

## Intrazeolite Photochemistry. 23. Transparent PDMS Films of Zeolites Incorporating Organic Guests: Quantitative Determination of Photophysical Parameters by Transmission Techniques

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*Received: February 16, 1998; In Final Form: July 13, 1998*

Zeolites containing embedded organics have been made into transparent films. These new materials have interesting properties that allow the measurement and quantification of optical and photophysical properties of the guest molecules that are either unattainable using current diffuse reflectance techniques or significantly less quantitative. These include the determination of the ground-state extinction coefficients and the quantum yield of triplet formation. It was determined that within experimental error, the values of the photophysical parameters of the guest molecules included within the zeolite are very similar to those measured in solution. This indicates that in the cases under consideration, incorporation of an organic molecule or cation into the zeolite pores does not significantly alter its molecular properties with respect to those in nonrigid media. These transparent films open the possibility of determining the extinction coefficient of cations that are not persistent in solution but can be formed within the zeolite pores. Further technical applications of these films, which show remarkable stability and fatigue resistance, can also be anticipated.

### Introduction

Incorporation of organic species within the micropores of zeolites and related solids such as clays or silicas has become a powerful methodology to gain control of the selectivity of photochemical reactions.<sup>1–8</sup> Up to now, photophysical studies on the resulting opaque powders have been possible by making use of diffuse reflectance or front-face excitation techniques instead of the transmission setup routinely employed for solution work. In this regard, time-resolved diffuse reflectance laser flash photolysis was a significant breakthrough in this area, because it allowed for the detection of short-lived (from the picosecond to the millisecond time scale) reaction intermediates in solid media, as well as the monitoring of their kinetics.<sup>9–11</sup> However, despite the valuable information provided by diffuse reflectance techniques, quantification of extinction coefficients and quantum yield measurements in this mode is difficult because of the nonlinear relationship between concentration and response intensities.

In this paper we report that by dispersing the zeolite opaque powder containing encapsulated organic chromophores into a poly(dimethylsiloxane) (PDMS) matrix, it has been possible to prepare transparent films. This is the first time that organic-embedded zeolite films have been made, and this novel type of material opens up exciting new possibilities for further applications that have been limited up to now by the lack of transparency of the powders, and the low mechanical resistance of self-supported wafers of zeolites. The resulting PDMS films containing doped zeolites are totally transparent in the UV–vis region down to 220 nm and have exceedingly good shaping and mechanical strength properties provided by the PDMS backbone. The new properties of the resulting composite can be readily applied to the development of electronic devices and

chemical sensors through the control of the molecular and photophysical properties of the guest that is exerted by incorporation in zeolites. The objective of this report is to show that these films can be characterized using transmission spectroscopy. This ultimately allows for the quantification of photophysical properties of the organic embedded in zeolite pores that cannot be measured using current diffuse reflectance techniques. A significant consequence of this quantification, which involves measurements such as extinction coefficients and quantum yields, is that a direct comparison of the properties of organic dyes in solution to those included within zeolites can now be made. Further, this new approach is less prone to detection problems caused by scattered light, which are very common with reflectance techniques. We anticipate that other spectroscopic techniques, such as circular dichroism, will be readily applicable in these films.

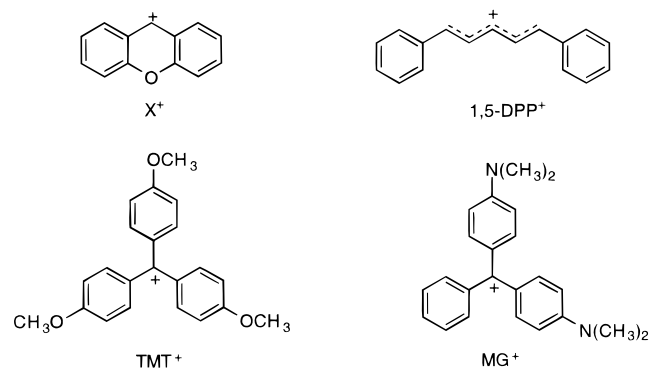
Although it has recently been reported that “empty” zeolites (zeolites that do not contain a guest molecule) can be dispersed into poly(dimethylsiloxane) (PDMS) or polyimide (PI) polymers forming a transparent film,<sup>12,13</sup> we have found no reports of using organic-embedded zeolites as the doping materials for these polymers. Whereas the “empty” zeolite films have been applied to controlling the transit of hydrocarbons or ethanol/water vapors across the membranes, we thought that organic-embedded zeolite films may have many other potential applications. What makes these materials so attractive to study is the fact that PDMS polymers do not contain any chromophore that could interfere in the UV–vis region, making them ideal materials for measuring and quantifying photophysical properties. In addition, the methylsiloxane backbone of the PDMS polymer provides a highly apolar surrounding for the dispersed zeolite particles, which may further protect the guest organic molecule from oxygen.

The films we have chosen to prepare contain organic-embedded zeolites that we have previously characterized in the

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## CHART 1



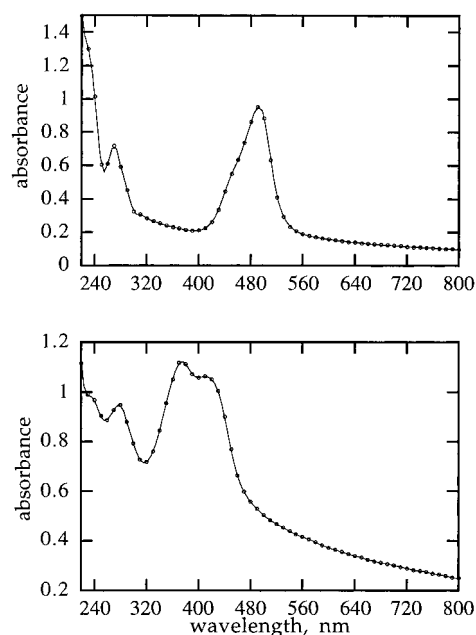
solid state using diffuse reflectance techniques. The organic cations that have been generated are shown in Chart 1. They have been prepared by functional group transformation of a convenient precursor into an acidic zeolite or through a more elaborate synthetic route that involves new C—C bond formation (ship-in-a-bottle synthesis)<sup>3</sup> when the size of the corresponding cation is larger than the window diameter of the faujasite supercage. We have shown that these organic cations trapped within the voids of zeolites are persistent cations and are stable due to the electrostatic field experienced within the zeolite as well as by the geometrical restraints imposed by the zeolite lattice.<sup>5,14,15</sup> This stability makes them ideal candidates for initial preparation and study of zeolite films. In this report, we will directly compare the ground state transient absorption and fluorescence spectra of the opaque zeolite solids to those of their corresponding transparent film. For all of the film samples, we have measured the extinction coefficient of the included dye, and we have also prepared a film of xanthone included in zeolite NaY for the purpose of calculating the quantum yield of triplet formation. These values, along with those obtained in solution, are discussed.

## Experimental Section

**Membrane Preparation.** The PDMS silicone (RTV 615) was obtained from GE Silicones. Hexane (Omnisolv grade) was purchased from VWR Scientific and dried over molecular sieves prior to use. In a typical preparation of zeolite films, 1 g of RTV 615A with 30–70 mg of the zeolite included complex and 1 g of dry hexane were sonicated for a period of 6 h. Then 100 mg of RTV 615B was added, and the mixture was sonicated for an additional 20 min. This mixture was cast onto a glass plate and heated at 60 °C overnight. Typically, film thicknesses range from 20 to 30  $\mu\text{m}$  from sample to sample and have zeolite loadings of less than 15% (w/w). The dye loading in the zeolite is approximately 5% based on composite weight, leading to a dye loading in the membrane of less than 1%. All films are air saturated. A zeolite/PDMS film of about 30  $\mu\text{m}$  thickness has an appearance similar to that of an overhead transparency, with a somewhat more rubbery texture. Films in the 1–2  $\mu\text{m}$  range have also been prepared by spin-coating on quartz disks, although these films are not the subject of the current report. The zeolite inclusion cations were prepared as described previously.<sup>5,14,15</sup>

Emission spectra were recorded with a Perkin-Elmer LS-50 spectrofluorimeter. Absorption spectra were measured with an HP 8451A photodiode array spectrometer.

The laser system consists of an Nd:YAG Surelite laser from Continuum for the 355 nm wavelength and a Lumonics EX-530 excimer laser for the 308 nm wavelength. All pulse



**Figure 1.** Ground-state absorption spectra of a PDMS film containing TMT<sup>+</sup>/HY. Composition of film: 30 mg of TMT<sup>+</sup>/HY (5% TMT<sup>+</sup> loading) in 1 g of polymer (top spectrum) and 40 mg of X<sup>+</sup>/HZSM5 (5% X<sup>+</sup> loading) in 1 g of polymer (bottom spectrum).

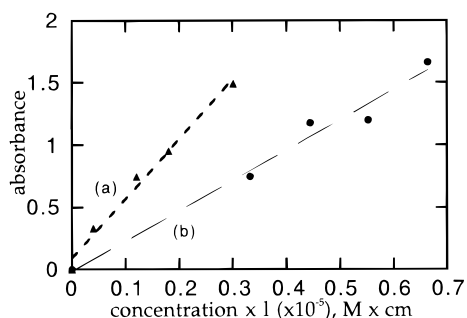
durations are less than 10 ns and typical pulse energies lie between 5 and 50 mJ. The signals from the monochromator/photomultiplier system are initially captured by a Tektronix 2440 digitizer and transferred to a PowerMacintosh computer that controls the experiment with software developed in the LabVIEW 3.1.1 environment from National Instruments.<sup>16,17</sup> Front-face excitation was used, with the film sample holder consisting of a stepping motor, which moves the film after each laser shot to ensure a fresh part of the sample is being irradiated.

The quantum yield for intersystem crossing was measured by matching the absorbance from xanthone encapsulated within NaY dispersed in a PDMS film with that of xanthone located on the outer surface of hydrated NaY also dispersed in a PDMS film. The NaY used for the latter sample was purposely not calcined prior to use to ensure that all of the xanthone remains on the outer surface. The zeolite was used in both film samples so that the xanthone molecule receives an equal laser dose. For this measurement, the film samples were prepared on the interior walls of a 3 mm  $\times$  7 mm quartz cell.

To determine how accessible gases are to the organic-encapsulated zeolite dispersed in a PDMS film, a NaY/xanthone film was prepared and placed in a quartz cell. This was subsequently purged with nitrogen for 1 h followed by oxygen purging for specified periods of time. This study was done with freshly prepared film samples as well as with those that had been aged for several months. The decay traces of the nitrogen- and oxygen-purged samples were monitored at 600 nm, where triplet xanthone absorbs. Triplet xanthone was used as the probe in this study, since it is known to be quenched by oxygen.

## Results and Discussion

**Measurement of Extinction Coefficients.** Transmission spectroscopy has been used to measure the absorption spectra of the organic molecules embedded inside the zeolite micropores using transparent zeolite films. Some of the spectra obtained are shown in Figure 1. The measurements were carried out by preparing film samples of a known area and thickness with



**Figure 2.** Determination of  $\epsilon$  for organic cation-included zeolites dispersed within a PDMS film: (a)  $\text{MG}^+/\text{HY}$  and (b)  $\text{X}^+/\text{HZSM5}$ . See text for description of method used to obtain  $\epsilon$  values.

varying amounts of organic guest. The value of  $\epsilon$  was determined as follows. From the Beer–Lambert equation, the path length,  $l$ , is equal to the film thickness. The concentration of the dye in the film, which is equal to the number of moles divided by the film volume (area of film  $\times$  thickness), is substituted into the Beer–Lambert equation. This yields an expression where a plot of the absorbance versus the number of moles of guest divided by the area of the film yields a slope  $\epsilon$ . The linearity of these plots for all of the samples studied is in accordance with the Beer–Lambert law as can be seen in Figure 2 for  $\text{MG}^+/\text{HY}$  and for  $\text{X}^+/\text{HZSM5}$ . A linear relationship between the thickness of the film and its absorption in the UV–vis spectrum has also been observed. A comparison of the log  $\epsilon$  values obtained for the organic cations in solution and those embedded in the zeolite films shows that they are identical within experimental error. The similarity between the extinction coefficients measured in solution and those measured in the zeolite films is noteworthy. This indicates that in the case of the zeolite/PDMS composites, we are measuring a physical property that is intrinsic to the organic chromophore and is not significantly affected by the optical properties of the composite. In addition, the fact that the spectra and extinction coefficients remain much the same as those in solution can be interpreted as meaning that in the examples under consideration, the frontier molecular orbitals of the guest as well as its preferred conformation are not significantly altered by the geometrical restraints due to the incorporation inside the zeolite voids. Conversely, our zeolite film technique can be used to obtain the extinction coefficient of organic species that can be prepared inside the zeolite micropores but are not persistent enough in homogeneous solution.

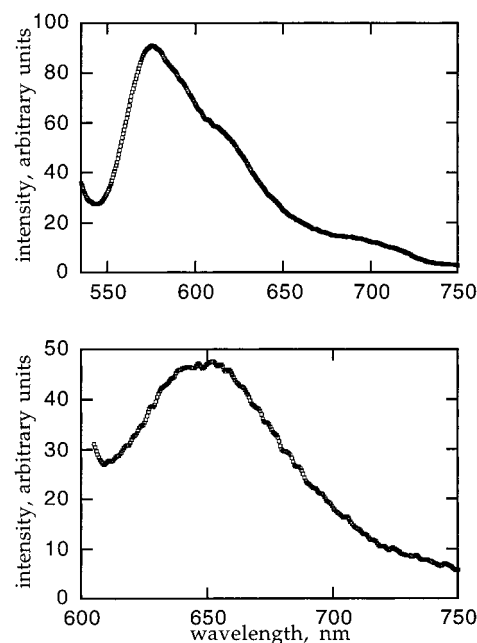
Attempts to prepare transparent zeolite films by pressing the zeolite powders (normal particle size from 0.1 to 2  $\mu\text{m}$ ) between 1 and 5  $\text{Ton cm}^{-2}$  were found to be unsuccessful in producing films that were sufficiently transparent for optical spectroscopy. Only very recently, it has been reported that special large crystals of NaY of 40  $\mu\text{m}$  can be packed into transparent layers suited for transmission absorption spectroscopy.<sup>18</sup> However, this method has only a very limited practical application because the usual crystal size of the zeolites synthesized by common hydrothermal procedures (including commercial samples) is much smaller than 1  $\mu\text{m}$ . By dispersing zeolite powder in a PDMS polymer, we have been able to prepare sufficiently transparent materials, regardless of the particle size of the crystals. The resulting zeolite/PDMS membranes have excellent mechanical properties compared to compressed, crispy wafers and can be handled without additional precautions.

**Fluorescence Spectroscopy.** The steady-state fluorescence spectra of the film samples was also recorded. The emission  $\lambda_{\text{max}}$  obtained when comparing the opaque solid zeolite powder

**TABLE 1: Fluorescence Data for Solid Zeolite<sup>a</sup> and Zeolite Film Samples<sup>b</sup>**

	solid $\lambda_{\text{max}}$ (nm)	film $\lambda_{\text{max}}$ (nm)
1,5-DPP <sup>+</sup> /HZSM5	575, 615 (sh)	575, 615 (sh)
TMT <sup>+</sup> /HY	570	570
MG <sup>+</sup> /HY	620	640
X <sup>+</sup> /HZSM5	495, 520	495, 520

<sup>a</sup> Data taken from previous work.<sup>5,14,15</sup> <sup>b</sup> For the film samples, the loading of the dye is 5% and the zeolite loading in the polymer is 15%.



**Figure 3.** Fluorescence spectra of PDMS film containing 1,5-DPP<sup>+</sup>/HZSM5 obtained using a  $\lambda_{\text{ex}}$  of 515 nm (top) and one containing MG<sup>+</sup>/HY obtained using a  $\lambda_{\text{ex}}$  of 590 nm (bottom). For both films, the loading of the organic in the zeolite is 5% and the zeolite loading in the polymer is 15%.

to the transparent film sample matched very well. A comparison of these values is presented in Table 1. The fluorescence spectra obtained for the 1,5-DPP<sup>+</sup>/HZSM5 and MG<sup>+</sup>/HY films are shown in Figure 3. Included in the Supporting Information are the fluorescence spectra for X<sup>+</sup>/HZSM5 and TMT<sup>+</sup>/HY.

**Laser Flash Photolysis.** A zeolite film containing xanthone encapsulated within the zeolite voids was also prepared, and its transient absorption was monitored. Xanthone was chosen as our standard probe molecule for two reasons. One is that xanthone has frequently been used as a standard molecule to calibrate photophysical parameters.<sup>19</sup> In addition, it has been well established that the xanthone triplet excited state is a highly sensitive probe to report on the polarity and other characteristics of the medium.<sup>16</sup> We used the NaY/xanthone film to measure the accessibility of small gases through the film membrane as well as to calculate the quantum yield for ISC ( $\Phi_{\text{ISC}}$ ); both are discussed below. The triplet absorption of xanthone in the NaY/xanthone film occurs at  $\sim 600$  nm, which is comparable to that observed for the opaque NaY/xanthone solid.<sup>20</sup>

To determine the quantum yield of triplet formation ( $\Phi_{\text{ISC}}$ ), we prepared two film samples containing both xanthone and NaY. The NaY used in the control sample was not calcined prior to use to ensure that the xanthone is located on the outer surface. It has been previously reported that the incorporation of an organic guest in the supercages of faujasite zeolites that are saturated with water is simply not possible and that the guest

**TABLE 2: Comparison of Transient Absorption  $\lambda_{\text{max}}$  and Rate Constants for Solid Zeolite<sup>a</sup> and Zeolite Film Samples**

	solid		film	
	$\lambda_{\text{max}}$ , nm	$k_{\text{obs}}$ (s <sup>-1</sup> )	$\lambda_{\text{max}}$ , nm	$k_{\text{obs}}$ (s <sup>-1</sup> )
1,5-DPP <sup>+</sup> /HZSM5	610 (triplet)	10 <sup>4</sup>	610, (triplet), 550 (bleaching)	~10 <sup>3</sup>
TMT <sup>+</sup> /HY	380, 440, 640 (triplet), 500 (bleaching)	2 × 10 <sup>4</sup>	370, 410, 520–640, 490 (bleaching)	1 × 10 <sup>4</sup>
MG <sup>+</sup> /HY	480, 530 (triplet)	1.2 × 10 <sup>4</sup>	470, 530 (sh), 610 (bleaching)	4 × 10 <sup>3</sup>
X <sup>+</sup> /HZSM5	300, 520–570 (triplet), 340 (radical), 370 (bleaching)	2 × 10 <sup>4</sup>	300 (triplet), 330 (radical), 375 (bleaching)	3 × 10 <sup>3</sup>

<sup>a</sup> Data taken from previous work.<sup>5,14,15</sup>

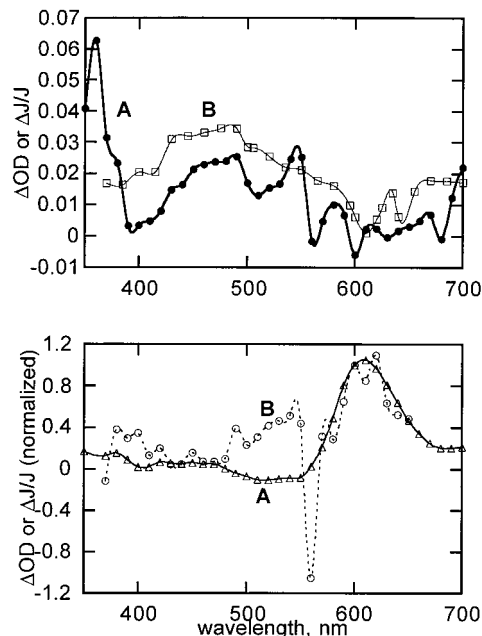
molecule is located on the exterior surface.<sup>21</sup> The second sample has xanthone incorporated within the zeolite. In both film samples, there is an equal amount of xanthone and zeolite. This was done so as to keep the physical properties, such as the refractive index, similar in both samples. Thus, any differences that may be seen in the amount of triplet formation would be a true reflection of the photophysical properties of the organic guest and not simply due to differences in sample content.

The xanthone triplet was monitored at 600 nm. Assuming that the extinction coefficient of the T–T absorption of the xanthone triplet is the same on the zeolite exterior and inside the zeolite cavities, which is a reasonable assumption based on our earlier results (*vide supra*), then our result establishes that  $\Phi_{\text{ISC}}$  is also the same within experimental error. This indicates again that  $\Phi_{\text{ISC}}$  of xanthone is not influenced significantly by its confinement within the large cavities of the Y zeolite.

Dispersion of zeolites (not containing any organic chromophore) into PDMS membranes has been used to control the traffic of vapors across the film, depending on the polarity of the individual components in the gas phase.<sup>12,13,22</sup> We wanted to establish whether the apolar threads of the PDMS polymer backbone effectively impede the accessibility of small gases to the target organic molecule immobilized inside the zeolite cavities. To test the permeability of the membrane/zeolite composite, a sample of a NaY/xanthone film was purged with nitrogen for at least 1 h. After this time, we detected the long-lived ( $t_{1/2} = 50 \mu\text{s}$ ) triplet of xanthone with a  $\lambda_{\text{max}}$  of ~590 nm, characteristic of zeolite inclusion. Purging with oxygen for 1 h led to partial quenching, with a weaker signal detected (~50%) and a minor reduction in triplet lifetime; this time should be adequate for full equilibration of the PDMS film. Work carried out over several days suggested that these qualitative observations were reproducible. The film was reexamined about 4 months later, and interestingly, the triplet of xanthone was completely quenched by oxygen purging, to the point that essentially no signal was detected. Under nitrogen, the film showed  $\lambda_{\text{max}} \sim 605 \text{ nm}$ . Combined, these observations imply that while the zeolite-containing films are stable over short periods (days), guest migration from the zeolite cavities to the polymeric matrix occurs over extended storage at room temperature. Such migration is probably strongly dependent upon the size of the guest as well as on its charge, since samples containing the cationic guests (see Chart 1), which are highly stabilized by the electrostatic field within the zeolite, appear stable over a similar period of time.

The spectroscopic and photophysical data of the solid zeolite samples using diffuse reflectance techniques and of the film samples using transmission techniques are compared and reported in Table 2.

As shown in Table 2, there is a very good correlation between the  $\lambda_{\text{max}}$  obtained in the transmission and diffuse reflectance transient absorption spectra. This is illustrated in Figure 4 for the MG<sup>+</sup>/HY and the 1,5-DPP<sup>+</sup>/HZSM5 samples. However, for some of the samples, there is a change in the relative intensity of the transient absorption peaks. In the case of X<sup>+</sup>/HZSM5,

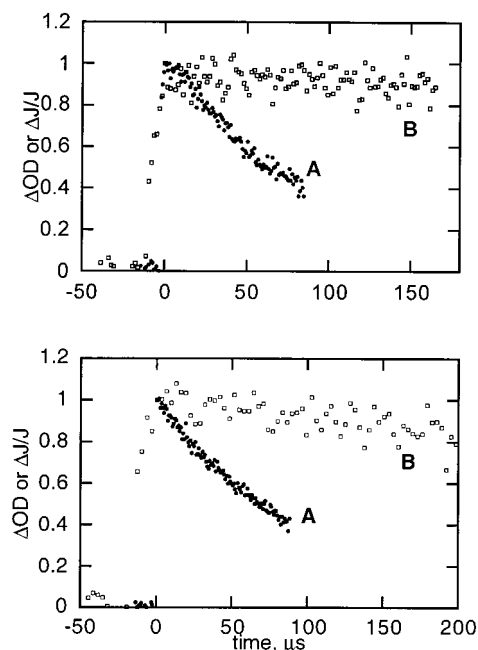


**Figure 4.** Transient absorption spectra for MG<sup>+</sup>/HY in (A) the solid state, 1  $\mu\text{s}$  after the laser pulse, and (B) transparent film, 24  $\mu\text{s}$  after the laser pulse (top). Excitation wavelength in both cases is 355 nm. Transient absorption spectra for 1,5-DPP<sup>+</sup>/HZSM5 in (A) the solid state, 6.4  $\mu\text{s}$  after the laser pulse, and (B) transparent film, 12  $\mu\text{s}$  after the laser pulse (bottom). The excitation wavelength for the solid is 355 nm and for the film is 308 nm. For both films, the loading of the organic in the zeolite is 5%. For MG<sup>+</sup>/HY, the zeolite loading in the polymer is 6%, and for 1,5-DPP<sup>+</sup>/HZSM5, this value is 15%.

the absorption in the 500 nm region is very weak in the transparent film compared to that observed in the opaque solid powder. A similar observation was already noted when comparing transient spectra for the same species in solution (transmission) and in zeolite powder (diffuse reflectance). For example, there is very weak absorption in the 540 nm region that has been reported for the triplet state of substituted X<sup>+</sup> in homogeneous solution.<sup>23</sup> In the case of TMT<sup>+</sup>/HY, there is also a weaker absorption in the longer wavelength region. Oxygen is known to quench the long wavelength band in the solid form. This band has been ascribed to the triplet, which may explain the weak bands seen in the air-saturated film samples. The transient absorption spectra of the film samples not shown in the figures are given in the Supporting Information.

Each of these film samples shows a bleaching effect corresponding to ground-state depletion. For the X<sup>+</sup>/HZSM5 and TMT<sup>+</sup>/HY samples, bleaching was recorded using indistinctly diffuse reflectance (for powders) or transmission (for films). However, in the case of MG<sup>+</sup>/HY and 1,5-DPP<sup>+</sup>/HZSM5, it was not possible to observe the bleaching in the diffuse reflectance mode, while it was readily recorded for the zeolite films in transmission mode. For the MG<sup>+</sup>/HY film, the bleaching is not as pronounced as it is in the case of the 1,5-DPP<sup>+</sup>/HZSM5 film, due to the transient absorbing in this region as well. The disappearance of the ground-state absorption bands





**Figure 5.** Normalized transient decay trace in (A) a solid zeolite sample and (B) a transparent zeolite film for (top)  $\text{MG}^+/\text{HY}$  monitored at 500 nm and (bottom)  $1,5\text{-DPP}^+/\text{HZSM5}$  monitored at 600 nm. Note that the lifetime of the transient in the film sample is considerably longer compared to the solid-state sample. The film compositions are the same as those stated in Figure 4.

has to occur during the laser pulse, and it has to be considered instantaneous in our time scale. The differences seen in the amount of bleaching in diffuse reflectance and transmission modes for these highly colored ground-state species may in fact be due to limitations of the diffuse reflectance setup. For each zeolite/PDMS film, the recovery of the bleaching correlates with the decay of the excited states.

Even though the transient spectra in diffuse reflectance and transmission modes were very similar, some differences in the kinetics were noticed. Thus, an effect that is observed for all of the cation-included zeolite film samples is that the traces do not decay back to their preexcitation level. This indicates that there is a residual population of transients that persists longer than the time scale monitored in a nanosecond laser flash experiment. In fact, the decay profiles of the transient absorptions for dyes incorporated in zeolite/PDMS films are in some cases even slower than those recorded by diffuse reflectance for the powders. This is more clearly seen when comparing the decay traces obtained for the transients in the solid zeolite complex and in the transparent zeolite film. This comparison is shown in Figure 5 for  $\text{MG}^+/\text{HY}$  and for  $1,5\text{-DPP}^+/\text{HZSM5}$ . It has already been reported that the lifetimes of many transients included inside zeolites are much longer than those measured in solution for the same species.<sup>19</sup> Transient kinetic traces for the film samples not presented in the figures are given in the Supporting Information.

## Conclusions

By dispersion of the zeolite particles containing organic cations in PDMS polymer, a transparent film can be prepared,

regardless of the particle size of the zeolite crystals. This simple procedure has allowed the use of quantitative transmission techniques instead of diffuse reflectance methods to monitor the transient species generated upon laser flash photolysis. New information concerning the extinction coefficients and quantum yields has been easily obtained in this way. Evidence has been obtained that these photophysical parameters of a guest molecule hosted in a zeolite can be very similar to the values in solution. Further applications of these zeolite/PDMS films to other instrumental techniques can be anticipated, particularly in the imaging and color display areas.<sup>24</sup>

**Acknowledgment.** Financial support from the Natural Sciences and Engineering Research Council of Canada through a research grant (J.C.S.) and a graduate scholarship (S.C.) and Spanish DGICYT (H.G., Project No. MAT97-1016-CO2) are gratefully acknowledged.

**Supporting Information Available:** Fluorescence spectra, transient absorption spectra, and kinetic traces not included in the figures are presented along with the kinetic traces used in determining the triplet yield for xanthone in film (5 pages). Ordering information is given on any current masthead page.

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