Coordination Chemistry Reviews, 97 (1990) 225–236
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE LOCATION OF ORGANIC GUESTS WITHIN X-TYPE FAUJASITE ZEOLITES *VIA* EXTERNAL HEAVY-ATOM INDUCED PHOSPHORESCENCE

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SUMMARY

Heavy-atom induced phosphorescence of naphthalene and related aromatic guest molecules included in X-type faujasite zeolites (M^+X^-, $M^+ = Li,^+ Na,^+ K^+, Rb^+, Cs^+, Tl^+$) has been studied and evidence has been obtained for direct interactions between the heavy-atom cations present within the zeolite supercage and the included organic guest. As expected for an external heavy-atom perturbed excited state, both singlet and triplet excited state lifetimes and emission efficiencies depend upon the identity and accessibility of the cation. The use of photophysical probes to monitor the guest's local environment and approaches to monitoring guest diffusion processes within zeolites *via.* phosphorescence are discussed.

INTRODUCTION

Since the discovery by Kasha (ref. 1) that spin-orbit coupling due to an external heavy-atom can significantly perturb the photophysical properties of the lowest triplet excited states of organic chromophores this effect has been the object of extensive investigation in a variety of different media including solution, low temperature glasses and crystals (ref. 2). In this paper we demonstrate that the cation exchanged X-Type faujasite zeolites (M^+X^-, $M^+ = Li,^+ Na,^+ K^+, Rb^+, Cs^+, Tl^+$) represent a novel new medium capable of yielding dramatic heavy-atom perturbation of organic chromophores. Furthermore we show that the spectroscopic and kinetic investigation of the perturbed organic triplet excited state in these zeolites provides a powerful new probe of the local environment of adsorbed organic molecules inside zeolite cavities.

The internal structure of the faujasite class of zeolites is characterized by a three dimensional network of "supercages" (large voids *ca.* 13 Å in diameter within which adsorbed guest molecules are located) interconnected by tetrahedrally disposed "windows" (*ca.* 8 Å diameter, see Fig. 1). Charge compensating cations are located at three different sites within the zeolite framework of which only two (Types II and III) are expected to be readily accessible to the interior of the supercages (ref. 3) and hence to the adsorbed organic. The zeolite samples used in this study had all three cation sites occupied. The site of adsorption of the organic guest within the zeolite is of course strongly dependent upon the guest's structure. While we will deal primarily with naphthalene as guest, we note that a variety of techniques have demonstrated that benzene in MX zeolites is preferentially adsorbed at the Type II cations inside the supercage

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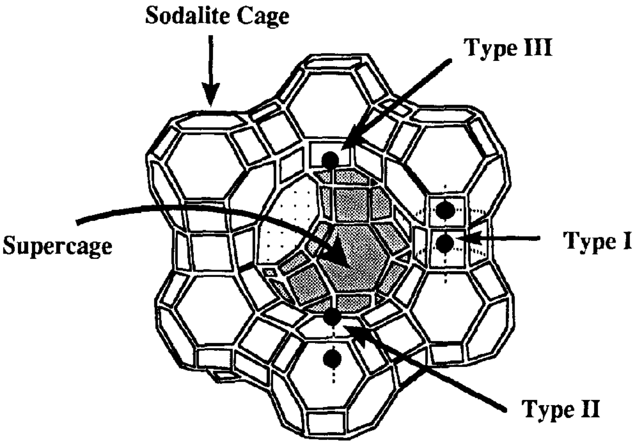


Fig. 1. Structure of the MX faujasite zeolites showing the locations of the three types of charge compensating heavy-atom cations.

with a minor secondary site located in the windows to the supercage (ref. 4, 5, 6, 7).

EXPERIMENTAL

Zeolite samples were prepared by conventional ion exchange of commercial NaX (Linde 13X) with the appropriate metal nitrate solution at 90 °C as described previously (ref. 8). The degree of exchange was determined by elemental analysis and ESCA spectroscopy. Samples of naphthalene included in the various zeolites were prepared from solution as described previously (ref. 8) or alternatively solid samples of the zeolite host and naphthalene were mechanically ground together to yield a uniformly dispersed sample. Luminescence properties of materials prepared by these two routes were identical. In all cases naphthalene loadings were intentionally kept low (0.25 per supercage) in order to minimize the possibility of bimolecular excited state reactions. Samples with controlled states of zeolite hydration were prepared by the grinding method using zeolite samples which had been dried at *ca* 500 °C under high vacuum for 12 hours. Following inclusion of naphthalene the samples were hydrated by exposure to water vapor, with the extent of hydration monitored by measuring the increase in the weight of the sample. Complete hydration of the samples typically yielded weight increases of 15-20% depending upon the choice of zeolite cation.

Emission spectra, corrected for detector sensitivity, were determined using a SPEX Fluorolog 222 Photon Counting Spectrofluorimeter with double grating monochrometers for both excitation and emission. Variable temperature studies were carried out using an Oxford Instruments CF1204 Continuous Flow Cryostat. Samples were mounted between sapphire windows sealed with indium wire to insure good thermal contact between the sample and the mount. Temperature control was typically accurate to ± 0.5 °K.

Phosphorescence lifetimes were measured with the optics described above using a xenon flash lamp (nominal 20 μs pulse duration) as excitation source (typically at 280 nm). Emission intensity was monitored at the vibronic origin of the phosphorescence spectrum (typically 467 nm). Time dependent decay profiles, F(t),were acquired by integrating the signal intensity, I(t), for sequentially increasing times following flash excitation.

$$F(t) = \int_0^t I(t)\,dt \tag{1}$$

The F(t) data were fit satisfactorily using unweighted least squares minimization to either mono- or bi-exponential kinetic models (Eq. 2, n=1 or 2) where τ_i is the phosphorescence lifetime and $I_i\tau_i$ is proportional to the phosphorescence quantum yield for the i^{th} pathway. Quality of the fits was judged by values of χ^2 and by inspection of plots of residuals.

$$F(t) = \sum_{i=1}^{n} I_i\,\tau_i\,[1 - \exp(-\frac{t}{\tau_i})] \tag{2}$$

Relative emission quantum yields as a function were determined both from integration of steady-state emission spectra and from the pre-exponential term ($I_i\tau_i$) obtained in the fits of phosphorescence lifetime data. The results obtained by the two techniques were identical within experimental error.

Diffuse Reflectance spectra were determined using a Cary 2400 spectrometer equipped with an integrating sphere and were referenced to a standard $BaSO_4$ scatterer. Samples were contained in 1mm quartz cuvettes and spectra were not corrected for scattering from the cell.

RESULTS AND DISCUSSION

As shown in Fig. 2, the emission spectrum of naphthalene is profoundly affected by inclusion in faujasites. For low mass cations such as Li^+ and Na^+, emission spectra show the typical naphthalene blue fluorescence. However, as the mass of the cation increases (*e.g.* Rb^+, Cs^+, Tl^+) there is a dramatic decrease in fluorescence intensity and a simultaneous appearance of a new vibronically structured low energy emission band which is readily identified as the $T_1 \rightarrow S_0$ phosphorescence of naphthalene (ref. 9, 10, 11).

The evidence that this phosphorescence is due to naphthalene included in the interior of the zeolite and not merely due to naphthalene adsorbed on the outer surface has been discussed elsewhere (ref. 12). Briefly, we find the effect is general. Intense phosphorescence is observed for a wide range of different organic guests such as naphthalene, anthracene, acenaphthene, phenanthrene, crysene and pyrene. The only examples of guests for which phosphorescence is not observed are for fused aromatics which are too large in diameter to fit through the 8 Å windows of the zeolites (*e.g.* coronene and triphenylene). In these cases the observed emission spectrum closely resembles that for the crystalline guest with no evidence of heavy-atom perturbation.

The correlation of the appearance of the phosphorescence with cation mass clearly suggests that the effect is due to an external heavy-atom perturbation (ref. 2). Diffuse reflectance measurements of naphthalene included in the cation exchanged zeolites show spectra essentially identical to naphthalene in solution demonstrating that naphthalene is not reacting chemically with the host. The emission spectra in Fig. 2 exhibit a distinct decrease in the vibronic structure of the phosphorescence with increasing heavy-atom mass, consistent with known heavy-atom effects on the electron-phonon coupling of naphthalene X-Traps (ref. 13).

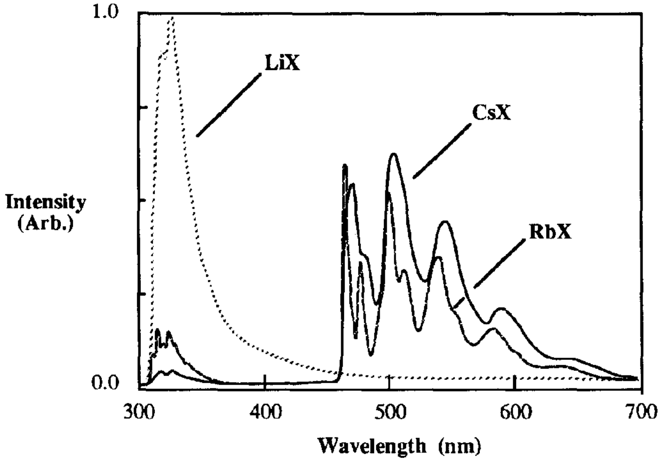


Fig. 2. Emission spectra of naphthalene included in cation exchanged X-type faujasite zeolites at 77 °K.

At low temperatures where the phosphorescence yield was independent of temperature (less than *ca.* 150 °K) the phosphorescence lifetime of naphthalene could be well represented by a single first order decay for all of the zeolite samples under study. However at higher temperatures lifetimes were composed of two independent first order decay pathways. The major pathway (as measured by phosphorescence yield) exhibited a pronounced temperature dependence of both the lifetime and emission yield while the minor pathway was independent of temperature. The phosphorescence lifetime of the minor pathway was similar in magnitude to the limiting low temperature lifetime for the major pathway. The similarity in the magnitudes of the two lifetimes at low temperatures precludes determining whether the minor pathway is present at all temperatures, as biexponential fits could not be statistically justified. Attempting to model the biexponential phosphorescence decays to a single second order kinetic model appropriate for a triplet-triplet annihilation decay path did not yield satisfactory results, consistent with the fact that none of our samples showed evidence of delayed fluorescence.

We believe that the results above favor the assignment of two adsorption sites for naphthalene in the MX zeolites. Support for this assignment comes from time resolved emission spectra of naphthalene-d_8 in CsX acquired at temperatures where emission signals from both the major and minor lifetime pathways are present (Fig. 3). Although the difference in the two spectra is subtle (2 nm red shift and a decrease in vibronic structure for the minor pathway), it is reproducible and appears to be consistent with emission originating from naphthalene adsorbed at two different sites within the zeolite. The absence of a temperature dependence of the lifetime for the minor site argues against an intramolecular origin for the observed temperature dependence of the major site lifetime. As external heavy-atom perturbation has its most pronounced influence on radiative rates (see below), the similarity of the phosphorescence lifetimes for the two sites suggests that the relative population of the two sites should be roughly equal to their relative emission efficiencies at low temperature which in turn implies that the minor site accounts for 1-10% of the included naphthalene.

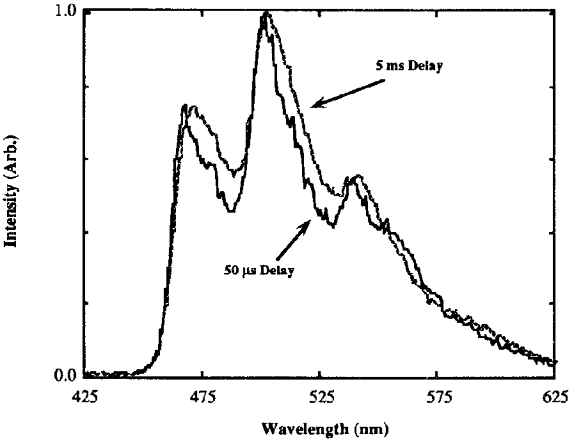
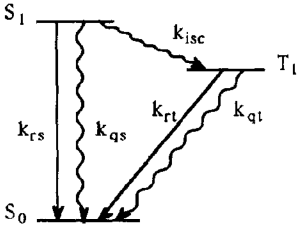


Fig. 3. Time resolved phosphorescence spectrum of naphthalene-d_8 included in CsX excited at 280 nm and recorded at 250 °K at which temperature both the major (50 μs delay) and minor (5 ms delay) naphthalene emission sites are detectable. Note the consistent 2 nm blue shift and the enhanced resolution of the emission bands of the major site.

In order to assess the effect of the local zeolite environment upon the naphthalene excited states, we investigated the relative emission quantum yields and excited state lifetimes of the S_1 and T_1 excited states as functions of temperature, state of zeolite hydration and identity of the heavy-atom perturber.

For all of the cations we studied (K^+, Rb^+, Cs^+, Tl^+), the relative emission quantum yield of the naphthalene singlet state is essentially temperature independent from 77-295 °K indicating that $S_1 \rightarrow S_0$ radiative and nonradiative rates and $S_1 \rightarrow T_1$ intersystem crossing rates are unaffected by temperature and that there are no thermally activated processes leading to population of the S_1 excited state from naphthalene triplet states. These observations also argue against any diffusional triplet-triplet annihilation contribution to naphthalene triplet decay in this temperature regime. Naphthalene singlet lifetimes decrease with cation mass in the order



Scheme I. Kinetic scheme for interconversion of the lowest energy naphthalene singlet (S_1) and triplet (T_1) electronic excited states with the ground state (S_0).

Na ≈ K > Rb > Cs (ref. 12), and while we have not measured absolute efficiencies, it is clear that the relative $S_1 \rightarrow S_0$ emission efficiencies decrease as the cation mass increases in the series $Li^+ \approx Na^+ \approx K^+ < Rb^+ < Cs^+ << Tl^+$. As the heavy-atom effect is not expected to significantly affect k_{rs} or k_{qs} (ref. 2), we interpret the decrease in singlet emission efficiency and lifetime to an increase in k_{isc} due to external heavy-atom perturbation.

While the naphthalene singlet emission quantum yields are independent of temperature, the relative phosphorescence yields ($\Phi_{rel}(T)$) and phosphorescence lifetimes ($\tau(T)$) are strongly influenced by temperature for all of the cations we have investigated (Figs.4, 5). The ratio $\tau(T)/\Phi_{rel}(T)$ is temperature-independent demonstrating that the temperature dependence must be due to the presence of a thermally activated nonradiative decay pathway. The naphthalene phosphorescence spectra show no unusual shifts in energy with temperature; only the expected thermal broadening consistent with thermally activated decay *via* a non-emitting state is observed.

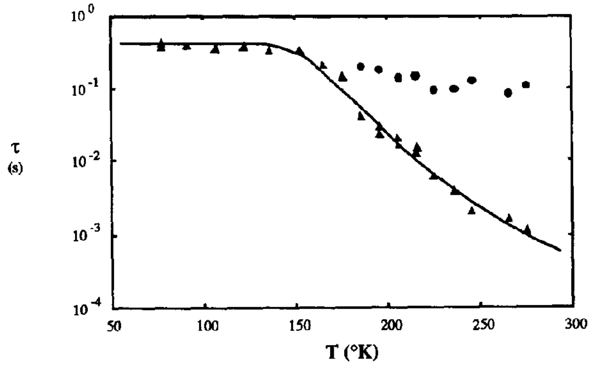


Fig. 4. Temperature dependence of the phosphorescence lifetime (τ) of naphthalene-d_8 included in CsX. (▲) Temperature dependent pathway. (—) Theoretical fit to eq. 3. (•) Temperature independent component observable only at higher temperatures.

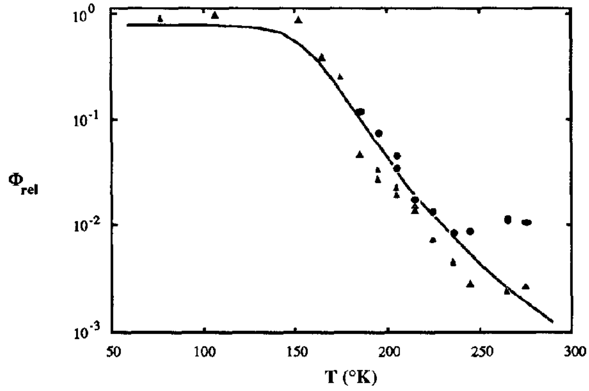


Fig. 5. Temperature dependence of the relative phosphorescence efficiency (Φ_{rel}) of naphthalene-d_8 included in CsX. (▲) Major phosphorescence component. (—) Calculated fit to eq. 4 obtained using the activation parameters obtained from the fit of τ(T) and adjusting the constant, c. (•) Minor phosphorescence pathway corresponding to the temperature independent lifetime component in Fig. 4.

Activation parameters for the naphthalene phosphorescence decay in various zeolites were obtained from fits of τ(T) to the expression for a manifold of two excited states in rapid thermal equilibrium (ref. 14, 15) neglecting degeneracies (eq. 3).

$$\tau(T) = \frac{1 + \exp[\frac{-\Delta E}{k_B T}]}{k_0 + k_1 \exp[\frac{-\Delta E}{k_B T}]} \tag{3}$$

$$\Phi_{rel}(T) = c\,\tau(T) \tag{4}$$

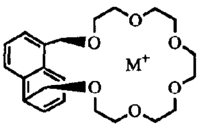
In Eq. 3, k_0 is the limiting triplet decay rate at low temperature ($k_0 = k_{rt} + k_{qt}$), ΔE is the activation barrier for the thermally activated decay process, k_1 is the limiting decay rate for the activated process and k_B is the Boltzman constant. The expression for $\Phi_{rel}(T)$, is simply τ(T) arbitrarily scaled by a constant, c (eq. 4). Relative emission quantum yields are experimentally more difficult to measure than lifetimes and in addition are susceptible to systematic errors due to the temperature dependent broadening of electronic absorption spectra. For this reason activation parameters were derived only from the lifetime data and emission yields were fit using these values allowing only the constant, c, to vary. Results of fitting τ(T) to eq. 3 using a weighted non-linear least squares procedure are summarized in Table I. The fitting procedure typically yields k_1 values with very large uncertainties. For this reason, this parameter is treated as a strictly empirical result.

TABLE I

Activation parameters for T_1 excited state decay determined from fits of the temperature dependence of naphthalene (Np) and naphthalene-d_8 (Np-d_8) phosphorescence lifetimes to eq. 3. Quoted uncertainties are 95% confidence limits. All zeolites were hydrated except for the anhydrous CsX sample (CsX, Anh.). Values of the spin-orbit coupling constants (ξ) for the perturbing heavy-atom cations are included for comparison.

Zeolite Host	**Guest**	ξ (cm^{-1})	$\mathbf{k_0}$ (s^{-1})	ΔE (cm^{-1})	$\mathbf{k_1}$ (s^{-1})
KX	Np	87	0.58 ± 0.08	3240 ± 420	$6.2 \pm 16 \times 10^9$
RbX	Np	360	1.39 ± 0.20	3310 ± 320	$2.1 \pm 4.1 \times 10^{10}$
CsX	Np	840	5.05 ± 0.52	2010 ± 240	$1.8 \pm 2.3 \times 10^6$
CsX, Anh.	Np	840	6.04 ± 0.33	2960 ± 200	$4.1 \pm 4.4 \times 10^8$
TlX	Np	7294	815 ± 54	610 ± 90	$3.7 \pm 1.7 \times 10^4$
RbX	Np-d_8	360	0.46 ± 0.18	2250 ± 780	$8.5 \pm 38 \times 10^7$
CsX	Np-d_8	840	2.45 ± 0.90	1630 ± 220	$5.1 \pm 7.6 \times 10^6$

In interpreting the trends in k_0 it is important to note that this term is the sum of radiative and nonradiative terms (k_{rt}, k_{qt}) which cannot be separated in the absence of absolute phosphorescence quantum yield measurements. External heavy-atom perturbation is expected to enhance radiative rates more than nonradiative (ref. 16, 17, 18, 19) and hence variations in k_0 between different heavy-atom cations should primarily reflect variations in k_{rt}, as long as the phosphorescence yields are significantly less than unity. It is well known that the effect of external heavy-atom perturbation scales with the square of the perturbers spin-orbit coupling constant, ξ^2 and that a log-log plot of k_0 *vs.* ξ^2 should be linear with a maximum predicted slope of unity (ref. 2). As shown in Figure 6, we observe the expected dependence. The magnitude of the heavy-atom effect we observe is significantly larger than that observed for the 1,5-naphtho-22-crown-6 (**1**) exchanged with heavy-atom cations (see Fig. 6) where the cation is rigidly held over the naphthalene π-face. In fact the zeolite samples show heavy-atom effects nearly as large as for a series of 1-halo-naphthalenes (2) where the perturbers are covalently attached to the chromophore. We attribute this result both to the close approach between naphthalene and the heavy-atom which is enforced by the zeolite supercage and to the presence of more than one heavy-atom cation per supercage which leads to high effective concentrations of the heavy-atom in the vicinity of the naphthalene.



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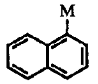

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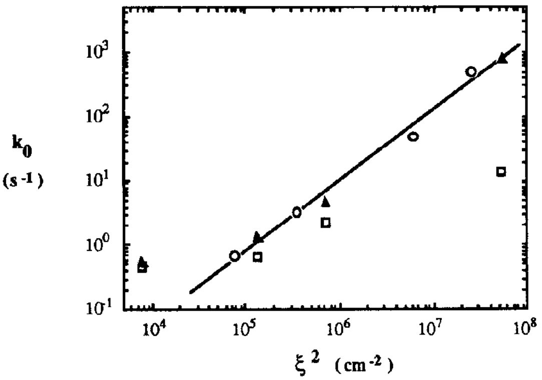

Fig. 6. Effect of spin-orbit coupling on phosphorescence lifetimes of naphthalene in different environments. (▲) Heavy atom exchanged faujasites. (o) 1-Halo-naphthalenes at 77 °K (ref. 20). (Squares) 1,5-Naphtho-22-crown-6 in ethanol at 77 °K with added metal chloride salts (ref. 21, 22). (—) Least squares fit to the data for the 1-halo-naphthalenes with slope = 1.09.

Comparison of k_0 values for naphthalene and naphthalene-d_8 (Table I) shows that there is a significant H/D kinetic isotope effect of 2.06 (CsX) and 3.02 (RbX) which appears to correlate inversely with the heavy-atom mass (and spin-orbit coupling). Comparison with isotope effects typically observed for naphthalene in doped crystals (7.8 in benzene at 77 °K (ref. 23), 6.9 in benzophenone at 77 °K (ref. 23), 6.5 in durene at 77 °K (ref. 24)) shows that the magnitude of the isotope effect in the zeolite samples is remarkably low; however, a detailed analysis requires the measurement of absolute phosphorescence yields in order to determine the partitioning of the isotope effect between k_{rt} and k_{qt}. These experiments are currently in progress.

The effect of included water on the heavy-atom perturbation of naphthalene included in faujasites is shown most clearly in the value of k_0 which is smaller by a factor of 1.2 in anhydrous CsX compared to hydrated CsX. Water will coordinate to the Cs^+ cations in the zeolite and the formation of this water shell is expected to hinder the approach of the naphthalene to Cs^+ and hence will increase the naphthalene-Cs^+ separation. It is known from IR spectroscopy that addition of NH_3 to benzene in NaY zeolite leads to displacement of the benzene from the Type II cations (ref. 25). In our case, the resulting decrease in k_0 is consistent with previous work which has demonstrated that the external heavy-atom effect is a strong function of the distance between the chromophore and the heavy-atom with the magnitude of the effect decreasing with increasing separation (ref. 26).

The values of ΔE in Table I show that the activation energy for phosphorescence decay depends upon the identity of the perturbing heavy-atom (Fig. 7) with the general trend that ΔE decreases with cation mass. However the trends may not be as simple as they appear at first glance, as the magnitude of ΔE also shows significant H/D isotope effects for deuteration of naphthalene (factors of 1.23 for CsX and 1.47 for RbX) and ΔE increases by a factor of 1.47

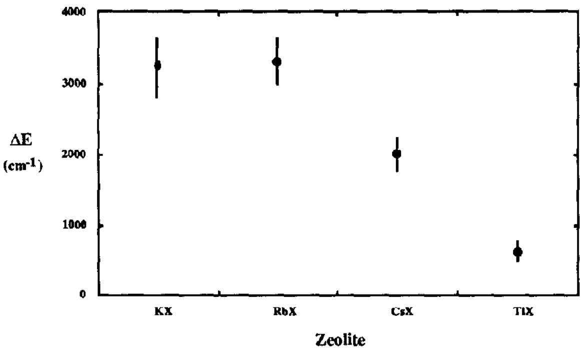

Fig.7. Dependence of the activation energy for naphthalene phosphorescence decay (ΔE) upon the identity of the heavy atom perturber. Error bars represent 95% confidence limits.

for anhydrous CsX compared to hydrated CsX. We believe that the origin of the systematic variations in ΔE is related to the magnitude of complexing interactions between naphthalene and the heavy-atom cations in the zeolite. Further investigation of these trends, including optically detected magnetic resonance studies aimed at establishing the geometry of the triplet naphthalene-cation complexes, is currently in progress.

CONCLUSION

We have demonstrated that heavy-atom exchanged faujasite zeolites are a versatile new medium for the observation of external heavy-atom perturbation of organic triplet excited states. Detailed investigation has revealed that the photophysical properties of naphthalene included in these zeolites is sensitive to the identity of the heavy-atom perturber and to the presence of water in the zeolite. We anticipate that the addition of other small molecules (*e.g.* NH_3, HCl) will also lead to detectable changes in phosphorescence photophysics and that phosphorescence measurements will provide an important new probe of the local environments of guests adsorbed in zeolites. The large magnitude of the external heavy-atom perturbation is not unique to the X-type faujasites; we have observed similar effects for organic guests included in Y-type faujasites and in pentasils (ref. 27).

Our results also provide the background for a new approach to monitoring diffusion of organic guests inside zeolites. Preparation of zeolite samples containing mixtures of more than one heavy-atom (*e.g.* Na^+ and Cs^+) such that the majority of supercages contain only the lighter cations should yield phosphorescence lifetimes which are bi-exponential under conditions where the adsorbed naphthalene cannot diffuse between cages within the excited state lifetime. As the temperature is increased and diffusion begins to allow the naphthalene triplet to encounter the heavier cation prior to decay, the phosphorescence kinetics will begin to change until reaching temperatures where diffusion becomes rapid on the excited state time scale. The phosphorescence lifetime will then become monoexponential with a value typical for a zeolite sample containing only the heavier cation. In principle this approach can be used as well for monitoring singlet lifetimes. The power of the technique derives from both the sensitivity to local environment and the range of time scales accessible, ranging from nanoseconds for singlet states up to seconds for triplets. In preliminary studies of this type we have found that for phenanthrene included in [Na,Cs]X zeolites where the Cs^+ content is low the triplet lifetime at 77 °K is biexponential and the two observed lifetimes (0.26 s and 2.0 s) are identical to those observed for phenanthrene included in pure CsX and NaX respectively. When the Cs^+ content is increased the 77 °K lifetimes become monoexponential with a value of 0.27 s indicating that all excited states are contacting Cs^+. Variable temperature studies and detailed analysis of these effects are now in progress.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the skilled technical assistance of D. Sanderson, A. Pittman, and P. Hollins.

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