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The Fluorescence Lifetimes of Jet-cooled Alkylnaphthalenes

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Synopsis. The measured fluorescence lifetime of the origin of jet-cooled 1-methylnaphthalene is close to that of naphthalene, whereas the corresponding lifetimes of the 2-substituted are longer. The fluorescence lifetime decreased with increasing excitation energy; this can be attributed to an increase in the rate of intersystem crossing with vibrational excitation.

Supersonic free jet experiments have been extensively applied to investigate the spectroscopic and molecular dynamical aspects of various size molecules. The supersonic molecular beam prepares isolated gas molecules of low internal temperature, which makes feasible the study of the dynamical behaviour of state selected single vibronic level.

The naphthalene molecule in jet-cooled conditions has recently been investigated by Smalley *et al.*[1] and Rice's group.[2] Many vibronic bands up to about 4000 cm^{-1} from the origin are assigned and intramolecular vibrational relaxation processes have an onset at about 2500 cm^{-1} above the origin. Measurements of fluorescence lifetime and quantum yield led to the radiationless decay rate and the radiationless process is postulated to be intersystem crossing to triplet manifolds, a similar process to that of benzene.

On the other hand, naphthalene derivatives have not been studied well in the jet. Very recently Small's group[3] has observed laser induced fluorescence of jet-cooled 1-methyl- and 2-methylnaphthalene derivatives. They suggested that in the first excited singlet state of 2-methylnaphthalene symmetry reduction-vibronically induced mode mixing should occur.

A previous paper[4] has demonstrated jet-cooled fluorescence excitation spectra associated with 1-methyl-, 2-methyl- and 2-ethylnaphthalene derivatives by monochromatized xenon lamp irradiation. In this paper fluorescence lifetimes were first measured for the origin bands and vibronic bands up to excess vibrational energy of 700 cm^{-1} to study substitution effect on radiative and nonradiative transitions in jet-cooled alkylnaphthalenes.

Experimental

The supersonic free-jet apparatus used in this experiment has been described elsewhere,[5] therefore only a brief description is given here.

The free-jet portion of the apparatus consists of a 50 cm diameter vacuum chamber, through one side of which is inserted a continuously operated supersonic nozzle. A large slit nozzle, 4 mm long and 380 µm wide, was used for these experiments. Back ground pressure in the expansion chamber was maintained in the region of 10^{-3} Torr (1 Torr= 133.322 Pa) by evacuation with a vapour booster (pumping speed 4000 l s^{-1}) backed by a rotary pump. The expansion mixture is argon, at a typical stagnation pressure of 50 Torr. Naphthalene derivatives were seeded into the argon by placing a sample tube heated at 75 °C in the argon feed line to the nozzle, giving a concentration of 2—4 mole%.

Fluorescence excitation spectra were measured by crossing the free jet at 90° with the light of a 450 W Xe lamp, dispersed by a 1 m monochromator with resolution 10 cm^{-1} FWHM. The excitation beam was mildly focused and crossed the jet 5 mm downstream from the slit nozzle. The crossing position is varied by the movement of a lens. Fluorescence was collected, at right angles to the free jet and the excitation beam, by an f/1 lens and focussed *via* a band pass filter (340±20 nm), onto a photomultiplier tube. The signal from the photomultiplier was processed by the photon counting technique. The fluorescence excitation spectrum was corrected for the spectral intensity distribution of the xenon lamp.

Fluorescence lifetimes were determined for each peak of the excitation spectra by the time correlated single photon counting techniques. The excitation source used was the frequency doubled output of a cavity dumped dye laser synchronously pumped by a mode-locked argon ion laser with resolution 3 cm^{-1} FWHM.

Samples of 1-methyl-, 2-methyl-, and 2-ethylnaphthalene were obtained from Aldrich and used without further purification. Stated purities of these samples ranged from 95% to 99%.

Results and Discussion

The positions of the observed origins for π-π^* electronic transitions of 1-methyl-, 2-methyl-, and 2-ethylnaphthalene are 31773, 31705, and 31749 cm^{-1}, respectively.[4] Relative frequencies of some vibronic bands <1000 cm^{-1} are listed in Table 1, together with frequencies and assignments of pertinent naphthalene transitions. Assignments of these naphthalene derivatives are tentative since we do not have reliable information on the vibrational structures of the methyl- and ethylnaphthalene molecules. The prominent Herzberg-Teller origin band 8 ($^1b_{1g}$) at 437 cm^{-1} for naphthalene[1,2] was observed at 422 cm^{-1} in the 1-methylnaphthalene spectrum with slight shift; for the 2-methyl and 2-ethyl derivatives only very weak features were observed at 429 and 421 cm^{-1}, respectively, which are tentatively assigned as the band. Assignments for 1-methylnaphthalene in Table 1 is based on the assumption that relative intensity of the vibronic bands are similar to that of naphthalene. For 2-methyl- and 2-ethylnaphthalene derivatives the frequency change of these vibronic bands is assumed to be small and hence similar to the frequency of 1-methylnaphthalene vibronic bands though relative intensity of the vibronic bands are drastically changed due to mode-mixing.[3,4] The fact that replacement of the 2-methyl group with an ethyl group produces only a minor change in the excitation spectrum is in agreement with the observations of Hopkins *et al.*[6] for jet-cooled alkylbenzenes.

TABLE 1. RELATIVE FREQUENCIES OF S_0—S_1 ABSORPTION BANDS AND FLUORESCENCE LIFETIMES FOR EXCITATION INTO THESE BANDS

Naphthalene[a)]			1-Methyl-Naphthalene		2-Methyl-Naphthalene		2-Ethyl-Naphthalene	
Assignment[b)]	$\Delta\nu$/cm^{-1}	τ/ns	$\Delta\nu$/cm^{-1}	τ/ns	$\Delta\nu$/cm^{-1}	τ/ns	$\Delta\nu$/cm^{-1}	τ/ns
	0	299	0	305	0	324	0	364
	—	—	77	324	173	190	35	315
	—	—	—	—	388	235	389	304
$8(b_{1g})^1$	437	317	422	281	429	222	421	259
	—	—	—	—	—	—	450	259
$2(b_{2g})^1$	485	120	485	—	482	194	482	219
	—	—	669	—	—	—	—	—
$8(b_{1g})^1 4(a_u)^2$	686	300	690	—	686	196	—	—
$8(a_g)^1$	704	309	—	—	719	187	720	—
	—	—	—	—	780	—	—	—
	—	—	822	—	819	—	—	—
	—	—	—	—	872	—	—	—
$7(b_{1g})^1$	911	262	910	—	—	—	—	—
	—	—	—	—	923	—	—	—
	—	—	—	—	—	—	938	—
$7(a_g)^1$	989	290	979	—	977	—	974	—

a) Reproduced from Ref. 2). b) Assignments for alkylnaphthalenes are tentative.

The results of fluorescence lifetime measurements are also shown in Table 1. The fluorescence lifetime of the origin of 1-methylnaphthalene is close to that of naphthalene, whereas the corresponding lifetimes of the 2-substituted are longer. The increase in transition moment of the origin resulting from alkyl substitution is accompanied by an increase in the radiative decay rate of S_1. The observed decrease in the fluorescence decay rate must therefore be due to a decrease in the rate of intersystem crossing in the alkyl substituted naphthalenes. Nonradiative transition in 0-0 bands of the alkylnaphthalenes can not be internal conversion in analogy to naphthalene[2)] though the frequency of these 0-0 bands is slightly red-shifted ($\approx$300 cm^{-1}) compared with that of naphthalene.

Reiser and Wright[7)] have theoretically predicted that the radiative decay rate increases by a factor of $\approx$2 for 1-methylnaphthalene and $\approx$3 for 2-methylnaphthalene, relative to naphthalene. They have shown these values to be consistent with radiative lifetimes measured in solution. Behlen and Rice[2)] have estimated the rate coefficient for radiative decay (k_r) of the S_1 origin of jet-cooled naphthalene to be 9.4×10^5 s^{-1}, and that for intersystem crossing (k_{isc}) to be 2.4×10^6 s^{-1}. On this basis the following values can be predicted: $k_r\approx2\times10^6$ s^{-1}, $k_{isc}\approx1\times10^6$ s^{-1} for the origin of jet-cooled 1-methylnaphthalene and $k_r\approx3\times10^6$ s^{-1}, $k_{isc}\approx1\times10^5$ s^{-1} for 2-methylnaphthalene. The implication is thus that 2-methyl substitution leads to an order of magnitude decrease in the rate of intersystem crossing from the origin level, giving a fluorescence quantum yield of $\approx$1. The effect of 2-ethyl substitution is expected to be similar, and the measured fluorescence lifetime indicates the upper limit for k_r to be 3×10^6 s^{-1} in this case.

For both of the 2-substituted naphthalenes studied, the fluorescence lifetime decreases with increasing excitation energy; this can be attributed to be an increase in the rate of intersystem crossing with vibrational excitation. The marked dependence of decay rate on population of particular vibrational modes which was observed in naphthalene[2)] (*e.g.* the sharp increase in k_{isc} on population of the $2(b_{2g})$ mode) was not observed for the 2-substituted molecules, presumably as a result of the mode-mixing which is induced by alkyl substitution.

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