

Effects of clustering of rare-gas atoms on the rate of S_1-T_2 intersystem crossing for 9-methylanthracene

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Abstract

Laser induced fluorescence excitation spectra for 9-methylanthracene (MEA) in a supersonic free jet were measured as a function of the stagnation pressure of Ar, Kr and Xe, used as carrier gas. The 0–0 excitation bands for complexes of type $MEA \cdot Ar_n$ were observed successively corresponding to an increase in coordination number n with increasing stagnation pressure. On the other hand, excitation bands associated with small clusters of Kr and Xe were scarcely observed, although strong excitation bands associated with larger clusters were observed at largely red-shifted wavelengths. These observations combined with the measurement of fluorescence lifetimes were interpreted in terms of two effects of the clustering of rare-gas atoms on the intersystem crossing rate; energy shift of S_1 relative to T_2 and heavy atom effect.

1. Introduction

The technique of a supersonic free jet has provided new information on solvation through the formation of isolated molecules and clusters [1–3]. The effects of microscopic solvation on the electronic relaxation of excited molecules have been studied by this technique combined with a laser induced fluorescence method [1,4–8]. The coordination of solvent molecules to an excited parent molecule influences the electronic energy of the excited molecule and the migration of intramolecular and intermolecular vibrational energies. When heavy atoms such as Kr and Xe are used as the coordinating molecule, the intersystem crossing (ISC) rate is usually increased owing to the enhancement of spin–orbit coupling [1,5–7].

The dynamics of anthracene compounds in the first excited singlet state (S_1) under jet-conditions have been studied by several research groups [5–12]. One of our purposes is to clarify the effect of microscopic solvation on the ISC rate of anthracene compounds, with the intention of a systematic understanding about this somewhat complicated process depending on the environment from gas to solution. It is well known that ISC in anthracene compounds proceeds from S_1 to the second triplet state (T_2) located close to S_1 [13]. For some 9-substituted anthracenes including 9-methylanthracene (MEA), S_1 is shifted above T_2 in the bare state by desolvation [12], while S_1 is located below T_2 in solution. In a previous paper [14], we reported that the excitation bands associated with MEA–Kr or MEA–Xe clusters were not observed under experimental condi-

tions in which the size of clusters formed was small owing to the use of a continuous supersonic jet. This observation was attributed to the enhancement of ISC rate due to the heavy atom effect in the condition where the energy of S_1 was higher than that of T_2 and, hence, ISC was allowed energetically. In the present work the effect of large clusters of rare-gas atoms on the ISC rate was investigated by the use of a pulsed supersonic jet, and the obtained results enabled a more thorough understanding about the solvent effect on the rate of S_1 - T_2 ISC upon variation of the medium from the isolated state to clusters and to solution.

2. Experimental

MEA (Aldrich) was purified by column chromatography. Experimental details on the instrumentation are given in previous papers [15–17]. MEA was heated at ca. 70°C in a furnace with a pulsed nozzle of aperture 100 μm diameter and was expanded into a vacuum in a chamber with a carrier gas. The nozzle-opening width was about 1.2 ms and the repetition rate was 50 Hz. The chamber was evacuated by using a Urneva CDP-3700 10 inch 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, QUI in dioxane) was used as the excitation source. 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 of 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 spectral and decay measurements, respectively). In the measurement of excitation spectra the output signal integrated with a PAR Model 162 boxcar averager was transferred to a personal computer continuously against the scanned laser wavelength. The fluorescence intensities were not corrected for the laser intensity. The fluorescence decays were measured by recording and averaging the output signals from R928 with a Lecroy digital oscilloscope 7200. The fluorescence lifetimes were

calculated by the iterative least-squares convolution method.

3. Results and discussion

The fluorescence excitation spectra of MEA measured as a function of the stagnation pressure of Ar, Kr and Xe gases are shown in Figs. 1–3. In Fig. 1 the electronic origin of a bare MEA molecule is seen at 371.20 nm. The excitation band at 365.92 nm is assigned to the 12_0^1 vibronic transition common to anthracene compounds [11,18]. All the bands seen at wavelengths longer than the origin of a bare MEA molecule are attributed to complexes of MEA with Ar atoms. The formation of $\text{MEA} \cdot \text{Ar}_n$ complexes is observed in correspondence to a successive increase of n as the stagnation pressure of Ar gas is increased. At high stagnation pressures the excitation band becomes broad, reflecting the overlap of various clusters different in size and in structure. The other broad band seen at shorter wavelengths by ca. 5 nm than the broad band associated with the elec-

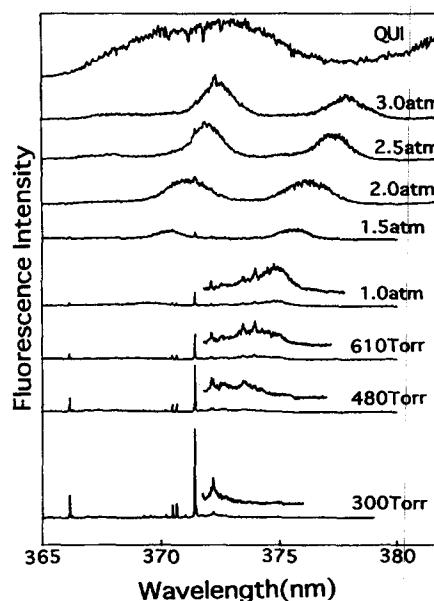


Fig. 1. Fluorescence excitation spectra of MEA seeded in Ar as a function of stagnation pressure. Parts of the spectra are expanded. QUI represents the variation of laser intensity with wavelength. The electronic origin for a bare MEA molecule appears at 371.20 nm as a sharp and intense peak at low stagnation pressures.

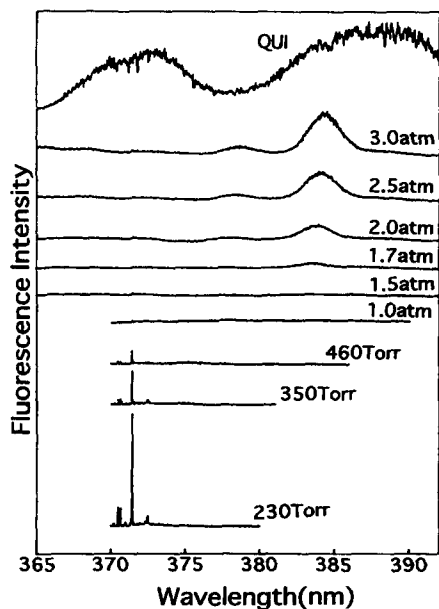


Fig. 2. Fluorescence excitation spectra of MEA seeded in Kr as a function of stagnation pressure. QUI represents the variation of laser intensity with wavelength.

tronic origin is a cluster band associated with the 12_0^1 transition. The successive appearance of excitation bands of $\text{MEA} \cdot \text{Ar}_n$ suggests that the fluorescence from the MEA moiety is not quenched strongly by complexation, irrespective of the size of Ar clusters. This is in contrast to the cases of Kr and Xe as described below. The fluorescence lifetimes (τ_f) measured at several wavelengths corresponding to different sizes from small to large clusters were in a range of 7–18 ns. The value of τ_f for the electronic origin of the bare MEA molecule is 18.7 ns and, indeed, any remarkable quenching due to the coordination of Ar atoms is not seen.

As seen in Fig. 2, no excitation bands of complexes of MEA with Kr atoms were observed besides that of the 1:1 complex ($\text{MEA} \cdot \text{Kr}$) at stagnation pressures no higher than 1.5 atm. The value of τ_f measured for the electronic origin of $\text{MEA} \cdot \text{Kr}$ at 372.30 nm was 7 ns, and was smaller than 18.7 ns for the bare molecule [14], suggesting that the ISC rate is increased because of a heavy-atom effect. Additional coordinations of Kr atoms are considered to enhance further the ISC rate and to lead to a shorter fluorescence lifetime. Therefore, the excita-

tion bands of $\text{MEA} \cdot \text{Kr}_n$ ($n > 1$) subsequent to the 1:1 complex are not observed till n exceeds a certain value. Above a stagnation pressure of 1.5 atm, a broad excitation band appears at largely red-shifted wavelengths, together with the other broad band associated with the 12_0^1 transition, and grows with increasing pressure. This observation implies that the ISC rate is not enhanced in the large clusters of $\text{MEA} \cdot \text{Kr}_n$. Indeed, the fluorescence lifetimes measured at several wavelengths within this band were in the range 12–25 ns. Similar phenomena were observed for the excitation spectra of Xe-clusters of MEA as seen in Fig. 3. The excitation bands associated with small clusters were not detected under the present experimental conditions. Above a stagnation pressure of 600 Torr, a broad band was observed at longer wavelengths and the fluorescence lifetimes measured at several wavelengths within this band were in the range 11–24 ns. Analogously to the case of Kr-clusters, the ISC rate of MEA is enhanced in small clusters of Xe atoms and diminished in the large clusters.

The results obtained in this work can be interpreted in terms of two effects in the clustering of

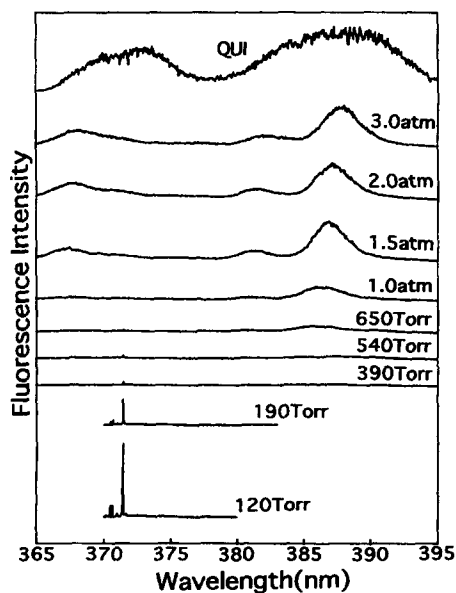


Fig. 3. Fluorescence excitation spectra of MEA seeded in Xe as a function of stagnation pressure. QUI represents the variation of laser intensity with wavelength.

rare-gas atoms toward an MEA molecule. One is the lowering of the S_1 energy relative to the T_2 energy by microscopic solvation and the other is a heavy-atom effect on the ISC rate. The S_1 state of MEA is located below the T_2 state in solution; for instance, the electronic energy gap between the S_1 and T_2 states was estimated to be $700\text{--}800\text{ cm}^{-1}$ in solution [13,19–22]. The S_1 energy of MEA is increased by approximately 1000 cm^{-1} in the isolated state owing to desolvation, resulting in the shift of S_1 above T_2 because the S_1 state undergoes a larger solvent shift than the T_2 state does. Therefore, ISC from the vibrationless level of S_1 to T_2 is energetically allowed and the fluorescence quantum yield for the bare MEA molecule is 0.57 at the electronic origin [23]. Both cases for the presence and absence of the heavy-atom effect on the nonradiative decay of anthracene compounds were found in the jet-experiment using rare gases. For anthracene [24], MEA [14] and 9-methoxyanthracene [6], the ISC rate is enhanced greatly by the coordination of Kr and Xe atoms because the ISC channel is open energetically for these molecules being in the condition $S_1 > T_2$. In contrast, for 9-cyanoanthracene [15], 9,10-dicyanoanthracene [25], 9,10-dichloroanthracene [26] and 9,10-dimethoxyanthracene [27], the fluorescence lifetimes of all the rare-gas complexes including the Xe-complex are almost equal to those measured for the bare molecules. This is because the energy of S_1 is already lower than that of T_2 for these molecules and the further lowering of S_1 relative to T_2 by the complexation of rare-gas atoms does not alter the situation of S_1 being located below T_2 ; i.e. ISC is not allowed energetically even though the spin-orbit coupling is enhanced owing to the heavy-atom effect.

The successive coordinations of rare-gas atoms to an MEA molecule cause the gradual lowering of the S_1 energy relative to the T_2 energy. Since the heavy-atom effect of the Ar atom is small, the complexation of Ar atoms leads to only a small increase in the ISC rate. Therefore, all excitation bands attributed to $\text{MEA} \cdot \text{Ar}_n$ are observed even under the condition $S_1 > T_2$, irrespective of cluster size. In contrast, the coordination of Kr and Xe atoms to MEA enhances the ISC rate greatly under the condition $S_1 > T_2$, and, hence, the excitation bands associated with small clusters of Kr and Xe are scarcely observed

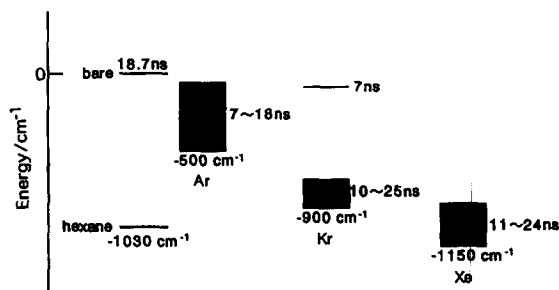


Fig. 4. Energy shifts and fluorescence lifetimes of the S_1 electronic origin of MEA upon clusterization. The energy region of cluster bands observed in fluorescence excitation spectra are shown with fluorescence lifetimes measured at different wavelengths in the region. The S_1 energy at the peak of the cluster band at the highest stagnation pressure of 3 atm is represented as a red-shift measured from the electronic origin of a bare MEA molecule.

because the S_1 state is still located above the T_2 state in the small clusters. As the size of the cluster becomes larger, the S_1 state comes closer to the T_2 state and, eventually, is shifted below the T_2 state. In the large clusters under the condition $S_1 < T_2$, the ISC from the lowest vibrational level of MEA is not allowed energetically. As a result, the fluorescence from MEA in the large clusters of Kr and Xe atoms is observed.

The energy shifts and fluorescence lifetimes of the S_1 electronic origin upon clusterization are shown in Fig. 4. The coordination number for clusters, in particular, for large clusters is not determined in this work. In this experimental condition, the highest coordination number at a stagnation pressure of 3 atm is considered to be no less than 20, on the basis of the previous study [17]. The magnitude of the energy shift of S_1 is dependent on the dispersive force of a rare-gas atom, its order being $\text{Xe} > \text{Kr} > \text{Ar}$. The S_1 energy of MEA in the large clusters of Kr and Xe formed in this work is close to or even lower than that in hexane, supporting that S_1 is located below T_2 in these large clusters as well as in solution. The natural radiative lifetime of the bare MEA molecule is calculated to be 32.8 ns from the fluorescence quantum yield of 0.57 [23] and the fluorescence lifetime of 18.7 ns [14]. The fluorescence lifetimes of MEA in the large clusters of Kr and Xe atoms are shorter than the natural radiative lifetime thus evaluated. This fact indicates that ISC indeed

proceeds though S_1 is located below T_2 . For the MEA molecule at the electronic origin, an ISC channel is closed under the condition $S_1 < T_2$, and its fluorescence lifetime should be almost equal to the natural radiative lifetime of 32.8 ns. The observed shorter fluorescence lifetimes suggest a possibility that the large clusters are not cooled completely and have a certain amount of excess thermal energy as a whole of a cluster, and, hence, the thermally assisted S_1-T_2 ISC proceeds in these clusters at an averaged rate which is determined mainly by both the electronic energy gap of S_1 and T_2 states and the amount of thermal energy available.

In previous studies, it has been shown that the S_1-T_2 level inversion is caused by coordination of one Xe atom for 9,10-dimethylantracene and 9,10-dibromoanthracene [12] and by coordination of several Xe atoms for 9,10-diphenylantracene [7]. In the bare state of these molecules the energy of S_1 is slightly higher than that of T_2 . In the present study on an MEA molecule having a larger energy gap between S_1 and T_2 in the bare state, S_1-T_2 level inversion was attained by the formation of large clusters of Kr or Xe atoms in a pulsed supersonic jet. In conclusion, the interpretation of the S_1-T_2 ISC in terms of the solvent-induced shift of the S_1 energy is consistent with the observed medium effect on the fluorescence decay ranging from a bare molecule to clusters and even to solution.

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