Ultrafast Dynamics of Pyrene Excimer Formation in Y Zeolites

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Pyrene excimer emission in alkali-metal-exchanged zeolites is readily observed to grow in using an ultrafast streak camera with 3.3 ps time-resolution. Rise-time constants range from 7 to 14 ps depending on the composition of the zeolite. These results show that two pyrene molecules in doubly occupied cavities must move from their pre-excitation orientation into the face-to-face orientation required for the excimer.

The photophysical properties of pyrene have been used in numerous studies to examine the microenvironment within the supercage interior of faujasite zeolites. This includes examining both the structured emission from the pyrene monomer between 375 and 420 nm and the broad, featureless excimer emission between 400 and 550 nm.[1−5] One aspect of the photophysics of zeolite-incorporated pyrene that has not yet been fully investigated is the nature of the formation of the excimer. In particular, attempts have been made using fast pulsed laser excitation to resolve the rise time of excimer emission,[6−11] which would show that the two pyrene molecules within doubly occupied zeolite cavities[6−10] must rearrange after absorption of light into the orientation required for excimer formation. However, although results from some studies suggest that excimer emission is not instantaneous,[10,11] the fast rise time of pyrene excimer emission has not been resolved. We have now examined pyrene emission using an ultrafast streak camera, and show that excimer formation can be fully resolved and that excimer formation is sensitive to the composition of the zeolite.

Faujasite zeolites are aluminosilicate materials with an open framework structure[12,13] composed of linked SiO_4^{4-} and AlO_4^{5-} tetrahedra arranged into sodalite cages.[14−17] The sodalite cages form the framework structure of large, spherical supercages that are linked in a tetrahedral arrangement via 7.4 Å pores. Pyrene can be readily incorporated into the supercages (13 Å diameter) where they can interact with the walls or the charge balancing cations located throughout the lattice.[7,9,18,19] Up to two pyrene molecules can be accommodated within one supercage, and intercavity movement is slow, on the order of 100 s.[10]

Emission produced upon pulsed irradiation of pyrene with 388 nm laser light[20] was monitored at both 500 and 420 nm. The emission at 500 nm is due exclusively to emission from the pyrene excimer, whereas that at 420 nm is primarily from excited monomer. As shown in Figure 1, the time-dependent profiles of the emission at these two wavelengths are considerably different. At 420 nm, the maximum emission intensity is almost fully formed promptly within the 3.3 ps time resolution of the streak camera. On the other hand, the 500 nm emission from the excited dimer shows *no prompt formation*. Instead, this emission develops in a first-order manner over a time period of approximately 20 ps that is considerably longer than the time resolution of the streak camera.

Rise time information can be extracted from the collected time trace at 500 nm by non-linear fitting techniques with
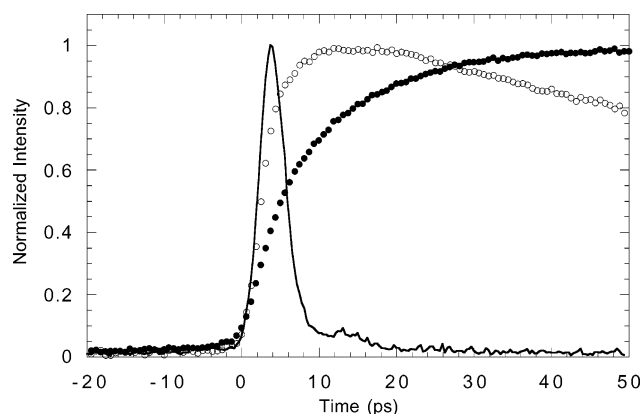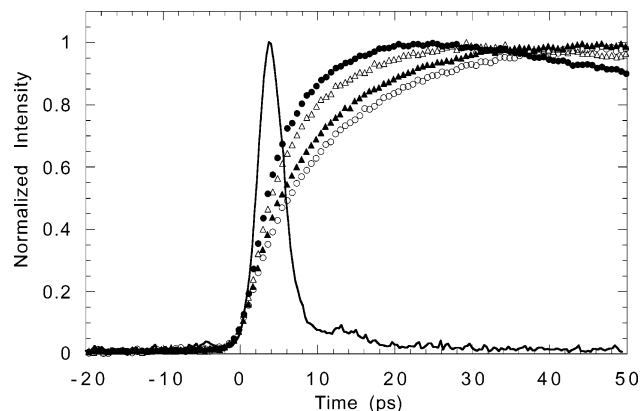
Figure 1. Rise-time traces for pyrene monomer emission at 420 nm (○) and excimer emission at 500 nm (●) obtained upon 388 nm femtosecond laser irradiation of pyrene incorporated in NaY under N_2. Every second data point is plotted. The figure also includes the instrument response function (—).

reconvolution. Using this treatment, the growth rate constant of excimer emission at 500 nm in NaY is 7.24×10^{10} s^{-1}, which corresponds to a rise time of 13.8 ps.[21] A time constant slightly longer than the time resolution of the streak camera was determined for the rise time at 420 nm. Prompt formation (within the laser pulse) of the monomer is expected. The observed non-instantaneous growth is due to slight contamination of the prompt monomer emission by the excimer band.

To further establish the veracity of the rise times measured in the dry NaY zeolites as being due to excimer formation, experiments were carried out in NaY containing varying amounts of two polar solvents, water and methanol. These solvents should affect the dynamics of excimer formation by modulating the ability of individual pyrene molecules to reorient within a zeolite cavity (vide infra). As shown in Figure 2, increasing methanol content from 2 to 20 methanol molecules/ cavity did indeed cause a change in excimer emission rise time, with the rise time decreasing from 13.8 ps in the absence of methanol to 7.9 ps upon the addition of 20 methanol molecules/ cavity. The addition of water also had a significant effect by reducing the excimer rise time from 13.8 ps in NaY in the absence of water to 10.6 ps upon the addition of 20 water molecules/cavity.

Excimer rise times were also observed in other alkali metal cation exchanged zeolites, LiY and KY, Table 1. These rise times exhibited trends upon the addition of methanol and water

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Figure 2. Rise-time traces for pyrene excimer emission at 500 nm obtained up 388 nm femtosecond laser irradiation of pyrene incorporated in NaY upon the addition of 2 (○), 5 (▲), 15 (△), and 20 (●) methanol molecules per cavity under dry nitrogen conditions. Every second data point is plotted. The figure also includes the instrument response function (—).

TABLE 1: Pyrene Excimer Emission Rise Times, τ (ps), Obtained upon 388 nm Femtosecond Laser Irradiation of Pyrene within Three Zeolites under Dry Conditions and as a Function of Cosolvent Incorporation (20 Molecules/Cavity)

	τ (ps)		
zeolite	dry	methanol	water
LiY	8.9	6.8	7.0
NaY	13.8	7.9	10.6
KY	11.0	9.7	7.5

similar to those observed in NaY. However, the rise times in dry LiY and dry KY were substantially shorter than those in NaY, suggesting that the nature of the cation has a significant influence on the dynamic process responsible for the formation of the excimer.

Because pyrene excimers within zeolites are only formed in doubly occupied supercages,[6–10] the prior inability of researchers to observe time-resolved excimer formation in previous studies led to the argument that pyrene exists as a ground state dimer within a doubly occupied supercage.[6,7,11,19] However, if this ground state dimer existed with the same structure as the excimer, excimer formation would be complete promptly within the laser pulse. The resulting rise time for the excimer emission would therefore appear to be instantaneous and identical to the prompt rise time for the fluorescence of the pyrene monomer. Our results therefore provide strong evidence that excimer formation is a dynamic process that involves initial excitation of a single pyrene molecule within a doubly occupied supercage, followed by reorientation of the excited and ground state pyrene monomers to give the emissive excimer. This reorientation requires the disruption of forces that hold the pyrene molecules in place within the zeolite cavities, such as π-cation interactions between the cations and the aromatic rings of pyrene, which ultimately renders excimer formation measurable on the early picosecond time scale.

This analysis is consistent with effect of polar solvents on the dynamics of excimer emission. Polar solvents are known to preferentially bind to alkali metal cations within zeolite cavities.[19,22–24] This would disrupt the π-cation interactions that exist between the pyrene and the intracavity cations, thus allowing the pyrene molecules to more easily adopt the orientation required for excimer formation. Similarly, in the absence of a polar solvent, binding between K^+ and pyrene would be expected to be weaker than that between Na^+ and pyrene.[25–31] Pyrene in KY would therefore be more mobile and

would have a greater ability to reorient as required for excimer formation. Binding of pyrene with Li^+ should be stronger than with Na^+, but the small size of Li^+ and its placement within the cavity walls presumably diminishes the strength of its interaction with the pyrene relative to the larger Na^+.

In summary, we have shown for the first time that intracavity excimer formation in Y zeolites does not occur simultaneously with the laser pulse but instead occurs over a time period of approximately 20 ps. This indicates that pyrene molecules in doubly occupied cavities are not present as ground-state dimers with the correct orientation for excimer formation: the two pyrene molecules must move from their pre-excitation orientation into the face-to-face orientation required for the excimer.

Supporting Information Available: Procedure for preparation of pyrene-zeolites samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Time-resolved luminescence measurements were performed using a Clark-MXR CPA-2001 laser (<150 fs, 775 nm pulses at 1 kHz, 800µJ per pulse) for sample excitation and a streak camera (Axis-Photonique) coupled to a CCD camera (SenSYS) for detection. The pulses are split by a beamsplitter; one of the pulses is frequency-doubled to 388 nm for sample excitation and the unchanged fundamental is used to trigger the G2 Jitter-Free Trigger Unit (Axis-Photonique). Front face excitation of the sample produced emission that was collimated and focused into the streak camera through the appropriate band-pass filter (420 ± 5 or 500 ± 12.5 nm).

(21) The error in rise times due to sample reproducibility is estimated to be 1 ps by comparing data from repeated trials.

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