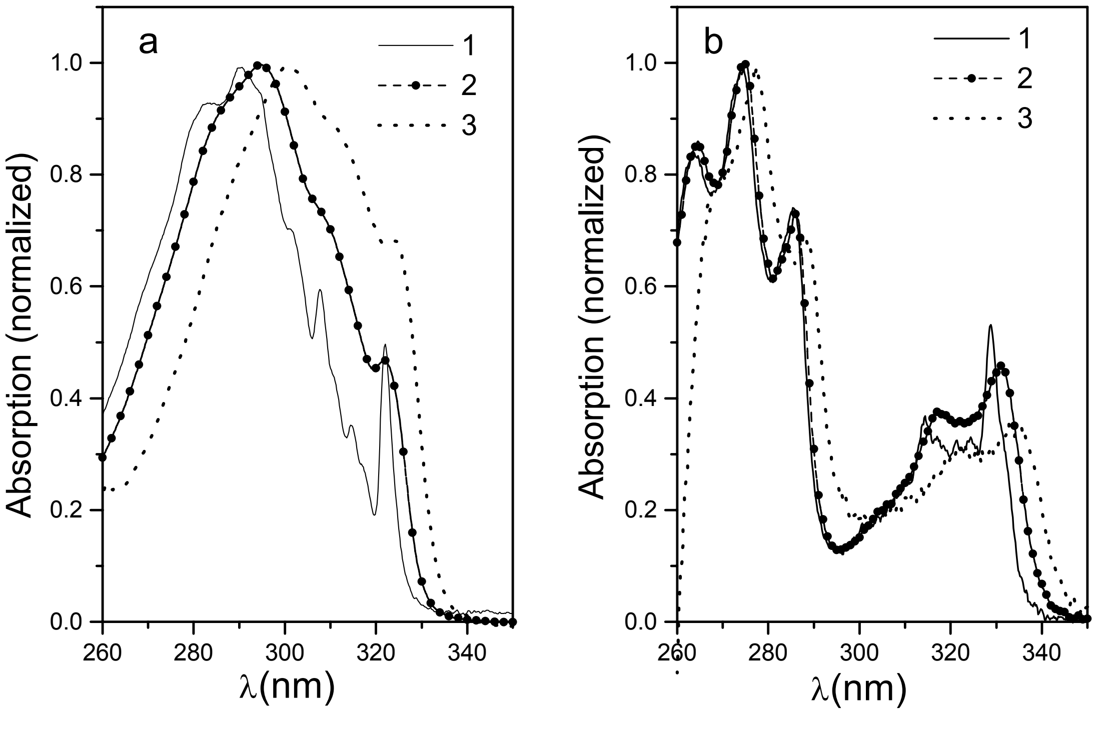


FIGURE 24. Absorption spectra of 1-naphthol (a); 2-naphthol (b); in several solvents of different polarity: 1- c-hexane, 2- acetonitrile, 3-DMSO (adopted from [51]).

This problem may be tackled by a more systematic analysis of the Stokes shift. Pines and co-workers[51] tactically assumed that the first absorption transition of 1-naphthol and the two absorption transitions of 2-naphthol may be described by Pekarian functions. These functions were analyzed by the Kamlet -Taft analysis, Figures 25 and 26.

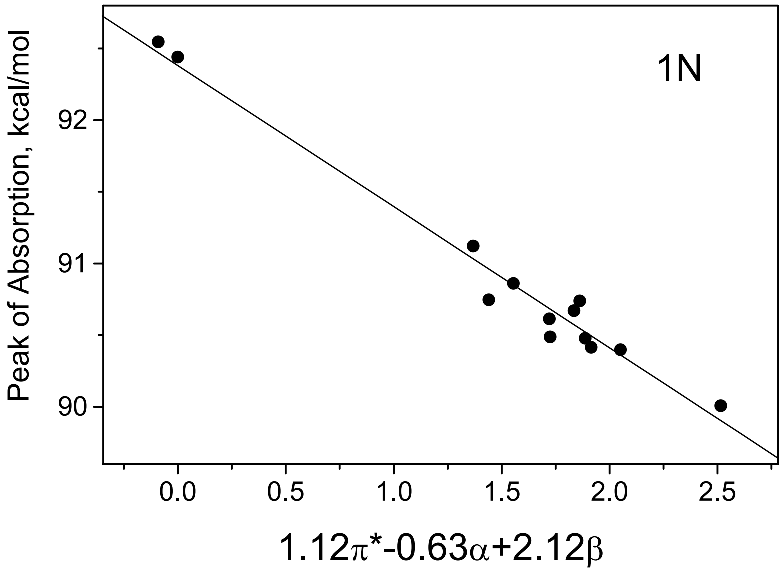


Figure 25. Correlation of the peaks of Pekarian functions (energy scale) used to approximate the UV-vis absorption spectra of 1-naphthol (adopted from [51]).

The analysis show the ^1L_a absorption transition of 1-naphthol to be more sensitive to solvent polarity than the ^1L_a or the ^1L_b absorption transition of 2-naphthol, indicating that it is the most polar of the three states. The comparison between the ^1L_b and ^1L_a states of 2-naphthol, show the ^1L_b state to be less polar than the ^1L_a state but considerably more sensitive to hydrogen-bonding interactions with the solvent. The greater sensitivity of the ^1L_b state to hydrogen-bonding interactions with bases is in quantitative agreement with the findings of

Suzuki and Baba[34] discussed above. In both cases the spectral shift due to hydrogen bonding interaction with the base was found to be three times larger in the ^1L_b state.

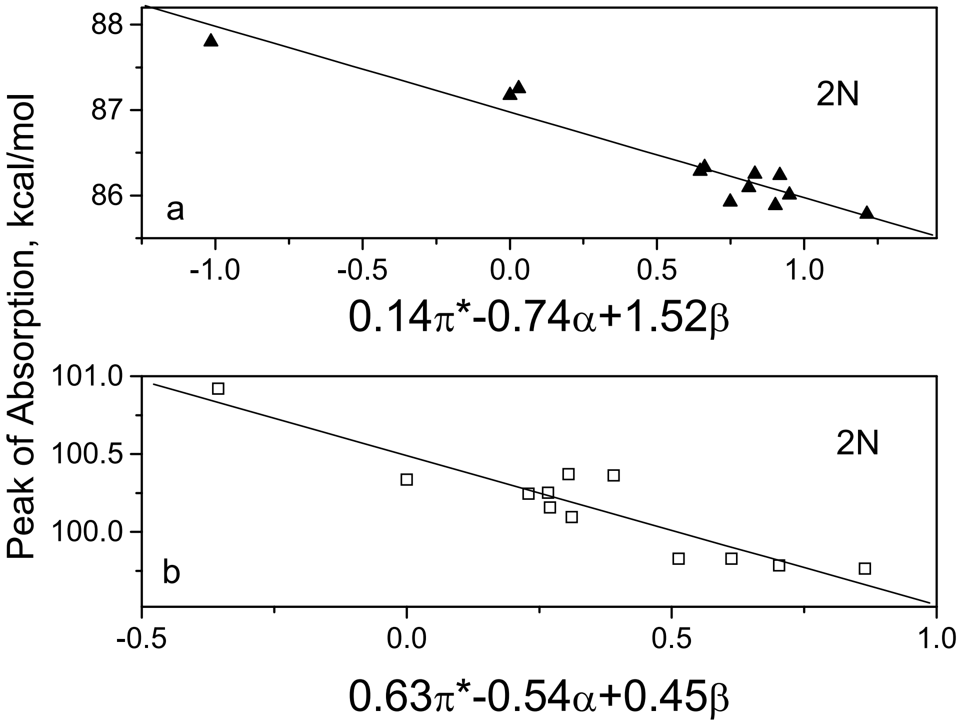


FIGURE 26. Correlation of the peaks of Pekarian functions (energy scale) used to approximate the UV-vis absorption spectra of 2-naphthol blue-band (a) and red-band (b) with Kamlet-Taft parameters [91]. See also Fig. 24 for the details of the absorption spectra.

These findings consist an argument against the idea that regularities in the photoacidity behavior of hydroxyarenes may be defined and quantitatively analyzed simply by assuming constancy in the properties of their two lowest electronic singlet states. Indeed, one can not even role out situations where the less polar state in terms of its dipole moment and CT properties is the more acidic one as the 2-naphthol case appears to be at least when photoacidity is judged by the strength of the hydrogen-bonding interactions of the acidic hydrogen atom of the –OH group.

An additional way to identify level crossing between the two lowest singlet states of hydroxyarenes as opposed to one emitting level gradually changing its properties was suggested by Hynes and co-workers[66]. They argued that ^1L_a to ^1L_b level switching may be demonstrated by comparing the free parameter in the Kamlet-Taft analysis (P^o_{s-s}, in equation (18), $P_{s-s} = P^o_{s-s} + s\pi^* + a\alpha + b\beta$, where P^o_{s-s} corresponds to the transition energy of the probe in cyclohexane) of the absorption spectra of the photoacid with the P^o_{s-s} found in the K-T analysis of the fluorescence spectra of the photoacid in the same set of solvents. In cases where level switching occurs in the excited-state of the photoacid, the absorption transition is assumed to be ^1L_b while the fluorescence transition is assumed to occur from a ^1L_a state. Assuming that level crossing does not occur in non-polar solvents, one expects the P^o_{s-s} of the fluorescence to be higher in energy then the P^o_{s-s} of the absorption, a situation which can not happen if absorption and fluorescence are to- and from the same electronic level. Hynes et al. argued that such a situation occurs in HPTS although the complexity of this system still resists clear cut conclusions.

V. FREE ENERGY CORRELATIONS BETWEEN PHOTOACIDITY AND REACTIVITY

Pines and Fleming have utilized a free-energy correlation between the excited-state equilibrium constant of the photoacid and the proton dissociation rate[83,97]. Such correlations are extensions of similar correlations existing between the equilibrium constant and reactivity of ground-state acids (the "Brønsted relation"[98]).

A “universal‘ correlation was suggested to exist between the excited-state proton-transfer rate and photoacidity in aqueous solutions, equation (19):

$$k_p \sim k_o \exp(-(\Delta G_a + w^r)/kT) \qquad (19)$$

where w^r is the so called “work function" of the work done when separating the two reactants to infinity and $(k_o)^{-1}$ is the reaction frequency prefactor which is assumed to depend on the solvent and to be identical for all photoacids of a given family in a given solvent. ΔG_a is the reaction free-energy given by Marcus' Bond-Energy-Bond-Order theory (MBEBO), eq.20, [99]:

$$\Delta G_a = \Delta G^o/2 + \Delta G_o^{\#} + \Delta G_o^{\#} \cosh[\Delta G^o \ln 2/(2\Delta G_o^{\#})] /\ln 2 \qquad (20)$$

where $\Delta G_o^{\#}$ is the activation free-energy of the symmetric transfer when the total free energy change following the proton-transfer is equal to zero, i.e., when ΔpK_a between the proton donor and the proton acceptor equal zero.

The above representative semi-empiric model for proton dissociation is supported by recent ab initio studies of Kiefer and Hynes[100,101]. Figure 27 shows the good correlation which was found between the excited-state pK^*_a of hydroxyarenes photoacids and their corresponding proton dissociation rate in aqueous solutions. The free-energy correlation seems to indicate that the equilibrium constant of the photoacid gives an excellent measure for its reactivity in the excited-state regardless if the emitting state being ^1L_b or ^1L_a. This draws a line between the fundamental question why a particular photoacids has a particular pK^*_a and the question how to estimate the reactivity of the photoacid, the latter property of the photoacid being proportional to its pK^*_a. It appears that as a general rule, one could estimate the relative reactivity of a group of substituted photoacids by using empiric correlations between structure and acidity found in ground-state acids such as the Hammett's sigma value of a substituent. Such an approach have been successfully utilized by Tolbert and co-workers who were able to synthesize "enhanced" photoacids by predicting their pK^*_a values from the sigma value of the introduced substituents [8,9,17].

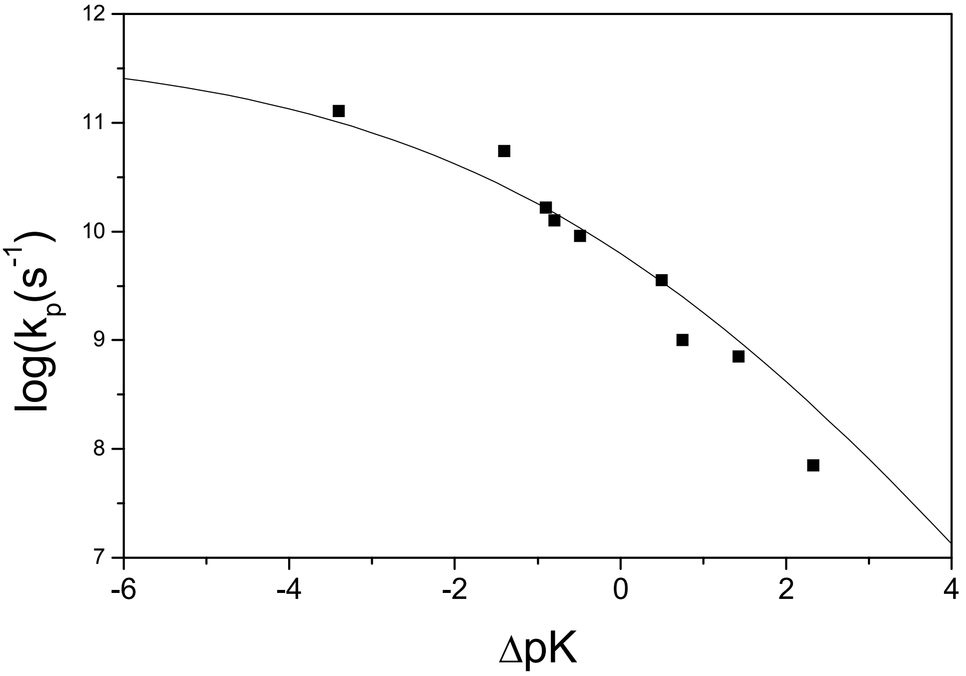


FIGURE 27. The free energy correlation found in dissociation reaction of hydroxyarenes photoacids in aqueous solutions taken at room temperature (squares). The parameters of the fits are $\log(k_o) = 11.7$, $\Delta G_o^{\#} = 2.5$kcal. $W_r = 0$ (adapted from [97]).

VI. CONCLUDING REMARKS: EVALUATION OF OUR CURRENT UNDERSTANDING OF THE PHOTOACIDITY OF HYDROXYARENES.

The photoacidity of hydroxyarenes has attracted consider interest over the past 50 years. Many conventions about photoacidy have their origins placed in the early studies of photoacidity. This conventions are now being critically examined by a new generation of researcher which have had in their disposal new experimental tools and enhanced computational capabilities. A fresh outlook is already emerging from these latest studies, an outlook which appreciates the great complexity of these seemingly simple aromatic molecules. New ingredients have been successfully integrated into the old concepts which have been used to describe photoacidity. This progress has not yet resulted in a coherent and full understanding of photoacidity, although the field is well prepared and poised for such a development to occur.

Hydroxyarenes photoacids may be divided into two group of molecules, the 1-naphthollike and the 2-naphthollike photoacids. The 2-naphthollike photoacids resemble ground-state photoacids in that the proton-transfer equilibrium takes place in one electronic level, presumably the ^1L_b state. There are many features common to ground-state acidity and the excited-state acidity of 2-naphthollike photoacids. Among these are the substituent effect through resonance and inductive interactions which their molecular mechanism do not seem to differ much from their respective mechanism in the ground-state, although it is important to point out that the magnitude of these effects is usually larger in the excited-state and ring positions should not necessary bear the same effects in the ground- and the excited-state of the photoacid due to differences between the ground- and excited-state electron distributions. In addition, solvent polarity seems to affect 2-naphthollike photoacid in a similar way that it affects ground state acids, thus making the effect of the solvent on the reactivity of the photoacid predictable from the corresponding ground-state data. Finally, the photo-physics and photochemistry of the first emitting state of 2-naphthollike photoacids appear to be simple with relatively small deactivation routes other than the radiative decay and adiabatic proton-transfer reaction. One may characterize 2-naphthollike photoacids as 'well- behaved' photoacids or as 'proper photoacids'. Substituted pyrenols also seem to fall under this category of well-behaved photoacids, although some of their electronic properties are still in debate.

The situation is drastically changed with 1-naphthollike photoacids which 1-naphthol is their best representative. 1-naphthol exhibit enhanced photoacidity, complex absorption and fluorescence spectra which is very sensitive to solvent and ring-substituents. The main route for its excited-state deactivation in aqueous solution is proton-quenching[102], a very intriguing phenomenon by its own merit which is not discussed in this review. The complexity found in the photo-physics and photochemistry of 1-naphthol is attributed to the complex structure of its first two electronic singlet states which is affected intermoleculary by polar interactions with the solvent and intramolecularly, by the chemical structure and the position of ring-substituents. The exact details of these interactions and their effect on the electronic structure of 1-naphthol and its photoacidity await further investigations. However, regularities which are found in the appearance of the 1-naphthol spectra and theoretical considerations from first-principles clearly point out the reason for this complexity. It is generally accepted that the lowest emitting state of 1-naphthol is sensitive to polar interactions, changing from being ${}^1L_b$-like in non-polar environments to being ${}^1L_a$-like in polar environment. The enhanced acidity of 1-naphthol over its 2-isomer is attributed to the ${}^1L_a$ state being more polar and of greater CT character the ${}^1L_b$ state. Correlation between the appearance of the fluorescence spectra of the photoacid and its excited-state reactivity is expected and indeed observed in the case of 1-naphthol, although it is not clear how general are these observations. Ring substituents seem to introduce a similar effect on the electronic-structure of excited 1-naphthol, however this effect has not yet been studied in details. An example is shown above in Figures 22 and 23. Förster cycle calculations and spectral appearance of the sulfonate-substituted 1-naphthols correlate with the expected inductive effect at each ring position in the excited-state, the migration of the electronic charge to the naphthalene ring expected to be the largest in the 5-substituted naphthol (Figure 23) and the smallest in the 2-substituted naphthol. This makes excited 5S1N the most ${}^1L_a$-like isomer, with almost featureless absorption and fluorescence spectra, and the excited 2-isomer the most ^1L_b-like isomer, with strong vibrational features both in the absorption and fluorescence spectra. The effect of the substituents on the Förster cycle acidity of 1-naphthol are resolved in methanol. The order of Förster cycle photoacidity in methanol is 5S1N > 4S1N > 1N > 3S1N > 2S1N, (Table 2).

The complex electronic structure of 1-naphthollike photoacids makes them non-conventional photoacids. In this case, photoacidity is influenced by additional factors not present in ground-state acids, namely electronic rearrangements occurring during the lifetime of the excited photoacids. Clearly, electronic rearrangements occurring in the short-lived excited-state of the photoacids (typically, the excited-state lifetime in the singlet state is not longer than a few nanoseconds) can affects both the dynamics of the excited-state proton-transfer reaction and the thermodynamics of the photoacids. The expected and observed non-trivial photoacidity of 1-naphthollike photoacids awaits further investigations.

Our final observation is that photoacids seem to generally resemble ground-state acids in most studied cases were proton-transfer reaction is observed. As in ground-state hydroxyarenes, Brønsted acidity is greatly affected by the stabilization of the conjugate base in polar solvents and by intramolecular charge transfer processes shifting some of the anionic charge away from the oxygen atom to the aromatic ring. The charge-transfer process is assisted by inductive and resonance processes occurring at the aromatic ring. Level mixing in the excited-state although very important in 1-naphthollike acids is secondary in importance to the acid being in the excited-state. Level dynamics, if indeed exist do not seem to introduce additional barrier to the proton-transfer reaction in polar solvents. Thus, level dynamics do not affect the generality of the above-stated observation. The extension of the photoacidity scale to less-polar environments where no proton-transfer is observed within the short lifetime of the excited photoacid is a desirable goal which may be achieved by scaling the hydrogen-bonding interaction of the photoacids or perhaps by calibrating their Förster cycle acidities using spectral analysis of their lowest optical transitions.

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