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Excitation Energy Dependence of Intramolecular Exciplex Formation and Electronic Relaxation in the Collision-free Vapor

Michiya Itoh*, Yukio Hanashima, Naoko Wada, and Ichiro Hanazaki†
Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920
†*Institute for Molecular Science, Myodaiji, Okazaki 444*

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The excitation energy dependence of the intramolecular exciplex formation and the electronic relaxation has been studied in the collision-free vapor of 1-(9,10-dicyano-2-anthryl)-3-(pentamethylphenyl)propane. The fluorescence quantum yields and lifetimes of the 9,10-dicyanoanthryl moiety and the intramolecular exciplex in the collision-free vapor were observed to depend on the excitation energy within the S_1 absorption band. From the quantum yields and the decay rate constants, the excitation energy dependence of the association and dissociation rate constants of the intramolecular exciplex formation were determined. The association rate constant of the exciplex formation increases more remarkably with increasing excitation energy than the nonradiative rate constants of 9,10-dicyanoanthryl moiety and the exciplex. The excitation energy dependence of the association rate constant was discussed in terms of the nonradiative transition from the initial optical state to the final exciplex and the level density of the final state, which were calculated in the simple model system by means of the semi-classical mechanics.

The exciplex formation in the vapor phase was reported in the 9-cyanoanthracene and/or substituted 9-cyanoanthracene and alkylamine systems[1,2] and in the tetracyanobenzene (TCNB) and *p*-xylene system.[3] Okajima and Lim[4] reported that the exciplex formed from the vibrationally hot S_1 state of TCNB and the ground state of *p*-xylene is almost nonfluorescent and decays rapidly via nonradiative process. Recently, Itoh *et al.*[5,6] reported that the intramolecular exciplex of 1-(9,10-dicyano-2-anthryl)-3-(1- or 2-naphthyl)propane ($\beta\alpha$- or $\beta\beta$-DCAN) in the collision-free vapor phase exhibits the excitation energy dependence of the fluorescence spectra and lifetimes of the exciplex. They suggested that exciplex formation from the vibrationally hot S_1 state of the electron acceptor and the ground state donor moieties followed by the fluorescent relaxation from the upper vibrational state of the exciplex takes place. In the intermolecular electron donor acceptor system, the concentration of the electron donor (or acceptor) amounts to 10^{-2}—10^{-3} mol dm^{-3} in the vapor phase, which corresponds to the gas pressure of approximately 50 Torr (1 Torr=133.322 Pa). The donor molecules in this pressure may act as a collisional relaxer of the vibrationally hot S_1 state of the acceptor.[7] Therefore, the vibrational effect on the exciplex formation and the electronic relaxation can not be measured in the intermolecular system. The electronic interaction between the electron donor–acceptor system can be investigated only in the isolated molecular condition of the intramolecular electron donor acceptor system. Further, Itoh and Hanashima[8] reported the excitation energy dependence of the rate constants of intramolecular exciplex formation in the collision-free vapor. The rate constant of the exciplex formation increases remarkably on the excitation of the upper vibrational S_1 state. Very recently, Felker *et al.*[9] also reported the excess energy dependence of the exciplex fluorescence in the jet-cooled molecules of the intramolecular electron donor acceptor system.

On the other hand, the excitation energy dependence of the fluorescence lifetimes, quantum yields, and the radiative and nonradiative rate constants has been reported in the single vibronic level (SVL) fluorescence of some aromatic compounds. Further, numerous investigations of the vibrational level dependence of the photochemical reaction such as dissociation and isomerization of small molecules have been published.[10] However, no excitation energy dependence of the molecular complex formation and bimolecular reaction in the excited state has been reported except two papers mentioned above, though the important role of the S_1 excess energy on the photochemical reaction was pointed out.[11] This paper is further concerned with the excitation energy dependence of the association and dissociation rate constants of the exciplex formation in the collision-free vapor of 1-(9,10-dicyano-2-anthryl)-3-(pentamethylphenyl)propane (DCAB).[12] The rate constants of the exciplex formation and dissociation increase with increasing vibrational energy of the S_1 state of the 9,10-dicyanoanthryl (DCA) moiety. In order to investigate the excitation energy dependence, the transition probability from the initial locally excited state of DCA to the final exciplex was estimated in the model system by means of the semi-classical mechanics. The results suggest that the excess energy dependence may be mostly attributable to the density of the vibrational levels of the exciplex state.

Experimental

Preparation and purification of the sample were described in the previous papers.[12] 2-Methyl-9,10-dicyanoanthracene was prepared by bromination and cyanogenation of 2-methylanthracene (Nakarai Chem. GR), and purified by repeated column chromatography (silica gel. benzene–hexane) followed by recrystallization. 1-(9,10-Dicyano-2-anthryl)-3-(pentamethylphenyl)propane was synthesized from the starting materials of 2-anthraldehyde and pentamethylacetylbenzene, and purified by repeated column chromatography and recrystallization.[12] The rectangular quartz cell (10 mm) with graded seals containing samples was degassed and sealed off from the vacuum line. Fluorescence and absorption spectra were measured in a quartz dewar at controlled temperature by heated air flow. The fluorescence and absorption spectra were measured by Hitachi MPF-4 and 220 spectrophotometers, respectively. The fluorescence lifetimes and decay curves were measured in the excitations by a nitrogen laser and its pumped dye laser (Molectron UV-12 and DL-14), and by an HTVR666 photomultiplier and a Tektronix 7904 (7A19 and 7B85) oscilloscope. Observed decay curves were analyzed by a computer-simulated deconvolution. The fluorescence quantum yields were determined by using a quinine sulfate solution as a standard (1×10^{-5} mol dm^{-3} in 0.25 mol dm^{-3} sulfuric acid; $\phi=0.54$ at room temperature)[13] where the fluorescence spectra of the standard solution were measured in the almost completely same experimental set-up as those of the vapor phase.

Results and Discussion

The absorption spectrum of DCAB in the vapor phase at 500—550 K shows a very weak absorption intensity as shown in Fig. 1, because of a very low vapor pressure. Assuming that the absorption intensity of DCAB in the vapor phase may be almost identical to that in the nonpolar solution, the concentration and pressure of DCAB in the vapor phase at this temperature were estimated to be 10^{-6}—10^{-7} mol dm^{-3} and 10^{-2}—10^{-3} Torr, respectively. Since the intermolecular collisional rate of the S_1 state of the molecule in the gas pressure of p is estimated to be 10^7p Torr^{-1} s^{-1} by a hard sphere collision model,[14] the molecules of DCAB in the experimental condition may be regarded to be an intermolecularly collision-free condition, that is the isolated molecular condition.

The fluorescence and excitation spectra of this collision free vapor of DCAB are shown in Fig. 1. The excitation spectra monitored at 450 and 500 nm are in good consistency with that of the absorption spectrum. Further, the fluorescence spectrum of 2-methylanthracene (2-Me-DCA) in the collision-free condition is also shown in Fig. 1. From comparison of the fluorescence spectrum of DCAB with that of 2-Me-DCA, the shorter wavelength fluorescence (400—460 nm) and the longer wavelength one (450—520 nm) are ascribed to the 9,10-dicyanoanthryl (DCA) moiety and the intramolecular exciplex in the vapor phase, respectively. The fluorescence intensity of the collision-free vapor of DCAB was observed to exhibit a remarkable excitation energy dependence. Figure 2 shows the relative fluorescence quantum spectra in the excitations at several wavelengths, the relative intensity decreases with increasing excitation energy. Further, the fluorescence spectral distribution shifts to the shorter wavelength region with increasing excitation energy, as shown in Fig. 3.

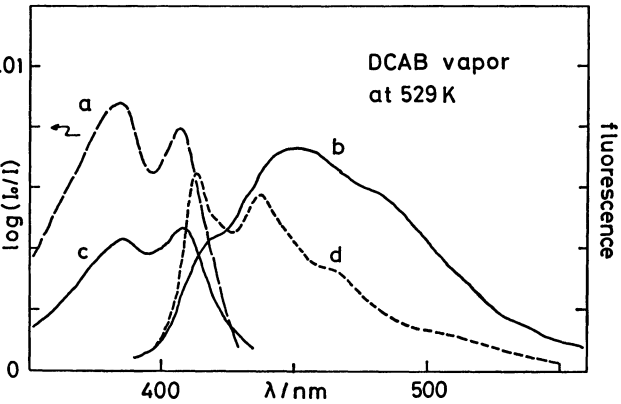

Fig. 1. (a) Electronic absorption spectrum of DCAB in the vapor phase. (b) Fluorescence (excited at 385 nm) and (c) excitation (monitored at 500 nm) spectra of the collision-free vapor of DCAB at 529 K. (d) Fluorescence spectrum of the collision-free vapor of 2-Me-DCA (excited at 385 nm) at 458 K. The fluorescence spectra are uncorrected.

The photochemical reaction scheme and kinetics in the intramolecular exciplex formation are expressed by the following wellknown equations;[15]

$$\begin{tikzcd}
 & D + A^* \arrow[rrr, shift left, "k_3"] \arrow[dl, "k_1"'] \arrow[dr, "k_2"] & & & (DA)^* \arrow[lll, shift left, "k_4"] \arrow[dl, "k_5"'] \arrow[dr, "k_6"] & \\
D + A + h\nu, & & D + A & D + A + h\nu', & & D + A
\end{tikzcd}$$

$$[A^*] = c_1\exp(-\lambda_1 t) + c_2\exp(-\lambda_2 t), \quad (1)$$

$$[(DA)^*] = c_3\exp(-\lambda_1 t) - c_3\exp(-\lambda_2 t), \quad (2)$$

$$2\lambda_1,\ 2\lambda_2 = (X+Y) \pm \{(Y-X)^2 + 4k_3k_4\}^{1/2},$$
$$X = k_1 + k_2 + k_3, \qquad Y = k_4 + k_5 + k_6,$$

where A and D are DCA and phenyl moieties, respec-

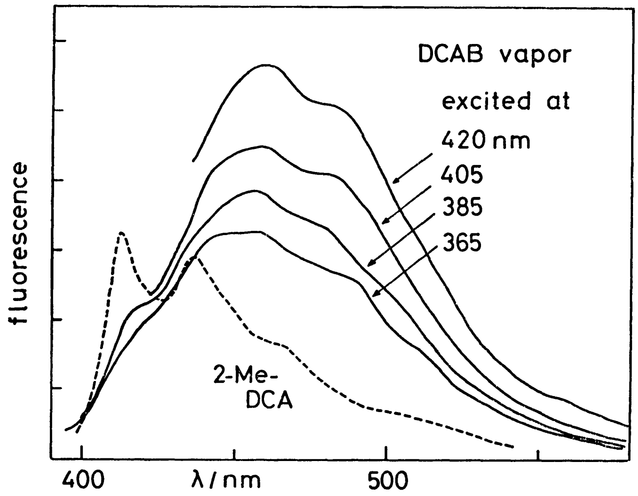

Fig. 2. The relative fluorescence quantum spectra of the collision free vapor of DCAB in the excitations at several wavelengths at 529 K. The spectra are corrected.

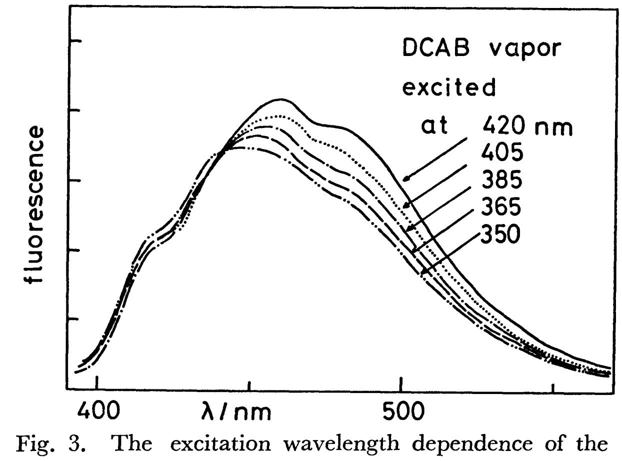

Fig. 3. The excitation wavelength dependence of the fluorescence spectral distribution of the collision-free vapor of DCAB at 529 K. The spectra are normalized in intensity at 440 nm and uncorrected.

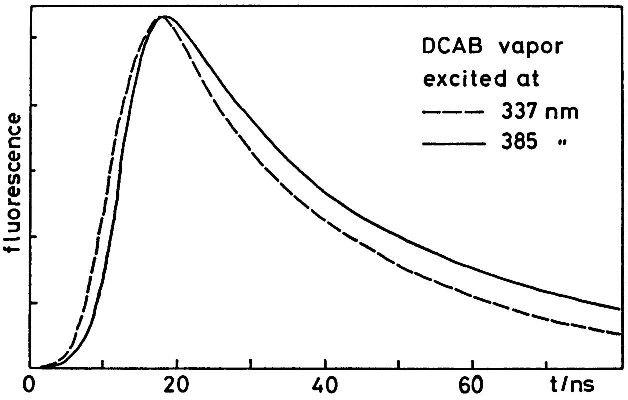

Fig. 4. Typical fluorescence decay curves (monitored at 430 nm) of the DCAB vapor at 525 K. The curve (— — —) was excited at 337 nm (pulse FWHM $\approx$10 ns) and analyzed for $A\exp(-\lambda_2 t)+(1-A)\exp(-\lambda_1 t)$, $\lambda_1^{-1}=28.94$, $\lambda_2^{-1}=1.47$ ns, and $A=0.7675$; the curve (——) excited at 385 nm (pulse FWHM $\approx$7 ns), $\lambda_1^{-1}=41.42$, $\lambda_2^{-1}=7.09$ ns, and $A=0.4984$.

tively. In the collision-free vapor, A* and (DA)* imply the upper vibrational states of their S_1 states depending on the excitation energy. Spears and Rice reported that the quantum yields and the lifetimes of the SVL fluorescence of benzene vapor exhibit different excitation energy dependences from each other according to the vibrational sequence.[16] However, the intramolecular vibrational energy redistribution (randomization) might take place at a rather high temperature.[17] If the considerable fast redistribution of the vibrational energy may take place, A* and (DA)* may be expressed by each sum of several vibrational states, and the decay of these states may be expressed by multi-exponential or an average from these vibrational states. The decay curves of A* and (DA)* were observed to be approximately double (at 430 nm) and single (at 580 nm) exponentials, respectively. Therefore, A* and (DA)* are considered as a quasi-single vibronic state in equilibrium. The typical decay curves of the collision-free vapor of DCAB excited at 337 and 385 nm are shown in Fig. 4. Therefore, the decay rate constants λ_1 and λ_2 were obtained from the A* fluorescence decay (Eq. 1) for respective excitation energies. However, no significant rise time (λ_2^{-1}) of the (DA)* fluorescence (Eq. 2) was observed because of the spectral overlap of A* and (DA)* fluorescences, as will be mentioned later, though the same decay rate constant λ_1 was obtained from the (DA)* fluorescence as that of A*. These decay rate constants are summarized in Table 1 for several excitation wavelengths.

The fluorescence quantum yield and lifetime of the collision free vapor of 2-Me-DCA were observed to depend on the excitation energy. From these excitation energy dependences, radiative and nonradiative rate constants were determined at 523 K, as summarized in Table 1. On the other hand, the fluorescence quantum yields of A* (ϕ_a) and (DA)* (ϕ_e) in DCAB are expressed as follows;

$$\phi_a = k_1Y/(XY-k_3k_4) \tag{4}$$

$$\phi_e = k_3k_5/(XY-k_3k_4). \tag{5}$$

TABLE 1. EXCITATION WAVELENGTH DEPENDENCE OF FLUORESCENCE QUANTUM YIELDS (ϕ_a AND ϕ_e), AND DECAY (10^7 s^{-1}) AND REACTION RATE CONSTANTS (10^7 s^{-1}) OF THE INTRAMOLECULAR EXCIPLEX FORMATION IN DCAB VAPOR AT 523—526 K

Excitation	337 nm	365 nm	385 nm	405 nm
ϕ_a[a)]	0.07	0.15	0.19	0.28
ϕ_e	0.23	0.33	0.33	0.27
k_1[a)]	1.8	2.5	2.7	2.8
k_2[a)]	11	6.8	5.8	4.3
λ_1	3.4	3.0	2.4	2.2
λ_2	66	18	14	10
k_3[b)]	50.6	8.5	5.6	3.3
k_4[b)]	5.8	0.9	0.2	—
k_5[b)]	2.3	2.4	2.1	1.7
k_6[b)]	0.4	0.3	0.2	2.3

a) Determined from the collision-free vapor of 2-Me-DCA; errors are approximately ±10%. b) Errors are approximately ±20%.

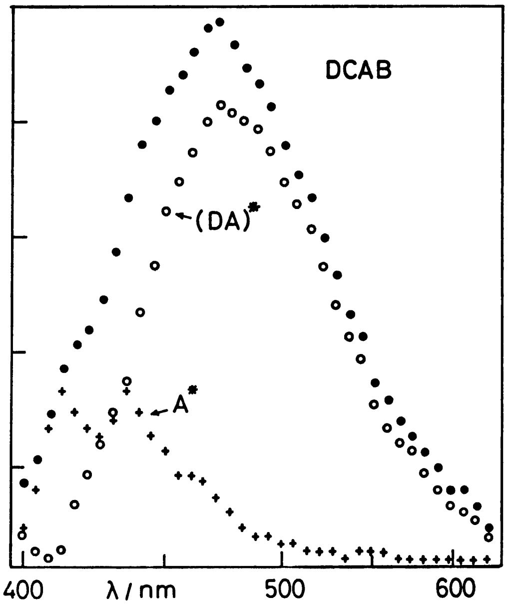

Fig. 5. An example of the separation of the fluorescence spectra (corrected) of the collision-free vapor of DCAB into those of DCA moiety and exciplex.

The fluorescence spectra of A* and (DA)* overlap very close each other. Therefore, assuming that the fluorescence spectrum of DCA moiety (A*) in DCAB is identical to that of 2-Me-DCA in the several excitation energies, the fluorescence spectrum (corrected) obtained was divided into the A* and (DA)* fluorescence spectra by the computer simulation as shown in Fig. 5. Then, the quantum yields ϕ_a and ϕ_e were obtained in the respective excitation energies. Furthermore, assuming k_1 and k_2 to be identical to the radiative and nonradiative rate constants of 2-Me-DCA, respectively, the rate constants k_3, k_4, k_5, and k_6 were determined from decay rate constants λ_1 and λ_2, and quantum yields (ϕ_a and ϕ_e). These data

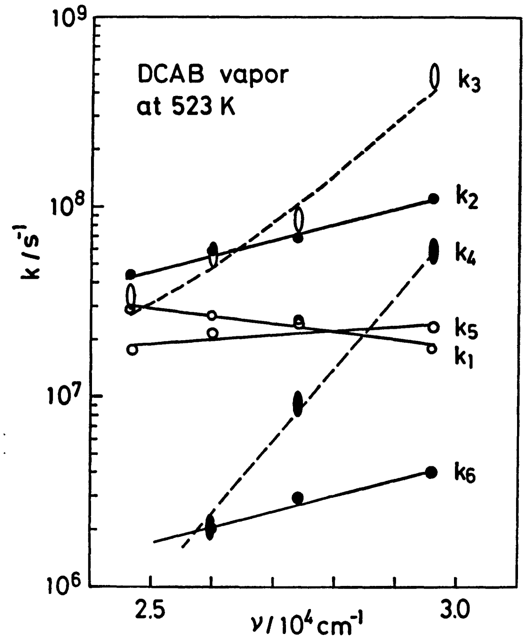

Fig. 6. The plots of rate constants *vs.* excitation energy (wavenumber unit) shown in Table 1.

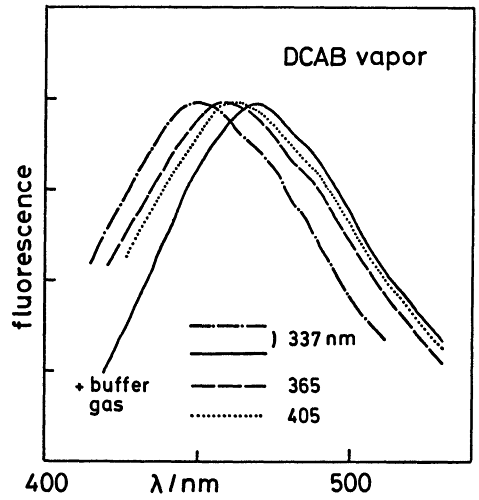

Fig. 7. Time-resolved fluorescence spectra of the DCAB vapor (523 K) in the excitations at several wavelengths. The spectra were depicted at 50 ns after a laser pulse; (—●—●—) 337 nm, (— — —) 365 nm, (······) 405 nm for the collision-free vapor. The spectrum (——) of the collisionally relaxed vapor by 50 Torr hexane gas excited at 337 nm. The spectra are normalized in intensity.

are summarized in Table 1.

The quantum yield of the DCA moiety, ϕ_a, decreases remarkably and λ_2 increases with increasing excitation energy. As the results, the association (k_3) and dissociation (k_4) rate constants of the exciplex formation increase with increasing excitation energy in the DCAB vapor. Similar excitation energy dependence of the exciplex formation in the collision-free vapor of *ββ*-DCAN and also the intramolecular excimer formation in *N,N,N′,N′*-tetramethylpropanediamine vapor were reported in the previous papers.[8,18] Figure 6 shows log plots of these rate constants *vs.* excitation energy (wave number). The nonradiative rate constants of the DCA moiety (k_2) and the exciplex (k_6) increase markedly with increasing excitation energy. The nonradiative rate constants of polyatomic molecules are known to depend linearly on the exponential of the excitation energy.[19,20] The observed excitation energy dependence of k_2 and k_6 exhibits a reasonable trend from this point of view. However, it is noteworthy that $\log k_3$ and $\log k_4$ increase extraordinarily with increasing vibrational energy level, and shows a significant deviation from a linear relationship with respect to the energy; the reason will be discussed later.

The collision-free vapor of DCAB shows the excitation energy dependence of the spectral distribution of the exciplex, as mentioned above. Figure 3 exhibits that the exciplex fluorescence seems to shift to the longer wavelength region with decreasing excitation energy, while the fluorescence of 2-Me-DCA was observed to exhibit conversely a little blue shift. In order to demonstrate the shift of the exciplex fluorescence, the time-resolved fluorescence (Fig. 7) was depicted at ≈50 ns after a laser pulse. The spectral distribution shows red shift with decreasing excitation energy. However, the spectra of the collisionally relaxed vapor of DCAB by the buffer gas (≈500 Torr hexane gas) shows the longest wavelength fluorescence irrespective of the excitation energy. Halpern and Gartmen reported the similar excitation energy dependence of the fluorescence spectrum of *N,N′*-dimethylpiperidine vapor and suggested it to be the fluorescence from the unrelaxed state.[21] The fluorescence spectral distribution depending excitation energy is attributable to the fluorescent deactivation from the upper vibronic S_1 states. The excitation energy dependence of the spectra provides an important information of potential energy surfaces of both ground and excited states of the exciplex. The fluorescence spectra of usual aromatic compounds such as 2-Me-DCA in the collision-free vapor exhibit a faint red shift with increasing excitation energy. The fact is usually interpreted by a consideration that the potential curve of the fluorescent state may be shallower than that of the ground state. In the exciplexes, however, the ground state corresponding to the exciplex is considered to be repulsive and very shallow. Therefore, the fluorescence from the upper vibrational level may shift to the shorter wavelength region than that from the lower level.

An extraordinary vibrational energy dependence of the rate constant was reported in an atom molecular reaction such as $KCl+H=K+HCl$.[22] The rate constant from the vibrational state $v=1$ of HCl is approximately 100 times as large as that from $v=0$. Numerous experimental and theoretical investigations have been reported in the vibrational and rotational energy dependence on the reaction rate constants.[23,24] However, it is not properly interpreted how these observed effects of vibrational energy to the reaction rate constants are to be attributable to the activation energy and/or the pre-exponential factor in the reaction rate equation. Further, in the excited-state electron donor–acceptor interaction, the rate constant of the exciplex formation between the vibrationally hot S_1 state (*via* S_2) of TCNB and the ground state of *p*-xylene (7×10^{12} mol^{-1} dm^3 s^{-1}) was suggested to be an order of magnitude greater than that from the vibrationally relaxed S_1 state (7×10^{11} mol^{-1} dm^3 s^{-1}).[4] It is noteworthy that these rate constants of the excited-state interaction show an unusual dependence on the vibrational energy of the S_1 state reported here and also in the previous papers.[8,18] Very recently, Felker *et al.* reported the excitation energy dependence of the exciplex fluorescence spectra and decay rate in the jet-cooled molecular EDA system, as mentioned in the introductory section. The extent of the excitation energy dependence of the exciplex fluorescence lifetimes seems to be more remarkable in the jet-cooled molecule than those in the collision-free vapor at rather high temperature,[6–8,18] though Felker *et al.* did not determine any excitation energy dependence of the association and dissociation rate constants of the exciplex in the jet-cooled molecule. These facts are quite reasonable in the jet-cooled molecule, because the randomization of the vibrational energy may be limited at low temperature. However, the kinetic determination of the association rate constant of the exciplex formation seems to be almost impossible, since the estimation of the fluorescence quantum yield is very difficult in the supersonic expansion.

The nonradiative rate constant of the electronic excited state is usually discussed in terms of the transition probability of the Fermi Golden rule for the nonradiative process.[25–28] Further, the excited-state proton transfer is also considered as the nonradiative process between the double minimum potential of the hydrogen bonding system.[29] However, this theory of the nonradiative transition can not be strictly applicable to (DA)* formation because of the repulsive potential in the initial optical state of A* and D, as shown in Fig. 8. In the excitation into the upper vibrational states of the 9,10-dicyanoanthryl moiety in DCAN and DCAB, which is connected to the electron donor moiety by trimethylene chain, the vibrational energy in the aromatic ring system seems to dissipate to the methylene chain by the vibrational-vibrational (*V*—*V*) energy transfer. Then, stretching and/or bending vibrations in trimethylene chain of DCAN and DCAB are induced by the *V*—*V* energy transfer. This means that the vibrational to translational (*V*—*T*) energy transfer occurs through the trimethylene chain, and that the DCA moiety obtains translational energy.

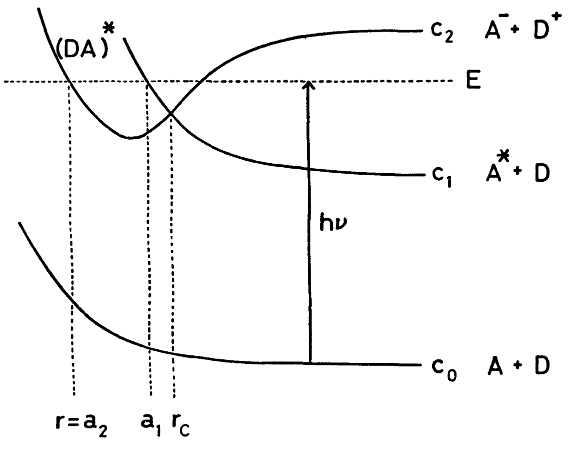

Fig. 8. Schematic potential energy curves of the exciplex formation.

In order to simplify the theoretical consideration, the electronic interaction between the electron donor acceptor is assumed to be a kind of Coulomb interaction between D and A* which are assumed simply to be two atoms. Figure 8 shows the potential energy curves of D+A (C_0), D+A* (C_1), and $(D^+ + A^-)^*$ (C_2) along the reaction coordinate. Here, the following assumptions are made in order to solve the problem by means of the semi-classical mechanics; the C_2 potential is considerably lower than C_1 at the stable interatomic distance of (DA)* and the CT interaction between C_1 and C_2 is small so that the potential curve for (DA)* can be approximately by C_2. The transition from the initial state (D+A*) to the complex state (DA)* occurs at the crossing point of $r=r_c$, where the energy and also momentum are conserved. According to the Landau's theory,[30] the transition probability (w) from the initial state (D+A*) to the (DA)* state is expressed as following equation;

$$w = \frac{2\pi}{h\nu}\left\{\left|\int X_2{}^* V(r) X_1 \mathrm{d}r\right|\right\}^2, \tag{6}$$

where $V(r)$ is a perturbation energy of interaction between two states, and X_1 and X_2 are semi-classical wave functions in the (D+A*) and (DA)* states, respectively. From the simple model calculation, the estimated transition probability (w) was ploted *vs.* the excess energy from the potential barrier, as shown in Fig. 9. The transition probability exhibits a considerable decrease with increasing excess energy, but does not depend greatly on the excess energy.

Okajima and Lim[4,31] suggested an importance of the Franck Condon factor associated with the transition

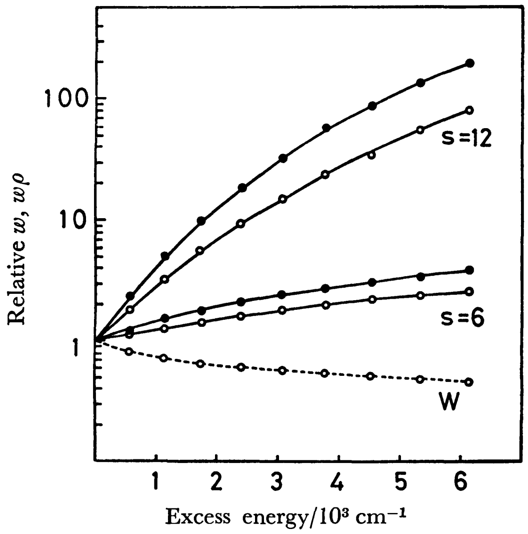

Fig. 9. Relative transition porbability (w, --○--○--) and the product of w and the level density (ρ) calculated by the semiclassical mechanics for the simple model system; (—●—●—) $\Delta E = 1800$ cm^{-1}, (—○—○—) $\Delta E = 2500$ cm^{-1}. Data are normalized at zero excess energy (see text).

from the uncomplexed to complexed component molecules in the vibrational energy dependence of the association rate constant (k_3). The Franck-Condon factor is expected to be large for a vibration. Further, they suggested that the vibrational excitation in a good accepting mode render the vibration a better accepting mode, then the rate constant may be increased by vibrational excitation.[31] On the other hand, since the actual molecules such as DCAB and DCAN have a large number of vibrational and rotational energy levels, the reaction rate constant of the exciplex formation may be proportional to the product of the transition probability (w) and the vibrational level density (ρ) of the final exciplex state. The semiclassical approximation for the density of vibrational energy levels of polyatomic molecules was proposed by Haarhoff,[32] where the density is expressed as follows;

$$\rho = (E+E_0)^{s-1}/[(s-1)!h\nu_i]. \tag{9}$$

Here ν_i is the wave number of normal mode i; s is the number of the vibrational freedom. In this paper, the level density of the final state (ρ) was estimated at several excess energies (E_x) for a simple model system of two atoms as mentioned above. Figure 9 shows the product of transition probability and the estimated level density *vs.* the excess energy from the potential barrier (ΔE), of which level is higher than the zero point energy; $E=E_x+\Delta E$. The excess energy dependence of $w\rho$ in the case of $s=10$—12 and $\Delta E=1800\ \mathrm{cm}^{-1}$ seems qualitatively to interpret that of the rate constant k_3 (Fig. 6), though the model calculation of $w\rho$ is not accurate and the profiles of the curves of the excess energy dependence are considerably different from each other. Therefore, Fig. 9 may tentatively suggest that the excess energy dependence of k_3 seems to be attributable to the level density of the final exciplex state.

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