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Photoionization mechanism of aniline derivatives in aqueous solution studied by laser flash photolysis

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Abstract

The photoionization mechanism of a series of aniline derivatives in aqueous solution was investigated by 266 or 308 nm laser flash photolysis to determine the molecular properties which play an important role in the photoionization of solute molecules in aqueous medium. The ionization potentials of the investigated compounds in the gas phase (IP_{gas}) are in the range 6.87–8.64 eV. In compounds with IP_{gas} values of less than approximately 7.8 eV, photoelectron ejection takes place mainly from the non-relaxed S_1 state by one-photon absorption at 266 nm (4.66 eV) or 308 nm (4.03 eV), showing that significant polarization stabilization of the cation as well as of the photoejected electron should occur in aqueous solution. Contrary to expectation, the hydrated electron yield ($\Phi_{e_{aq}^-}$) determined from transient absorption measurements tends to increase with increasing IP_{gas}. The $\Phi_{e_{aq}^-}$ value increases with increasing positive charge (i.e. formal charge) on the nitrogen atom of the resulting cations, indicating that the interaction between the local positive charge on the cation and the solvent water molecules is one of the key factors in the photoionization of aqueous aniline derivatives. © 1997 Elsevier Science S.A.

Keywords: Aniline derivatives; Aqueous medium; Laser flash photolysis; Photoionization mechanism

1. Introduction

The photoionization process of a solute molecule in the liquid phase is strongly affected by the ambient solvent molecules, so that the ionization mechanism and threshold energy of ionization are significantly different from those in the gas phase [1–6]. In polar media, especially in aqueous solution, the photoionization threshold (IP_{liq}) of a solute molecule is substantially lower than that (IP_{gas}) in the gas phase due to polarization stabilization of the cation and electron pair in condensed media. Therefore the photoionization process often becomes an important relaxation pathway in aqueous solution, competing with fluorescence, intersystem crossing and internal conversion in the excited state of the solute molecule. Hence photoionization in aqueous solution has been studied extensively [7–25].

As a characteristic feature of photoionization in aqueous solution, one-photon ionization of solute molecules on UV irradiation has been reported for various compounds, such as indole [7–11], tryptophan [8,9,11,12], phenol [13–15], β-naphtholate anion [16–19] and aromatic amines [20–22]. Several possible ionization mechanisms have been proposed [8,26]. From thermochemical considerations, the difference between IP_{gas} and IP_{liq} is usually expressed by the following equation [27,28]

$$IP_{liq} = IP_{gas} + P_+ + V_0 \tag{1}$$

where P_+ is the adiabatic electronic polarization energy of the medium by the positive ion and V_0 is the minimum energy of a ‘‘quasi-free’’ electron in the liquid relative to an electron in vacuum. Since the V_0 value in water has been estimated to be −1.2 eV by Grand et al. [29], it can be anticipated that the polarization stabilization (P_+) of a cation in aqueous solution should be larger than that of an electron. Within the framework of the theoretical model regarding solvents as a dielectric continuum, P_+ can be estimated from Born’s equation [30]

$$P_+ = -\frac{e^2}{2r_+}\left(1 - \frac{1}{\epsilon_{op}}\right) \tag{2}$$

where e is the electronic charge, r_+ is the effective ionic radius and ϵ_{op} is the optical dielectric constant of the solvent. For aqueous indole, Bernas and coworkers [7,29] have reported the photoionization threshold as 4.35 eV. To explain the large negative P_+ value (−2.35 eV) deduced from the observed IP_{liq} (4.35 eV) and reported IP_{gas} (7.9 eV) values, the r_+ value of aqueous indole was estimated to be 1.4 Å, which is much smaller than that (3.36 Å) calculated from

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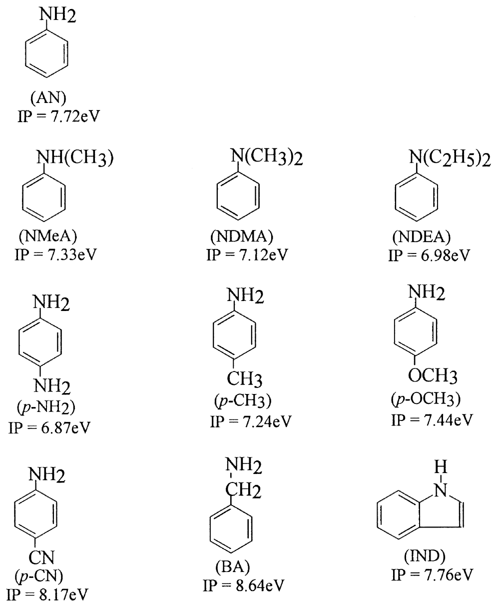

Scheme 1.

the molecular volume [7,29]. It was suggested that the r_+ value could be attributed to the positive charge localized around the nitrogen atom [7]. However, P_+ is also affected by the solvent dielectric constant, which varies from the high-frequency limit (ϵ_{op}) to the static limit (ϵ_S) depending on the solvent relaxation during electron ejection from the excited solute molecule. Although a large number of studies on the photoionization of solute molecules in aqueous solution have been reported, the effect of the electronic structure of the parent molecule and the role of the solvent water molecules on the photoionization are not yet fully understood.

Recently, we found that aqueous aniline is ionized by 266 or 308 nm laser photolysis with a relatively high photoionization quantum yield ($\Phi_{e_{aq}^-}$ of 0.18 and 0.16 at 266 and 308 nm respectively) [31]. Furthermore, it was revealed that the photoionization of aqueous aniline took place from the non-relaxed S_1 state through one-photon absorption. In this paper, the photoionization of aniline derivatives in aqueous solution is investigated in order to clarify the following points:

1. the contribution of photoionization to the various relaxation processes in the excited state;
2. the photoionization mechanism of aniline derivatives in aqueous solution;
3. the effect of the electronic structure of the parent molecule and its cation on the photoionization yield;
4. the role of water molecules in photoionization.

The sample molecules investigated are listed in Scheme 1, together with the abbreviations used and their IP_{gas} values. The gas phase ionization potentials of these compounds are in the range 6.87–8.64 eV.

2. Experimental details

Aniline (AN; Kanto), *N*-methylaniline (NMeA; Tokyo Kasei), *N*,*N*-dimethylaniline (NDMA; Wako), *N*,*N*-diethylaniline (NDEA; Wako) and benzylamine (BA; Kanto) were purified twice by vacuum distillation. *p*-Phenylenediamine (*p*-NH_2; Kishida), *p*-toluidine (*p*-CH_3; Kanto), *p*-methoxyaniline (*p*-OCH_3; Tokyo Kasei), *p*-cyanoaniline (*p*-CN; Wako) and indole (IND; Kishida) were purified twice by recrystallization from ethanol and *n*-hexane and sublimated in vacuum. Deionized water (H_2O) was purified by a Milli-Q Lab (Millipore). Cyclohexane (CH; Wako spectrosol) was purified by fractional distillation. Cs_2SO_4 (Fluka, 99.9%) was used as received. The pH of the aqueous sample solutions ranged from pH 6.5 to pH 7.5, except for the aqueous BA solution (pH 10.4). Since the pK_a values of the aniline derivatives investigated are reported to be in the range 4.6–6.2, the presence of protonated amines was negligible under the present experimental conditions (partial protonation was involved in aqueous BA ($pK_a = 9.2$)). All sample solutions were thoroughly degassed by freeze–pump–thaw cycling on a high-vacuum line.

The absorption and fluorescence spectra were recorded on a Jasco Ubest-50 spectrophotometer and a Hitachi F-4010 spectrofluorometer with a rhodamine B accessory for spectral correction respectively. The AN–CH system ($\Phi_f = 0.17$ in CH at 293 K [32]) was used as a reference to determine the fluorescence quantum yields of the samples. The fluorescence lifetime was measured with a time-correlated single-photon counter (Edinburgh Instruments, FL900CD).

The nanosecond laser flash photolysis experiments were carried out using the fourth harmonic (266 nm) of an Nd^{3+}:YAG laser (Spectra-Physics, GCR-130; pulse width, 6 ns) and 308 nm pulses from an XeCl excimer laser (Lambda Physik, Lextra 50; pulse width, 17 ns) as excitation sources. The monitoring system for the transient species consisted of a pulsed xenon lamp (Ushio, UXL-151D), a monochromator (Ritsu, MC-20N) and a photomultiplier (Hamamatsu, R928). The timing sequence between the laser pulse and the xenon flash lamp was controlled by a digital delay pulse generator (Stanford Research Systems, model DG-535). The transient signals were recorded with a digitizing oscilloscope (Tektronix, TDS-744; 500 MHz, 2 giga samples s^{-1}) and transferred to a personal computer (NEC, PC-9821Ap) to analyse the data. The signals were averaged over five to ten laser shots to improve the signal-to-noise ratio. The laser power was measured using a pyroelectric detector (Scientech, P25/S200).

3. Results and discussion

3.1. Absorption and fluorescence spectra

Fig. 1 shows the absorption and fluorescence spectra of the aromatic amines in aqueous solution. The first and second absorption bands can be assigned to the $^1L_b \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$ transitions respectively [33]. Both transitions have intramolecular charge transfer character. It can be seen from Fig. 1 that alkyl substitution on the amino group causes a red

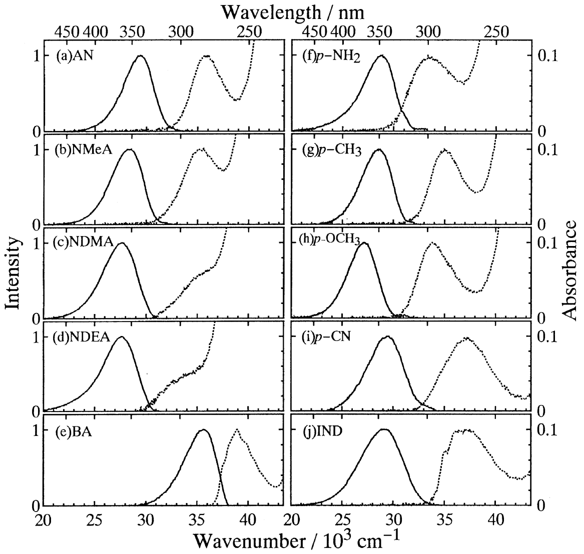

Fig. 1. Absorption (dotted line) and fluorescence (full line) spectra of aniline derivatives and related compounds (BA and IND) in aqueous solution at 298 K.

shift in both the absorption and fluorescence spectra compared with those of AN. The electron-donating substituent on the para position of the benzene ring also produces a red shift. The large Stokes shifts in aqueous solution indicate the large difference in dipole moment between the ground and excited states mainly due to the charge transfer character in the S_1 state. The fluorescence decay profiles in CH and aqueous solutions at 298 K were obtained by the time-correlated single-photon counting method. The fluorescence lifetimes are listed in Table 1, together with the fluorescence quantum yields and Stokes shifts. The fluorescence lifetime and quantum yield tend to be small in aqueous solution compared with those in non-polar CH, suggesting that efficient radiationless processes in the excited singlet state are involved in aqueous solution. Such a solvent effect was found to be remarkable only in compounds having N–H bond(s), and was not observed in NDMA and NDEA. Köhler [34] has reported that hydrogen bonds between aniline (proton donor) and ethanol in binary ethanol–*n*-hexane solvent mixtures become stronger in the excited state by virtue of an increased charge acceptor strength. These observations suggest that the hydrogen bonds between the hydrogen atom on the amino group and the water molecules play an important role in water-induced radiationless processes [35].

3.2. Transient absorption spectra

Fig. 2 shows the transient absorption spectra obtained by 308 and 266 nm laser photolysis of the sample compounds in CH at 298 K. The most dominant bands in the transient absorption spectra are quenched by dissolved oxygen, so that they can be ascribed to $T_n \leftarrow T_1$ absorption as in the case of AN [31]. It can be seen that long-lived components are superimposed on the $T_n \leftarrow T_1$ absorption bands of AN, NMeA, *p*-NH_2, *p*-CH_3, *p*-OCH_3, *p*-CN and IND. These components are considered to be due to neutral radicals produced by N–H bond fission in the excited state in CH [31,36–38]. This is supported by the fact that the long-lived components are absent in NMDA and NDEA which have no N–H bond. Thus the transient absorption spectra of the sample compounds in CH are mainly due to $T_n \leftarrow T_1$ absorption.

The transient absorption spectra in aqueous solution are shown in Fig. 3, and are markedly different from those in CH

Table 1
Fluorescence lifetime (τ_f), fluorescence quantum yield (Φ_f), absorption ($\bar{\nu}_a$) and fluorescence ($\bar{\nu}_f$) peaks and Stokes shift ($\Delta\bar{\nu}$) of aniline derivatives in cyclohexane (CH) and aqueous (H_2O) solutions at 298 K

Sample	Solvent	τ_f (ns)	Φ_f (10^{-1})	$\bar{\nu}_a$ (10^4 cm^{-1})	$\bar{\nu}_f$ (10^4 cm^{-1})	$\Delta\bar{\nu}$ (10^3 cm^{-1})
p-NH_2	CH	3.10	0.86	3.16	2.73	4.3
	H_2O	1.35	0.11	3.33	2.88	4.5
NDEA	CH	2.51	0.77	3.29	2.99	3.0
	H_2O	2.29	0.49	3.37	2.76	6.1
NDMA	CH	2.42	0.82	3.39	3.01	3.8
	H_2O	2.24	0.42	3.45	2.77	6.8
p-CH_3	CH	3.84	1.28	3.39	3.07	3.2
	H_2O	0.57	0.16	3.50	2.87	6.3
NMeA	CH	3.42	1.19	3.39	3.07	3.2
	H_2O	1.22	0.32	3.56	2.85	7.1
p-OCH_3	CH	2.15	0.84	3.31	2.92	3.9
	H_2O	0.67	0.19	3.37	2.72	6.5
AN	CH	4.34	1.7	3.48	3.15	3.3
	H_2O	0.93	0.32	3.59	2.94	6.5
IND	CH	8.58	4.17	3.88	3.34	5.4
	H_2O	4.10	2.1	3.75	2.92	8.3
p-CN	CH	5.43	2.23	3.45	3.11	3.4
	H_2O	0.11 (90%) 3.16 (10%)	0.07	3.73	2.95	7.8
BA	CH	28.3	1.04	3.86	3.52	3.4
	H_2O	3.69	0.09	3.89	3.56	3.3

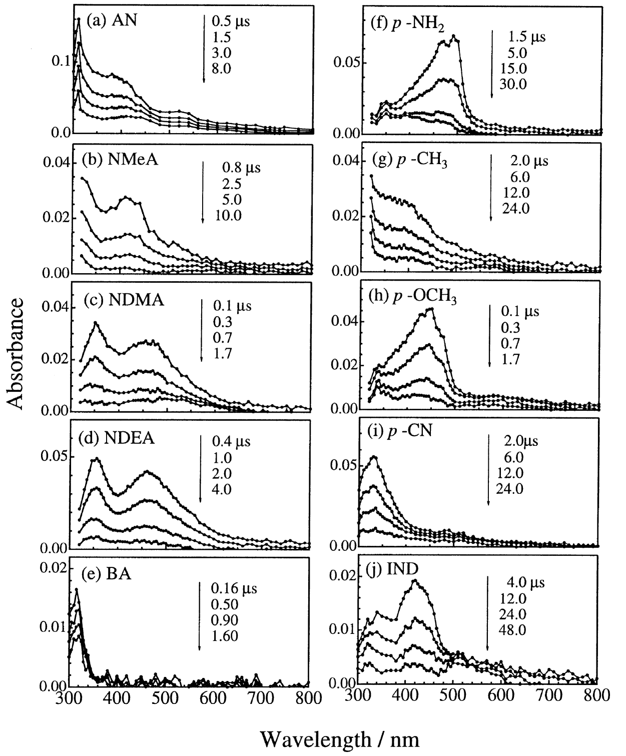

Fig. 2. Transient absorption spectra obtained by 266 nm laser photolysis of AN (a), BA (e), p-CN (i) and IND (j) and by 308 nm laser photolysis of NMeA (b), NDMA (c), NDEA (d), p-NH_2 (f), p-CH_3 (g) and p-OCH_3 (h) in CH at 298 K.

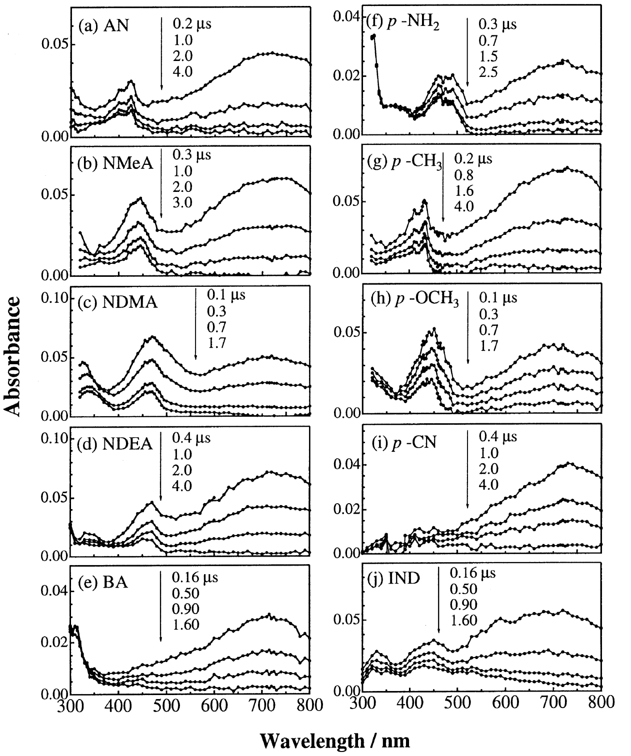

Fig. 3. Transient absorption spectra obtained by 266 nm laser photolysis of AN (a), NDEA (d), BA (e), p-CN (i) and IND (j) and by 308 nm laser photolysis of NMeA (b), NDMA (c), p-NH_2 (f), p-CH_3 (g) and p-OCH_3 (h) in aqueous solution at 298 K.

(Fig. 2). The broad absorption band with a peak at 720 nm [39] in Fig. 3 has the characteristic spectral shape of the hydrated electron (e_{aq}^-) and can be assigned to this species. The cation radicals produced by photoionization show band peaks at 425 nm for AN [31,37,40], 459 nm for NMeA [41], 473 nm for NDMA [41], 480 nm for p-NH_2 [42,43], 440 nm for p-CH_3, p-OCH_3 and p-CN [41,43] and 340 and 565 nm for IND [11,41]. By comparing the transient absorption spectra in aqueous solution (Fig. 3) with those in CH (Fig. 2), we can deduce that the transient absorption bands with maxima in the range 300–500 nm in aqueous medium are due to the cation radicals and $T_n \leftarrow T_1$ absorption. The formation of e_{aq}^- and cation radicals reveals that aniline derivatives in aqueous medium are ionized by 266 or 308 nm laser photolysis.

3.3. Photoionization mechanism in aqueous solution

The laser power dependence of the hydrated electron yield was examined in order to distinguish between one- and two-photon ionization mechanisms. Fig. 4 shows the laser power dependence of the hydrated electron yield in aqueous solution at 298 K. Both BA and p-CN, which have relatively large gas phase ionization potentials ($IP_{gas} = 8.64$ and 8.17 eV respectively), exhibit quadratic power dependences with slopes of 2.12 and 2.27 respectively (see Fig. 4(c) and Fig. 4(d)). This shows that the photoionization of BA or p-CN in aqueous solution takes place via a two-photon absorption process. In contrast, the other compounds, with relatively low gas

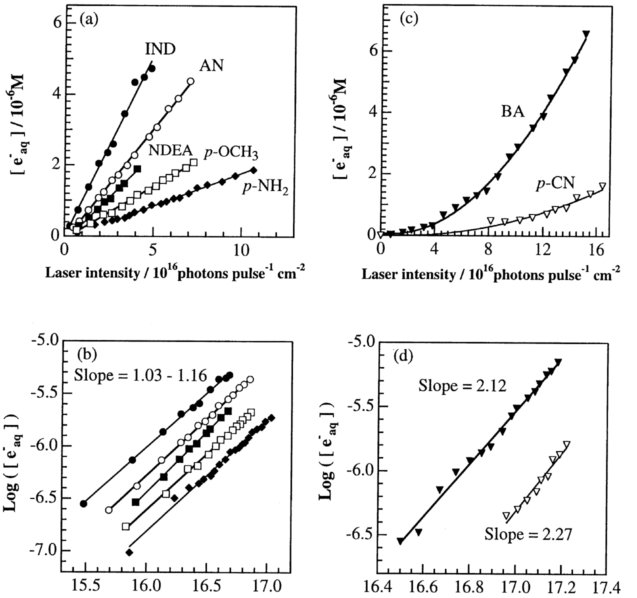

Fig. 4. (a) Laser power dependence of the e_{aq}^- concentration generated by 266 nm laser photolysis of aqueous IND (●) and by 308 nm laser photolysis of aqueous AN (○), NDEA (■) in water–ethanol (95 : 5, v/v) mixed solvent, aqueous p-OCH_3 (□) and aqueous p-NH_2 (◆), and their log–log plots (b). (c) Laser power dependence of the e_{aq}^- concentration generated by 266 nm laser photolysis of BA (▼) and p-CN (▿) in aqueous solution, and their log–log plots (d).

phase ionization potentials ($IP_{gas}=6.87$–7.76 eV), show almost linear laser power dependences as illustrated in Fig. 4(a) and Fig. 4(b). The slopes of the straight lines in Fig. 4(b) are 1.03–1.16. Although the data are not shown in Fig. 4, NMeA, NDMA and p-CH_3 also exhibit linear laser power dependences. These observations indicate that the investigated compounds, except BA and p-CN, are ionized in aqueous solution by one-photon absorption of a 308 or 266 nm photon. Thus the ionization thresholds for the one-photon ionized molecules in aqueous solution are less than 4.03 eV (308 nm) (for IND, less than 4.66 eV (266 nm)).

The quantum yields of e_{aq}^- formation ($\Phi_{e_{aq}^-}$) on 266 or 308 nm excitation were determined using the $T_n \leftarrow T_1$ absorption of naphthalene (NAP) in CH as an external actinometer. The quantum yield of intersystem crossing (Φ_{isc}^{NAP}) and the molar extinction coefficient ($\epsilon_{^3NAP^*}^{415}$) of the $T_n \leftarrow T_1$ absorption of NAP at 415 nm in CH have been reported as 0.75 and 24 100 $M^{-1}\,cm^{-1}$ respectively [44,45]. Since the absorbance of the sample solution at 266 nm (or 308 nm) is adjusted to be equal to that of NAP in CH, $\Phi_{e_{aq}^-}$ is given by

$$\Phi_{e_{aq}^-}=\left(\frac{\Delta A(0)_{e_{aq}^-}^{720}}{\Delta A(0)_{^3NAP^*}^{415}}\right)\left(\frac{\epsilon_{^3NAP^*}^{415}}{\epsilon_{e_{aq}^-}^{720}}\right)\Phi_{isc}^{NAP} \qquad (3)$$

where $\Delta A(0)_{e_{aq}^-}^{720}$ and $\Delta A(0)_{^3NAP^*}^{415}$ are the initial absorbances of e_{aq}^- at 720 nm and triplet naphthalene at 415 nm respectively and $\epsilon_{e_{aq}^-}^{720}$ is the molar extinction coefficient of e_{aq}^- at 720 nm (18 500 $M^{-1}\,cm^{-1}$ [46]). The values of $\Phi_{e_{aq}^-}$ obtained are listed in Table 2. The solubility of NDEA in water was too low to carry out laser experiments; instead, a water–ethanol (95 : 5, v/v) mixed solvent was used for the determination of $\Phi_{e_{aq}^-}$. For all the one-photon ionized molecules, $\Phi_{e_{aq}^-}$ is found to be larger than 0.1 on 266 nm excitation, indicating that the photoionization process is one of the dominant relaxation pathways in the excited singlet state.

In Table 2, relatively large wavelength dependences of $\Phi_{e_{aq}^-}$ are observed for p-NH_2, NDEA and NDMA, which can be explained by considering the difference in the electronic states. As can be seen from Fig. 1, the 266 nm excitation can reach the second absorption band of p-NH_2, NDEA and NDMA. The S_2 state of NDEA, originating from valence electron excitation, has intramolecular charge transfer character [47]. Furthermore, s-type Rydberg states can be superimposed in the energy region higher than 36 520 cm^{-1} [48]. Therefore the increase in $\Phi_{e_{aq}^-}$ at 266 nm may result from the difference in the electronic structures and from the involvement of autoionization. Such excitation wavelength dependences of the photoionization yield for aqueous aromatic amines have also been reported on steady state irradiation [21,22].

The increase in $\Phi_{e_{aq}^-}$ on S_2 state excitation suggests that a photoelectron is ejected before relaxation to the fluorescent state. In order to clarify whether the photoionization takes place from the relaxed or non-relaxed excited singlet state, we examined the effect of Cs^+ ion on $\Phi_{e_{aq}^-}$ as in the case of AN [31]. The Cs^+ ion is an effective singlet quencher increasing the intersystem crossing rate. If photoionization of the aniline derivatives in aqueous medium occurs from the relaxed S_1 state (i.e. fluorescent state), the Cs^+ ion effect should follow the Stern–Volmer relationship

$$\frac{\tau_f^0}{\tau_f}=\frac{\Phi_{e_{aq}^-}^0}{\Phi_{e_{aq}^-}}=1+k_q\tau_f^0[Cs^+] \qquad (4)$$

where τ_f and τ_f^0 denote the fluorescence lifetimes with and without Cs^+ respectively and k_q is the fluorescence quenching rate constant by Cs^+. Fig. 5 shows plots of τ_f^0/τ_f and $\Phi_{e_{aq}^-}^0/\Phi_{e_{aq}^-}$ of NDEA and BA as a function of the Cs^+ concentration at 298 K. From the slopes of the straight lines for τ_f^0/τ_f, the k_q values are obtained as 1.6×10^9 and 1.4×10^8 M^{-1}

Table 2
Hydrated electron yield ($\Phi_{e_{aq}^-}$), gas phase ionization potential (IP_{gas}), formal charge on the N atom in the cation and cation radius (r_+) of aniline derivatives in aqueous solution at 298 K

Compound	$\Phi_{e_{aq}^-}$		IP_{gas}^a (eV)	Formal charge on N atom[b]	r_+^c (Å)
	266 nm	308 nm			
p-NH_2	0.12 (0.10)[e]	0.047 (0.032)	6.87	0.347	3.35
NDEA	0.30 (0.22)	(0.12)	6.98	0.367	3.98
NDMA	0.20 (0.18)	0.12 (0.09)	7.12	0.396	3.69
p-CH_3	0.17 (0.14)	0.13 (0.11)	7.24	0.434	3.52
NMeA	0.19 (0.19)	0.15 (0.13)	7.33	0.420	3.50
p-OCH_3	0.12 (0.11)	0.075 (0.062)	7.44	0.400	3.58
AN	0.18 (0.17)	0.16 (0.13)	7.72	0.462	3.31
IND	0.27	–	7.76	0.511	3.36[f]
p-CN	0.013[d]	–	8.17	0.459	–
BA	0.022[d]	–	8.64	0.364	3.51

[a] Taken from Ref. [49].
[b] Calculated by the PM3 method.
[c] Estimated according to Eq. (5).
[d] Apparent hydrated electron yield by two-photon ionization.
[e] In parentheses: determined in mixed solvent, H_2O–EtOH (95 : 5, v/v).
[f] Taken from Ref. [29].

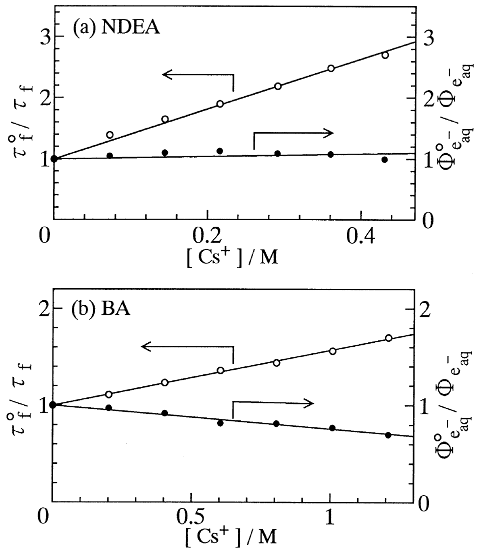

Fig. 5. (a) Plots of τ_f^0/τ_f (○) and $\Phi^0_{e_{aq}^-}/\Phi_{e_{aq}^-}$ (●) as a function of [Cs$^+$] for NDEA in water–ethanol (95 : 5, v/v) mixed solvent at 298 K (excitation wavelength, 308 nm). (b) Plots of τ_f^0/τ_f (○) and $\Phi^0_{e_{aq}^-}/\Phi_{e_{aq}^-}$ (●) as a function of [Cs$^+$] for aqueous BA at 298 K (excitation wavelength, 266 nm).

s^{-1} for NDEA and BA respectively. It should be noted from Fig. 5(a) that the effect of Cs$^+$ on $\Phi_{e_{aq}^-}$ is much smaller than that on τ_f, indicating that photoionization of aqueous NDEA originates from the non-relaxed S$_1$ state. Similar results were obtained for other aniline derivatives and IND as for AN [31]. However, $\Phi_{e_{aq}^-}$ of BA increases with increasing [Cs$^+$] as shown in Fig. 5(b). This implies that aqueous BA is ionized mainly by sequential two-photon absorption through the T$_1$ state.

It can be expected from Eq. (1) that $\Phi_{e_{aq}^-}$ will depend on the values of IP$_{gas}$ and P_+ (see Eq. (2)), as V_0 should be the same for all the molecules investigated. If IP$_{gas}$ is the most dominant factor determining the hydrated electron yield, $\Phi_{e_{aq}^-}$ will increase with decreasing IP$_{gas}$. However, the plots of $\Phi_{e_{aq}^-}$ as a function of IP$_{gas}$ for one-photon ionized molecules give a relation contrary to expectation as shown in Fig. 6. This observation indicates that P_+ is the more important factor determining the photoionization yield of the aniline derivatives in aqueous medium.

In order to determine the dominant factors affecting P_+, we plotted the $\Phi_{e_{aq}^-}$ values against the cation radius (r_+). If the electronic charge in the cation is delocalized over the whole molecule, $\Phi_{e_{aq}^-}$ will be expected to decrease with increasing r_+, which can be deduced from the molecular volume as

$$r_+ = \left(\frac{3M}{4\pi\rho N}\right)^{1/3} \tag{5}$$

where ρ and M are the density and molecular weight of the sample and N is Avogadro's number. The r_+ values estimated from Eq. (5) are listed in Table 2. The relationship between $\Phi_{e_{aq}^-}$ and r_+ is shown in Fig. 7, where a correlation such that $\Phi_{e_{aq}^-}$ decreases with increasing r_+ cannot be seen clearly. This means that the r_+ value estimated from Eq. (5) is not adequate for the calculation of P_+ using Born's equation (Eq. (2)). Since the interactions between the local charge in the cation and the water molecules may play an important role in the stabilization of charged species in polar media, we plotted the $\Phi_{e_{aq}^-}$ values as a function of the formal charge on the N atom of the aromatic amine cations calculated by the PM3 method as shown in Fig. 8. The $\Phi_{e_{aq}^-}$ values tend to increase with increasing formal charge on the N atom of the cations. This result indicates that the formal charge on the N atom is an important factor for both P_+ and $\Phi_{e_{aq}^-}$. Thus the charge localization on the nitrogen atom of the cation produced by photoionization is an important factor determining the ionization threshold and efficiency of aromatic amines.

Fig. 9 shows the relationship between the Stokes shifts ($\Delta\bar{\nu}$) and $\Phi_{e_{aq}^-}$ for aniline derivatives and IND in aqueous solution. Compounds with large Stokes shifts give large

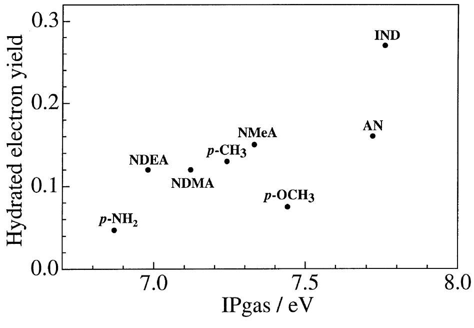

Fig. 6. Plots of $\Phi_{e_{aq}^-}$ vs. IP$_{gas}$ for one-photon ionized molecules in Table 2 at 298 K.

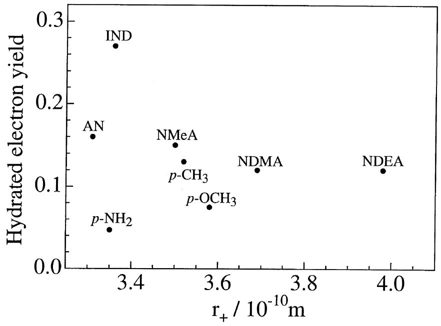

Fig. 7. Plots of $\Phi_{e_{aq}^-}$ as a function of r_+ estimated from Eq. (5) (for details, see text).

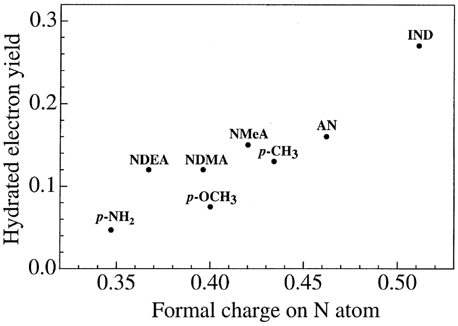

Fig. 8. Plots of $\Phi_{e_{aq}^-}$ as a function of the formal charge on the N atom in the cation produced by one-photon ionization of the samples at 298 K (for details, see text).

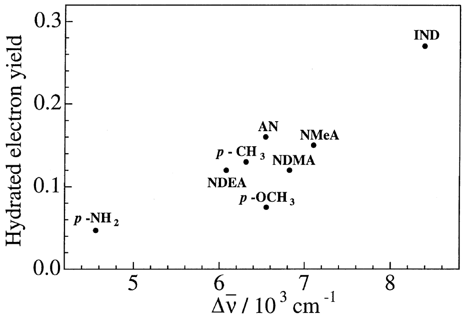

Fig. 9. Plots of $\Phi_{e_{aq}^-}$ as a function of the Stokes shift ($\Delta\bar{\nu}$) for one-photon ionized samples at 298 K.

hydrated electron yields, indicating that the electron ejection in the excited aromatic amines in aqueous solution occurs effectively from the S_1 state with charge transfer character. According to PM3 calculations for the cation radicals, the charge distribution in the S_1 state, characterized by intramolecular charge transfer from the nitrogen atom to the benzene ring, seems to be similar to that of the cation radicals produced by photoionization.

Therefore during solvent relaxation from the Franck–Condon state to the fluorescent state, solvent reorientation may act favourably for electron ejection of the excited aromatic amines to produce cation radicals. The photoelectron ejection should occur before completion of the orientational relaxation of the solvent molecules, because $\Phi_{e_{aq}^-}$ is hardly affected by Cs^+.

4. Conclusions

The following conclusions can be drawn from laser flash photolysis studies on the photoionization of aniline derivatives in aqueous medium:

1. the photoionization of aniline derivatives in aqueous medium, with the exception of *p*-CN, originates from the non-relaxed S_1 state by one-photon absorption of a 266 or 308 nm photon;
2. for one-photon ionized aniline derivatives, the hydrated electron yields are found to be greater than 0.1 on 266 nm laser excitation, indicating that the photoionization process is one of the dominant relaxation pathways in the excited singlet state in aqueous solution;
3. the local interaction between the positive charge on the N atom of the cations and the water molecules, resulting in an increase in the polarization stabilization, is one of the key factors in the photoionization of aromatic amines in aqueous medium;
4. the quantum yield of hydrated electron formation depends on the electronic structure of the excited singlet state.

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