Photodissociation of Jet-Cooled Intramolecular Exciplex in 1-(9-Anthryl)-3-(*p*-(*N*,*N*-dimethylamino)phenyl)propane: Formation of Excited-State Anthryl and Deuteration Effect

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The jet-cooled intramolecular exciplex formation and photodissociation were examined in deuterated anthryl bichromophoric EDA systems 1-(9-anthryl-d_8)-3-(*p*-(*N*,*N*-dimethylamino)phenyl)propane (9-An-*d*-DMA) in comparison with the undeuterated compound (9-An-DMA) reported previously. The excess vibrational energy threshold for the exciplex formation in the former was considerably smaller than that of the latter. The photodissociation of the jet-cooled exciplex leading to the anthryl moiety fluorescence was observed in the excitation of the transient absorption band of the exciplex ($S_n \leftarrow S_1$). It is noteworthy that very short decay times of anthryl fluorescence were observed upon photodissociation of the exciplex. The deuterated effect of the anthryl moiety on the formation and photodissociation of the exciplex may be attributable to the role of the vibrational level density of the anthryl in these excited-state reaction dynamics.

Introduction

The intramolecular exciplex formation and excess vibrational energy dependence have been reported in several bichromophoric EDA systems in supersonic expansion,[1] since pioneering works of the intramolecular exciplex formation in jet-cooled 1-(9-anthryl)-3-(*p*-(*N*,*N*-dimethylamino)phenyl)propane (abbreviated to 9-An-DMA) by Zewail and his co-workers.[2,3] We have reported that the existence of multiconformations of jet-cooled bichromophoric EDA compounds is demonstrated by fluorescence hole burning depletion spectra and that the vibrational energy thresholds for exciplex formation is dependent on their ground-state conformations.[4−6]

Zewail and his co-workers[3] proposed a simple theory to describe the excess energy dependence of the rate constant of the jet-cooled exciplex formation in 9-An-DMA. An activation type rate equation could be applied to isolated molecules to describe the rate constant at a given excess energy, if an effective temperature was defined according to the number of vibrational modes involved. Itoh et al.[7] reported excitation energy dependence of intramolecular exciplex/excimer formations in the static vapor of bichromophoric EDA systems. They indicated that the reaction rate constant of the exciplex formation may be proportional to the product of transition probability and the calculated relative vibrational level density of the final exciplex state.

Saigusa et al.[8] and Saigusa and Lim[9] have reported photodissociation spectroscopy of napththalene clusters (excimer) leading to the excited state of naphthalene in the excitation of the excimer state (B_{3g}) to its higher electronic state (B_{2u}). This fact was ascribed to the consideration that both states originate from the interaction of the ^{1}La and the charge resonance state (CR), and the excitation of the B_{2u} state means the excitation of the dissociative or weakly bound state of the excimer. This paper presents the supersonic jet spectroscopy of intramolecular exciplex formation and photodissociation in the deuterated anthryl bichromophoric EDA system 1-(9-anthryl-d_8)-3-(*p*-(*N*,*N*-dimethylamino)phenyl)propane (abbreviated to 9-An-*d*-DMA) in comparison with the undeuterated compound (9-An-DMA).

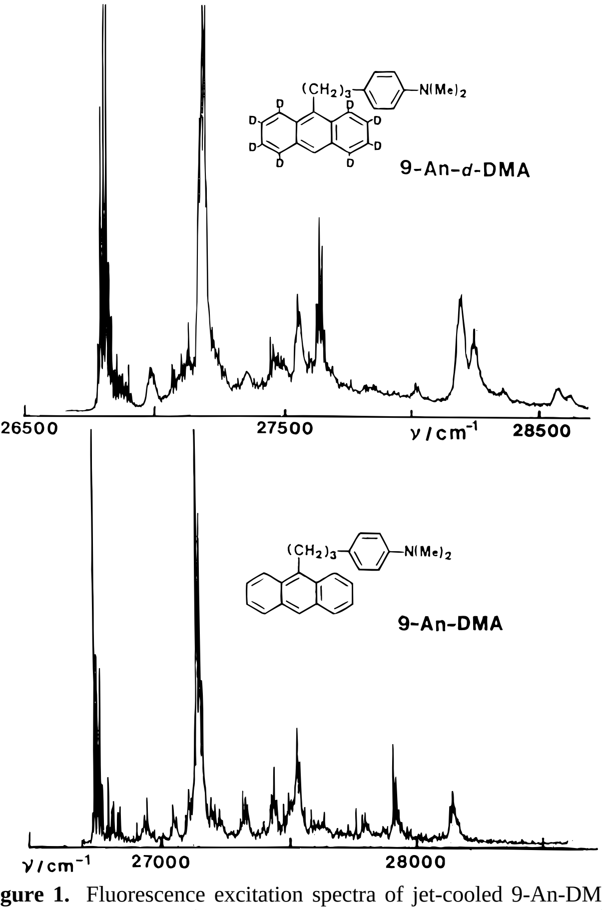

Figure 1. Fluorescence excitation spectra of jet-cooled 9-An-DMA (an origin, 26 683 cm^{-1}) and 9-An-*d*-DMA (an origin, 26 735 cm^{-1}). In both spectra, fluorescence was detected in peaks at 395−397 nm (25 316−25 189 cm^{-1}).

In the bichromophoric compound with deuterated anthryl, the excess energy threshold for the exciplex formation was considerably smaller than that of the undeuterated compound. Further, this paper is concerned with photodissociation spectroscopy of the jet-cooled exciplex by excitation of the transient absorption band of the exciplex ($S_n \leftarrow S_1$) in both deuterated

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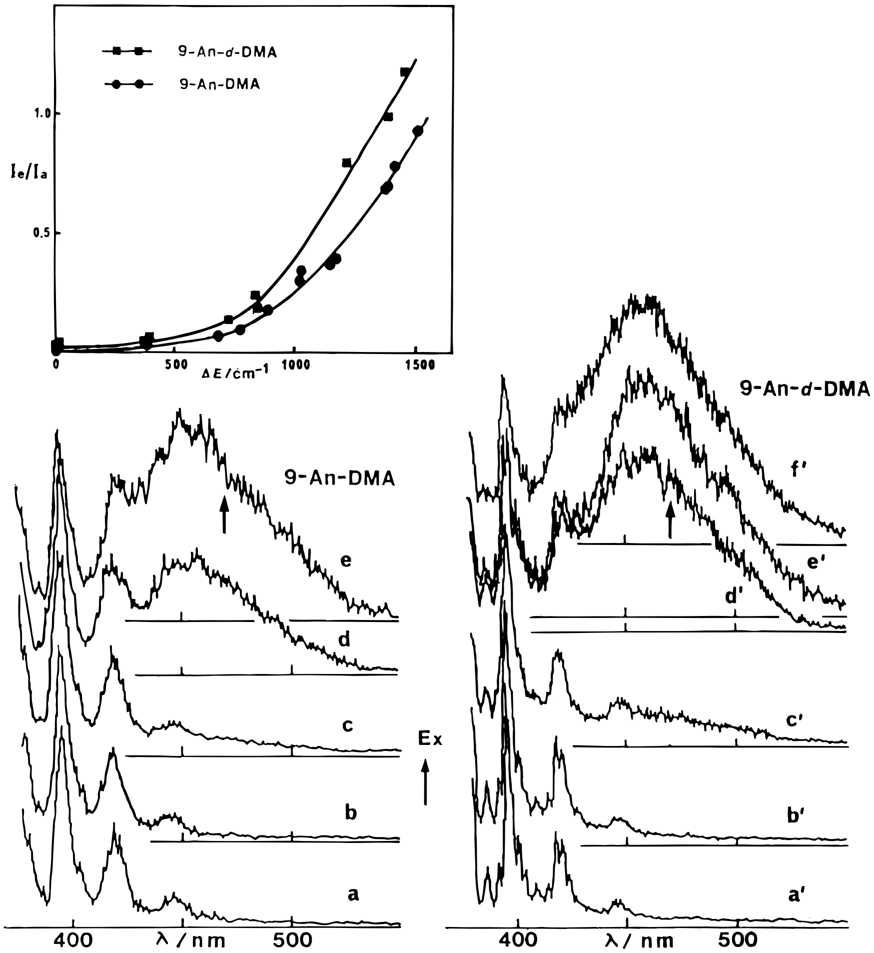

Figure 2. Dispersed fluorescence spectra of 9-An-DMA and 9-An-*d*-DMA in supersonic expansion. Spectra of the former were obtained in excitations at (a) 26 683 cm^{-1}, (b) 27 078 cm^{-1}, (c) 27 472 cm^{-1}, (d) 27 850 cm^{-1}, and (e) 28 076 cm^{-1} (356.18 nm). Those of the latter were obtained in excitations of bands at (a′) 26 734 cm^{-1}, (b′) 27 109 cm^{-1}, (c′) 27 571 cm^{-1}, (d′) 28 130 cm^{-1} (355.48 nm), (e′) 28 176 cm^{-1}, and (f′) 28 509 cm^{-1}. The inset shows the ratio of relative intensity of the exciplex and anthryl moiety fluorescence of both compounds *vs* excess vibrational energy. The exciplex (I_e) and anthryl moiety (I_a) fluorescence was detected at 470 nm and at a peak at 390−400 nm. The errors of these fluorescence intensity ratios are approximately 10%.

and undeuterated compounds. The photodissociation of the exciplex leading to anthryl fluorescence with very small decay time was observed in the excitation of the transient absorption band of the exciplex ($S_n \leftarrow S_1$). The effect of deuteration of the anthryl moiety on the photodissociation dynamics of the exciplex was observed in these bichromophoric compounds. The different features of the excess energy threshold for the formation and photodissociation of the exciplex between deuterated and nondeuterated compounds are discussed in terms of the role of level density in the reaction dynamics in the excited state.

Experimental Section

Materials. The bichromophoric EDA compound with deuterium-substituted anthryl, 9-An-*d*-DMA, was synthesized from respective *p*-(*N*,*N*-dimethylamino)acetophenone and 9-anthryl-d_9-aldehyde by methods and procedures similar to those described in previous papers. The latter deuterated compound was prepared from anthracene-d_{10} (C/S/N Isotopes Inc. 99.5 atom % D) by *N*-methylformanilide and $POCl_3$ in *o*-dichlorobenzene. In the hydrogenation reaction of the carbonyl group of 1-(9-anthryl-d_9)-3-(*p*-(*N*,*N*-dimethylamino)phenyl)propan-1-one by hydrazine in diethylene glycol, a deuterium atom at the 10 position of deuterated anthryl was substituted by a hydrogen atom. Then, 1-(9-anthryl-d_8)-3-(*p*-(*N*,*N*-dimethylamino)phenyl)propane was obtained. The structure and purity of the compound were confirmed by elementary analysis and mass and NMR (270 and 500 MHz) spectroscopies before use. Elementary analysis and melting points are as follows: 1-(9-anthryl-d_8)-3-(*p*-(*N*,*N*-dimethylamino)phenyl)propane, mp 102−103.5 °C. Calcd, for $C_{25}H_{17}D_8N$: C, 86.40; H, 4.93; D, 4.64; N, 4.03. Found: C, 86.33; H, 5.07; D, 4.51; N, 4.08.

General Procedures. The experimental setup and procedures of fluorescence spectroscopy of the pulsed supersonic free jet were completely the same as those described in the previous papers.[5,6,10] The 10-Hz pulsed supersonic free jet backed by He (2−3 atm) was excited at 10−12 mm downstream of a nozzle by an excimer laser pumped dye laser (Lambda Physik Compex 102/FL3002). The setup and procedures of the laser-induced fluorescence spectra and decay were the same as those described in the previous papers. The setup and procedures of the photodissociation of the exciplex were almost similar to those of the fluorescence hole burning depletion spectroscopy.[6,10] An excimer laser pumped dye laser (Lambda Physik EMG 53MSC/FL 2002) was used as a photodissociation laser of the exciplex. The pump and dissociation laser beams were counterpropagated and slightly focused through 50/60-cm lenses on the free jet 10−12 mm downstream from the nozzle. Delay time between laser pulses was approximately 50−150 ns. Since time jitters between two laser pulses were very important, a digital oscilloscope (Tektronix TDS 520) for detecting the fluorescence signal in the photodissociation of the exciplex was triggered by a dissociation laser pulse, and the output of signal was processed by a personal computer. The photodissociation experiment of the exciplex in solution was examined by the same setup as the two-step laser-induced fluorescence (TS-LIF) spectroscopy described in the previous papers.[11,12] Fluorescence decays were determined by using a high-speed photomultiplier (Hamamatsu H3284, a rise time of 0.4 ns) through a monochromator and the digital oscilloscope and were processed by a computer-simulated convolution. The shortest fluorescence decay time that can be obtained is at least 1 ns by the computer-simulated convolution, although fwhm of the dye laser pulse may be 5−7 ns. The errors of the decay times are approximately 10%.

Results and Discussion

Excess Vibrational Energy Dependence for the Exciplex in 9-An-*d*-DMA. Figure 1 shows UV fluorescence excitation spectra of 9-An-*d*-DMA with the deuterated anthryl-d_8, in comparison with the undeuterated compound (9-An-DMA) in supersonic expansion. These spectra are essentially similar to each other, but the former exhibits a 40−60 cm^{-1} blue shift and somewhat different intensity distribution from the latter.[13] For instance, low-frequency vibrations with 10−11-cm^{-1} spacing in the origin band region were observed in 9-An-*d*-DMA, which were suggested to be vibrational coupling of anthryl with two hydrogen atoms in the center carbon atoms of $-CH_2-CH_2-CH_2-$ in 9-An-DMA by Syage et al.[3] In 9-An-*d*-DMA, however, the intensity distribution of this low-frequency vibration was considerably different from that of 9-An-DMA. This fact indicates that the Franck-Condon profile in the former is considerably different from that of the latter. Thus, a band with the largest intensity at 374.05 nm (26 734 cm^{-1}) was tentatively assigned to the origin band in the deuterated compound, 9-An-*d*-DMA. The fluorescence decay time of the anthryl-d_8 moiety was observed to be considerably smaller (11.9 ns at the origin region) than that of the undeuterated compound (20.0 ns).[5]

As mentioned in the previous paper, the hole-burning depletion spectrum of 9-An-DMA indicated only one ground-state chain conformer in the jet-cooled condition of 2−3 atm He backing pressure. The deuterated anthryl compound, 9-An-*d*-DMA, was also only one conformer in the ground state. The visible (470 nm) fluorescence excitation spectrum of the deuterated compound exhibits a remarkable increase in intensity in the vibronic band region. The excess vibrational energy dependence of the exciplex formation in 9-An-*d*-DMA was examined in comparison with that of the undeuterated compound,[2,3,5] as shown in Figure 2. The excess energy threshold for exciplex formation was found to be approximately 750 cm^{-1} in 9-An-*d*-DMA from plots of the intensity ratio of the exciplex and the anthryl fluorescence (I_e/I_a) *vs* excess vibrational energy (ΔE), as shown in an inset of Figure 2. The obtained energy threshold in the deuterated compound is smaller than that of 9-An-DMA (900−1000 cm^{-1}).[2,3,5] The smaller excess energy threshold for the exciplex formation in 9-An-*d*-DMA may be attributable to the vibrational level density of the anthryl-d_8 moiety and also probably the Franck−Condon profile, as will be mentioned later.

The Photodissociation of the Jet-Cooled Intramolecular Exciplex. The photodissociation of the exciplex in 9-An-DMA and 9-An-*d*-DMA was examined in the excitation of transient absorption of the exciplex ($S_n \leftarrow S_1$) in supersonic expansion. Since it is very difficult to observe the transient absorption spectrum of the jet-cooled molecule, the transient absorption spectra of these compounds were measured in 3-methylpentane solution at room temperature. Two transient absorption bands were observed at 700−800 and 460−475 nm in both compounds in addition to the considerably sharp band at 424 nm. Since the transient absorption band at 424 nm was assigned to the $S_n \leftarrow S_1$ transition of anthracene by Kliger and Albrecht,[14] the observed 424-nm band may be ascribed to the transient absorption of the anthryl moiety of these compounds. The 700−800- and 460−475-nm absorption bands are very similar to the absorption bands of anthryl anion and *N*,*N*-dimethylaniline (DMA) cation radicals, respectively.[15] Therefore, the transient absorption bands in solution suggest a considerable charge transfer character in the exciplex state (S_1).

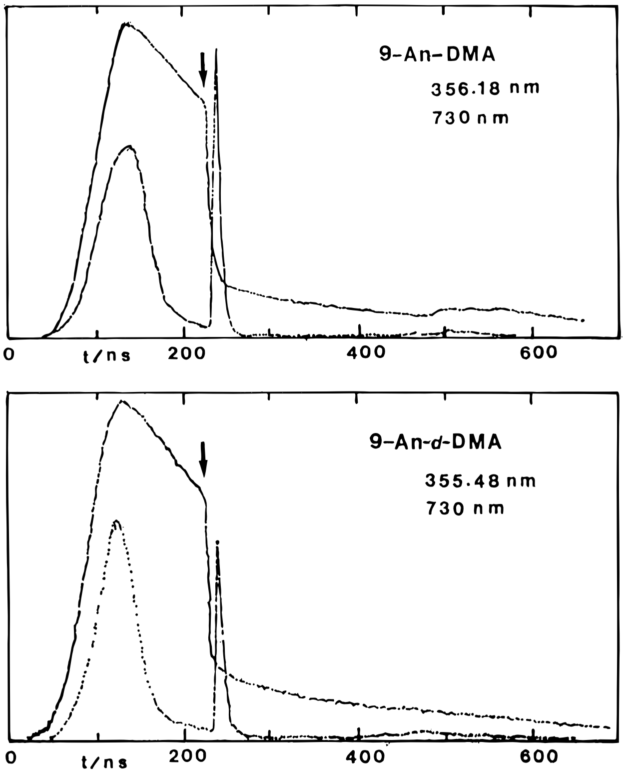

Figure 3. Typical time-resolved photodissociations of the exciplex fluorescence and fragment signals of anthryl fluorescence for jet-cooled 9-An-DMA and 9-A-*d*-DMA. The times of the dissociation laser pulse (730 nm) are indicated by arrows. The exciplex fluorescence decay curves determined are indicated by arrows in Figure 2 (e, for 9-An-DMA, and d′, for 9-An-*d*-DMA). The anthryl fluorescence was not detected by the second laser excitation without the first one.

The fluorescence spectra of the exciplex was observed by the excitations of vibronic bands with considerable excess vibrational energy, as shown in Figure 2. The exciplex was excited by the second laser pulse (730 nm) within the decay time of the exciplex. The wavelength of the second laser corresponded to the transient absorption band of the exciplex mentioned above. Since exciplex decay times (250−270 ns) of the deuterated 9-An-*d*-DMA were not so different from those of the undeuterated compound,[5] delay times of the dissociation laser pulse were approximately 100−150 ns after the first one. Figure 3 shows typical time-resolved detections of the photodissociation of the exciplex of 9-An-*d*-DMA in comparison with those of the undeuterated compound. A pronounced depletion of the exciplex fluorescence amounts to approximately 70−80%, and the anthryl fluorescence was observed simultaneously with the depletion of the exciplex by the excitation of the transient absorption band (730 nm). Further, since no significant anthryl fluorescence was detected by the second laser excitation without exciplex formation by the first laser excitation, the

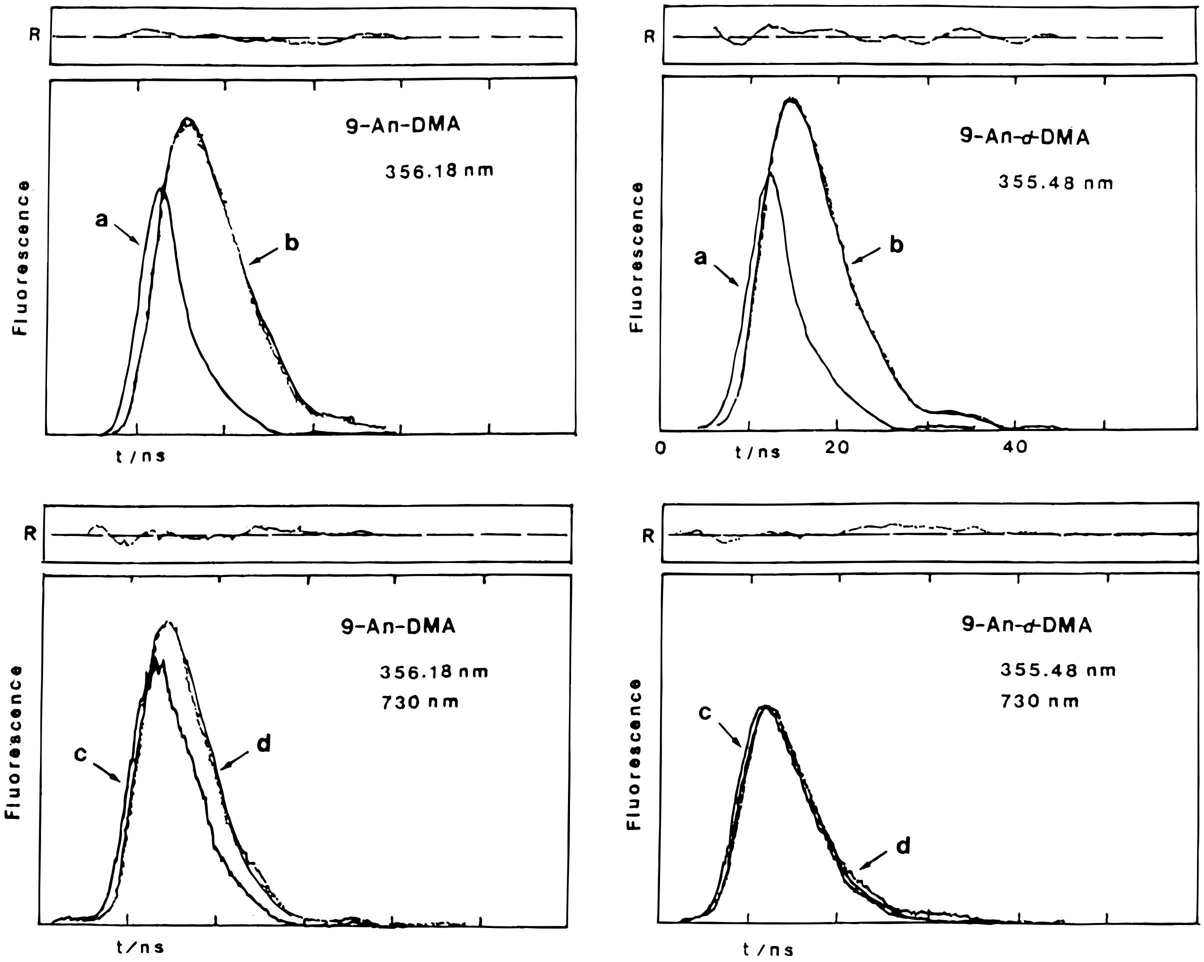

Figure 4. Time-resolved fluorescence decay curves of the anthryl moiety generated by the photodissociation of the exciplex in 9-An-DMA and 9-An-*d*-DMA. (a) Excitation laser pulse for the exciplex formation; (b) fluorescence decay curves of anthryl moieties for the exciplex formations; (c) photodissociation laser pulse (730 nm) of the exciplex, and (d) fluorescence decay curves of anthryl fragments generated by the exciplex dissociation.

observation of anthryl fluorescence shown in Figure 3 was ascribed to the photodissociation of the exciplex. The exciplex fluorescence depletion was examined at several wavelengths (700−800 nm) of the second laser. The photodepletion efficiency curve *vs* wavelength of the dissociation laser was essentially similar to the transient absorption band (700−800 nm) in the 3-methylpentane solution. These facts demonstrate that the pronounced depletion of the exciplex fluorescence (Figure 3) followed by the simultaneous formation of anthryl may be attributable to the dissociation of the exciplex in the higher electronic state of the exciplex. The dispersed fluorescence spectrum of the anthryl moiety was examined to detect the photodissociation of the exciplex. Very broad and congested anthryl fluorescence spectra without vibrational structure were observed at 380−440 nm, although considerably intense exciplex fluorescence remained in the >440-nm region. Figure 4 shows typical decay curves of the anthryl fluorescence generated by the photodissociation of the exciplex in 9-An-DMA and 9-An-*d*-DMA. The anthryl fluorescence decay time upon photodissociation was found to be 1.3 ns, while the corresponding decay time leading to the exciplex formation was 4.7 ns in the excitation of the vibronic band ($\Delta E = 1390$ cm^{-1}) of 9-An-DMA. In the deuterated compound, 9-An-*d*-DMA, the anthryl decay time upon exciplex dissociation was less than 0.5 ns, probably within the picosecond time domain, although that for the exciplex formation was 3.6 ns in the excitation at $\Delta E =$ 1405 cm^{-1}. It is noteworthy that very short decay times of anthryl were generated by the photodissociation of the jet-cooled exciplex and that the remarkable deuteration effect on their decay times was observed. The errors and limitation of the short decay times were mentioned in the Experimental Section.

Saigusa et al.[8] and Saigusa and Lim[9] reported the fluorescence depletion of the jet-cooled excimer generated from the naphthalene cluster in the excitation of the excimer state (B_{3g}) to its higher electronic state (B_{2u}). In the photodissociation of naphthalene excimer, a fragment fluorescence of naphthalene was detected. This fact was ascribed to the interpretation that the B_{2g} and B_{2u} states originate from the interaction between the ^{1}La molecular exciton states and charge resonance state (CR), and the upper excimer state is dissociative or weakly bound.[8,9] In the photodissociation of jet-cooled exciplex reported here, the mechanism of the photodissociation may be considerably different from that of the excimer, although the character of the higher electronic state of the exciplex (S_n) will be discussed in the next section. The excitation of the exciplex to the upper level of the transient absorption band leads to the higher vibrational continuum of the anthryl S_1 state through very fast intramolecular vibrational energy redistribution (IVR) and/or internal conversion. Then, the remarkable exciplex depletion followed by anthryl fluorescence with a very short decay time was obtained by a level crossing between the higher exciplex state and the higher vibrational S_1 state of anthryl, as will be mentioned later.

Similar photodissociation of the exciplex of 9-An-DMA and 9-An-*d*-DMA in solution such as hexane and acetonitrile was examined by using the optical setup of the two-step laser-induced fluorescence (excitation wavelength 308/730 nm). Further, the same experiment was also performed by picosecond depletion laser excitation (700 nm pulse, fwhm 10 ps, 0.5 mJ) and by using a streak camera (ns/ps TS-LIF).[11,12] However, neither depletion of the exciplex fluorescence nor increment of anthryl moiety fluorescence was detected, because not only ionic dissociation and/or relaxation of the exciplex but internal conversion probably takes place very fast within the pico- or femtosecond time domain in solution.

Anthryl Deuteration Effects on Exciplex Formation and Photodissociation. As mentioned in the Introduction, a simple theory to describe the excess energy dependence of the rate constant of the jet-cooled exciplex formation in 9-An-DMA was proposed by Zewail and his co-workers.[2,3] From the results of electron transfer rate *vs* the excess vibrational energy, it was shown that the folding of the two chromophores is crucial to bring about the intramolecular encounter necessary for the exciplex formation. This folding is the result of IVR from the anthryl moiety to the methylene chain, as pointed out by Zewail's[3] and also Itoh's[7] group. The rate of IVR is faster than the reaction rate with excess energy, since no significant mode selectivity of state in the exciplex formation was observed at any given energy. On the other hand, Peng et al.[13] reported the dynamics of IVR in deuterated anthracene. They indicated that approximate densities of state of S_1 in anthracene-d_{10} remarkably increased with increasing excess vibrational energy (ΔE), for instance 15/cm^{-1} at $\Delta E = 770$ cm^{-1}, 901/cm^{-1} at $\Delta E = 1420$ cm^{-1}, and 6680/cm^{-1} at $\Delta E = 1790$ cm^{-1}. The extent of increase of the density of state in the higher vibrational states was much greater in the deuterated anthracene than in undeuterated anthracene (6/cm^{-1} at $\Delta E = 770$ cm^{-1}, 233/cm^{-1} at $\Delta E = 1420$ cm^{-1}, and 1443/cm^{-1} at $\Delta E = 1790$ cm^{-1}). The increase of the density of state in the deuterated anthryl moieties seems to promote the rate of IVR of anthryl to the folding of the methylene chain, leading to the exciplex formation.[3,7] On the other hand, Okajima and Lim[16] suggested an importance of the Franck−Condon factor associated with the transition from the uncomplexed to the complexed component molecules in vibrational energy dependence of the association rate constant in the intermolecular exciplex formation in the static vapor phase. Therefore, the smaller excess energy threshold for the exciplex formation in the deuterated compound may be qualitatively attributable to the higher density of state in the deuterated anthryl moiety. Further, the different Franck−Condon profile between the deuterated and undeuterated anthryl/DMA systems may be taken into account for the deuterium effect of the exciplex formation, as mentioned above.

Transient absorption spectra of the exciplex in solution spectroscopy indicate that anion and cation characters of their component moieties, $(D^+, A^-)^*$, are involved in the exciplex state (S_1). The facts suggest that the upper states (S_n) of the transient absorption spectrum of the exciplex may have locally excited characters of cation and anion of the component moieties: (D^{+*}, A^-) and/or (D^+, A^{-*}) states. Another possibility of the upper excited states of the exciplex may be the involvement of the reverse charge transfer states such as (D_i^*, A) and (D, A_i^*). (D_i^*, A) and (D, A_i^*) represent the higher singlet excited states of the DMA and anthryl moieties, respectively. Absorption bands that might be ascribed to transitions of the reverse CT states were reported in addition to the localized ionic transitions by Ottolenghi et al.[17] In the solution spectroscopy, however, neither donor nor acceptor fluorescence has been observed in the excitation of the transient absorption band of the exciplex as mentioned in the last section. It is likely because the further anion and cation recombination and/or internal conversion take place within the pico- or femtosecond time domain, although the reverse CT might occur in solution.[18]

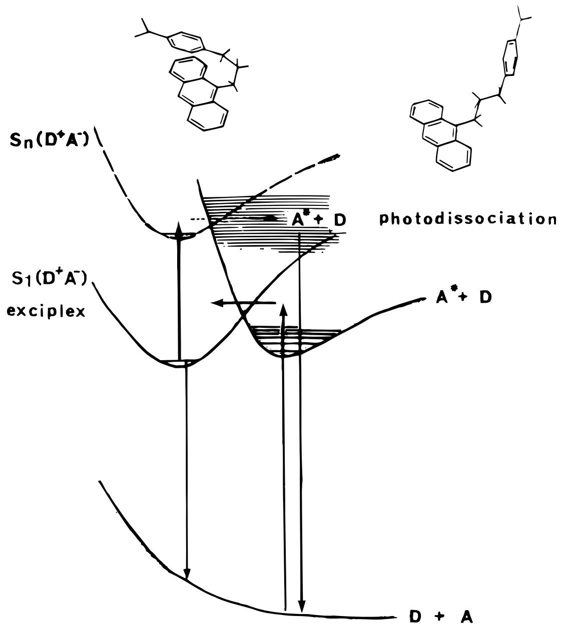

Figure 5. Schematic potential energy curves illustrating the formation and photodissociation of the intramolecular exciplex.

The pronounced depletion of the exciplex leading to the simultaneous formation of the excited-state anthryl was observed by the excitation of the transient absorption band of the exciplex in the jet-cooled 9-An-DMA, as presented in this paper. The very short decay times and also very broad congested dispersed fluorescence of the anthryl moiety were observed upon photodissociation of the exciplex. Further, the anthryl decay times upon photodissociation remarkably decreased in 9-An-*d*-DMA with deuterated anthryl, as mentioned above. These spectral and decay features suggest that the fluorescence relaxation takes place from the upper vibrational energy levels of the anthryl moiety. The transient absorption band excitation (730 nm) of the exciplex leads to the locally excited state with anthryl ionic character, (D^+, A^{-*}). The energy level of this state may correspond to the higher vibrational continuum of the exciplex and also probably to those of the reverse CT stae (D, A_i^*). As shown in the potential energy curves of Figure 5, the IVR and/or internal conversion take place from the upper electronic states of the exciplex to the higher vibrational continuum states of the anthryl S_1 state. On photodissociation of the exciplex, the anthryl fluorescence with very short decay times emits from certain vibrational states of the upper energy levels in the anthryl moieties. Further, the higher density of states in deuterated anthryl may be responsible for very short decay times observed in the exciplex photodissociation, as mentioned above.

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