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Ionization of Aniline in Nonpolar Hydrocarbon Solvents as Studied by Two-Photon Ionization Spectra

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Two-photon ionization spectra (wavelength dependence of photoionization efficiency) of aniline were measured in several hydrocarbon solvents in the excitation wavelength region of 360−430 nm (two-photon energy = 5.77−6.89 eV, a nonresonant process). There were two thresholds in saturated hydrocarbons, one at 6.4−6.6 eV and the other at 5.6−6.1 eV. The former was assigned to the direct ionization because the thresholds agreed with those calculated with the electron affinity of solvents and the polarization energy of aniline cation. The latter was assigned to an unidentified ion-pair formation process between aniline and saturated hydrocarbon. The spectrum in benzene, however, showed only one threshold at 6.16 eV, and this threshold was assigned to the direct ionization.

1. Introduction

The ionization process in liquid is different from that in the gas phase. The ionization potential of an aromatic molecule is lower by a few electronvolts than that in the gas phase, because a Coulombic field of the cation induces a large solvation energy even in nonpolar solvents and an electron may be stabilized in them.[1,2] The ionization potential in solution, IP_L, can be related to the ionization potential in gas phase, IP_G, the polarization energy of the cation, P_+, and the electron affinity of the solvent, V_0, as

$$IP_L = IP_G + P_+ + V_0 \qquad (1)$$

where P_+ is typically −1 to −2 eV and V_0 is typically −0.6 to +0.1 eV.[1−4] P_+ may be expressed by the Born equation,[5] which is expressed in atomic unit as follows:

$$P_+^{\mathrm{Born}} = -(1/2r_+)(1 - 1/\epsilon) \qquad (2)$$

where r_+ denotes the radius of the cation; r_+ can be obtained from the molecular volume. The first ionization potential of most aromatic molecules in the gas phase lies above 7 eV, and that in solution lies mostly around 6 eV.

Determination of the ionization potential in solution requires a stable and tunable light source around 200 nm and can be carried out by using either a discharge lamp[6,7] or a synchrotron radiation source.[3,4] On the other hand, the ionization potential in solution can be determined by using lasers through a two-photon excitation process.[8−10] Although two-photon absorption is much weaker than one-photon absorption, the laser two-photon ionization is a very sensitive process because an intense and tunable solid-state laser is now available in the 360−500 nm region and the ionization can be detected efficiently through photocurrent measurements.[11−14] The two-photon ionization spectrum[8,9,15,16] (wavelength dependence of photoionization efficiency) can disclose the ionization process of an aromatic molecule in solution in detail.

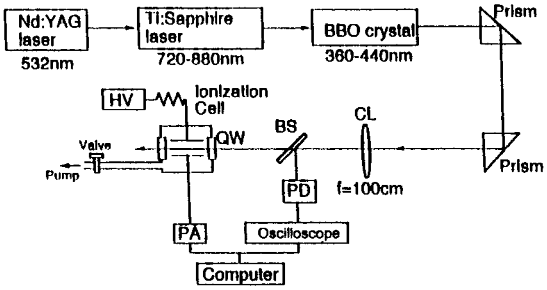

Figure 1. Schematic diagram of experimental apparatus: QW, quartz window; BS, beam splitter; CL, cylindrical lens; PD, photodiode; PA, picoammeter; HV, high-voltage supply unit.

In the present work, we have measured two-photon ionization spectra of aniline in several saturated hydrocarbons and benzene in the wavelength region 360−430 nm (two-photon energy of 5.77−6.89 eV). We have found two thresholds in the spectra and discussed their assignments and ionization processes of aniline.

2. Experimental Section

The schematic diagram of the experimental apparatus is shown in Figure 1. The second harmonic of a Ti:sapphire laser (Continuum TS60: 700−900 nm, 60−100 mJ/pulse, 10 Hz, 4−5 ns pulse width), which was pumped by a Nd:YAG laser (Continuum NY81C-10), was used as a light source between 360 and 440 nm. The laser beam was softly focused by a cylindrical lens (f = 1 m) and introduced into an ionization cell through a quartz window. The pulse energy of the laser beam was monitored with a photodiode and a digital scope (Kenwood DCS-8200, 500 MHz). The sensitivity of the

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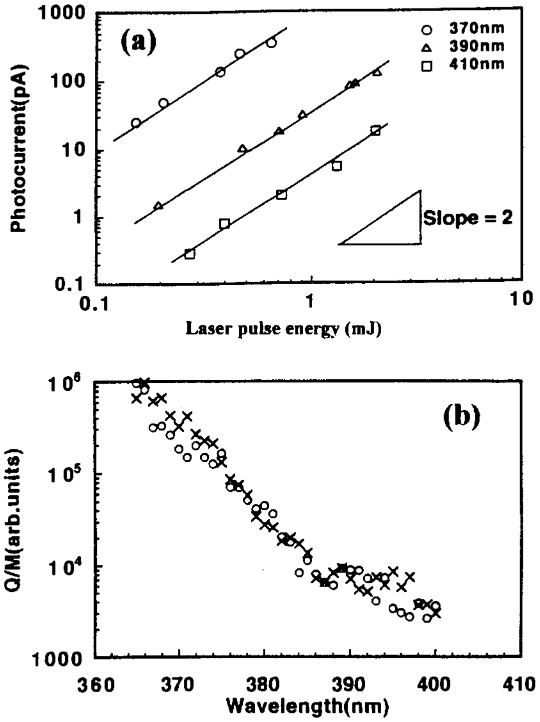

Figure 2. Dependence of photocurrent (*Q*) on laser pulse energy and concentration: (a) laser pulse energy dependence at three laser wavelengths, solvent is 2,2,4-trimethylpentane, concentration of aniline = 10^{-4} M; (b) concentration (*M*) dependence of photoionization spectra, *Q*/*M* is shown to normalize the concentration, solvent is pentane, concentration = (○) 10^{-4} M, (×) 10^{-5} M(×10).

photodiode at each wavelength was calibrated by a power meter (Molectron 5100).

The stainless steel ionization cell has a pair of stainless steel electrodes of 5 mm radius, four quartz windows, and an arm inlet for sample solution. The electrodes were insulated from the cell, and their spacing was 3 mm. An electric field of 1.5 kV was applied at one electrode. Photocurrent was measured through another electrode as dc current averaged over 150−300 laser pulses using a picoammeter (Takeda Riken TR8652). All instruments were controlled with a microcomputer (Compaq Prolinea 25).

Aniline (Wako Chemical, Research grade) was used after distillation under vacuum followed by deoxidization using zinc powder. The solvents, *n*-pentane, *n*-hexane, *n*-octane, 2-methylpentane, 3-methylpentane, 2,2,4-trimethylpentane, cyclopentane, cyclohexane, and tetramethylsilane (Kishida Chemical, research grade), and 2,2-dimethylbutane (Kishida Chemical, extra grade), were purified by percolation through a silica gel column. Benzene (Kishida Chemical, research grade) was distilled, dried over molecular sieves, and then percolated through a silica gel column. The solution was degassed in freeze−pump−thaw cycles with a turbo molecular pump. All measurements were carried out at room temperature.

3. Results

Dependence on the Laser Pulse Energy. Typical examples of the dependence of photocurrent on the laser intensity are shown in Figure 2a; the sample is 1 × 10^{-4} mol/dm^3 aniline in 2,2,4-trimethylpentane at 370, 390, and 410 nm. The typical photocurrent was 0.3−300 pA. The photocurrent was quadratically proportional to the pulse energy, and it should come from a two-photon excited process. The dark current (signal without laser irradiation) of this solution was about 0.4 pA, and its fluctuation was about 0.1 pA. The photocurrent without the solute,which would be due to three-photon excited ionization of the solvent,[17] was smaller than that of the solutions typically by 1/20 and was negligible.

Because aniline has no absorption in the wavelength region used (absorption edge, 320 nm), the process we have observed should be a nonresonant (simultaneous) two-photon process. Thus, the total excitation energy is definitely equal to twice the laser photon energy. This is true for all cases measured in the present study.

The photocurrent becomes smaller as the laser wavelength increases and is very small near the threshold. Thus, it should be measured at a high sensitivity. There are two major sources of noise; one is dark current of solution, and the other is three-photon excited photocurrent due to ionization of the solvent. Because the two-photon excited photocurrent of the probe molecule is proportional to the square of the laser pulse energy, an intense and focused laser beam may be advantageous to overcome the fluctuation of the dark current of the solution. However, a three-photon excited process gains more intensity at a higher pulse energy in a smaller spot. Thus, the laser intensity should be kept high enough to overcome the fluctuation of the dark current but low enough to suppress the three-photon process of the solvent. Thus, in the present study, the laser beam was softly focused, and the dependence of the photocurrent on the laser intensity was always examined. All measurements were carried out only in the region where the photocurrent was quadratically proportional to the laser intensity.

Although the photocurrent was quadratically proportional to the laser intensity at 430 nm, it was sometimes cubically proportional at 435 nm. This finding indicates that photoionization above 435 nm is a three-photon process. The photocurrent of aniline in 2,2,4-trimethylpentane was cubically proportional to the laser intensity when it is high, even at 430 nm. At the focus condition used in the present study, the two-photon signal (0.5 pA) in 2,2,4-trimethylpentane was about 3 times larger than the three-photon signal at 0.75 mJ/pulse, but they are approximately equal at 2 mJ/pulse. Because the three-photon signal should be negligibly small for the analysis of the two-photon ionization threshold, we removed any data taken at 430 nm and longer and used the data taken at 425 nm and shorter for the analysis of the photoionization processes in 2,2,4-trimethylpentane. The two-photon energy of 425 nm is 5.83 eV, which is slightly larger than the two-photon ionization threshold of aniline (5.73 eV), as described later. A similar analysis was carried out for all solvents used, and the longest wavelength used for analysis was 0.05−0.15 eV higher than the two-photon ionization threshold of aniline in that solvent. Benzene is rather exceptional because the two-photon signal from aniline was weak and the three-photon process of benzene itself was not negligible above 6.55 eV. Nevertheless, it has been possible to determine the two-photon ionization threshold within an accuracy of 0.01−0.03 eV, as shown later.

Concentration Dependence. The photocurrent was proportional to the concentrations of aniline. A typical example of the concentration dependence of photocurrent is shown in Figure 2b. Thus, only one aniline molecule should be involved in the photoionization process and any bimolecular secondary process should be negligible.

Two-Photon Ionization Spectra. Figure 3 shows two-photon ionization spectra of aniline in three hydrocarbons in the region of 365−420 nm; the photocurrent signal is quadratically proportional to the laser pulse energy in all cases. The photocurrent was normalized to the laser pulse energy in a

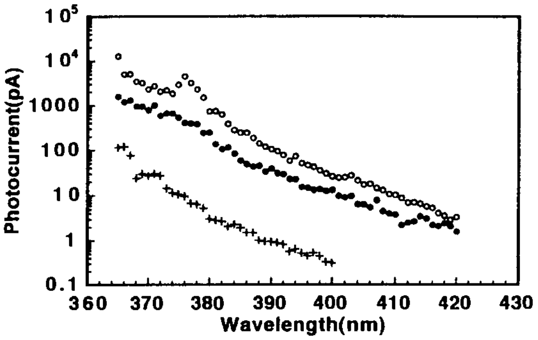

Figure 3. Typical photoionization spectra of aniline (10^{-4} M). Solvent: (○) isooctane, (●) cyclopentane, (+) pentane.

photon number of 2.0×10^{15} photons/pulse, which corresponds to about 1 mJ/pulse at 400 nm. The photocurrent was larger in a solvent with a low V_0 value such as 2,2-dimethylbutane and smaller in a solvent with a high V_0 value such as *n*-hexane. A small value of V_0 indicates a small value of IP_L, as shown in eq 1, and a solvent with a small value of V_0 has a large electron mobility.[1,2] The probability of geminate separation increases in these solvents, and thus both photocurrent and photoionization yield at a given wavelength increase when V_0 of the solvent is small.[1,2]

Power Law Plot and Photoionization Threshold. Photocurrent (I) near ionization threshold is proportional to the 5/2 power of the excess energy for photoionization (power law)[3] as

$$I = c(2h\nu - IP_L)^{5/2} \tag{3}$$

where c is a proportionality constant, and $h\nu$ is the photon energy. Thus, $I^{2/5}$ is plotted over $2h\nu$ as shown in Figure 4.

If there is only one photoionization process, the plot should give a single straight line and its intersection with the abscissa gives the ionization threshold, because $2h\nu - IP_L = 0$ at the intersection. Every plot in saturated hydrocarbons, however, has two thresholds, which indicates the existence of two photoionization processes.[18,19] The plot in benzene, on the other hand, showed only one threshold in the observed region, and there should be only one photoionization process of aniline in benzene below 6.52 eV.

The plot in 2,2,4-trimethylpentane has a maximum at 6.6 eV. Such a maximum has been found occasionally and assigned to autoionization of neutral excited states.[4,18,20] The data between 6.53 and 6.62 eV were excluded in the following analysis.

When there were two photoionization thresholds, the observed plots were simulated using the following equation:

$$I = c_1(2h\nu - IP_{L1})^{5/2} + c_2(2h\nu - IP_{L2})^{5/2} \tag{4}$$

where IP_{L1} and IP_{L2} are the first and second ionization thresholds and c_1 and c_2 are proportionality constants indicating the relative contribution of the two processes. The second ionization threshold can be determined as the energy at the bending point of the plot on the simulation. The simulation was carried out by using two c's as parameters, and the best fit is shown as a solid line in Figure 4. The simulated lines and the observed data agreed well, confirming the existence of two thresholds in saturated hydrocarbons.

The observed values of c's are shown in Table 1 together with the electron affinity (V_0), the dielectric constant (ϵ), and the electron mobility (μ_e) of solvents; c_1 and c_2 are normalized so that c_2 in *n*-pentane is unity. The polarization energy of the cation (P_+) can be calculated based on eq 1 using the observed values of IP_L and IP_G (7.72 eV[21]) and the known value of V_0, as shown also in Table 1. The single photoionization process in benzene should correspond to the second one in other solvents based on the P_+ value, as shown later.

Effect of Impurities. If there is an impurity in aniline, there should be some difference in photocurrent for purified and unpurified aniline in *n*-pentane. However, there was no difference in two two-photon ionization spectra taken for purified and unpurified aniline in *n*-pentane. Thus, there should be no impurity in aniline that gave an appreciable effect in photoionization.

Because no appreciable photoionization signal was obtained without aniline, there was no impurity in the solvent, which showed any appreciable effect by itself. An electron acceptor (Y) such as oxygen in the solvent may affect the photoionization process of aniline as follows:

$$C_6H_5NH_2 + Y + 2h\nu \rightarrow C_6H_5NH_2^{\ +} + Y^- \tag{5}$$

We have measured the two-photon ionization spectra in purified and degassed solvent, in purified and air-saturated solvent, and in unpurified and degassed solvent for *n*-pentane and 2,2,4-trimethylpentane. No obvious difference was found among them.

Thus, the impurity should not affect the observed results in any appreciable way.

4. Discussion

Assignment of Ionization Processes. Two ionization thresholds were observed in several investigations;[18,19] the first one was assigned to the formation of the ground-state cation and the second one to that of the excited cation. If the second process should create an excited cation, the second ionization potential (ca 1.2 eV above the first one[22]) should be used for an estimation of P_+. However, the absolute value of P_+ became too large ($P_+ < -2.5$ eV) by using the second ionization potential. Thus, the second process should not be related to the formation of an excited cation. The values in Table 1 were calculated using the first ionization potential of aniline and are reasonable, compared with the others. This finding indicates that the second ionization threshold can be related with the formation of the ground-state cation.

To assign the second threshold, we have plotted the observed value of P_+ to the dielectric constant (ϵ) of the solvent as shown in Figure 5; the solid circles are P_{+1} for the first threshold and the open circles are P_{+2} for the second threshold. Predicted values of P_+ (P_+^{Born}) based on the Born equation[5] (eq 2) were also shown in Figure 5 as a broken line. They were small for P_{+2} and very small for P_{+1} in the absolute value.

The Born equation assumed a point charge for the ion and included no contribution for the dipole moment of the aniline cation. The dipole moment (μ) of the aniline cation was calculated by a semiempirical molecular orbital method at the UHF/PM3 level using the MOPAC package[23] as $\mu = 4.97$ and $D = 1.96$ au. The solvation energy (E_s) induced by a dipole moment can be calculated as[24]

$$E_s = \{2(\epsilon - 1)\mu^2\}/\{2(\epsilon + 1)r_+^{\ 3}\} \tag{6}$$

The calculated value of E_s was about -0.2 eV for $\epsilon = 2.0$, which was about 20% of the estimated value of P_+^{Born}, and was not negligible. The estimated value of P_+ should be the sum of P_+^{Born} and E_s and is shown in Figure 5 as a solid line.

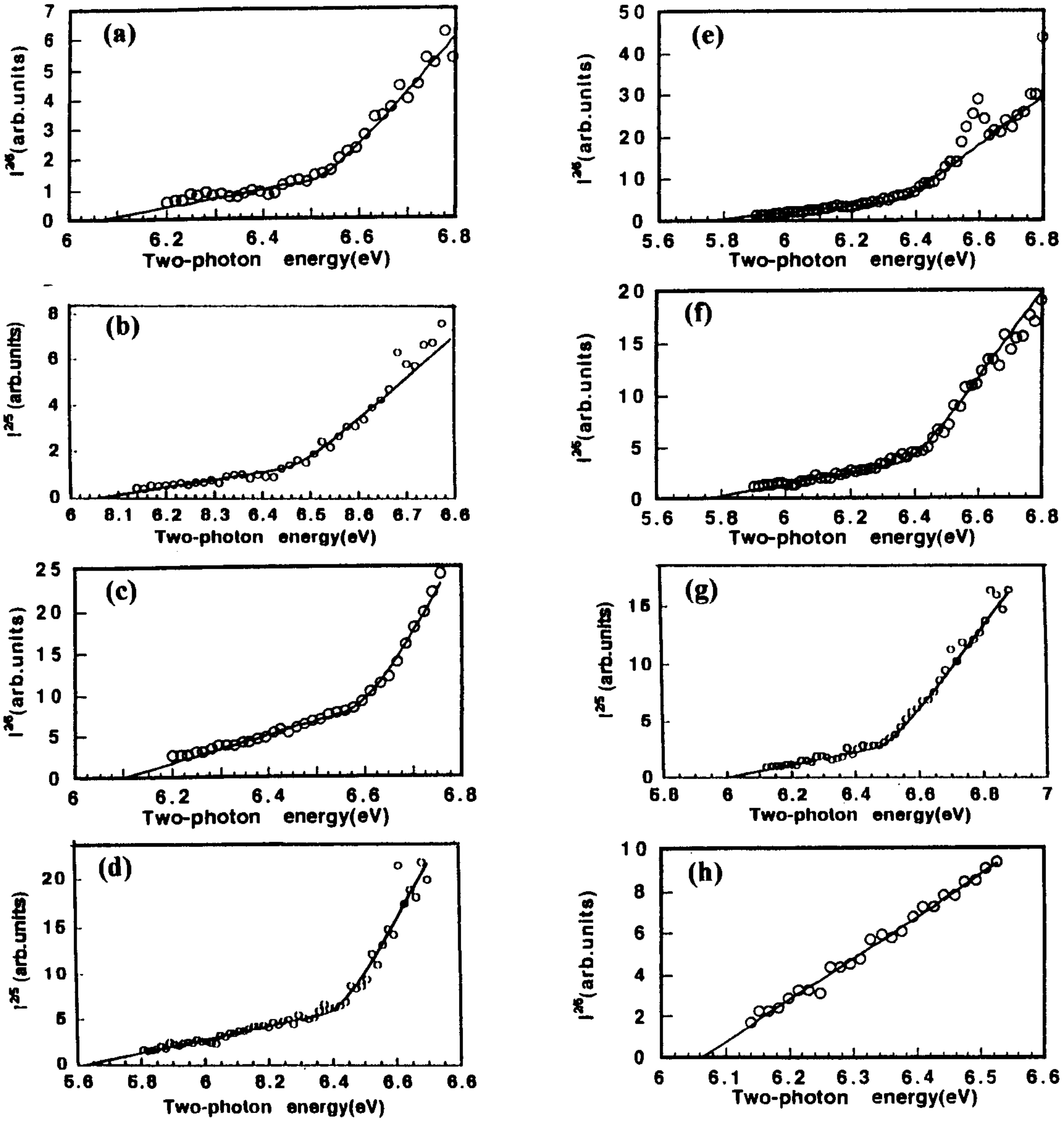

Figure 4. Dependence of the 2/5 power of photocurrent on two-photon energy. Solvent: (a) *n*-pentane, (b) *n*-hexane, (c) *n*-octane, (d) 2,2-dimethylbutane, (e) 2,2,4-trimethylpentane, (f) cyclopentane, (g) cyclohexane, (h) benzene. Concentration of aniline: 10^{-4} M, except in benzene of 10^{-3} M.

TABLE 1: Photoionization of Aniline in Various Solvents ($IP_G = 7.72$ EV)

solvent	V_0, eV	ϵ	μ^e, cm^2/Vs	IP_{L1}, eV	P_{+1}, eV	IP_{L2}, eV	P_{+2}, eV	c_1	c_2
1. *n*-pentane	-0.01^a	1.84	0.154	6.06	−1.66	6.49	−1.22	0.009	1.0
2. *n*-hexane	0.04^b	1.88	0.074	6.05	−1.71	6.43	−1.33	0.01	0.94
3. *n*-octane	0.13^c	1.95	0.038	6.09	−1.76	6.55	−1.30	0.04	0.44
4. 2-methylpentane	-0.20^d	1.88	0.29	5.88	−1.64	6.38	−1.14	0.03	6.3
5. 3-methylpentane	0.01^c	1.90	0.2	5.85	−1.88	6.40	−1.33	0.06	4.4
6. 2,2-dimethylbutane	-0.20^b	1.87	12	5.62	−1.90	6.36	−1.16	0.09	18.8
7. 2,2,4-trimethylpentane	-0.18^b	1.94	6.5	5.73	−1.81	6.30	−1.24	0.12	16.3
8. cyclopentane	-0.21^c	1.97	1.13	5.75	−1.78	6.34	−1.19	0.05	7.5
9. cyclohexane	0.01^c	2.02	0.28	5.99	−1.74	6.45	−1.28	0.04	5.0
10. benzene	-0.14^d	2.27	0.125			6.06	−1.52		0.11
11. tetramethylsilane	-0.55^a	1.92	103	5.05	−2.12	5.98	−1.19	0.05	15.0

[a] Reference 28. [b] Reference 29. [c] Reference 30. [d] Reference 31. [e] Reference 25.

The sum agreed well with P_{+2}. Thus, the second threshold should be assigned to the formation of the ground-state ion. The threshold observed in benzene should also be assigned to the formation of the ground-state ion as indicated by the value of P_+. A spherical cavity of solvent was assumed in eqs 2 and 6. The published value of P_+ of polar and nonpolar aromatic molecules agreed with those estimated on this assumption within 20%.[4,6,20] Thus, this model should be suitable for the aniline cation.

The relative contribution of the two processes, c_1 and c_2, depends on solvents, as shown in Table 1. There is a linear correlation between the logarithmic value of c_1 and c_2 on μ_e, as

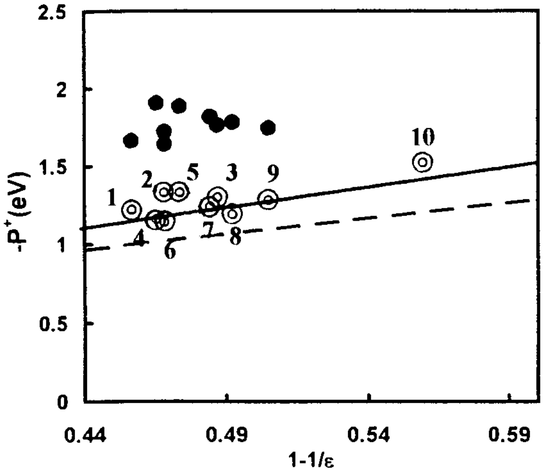

Figure 5. Dependence of P_+ determined for the two ionization thresholds on dielectric constant of solvents: P_{+1} (●), P_{+2} (◎); solid line, $P_+^{\mathrm{Born}} + E_s$, broken line, P_+^{Born}. Numbers in the figure are identical with the entry number of Table 1.

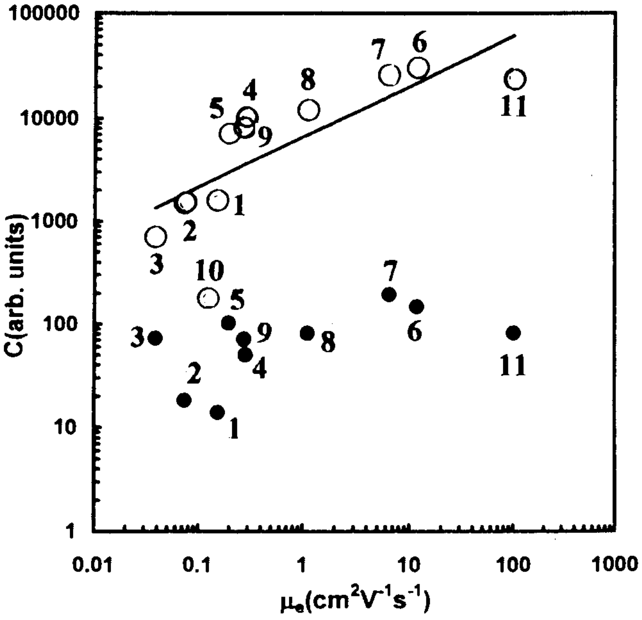

Figure 6. The relative contribution of the two ionization processes and the electron mobility of solvents: c_1 (●), c_2 (○). c_2 of pentane was set to 1.0. Numbers in the figure are identical with the entry number of Table 1.

shown in Figure 6. The least-squares fit to the observed data gave the following relationship, as shown in the full line in Figure 6:

$$c_2 \propto \mu_e^{0.48\pm0.10} \tag{7}$$

Although few studies have been carried out on the μ_e dependence of the photoionization probability of solute, there are a number of investigations on the radiation-induced ionization of neat liquids. Correlation between μ_e and the radiation-induced free-ion yield (G_{fi}) indicated that G_{fi} depended on μ_e as $G_{\mathrm{fi}} \propto \mu_e^{0.31\pm0.05}$ for 52 nonpolar liquids of which μ_e are larger than 0.1 cm^2 V^{-1} s^{-1}.[25] Although G_{fi} and c_2 are not identical quantities because the former is the probability for a pure liquids to produce a free-ion pair by radiation and the latter is the ionization efficiency of the solute, the similarity of their dependence on μ_e should indicate a similarity in their origin.

Assignment of the First Threshold. Although the photocurrent below the second threshold was weak, it was not due to any impurity. Two ionization thresholds at 7.4[26] and 7.65 eV[27] were reported in neat benzene, and the former was assigned to the formation of an ion-pair state.[26] However, aniline should not produce an ion-pair state in saturated hydrocarbon solvents because no anion state that lies below V_0, is known in saturated hydrocarbons. In addition, the fact that there was no first threshold in benzene should disclaim the ion-pair formation. The relative contribution of the first process, c_1, depended little on μ_e, as shown in Figure 6. Thus, the first process is not the ionization, that is, the formation of a cation and an electron.

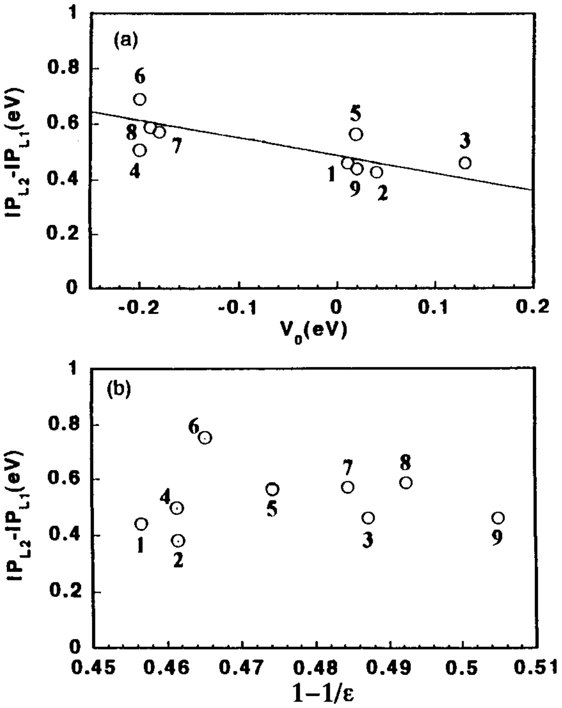

Figure 7. Dependence of the difference between the two ionization thresholds on the electron affinity (V_0) and dielectric constant (ϵ) of solvents. Numbers in the figure are identical with the entry number of Table 1.

The photocurrent below the ionization threshold may be explained by thermal dissociation of a low-energy geminate pair or a hot-band transition. Photoionization spectra of *N*,*N*,*N*′,*N*′-tetramethylphenylenediamine in various solvents showed that photocurrent could be observed in a wide range of temperature and should depend on the excitation energy as $\exp\{(E - \mathrm{IP})/kT\}$.[28] However, the photoionization spectra obtained in the present study agreed with eq 3 and decreased much more slowly with the excitation energy than expected for a thermal process. Thus, the thermal process should not be the origin of the first threshold.

The first process may originate from an ion-pair formation through a proton transfer induced by photoexcitation.

$$C_6H_5NH_2 + 2h\nu \rightarrow C_6H_5NH_2^{**}$$

$$C_6H_5NH_2^{**} + RH \rightarrow C_6H_5NH_3^{+} + R^{-} \tag{8}$$

where ** denotes a highly excited state. This mechanism is consistent with the finding that there is no first process in benzene because the C−H binding energy is larger in benzene than in saturated hydrocarbons.

The difference between two ionization potentials, ΔIP, is larger in solvents with a low value of V_0, as shown in Table 1, and depends on V_0 and ϵ, as shown in Figure 7. ΔIP depended linearly on V_0 but not on ϵ. A least-squares fit gave the relation

$\Delta IP = -0.48 \pm 0.10 + (0.74 \pm 0.15)V_0$, as shown in a full line in Figure 7a. Together with eq 1, this relation means $IP_{L1} = IP_G + P_+ + 1.74V_0 - 0.48$. If the first process is an ion-pair formation, the threshold energy may depend on P_+ and V_0. However, it is difficult to explain why V_0 has a factor of 1.74.

5. Conclusion

The two-photon ionization spectra of aniline has two thresholds, except in benzene. The higher threshold can be assigned to the formation of an aniline cation and an electron due to its dependence on P_+ and V_0. The lower threshold is too low to be a direct ionization of aniline and should be assigned to an ion-pair formation based on a proton transfer.

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