

Ground and Excited States Proton Transfer Reactions of 1,8-Diaminonaphthalene in Perchloric Acid Solutions

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The proton-transfer reaction of 1,8-diaminonaphthalene (1,8-DAN) in acidic medium was studied by means of fluorescence and picosecond spectroscopic techniques. It has been found that there are three different forms of 1,8-DAN in the ground state, but only two different forms in the excited state. The absorption of the mono-cation form of 1,8-DAN is found to be a mixture of the neutral form and the di-cation form. However, the emission is found to be the same as the neutral form, due to the fast dissociation of the mono-cation form once it is excited. The fluorescence of the mono-cation form of 1,8-DAN shows a small shift under different excitation wavelengths. The di-cation form only fluoresces if no free water cluster is available as a proton acceptor. The reaction in the excited state is shown to be a diabatic quenching reaction. With the help of quantum yields and fluorescence lifetime measurements these results are interpreted in terms of a new photochemical scheme. All dissociation and quenching rate constants, pK_a and k_q , have been determined.

KEY WORDS: Proton transfer; fluorescence; 1,8-diaminonaphthalene; quenching; lifetime.

INTRODUCTION

Proton transfer reactions have been the subject of many studies over the years [1–20]. Intermolecular proton transfer between excited molecules and solvents has been investigated in the past few years by means of the picosecond spectroscopic techniques. Studies were extended to alcohol–water mixtures [10–15].

The proton transfer reaction from the excited state of 4-hydroxy-1-naphthalenesulphonate has been investigated in alcohol–water mixtures at different temperatures [10–15]. Two new models and two possible mechanisms have been proposed to explain the proton transfer process of the probe molecule in methanol–and ethanol–water mixtures [10].

Recently there has been renewed interest in the photophysical behavior of 1-aminonaphthalene (1-AN) [6,7]. 1-ANH⁺ is a very strong acid in the excited state and was shown to have, besides the expected excited acidic form, a new form X which is an adduct between the excited acid and the anion ClO₄⁻, i.e., X ≡ RNH₂–H⁺–ClO₄⁻, while the X-form was specifically found in solutions like H₂ClO₄. This molecule in the acidic form and the X-form is successfully applied to study the acidity of zeolite Y (NaY, HY) catalysts [7,8]. Therefore, the objective of our group is to investigate a new probe molecule. Paul *et al.* have shown the effects of solvent and acid concentration on absorption and fluorescence spectra of 1,8-diaminonaphthalene (1,8-DAN) and other molecules [9]. However, some of their findings are controversial.

Our current work is carried out in two parts: first, to reinvestigate 1,8-DAN and set up a revised and improved reaction scheme of 1,8-DAN in the ground and excited state with varying acidity. Second, to perform a photochemical investigation of 1,8-DAN on zeolite Y, based on fluorescence properties. These will be done by measuring the interaction of the probe molecules with the acidic sites

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of the catalyst, i.e., the proton transfer reactions between the zeolite and 1,8-DAN in the ground and excited state, using laser-induced picosecond spectroscopy. In this paper we present the results of the first part of our work.

EXPERIMENTAL

Materials

The probe molecule, 1,8-DAN, was provided by Fluka company and was used after recrystallization from ethanol–water followed by sublimation. Perchloric acid, HClO_4 (>70%) Fluka, was used for varying the acid concentrations.

Purification and Stability

Since 1,8-diaminonaphthalene is readily oxidized, it needs to be purified before use. Recrystallization from ethanol–water for many times and sublimation are two possible methods. Deoxygenated water is used to keep the solutions stable for longer time.

Solution Preparations

1,8-DAN was first dissolved in methanol–water (<1 wt.%) and then diluted to different concentrations by distilled water. A diluted solution of the acid was used to prepare samples of pH 5.0–2.0. For pH values from 3.0 to 9.0, buffer (pH 3, 6, and 9) solutions were used. Highly acidic solutions, pH 1.0 to pH –1.1, of 1,8-DAN were prepared by adding different volumes of concentrated perchloric acid. Different acidic molarities were prepared starting from 0.01 to 11.8 M. The 1,8-diaminonaphthalene concentration was kept at 8.0×10^{-5} M.

UV–Vis Absorption Measurements

Steady-state UV–Vis absorption measurements for solutions were obtained using a Lambda-5 and a Lambda EZ 210 (Perkin-Elmer) Spectrophotometer.

Fluorescence Emission Measurements

Fluorescence spectra were recorded with a SPF-500 spectrofluorometer from SLM Instruments. The fluorescence spectra were corrected for the intensity of the lamp and the sensitivity of the photomultiplier tube.

Fluorescence Decay Time Measurements

A mode-locked Nd:YAG laser (Spectra-Physics model 3800) with a mode locker (Spectra-Physics model 451) operating at 41 MHz repetition rate was used to pump a Rhodamine 6G dye laser. Cavity dumping at 4 MHz was performed. The output pulses were frequency doubled (Spectra-Physics model 390 frequency doubler). The excitation wavelength was 300 nm and the fluorescence decay signals of the probe molecule were collected at the wavelength of maximum fluorescence emission. Lifetimes were measured using the Applied Photophysics photon-counting spectrometer system, model PS 60, equipped with a XP 2020Q photomultiplier. The actual pulse width of the excitation pulse is less than 10 ps; however, due to the response time of the photon counting system, it is broadened to 350 ps. Data were collected through a multichannel analyzer and then transferred to a computer for analysis.

RESULTS AND DISCUSSIONS

Absorption Spectra

Absorption spectra of 1,8-DAN in water shows a band at ~ 330 nm which correspond to the neutral form of the molecule. By increasing the acidity of the solution from neutral to 11.8 M HClO_4 we found a steady decrease of the band at 330 nm and the appearance of a band at 280 nm with an isobestic point at 295 nm as shown in Fig. 1. The absorption spectrum of the mono-cation form is a mixture of two transitions, the neutral transition at 330 nm and the di-cation transition at 280 nm. A proposed

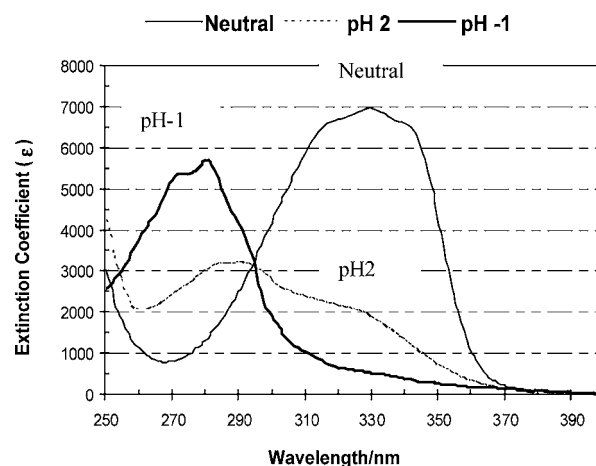
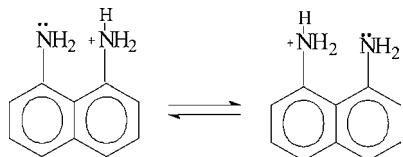


Fig. 1. Absorption spectra of the three different forms 1,8-DAN at 8.0×10^{-5} M, in terms of the extinction coefficient (ϵ).



Scheme 1. Proposed structure for mono-cation 1,8-DAN.

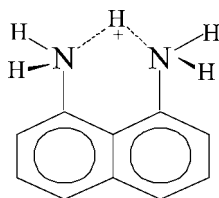
structure of the mono-cation form is suggested according to the absorption spectra. The proton is attached either to one or the other nitrogen atom. Both forms are in equilibrium, see Scheme 1. However, if the proposed structure by Paul *et al.* (Scheme 2) is true, only one transition should occur in the absorption spectrum, which is not the case.

Fluorescence Spectra

Fluorescence emission spectra of the neutral form and the mono-cation form show the same emission at a maximum wavelength of $\lambda_{Em} = 440$ nm, where exciting at wavelength of $\lambda_{Ex} = 340$ nm (Fig. 2). However, exciting at wavelength $\lambda_{Ex} = 300$ nm, the mono-cation shows a small red shift and fluorescence at wavelength $\lambda_{Em} = 452$ nm, which is due to solvent relaxation (Fig. 3). This red shift is in agreement with what was previously reported by Paul *et al.* [9]

The fluorescence spectrum of the di-cation form shows a band with a maximum at $\lambda_{Em} = 340$ nm. This blue shift is due to the localization of the N-lone pairs by reacting with H^+ .

Increasing the hydrogen ion concentration lead to a decrease in the emission intensity of the neutral form with insignificant increase in the fluorescence of the di-cation form (Fig. 4). The emission of the di-cation form appears at a concentration of around 1 M $HClO_4$ until it reaches the maximum emission at 11.8 M $HClO_4$. However, the quenching effect of the di-cation form is visible upon increasing free water, i.e., diluting the 11.8 M $HClO_4$ with water, without an increase in the emission of the neutral form.



Scheme 2. Proposed structure by Paul *et al.* for the mono-cation of 1,8-DAN [9] which should display only one transition.

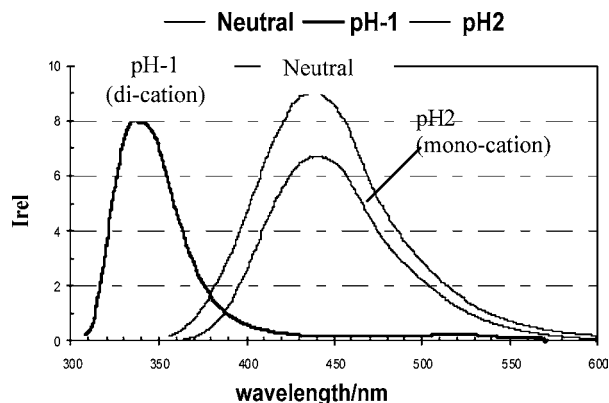


Fig. 2. Fluorescence emission spectra of different forms of 1,8-DAN. $\lambda_{Ex} = 340$ nm for the neutral and mono-cation form. $\lambda_{Ex} = 285$ nm for the di-cation form.

Fluorescence Decay Measurements

All measurements of the fluorescence decays are with fixed excitation wavelength $\lambda_{Ex} = 300$ nm. Fluorescence decays of the neutral form 1,8-DAN, pH 5.8, and the mono-cation form, pH 2.0, have very similar decays (Fig. 5). The emission wavelength of both is at $\lambda_{Em} = 460$ nm. Both are single-exponential.

The fluorescence decay for the di-cation form having pH -1.0 , shows a bi-exponential behavior with emission wavelength $\lambda_{Em} = 360$ nm and satisfy the equation:

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (1)$$

where $\lambda_{Ex} = 300$ nm for all measurements; $\lambda_{Em} = 460$ nm for the neutral form and mono-cation form; $\lambda_{Em} = 360$ nm for the di-cation form.

El-Rayyes *et al.* have found a bi-exponential decay for 1-AN at high acid concentrations, which was attributed to the formation of the X-form [6]. This was identified

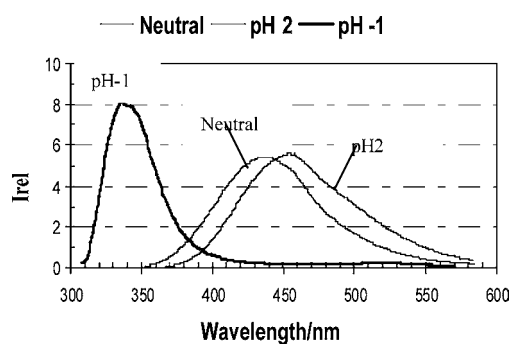


Fig. 3. Fluorescence emission spectra of different forms of 1,8-DAN. $\lambda_{Ex} = 300$ nm for the neutral and mono-cation form. $\lambda_{Ex} = 285$ nm for the di-cation form.

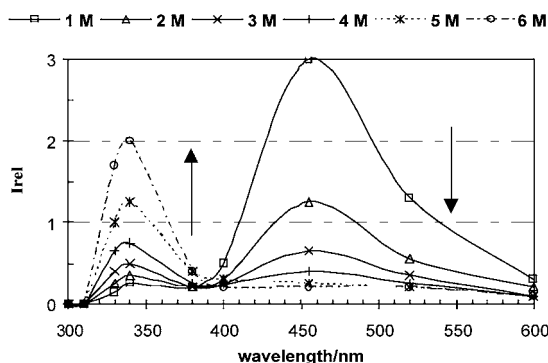


Fig. 4. Fluorescence emission spectra of different acid concentrations, from 1 to 6 M, showing the quenching between neutral and di-cation.

by absorption and emission spectroscopy. However, in our case such spectroscopic identification is not possible, which leaves the understanding of the bi-exponential decay open.

Determination of the Dissociation Constants (pK_a) in the Ground State

The values of the dissociation constants, pK_1 and pK_2 , in the ground state (S_0) were determined by plotting the absorbance differences of 1,8-DAN, at $\lambda = 330$ nm for pK_1 and $\lambda = 270$ nm for pK_2 , against pH values. Sigmoidal curves with inflections at pH 4.0 and -0.1 were obtained, which are the values of pK_1 and pK_2 at the ground state. These values of 1,8-DAN agree well with the literature values of 4.15 and -0.1 for pK_1 and pK_2 , respectively [9].

Determination of the Dissociation Constants pK_a^* in the Excited State

From the dissociation constants in the ground state the dissociation constants in the excited state can be de-

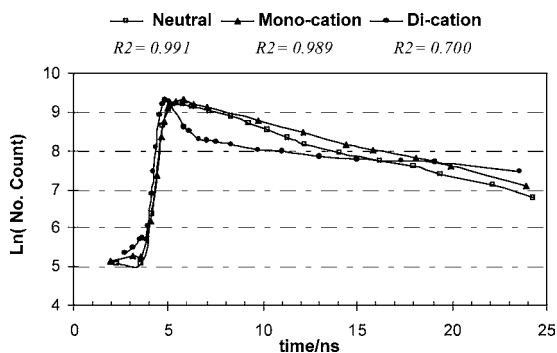


Fig. 5. Emission decay profiles of different forms of 1,8-DAN.

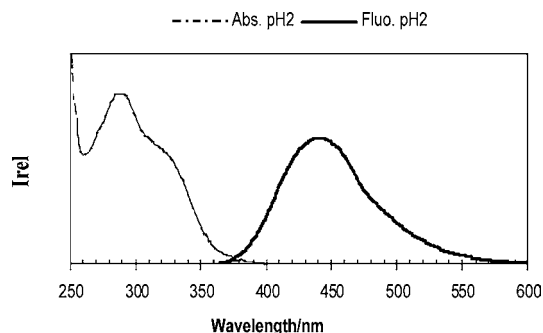


Fig. 6. Absorption and fluorescence spectra of the mono-cation of 1,8-DAN expressed in wavelength (nm), the absorption shows a mixture of two forms but the emission shows only one form.

termined using the Forster cycle:

$$pK_a^* = pK_a - hCN_A (\lambda_{HA}^{-1} - \lambda_A^{-1}) / 2.303RT \quad (2)$$

where λ_{HA} and λ_A are the wavelengths taken at the 0–0 transition between the absorption and the corresponding emission spectra of the acid and the base, respectively, pK_a and pK_a^* are the dissociation constants in the ground and excited state, respectively, h is the Planck's constant, C is the speed of light, N_A is the Avogadro's number, R is the gas constant, T is the temperature in Kelvin.

Determination of Fluorescence Quantum Yields

Fluorescence quantum yields were determined by comparing the fluorescence intensity of 1,8-DAN solutions to a reference solution. Quinine sulphate dissolved in 1N H_2SO_4 was used as fluorescence [21]. The absorbance of the sample and the reference must be the same at the excitation wavelength, which was chosen at $\lambda_{Ex} = 330$ nm for the neutral form and at $\lambda_{Ex} = 288$ nm for the mono-cation and the di-cation forms (Fig. 6).

Determination of k_q for the Neutral Form Using Quantum Yield Intensities

Appreciable proton-induced quenching has been observed for the fluorescence of the mono-cation form in the proton concentration range 0.01–1.2 M, prior to the formation of the di-cation. There is no quenching effect due to the counter ion ClO_4^- under the experimental conditions employed. The quenching constant can be determined using the model suggested by Shizuka [4] or by using a simple Stern–Volmer plot (Fig. 7) under the condition where the H^+ concentration is too small to give any

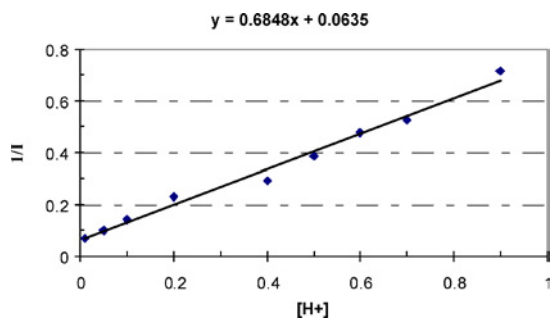


Fig. 7. Stern–Volmer plot of $1/I$ for 1,8-DAN vs. $[H^+]$.

backward reaction [9].

$$\frac{1}{\eta} = \frac{1}{\eta_0} + \frac{k_q \tau_0}{\eta_0} [H^+] \quad (3)$$

Plotting $1/\eta$ vs. $[H^+]$, gives slope = $k_q \tau_0 / \eta_0$

Then,

$$k_q = \frac{\text{slope} \times \eta_0}{\tau_0}$$

where η and η_0 are the fluorescence yield with and without quencher, respectively, k_q is the rate constant for proton-induced fluorescence quenching and τ_0 is the natural lifetime of the neutral species. (Note: Actual quantum yields are not needed. As they are proportional to the height of the spectrum, heights at $\lambda_{EM} = 455$ nm are used). Using slope = 0.685, $\tau_0 = 7.70 \times 10^{-9}$ s and $I_0 = 14.2$ cm at $\lambda = 455$ nm Then, $k_q = 1.26 \times 10^9$ M⁻¹ s⁻¹, which is in good agreement with the value of the quenching constant of 1.0×10^9 M⁻¹ s⁻¹ measured by Paul *et al.* [9]

Determination of k_q for the Neutral Form Using Lifetime Measurements

The quenching constant k_q can be also determined using a Stern–Volmer plot in terms of τ_0/τ vs. $[H^+]$ (Fig. 8).

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [H^+] \quad (4)$$

where τ_0 is the actual lifetime in the neutral species, i.e., without quenchers H^+ , τ is the actual lifetime in the mono-cation species, i.e., with quenchers H^+ , and k_q is the quencher rate constant of the neutral form. Plotting τ_0/τ vs. $[H^+]$, gives slope = $k_q \tau_0$. So, $k_q = \text{slope}/\tau_0$. Using slope = 9.92 and $\tau_0 = 7.70 \times 10^{-9}$ s, yields, $k_q = 1.29 \times 10^9$ M⁻¹ s⁻¹, which is in excellent agreement with the value of the quenching constant calculated from the quantum yield intensities, which gives $k_q = 1.26 \times 10^9$ M⁻¹ s⁻¹, within an error of 2%.

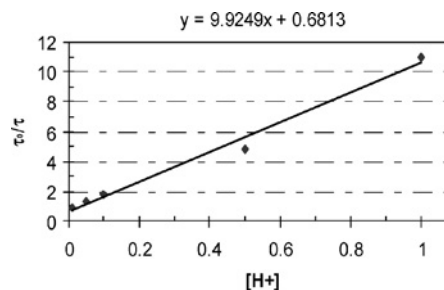


Fig. 8. Stern–Volmer plot of τ_0/τ for 1,8-DAN vs. $[H^+]$.

Determination of the Quenching Constant k'_q for the Protonated Form

In a previous study on 1-AN, El-Rayyes *et al.* [6] have shown that the rise of the fluorescence intensity of the protonated form on increasing the acid concentration is due to a decrease of the free water clusters capable of accepting the proton. Once the proton is transferred to a water cluster it acts as a quencher of the excited neutral form, i.e., we have diabatic reprotonation of the neutral form. They also observed that the fluorescence intensity of the protonated excited 1-AN goes through a maximum. This was attributed to the formation of X, an adduct between the excited acid and the anion. 1,8-DAN shows a similar behavior, i.e., the fluorescence intensity of the di-cation form rises on increasing the acid concentration, however, it does not go through a maximum. This suggests that there is only little X formed if at all in the case of di-cation 1,8-DAN, because of the repulsion of the two anions i.e., two ClO_4^- . A stable complex X-form cannot be found as in the case of 1-AN.

On the other hand, it is obvious that we should apply their quenching model through free water clusters, $[H_2O]_{free}$,

$$\frac{\eta_0}{\eta} = 1 + k_1 \tau_{acid} \gamma [H_2O]_{free} \quad (5)$$

where $k_1 = k'_q \times 55.5$, k'_q is the diabatic quenching constant, τ_{acid} is the lifetime of the pure di-cation form and $\gamma [H_2O]_{free}$ is the mole fraction of free water as a function of the $[HClO_4]$ which is taken from El-Rayyes *et al.* work [6] (Fig. 9).

This is in good agreement with the value of the quenching constant of 3.8×10^8 M⁻¹ s⁻¹ for 1-aminonaphthalene reported by El-Rayyes *et al.* [6]. This proves that the free water cluster model is applicable to 1,8-DAN and may be used as a general model for a strong acid in the excited state undergoing a diabatic quenching (Fig. 10, Tables I–III).

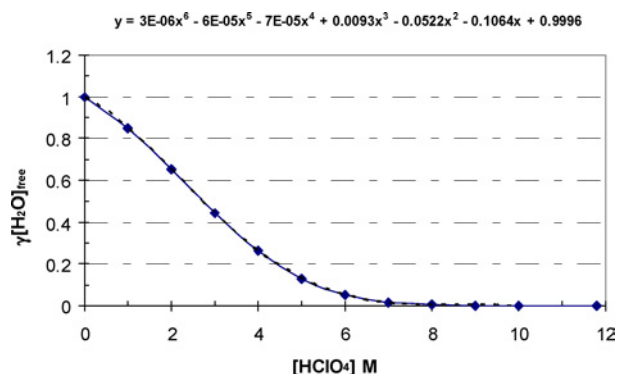


Fig. 9. Mole fractions of $[\text{H}_2\text{O}]_{\text{free}}$ vs. the perchloric acid concentrations.

Energy Surface Diagrams of 1,8-DAN

According to the spectroscopic measurements we got, there are three different forms of 1,8-DAN in the ground state, i.e., the neutral, the mono-cation and the di-cation form. However, there are only two different forms of 1,8-DAN in the excited state, i.e., the neutral and the di-cation form. The mono-cation form in the excited state becomes more acidic. The estimated value of k_d^* is 10^{17} s^{-1} , which was estimated by using the $\text{p}K_a^*$ of the aminonaphthalene (1-AN). Hence, it loses the proton very fast to form the neutral form which actually gives the emission (Fig. 2). On the other hand, Fig. 3 shows a red shift of the mono-cation emission due to solvent relaxation. According to these information, schematic energy surface diagrams of the mono- and the di-cation form were sketched (Figs. 11–12).

Kinetic Model of the Proton Transfer Reactions For 1,8-DAN

According to the preceding discussion, we propose the following scheme for the proton transfer reactions.

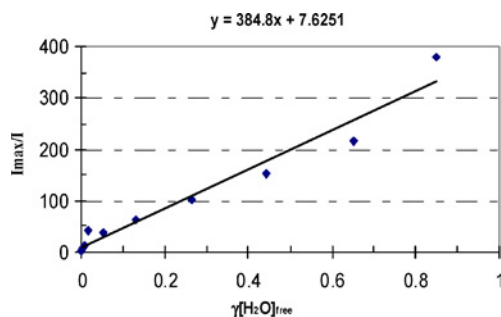


Fig. 10. I_0/l vs. mole fraction $[\text{H}_2\text{O}]_{\text{free}}$. Slope = $k_1 \times \tau_{\text{acid}}$, $k_1 = 384.8/22.2 \times 10^{-9} \text{ s} = 1.73 \times 10^{10} \text{ s}^{-1}$, $k'_q = k_1/55.5 = 3.12 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

Table I. Lifetimes of the Different Forms of 1,8-DAN

pH	τ_1 (ns)		τ_2 (ns)	
	Paul <i>et al.</i>	Our work	Paul <i>et al.</i>	Our work
5.8 (neutral)	1.6	7.7	—	—
2.0 (mono-cation)	7.4	8.3	—	—
−1.1 (di-cation)	—	1.6	—	22.2

As spectroscopic data suggest, the mono-cation form of 1,8-DAN in the excited state undergoes fast dissociation to the neutral form which gives the emission of the neutral form. Upon increasing the concentration of H^+ this form is quenched. On the other hand, the di-cation form of 1,8-DAN loses its excitation when a proton acceptor (i.e., free water) is present. There is no equilibrium between the di- and mono-cation forms in the excited state, i.e., it is a diabatic process (see Scheme 3). Table IV shows all the kinetics constants were determined.

CONCLUSION

The proton-transfer reaction kinetics of 1,8-diaminonaphthalene in acidic medium was studied by means of absorption and emission spectra and by laser-induced picosecond spectroscopy. We found that there are three different forms of 1,8-DAN in the ground state, but only two different forms in the excited state.

The absorption of the mono-cation form of 1,8-DAN is found to be a mixture of two transitions, i.e., the neutral form transition and the di-cation form transition, which disproves the scheme proposed by Paul *et al.* [9], i.e., the proton is shared between the two nitrogen atoms. However, the emission is found to be only from the neutral form, due to the instant dissociation of the mono-cation form once it is excited. The reaction of the excited neutral form with H^+ does not lead to an excited mono-cation

Table II. Acidity Constants in the Ground and First Excited States of 1,8-DAN

Equilibrium	$\text{p}K_a$		$\text{p}K_a^*$	
	Paul <i>et al.</i>	Our work	Paul <i>et al.</i>	Our work
$\text{DANH}^+ \leftrightarrow \text{DAN} + \text{H}^+$	4.2	4.0	—	−9.7 ^a
$\text{DANH}_2^{2+} \leftrightarrow \text{DANH}^+ + \text{H}^+$	−0.1	−0.1	−6.5	−10.7

Note. $\text{p}K_a^*$ values are theoretical values obtained by Forster cycle.

^aUsing the 1-AN spectrum which has a similar transition as 1,8-DAN at around 276 nm.

Table III. Quantum Yields of Different Forms of 1,8-DAN

Form of 1,8-DAN	Quantum yield Φ_f^S
Neutral (1,8-DAN)	0.061 ^a
Mono-cation (1,8-DANH ⁺)	0.136
Di-cation (1,8-DANH ₂ ²⁺)	0.047

Note. Quantum yield of quinine sulphate $\Phi_f^S = 0.55$ and refractive index of water $n_{\text{H}_2\text{O}} = 1.33$.

^aAgrees well with the earlier finding by Paul *et al.* who reported a value of 0.061 [9].

form (adiabatic reaction), rather it leads to the unexcited mono-cation form (diabatic quenching reaction).

Higher energy excitation of the mono-cation form gives a red shift emission due to solvent relaxation, as reported before by Paul *et al.* [9] However, lower energy excitation of the mono-cation form gives the unshifted neutral emission which was not reported before.

A kinetic scheme for the protonation/deprotonation of 1,8-DAN in the ground and excited states is proposed. According to the scheme, there is no equilibrium in the excited state between the different forms of 1,8-DAN, i.e., no adiabatic processes are observed. Energy surface schemes for the mono- and the di-cation forms are proposed based on absorption and emission spectra.

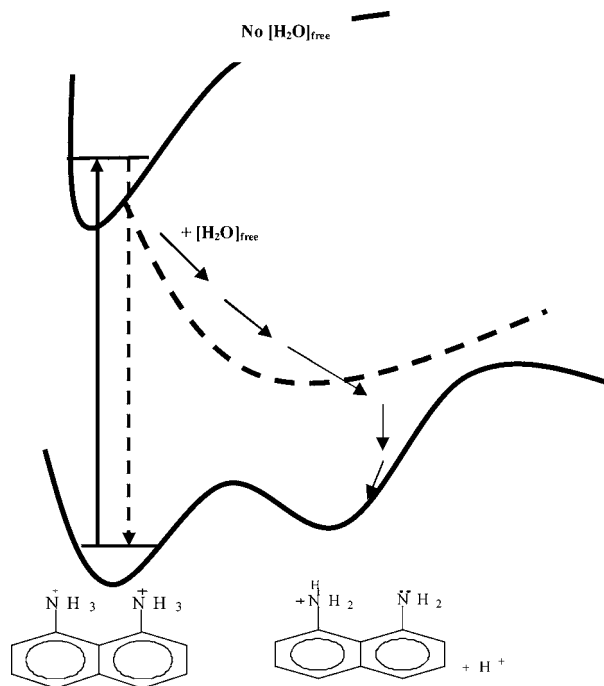


Fig. 12. Schematic energy surface of the di-cation form in the presence and absence of free water molecules, where $\lambda_{\text{Ex}} = 285 \text{ nm}$ and $\lambda_{\text{Em}} = 340 \text{ nm}$.

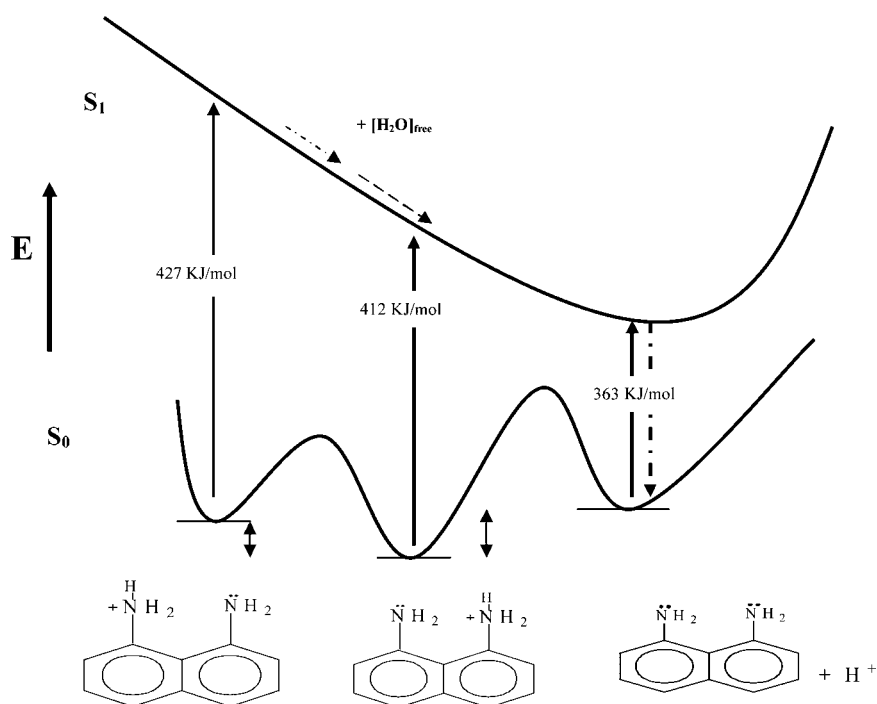
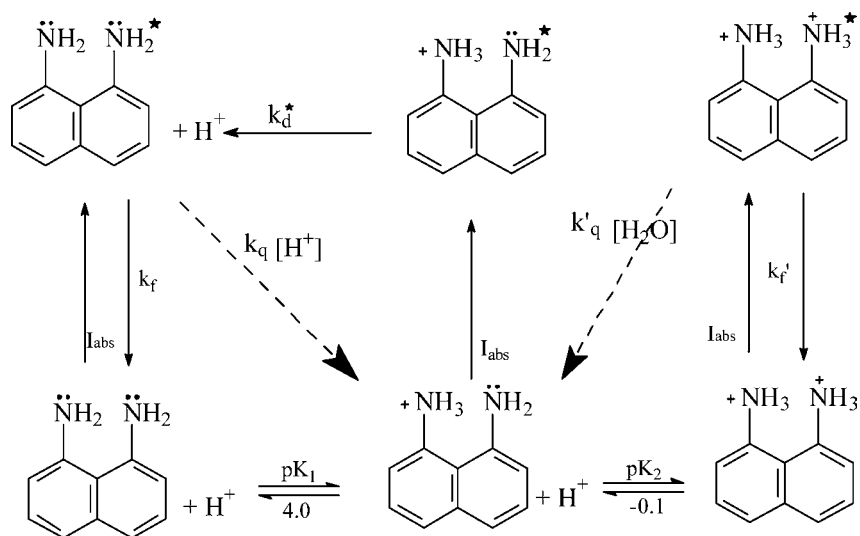


Fig. 11. Schematic energy surface diagram for the mono-cation form in the ground and excited state, where $\lambda_{\text{Ex}} = 340 \text{ nm}$, $\lambda_{\text{Em}} = 440 \text{ nm}$.



Scheme 3. Proton transfer reactions of 1,8-DAN in the ground and excited states. pK_1 and pK_2 are the dissociation constants in the ground state, k_d^* is the rapid deactivation constant of the mono-cation form in the excited state, k_f and k'_f are the fluorescence rate constants, for neutral and protonated forms, respectively, k_q and k'_q are the quenching rate constants, deactivation, for neutral and protonated forms, respectively, I_{abs} is the absorption intensity, which indicate where excitation can be done.

Table IV. Kinetics Constants

Form of 1,8-DAN	Neutral	Mono-cation	Di-cation
τ (ns)	7.7	8.3	1.6, 22.2
$k_f(\eta)$ (10^8 s^{-1})	1.3	1.2	6.3, 0.450
pK_a	4.0	—	-0.1
pK_a^*	-9.7	—	-10.7
Φ	0.061	0.136	0.047
K_q ($\text{M}^{-1} \text{ s}^{-1}$)	1.26×10^9	10^{17}	3.12×10^8

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