Fluorescence Lifetimes of 9-Methylanthracene in Supersonic Free Jets. A Level Inversion between S_1 and T_2 States upon the Phase Change from Solution to Gas

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Synopsis. Fluorescence lifetimes measured for 9-methylanthracene in supersonic free jets confirm the occurrence of nonradiative decay at the vibrationless level of S_1 that has been suggested from the measurement of the fluorescence yield. The nonradiative decay constants in the isolated and condensed phases have been compared from the viewpoints of relative positions of S_1 and T_2 levels and of the magnitude of the energy gap.

The fluorescence quantum yield (Φ_f) and lifetime (τ_f) for 9-substituted anthracenes strongly depend on temperature and medium.[1-8] In solution this behavior has been explained in terms of the intersystem crossing (ISC) from S_1 to T_2 lying above S_1. A recent measurement in supersonic free jets[9] showed that Φ_f of 9-methylanthracene(9MA) at the vibrationless level of S_1 is only 0.57 although the molecule is supercooled, making a sharp contrast to a Φ_f-value of unity at 77 K in the condensed phase.[1] On the basis of the solvent and pressure effects on the ISC rate, Tanaka et al. have suggested that S_1 should lie above T_2 in the isolated state as predicted from a large blue shift of the 0-0 band.[10] The fluorescence behavior of other 9-substituted anthracenes in solution and vapor phases has been interpreted similarly in terms of a S_1-T_2 level inversion model.[11] In the present work, in order to confirm these suggestions, the fluorescence lifetimes of 9MA in supersonic free jets have been measured and the heavy atom effect in the rare gas clusters has been investigated as well, along with the additional lifetime measurements in solutions. The radiative and nonradiative decay constants (k_r and k_{nr}) in the isolated and condensed phases were estimated, and the values of k_{nr} were compared from the viewpoints of relative positions of S_1 and T_2 levels and of the magnitude of the energy gap.

Experimental

9MA purchased from Tokyo Kasei was purified by column chromatography. The apparatus and the measurement system for laser induced fluorescence studies of jet-cooled molecules at the Institute for Molecular Scienece were described previously.[12] 9MA heated to ca. 80 °C in a furnace was expanded into vacuum with a carrier gas through a 150 μm nozzle.

The fluorescence lifetime in solution was measured by a time-correlated single photon counting system at Kyoto Institute of Technology.[13] Solvents of a spectroscopic grade were used. The composition of EPA was 5:5:2 in volume for diethyl ether, isopentane, and ethyl alcohol. Sample solutions of 2.5×10^{-5} mol dm^{-3} were deaerated by freeze-pump-thaw cycles.

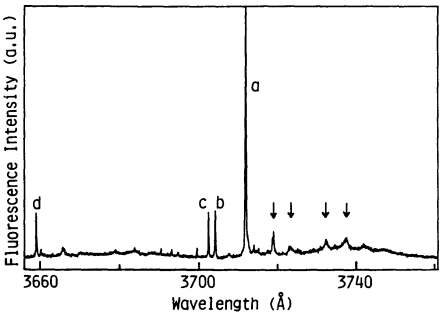

Fig. 1. The fluorescence excitation spectrum of 9MA expanded with 600 torr of Ar. The arrows indicate the Ar cluster bands of 9MA where the fluorescence lifetime was measured.

Table 1. Fluorescence Lifetimes for 9MA and Its Ar Clusters in Supersonic Free Jets

Bare 9MA		Ar Cluster	
Band position cm^{-1}	τ_f ns	Band position cm^{-1}	τ_f ns
26939 (a)	18.7	26891	11.6
26995 (b)	25.8	26859	13.2
27008 (c)	23.2	26797	13.3
27328 (b)	15.6	26758	14.3

Results and Discussion

The fluorescence excitation spectrum of 9MA expanded with 600 Torr (1 Torr=133.322 Pa) of Ar is shown in Fig. 1. The electronic origin band (a) of bare 9MA is located at 371.2 nm with a blue shift exceeding 1000 cm^{-1} from the corresponding transition in solution. The bare 9MA bands (a,b,c,d) are in good agreement with those reported by other investigators.[14,15] The Ar cluster bands on the longer-wavelength side of the origin band become prominent as the Ar pressure is increased.

Fluorescence lifetimes for the bare and cluster bands are listed in Table 1. τ_f for the 0-0 band is 18.7 ns while Zeweil et al. have obtained a value of 21 ns.[15] The vibronic bands b and c have longer lifetimes, and the vibronic band d has a shorter lifetime. Such an irregular change in the lifetime for 9MA, as well as for anthracene,[16] with an excess vibrational energy was observed in a wider range of excess energy.[15] The existence of longer lifetimes of 25.8 and 23.3 ns for b and c bands indicates that the lifetime of 18.7 ns for the 0-0 band contains the contribution from a nonradiative decay process besides radiative one. Sonnenschein et al.

Table 2. Radiative and Nonradiative Decay Constants for the S_1 Electronic Origin of Jet-Cooled 9MA and the Solution Values

Medium	temp °C	λ_{0-0}[a] nm	Φ_f	τ_f ns	k_r $\times10^7\,s^{-1}$	$k_r\cdot(1/n^2)$ $\times10^7\,s^{-1}$	k_{nr} $\times10^7\,s^{-1}$
Isolated		371.2	0.57[b]	18.7[c]	3.1		2.3
Pentane[d]	22	385.0	0.24	3.69	6.5	3.5	21
Hexane	R.T.[g]	385.6	0.29[e]	4.25[c]	6.8	3.6	17
Methylcyclohexane	R.T.	386.7	0.33[e]	5.20[c]	6.3	3.1	13
Toluene	R.T.	389.4	0.71[e]	9.20[c]	7.7	3.4	3.2
EPA	−196		1[f]	13.0[c]	7.7		≈0

a) Values from the absorption spectra. b) Ref. 9. c) Present work. d) Ref. 7. e) Ref. 5. f) Ref. 1. g) 20—25 °C.

obtained a value of Φ_f=0.57 for the 0-0 band of jet-cooled 9MA.[9] The present lifetime data are consistent with their result, concerning the occurrence of nonradiative decay from the vibrationless level of S_1. The radiative and nonradiative decay constants in solution and in free jet are compared in Table 2. Although the radiative decay constant for the jet-molecule is fairly smaller than that in solution, these values become comparable, after correcting for the refractive index, i.e. multiplying by $1/n^2$.[17]

The nonradiative decay route is the ISC from S_1 to T_2. In solution k_{nr} decreases as the S_1 energy is lowered from pentane to toluene since the S_1–T_2 energy gap increases when $S_1<T_2$.[5,10] The long lifetime in EPA at 77 K reflects only a radiative decay constant as indicated by the fluorescence quantum yield of unity at this temperature.[1]

Since an apparent activation energy of ca. 800 cm^{-1} has been obtained from the temperature dependence of k_{nr} in pentane and the S_1–T_2 gap has been estimated to be ca. 400 cm^{-1} by considering the shift of S_1 due to the temperature dependence of a dielectric constant,[7] the blue shift of ca. 1000 cm^{-1} in going from pentane solution to the isolated state probably results in the elevation of the S_1 energy above the T_2 level. This S_1–T_2 level inversion will enable energetically the ISC to occur in the isolated 9MA even though 9MA is supercooled.

Another evidence for the level inversion is provided by the fluorescence behavior of the rare gas clusters of 9MA. The fluorescence lifetimes at the Ar cluster bands are shorter compared with the value at the vibrationless bare band. If the vibrationless level of S_1 of bare 9MA lies below T_2, this result can not be understood since the lowering of the S_1 energy level by cluster formation will leave the ISC channel closed. Furthermore, when Kr or Xe was used as a carrier gas, no cluster bands were observed. This finding does not necessarily mean that no clusters are formed. On the contrary, it is reasonable to consider that Kr and Xe clusters are formed but their fluorescence intensities are very low since the ISC rates are extremely raised. In fact, as the pressure of Kr or Xe increases the 0-0 band intensity of the bare 9MA decreases significantly, indicating the formation of 9MA-Kr or Xe atom van der waals clusters which exhibit very short-lived excited states. These observations on the clusters of 9MA contrast with the case of 9-cyanoanthracene (9CNA).[12] For 9CNA its cluster bands with Ar, Kr, and Xe were detected and those lifetimes were almost identical with that (28 ns) of the vibrationless bare band, indicating the absence of the heavy-atom effect. In a supersonic free jet the fluorescence yield at the vibrationless level of bare 9CNA was found to be unity.[9] These results for 9CNA indicate that the ISC from S_1 to T_2 is energetically prohibited since $S_1<T_2$, and hence the heavy-atom effect was not observed. Conversely, for 9MA where the ISC route is open in the isolated state ($S_1>T_2$), the heavy-atom effect by Kr or Xe enhances the ISC rate remarkably. The shortened lifetime for the Ar clusters of 9MA may be ascribed to the change in the Franck-Condon factor between S_1 and T_2 caused by the decrease in the S_1–T_2 energy gap under the condition of $S_1>T_2$ because the heavy-atom effect by Ar, if any, seems to be insignificant.[18]

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