

# Hypermobility of Aromatic Guest Species in Zeolite as Observed from Anthracene Triplet Self-Quenching within NaY in the Presence of Critical Amounts of Coadsorbed Solvents<sup>†</sup>

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The decay kinetics was investigated of triplet-state anthracene adsorbed into the cavities of a faujasite zeolite, NaY, both in the absence and in the presence of various quantities of water and other coadsorbed inert solvent molecules. It was found that at a sufficiently low loading level of anthracene the decay rate is dependent on the amount of water, methanol, and pyridine but is scarcely affected by *n*-hexane. When the decay rates are plotted versus the amount of solvents introduced, convex curves were obtained with a peak at ca.  $0.1 \text{ cm}^3 \cdot \text{g}^{-1}$ , which is approximately a quarter of the total pore volume of NaY ( $0.378 \text{ cm}^3 \cdot \text{g}^{-1}$ ). The enhanced triplet decay rate was found to be ascribable to a self-quenching event, i.e., the triplet quenching by ground-state anthracene. Thus a picture was given that anthracene molecules are highly mobile when the zeolite cavities are loaded with the coadsorbed solvents in quantities sufficient to shield the cationic sites at which anthracene is supposed to be adsorbed. The kinetic analysis of the triplet quenching process revealed that the inter-cage mobility in the presence of  $0.1 \text{ cm}^3 \cdot \text{g}^{-1}$  of water is more than 100 times higher than that in the presence of  $0.3 \text{ cm}^3 \cdot \text{g}^{-1}$  of water. The high mobility of the guest species is presumably caused by the liberation of adsorption interaction of anthracene with the zeolite walls by the action of small quantities of the solvent molecules with strong affinity toward the zeolite frameworks. By contrast, large quantities of the coadsorbed solvents are expected to interfere with the movement of anthracene in the cage networks because they are crowded enough to fill the interconnecting windows between cages as well as a large portion of the cage volume. The dramatic effect of coadsorbed water and other solvents on the diffusional motion of anthracene within the zeolite supercage networks depending on the quantity adsorbed is described.

## Introduction

Medium control of photophysical and photochemical events of organic molecules is currently an important subject in photochemistry.<sup>1</sup> As one of such reaction media, zeolites have attracted considerable attention in photochemical research<sup>2</sup> because they host various organic transformations in their cavities and channels, often providing product distributions strikingly different from those in solutions. The confinement of molecules within the constrained space and the catalytic properties of the surface adsorption sites were considered decisive for the product distribution unique to zeolites. Despite the fascinating features of the zeolites as a novel solid reaction medium, there still remain gaps between our understanding of photophysics within zeolites and that of the outcome of reactions. Thus, much effort has been devoted in recent years to establishing the correlation of the mechanistic aspects of photophysical and photochemical processes in zeolite-adsorbed systems with the remarkable specificity and selectivity of photochemical reactions.<sup>3</sup>

Kinetic analysis of the dynamics of the excited-state processes within zeolites is essential for better understanding of the reaction mechanisms as well as for utilizing intrazeolite chemistry for practical applications. However, a simple analysis has been hampered by the problem of a heterogeneous distribution: nonexponential decays were commonly observed<sup>4</sup> due to

the distribution of molecules at various adsorption sites with differing environment (differing interaction with the host) and similarly with other solid support such as silica gel.<sup>5</sup> For analyzing the experimental decay curves, the statistical distribution of lifetimes<sup>6</sup> or decay rates<sup>2c</sup> was assumed. Thus the experimental data were well fitted with mathematical functions based on the models; however, the physical meaning of parameters obtained were still unclear.

Besides the distribution problem, the slow diffusion rate of molecules within zeolites was considered to be a major obstacle to investigation with a luminescence quenching method. This method basically detects the motion of molecules in short time scales of nano- to microseconds, and hence is inappropriate for applying to zeolites for obtaining information about the slow transport of guest species. So far, we know little about the rate of the intra-cage quenching process of the excited-state species distinguished from that of inter-cage migration of molecules which eventually react to deactivate the excited-state species, except for only a few cases. For instance, we observed with the transient absorption study the intra-cage quenching of excited singlet-state anthracene with anthracene in the ground state resulting in the formation of anthracene excimer within the picosecond time scale.<sup>7</sup> We also detected the intra-cage quenching of S<sub>1</sub>-state pyrene by the same molecule in the ground state leading to the formation of radical ion pairs of pyrene in the nanosecond time scale.<sup>8</sup> These cases are exceptionally fast due to the confinement of molecules within the restricted space; usually a much longer time scale is necessary for observing reactions due to the diffusional motion of molecules within

<sup>†</sup> This paper is dedicated to Professor Kerry Thomas on the occasion of his 65th birthday.

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zeolites. This process is more popular and important for reactions within zeolites.

Reaction kinetics in organized assemblies such as micelles and microemulsions have been studied for more than two decades. Luminescence quenching studies in the organized assemblies showed the peculiar deactivation kinetics of excited-state probes, markedly different from observation in homogeneous solution.<sup>1</sup> Theoretical treatments which properly handle the equilibrium distribution (occupation statistics) of reactants, various mechanisms of solute exchange, and the reaction dynamics between solubilized molecules have been developed.<sup>1,9</sup> The reactions in the organized assemblies have similarities with those in zeolites in many respects: the compartmentalization of molecules into cells according to a certain distribution law, exchange of solutes between the cells, the reaction of solutes within the same cell and that of molecules originally contained in different cells through a diffusional motion of reactants. Especially, micelle clusters with indefinite size rather than simple monodisperse micelles are very similar to zeolites in structure. Theoretical treatment of the decay kinetics of excited species has been extended to the micelle clusters.<sup>9</sup>

We have initiated the investigation of the relaxation processes of the excited states of simple aromatic molecules doped within zeolites with emphasis on the decay kinetics in micro- to millisecond time domain where the inter-cage diffusion can be responsible for reactions. Triplet-state anthracene might be suited for this type of investigation with zeolites because it is basically unreactive toward chemical reactions, possessing strong absorption bands in the visible region with a long lifetime at room temperature.<sup>10</sup> These advantageous features enable the detection of the triplet with minimum disturbance from side reactions with the transient absorption spectroscopy based on a diffuse reflectance technique<sup>11</sup> for powdered samples. Interestingly, there have been only a few works that concentrate on the kinetic behavior of the triplet states within zeolites.<sup>12</sup>

As is made clear by the work to be described, we observed that the amounts of water and some solvent molecules introduced into the zeolite critically affect the observed triplet decay constants. We found that the critical amounts of solvents facilitate the diffusional motion of guest anthracene by liberating the molecule from the zeolite frameworks, leading to the dynamic triplet quenching by the molecules in the ground state even at sufficiently low loading levels of anthracene. This finding has two significant meanings. First, the solvents with strong interaction with the zeolite walls have ability to control the rates of intra-cage reaction and inter-cage migration of guest aromatic species. A different type of solvent effect has been observed recently by Sciano and co-workers<sup>12c</sup> for triplet-state xanthone and *p*-methoxy- $\beta$ -phenylpropiophenone in NaY by pyridine which reduced the decay rate of the triplet states by blocking the acid sites on the zeolite surface for xanthone or by restricting the internal motion for *p*-methoxy- $\beta$ -phenylpropiophenone. Second, although no intact zeolite was employed in our study, the kinetics of the quenching of the excited state characteristic to zeolite system was observed for the first time to be similar to those in micelle clusters.<sup>9</sup> The observed quenching kinetics can be generally applicable to zeolites if a proper system with probe excited-state lifetimes long enough to compete with the migration rate of quenchers within zeolites or with quenchers moving fast enough to compete with the excited-state lifetime of a given guest molecule is employed.

This paper describes the dramatic effect of coadsorbed water and other solvents (methanol, pyridine) on the self-quenching reaction of triple-state anthracene in NaY zeolite. A relatively

small amount of the solvents is found to enhance the mobility of the simple aromatic guest, anthracene, within the zeolite supercage networks. The enhanced mobility is responsible both for intra-cage reactions and for inter-cage migration of the guest species. We also found the effect of a relatively large amount of the solvents which interfere with the diffusional motion of anthracene by blocking inter-cage migration and also by reducing the free volume inside the cages. Thus a general picture which describes the kinetic mechanism of reactions in zeolite is revealed.

## Experimental Section

Anthracene (Merck, scintillation grade) was used as received whereas azulene (Tokyo Kasei) was sublimed prior to use. *n*-Hexane (Wako chemicals, HPLC grade) was distilled and stored over molecular sieves 4A, water doubly distilled, and methanol distilled from magnesium methoxide. Pyridine (Tokyo Kasei, extra pure) was used as received. Zeolite NaY (unit cell contents  $\text{Na}_{51}\text{Al}_{51}\text{Si}_{141}\text{O}_{384} \cdot x\text{H}_2\text{O}$ ) was obtained from Tosoh Co. Zeolite was calcined in air at 500 °C for 6–8 h just before sample preparation.

Anthracene-doped zeolite samples were prepared by adsorption from *n*-hexane solution: the dehydrated zeolite powder was stirred in *n*-hexane solution of anthracene in a stoppered vial at room temperature for 10 min; the sample was filtered and the solid washed twice with *n*-hexane. All of the procedure was carried out in a nitrogen-filled glovebox. The samples were contained in 2-mm-thick Suprasil cells and were evacuated at <0.4 Pa for 12 h at 100 °C. The water content in the dehydrated samples is estimated to be less than 0.4 wt % with <sup>1</sup>H NMR measurements using anthracene as an internal standard. A weighed amount of water and other solvents which were thoroughly degassed by repeated freeze–thaw cycles were admitted through a vacuum line into a cell with samples before sealing for the experiments with zeolites containing coadsorbed solvents. Azulene was adsorbed by sublimation into the zeolite doped with anthracene in the vacuum line before water was introduced.

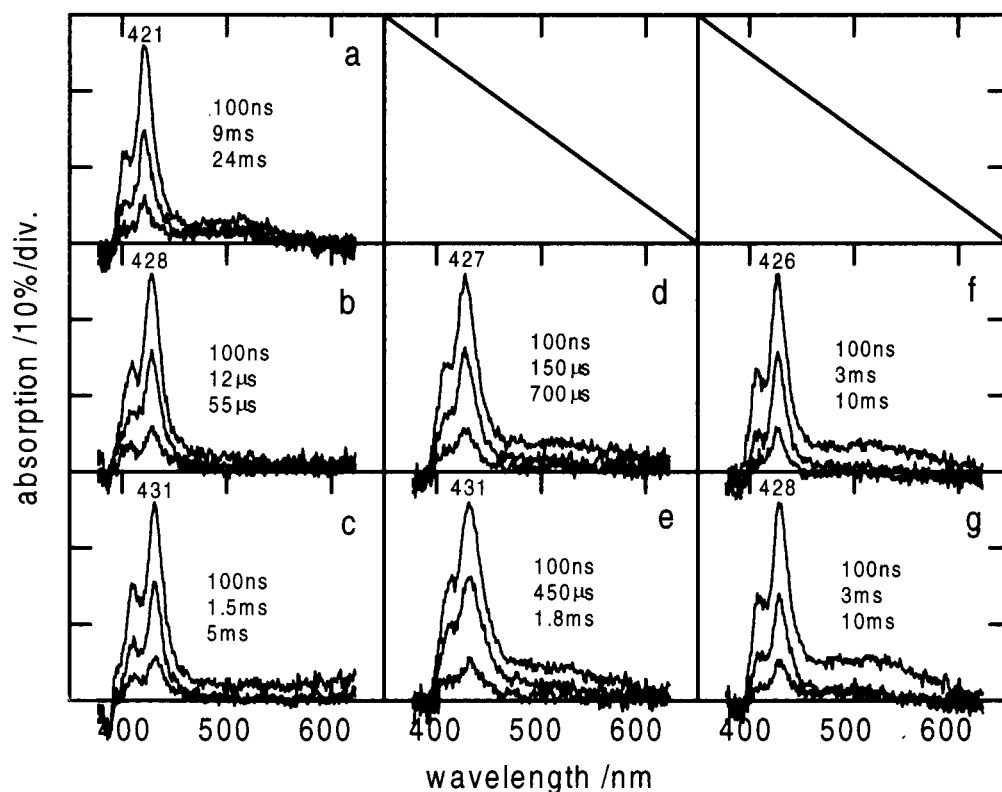
The experimental setup for nanosecond diffuse reflectance laser photolysis, which is applicable to the detection of transient species in optically inhomogeneous and light-scattering systems, was similar to the one described previously.<sup>13</sup> We adopted an approach by Wilkinson and co-workers<sup>11</sup> in which the percentage absorption (absorption (%)) is employed to describe the transient optical absorption signal following a laser excitation of guest-doped zeolites. The absorption (%) is defined as

$$\text{absorption (\%)} (\lambda, t) = 100[1 - R(\lambda, t)/R_0(\lambda, t)]$$

where *R* and *R*<sub>0</sub> denote the intensities of diffusely reflected light with and without excitation, respectively. The previous theoretical estimation by Wilkinson and co-workers<sup>11</sup> showed that a linear relationship can be held between the value of absorption (%) and the amount of transient species present for at least up to 10%. Yet, a linearity between the absorption (%) and the laser intensity has been confirmed experimentally up to 25%.<sup>14</sup> We obtained similar results for the triplet state of both anthracene and benzophenone doped in zeolite NaY with little change in their spectral bandwidths. We employed sufficiently low laser powers of 0.3–1.0 mJ·cm<sup>−2</sup>. All the measurements were carried out at ambient temperature (23–25 °C).

## Results and Discussion

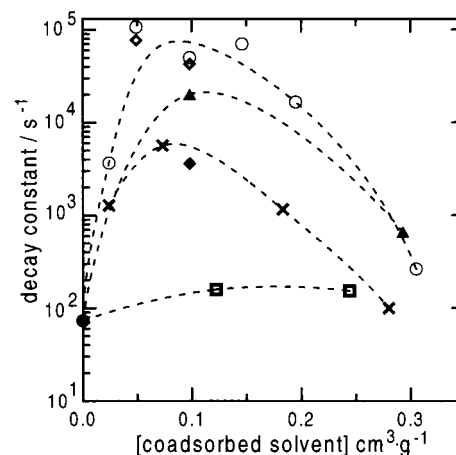
**Triplet Decay Rates in Dehydrated NaY and NaY with Coadsorbed Solvents.** The transient absorption spectra were



**Figure 1.** Transient absorption spectra of  $1.0 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}$  anthracene in NaY with various amounts of coadsorbed solvents at various delays ( $\lambda_{\text{ex}} = 355 \text{ nm}$ ). Key: a, dehydrated; b,  $0.10 \text{ cm}^3 \cdot \text{g}^{-1}$  hydrated; c,  $0.30 \text{ cm}^3 \cdot \text{g}^{-1}$  hydrated; d,  $0.075 \text{ cm}^3 \cdot \text{g}^{-1}$  pyridine; e,  $0.18 \text{ cm}^3 \cdot \text{g}^{-1}$  pyridine; f,  $0.12 \text{ cm}^3 \cdot \text{g}^{-1}$  *n*-hexane; g,  $0.24 \text{ cm}^3 \cdot \text{g}^{-1}$  *n*-hexane.

measured of anthracene doped in NaY in the absence and presence of various amounts of water and a few other solvents. We employed the anthracene loading level of  $1.0 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}$ , which is considered sufficiently low compared with the supercage concentration of  $6.3 \times 10^{-4} \text{ mol} \cdot \text{g}^{-1}$  ([guest]/[supercage]=0.016) for NaY. In fact, monomer-like fluorescence spectra detected at this loading level suggest the absence of guest–guest interaction while the contribution of excimer-like emission is noted more or less depending on the amount of coadsorbed solvents at loading levels  $> 1.0 \times 10^{-4} \text{ mol} \cdot \text{g}^{-1}$ . Note that the fluorescence decay curves at  $1.0 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}$  anthracene are practically the same regardless of the amount of the coadsorbed solvents.

The transient absorption spectra, depicted in Figure 1, can safely be assigned to those of the triplet–triplet absorption ( $T_1-T_n$  absorption) of anthracene on the basis of the similarity of the spectra obtained in solutions.<sup>15</sup> It is known that the  $T_1-T_n$  absorption spectrum has a maximum peak at 422.5 nm with a notably large  $\epsilon$  of  $64\,700 \text{ M}^{-1} \cdot \text{cm}^{-1}$  in cyclohexane.<sup>15</sup> In NaY-adsorbed systems, the transient spectra simply decayed without changing their shape; no new spectra arose as a result of the decay. Thus the decay was simply ascribed to the intersystem crossing to the ground-electronic state,  $S_0$ . The time-dependent decays of the  $T_1-T_n$  absorption were measured at various delays, and the triplet decay constants were obtained. In Figure 2 are shown the decay constants for  $1.0 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}$  anthracene at similar excitation intensities as a function of the quantity of the solvents introduced into the zeolite. These solvents are considered inert to the excited-state behavior of anthracene. Average decay constants are employed in Figure 2 when the decays showed nonexponential behavior.<sup>16</sup> Surprisingly, the triplet decay rate is significantly affected by the nature and amount of the coadsorbed solvents. A few remarks can be

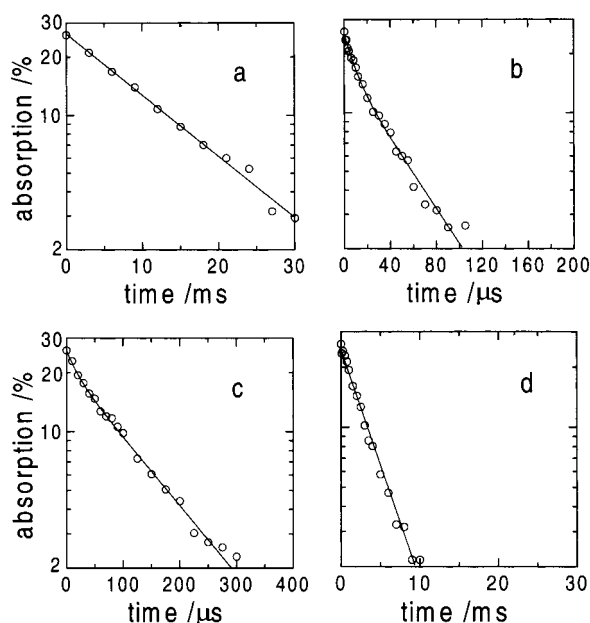


**Figure 2.** Decay constants of triplet-state anthracene plotted as a function of the quantities ( $\text{cm}^3 \cdot \text{g}^{-1}$ ) of various solvents for samples with anthracene loading level of  $1.0 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}$  in NaY at similar laser intensities. Key:  $\circ$ ,  $\text{H}_2\text{O}$ ;  $\diamond$ ,  $\text{D}_2\text{O}$ ;  $\blacktriangle$ , methanol;  $\times$ , pyridine;  $\blacklozenge$ , acetonitrile;  $\square$ , *n*-hexane;  $\bullet$ , dehydrated.

made which characterize the triplet decay dependence on the solvents.

First of all, the decay constant in dehydrated NaY is remarkably small. Second, with increasing amount of water, methanol, and pyridine, a convex curvature was observed: an initial increase in the decay constant was followed by a decrease while only a minute increase was observed in the presence of *n*-hexane. A remarkable increase in the decay constant of over 3 orders of magnitude was observed particularly for water and methanol. We should point out that the nonexponential nature of the decay was appreciable at large decay rates, although the decay was approximated by a single-exponential function when the value of decay constant is as small as  $< 5 \times 10^2 \text{ s}^{-1}$  (see





**Figure 3.** Decay curves of the triplet-triplet absorption of anthracene ( $1.0 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}$ ) in dehydrated and hydrated NaY. Key: a, dehydrated; b,  $0.10 \text{ cm}^3 \cdot \text{g}^{-1}$  hydrated; c,  $0.20 \text{ cm}^3 \cdot \text{g}^{-1}$  hydrated; d,  $0.30 \text{ cm}^3 \cdot \text{g}^{-1}$  hydrated.

Figure 3). Third, the  $T_1$ – $T_n$  absorption spectra afforded a continuous red shift with increasing amount of coadsorbed solvents (see Figure 1).

The important points that need to be elucidated are (a) the small triplet decay constant in the dehydrated zeolite, (b) the red shift in the  $T_1$ – $T_n$  absorption observed on addition of coadsorbed solvents, and (c) the origin of the different decay rates of the triplet in the presence of various inert solvents. We will refer to these points in due order.

First, the triplet decay constant of anthracene in dehydrated NaY (Figure 3a,  $60 \pm 10 \text{ s}^{-1}$ ) was measured to be so small as to be compared with that ( $38$ – $83 \text{ s}^{-1}$ ) observed in rigid plastic such as PMMA (poly(methyl methacrylate)) at  $300 \text{ K}$ .<sup>17</sup> Similar values have been obtained in solutions at room temperature<sup>15b,18</sup> despite the fact that it is difficult to obtain purely unimolecular decay constants of the triplet state in solutions because the simultaneously occurring bimolecular annihilation (triplet-triplet annihilation) process cannot be avoided even at low excitation intensities, in addition to a possible quenching by impurities. Although previous studies<sup>19</sup> have shown that the triplet lifetimes of aromatic species adsorbed on oxide surfaces including silica and alumina are well compared with those in solutions and rigid plastic media, few definitive studies have been carried out on the triplet lifetimes in zeolites. It is reasonable that the small decay rate analogous to that on oxide surfaces is obtained in the zeolite considering the fact that the chemical properties of the surface, e.g., acid–base properties, as well as the chemical composition are similar to other oxides. On the contrary, Sciano and co-workers<sup>12e</sup> obtained at least an order of magnitude larger decay constants for triplet xanthone and benzophenone adsorbed in NaY than those in solution. They ascribed this result to the possible quenching effect by the acid sites on the dry zeolite surface. Thus, we expect that the triplet state of simple aromatic hydrocarbons which are free from the quenching by the acid sites should have a sufficiently long lifetime in zeolites, and if this is not the case there should exist a certain effect of remaining solvents employed for adsorption or of water unintentionally introduced from moisture. We actually observed various short lifetimes of anthracene triplet

in NaY-adsorbed systems depending on the period and temperature of evacuation in sample preparation procedures.

It is interesting to note that the singlet lifetimes of aromatic hydrocarbons adsorbed on silica<sup>5</sup> and alumina<sup>20</sup> have been measured to be remarkably short compared with those in solutions. This is also the case for pyrene and other aromatic species included within zeolites.<sup>4,21</sup> The short lifetimes have been ascribed to the enhanced nonradiative deactivation rate presumably due to the adsorption interaction with the host materials.<sup>5c</sup> At the present stage of investigation, it is not obvious why the decay rate of the triplet state of aromatic species is so different from that of singlet state in zeolites and other surfaces.

The second issue is the red shift of the  $T_1$ – $T_n$  absorption spectra in NaY containing coadsorbed solvents. This finding can be explained either by the change in the medium polarity inside the supercages caused by the introduction of the solvents or by the formation of complexes between anthracene and solvent molecules within the supercages. The change in the polarity inside the zeolite cavities should be minor: the polarity in the cavities of NaY has been estimated to be high enough to be compared with that in the mixture of water and methanol.<sup>22</sup> Thus no significant change in polarity can be expected by introducing polar solvents into the cavities. It is reasonable to assume that a sort of complexes is formed in NaY in the presence of various amounts of coadsorbed solvents. The fluorescence spectra showed the gradual red shift, which is reminiscent of the phenomenon in the clusters of aromatic hydrocarbons with various numbers of solvent molecules such as *n*-hexane in supersonic jet,<sup>23</sup> with increasing amount of the solvents except water. Note that the  $T_1$ – $T_n$  absorption spectra (Figure 1) as well as the fluorescence spectra in NaY with coadsorbed *n*-hexane is appreciably red-shifted compared to those observed in *n*-hexane solution at room temperature. Thus the complexes with specific geometry should be formed within the zeolite cavities in the presence of *n*-hexane. Similar arguments can be applied to the cases of other solvents. We should point out that the supercages of the zeolite have the ability to hold this type of complexes, which are formed only in low-temperature glassy matrixes or supersonic jet, by restricting thermal motions of adsorbed molecules even at room temperature. However, the complex formation does not necessarily lead to the significantly enhanced decay rate of anthracene triplet. Obviously, the enhanced decay was only observed when certain critical amounts of specific solvents are introduced, and the slow decays were generally observed when the solvents are contained in large quantities.

The third issue of the enhanced decay rates in the presence of coadsorbed solvent molecules will be discussed at this point. Coadsorbed solvents have a remarkable effect on the state of adsorption of aromatic species within the zeolite host. With fluorescence spectroscopy, we revealed<sup>24</sup> that anthracene molecules are primarily adsorbed at  $\text{Na}^+$  cationic sites such as the type II sites in NaY through the cation  $\pi$  interaction. On introducing increasing amounts of water or other solvents (e.g., methanol, acetonitrile, pyridine), the adsorbed molecules are suggested to be gradually liberated from the interaction with the zeolite frameworks and replaced by the coadsorbed solvent molecules which can lie on the zeolite walls with strong interaction. Finally, anthracene crystals were formed in the presence of these solvents, the amount of which being close to filling the total pore volume of the zeolite ( $0.378 \text{ cm}^3 \cdot \text{g}^{-1}$ ). On the other hand, *n*-hexane was found to be different: the stronger interaction of anthracene with NaY than that of *n*-hexane with NaY prevents anthracene from being replaced by *n*-hexane and

released from the zeolite walls. The difference in the adsorbed state of anthracene within the zeolite depending on the nature and quantity of various solvents provides a clue to the notable triplet decay behavior in question.

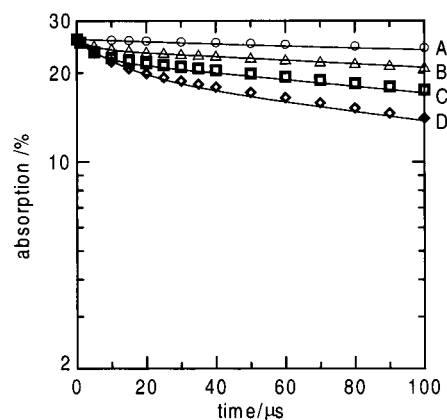
Anthracene molecules are expected to acquire large mobility within the supercage networks of NaY in the presence of water and a few other coadsorbed solvents which possess greater affinity toward the zeolite frameworks than anthracene does. This conclusion was drawn from the decay behavior of triplet-state anthracene. The decay of triplet-state anthracene in the presence of a large quantity of water was well approximated by a single-exponential function with a long lifetime. For example, the decay constant of  $2.6 \times 10^2 \text{ s}^{-1}$  was obtained in NaY in the presence of  $0.30 \text{ mol}\cdot\text{g}^{-1}$  water (Figure 3d). A similar value of the decay constant was measured for anthracene loading levels ranging from  $1.0 \times 10^{-6} \text{ mol}\cdot\text{g}^{-1}$  to  $1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$ . Thus, at anthracene loading levels of  $\leq 1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$ , the triplet decay kinetics can be regarded as the unimolecular process free from bimolecular quenching events under the condition that the zeolite is coadsorbed with a large quantity of water such as  $0.30 \text{ mol}\cdot\text{g}^{-1}$ . This conclusion applies also for the system containing methanol and pyridine. However, at loading levels  $\geq 5.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$ , the faster decays were observed with increasing loading levels of anthracene, suggesting the presence of a concentration quenching by the ground-state species at higher loadings. It turned out that the same process is the major cause of the various triplet decay rates dependent on the quantity of the coadsorbed solvents.

Although the loading level of anthracene was kept constant, the triplet decays were remarkably fast and carried a nonexponential character in the presence of relatively small quantities of the solvents except *n*-hexane as already shown (Figure 2). At first, the triplet quenching by ground-state anthracene was considered unlikely similar with the system with a large quantity of solvent. Besides, the samples were prepared under similar conditions and therefore both the quantity of impurities in the zeolite and the trace amount of oxygen remaining should be similar. Nonetheless, any environmental effect which enhances the unimolecular triplet decay rate, i.e.,  $T_1 \rightarrow S_0$  intersystem crossing rate, is hard to speculate. For instance, we saw exactly the same effect of  $\text{D}_2\text{O}$  on the triplet decay as that of  $\text{H}_2\text{O}$  (Figure 2). Thus no other possibility than concentration quenching can be considered although it has been reported that concentration quenching of triplet-state anthracene takes place with a considerably small rate constant of  $1.1 \times 10^6 \text{ M}^{-1}\cdot\text{s}^{-1}$  in cyclohexane solution at 296 K.<sup>25</sup> We carried out the triplet decay measurement in NaY at further low loading levels of anthracene, and indeed, we observed appreciably slow decay at low loadings compared with that at  $1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$  in the presence of a relatively small amount of water, e.g.,  $0.10 \text{ cm}^3\cdot\text{g}^{-1}$ .<sup>26</sup>

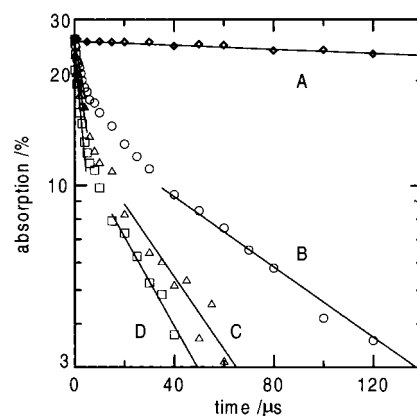
#### Quenching of Triplet-State Anthracene in Hydrated NaY.

We investigated the quenching process of triplet-state anthracene in hydrated NaY to acquire a picture that properly describes the dynamic nature of the host–guest–coadsorbates ternary system. We chose two conditions under which the kinetic behavior of triplet-state anthracene is markedly different:  $0.30 \text{ cm}^3\cdot\text{g}^{-1}$  water in NaY (system A) and  $0.10 \text{ cm}^3\cdot\text{g}^{-1}$  water in NaY (system B).

The decay of triplet-state anthracene was measured in system A at different loading levels of anthracene above  $1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$ , and the decay curves at early time domain are depicted in Figure 4. The decay is represented by nearly a single-exponential function at  $1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$  anthracene. The



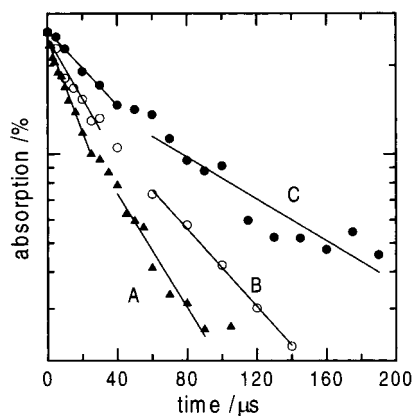
**Figure 4.** Decay curves of triplet-state anthracene in  $0.30 \text{ cm}^3\cdot\text{g}^{-1}$  hydrated NaY at various loading levels of anthracene. Key: A,  $1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$ ; B,  $5.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$ ; C,  $1.0 \times 10^{-4} \text{ mol}\cdot\text{g}^{-1}$ ; D,  $1.5 \times 10^{-4} \text{ mol}\cdot\text{g}^{-1}$ . More reduced laser intensities were employed at higher loadings.



**Figure 5.** Decay curves of triplet-state anthracene in  $0.30 \text{ cm}^3\cdot\text{g}^{-1}$  hydrated NaY at various loading levels of azulene at similar laser intensities. Key: A,  $1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$  anthracene in the absence of azulene; B,  $1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$  anthracene in the presence of  $5.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$  azulene; C,  $1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$  anthracene in the presence of  $1.0 \times 10^{-4} \text{ mol}\cdot\text{g}^{-1}$  azulene; D,  $1.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$  anthracene in the presence of  $1.5 \times 10^{-4} \text{ mol}\cdot\text{g}^{-1}$  azulene.

decay becomes fast with increasing loading levels and can be represented by two components with different decay constants: an initial fast decay is followed by a slow decay. Obviously, the triplet state of anthracene is dynamically quenched by anthracene in the ground state. The result suggests that anthracene within the zeolite is mobile enough to cause the collisional deactivation of triplet state with sufficiently long lifetimes.

We also measured the decay of triplet-state anthracene in system A in the presence of various loading levels of azulene. Azulene is known to induce the quenching of triplet-state anthracene in solution through the triplet–triplet energy-transfer mechanism with a rate constant close to that of the diffusion-controlled reaction ( $k_q = 6.7 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$  in benzene at room temperature<sup>27</sup>). As shown in Figure 5, an increase in the decay rate of the triplet is observed with increasing loading level of azulene. Again the decay in the presence of azulene shows the two-stage behavior: the fast and slow decays. In addition, the decay in the presence of azulene is definitely faster than that in the presence of a similar loading level of anthracene acting as a triplet quencher. A more efficient triplet quenching observed for azulene than for anthracene implies that the mobility of quenchers in the zeolite plays an important role for the



**Figure 6.** Decay curves of triplet-state anthracene in 0.10 cm<sup>3</sup>·g<sup>-1</sup> hydrated NaY at various loading levels of anthracene at constant laser intensities. Key: A, 1.0 × 10<sup>-5</sup> mol·g<sup>-1</sup>; B, 5.0 × 10<sup>-6</sup> mol·g<sup>-1</sup>; C, 1.0 × 10<sup>-6</sup> mol·g<sup>-1</sup>.

quenching because the smaller molecular size than that of anthracene enables azulene to move faster.<sup>28</sup>

In system B with a relatively small amount of coadsorbed water, the triplet decay is significantly fast even at the low loading level of 1.0 × 10<sup>-5</sup> mol·g<sup>-1</sup> anthracene. In this case, we measured the decay of triplet-state anthracene with samples in which the loading level of anthracene is <1.0 × 10<sup>-5</sup> mol·g<sup>-1</sup> to see if the decay becomes slow. Indeed, the slower decay was observed as the anthracene loading is decreased,<sup>29</sup> as shown in Figure 6. The result unequivocally shows that the self-quenching mechanism also applies to this system. The decay is very fast even at a considerably low loading level of anthracene, suggesting that the molecular movement of adsorbed anthracene is surprisingly fast compared with that in the zeolite with a large amount of adsorbed water.

The continuous time random walk (CTRW) model proposed by Barzykin and Tachiya<sup>30</sup> was applied for analyzing the decay curves of the triplet quenching. The model essentially describes the deactivation of static excited probes by randomly walking quenchers within the infinite lattice structures: the probes can be deactivated by the quenchers that visit the sites where the probes are located. This model is also applicable to mobile probes in the limit of low quencher concentration. The advantage of this model over others is that the physical meaning of the parameters is clearly defined enough to visualize the quenching event within zeolite.

Zeolite Y basically consists of a three-dimensional network of nearly spherical supercages of ca. 1.3 nm in diameter connected tetrahedrally through 0.74 nm windows.<sup>31</sup> When the quencher molecules distribute themselves according to the Poisson statistics into the cages, the CTRW theory predicts the time-dependent decay of the excited probes as

$$[T] = [T]_0 \exp(-k_0 t - \bar{n} S(t)) \quad (1)$$

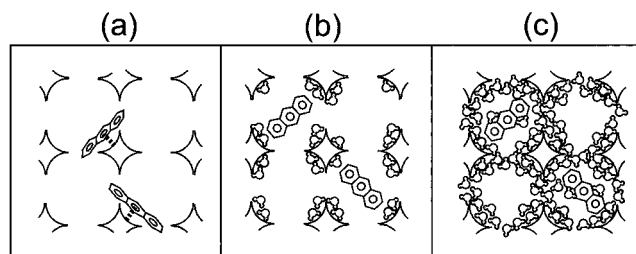
where  $[T]$  denotes the concentration of the triplet probes at time  $t$ ,  $[T]_0$  the concentration of the triplet probes at time zero,  $k_0$  the decay constant in the absence of a quencher,  $\bar{n}$ : a mean occupation number of quencher per supercage ( $\bar{n} = [\text{quencher}]/[\text{cage}]$ ) and  $S(t)$  a time-dependent function, an approximate solution of which will be given in the following. We tentatively assume that the distribution of anthracene in the zeolite cages obeys Poisson statistics. It is pertinent to note that the distribution of Xe atoms in NaA zeolite has been shown with NMR spectroscopy to obey Poissonian statistics for mean occupancies less than about three Xe atoms per  $\alpha$ -cage.<sup>32</sup>

**TABLE 1: Rate Parameters Obtained from Decay Curve Analysis on the Basis of the CTRW Model**

H <sub>2</sub> O/ cm <sup>3</sup> ·g <sup>-1</sup>	quencher	$k_0/\text{s}^{-1}$	$k_q/\text{s}^{-1}$	$k_j/\text{s}^{-1}$
0.10	anthracene	$6.9 \times 10^3 - 1.2 \times 10^4$	$1.5 \times 10^6$	$5.5 \times 10^6$
0.30	anthracene	$3.0 \times 10^3 - 7.0 \times 10^2$ ( $2.6 \times 10^2$ ) <sup>a</sup>	$5.8 \times 10^4$	$2.0 \times 10^4$
0.30	azulene	$3.1 \times 10^3 - 1.5 \times 10^4$ ( $2.6 \times 10^2$ ) <sup>a</sup>	$7.1 \times 10^5$	$2.3 \times 10^5$

<sup>a</sup> The value observed at the loading level of 1.0 × 10<sup>-5</sup> mol·g<sup>-1</sup> anthracene.

**CHART 1: Pictorial Representation of Anthracene Adsorbed in (a) Dehydrated NaY, (b) 0.10 cm<sup>3</sup>·g<sup>-1</sup> Hydrated (8 Water/Cage) NaY, and (c) 0.30 cm<sup>3</sup>·g<sup>-1</sup> Hydrated (26 Water/Cage) NaY**



When the short-time decay behavior and the long-time behavior is well-separated, eq 1 can be approximated by

$$[T] \approx [T]_0 \exp(-k_0 t - \bar{n} k_q t) \quad \text{for } t \rightarrow 0 \quad (2)$$

$$[T] \sim \exp\left(-k_0 t - \bar{n} \frac{k_j k_q}{k_j + u_0 k_q} t\right) \quad \text{for } t \rightarrow \infty \quad (3)$$

where  $k_j$  represents a the total jump frequency (s<sup>-1</sup>), i.e., the sum of the jump frequencies of the probe and the quencher between the nearest neighboring cages (double jump frequency in the case of self-quenching),  $k_q$  the first-order quenching rate constant within the same cage, and  $u_0$  a constant associated with the lattice structure ( $u_0 = 1.79$  for the diamond lattice<sup>33</sup>). The experimental decay curves (Figures 4–6) were fitted using eq 2 for the fast decaying part and eq 3 for the slow part of the decays because the two-stage time-dependent decay patterns were always observed.

The values of the rate parameters  $k_0$ ,  $k_j$ , and  $k_q$  thus evaluated are listed in Table 1. We mentioned earlier that the mobility of guest aromatic species within the zeolite is a decisive factor for the observation of the triplet quenching. The mobility responsible for the quenching has two aspects: one representing a movement within the supercage stands for  $k_q$  and the other representing a movement between the cages corresponds to  $k_j$ . The  $k_q$  value is a measure of the efficiency of the quenching of a triplet probe by one quencher molecule within the supercages while the value of  $k_j$  is a measure of the migration rate of the molecules from one cage to one of the nearest neighboring cages. The 2 orders of magnitude larger values of both  $k_q$  and  $k_j$  were obtained in system B (0.10 cm<sup>3</sup>·g<sup>-1</sup>) than in system A (0.30 cm<sup>3</sup>·g<sup>-1</sup>). The rate parameters lead to the following picture that envisages the state of adsorption and the movement of guest molecules in the zeolite at the different hydration levels (see Chart 1).

When the amount of water is as small as 0.10 cm<sup>3</sup>·g<sup>-1</sup>, an average occupation number of water molecules per supercage is estimated to be 8. One supercage has four type II Na<sup>+</sup> cationic sites acting as the primary sites of adsorption for aromatic species such as anthracene. Water molecules are likely to be



attracted in the first place by the cationic sites which is a representative Lewis acid site within the zeolite, and the introduction of water of 8 molecules per supercage can be sufficient for blocking the type II sites, leading to the liberation of anthracene adsorbed. This process was easily monitored by the sharpening of the vibrational fine structure in the fluorescence spectrum of anthracene with increasing quantity of water.<sup>24</sup> Thus, when the amount of water adsorbed is small, the four windows connecting supercages are wide open. This enables the smooth passage of the guest molecules.

On the contrary, at the loading level of coadsorbed water molecules of  $0.30 \text{ cm}^3 \cdot \text{g}^{-1}$ , which is equivalent to 26 water molecules per supercage, the free volume within the cages is expected to be significantly small and the windows connecting supercages are possibly blocked by the water molecules. The significantly reduced rates of both  $k_q$  and  $k_j$  suggest that the intra-cage reorientational motion as well as the translational motion of anthracene is severely hindered in this case. Interestingly, the reduced free volume within the supercage does not lead to an increased rate of intra-cage quenching. This suggests that the water molecules serve as an obstacle to the motion of anthracene within the same cage.

It has been suggested<sup>34</sup> that water molecules adsorbed on the surface of microporous materials can be characterized by a certain ordered structure different from that of bulk liquid due to the adsorption interaction with the surface. By analogy, we assume that the water molecules are regarded as possessing the nature of the ordered surface water when the zeolite is adsorbed with water in small quantities as to just cover the zeolite surface. On the other hand, a large portion of them is characterized by a bulk fluidlike nature when the zeolite is adsorbed with water in large quantities close to filling the pore volume. We assume that the former enhances the movement of anthracene by reducing the guest–zeolite interaction whereas the latter hinders anthracene from moving quickly.

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$$T(t) = T_0(A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2})$$
 where  $T(t)$  is the absorption intensity at time  $t$ ,  $T_0$  is the absorption intensity at time 0,  $A_1$  is the amplitude of a component with lifetime  $\tau_1$ , and  $A_2$  is the amplitude of a component with lifetime  $\tau_2$ . Thus the average lifetime was represented by
 
$$\bar{\tau} = \frac{A_1}{A_1 + A_2} \tau_1 + \frac{A_2}{A_1 + A_2} \tau_2$$
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