Radiative lifetime and electronic relaxation of 9-cyanoanthracene in rare-gas clusters and in rare-gas matrices

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Laser-induced fluorescence (LIF) excitation spectra and fluorescence lifetimes were measured for rare-gas (Ar, Kr and Xe) clusters of 9-cyanoanthracene (9CNA) generated in supersonic free jets and for 9CNA isolated in rare-gas matrices at 15 K. The natural radiative lifetime, τ_r, of the 9CNA clusters was not influenced greatly by complexation with rare-gas atoms of any kind. The values obtained for the most highly coordinated clusters were 26.5 ± 0.3, 28.2 ± 0.6 and 28.4 ± 0.3 ns for Ar, Kr and Xe, respectively. These values are approximately equal to the value for τ_r at the electronic band origin of the bare 9CNA molecule, but are almost two times larger than the radiative lifetimes of 9CNA found in the rare-gas matrices at 15 K, in which the radiative lifetimes measured are correlated satisfactorily through the square of the refractive index. Nevertheless, the relaxation process from higher vibronic levels as well as the spectral band positions of these clusters are similar to those found in the rare-gas matrices.

1. Introduction

The clarification of the effect of microscopic molecular environments on the dynamics of electronically excited molecules may be accomplished by comparing the dynamics in supersonic free jets with those in homogeneous condensed phases [1-3]. As one such approach it is interesting to quantify the effect of medium and/or coordinated molecules on the natural radiative lifetime, τ_r, of a given photoexcited molecule [4]. It has been established experimentally that the value of τ_r for a given anthracene derivative in vacuum is approximately two times larger than that of the same molecule in the condensed phase [5]. More specifically, the rate constant of the natural radiative process, τ_r^{-1}, is found to be proportional to the square of the refractive in-

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dex [6-9]. The values of τ_r for 9,10-dichloroanthracene (DCLA) coordinated with a number of Ar atoms in supersonic free jets were measured recently by Penner et al. [10]. However, the values of τ_r for large clusters reported by these authors are larger than the value for the bare molecule in the electronic origin and do not appear to show a smooth transition toward the value for τ_r in solution. This implies that the nature of the molecular environment provided by an ensemble of coordinated Ar atoms is still very different from that in the condensed phase.

In this paper we report the values for τ_r and discuss the relaxation process from the vibronic levels of super-cooled rare-gas (Ar, Kr and Xe) van der Waals (vdW) clusters of 9-cyanoanthracene (9CNA), as well as 9CNA isolated in the rare-gas matrices at 15 K. 9-cyanoanthracene was chosen for this work because the fluorescence quantum yield, ϕ_f, of the 0-0 band of the super-cooled bare 9CNA molecule is reported to be unity [11,12] and, hence,

the fluorescence lifetime, τ_f, of this band can be regarded as equal to τ_r. This will also be the case in matrices at low temperatures [5]. In addition, the values of τ_f obtained for single vibronic levels of 9CNA exhibits an excess energy dependence [13,14] which is expected to be influenced by complexation with the rare-gas atoms. Thus it was anticipated that 9CNA would provide a suitable system for which to examine the effect of microscopic molecular environments on the relaxation of excess excitation energy [2,15].

2. Experimental

The bare 9CNA molecule and its vdW complexes were prepared by supersonic expansion of gases into a vacuum. The chamber was evacuated by using a Urneva 4000 10-inch diffusion pump (pumping speed 4000 dm^3 s^{-1}) backed by an Ulvac D-650 rotary pump. The beam source was a furnace with a pulsed nozzle (automobile fuel injector) having an aperture of 130 μm diameter. The pulse width during which the nozzle was open was about 1 ms and the repetition rate of 50 Hz. The beam source was heated to 130°C. The rare-gas backing pressure was approximately 2280 Torr. A Lambda Physik EMG MSC 104+FL3002 excimer-pumped dye laser (QUI or PBBO in dioxane) was used as the excitation source. The laser pulse was synchronized with the electric pulse used to drive the nozzle, and its timing with the pulsed 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 rare-gas matrices were prepared by depositing a gaseous mixture of a rare-gas and 9CNA onto the cold surface of a copper plate (2 cm in diameter) of a home-built cryostat installed in the same vacuum chamber as that used for the supersonic free expansion. The copper plate was cooled to 15 K by flowing liquid helium into the cryostat. The temperature of the plate was monitored using a thermocouple (Chromel versus Au+0.07 at% Fe). The same beam source as used for the supersonic expansion was used for the deposition. In this case the nozzle was opened for about 2 ms at a repetition rate of 10 Hz. The furnace was heated to 70°C and the rare-gas backing pressure was approximately 1200 Torr. The tip of the nozzle was 3 cm away form the cold plate and the sample was deposited over a period of 50 min.

Details of the fluorescence emission detection and nanosecond fluorescence lifetime measurement systems are given in a previous paper [12]. The laser-induced fluorescence (LIF) excitation spectra were not corrected for laser intensity. 9-cyanoanthracene (Aldrich Chemical Co. Inc.) was purified by recrystallization from acetic acid. The rare gases (Nihon Sanso Co. Lot.) were used as received.

3. Results and discussion

3.1. Rare-gas clusters of 9CNA

The LIF excitation spectra of the bare 9CNA molecule and its rare-gas (X) vdW clusters ($9CNA:X_m$) were measured and some of the results for the Ar clusters (X=Ar) are presented in fig. 1. When the laser excitation pulse (pulse width ≈ 7 ns at fwhm) was delayed with respect to the pulse of the supersonic free jet (electronic pulse width=1.2 ms) by delay times ranging from 1.2 to 1.5 ms, the LIF excitation spectra changed dramatically as shown in fig. 1. The spectrum of the bare 9CNA molecule was obtained as shown in fig. 1i by using the shortest delay time. Band (a) in fig. 1i is assigned to the 0-0 band (26173 cm^{-1}) of bare 9CNA [11]. The bands (c), (d), (e), (f) and (g) are ascribed to the transitions of 12^1_0, 11^1_0, 12^2_0, 8^1_0 and 6^1_0, respectively [13,16]. The LIF excitation spectrum becomes dominated by bands associated with the vdW clusters as the delay time is increased. Based on the order of appearance [1], most of the new bands located to the red of the electronic origin of the bare 9CNA can be assigned to one of the Ar clusters ($m \leq 14$) (see figs. 1ii–1v). The clusters having coordination numbers, m, ranging from 1 to 8 are labeled in fig. 1iii. The LIF excitation spectrum shown in fig. 1viii was recorded using a delay time of 1.5 ms. The observed LIF spectrum did not change in shape when delay times longer than 1.5 ms were used. Therefore, fig. 1viii can be regarded as the LIF excitation spectrum of the most highly coordinated $9CNA:Ar_m$ cluster generated for the experimental conditions used in this work. Although the coordination number, m, is not known
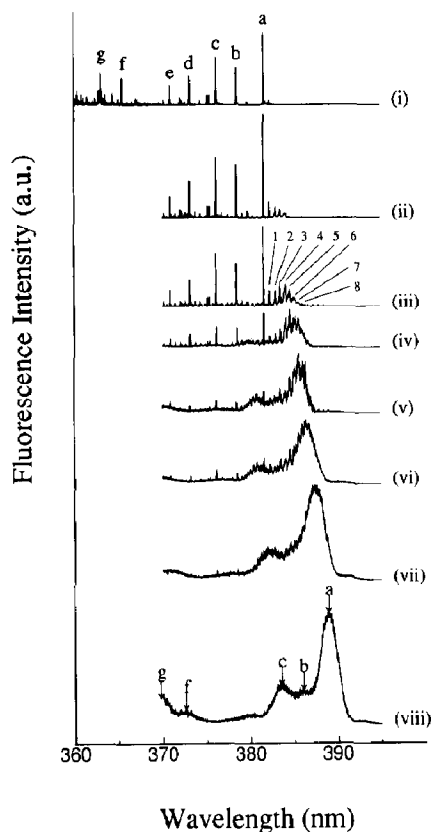
Fig. 1. LIF excitation spectra of the Ar clusters of 9CNA. The fluorescence emission was monitored at 414 nm (band pass 7 nm). The top (i) and bottom (viii) spectra are those recorded for the bare 9CNA molecule and the most highly coordinated cluster ($m > 20$), respectively. The positions of the bands labeled (a) to (g) are given in table 1.

precisely in this case, the value of m for this cluster is estimated to be not less than 20 by extrapolation of the relationship between m and the values for the red-shift of the 0–0 bands [2] measured for the smaller 9CNA:Ar_m ($m \leqslant 14$) clusters. The bands labeled from (a) to (c) and bands (f) and (g) in fig. 1viii correspond to the same vibronic transitions as for the bare 9CNA molecule, the positions of which are listed in table 1. The 0–0 band (band (a) in fig. 1viii) of the most highly coordinated Ar cluster is assigned tentatively to the band peak at 25678 cm^{-1}. Similar results were obtained for Kr and Xe clusters and the values of m for the most highly coordinated Kr and Xe clusters generated in this work are also estimated to be larger than 20. The procedure used in this work for the generation of large clusters dis-

penses with the necessity of employing backing pressures of a few tens atmosphere [10].

In contrast to the fluorescence spectra of the bare 9CNA molecule, which are strongly dependent on the excitation wavelength [13,14], the shape of the fluorescence spectrum of the most highly coordinated clusters is independent of excitation energy within the spectral resolution of 1 nm. This can be seen from fig. 2 in which the dispersed fluorescence spectra measured by excitation at bands (a) (25678 cm^{-1}) and (c) (26012 cm^{-1}) shown in fig. 1viii are compared.

The LIF excitation spectrum of 9CNA isolated in an Ar matrix at 15 K is shown in fig. 3. This spectrum was recorded by monitoring the fluorescence emission at 415.6 nm (band pass 0.1 nm). The 0–0 band (band (a)) for 9CNA in the Ar matrix is located at 25469 cm^{-1}. The vibrational bands labeled from (a) to (c) and from (f) to (i) correspond to those of the bare 9CNA molecule, the wavelengths of which are listed in table 1.

The values of τ_f for the main vibronic bands that are located within an excess energy of 1730 cm^{-1} are summarized in table 1 for the Ar clusters ($m > 20$) and 9CNA in the Ar matrix, together with relevant data for the bare 9CNA molecule adapted from ref. [13]. The dependence of the value of τ_f for the bare 9CNA molecule on the excess energy above the electronic origin, as is found for most anthracene derivatives, is seen from the data presented in table 1 [15]. On the other hand, the value of τ_f for the most highly coordinated 9CNA:$Ar_{m>20}$ cluster and 9CNA isolated in the Ar matrix does not show any excess energy dependence. These results, combined with the excitation energy insensitivity of the fluorescence emission spectra shown in fig. 2, indicate that the redistribution of excess excitation energy in those molecular environments which are provided by more than twenty coordinated rare-gas atoms takes place as rapidly as in the condensed phase. This result suggests that the vibrational relaxation of the excess excitation energy in S_1 of 9CNA coordinated with 20–30 rare-gas atoms, which is sufficient to form the first coordination shell when most closely packed, is already similar to that in condensed phase.

The values of τ_f measured for 9CNA:$Ar_{m=1,2}$ by excitation at the vdW bands associated with band (b) of the bare 9CNA molecule are 14.9 ns and 14.8

Table 1
Vibronic band positions and fluorescence lifetimes of the bare 9CNA, the Ar cluster ($m > 20$) and 9CNA isolated in an Ar matrix

Band (normal mode)	Bare 9CNA [a]			9CNA:Ar$_{m>20}$ cluster			9CNA in Ar matrix		
	$\bar{\nu}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	τ_f (ns)	$\bar{\nu}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	τ_f (ns)	$\bar{\nu}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	τ_f (ns)
a (0_0^0)	26173	0	28.0±0.2	25678	0	26.5±0.3	25469	0	16.2±0.1
b	26387	214	25.2±0.1	– [b]		– [c]	25693	224	16.5±0.1
c (12_0^1)	26549	376	27.3±0.1	26012	334	26.7±0.3	25857	388	16.2±0.1
d (11_0^1)	26766	593	25.5±0.2						
e (12_0^2)	26924	751	23.1±0.1						
f (8_0^1 or 7_0^1)	27332	1159	11.5±0.1	– [b]		– [c]	26639	1170	16.0±0.1
g (6_0^1)	27540	1367	11.2±0.1	26995	1317	26.0±0.2	26838	1369	16.2±0.1
h	27748	1575	5.0±0.1				27065	1596	14.8±0.1
i ($12_0^1 + 6_0^1$)	27903	1730	4.4±0.1				27218	1749	15.9±0.1

[a] Ref. [11]. Alphabetical labelling in this table is different from that in ref. [11].

[b] Bands are too broad to determine peak positions.

[c] Not measured.
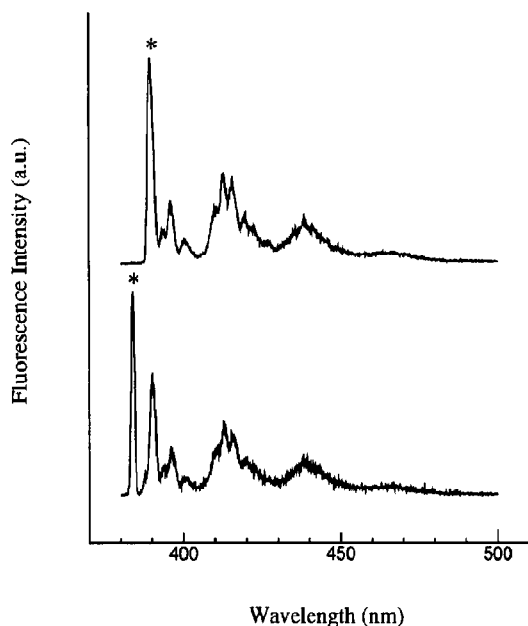
Fig. 2. Fluorescence spectra of the most highly coordinated 9CNA:Ar$_m$ cluster observed upon excitation at the band (a) (top figure) and band (c) (bottom figure) of fig. 1viii. The band positions of excitation are marked with an asterisk.

Fig. 3. LIF excitation spectrum of 9CNA isolated in an Ar matrix at 15 K. The positions of the bands labeled (a) to (i) are given in table 1.

ns for $m = 1$ and 2, respectively, and are much shorter than the corresponding value of 25.2 ns for bare 9CNA. Thus, complexation in this case appears to facilitate radiationless processes from the pumped vibronic levels [15]. When excited at the vdW band associated with band (g), however, the values for τ_f
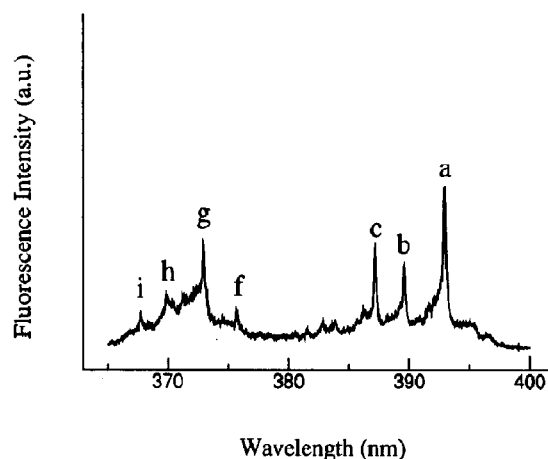
(18.9 ns for $m = 1$ and 23.4 ns for $m = 2$) are much larger than the corresponding value of 11.2 ns for the bare 9CNA molecule. This is presumably due to the photo-detachment of a coordinated Ar atom [17]. The excess energy at band (g) is 1367 cm^{-1}, which is large enough to break a vdW bond between 9CNA and an Ar atom [18]. Such a lengthening of the apparent fluorescence lifetime is always observed when vdW complexes dissociate upon photo-excitation [19,20] to yield a "parent molecule" or vdW complexes with very small or zero excess energy.

3.2. Radiative lifetime of 9CNA in rare-gas matrices

The values for the wavelength of the band origin for 9CNA in the rare-gas matrices and in the most highly coordinated clusters, together with the corresponding measured fluorescence lifetimes, are summarized in table 2. The fluorescence lifetimes measured for the matrices can be regarded as the radiative lifetimes of 9CNA in these matrices since the fluorescence quantum yield of 9CNA in solution is close to unity [5] and radiationless deactivation from S_1 will be negligible at very low temperatures [21]. The fluorescence quantum yield for the 0–0 band of the bare 9CNA molecule is reported to be unity [11]. In addition, complexation with Xe does not lead to any reduction in the value of τ_f, implying that the intersystem crossing process is not involved in the electronic relaxation from the electronic origin of 9CNA [12]. Consequently, the values for τ_f obtained for the band origins of the most highly coordinated clusters can also be considered to be equal to the radiative lifetime, τ_r. This is in accordance with the case for DCLA reported by Penner et al. [10]. However, in the case of anthracene the values of τ_f reported for the Ar clusters cannot be regarded as the radiative lifetime [22]. It is important, therefore, to distinguish between radiative and apparent fluorescence lifetimes when discussing the effect of molecular environment on fluorescence decay processes.

The fluorescence lifetimes measured for the electronic origins of the rare-gas clusters of $9CNA:X_{m<14}$ were all in the range of 25.7 to 31.7 ns. There is no distinct trend in the values of these fluorescence life-

times with increasing m. The values of τ_r ($=\tau_f$ in the present case) measured at the electronic origin for the most highly coordinated clusters, $9CNA:AR_{m>20}$, $9CNA:KR_{m>20}$ and $9CNA:XE_{m>20}$, given in table 2 are almost two times longer than those obtained for 9CNA isolated in Ar, Kr or Xe matrices. The 0–0 band positions of these clusters are comparable in energy to those in the corresponding matrices, with the magnitudes of the red-shift being 70.3%, 78.3% and 81.9% of those found in Ar, Kr and Xe matrices, respectively. However, the magnitude of the red-shift of the 0–0 band does not correspond to the variation in the values for τ_r. Furthermore, the variation in the values of τ_r for these clusters ($m>20$) does not correspond to the variation in the polarizabilities of the rare-gas atoms [10,23].

The reciprocal values for τ_r are plotted against the square of the refractive index, n^2, in fig. 4. The values of n for the Ar, Kr and Xe matrices are 1.28, 1.37 and 1.48, respectively [10]. The straight line shown in fig. 4 is the linear least-squares best-fit of eq. (1) to the data. The slope of this line is 3.55×10^{-2} ns^{-1}, which is very similar to the value of τ_r^{-1} for the bare 9CNA molecule.

$$\tau_r^{-1}(\text{condensed phase}) = n^2 \tau_r^{-1}(\text{bare}) . \qquad (1)$$

The radiative lifetime for 9CNA in methylcyclohexane is also shown in fig. 4 for comparison. It has already been shown for several anthracene deriva-
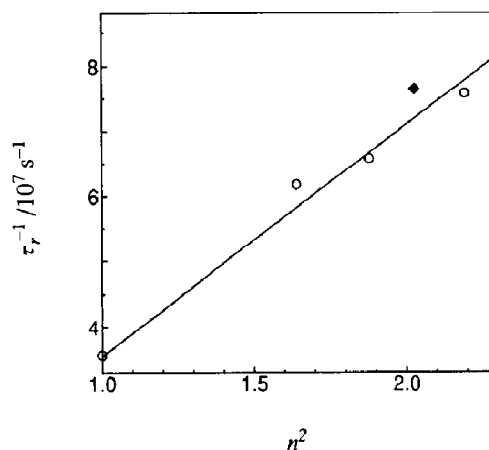
Table 2
Radiative lifetime of the rare-gas clusters of $9CNA:X_{m>20}$ and 9CNA isolated in the rare-gas matrices

Molecular state	$\bar{\nu}$ (cm^{-1})	τ_f (ns)
bare 9CNA	26173	28.0±0.2
$9CNA:Ar_{m>20}$ cluster	25678	26.5±0.3
9CNA in Ar matrix	25469	16.2±0.1
$9CNA:Kr_{m>20}$ cluster	25355	28.2±0.6
9CNA in Kr matrix	25128	15.2±0.1
$9CNA:Xe_{m>20}$ cluster	25060	28.4±0.3
9CNA in Xe matrix	24814	13.2±0.1

Fig. 4. Natural radiative rate constant (τ_r^{-1}) obtained for the rare-gas matrices and plotted as a function of the square of the refractive index, n^2. The radiative lifetime for 9CNA in methylcyclohexane (◆) is also shown for comparison.

tives that the values of τ_r for the bare molecules can be related to the values for τ_r in condensed phase by eq. (1) [5]. It is found in this work that eq. (1) is also a good description [24] of the radiative lifetime of 9CNA in the rare-gas matrices.

4. Summary

It is clear from a comparison of the values of τ_r for 9CNA in the clusters and matrices that the molecular environment which determines τ_r must be significantly larger than the first coordination shell of clusters. The probability of the emission of photons via the natural radiative process (τ_r^{-1}) is far less sensitive to the microscopic molecular environment around the fluorophore than the spectral red-shift or of the relaxation of excess excitation energy. From the results presented in this work it appears that a sheath of solvent molecules significantly larger than the first coordination shell around the fluorophore is required in order to quantify the effects of microscopic molecular environment on τ_r.

The refractive index, n, is a macroscopic quantity and cannot be defined for such small clusters as those examined in this work. The size of the cluster required for n to be defined is probably the order of a radiation wavelength in diameter [4] and, consequently, a substantial change in the radiative lifetime is expected to be observed only for clusters of comparable size. Further experiments using clusters with values of m much larger than twenty are required in order to create a phase in which τ_r assumes a value intermediate between those in the gas phase and condensed phase.

Acknowledgement

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