

Comparative study on the photodynamics of chloromethylanthracenes in a supersonic free jet and solution

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Fluorescence excitation spectra and fluorescence decays of 9-chloromethylanthracene (CMA) and 9-methyl-10-chloromethylanthracene (MCMA) were measured in a supersonic free jet. Excitation bands associated with the bare molecules were observed only at excess vibrational energies at less than 530 cm^{-1} for CMA and 400 cm^{-1} for MCMA. All the bands of the bare CMA molecule yielded fluorescence lifetimes (τ_f) shorter than 3 ns. The τ_f of the bare MCMA molecule was 16.6 ns at the electronic origin and it was shortened by increasing the excess energy. The excitation bands attributed to van der Waals (vdW) complexes of MCMA with rare-gas atoms were observed with fluorescence lifetimes longer than those of the bare molecule, whereas fluorescence from vdW complexes of CMA was observed only for large complexes of Kr and Xe atoms. Activation energies for the radiationless transition obtained from the temperature dependence of the fluorescence lifetime in solution were $610\text{--}650\text{ cm}^{-1}$ for CMA and $520\text{--}610\text{ cm}^{-1}$ for MCMA, and large values exceeding 10^{11} s^{-1} were obtained as the frequency factor. These results obtained in jets and solution are discussed from the viewpoint of the effects of medium on the photodissociation and intersystem crossing (ISC) processes.

Since the advent of supersonic free jet expansion, and when combined with laser induced fluorescence, it has become feasible to investigate the photodynamics of isolated molecules and vdW complexes excited state selectively.^{1–6} This method is particularly effective for large molecules which have low vapour pressure and spectroscopic complexities. It is interesting to compare photodynamics of such large molecules in a jet and solution. Of interest is how the kinetic parameters of activation energy and frequency factor in solution are related to state-selective rates measured for an isolated molecule. Also of interest is the effect of medium, which can be brought about by variations in electronic energy and vibrational relaxation. From these viewpoints, we have studied electronic relaxation from the first excited singlet state (S_1) of *meso*-substituted anthracenes in a jet and in solution.^{7–13} In this work, chloromethylanthracenes substituted at the *meso*-position (CMA and MCMA), which undergo photodissociation of the C–Cl bond in the S_1 state, were chosen as target molecules. The first objective is to examine the mechanism of this apparently simple photoreaction, in connection with the possibility of the involvement of ISC. The second is to interpret the activation energy and frequency factor in terms of the dependence of the deactivation rate on the S_1 vibrational level. The third is to examine the effect of medium on the radiationless transitions including photodissociation, by comparing the isolated molecule, the vdW clusters formed by coordination of different types and numbers of rare-gas atoms, and the solution.

Experimental

CMA was obtained from Tokyo Chemical Industry (TCI) and MCMA was prepared by a literature method.¹⁴ A small quantity of fluorescent impurities, which were thought to be

anthracene derivatives, could not be removed because purification of CMA and MCMA was restricted by the lability of the chloromethyl group; *i.e.*, column chromatography could not be used for purification. 3-Methylpentane and methylcyclohexane of guaranteed grade (TCI) were used after dehydration by molecular sieves. The reduction of trace water in the solvent was important in order to suppress hydrolysis of the chloromethyl group in CMA and MCMA.¹⁵

Fluorescence decays in solution were measured by a system consisting of a Ti : sapphire laser (Spectra-Physics Tsunami) and a streakscope (Hamamatsu C4334-2). Picosecond-pulses (repetition rate 80 MHz) generated from a Ti : sapphire mode-locked laser were frequency doubled by a frequency doubler (Model 3980) and the repetition rate was reduced to 4 MHz by a pulse selector. The temporal width of the second-harmonic pulse was about 20 ps. The fluorescence collected by the lens was detected at right angles to the excitation laser through a monochromator, using the streakscope operating in photon-counting mode. Fluorescence decay curves were analysed by the convolution method. The sample solution was deaerated by freeze–pump–thaw cycles. The measurement temperature was in a range 121–233 K for 3-methylpentane and 142–225 K for methylcyclohexane, where the solvents did not freeze. Low temperatures were attained by flowing cold nitrogen gas into a transparent Dewar vessel into which a sample cell was placed. The gas flow rate was controlled by adjusting the voltage supplied to a heater, which was dipped in liquid nitrogen in a 10 litre metal Dewar.

The measurement of transient absorption in the solution was carried out in the nanosecond time range with a system consisting of a nitrogen laser (pulse width 8 ns) as the excitation source, a flash lamp as the monitoring light source, a monochromator (JASCO CT-25N), a photomultiplier (Hamamatsu R928) and a storage scope (Iwatsu TS 8123).

An experimental description of the instrumentation for the measurement of fluorescence excitation spectra and fluorescence decays in a jet has been given elsewhere.^{7,11,16} In this

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work both continuum and pulsed supersonic jets were used. The experimental method in the pulsed supersonic jet is described briefly herewith. CMA and MCMA were heated at *ca.* 100 °C and *ca.* 120 °C, respectively, in a furnace with a pulse nozzle, with an aperture of 100 μm diameter. They were expanded into a vacuum in a chamber using a carrier gas. The nozzle-opening time was 2 ms and the repetition rate was 50 Hz. The chamber was evacuated by using a Urneva CDP-3700 10 in diffusion pump (pumping speed 4000 $\text{dm}^3 \text{s}^{-1}$) backed by an Ulvac D-650 rotary pump. A Lambda Physik excimer laser pumped dye laser [LPX205 + LPX105, 2-methyl-5-*tert*-butyl-*p*-quaterphenyl (DMQ) and 3,5,3''',5'''-tetra-*tert*-butyl-*p*-quinquephenyl (QUI) in dioxane] was used as the excitation source for the measurement of fluorescence excitation spectra and decays. The laser pulse was synchronized with the electronic pulse used to drive the nozzle, and its timing with the pulse jet was controlled by a digital delay generator (EG&G model 9650). The laser beam crossed the supersonic free jet 7 mm downstream from the nozzle. The fluorescence was collected through a lens and a cut-off filter and detected with a photomultiplier (Hamamatsu R331 and Hamamatsu R928 for the excitation and decay measurements, respectively). In the measurement of the excitation spectra, the output signal was integrated with a PAR Model 162 boxcar averager and was continuously transferred to a personal computer *vs.* the scanned laser wavelength. The fluorescence intensities were not corrected for variation of laser intensity with scanned wavelength. The fluorescence decays were measured with a nanosecond lifetime measuring system developed in the Instrument Centre at the Institute for Molecular Science. The fluorescence lifetimes were obtained by a conventional convolution method. When fluorescence lifetimes were longer than 3 ns, errors associated with the best-fit lifetime were 0.1–0.3 ns.

Results

Temperature dependences of fluorescence lifetime in solution

The fluorescence intensity of CMA and MCMA in 3-methylpentane and methylcyclohexane was very low at room temperature as reported previously for MCMA¹⁵ and it increased greatly with decreasing temperature. The fluorescence quantum yield at 77 K in glassy solutions of 3-methylpentane and methylcyclohexane was estimated to be almost unity by comparison with 9-cyanoanthracene and 9-methylanthracene whose fluorescence quantum yield is unity at 77 K. The presence of fast radiationless decays from the S_1 state at room temperature is implied by the low efficiency of fluorescence, and photodissociation and ISC are expected as the radiationless processes. In order to obtain information about the radiationless process, we performed nanosecond laser flash photolysis. The spectra of transient absorption measured for CMA and MCMA in methylcyclohexane at 25 °C are shown in Fig. 1. These spectra resemble the triplet-triplet (T-T) absorption spectra of anthracene compounds. However, the transient absorption of CMA and MCMA was not quenched by molecular oxygen and ferrocene, both of which are good triplet quenchers, though the T-T absorption of 9-methylanthracene was readily quenched. Consequently, the transient absorption obtained for CMA and MCMA cannot be attributed to T-T absorption. The transient species is thought to be an anthrylmethyl radical produced by photodissociation of the C-Cl bond, as reported for CMA by other workers.¹⁷ An involvement of photodissociation in the radiationless decay from the S_1 state was therefore suggested.

The fluorescence decays of CMA and MCMA in 3-methylpentane and methylcyclohexane were measured as a function of temperature using a picosecond fluorescence measurement system. The measurement was made for deaerated solutions at temperatures not higher than 233 K. The fluorescence decay curve measured for CMA in 3-methylpentane at

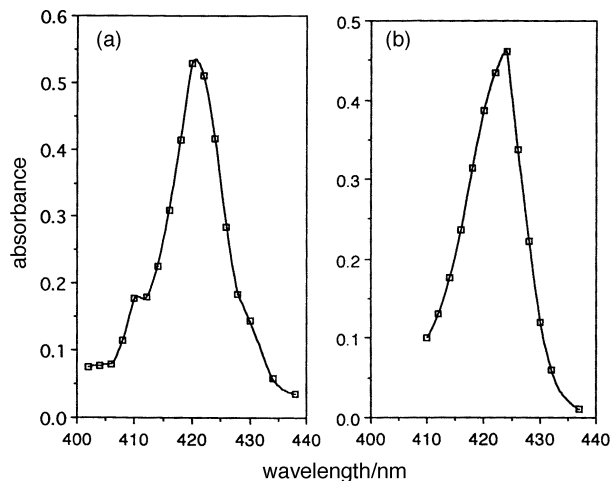


Fig. 1 Transient absorption spectra of (a) CMA and (b) MCMA in methylcyclohexane at 25 °C. The concentration of sample solutions was 10^{-3} M. The spectra were obtained at 100 ns after the excitation pulse. The spectra were not quenched by oxygen and ferrocene.

233 K is shown in Fig. 2. As a small amount of a slow decay component (attributed to impurities) exists, the decay curve was fitted to a double exponential function. The fluorescence lifetime obtained from the short decay component was 71 ps at this temperature, whereas the fluorescence lifetime and the relative pre-exponential factor for the impurities were 4.6 ns and 1.3%, respectively. The fluorescence lifetime increased dramatically with decreasing temperature and its value was 10.5 ns in glassy solution at 77 K. The fluorescence lifetime for MCMA in 3-methylpentane showed a similar temperature dependence, yielding 101 ps at 212 K and 10.6 ns at 77 K. The measurements on CMA and MCMA in methylcyclohexane also gave similar results. The long fluorescence lifetimes obtained at 77 K are considered to be equal to the natural radiative lifetime, and all of the radiationless channels from the S_1 state are closed at this low temperature. The radiationless rate constant (k^{nr}) is expressed by an observed fluorescence decay constant ($k^{obs} = 1/\tau_f$) and a radiative rate constant (k^r).

$$k^{nr} = k^{obs} - k^r \quad (1)$$

The value of k^r was taken as the reciprocal of the fluorescence lifetime at 77 K. Assuming an Arrhenius equation [eqn. (2)],

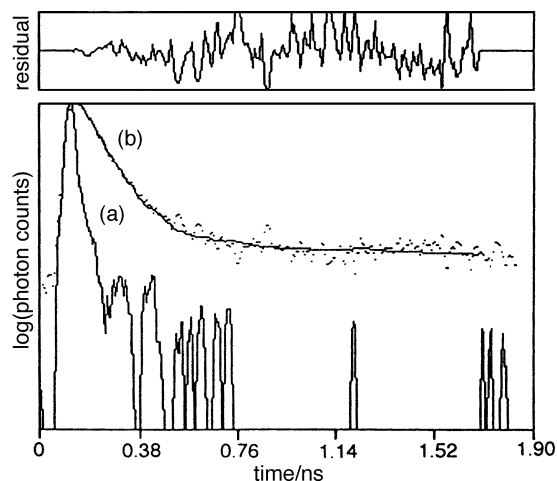


Fig. 2 Fluorescence decay curve measured for CMA in 3-methylpentane at 233 K. The excitation wavelength was 388 nm. The concentration of sample solution was approximately 10^{-5} M. The decay curve was fitted by a double exponential function owing to the presence of a slow decay component due to impurities. (a) Pump pulse; (b) fluorescence decay data.

$\ln k^{nr}$ was plotted against $1/T$ as shown in Fig. 3 for CMA in 3-methylpentane.

$$k^{nr} = A \exp(-E_a/RT) \quad (2)$$

Values of the frequency factor (A) and the activation energy (E_a) obtained for CMA and MCMA in 3-methylpentane and methylcyclohexane are listed in Table 1. The large values (3.5 – $8.5 \times 10^{11} \text{ s}^{-1}$) obtained for A suggest that the radiationless process is very fast when the thermal energy required is supplied to the molecules in the S_1 state; these values are one or two orders of magnitude larger than the values of A obtained for 9-methylanthracene and 9-chloroanthracene whose radiationless decay is entirely *via* ISC. For the *meso*-substituted anthracenes, whose radiationless process from S_1 is ISC, it is known that the activation energies associated with ISC are significantly larger for di-substituted anthracenes than for mono-substituted ones. This general tendency is not seen for CMA and MCMA.

Fluorescence excitation spectra and fluorescence lifetimes in a supersonic free jet

The fluorescence excitation spectra measured for CMA and MCMA molecules seeded in neon under a continuous free jet are shown in Fig. 4 and 5, respectively. The electronic origin of the bare molecule is located at 376.27 nm for CMA and at 386.80 nm for MCMA. Several vibronic bands are seen at vibrational energies below 530 cm^{-1} for CMA and 400 cm^{-1} for MCMA but at higher vibrational energies no excitation band was observed, suggesting the existence of fast radiationless decay.

The fluorescence lifetimes measured for the main bands are shown in Tables 2 and 3. All the bands measured for CMA, including the electronic origin, gave a fluorescence lifetime of shorter than 3 ns, which is the shortest value attainable reliably in the present apparatus. Although it is unknown how short the fluorescence lifetime of CMA is, it is definitely short as compared with those for other 9-substituted anthracenes; the fluorescence lifetime of the electronic origin is 18.7 ns for

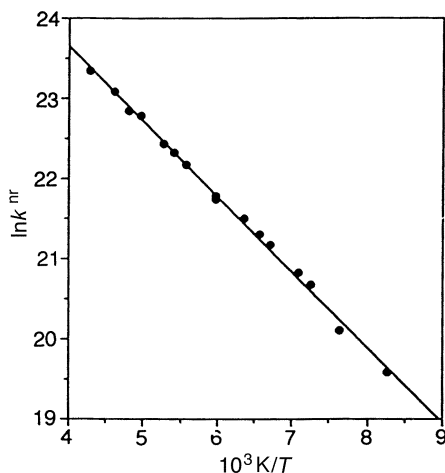


Fig. 3 Arrhenius plot ($\ln k^{nr}$ vs. $1/T$) for CMA in 3-methylpentane

Table 1 Energies of 0–0 bands (ν_{0-0}) for absorption spectra, fluorescence lifetimes (τ_f) at 77 K of CMA and MCMA in 3-methylpentane (MP) and methylcyclohexane (MCH), and activation parameters (A , E_a) for radiationless rate constants (k^{nr})

compound	solvent	ν_{0-0}/cm^{-1}	τ_f/ns	$A/10^{11} \text{ s}^{-1}$	E_a/cm^{-1}
CMA	MP	25 670	10.5	8.0	650
	MCH	25 590	10.6	7.1	610
MCMA	MP	25 000	10.4	3.5	520
	MCH	24 930	10.6	8.5	610

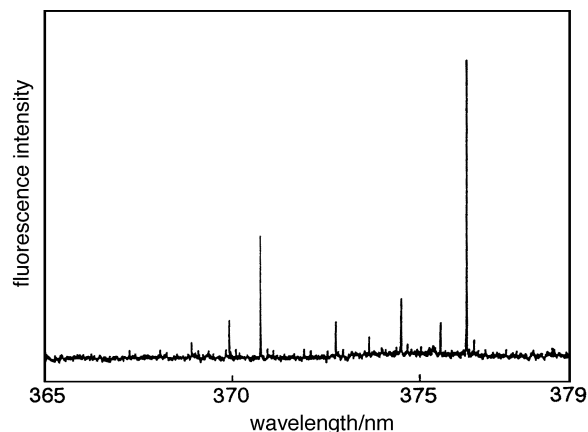


Fig. 4 Fluorescence excitation spectrum measured for CMA seeded in neon at a pressure of 620 Torr under continuous jet conditions

9-methylanthracene⁸ and 10.4 ns for 9-chloroanthracene.¹² On the other hand, the fluorescence lifetime for MCMA is as long as 16.7 ns at the electronic origin and it decreases rapidly with increasing vibrational energy. The value measured for the electronic origin of 9,10-dimethylanthracene is *ca.* 19.5 ns.¹²

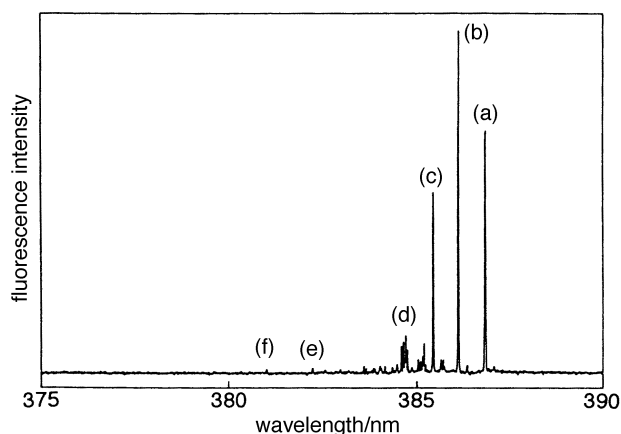


Fig. 5 Fluorescence excitation spectrum measured for MCMA seeded in neon at a pressure of 690 Torr under continuous jet conditions. The fluorescence lifetime was measured for the bands marked (a)–(f).

Table 2 Positions and fluorescence lifetimes of the bands associated with bare CMA and vdW complexes with rare-gas atoms

	band position ν/cm^{-1}	excess energy ^a $\Delta\nu/\text{cm}^{-1}$	τ_f/ns	
bare	26 576	0	<3	
	26 629	53	<3	
	26 702	126	<3	
	26 763	187	<3	
	26 827	251	<3	
	26 972	396	<3	
	27 033	457	<3	
	27 105	529	<3	
	Kr: 1.5 atm	25 940	–640	13.9
1.7 atm		25 940	–640	15.8
2.0 atm		25 900	–680	17.9
3.0 atm		25 820	–760	21.0
Xe: 0.8 atm		25 800	–780	17.3
		1.0 atm	25 710	–870
	2.0 atm	25 610	–970	23.9
3.0 atm	25 540	–1040	24.2	
	25 910(12 ₀)	–670	24.0	
	26 930(6 ₀)	350	23.9	

^a Measured from the 0–0 band position of the bare molecule.

Table 3 Positions and fluorescence lifetimes of the bands associated with bare MCMA and vdW complexes with rare-gas atoms

	band position ^a ν/cm^{-1}	excess energy ^b $\Delta\nu/\text{cm}^{-1}$	τ_f/ns
bare	25 853(a)	0	16.7
	25 902(b)	49	12.4
	25 947(c)	94	8.3
	25 997(d)	144	4.7
	26 166(e)	313	< 3
	26 249(f)	396	< 3
Ar ($n = 1$)	25 784(a')	-69	19.6
	25 832(b')	-21	18.8
	25 879(c')	26	17.2
Ar (140 Torr)	27 200(6_0^1)	1350	(8.3, 20.1) ^c
	27 520($6_0^1 + 12_0^1$)	1670	(5.6, 18.5) ^c
Xe ($n = 1$)	25 703(a')	-150	21.6
	25 752(b')	-101	20.8
	25 801(c')	-52	20.5
	26 098(f')	245	10.3
	26 148(g')	295	6.6
	26 196(h')	343	5.4
Xe ($n = 2$)	25 649(a'')	-204	22.3
Xe (40 Torr)	27 080(6_0^1)	1230	(6.9, 23.6) ^c
	27 320($6_0^1 + 12_0^1$)	1470	(8.8, 25.2) ^c

^a The notations in parentheses correspond to the bands shown in Fig. 5 and 7. ^b Measured from the 0–0 band position of the bare molecule. ^c Fitted by the double exponential function.

The measurement of the fluorescence excitation spectra was carried out in neon mixed with argon and xenon under a continuous jet, with the aim of investigating the effect of complexation of argon and xenon atoms. Fluorescence excitation bands that could be attributed to Ar- and Xe-complexes of CMA were not observed; however, excitation bands attributed to 1:1 complexes with MCMA (MCMA-Ar₁ and MCMA-Xe₁) were easily detected in neon mixed with argon of 140 Torr and xenon of 40 Torr at longer wavelengths as compared with the bare MCMA (see Fig. 6 and 7). The red-shift of the electronic origin upon complexation is 69 cm⁻¹ for MCMA-Ar₁ and 150 cm⁻¹ for MCMA-Xe₁. The fluorescence lifetimes measured for several of the bands of MCMA-Ar₁ and MCMA-Xe₁ are longer than those corresponding to the bare MCMA molecule, as shown in Table 3. The fluorescence lifetime of 21.7 ns for the electronic origin of MCMA-Xe₁ is close to the natural radiative lifetime because the latter when measured in a supersonic jet is expected to be approximately two times larger than the 10.6 ns measured in solution (when the difference in the refractive index between solution and

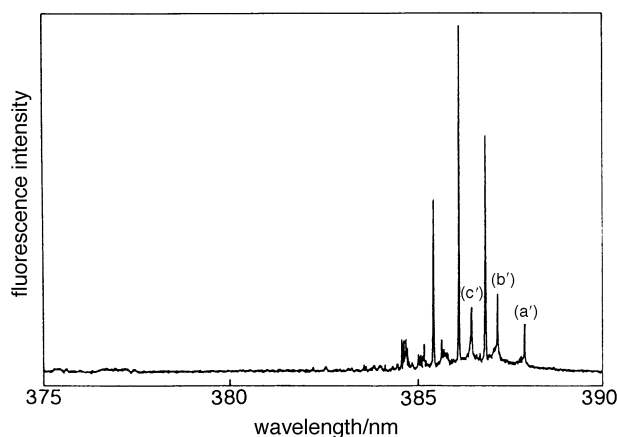


Fig. 6 Fluorescence excitation spectrum measured for MCMA seeded in a mixture of argon (140 Torr) and neon (420 Torr) under continuous jet conditions. The notation (a')–(c') for MCMA-Ar₁ represents bands associated with the bands marked in Fig. 5.

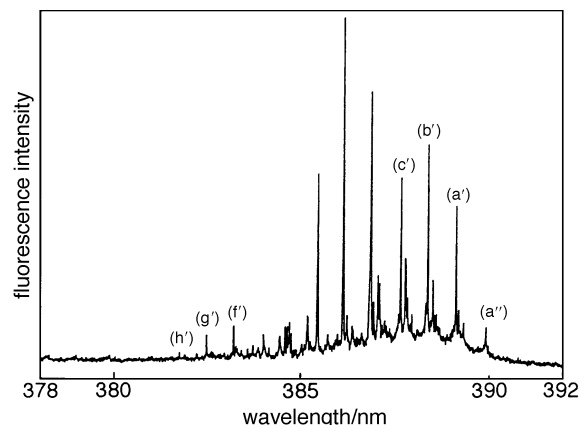


Fig. 7 Fluorescence excitation spectrum measured for MCMA seeded in a mixture of xenon (40 Torr) and neon (560 Torr) under continuous jet conditions. The notation (a')–(h') and (a'') for MCMA-Xe₁ and MCMA-Xe₂ represents bands associated with the bands marked in Fig. 5.

vacuum is taken into account).¹⁸ The band (a'') assigned to the electronic origin of MCMA-Xe₂ also has a long fluorescence lifetime (22.3 ns). A similar lengthening of the fluorescence lifetime by coordination of one Xe atom was observed for 9,10-dimethylanthracene.¹² The three bands (f'), (g'), (h') seen in the range 381.7–383.2 nm (Fig. 7), which correspond to the three bands (a'), (b'), (c') including the electronic origin, are associated with the 12₀¹ transition characteristic of anthracene compounds (refer to ref. 19 regarding vibrational assignments). Appearance of these bands indicates that the radiationless decay from the ν_{12} vibrational level is greatly suppressed by complexation of one Xe atom and, indeed, the fluorescence lifetimes of these bands are fairly long (as shown in Table 3). In contrast to MCMA-Xe₁, the 12₀¹ bands associated with MCMA-Ar₁ were not observed (see Fig. 6).

With increasing pressure of argon and xenon, the excitation bands associated with the Ar- and Xe-complexes of MCMA became broad and gradually red-shifted. In addition, new broad bands, attributed to the 6₀¹ and 6₀¹ + 12₀¹ vibronic bands of the Ar- and Xe-complexes, appeared over a range of short wavelengths from 360 to 375 nm, as can be seen in the two spectra in Fig. 8 measured at 500 Torr of argon and 200 Torr of xenon. The fluorescence decay curves measured for these

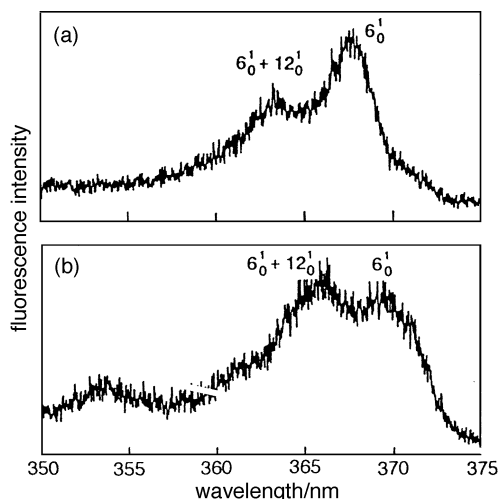


Fig. 8 Fluorescence excitation spectra measured in a region of short wavelengths for MCMA seeded in argon and xenon under continuous jet conditions. (a) Ar (500 Torr); (b) mixture of Xe (200 Torr) and Ne (250 Torr).

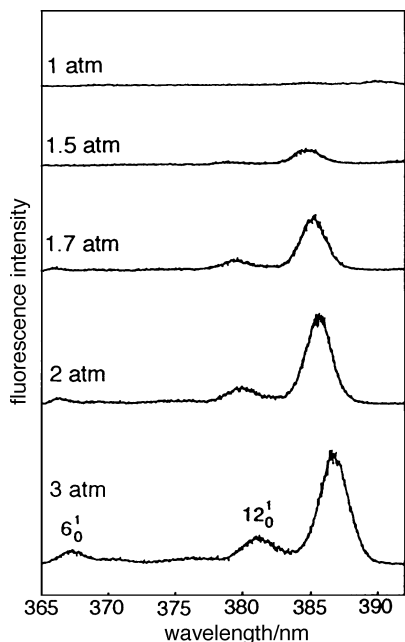


Fig. 9 Fluorescence excitation spectra measured for CMA seeded in krypton at different pressures of stagnation under pulsed-jet conditions

broad bands were fitted by the double exponential function with two long lifetimes as shown in Table 3. This result indicates that the coordination of several rare-gas atoms to MCMA greatly suppresses the radiationless decay from the ν_6 and $\nu_6 + \nu_{12}$ vibrational levels, which are located *ca.* 1400 and 1800 cm^{-1} above the electronic origin, respectively.

As described above, no excitation bands were observed for the complexes of CMA with Ar and Xe under the stagnation pressures used in the continuous jet. In order to obtain information about the larger rare-gas complexes of CMA, the measurement of fluorescence excitation spectra was carried out at

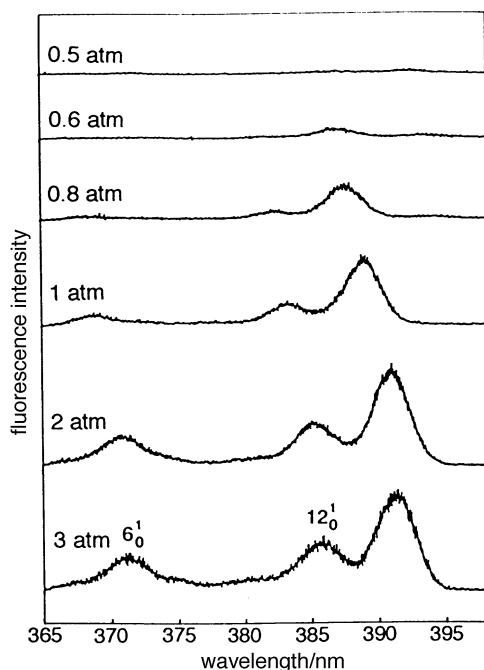


Fig. 10 Fluorescence excitation spectra measured for CMA seeded in xenon at different pressures of stagnation under pulsed-jet conditions

stagnation pressures up to 3 atm in a pulsed jet. When argon was used as the carrier gas, no excitation bands were observed. The spectra measured as a function of stagnation pressure of Kr and Xe are shown in Fig. 9 and 10. No excitation bands are seen at stagnation pressures lower than 1 atm for Kr and 0.5 atm for Xe. Above these pressures, three broad bands associated with the electronic origin, and with the 12_0^1 and 6_0^1 vibronic transitions appear at largely red-shifted wavelengths, and they grow and red-shift with increasing pressure. This observation indicates that the radiationless decay is greatly suppressed in large clusters of CMA with Kr and Xe. Indeed, the fluorescence lifetimes measured for these broad bands were in the range 13.9–21.0 ns for Kr-complexes and 17.3–24.2 ns for Xe-complexes, as shown in Table 2. A similar phenomenon associated with large clusters of Kr and Xe was observed for 9-methylanthracene, whose radiationless process is only ISC.¹³ However, there is a difference between CMA and 9-methylanthracene in that the excitation bands for the Ar-clusters of 9-methylanthracene were observed successively, and corresponded to the increase in coordination of the Ar atoms.

Discussion

Radiationless processes in solution

Two processes considered for the radiationless decay of CMA and MCMA are ISC and photodissociation. For most anthracene compounds, ISC is the transition from the S_1 state to the T_2 state located close to S_1 .²⁰ For *meso*-substituted anthracenes in solution, the S_1 state is located below the T_2 state and, hence, S_1 – T_2 ISC is a process for which thermal activation is required. Which of either ISC or photodissociation is the predominant process in solution? As described above, the A values (3.5 – $8.5 \times 10^{11} \text{ s}^{-1}$) obtained for CMA and MCMA in solution are two orders of magnitude larger than the A values reported for 9-methylanthracene ($4.0 \times 10^9 \text{ s}^{-1}$, $4.8 \times 10^9 \text{ s}^{-1}$)^{20,21} and 9,10-dimethylanthracene ($1.1 \times 10^9 \text{ s}^{-1}$)²¹ and they are also larger than the values for 9-chloroanthracene ($8.0 \times 10^{10} \text{ s}^{-1}$)²¹ and 9,10-dichloroanthracene ($1.7 \times 10^{11} \text{ s}^{-1}$)²¹ which are increased by enhancement of spin-orbit coupling due to a heavy-atom effect. By comparison with the A values of these compounds whose radiationless decay is caused only by ISC, the large A values obtained for CMA and MCMA suggest that the main radiationless process in solution is not ISC.

The E_a -values obtained also suggest that the T_2 state is not involved in the radiationless process, as stated below. The values of E_a reported for the S_1 – T_2 ISC are 710 and 770 cm^{-1} for 9-methylanthracene, 1550 cm^{-1} for 9,10-dimethylanthracene, 980 cm^{-1} for 9-chloroanthracene and 1570 cm^{-1} for 9,10-dichloroanthracene.^{20,21} These activation energies correspond approximately to the electronic energy gaps between S_1 and T_2 . As the lowering of the S_1 energy by substitution is larger than that of the T_2 energy, the S_1 – T_2 energy gap is large for anthracene derivatives having low S_1 energies. Therefore, the activation energies of 9,10-dimethyl- and 9,10-dichloro-anthracene are larger compared with those for 9-methyl- and 9-chloro-anthracene, corresponding to the red-shift of *ca.* 800 cm^{-1} in the absorption spectrum in going from the mono- to the di-substituted anthracenes. On the other hand, there is no significant difference seen between the E_a values obtained for CMA and MCMA, even though the S_1 energy of MCMA is lower than that of CMA by 610 cm^{-1} in 3-methylpentane and by 690 cm^{-1} in methylcyclohexane. Thus we arrived at the conclusion that the T_2 state does not participate in the main radiationless process in solution. On the basis of these considerations concerning the magnitudes of both A and E_a , it is also concluded that the radiationless process from the S_1 state of CMA and MCMA in solution is

predominantly photodissociation caused by a mechanism in which the T_2 state is not involved.

Radiationless processes in a supersonic free jet

CMA and MCMA molecules in the isolated state did not show any fluorescence at excess vibrational energies above 530 cm^{-1} and 400 cm^{-1} , respectively. The absence of fluorescence excitation bands is caused by fast radiationless decays at the corresponding vibrational levels. The appearance of three excitation bands associated with the 12_0^1 transition for MCMA-Xe₁, located at 396, 445 and 493 cm^{-1} above the electronic origin, suggests that the radiationless decay at these vibrational levels is significantly slower than those from higher vibrational levels; *i.e.*, the radiationless decay for a bare MCMA molecule is considered to be extremely fast at vibrational levels higher than *ca.* 500 cm^{-1} . The absence of fluorescence upon excitation above an excess energy of 790 cm^{-1} was shown previously for photoreactive 9-*tert*-butylanthracene.¹¹ The extremely fast radiationless decay for CMA and MCMA that occurs when excited with excess energy is thought to be associated with photodissociation rather than with ISC, when taking into account the results in solution. In that the photodissociation of the S_1 state is not a barrierless reaction but some energy is required, the attribution of radiationless decay at vibrational levels above the excess energies of *ca.* 530 cm^{-1} for CMA and *ca.* 500 cm^{-1} for MCMA to the photodissociation is consistent with the activation energies of $520\text{--}650\text{ cm}^{-1}$ obtained for the radiationless decay of these compounds in solution. Although the actual rate constants cannot be estimated for this fast radiationless process, the absence of fluorescence might reflect the large rate constants of $3.5\text{--}8.5 \times 10^{11}\text{ s}^{-1}$ obtained as a frequency factor for the radiationless decay in solution, attributed to photodissociation.

With regard to the excitation bands of the bare molecules that appear at the electronic origin and low excess energies, the radiationless processes at these vibrational levels are attributed to ISC involving the T_2 state, when the influence of the medium on the radiationless rate is taken into account. We first consider MCMA. The fluorescence lifetime of MCMA at the electronic origin is slightly shorter than a natural radiative lifetime and it is markedly decreased with a small increase of excess energy and, in addition, it is lengthened by coordination of Ar or Xe atoms. These features of fluorescence lifetimes resemble the results reported for 9,10-dimethylanthracene¹² and the previous interpretation based on the $S_1\text{--}T_2$ ISC can be used to understand the radiationless decays of MCMA. The S_1 electronic level of MCMA is elevated by 850 and 920 cm^{-1} upon a change of medium from 3-methylpentane and methylcyclohexane to the isolated state, respectively. Since the influence of medium on the T_2 energy is smaller compared with S_1 , the S_1 state is shifted toward a slightly higher level than the T_2 state by desolvation. Owing to this $S_1\text{--}T_2$ level inversion from $S_1 < T_2$ in solution to $S_1 > T_2$ in the isolated state, ISC at the electronic origin of the bare MCMA molecule is energetically allowed. This is in contrast to the absence of radiationless decay at 77 K in the condensed phase. The enhancement of the ISC rate caused by the increase in excess energy is remarkable such that the excitation to the 313 cm^{-1} band leads to a fluorescence lifetime significantly shorter than 3 ns.

The coordination of Ar or Xe atoms to the MCMA molecule reduces the ISC rates of the electronic origin and low vibronic levels. The long fluorescence lifetimes at the electronic origin for MCMA-Xe₁ and MCMA-Xe₂ are considered to represent the natural radiative lifetime. This suppression of ISC is attributed to the red-shift of S_1 to below T_2 caused by the coordination of Xe atoms. When Ar- and Xe-complexes are excited to vibronic levels, the vibrational

energy given initially to the MCMA moiety may be transferred to intermolecular vibrational modes between the MCMA and the rare-gas atoms, *i.e.*, vdW vibrational modes, resulting in a reduction of the vibrational energies in the MCMA moiety. The decrease of ISC rates for vibronic levels by complexation is thus caused by the transfer of vibrational energy to the vdW low frequency vibrational modes. In particular, the appearance of excitation bands associated with 12_0^1 upon complexation of one Xe atom and their largely lengthened fluorescence lifetimes (as seen in Fig. 7 and Table 3), represent a remarkable effect of vibrational energy transfer on the ISC rate. The corresponding bands for MCMA-Ar₁ did not appear, probably, because the amount of vibrational energy transferred in MCMA-Ar₁ is small compared with that for MCMA-Xe₁ owing to the reduction of red-shift and binding energy.²

In contrast to MCMA, an efficient radiationless decay occurs at the electronic origin of bare CMA molecules as shown by the fact that the fluorescence lifetimes are shorter than 3 ns. The $S_1\text{--}T_2$ ISC is energetically possible because the S_1 energy of CMA is higher by 723 cm^{-1} than that of MCMA, and the elevation of the S_1 state may result in the enhancement of ISC. This might be related to a shortening of the fluorescence lifetime of MCMA to less than 3 ns when excited to 313 cm^{-1} above the electronic origin. Since the 0-0 band and several subsequent bands are actually detected in the fluorescence excitation spectrum (with reasonable intensities), it is unlikely that the radiationless rate constants associated with these bands have large values (exceeding 10^{11} s^{-1}), which were obtained as the frequency factor for photodissociation in solution. When the predominant radiationless process for CMA at low excess energies, as deduced for MCMA, is attributed to $S_1\text{--}T_2$ ISC, the influence that clustering of rare-gas atoms has on the fluorescence excitation spectrum and on the fluorescence lifetime of CMA can be understood in terms of the $S_1\text{--}T_2$ level inversion.

The S_1 state is located higher above T_2 for CMA compared with MCMA and, hence, the red-shift required to lower the S_1 state of CMA below T_2 will be attained only by formation of large clusters of rare-gas atoms, as shown previously for 9-methylanthracene.¹³ The fluorescence excitation bands associated with Ar-clusters of CMA were not observed even if the stagnation pressure was raised up to 3 atm. The lowering of the S_1 energy is predicted to be *ca.* 500 cm^{-1} at 3 atm of argon gas from the result obtained for 9-methylanthracene.¹³ The absence of fluorescence from the Ar-clusters indicates that the S_1 state remains above T_2 and the $S_1\text{--}T_2$ ISC is an efficient radiationless process irrespective of the number of coordinated Ar atoms. For the Kr- and Xe-clusters the lowering of the S_1 energy is larger compared with the Ar-clusters owing to the increasing dispersion force of Kr- and Xe-atoms. As a result, the fluorescence excitation bands associated with the large Kr- and Xe-clusters formed at high stagnation pressures appear at largely red-shifted wavelengths, suggesting a suppression of $S_1\text{--}T_2$ ISC due to the shift of S_1 below T_2 . Indeed, the fluorescence lifetime of 24.2 ns measured for the electronic origin at 3 atm of xenon gas is as long as the natural radiative lifetime. The red-shifts obtained from the wavelength at the peak of the broad band are 750 and 1050 cm^{-1} for Kr and Xe, respectively, at a stagnation pressure of 3 atm. Under these experimental conditions, the coordination number is considered to be no less than 20, on the basis of a previous study.¹⁶

Comparative consideration about radiationless processes in a supersonic free jet and solution

The energy diagrams concerning the electronic states involved in the radiationless processes are shown in Fig. 11. Under the above consideration, the photodissociation process for CMA

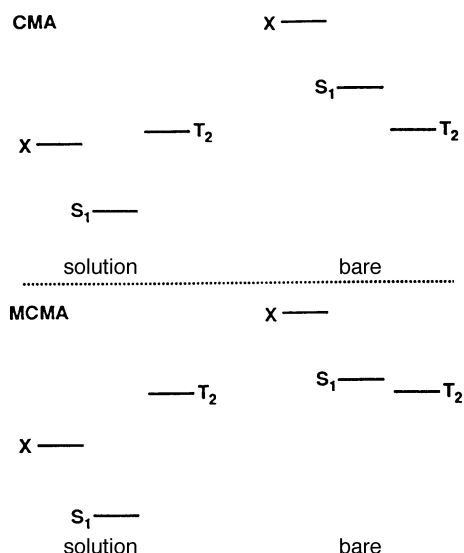


Fig. 11 Energy diagrams for electronic states associated with radiationless processes. The state leading to photodissociation is represented by X.

and MCMA occurs through an intermediate state other than the T_2 state (we call this state X). The gap in the electronic energy between X and S_1 is *ca.* $500\text{--}650\text{ cm}^{-1}$, and it is approximately the same for CMA and MCMA and it is not significantly influenced by the variation of medium. On the other hand, the energy gap between S_1 and T_2 depends strongly on both compound and medium.

The predominant radiationless process in solution is photodissociation, which is not competitive with $S_1\text{--}T_2$ ISC owing to the smaller frequency factors for CMA and MCMA, and the larger activation energies for MCMA, than those for photodissociation.

Bare CMA and MCMA molecules excited to vibrational levels higher in energy than the X state undergo fast photodissociation. The radiationless process for bare molecules excited to vibrational levels lower in energy than the X state is $S_1\text{--}T_2$ ISC under the condition of $S_1 > T_2$.

The S_1 state of MCMA is shifted below T_2 by coordination of a small number of rare-gas atoms, and a similar shift for CMA is attained by coordination of a large number of Kr or Xe atoms. The ISC at the vibrationless state for these complexes under the condition of $S_1 < T_2$ is suppressed, being analogous to the case in solution at 77 K.

When a parent molecule in a vdW complex is excited to vibrational levels higher than the binding energy of the complex, the intramolecular vibrational energy of the parent molecule is largely reduced by vibrational predissociation.⁶ The binding energies of 1:1 complexes between anthracene and rare-gas atoms in the S_0 state are estimated to be 519 , 612 and 753 cm^{-1} for Ar, Kr and Xe, respectively.² Adding the values of the red-shift to these values,^{2,22} the binding energies in the S_1 state are tentatively estimated to be 590 cm^{-1} for MCMA-Ar₁ and 900 cm^{-1} for MCMA-Xe₁. When the number of coordinated rare-gas atoms is increased, the vibrational energy transfer will become more efficient and then vibrational predissociation occurs before the radiationless decay in the parent molecule. For complexes of MCMA, which are probably coordinated with several Ar or Xe atoms (Fig. 8), the fluorescence lifetimes of the 6_0^1 and $6_0^1 + 12_0^1$ bands are as long as those measured for bare MCMA molecules having low excess energies ($0\text{--}100\text{ cm}^{-1}$). This indicates that most of the excess energy of *ca.* 1400 cm^{-1} (6_0^1) and *ca.* 1800

cm^{-1} ($6_0^1 + 12_0^1$) given to the MCMA moiety is lost by releasing a rare-gas atom or atoms before the dissociation of the C-Cl bond in the MCMA molecule.

Since the radiationless rate for CMA is fast even at low vibrational levels (including the electronic origin), the influence of vibrational energy transfer is not observed for complexes of CMA until the S_1 state is lowered below T_2 by the formation of significantly large Kr- and Xe-clusters. The fluorescence lifetimes measured for the 12_0^1 and 6_0^1 bands of CMA at 3 atm of xenon are as long as *ca.* 24 ns, indicating that most of the excess vibrational energy *ca.* 400 cm^{-1} or *ca.* 1400 cm^{-1} given to the CMA molecule in the large Xe-clusters is lost by the vibrational energy transfer.

Conclusions

For the photodissociation of CMA and MCMA, the activation energies in solution are almost consistent with the excess vibrational energies required for the reaction of the bare molecules. The clustering of the rare-gas atoms suppresses the photodissociation through vibrational predissociation. The radiationless process at low vibrational levels for the bare molecules is $S_1\text{--}T_2$ ISC, and this process is suppressed when the S_1 state is shifted below the T_2 state by coordination of the rare-gas atoms.

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