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Intersystem crossing in jet-cooled naphthalene clusters as studied by sensitized phosphorescence excitation spectroscopy

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Abstract

The fluorescence excitation and sensitized phosphorescence excitation spectra of jet-cooled naphthalene clusters were measured. The intensity of the cluster bands in the sensitized phosphorescence excitation spectrum depends on both the cluster size and the excess vibrational energy. The intensity of the trimer is 1.3 times larger than that of the monomer in the $\bar{8}_0^1$ region. However, the intensity of the tetramer is weaker than that of the monomer in the same excitation region. The trimer band intensity in the sensitized phosphorescence excitation spectrum decreases with an increase in the excitation energy compared with that in the fluorescence excitation spectrum. These results indicate that intersystem crossing of the clusters competes with faster relaxation at higher excitation energies. It is considered that the fast process is associated with the relaxation of the clusters to an excimer state. © 1997 Elsevier Science S.A.

Keywords: Intersystem crossing; Jet-cooled naphthalene clusters; Sensitized phosphorescence excitation spectroscopy

1. Introduction

Molecular clusters as an intermediate state between gaseous and condensed phases have attracted considerable attention [1]. The dynamic properties of the clusters depend on their size and structure. Studies on the dynamics of various singlet clusters have been carried out by several methods, such as measurement of the fluorescence lifetime and dispersed fluorescence [2]. However, few studies on the intersystem crossing (ISC) of clusters have been reported. Our goal was to obtain the efficiency of ISC in a supersonic jet using naphthalene clusters.

Sensitized phosphorescence is one of the most useful methods of measurement of the efficiency of ISC in a bulk system. However, this method is difficult to apply to supersonic jet spectroscopy. This difficulty was overcome by Abe et al. [3] using sensitized phosphorescence excitation spectroscopy. In this technique, an isolated molecule in a jet is excited to its S_1 state, and the triplet molecule is produced by ISC. The triplet molecules are detected by measuring the sensitized phosphorescence resulting from the collision of the triplet molecule with a phosphor placed downstream of the jet. By comparing the fluorescence intensity and sensitized phosphorescence intensity measured simultaneously, we can obtain the efficiency of ISC. Using this method, the ISC efficiencies of clusters and monomers can be obtained simultaneously.

There are several reasons why naphthalene is the best sample for studying the ISC of clusters. First, the ISC of monomeric naphthalene has been extensively studied by many researchers [4,5]. The rate of ISC subsequent to excitation of individual vibronic bands has been determined from the quantum yield of singlet vibronic fluorescence by Stockburger et al. [4]. The ratio of the fluorescence intensity to the sensitized phosphorescence intensity in a supersonic jet has been reported by Suzuki et al. [5]. Second, naphthalene clusters are one of the most investigated van der Waals' (vdW) clusters. The $S_1 \leftarrow S_0$ vibronic structure has been analysed by mass-selected resonance-enhanced multiphoton ionization (REMPI) [6,7] and fluorescence excitation [8] experiments. Syage and Wessel [6,7] measured the mass-selected MPI spectra of naphthalene from the dimer to the pentamer. They predicted that the structures of the tetramer and trimer are herringbone and linear respectively from their fine analysis [7]. The dynamics of naphthalene clusters in the S_1 state have also been reported by Saigusa and Lim [8,9]. They showed that the excimer formation from naphthalene vdW clusters depends on the cluster size and excess vibrational energy.

We are interested in the dependence of the ISC of clusters on the cluster size and excitation energy. In this paper, we

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report the ISC efficiency of naphthalene clusters studied by sensitized phosphorescence spectroscopy.

2. Experimental section

The supersonic apparatus for the simultaneous measurement of the fluorescence excitation and sensitized phosphorescence excitation spectra was the same as described elsewhere [10,11]. Briefly, naphthalene seeded in 5 atm of helium was heated to approximately 80 °C. Naphthalene clusters were generated by expanding the sample vapour into a vacuum chamber at 10^{-5} Torr through a pulse nozzle. A frequency-doubled dye laser (Lambda Physik LPD 3002) pumped by an excimer laser (Lambda Physik LEXTRA 50) was used as excitation light. The laser beam crossed the jet 15 mm downstream, and the naphthalene clusters were excited to their S_1 vibronic levels. The fluorescence excitation spectrum was obtained by monitoring the total fluorescence with a photomultiplier (Hamamatsu Photonics R 928). The signal was averaged by a boxcar integrator (Stanford Research Systems SR 250). The sensitized phosphorescence excitation spectrum was obtained by the method developed by Abe et al. [3]. The triplet molecules produced by ISC from the S_1 state travelled 3 cm downstream from the position of excitation and collided with a liquid-nitrogen-cooled copper surface covered with biacetyl (phosphor). Sensitized phosphorescence was emitted when the triplet molecule collided with the phosphor. The sensitized phosphorescence detected by a photomultiplier (Hamamatsu Photonics R 562) was averaged with a boxcar integrator.

3. Results and discussion

Fig. 1 shows the fluorescence excitation (Fig. 1(a)) and simultaneously measured sensitized phosphorescence excitation (Fig. 1(b)) spectra of naphthalene in the $\bar{8}_0^1$ region of $S_1 \leftarrow S_0$ $(0,0+400\ cm^{-1})$. All bands in the fluorescence excitation spectrum (Fig. 1(a)) can be assigned by comparison with the mass-selected REMPI spectra of Syage and Wessel [6,7] and Saigusa et al. [8]. The strongest band shown in Fig. 1(a) is assigned to the $\bar{8}_0^1$ band of the monomer, which is located at 435 cm^{-1} from the origin band of the monomer. The band located at $-81\ cm^{-1}$ from the monomer $\bar{8}_0^1$ band is assigned to the trimer $\bar{8}_0^1$ band. The bands appearing between $-200\ cm^{-1}$ and $-100\ cm^{-1}$ from the monomer band are assigned to tetramer $\bar{8}_0^1$ bands. The very broad band similar to background appearing between 311 and 308 nm is assigned to the dimer $\bar{8}_0^1$ band. It is conspicuous that the simultaneously measured sensitized phosphorescence excitation spectrum reveals very different features from the fluorescence excitation spectrum as shown in Fig. 1(b). Although the monomer and trimer peaks appear prominently in the spectrum, the intensity of the tetramer band is very weak and the dimer band is almost missing in the sensitized

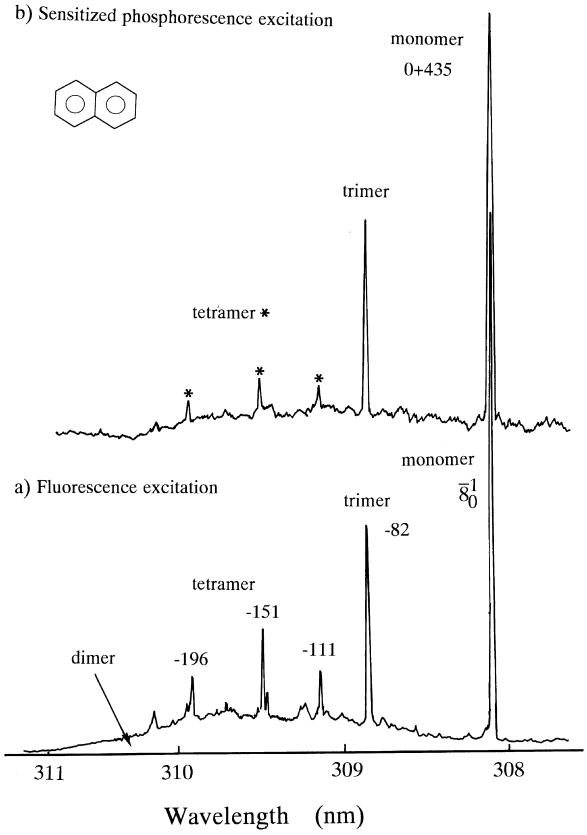

Fig. 1. Fluorescence excitation (a) and simultaneously measured sensitized phosphorescence excitation (b) spectra of naphthalene in the $\bar{8}_0^1$ region of $S_1 \leftarrow S_0$ $(0,0+400\ cm^{-1})$.

phosphorescence excitation spectrum. These results reveal that the intensity of the sensitized phosphorescence depends on the size of the cluster.

The ratio of the sensitized phosphorescence intensity to the fluorescence intensity (I_p/I_f) of each band is given by the following equation

$$I_p/I_f = Ck_{isc}[Y_{ET}\exp(-k_T t)]/k_f \quad (1)$$

where k_f and k_{isc} are the radiative and intersystem crossing rates respectively, Y_{ET} represents the energy transfer efficiency from the triplet molecule to the phosphor, k_T is the deactivation rate constant of the triplet molecule and C is a constant. Suzuki et al. [5] suggested that the term in the bracket of Eq. (1) is constant and k_f does not vary greatly in the S_1 region of the naphthalene monomer. Therefore I_p/I_f gives the efficiency of ISC approximately. To compare the efficiency of ISC of the clusters with that of the monomer, the ratio of I_p/I_f of the cluster to that of the monomer is deduced. The term in the bracket of Eq. (1) is almost the same for the monomer and the trimer, because the lifetime of triplet naphthalene is much longer than the flight time from the excitation position to the phosphor [5]. Therefore the ratio is given by

$$\frac{(I_p/I_f)_{cluster}}{(I_p/I_f)_{monomer}} = \frac{k_{isc}^{cluster}}{k_{isc}^{monomer}} \frac{k_f^{monomer}}{k_f^{cluster}} \quad (2)$$

The ratio of $(I_p/I_f)_{monomer}$ to $(I_p/I_f)_{trimer}$ in the $\bar{8}_0^1$ band, as shown in Fig. 1, is evaluated to be about 1.3. Assuming that the radiative rate is almost the same between the trimer and the monomer, the ratio of I_p/I_f of the trimer to that of the monomer gives the relative ISC rate. This means that k_{isc} of the trimer is 1.3 times larger than that of the monomer in the $\bar{8}_0^1$ region. It is considered that this corresponds to the clustering effect as a result of an increase in the density of state of the trimer due to the inclusion of intermolecular vibration.

In contrast, the ratio of I_p/I_f of the tetramer to that of the monomer in the $\bar{8}_0^1$ region was found to be approximately 0.5. This indicates that the phosphorescence yield of the tetramer is much lower than that of the monomer and trimer in this excess energy region. This is the first observation indicating that the intensity of sensitized phosphorescence depends predominantly on the cluster size. According to Eq. (1), we can generally attribute the low phosphorescence yields to the low efficiency of ISC. However, as the density of state of the tetramer is larger than that of the trimer, the ISC rate of the tetramer should not be 33% smaller than that of the trimer. Therefore there must be another route leading to a decrease in the intensity of sensitized phosphorescence of the tetramer, other than the low efficiency of ISC. One candidate for the fast reaction is excimer formation. Indeed, Saigusa et al. [8] observed excimer fluorescence from the tetramer following excitation into the $\bar{8}_0^1$ transitions. Thus the sensitized phosphorescence intensity of the tetramer $\bar{8}_0^1$ band decreases because ISC competes with excimer formation from the excited tetramer. Since the trimer does not form excimers in the $\bar{8}_0^1$ region [8], the I_p/I_f ratio of the trimer is greater than that of the monomer in this region.

If the trimer is excited to a higher vibronic band of the S_1 state, the cluster can cross the barrier of excimer formation losing excess energy. In order to ascertain whether or not ISC competes with excimer formation as described above, we measured the sensitized phosphorescence excitation spectrum in the higher excitation region. Fig. 2 shows the fluorescence excitation (Fig. 2(a)) and simultaneously measured sensitized phosphorescence excitation (Fig. 2(b)) spectra of naphthalene from the $\bar{7}_0^1$ region to the $\bar{8}_0^1 8_0^1$ region ($0,0+900\ cm^{-1}$ to $0,0+1100\ cm^{-1}$). The monomer $\bar{7}_0^1$ and $\bar{8}_0^1 8_0^1$ bands appear at 911 cm^{-1} and 1135 cm^{-1} respectively from the 0,0 band of the monomer in the fluorescence excitation spectrum (Fig. 2(a)). The band whose frequency shift is $-82\ cm^{-1}$ with respect to the monomer $\bar{7}_0^1$ band is assigned to the trimer $\bar{7}_0^1$ band, and the band whose frequency shift is $-75\ cm^{-1}$ with respect to the monomer $\bar{8}_0^1 8_0^1$ band is assigned to the trimer $\bar{8}_0^1 8_0^1$ band. Compared with the fluorescence excitation spectrum, the intensities of both the trimer bands ($\bar{7}_0^1$ and $\bar{8}_0^1 8_0^1$) are very weak in the sensitized phosphorescence excitation spectrum. The intensity ratios of the trimer $\bar{7}_0^1$ and $\bar{8}_0^1 8_0^1$ bands in the sensitized phosphorescence excitation spectrum vs. the fluorescence excitation spectrum (I_p/I_f) are 0.4 and 0.2 respectively, compared with those of the monomer. The sensitized phosphorescence of the cluster depends on the excess vibrational energy as well as the cluster size. Although I_p/I_f of the monomer gradually increases with increasing excitation energy, the ratio of I_p/I_f of the trimer to that of the monomer decreases. This shows that the ISC rate of the trimer in this excitation region becomes larger than that of the monomer with an increase in the excitation energy. Therefore the low intensity of sensitized phosphorescence of the trimer in the $\bar{7}_0^1$ and $\bar{8}_0^1 8_0^1$ region is due to excimer formation, as well as in the $\bar{8}_0^1$ region of the tetramer. Indeed, Saigusa et al. [8] reported that the trimer forms an excimer following excitation into the $\bar{7}_0^1$ transition on the blue side of $\bar{8}_0^1$. Therefore it was confirmed that ISC competes with excimer formation and results in a low intensity of sensitized phosphorescence.

Since excimer formation from the excited trimer does not occur in the $\bar{8}_0^1$ region, the ISC rate is 1.3 times larger than

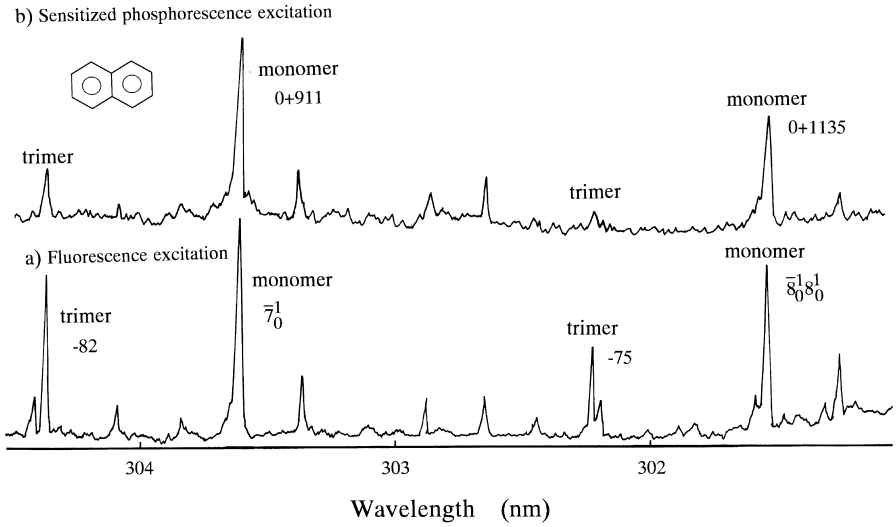

Fig. 2. Fluorescence excitation (a) and simultaneously measured sensitized phosphorescence excitation (b) spectra of naphthalene from the $\bar{7}_0^1$ region to the $\bar{8}_0^1 8_0^1$ region ($0,0+900\ cm^{-1}$ to $0,0+1100\ cm^{-1}$).

that of the monomer. Although the excimer of the trimer is formed in both the $\bar{7}_0^1$ and $\bar{8}_0^1 8_0^1$ regions, the ratio in the $\bar{8}_0^1 8_0^1$ region is smaller than that in the $\bar{7}_0^1$ region. It is considered that the decrease in the sensitized phosphorescence is associated with the rate of excimer formation. Saigusa et al. [12] reported that the buildup times of excimer fluorescence are 32 ns and less than 3 ns in $\bar{7}_0^1$ and $\bar{8}_0^1 8_0^1$ respectively, indicating that the rate of excimer formation increases with an increase in the excitation energy. Thus the amount of triplet molecules produced by ISC in $\bar{8}_0^1 8_0^1$ is smaller than that in $\bar{7}_0^1$, assuming that ISC is not very different between these excess energies. This results in a low intensity of the trimer band in the sensitized phosphorescence spectrum with an increase in the excitation energy.

$(I_p/I_f)_{tetramer}/(I_p/I_f)_{monomer} = 0.5$ on excitation at the $\bar{8}_0^1$ region. Saigusa et al. [12] estimated that excimer formation from a vdW tetramer excited at the $\bar{8}_0^1$ band occurs in less than 1 ps. Therefore the intensity of the tetramer band in the sensitized phosphorescence spectrum is weak. In the dimer, excimer formation takes place even on excitation in the 0,0 band [8,12]. It is estimated that the excimer is formed very rapidly from the dimer excited to the $\bar{8}_0^1$ band. Consequently, the dimer band is almost absent in the sensitized phosphorescence excitation spectrum.

Finally, we explain these results using the energy diagram of the trimer (Fig. 3). Since the trimer cannot reach the excimer crossing potential barrier by excitation into the $\bar{8}_0^1$ band, the ISC rate of the trimer is 1.3 times larger than that of the monomer. However, since the trimer can cross the barrier of excimer formation following excitation into the higher vibronic band ($\bar{7}_0^1$ and $\bar{8}_0^1 8_0^1$) transition, the quantity of triplet molecules decreases because the rate of excimer formation is faster than that of ISC. Therefore, when the trimer can form an excimer, the sensitized phosphorescence decreases. As ISC competes with excimer formation, the intensity of sensitized phosphorescence depends on the rate of excimer formation. The ratio of I_p/I_f of the trimer to that of the monomer in $\bar{7}_0^1$ is larger than that in $\bar{8}_0^1 8_0^1$ because the $\bar{8}_0^1 8_0^1$ level has a larger excess energy than the $\bar{7}_0^1$ band, which is sufficient to cross the barrier.

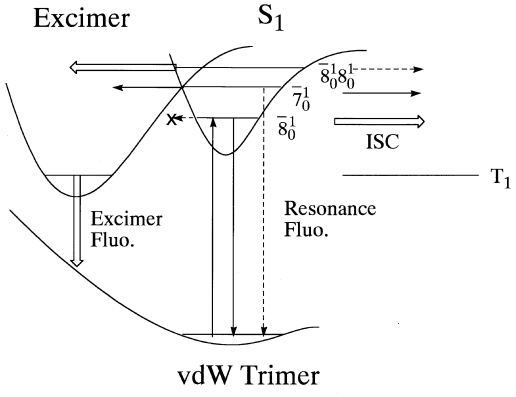

Fig. 3. Energy diagram of naphthalene trimer.

4. Conclusions

We obtained the relative ISC rate constant of the naphthalene trimer by sensitized phosphorescence excitation spectroscopy. The sensitized phosphorescence of the cluster depends on the cluster size and the excess vibrational energy.

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