Microscopic Solvation of Acetonitrile to 9,9′-Bianthryl Studied in Gas Phase Clusters: Polar Excited State Formation†

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Dynamics of the electronically excited state of 9,9′-bianthryl(BA) was studied in gas-phase clusters with acetonitrile (ACN), BA-$(ACN)_n$ ($n = 1-5$). The gas-phase clusters were formed by supersonic expansion of BA/acetonitrile/He mixtures. In the laser-induced fluorescence spectra, new absorption bands ascribed to the BA-$(ACN)_n$ clusters were observed at longer wavelength side of the S_1-S_0 transition of BA. The mass-selected two-color resonance-enhanced multiphoton ionization (REMPI) spectra were measured to determine the absorption band for the cluster of BA with the specific number of the acetonitrile molecules. The dispersed fluorescence (DF) spectra and lifetimes were measured for these absorption bands to study the dynamics of the excited state of BA in the clusters, BA-$(ACN)_n$. For all clusters studied, the DF spectra of BA were broad and largely red shifted compared with that of unclustered BA. The fluorescence lifetimes of BA in the clusters were considerably longer than that of unclustered BA. These results suggest that the photoexcited state of BA in the clusters change to the polar excited state which is analogous to the twisted intramolecular charge transfer (TICT) state of BA in the acetonitrile solution. The Stokes shift and lifetime of the BA-$(ACN)_1$ suggested that the charge-transfer reaction becomes possible by adding one acetonitrile. However, these two properties of the larger clusters do not show monotonic change toward those of BA in acetonitrile solution. These results implied that the structure and dynamics of the clusters play some important roles in the charge-transfer reaction.

Introduction

The supersonic jet technique combined with the laser spectroscopy has enabled us to study solute−solvent clusters as a model of solution in the isolated conditions where a solute molecule interacts only with the small number of “solvent” molecules. As far as the room temperature solution is used, we can only observe the behavior of solute molecules as an average over the ensembles in which the solute molecules interact with various number of solvent molecules with various configuration. One advantage to study the gas-phase solute−solvent clusters is that the number of solvent molecules interacting with the solute molecule can be specified and, in favorable cases, the structure of the solute−solvent cluster is also provided.[1] By taking this advantage, the effect of stepwise solvation have been studied in both unimolecular[2,3] and bimolecular reactions,[4−7] and provided basic information about the role of solvents in the reactions.

In the present paper, we present the experimental study of the dynamics of the excited state of 9,9′-bianthryl (BA) following to the photoexcitation in its clusters with acetonitrile (ACN). In polar solvents, the photoexcited BA is known to show red-shifted fluorescence which has been ascribed to the formation of so-called “twisted intramolecular charge-transfer (TICT)” state.[8−21] The first direct evidence of the charge-separated character was given by a picosecond transient absorption spectrum of the excited state by Mataga’s group.[9] They measured the $S_n \leftarrow S_1$ absorption spectra of BA in acetone solution and observed that they were similar to the superposition of spectra of anthracene anion and cation. Because two anthryl moieties are equivalent, the “charge-transferred” state of BA consists of two degenerated CT states, i.e., a pair of linear combinations of the states where an electron is transferred from one anthracene moiety to the other and vice versa. Thus, a mechanism to break this symmetry is necessary to exhibit net large polarity following the photoexcitation.[10,12] The importance of the broken symmetry was supported indirectly by the experimental study of the charge-transfer reaction in the symmetry-disturbed derivatives of BA.[14] Mataga et al. observed that the charge transfer reaction rate is enhanced in some symmetry-disturbed derivatives of BA. This result indicated that the light absorption of these compounds projects the ground state equilibrium distribution onto a nonzero gradient of the excited state potential or the slightly presolvated state for these symmetry-disturbed compounds will facilitate the CT process. The importance of the solvent dynamics, which is expected to induce broken symmetry, has also been suggested by the transient fluorescence studies.[19,20] The CT rates of BA in polar solvents were observed to be similar to the microscopic solvation times of the solvents, and high correlation between the CT process and the solvent dynamics was suggested.

In the gas-phase clusters of BA, the fluorescent behavior of BA has been reported to be quite similar to that of BA in solution. Although free BA and its clusters with nonpolar molecules showed the fluorescence from the photoexcited state, the red-shifted fluorescence was observed in the clusters of BA with polar molecules, such as acetone,[2,22,23] and water.[24] In the case of acetone, the red-shift of the fluorescence and the fluorescence lifetime were measured for the clusters of the specific number of the acetone molecules and these two properties were observed to change gradually from those of free BA to those of solution.[2] These results indicated that the polar excited state formation analogous to the CT process in solution

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occurred even though the solvent motion was highly restricted under the low-temperature cluster condition.

In the present study, we wish to present experimental study of the polar excited state formation in the BA cluster with acetonitrile (ACN). The BA-$(ACN)_n$ clusters containing the specific number of acetonitrile were selectively photoexcited and the dispersed fluorescence spectra were measured. The Stokes shift and fluorescence lifetime were determined as a function of the number of acetonitrile molecules. Compared with acetone, acetonitrile has larger dielectric constant, and as a result of this larger polarity, the Stokes shift of the CT emission of BA in acetonitrile solution (around 4000 cm^{-1}) is larger than that in acetone solution (3400 cm^{-1}).[8,9] In the molecular level, the dipole moment of acetonitrile is also larger than that of acetone and the polar excited state of BA is expected to be stabilized more in the cluster with acetonitrile if the configuration in the cluster is favorable to the dipole−dipole interaction.

Experimental Section

Experiments were carried out by using two apparatus. A single chamber apparatus was used for LIF and dispersed fluorescence measurements.[25] A high temperature pulsed nozzle (0.8 mm i.d.), with a sample reservoir was equipped on the top of the chamber and operated typically at 200 C and 10 Hz. The chamber was evacuated by a 10 in. oil diffusion pump (Edwards Difstak 250/2000). The beam of BA was generated by a free jet expansion of the BA vapor diluted in He through the pulsed nozzle. In the case of the BA-acetonitrile clusters, the He carrier gas was passed through a bottle containing acetonitrile, and the concentration of acetonitrile was controlled by changing the temperature of the bottle.

The free jet containing BA and BA-acetonitrile clusters was irradiated by tunable laser light from a dye laser (Lambda Physik, SCANmate: Butyl-PBD) pumped by a XeCl excimer laser (Lambda Physik, COMPex100). The fluorescence from the laser irradiation region was collected by a quartz lens system and detected by a photomultiplier tube (HAMAMATSU R-928). A monochromator (NIKON P-250) was used to measure dispersed fluorescence (DF) spectra. The fluorescence signal was preamplified and fed into a boxcar integrator (SRS SR-250). The laser intensity was measured by a fast photodiode and its signal was also averaged by another boxcar integrator. The averaged signals of the fluorescence and laser intensities were stored in a computer for further analysis.

The lifetime measurement was carried out by using the same arrangement as that for the measurement of the DF spectra. The time evolution of the fluorescence was stored into a digital storage oscilloscope (LeCroy 9450, 2.5ns time resolution), and the decay curve was deconvoluted with respect to the excitation laser profile which was also measured.[26]

Mass selected resonance enhanced multiphoton ionization (REMPI) spectrum was measured by another apparatus consisting of a source and an ionization-TOF (time-of-flight) chambers. The source chamber was pumped by a 10 in. diffusion pump (ANELVA CDP-3700) with a water-cooled baffle. The free jet of BA from the high-temperature nozzle was collimated by a skimmer (Beam Dynamics, 1 mm dia.) and fed into the TOF chamber that was differentially pumped by a diffusion pump (Difstak 100/300M). Typical vacuum conditions of both chambers with the beam on condition were 2×10^{-5} and 1×10^{-7} Torr, respectively. The BA and BA-acetonitrile clusters were ionized by a two-color REMPI method in an ionization region of a homemade TOF spectrometer. The flight length of the TOF tube is 56 cm. Ions were detected by a Ceratron multiplier and amplified by a fast preamplifier (Ortec VT120B). The amplified signals were fed into a digital storage oscilloscope (LeCroy 9361) for the TOF spectra or averaged by the boxcar integrator for the REMPI spectra.

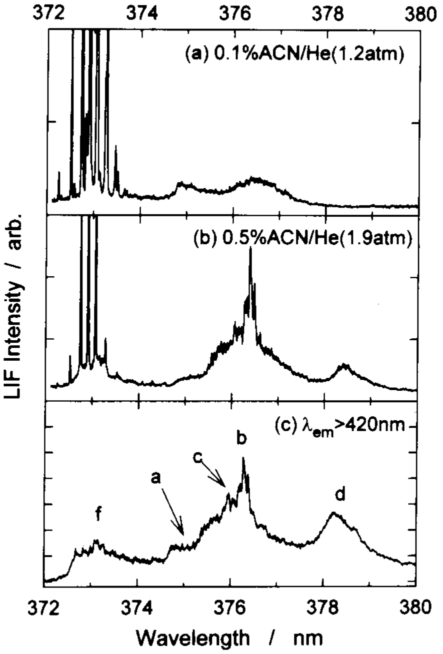

Figure 1. Laser-induced fluorescence (LIF) spectra of the BA-acetonitrile clusters. (a) LIF spectrum measured under low concentration of acetonitrile. (b) LIF spectrum measured under relatively high concentration of acetonitrile. (c) LIF spectrum measured by monitoring only emission wavelength longer than 420 nm. Nozzle condition is similar to that of (b).

The two-color REMPI was achieved by two synchronously operating tunable lasers, one used for the $S_1 \leftarrow S_0$ excitation and the other for the ionization. The output of a titanium sapphire laser (Continuum TS-60) pumped by a YAG laser (Continuum NY-82) was frequency doubled to obtain 370−382 nm and used for the excitation of BA or BA-acetonitrile clusters. For the ionization, a dye laser (Continuum ND-6000, DCM of dye) pumped by another YAG laser was used after the frequency doubling. The laser radiation at 310 nm was used for the ionization.

Bianthryl was prepared by the reduction of anthrone in acetic acid,[27] and recrystallized from toluene and chloroform. Special grade acetonitrile (Wako Co.) and high purity helium (99.999%) were used without further purification.

Results

Laser-Induced Fluorescence Spectra of the BA-Acetonitrile Clusters. Laser-induced fluorescence spectra measured for the supersonic jet of BA with acetonitrile are shown in Figure 1. Free BA has its 0−0 transition around 373 nm,[28−30] which consists of a train of sharp peaks owing to the torsional motion around the 9,9′-axis. This train of sharp peaks is seen in Figure 1, parts (a) and (b), which were measured by monitoring total fluorescence. In addition to the sharp peaks of free BA, new broad bands appear at longer wavelength region, i.e., the bands around 375 and 376.5 nm in Figure 1(a). With the increase of the acetonitrile concentration in the carrier gas, the band around 376.5 nm becomes more intense and some sharp features are also discernible, whereas the sharp peaks of free BA become less intense, Figure 1(b). In this acetonitrile concentration, one more new band appears at around 378.5 nm. The further increase of the acetonitrile concentration gives another band around 381.5 nm (not shown in this figure) and also increases intensity of very broad absorption band extending from 376 to 382 nm. These bands are ascribed to the clusters of BA with acetonitrile, and their dependence on the acetonitrile concentration suggests that the number of acetonitrile molecules increases from the cluster responsible for the band around 375 nm to those responsible for the band around 381.5 nm.

One interesting feature was observed in the LIF spectrum measured by monitoring fluorescence at longer wavelengths, viz., the wavelengths longer than 420 nm. The spectrum is shown in Figure 1(c). Because most parts of the emission of free BA appear at wavelengths shorter than 420 nm,[2,22,24] the band assigned to free BA is expected to be suppressed. In this spectrum, one broad band appears around 373 nm (band f) instead of the train of sharp peaks. Because of its dependence on the concentration of acetonitrile, this band is likely to originate from the BA-acetonitrile clusters. If this cluster band corresponds to the 0−0 band of free BA, the absorption band of BA in this cluster shows almost no spectral shift by the interaction with the acetonitrile molecules.

Mass Selected Resonance Enhanced Two-Photon Ionization Spectra. For the measurements of the two-color REMPI spectra, the ionization laser was fixed at 310 nm. Ionization energy of BA in the gas phase was reported to be 7.14[2] or 7.24 eV.[31] These values require 324 or 317 nm as the second photon for the ionization via the lowest singlet state of BA, and the photon of 310 nm has high enough energy to convert the first excited state to the ion. Preliminarily, we measured ionization efficiency curves of the BA-$(ACN)_n$ clusters. The wavelength of the excitation laser was fixed at the absorption band of one cluster and the wavelength of the ionization laser was scanned. For the clusters having one to four acetonitrile molecules, the onset of ions were observed around 330 nm. Hence, the ionization photon at 310 nm is believe to be high enough to ionize the excited state of the BA-acetonitrile clusters.

The mass-selected REMPI spectra are summarized for BA and BA-$(ACN)_n$ ($n = 1-4$) in Figure 2. The LIF spectrum is also shown in this figure for comparison. Compared with the LIF spectrum, the REMPI spectra are a little noisy. It is also noted that the bandwidths are a little wider in the REMPI spectra. This is because the temperature of the supersonic jet in the TOF apparatus is not so low as that in the LIF apparatus. It was observed that the interaction of the supersonic beam containing BA or BA-acetonitrile clusters with the skimmer was critical and this interaction heated the beam significantly. This effect is clearly seen in the spectrum of BA^+ compared with the LIF spectrum. In the former spectrum, some structure originates from hot band transitions which can be seen in the longer wavelength side. The wider band in the REMPI spectra may also originate from the contamination by the fragmentation of larger clusters. The ionization laser, 310 nm, supply sufficient energy to cause the fragmentation.

The REMPI spectrum measured by monitoring BA-$(ACN)_1^+$ shows a prominent broad band from 374.5 to 378.0 nm. This band is resemble to the band in the LIF spectrum measured at the low concentration of acetonitrile, Figure 1(a). This similarity is reasonable because the 1:1 BA-acetonitrile cluster is presumably dominant at the low concentration of acetonitrile. In the spectrum of BA-$(ACN)_1^+$, also seen is a weak feature around 372.5 nm. The spectrum of BA-$(ACN)_2^+$ shows two bands in this wavelength region, one at 373.2 nm and the other at 376.5 nm. The latter band shows good correspondence with the sharp band in the LIF spectrum (band b). The band at 373.2 nm is also similar to that appears in the LIF spectrum measured by monitoring longer wavelength emission, band f in Figure 1(c). The spectrum of BA-$(ACN)_3^+$ again shows rather narrow band around 376 nm, which is blue-shifted with respect to the band of BA-$(ACN)_2^+$. The broad band extending from 375 to 378 nm, and a weak shoulder like feature around 373.5 nm are also discernible. The absorption band measured for BA-$(ACN)_4^+$ is very broad and largely red-shifted, i.e., peaking around 379 nm. The correspondence of this band to the band in the LIF spectrum is not very good, probably because of the fragmentation of larger clusters ($n > 4$) in some extent and incomplete cooling of this large cluster in the TOF apparatus. However, the LIF band appears at 378.5 nm in the LIF spectrum (band d) could be assigned to be BA-$(ACN)_4$ because the short wavelength onsets of both bands agree with each other.

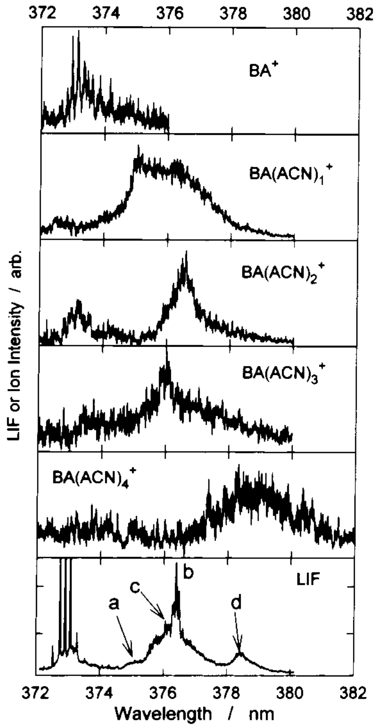

Figure 2. Mass-selected resonance enhanced two-photon ionization (REMPI) spectra of the BA-acetonitrile clusters. Monitored ion is shown in each figure, and LIF spectrum is also shown.

As we mentioned in the previous paragraph, the mass selected REMPI spectra could be contaminated by the fragmentation of the larger clusters. The bands observed in the spectra of BA-$(ACN)_n^+$ ($n = 1-3$) are overlapped in the wavelength region of 375 to 377 nm. The shoulder at 376 nm in the spectrum of BA-$(ACN)_1^+$ overlaps with the band in the spectrum of BA-$(ACN)_2^+$. However, other unique features appear in the BA-$(ACN)_2^+$, for instance the band around 373.2 nm is not reproduced in the spectrum of BA-$(ACN)_1^+$. Thus, the shoulder at 376 nm in BA-$(ACN)_1^+$ in unlikely to originate from the fragmentation of BA-$(ACN)_2$. Because the band of BA-$(ACN)_4^+$ is well separated from those of the smaller clusters, the contribution of the fragmentation from BA-$(ACN)_4$ is negligible in the spectra of the smaller ones. The only possible contribution of the fragmentation may come from the clusters with more than four acetonitrile molecules. Because the mass-selected REMPI spectrum could not be measured for the larger clusters, the spectrum of BA-$(ACN)_4^+$ may be contaminated by the clusters larger than $n = 4$.

From these results, we could select the wavelengths which were used to excite the BA-$(ACN)_n$ clusters with the specific

TABLE 1: Absorption Wavelengths and Spectral Shifts of BA-(acetonitrile)$_n$

n	peak wavelength/nm	$\Delta\nu$/cm^{-1a}
1	375.0	−41
2	376.6	−155
3	376.0	−112
4	379.0	−323

[a] Spectral shifts are given with respect to the 0-0 band of free BA, 26708 cm^{-1}.

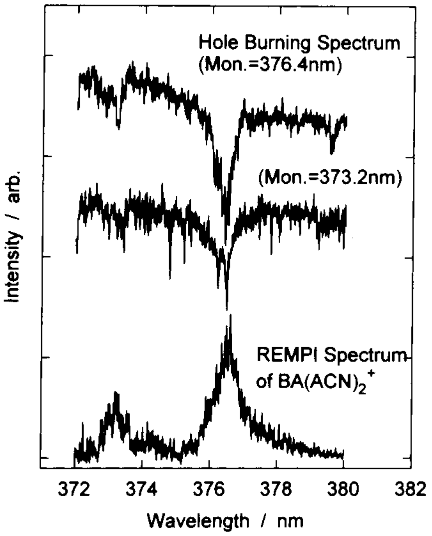

Figure 3. Optical hole burning spectra of the BA-acetonitrile clusters. The topmost and middle figures are the hole burning spectra by monitoring the emission at 376.4 and 373.2 nm, respectively. Mass-selected REMPI spectrum of BA-(acetonitrile)$_2$ is also shown in the bottom.

number of acetonitrile molecules. The most prominent characteristic bands were selected for the excitation and shown in the LIF spectra, Figs. 1(c) and 2, i.e., a, b, c, and d correspond to the absorption bands for $n = 1$, 2, 3, and 4, respectively. The wavelengths and energy shifts from the 0−0 band of BA, 26 708 cm^{-1}, are summarized in Table 1. The band designated as f in Figure 1(c) is also assigned to be $n = 2$, and the origin of this band will be discussed in the next section.

Assignment of the Band at 373 nm in the BA-(Acetonitrile)$_2$ Cluster. Two absorption bands were observed for BA-(ACN)$_2$ in the wavelength region measured here, i.e., 373.2 and 376.4 nm. They could be either the absorption bands of two isomers or vibronic bands of a single species. One useful experimental technique to discriminate between these two possibilities is the measurement of an optical hole burning spectrum. The hole-burning spectroscopy involved two laser pulses, a strong tunable pump pulse and a weak fixed-wavelength probe pulse. The probe laser was tuned to one of the absorption bands, 373. 2 or 376.4 nm, whereas the pump laser scanned the wavelength to search the electronic transition, 372−380 nm. The time-integrated fluorescence of the probe pulse was recorded, and the depletion of the probe signal induced by the pump pulse gave the saturated absorption spectrum of the selected species. The output of the dye laser pumped by the excimer laser was used for the probe pulse and the frequency doubled output of the titanium-sapphire laser was used for the pump pulse. The delay between the pump and the probe pulses were selected to be 500 ns.

The results are shown in Figure 3. The REMPI spectrum of BA-(ACN)$_2$ is also shown for comparison. The topmost spectrum was obtained by using the probe pulse at 376.4 nm. In this spectrum, two depletions can be seen. The wavelengths and the relative intensities of these two agree quite well with those of the REMPI spectrum shown on the bottom. The hole burning spectrum measured by the probe pulse at 373.2 nm, the middle of Figure 3, also shows two depletions that agree with both the hole burning spectrum measured by probing 376.4 nm and the REMPI spectrum. These results confirm that the two bands of BA-(ACN)$_2$ originate from not by their isomers but by a single species. Since the band appears at 376.4 nm corresponds to the 0−0 band of free BA, that appears at 373.2 nm is ascribed to the absorption to a vibrationally excited state.

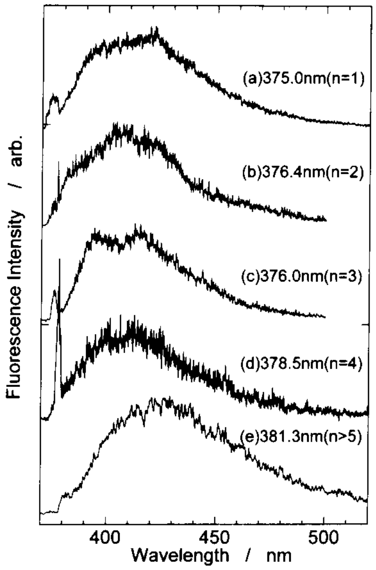

Figure 4. Dispersed fluorescence (DF) spectra of the BA-acetonitrile clusters. Shown in the figure are the wavelengths for excitation and the number of acetonitrile molecules in the clusters.

As we mentioned in the previous section, weak bands were also discernible for BA-(ACN)$_n$ ($n = 1$ and 3) around 373 nm. Although the hole burning spectrum could not be measured for them, they are also likely to be vibronic bands of these clusters.

Dispersed Fluorescence Spectra and Fluorescence Lifetimes. To clarify the properties of the excited states of the BA-(ACN)$_n$ clusters, we measured dispersed fluorescence spectra and fluorescence lifetimes. Dispersed fluorescence spectra measured by the excitation at four wavelengths shown as a−d in Figures 1(c) and 2 are summarized in Figure 4. As we described in the previous section, these excitation wavelengths correspond to $n = 1$−4 of BA-(ACN)$_n$. These DF spectra are very broad, structureless, and red-shifted compared with the dispersed fluorescence of free BA. Peak wavelengths and widths at half-maximum were determined for several spectra and averaged values are summarized in Table 2. The amounts of the red-shift (the Stokes shift), $-\Delta\nu$, and the widths of the spectra are plotted as a function of the number of solvent molecules in Figure 5(a) and (b), respectively.

For the absorption bands a−d, the lifetimes were measured and the results are summarized in the last column of Table 2 and plotted as a function of the number of acetonitrile in Figure 5(c). Also shown in Figure 5(c) is the lifetime of free BA, 11.3 ± 0.8 ns, which is consistent with both the previous measurement under the supersonic jet condition[22] and the lifetime in nonpolar solution. It is clear from Figure 5(c) and Table 2 that the lifetimes of BA-(ACN)$_n$ are longer than that of free BA.

For the cluster of $n > 4$, the REMPI spectrum could not be measured because of their weak intensities. However, DF spectra

TABLE 2: Peak Wavelengths, Widths of the Emission Bands, and Fluorescence Lifetimes of the BA-(acetonitrile)$_n$ Clusters

excitation (nm)	n	peak of emission (nm)	$-\Delta\nu$ (cm^{-1})	width (cm^{-1})	lifetime (ns)
375.0	1	412	2366 ± 42	3700 ± 70	22.8 ± 0.6
376.4	2	408	2190 ± 446	3250 ± 47	25.0 ± 0.8
376.0	3	407	2090 ± 85	3400 ± 75	29.2 ± 0.4
378.5	4	420	2420 ± 300	3810 ± 390	24.9 ± 1.7
381.3	5[a]	430	2950 ± 270	4100 ± 390	34.1 ± 0.3
379	>5[b]	450	3870 ± 490	5100 ± 920	50.4 ± 1.4
solution			4389[b], 4300[c], 4040[d]		43[e],45[f],35[d],35[g]

[a] This is the temporary assignment and see detail in text. [b] Catalan, J.; Diaz, C.; Lopez, V.; Perez, P.; Claramunt, R. M. *J. Phys. Chem.* **1996**, *100*, 18 302. [c] Ref 9. [d] Ref 8. [e] Schutz, M.; Schmidt, R. *J. Phys. Chem.* **1996**, *100*, 2012. [f] Visser, R. -J.; Weisenborn, P. C. M.; van Kan, J. M.; Huizer, B. H.; Varma, C. A. G. O.; Warman, J. M.; de Haas, M. P. *J. Chem. Soc. Faraday Trans. 2* **1985**, *81*, 689. [g] Ref 37.

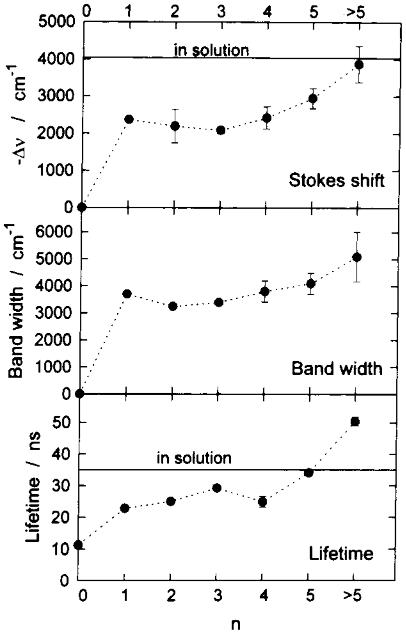

Figure 5. Fluorescence properties are summarized as a function of the number of acetonitrile molecules. (a) The Stokes shift of the DF spectra. The shift observed in solution is also shown. (b) Bandwidths of the DF spectra. (c) Lifetimes. The lifetime reported for the acetonitrile solution is shown as a horizontal line.

and lifetimes were measured for the absorption bands appeared at higher concentrations of acetonitrile. The spectrum shown in Figure 4(e) was measured by the excitation at 381.3 nm. This is the peak wavelength of the LIF band appeared after the band d by increasing the concentration of acetonitrile and is likely to be BA-(ACN)$_5$. This DF spectrum shows larger red-shift compared with the DF spectra of the clusters containing one to four acetonitrile, viz. 3810 cm^{-1}. The lifetime, 34.1 ns, is also significantly longer than those of the clusters of $n = 1-4$.

As we described in the LIF section, further increase of the concentration of acetonitrile did not provide an isolated absorption band but broad background like feature increases the intensity from 375 to 382 nm. The contribution of this broad absorption in the DF spectrum could be recognized in Figure 6. Two spectra measured at the two different concentration of acetonitrile are compared in this figure. Even though the same excitation wavelength, 379 nm, was used for both spectra, significant differences can be seen in the longer wavelength region of the DF spectra. The spectrum measured with the higher vapor pressure of acetonitrile, Figure 6(a), has larger intensity at longer wavelength. Because the number of acetonitrile molecules is not specified for this emitting species, the Stokes shift and the lifetime of this emission are listed as those for n > 5 in Table 2 and Figure 5. The Stokes shift is very large and becomes almost 90% of the value of acetonitrile solution and the lifetime is elongated further from that of $n = 5$ and becomes even longer than that in solution.

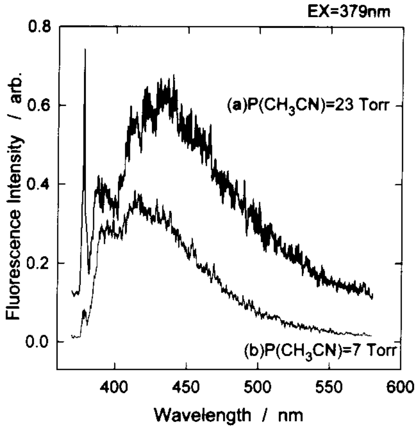

Figure 6. DF spectra of the BA-acetonitrile clusters. The same excitation wavelength was used, 379 nm, for different concentration of acetonitrile in the nozzle.

The results of DF spectra and lifetimes are summarized as the following.

(1) One acetonitrile molecule makes drastic changes in the DF spectra and lifetimes, i.e., the large red-shift (2366 cm^{-1}) and longer lifetime (22.8 ns).

(2) Second to fourth acetonitrile molecules add little effect on the DF spectra and lifetimes.

(3) The DF spectra and lifetimes become to change in the clusters containing more than four acetonitrile, i.e., the larger red-shifts and longer lifetimes.

Discussion

Mechanism of the Charge-Transfer Reaction in the Gas-Phase Clusters. In all clusters of BA with acetonitrile observed in the present study, the dispersed fluorescence showed broad spectra with large Stokes shift, and their fluorescence lifetimes are much longer than that of free BA. These results are similar to the fluorescence properties observed in the clusters of BA with water[24] and ketones,[2,22,23] and suggest that the charge-transfer reaction occurs following the photoexcitation of BA in the clusters with acetonitrile. The charge-transfer state of BA is stabilized by the interaction with polar solvent molecules, and accessible from the initially photoexcited state. Because the transition between the ground state and the charge-transfer state is forbidden, the increase of the charge-transfer character in the excited-state elongates the fluorescence lifetime.

In the CT reaction from the photoexcited state of BA in solution, solvent plays two essential roles. Solvent polarity is primarily important to stabilize the CT state to have lower energy than the initially photoexcited state. The second role of the solvent is to remove the degeneracy of the CT state. The

CT state of BA originates from a pair of linear combination of states where an electron is transferred from one anthracene moiety to the other and vice versa. Without any perturbation from the surroundings, these two states are completely degenerated. The solvent fluctuation is effective to remove the degeneracy of these two and stabilize the one charge transfer state over the other.[10−13] After the one state is stabilized and the charge separation is emerged, surrounding solvents rearrange to a more favorable orientation and position for the CT state of BA. This further stabilization of the CT state opens the nonadiabatic conversion channel toward this state without the energy barrier from the initially photoexcited state.[19,20]

These two essential roles of solvents for the CT reaction are likely to couple together in the gas-phase clusters of BA. Any solvent molecule is effective in breaking the symmetry because it is very likely for the gas-phase clusters to have asymmetric structure.[32] Some polar environment could be created by one polar solvent molecule, acetonitrile. However, it is noted that the acetonitrile molecule attaches to BA in its ground electronic state which has no dipole moment. The polar environment created by the acetonitrile molecule is not necessarily favorable to the CT reaction. In the clusters of BA with acetone[2] or diethyl ketone,[23] two isomeric clusters were observed and sharp contrast in fluorescence behavior was seen for them. One isomeric clusters showed structured LIF band and the others provided the broad spectrum. The red-shifted emission consistent with the CT reaction was observed only for the latter isomers, whereas the former isomers showed emission spectrum similar to free BA. These results suggested that the attachment of the polar molecules, acetone or diethyl ketone, was not enough to lead to the CT reaction in these isomeric clusters.

In the clusters with acetonitrile, no isomeric clusters were observed. Because the CT reaction seems to occur in all clusters, the polar environment created by the acetonitrile molecules may be useful in their original configuration to stabilize the CT state of BA to emerge after the photoexcitation. Once the CT reaction is initiated the acetonitrile molecules are able to relax their configuration to stabilize the CT state effectively.

If the configuration of the acetonitrile molecules is not favorable to stabilize the CT state lower than the initially photoexcited state, the relocation or reorientation of acetonitrile is necessary for the CT reaction. Because of the low temperature of the clusters,[33] such solvent motions are highly restricted without the excess energy provided by the vibronic excitation. Because the 0−0 band region is used for the excitation of BA in the present study, only available excess energy can originate from the excitation of torsional motion with respect to the 9,9′-axis. Because the equilibrium torsional angles of the ground and electronically excited states are different, i.e., 90 and 70 degree, respectively,[28,29,34] the vertical transition from the vibrationless ground state leads to the torsional excitation, viz. 116 cm^{-1}.[34]

Deformation of the torsional potential by attaching a solvent molecule, rare gases or simple molecules, has been suggested by experimental studies combined with a minimum energy structure calculation.[35,36] According to these studies, the molecule attaches to the terminal benzene ring of one anthryl moiety. Although the 1:1 cluster formation gives only a small change in the ground state torsional potential, the torsional motion in the excited state is significantly affected by the cluster formation due to steric repulsion between the “solvent” molecule and the anthracene ring. In cases of N_2 and H_2O, the 1:1 cluster formation results in the reduction or loss of one wing of the potential valleys of the double minimum torsional potential in the excited state.[36] This deformation of the torsional potential of the excited state leads to even higher excess energy for the vertical excitation, i.e., about 220 cm^{-1} in the case of water.[35,36] Comparable or more excess energy is expected for the clusters with acetonitrile, and this excess energy is probably utilized to assist the initial rearrangement of the solvent molecules. The CT reaction can start with this solvent rearrangement. Once the CT state is reached, the additional stabilization energy is released, which accelerates the motion of the solvents to reach the best stabilizes the CT state by the dipole−dipole interaction.

Because no information is available for the configuration of the clusters in their ground state, it is difficult to state whether the solvent rearrangement is necessary to initiate the CT reaction in the BA-$(\text{ACN})_n$ clusters. One relevant information has been provided by the picosecond fluorescence measurements of the BA-H_2O and BA-acetone clusters.[24,35] In the BA-H_2O cluster, the time constants for the IVR process in the initially photoexcited state and for the CT reaction were determined to be 16 and 50 ps, respectively. Because only the torsional vibration and van der Waals modes were available for the IVR process, the torsional relaxation and solvent rearrangements were suggested to occur prior to the CT reaction in the BA-H_2O cluster. The CT reaction in the BA-$(\text{acetone})_1$ cluster was also suggested to occur in the longer time scale than the IVR process, 38 ps.[35] Therefore, the torsional relaxation and the solvent rearrangement are likely to be also necessary for the CT reaction in the BA-$(\text{ACN})_n$ clusters.

Stabilization Energy of 1:1 Cluster. Another question is whether the stabilization by only one or a few acetonitrile molecules is enough to lower the energy of the CT state below the initially photoexcited S_1 state. Recent semiempirical calculation has suggested the energy of a charge-transfer state, $D^+{-}A^-$, to be 4.18 eV.[37] In the BA-$(\text{ACN})_1$ cluster, this state is stabilized dominantly by the dipole−dipole interaction. Because the energy of the initially excited state of BA-$(\text{ACN})_1$ is estimated to be 3.31 eV (375 nm) from the maximum of the absorption band, the CT state must be stabilized by more than 0.87 eV to become lower than the initially photoexcited state. If we use the wavelength of the fluorescence maximum as the energy of the stabilized CT state, then the CT state is lower to be 3.01 eV, then more than 1.17 eV must come from the dipole−dipole interaction between an acetonitrile molecule and a BA molecule in the CT state.

If we assume that the charge is located at the center of gravity of each anthryl moiety, then the dipole moment of the CT state of BA is estimated to be 20.6 D. By using 3.92 D for the dipole moment of acetonitrile, the interaction energy of more than 1.1 eV can be attained if the acetonitrile molecule lies within several Angstrom from BA and BA and acetonitrile has a favorable configuration. According to the calculation for BA-H_2O, the distance between water and anthracene plane is 3.14 A.[35] Therefore, it is likely that the acetonitrile molecule rearranges its orientation to the favorable configuration and the BA-acetonitrile distance is short enough to stabilize the CT state lower than the photoexcited state in the BA-$(\text{ACN})_1$ cluster.

Effect of Successive “Solvation”. One puzzling result is the effect of second to fourth acetonitrile molecules on the spectral shift of the fluorescence from the CT state. In the case of acetone, it was observed that second acetone molecule leads to larger Stokes shift which is ascribed to the further stabilization of the CT state.[2] However, no apparent change was observed in the emission spectra by adding second to fourth acetonitrile molecules as shown in Figure 5. These results suggest that the second to fourth acetonitrile molecules add little effect to stabilize the CT state. As we discussed in the previous section, the rearrangement of solvents takes place after the CT reaction. One acetonitrile molecule is effective enough to stabilize the CT state to show the red-shifted emission. However, even after the rearrangement, the interaction between more than two dipoles may lead to the configuration in which the CT state is not fully stabilized by two to four acetonitrile molecules.

The results of the Stokes shift and lifetime suggest that some change occurs in the clusters containing five or more acetonitrile molecules. The Stokes shift becomes larger and the lifetime becomes longer. The change is more prominent in the lifetime, i.e., the lifetime of the BA-$(ACN)_5$ cluster becomes almost the same value as that observed in the acetonitrile solution and the cluster with more than five acetonitrile molecules shows even longer lifetimes. The lifetime longer than that in solution was also observed in the cluster of BA with acetone.[2] The cluster having more than three acetone molecules showed the lifetimes longer than that observed in the acetone solution, and they were ascribed to the low temperature of the clusters. As we discussed in the first part of the Discussion, the CT reaction produces the excess energy in the cluster, and it is very likely that the solvent molecules are movable in the cluster. However, it is not true if the dissociation of clusters occurs. If the excess energy becomes large enough to dissociate one or more intermolecular bonds, the elimination of one or more solvent molecules occurs. The temperature of the remaining cluster becomes lower and the solvent motion could be restricted after the solvent elimination. In the BA-$(ACN)_n$ clusters, no dissociation of clusters were suggested up to $n = 4$ because no discernible effect of fragmentation was observed in the mass-selected REMPI spectra. However, the solvent elimination may take place in the clusters having more than four acetonitrile molecules. After the elimination, the CT state in the cluster is fully relaxed and its electronic character may appear more explicitly because of the lack of the mixing with the S_1 state. The emission from this state must be longer lifetime and further red-shifted.

Summary

Excited-state behaviors were studied for the gas-phase cluster of 9,9′-bianthryl with the specific number of acetonitrile molecules. The mass-selected REMPI spectra were measured to determine absorption bands for the clusters having 1 to 4 acetonitrile molecules. Fluorescence properties, dispersed fluorescence spectra and fluorescence lifetimes, were measured for the excitation of these bands. The same measurements were also achieved for the absorption bands of larger clusters, i.e., the clusters with more than 4 acetonitrile molecules.

In all clusters studied here, i.e., the clusters having 1 to more than 5 acetonitrile molecules, the emission spectra were largely red-shifted and the elongated fluorescence lifetimes were observed. These fluorescence properties were ascribed to the formation of the polar excited state that was analogous to the charge-transfer state observed in the room-temperature solutions of polar solvents. Even in the very cold gas-phase clusters, the excess energy come from the torsional motion characteristic of BA was proposed to be utilized to rearrange the BA-acetonitrile configuration favorable in stabilizing the charge-transfer state of BA. Second to fourth acetonitrile molecules added little extra effect on the fluorescence properties, i.e., the Stokes shifts and lifetimes of these clusters were almost identical to those of BA-$(ACN)_1$. These properties started to change for the clusters with more than four acetonitrile molecules. Although these results were discussed by the structure of the clusters and the occurrence of the elimination of the acetonitrile molecules, further information about the configuration of the clusters are essentially important.

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References and Notes

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