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Zeolite Photochemistry: Energy Transfer between Rare-Earth and Actinide Ions in Zeolites

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Energy transfer is an important process in various display and luminescence devices. This paper shows that energy transfer efficiencies can be controlled by selectively placing certain inorganic ions in zeolite molecular sieves. The energy transfer in these zeolites occurs between uranyl ions and europium(III) ions in various zeolites. It has been observed that energy transfer is most efficient in solution-like amorphous environments in zeolites. Three-dimensional channels in crystalline materials provide better interactions for energy transfer than two-dimensional or zigzag channels such as in mordenite and ZSM-5. Different synthetic procedures involving simultaneous and sequential ion exchange yield different efficiencies of energy transfer. The mechanism is believed to be of the short-range electron-exchange type for crystalline ZSM-5, mordenite, and Y zeolite and of the long-range type for amorphous materials derived from zeolite A.

Photochemical activation of molecules in controlled molecular environments is becoming an increasingly important area of research as nonrenewable energy supplies are being diminished. Many different molecular environments such as micelles, thin films, vesicles, and bilayers are available for use as models of the photochemical processes that occur in photosynthesis and in solar energy devices. Studies of fundamental photophysical and photochemical processes such as electron transfer and energy transfer in these molecular environments are still in their infancy. A type of controlled molecular environment that is stable and robust with respect to both thermal and photochemical activation is a zeolite molecular sieve.

Long-range energy transfer transfer between copper(I) ions and oxygen has recently been observed in zeolite Y.[1] This is the only report involving energy transfer in zeolites and has provided impetus for the present study. The research reported in this paper provides evidence that energy transfer can occur between two cations in the pores of several different zeolite lattices. The efficiency of energy transfer is controlled by the size of the pores of the zeolite and by the type of pore. That is, some pores are three-dimensional; others are more restrictive and are of lower dimensionality.

Table I. Energy-Transfer Efficiencies (η_t)[c] for Simultaneous Ion Exchange of Uranyl and Europium(III) Ions in Zeolites

	$[UO_2^{2+}]$, M				
zeolite	0.095	0.075	0.050	0.025	0.005
Na-Y	0.17	0.20	0.31	0.32	0.40
Na-A	0.43	0.90	0.86	0.89	0.93
Na-mordenite	*b*	0.07	0.09	0.10	0.21
Na-ZSM-5	0.13	0.10	0.14	0.22	0.33

[a] The molar concentration of Eu^{3+} is 0.1 M − $[UO_2^{2+}]$. [b] No emission for Eu^{3+} was observed. [c] Energy-transfer efficiencies were calculated by the formula $1 - A_0/(A_0 + A)$, where A is the intensity measured in peak area of the acceptor in the presence of the donor and A_0 is the intensity measured in peak area of the donor.[22]

In addition, a wealth of information concerning the diffusion of these ions through the lattice is available from luminescence emission studies. Reliable diffusion coefficients in porous zeolite molecular sieves are very difficult to measure. In fact, variations in reported diffusion coefficients[19] exceeding 3 orders of magnitude are not uncommon. Provided that the mechanism for energy transfer is short-ranged, some information regarding diffusion can be obtained.

We have recently reported that uranyl-exchanged zeolites can be used in the photoassisted catalytic oxidation of isopropyl alcohol.[5,6] As a consequence of these luminescence emission and X-ray powder diffraction studies, it was shown that certain zeolites behave like solids and that others have a solution-like environment. Others have proposed that zeolites have solution properties[7,8] and this behavior may be of importance in the design of catalytic and photocatalytic systems. In order to understand the nature of the interaction of light with zeolite molecular sieves, we have investigated the behavior of rare-earth and actinide ions in zeolites. The visible emission of rare-earth ions like Sm^{3+} or Eu^{3+} is of practical importance[2] in various display and fluorescence devices. The optical properties of trivalent rare-earth ions in solids are also important because of possible applications in devices such as quantum counters, infrared upconvertors, lasers, and solar luminescent collectors.[3,4] In this paper we report that energy transfer is very efficient between uranyl ions and europium(III) ions in several zeolites, especially if the ions are in a solution-like or amorphous environment.

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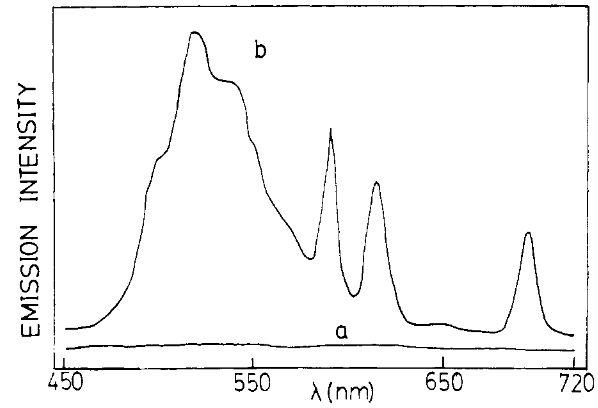

Figure 1. Emission spectra (excited wavelength 425 nm): (a) Eu^{3+}–Y zeolite; (b) UO_2^{2+},Eu^{3+}–Y zeolite.

Energy transfer between uranyl ions and europium(III) ions in water and acetic acid solution has been observed.[9] A short-range electron-exchange mechanism that occurs only when the ions are at collisional diameters has been proposed. Rate constants for energy transfer were determined to be 10^7 M^{-1} s^{-1}, which are lower than the diffusion-controlled rate due to mutual ion–ion repulsion. Energy transfer between rare earths and actinides has also been shown to occur in solids[10] like $SrZnP_2O_7$:UO_2^{2+} and in phosphate glasses.[11] None of these studies involves the incorporation of uranyl or europium(III) ions in a controlled molecule environment like a zeolite.

An emission spectrum of a europium(III)-exchanged Y zeolite when excited at 425 nm is shown in Figure 1a. The characteristic europium(III) emission bands are not observed. However, on simultaneous exchange of uranyl ions and europium(III) ions in zeolite Y and subsequent excitation at 425 nm, a broad emission around 520 nm for the UO_2^{2+} ion in the zeolite and peaks at 595, 615, and 695 nm indicative of europium(III) ions are observed as in Figure 1b. This type of experiment demonstrates that energy transfer has occurred in the Y zeolite system. Energy transfer between UO_2^{2+} and Eu^{3+} ions is not limited to zeolite Y. As reported in Table I, transfer efficiencies are quite different for different zeolites. The most efficient transfer occurs in the material derived from zeolite A that has uranyl ions in a solution-like (amorphous) surface environment.[5]

After exchange with uranyl ions the X-ray powder pattern does not contain sharp diffraction peaks, but rather a broad band around 25° 2θ. We believe that the uranyl moiety is on the external surface of zeolite A due to size restrictions of the aluminosilicate lattice. The other three zeolites are all crystalline, and the efficiency here seems to be controlled by the framework structure. For instance, the presence of zigzag channels in both ZSM-5[12] and mordenite[13] may explain why the efficiency of energy transfer is lower in these zeolites. The concentrations listed in Tables I and II represent molarities used during the ion-exchange procedure.

The behavior of other rare-earth ions such as Sm^{3+}, Tb^{3+}, and Dy^{3+} when ion-exchanged into zeolites is not as predictable as the UO_2^{2+} and Eu^{3+} ions. Energy transfer in zeolites between uranyl and other rare-earth ions besides europium(III) has yet to be observed[20] except for samarium(III).

The method of preparation of these materials is certainly a major factor in the efficiency of energy transfer. Three different procedures of preparation and the corresponding energy-transfer efficiencies are described in Table II. Sequential ion exchange using either uranyl or europium(III) ions first decreases the efficiency with respect to the simultaneous introduction of both ions. This result is expected since it is known that ion exchange of multivalent ions causes these ions to remain in the intracrystalline environment in preferred locations[23] unless severe conditions are then imposed.[24] Indirect evidence of this result is obtained from solution leaching studies.

Table II.[14] Energy-Transfer Efficiencies for Simultaneous and Sequential Ion Exchange of Uranyl and Europium(III) Ions in Zeolites

	η_t[a]		
zeolite	simultaneous	sequential[b]	sequential[c]
Na-Y	0.31	0.17	0.11
Na-A	0.86	0.51	0.78
Na-mordenite	0.09	0.04	*d*
Na-ZSM-5	0.14	0.25	0.10

[a] All transfer efficiencies reported above are obtained from the following concentrations: $[UO_2^{2+}] = 0.05$ M; $[Eu^{3+}] = 0.05$ M. [b] Uranyl ions exchanged first; 24-h exchange for both ions; zeolite filtered and washed between exchanges. [c] Same as footnote *b* except europium(III) ions exchanged first. [d] No emission for Eu^{3+} was observed.

Further studies of these systems show that the efficiency of energy transfer decreases as the temperature of the sample is lowered. The efficiency is also lowered by a factor of about 3 in zeolite Y if the europium(III) ions are exchanged first, followed by dehydration to lock the Eu^{3+} ions into the sodalite cages,[15] followed by exchange with uranyl ions. All of these factors point, as in the case of energy transfer in solution,[9] to a collisioinal or nonradiative short-range exchange mechanism. Diffusion is usually important in the short-range electron-exchange mechanisms.[9]

Static quenching via ground-state association between UO_2^{2+} and Eu^{3+} ions is another possible quenching mechanism. If static quenching were important in the zeolite systems described here, then it would be expected that the excitation spectrum of a uranyl- and europium(III)-exchanged zeolite would be different from the excitation spectrum of a uranyl-exchanged zeolite. This is not the case. Another method that is commonly used to observe whether static quenching is important involves Stern–Volmer analysis.

In each of the reports of the quenching of luminescent ions in zeolites such as $Ru(bpy)_3^{2+}$[17,18] and UO_2^{2+},[5] Stern–Volmer plots have yielded nonlinear plots. This is true if both the ions and quenchers are not too large to exist in the zeolite pores. The interpretation of the nonlinear Stern–Volmer plots is that the first linear region of quenching is due to quenching of external ions and the second linear region (which is separated from the first region by a nonquenching region) involves internal ions sites being quenched.

Similar nonlinear plots have been obtained for the quenching of uranyl ions (at constant $[UO_2^{2+}]$) by europium(III) ions in solution. There is no evidence of ground-state association of UO_2^{2+} and Eu^{3+} ions in these zeolites on the basis of these Stern–Volmer plots. Stern–Volmer analyses derived from lifetime measurements are also consistent[21] with a nonstatic quenching mechanism.

Although the Stern–Volmer plots are nonlinear, one can compare the relative $[Eu^{3+}]$ concentration needed to reach a certain I_0/I value. These concentrations perhaps give some indication of the relative rate of diffusion in these systems. For zeolite A, $I_0/I = 3$ when $[Eu^{3+}] = 0.074$ M. For zeolite Y, $I_0/I = 3$ when $[Eu^{3+}] = 0.11$ M. Even when $[Eu^{3+}] = 0.15$ M, zeolite ZSM-5 has an I_0/I value of only 2.3. These and other observations imply that diffusion is more rapid on the surface of zeolite A than for

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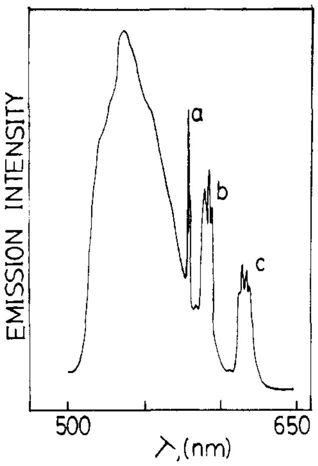

Figure 2. Emission spectrum of Eu^{3+}–A zeolite at 4 K (excitation wavelength 425 nm): (a) $^5D_0 \rightarrow {}^7F_0$ transition; (b) $^5D_0 \rightarrow {}^7F_1$ transition; (c) $^5D_0 \rightarrow {}^7F_2$ transition.

the same ions in the pores of ZSM-5 and Y. Diffusion in Y appears to be greater than that in ZSM-5. This is consistent with the sizes of the pores of these zeolites.

Evidence of association between europium(III) and uranyl ions was obtained, however, when the uranyl- and europium(III)-exchanged Y zeolite was thermally treated to 350 °C. The intention of this experiment was to move the europium(III) ions into the sodalite cages from the supercage and then observe the effect of the energy-transfer efficiency. After thermal treatment the uranyl moiety was decomposed, as evidenced by a very weak excitation and emission spectrum. This was surprising since thermal treatment of UO$_2$–Y[5,6] zeolite produces a stable luminescent uranyl–Y zeolite that, when rehydrated, can regenerate the starting material. Thermal treatment[15] of Eu(III)Y to 375 °C also produces a stable material. The above observation must mean that uranyl and europium(III) ions react with one another perhaps by an inner-sphere mechanism during thermal treatment. Bridging hydroxyl uranyl/europium(III) oligomers in aqueous solution[16] have indeed been suggested recently.

For systems in which there is only type of Eu^{3+} binding site, the $^5D_0 \rightarrow {}^7F_1$ europium transition at 595 nm and the $^5D_0 \rightarrow {}^7F_2$ europium transition at 615 nm split into three and five peaks, respectively, under high-resolution conditions.[14] Group-theoretical calculations indicate that the site must be of C_2 or lower symmetry if these splittings are observed. The emission spectrum in Figure 2 of UO$_2^{2+}$,Eu^{3+}–A zeolite at 4 K under high resolution indicates that the europium(III) ion is likely in a symmetry of at least C_2 or lower due to the number of splittings observed. The transition at 595 nm splits into three peaks, and the 615-nm transition does not split but has some shoulders. Another criterion for single siting is that the $^5D_0 \rightarrow {}^7F_0$ europium peak at 580 nm must not split. This is also true for the A zeolite system. This europium ion site must be in the supercage of zeolite A. EXAFS and luminescence lifetime measurements[8e,25] indicate that the europium(III) ion site has three water molecules and three framework oxygen atoms. The efficiency of energy transfer is noticeably reduced at this temperature. These results suggest that energy transfer in the material derived from zeolite A proceeds via a long-range mechanism.

Energy transfer in these zeolites occurs betwen the $\Omega = 4$ level of UO$_2^{2+}$ and the group of Eu^{3+} levels $^5D_2$, $^5D_3$, and $^5L_6$.[16] Phonon-assisted processes are possible[16,26] since some of these levels are higher than the $\Omega = 4$ level. It is exciting that the efficiency of energy transfer can be controlled by the method of preparation and by the structural framework of the particular zeolite. These observations imply that solution-like environments do exist in zeolites and that fundamental photochemical processes like energy transfer that abound in solution can also occur to a certain extent in zeolite molecular sieves.

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Registry No. UO$_2^{2+}$, 16637-16-4; Eu^{3+}, 22541-18-0.

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Luminescence of Ruthenium(II) Tris Chelate Complexes Containing the Ligands 2,2′-Bipyridine and 2,2′-Biisoquinoline. Behavior of the Ru(bpy)$^{2+}$ and Ru(bpy)$_2^{2+}$ Emitting Units

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The absorption spectra, emission spectra, emission lifetimes, and the temperature dependence of the emission intensity and lifetime (between 84 and 330 K) of the complexes Ru(bpy)$_2$(*i*-biq)$^{2+}$, Ru(bpy)(*i*-biq)$_2^{2+}$, and Ru(*i*-biq)$_3^{2+}$ (bpy = 2,2′-bipyridine, *i*-biq = 2,2′-biisoquinoline) have been studied and compared with those of the previously studied Ru(bpy)$_3^{2+}$. The electrochemical behavior of the same complexes has also been investigated. The spectroscopic results show that the *i*-biq ligand is not involved in the low-energy excited states that are responsible for the luminescence emission of the mixed-ligand complexes, and the electrochemical data show that the presence of one or two *i*-biq ligands affects only slightly the density of charge on the Ru ion compared with the situation found for Ru(bpy)$_3^{2+}$. Ru(bpy)(*i*-biq)$_2^{2+}$ can thus be regarded as containing the Ru(bpy)$^{2+}$ emitting unit in a situation that, except for ligand–ligand interaction, is essentially the same as that experienced by such a unit in the Ru(bpy)$_2$(*i*-biq)$^{2+}$ and Ru(bpy)$_3^{2+}$ complexes. The electrochemical and spectroscopic results suggest that Ru(bpy)(*i*-biq)$_2^{2+}$, Ru(bpy)$_2$(*i*-biq)$^{2+}$, and Ru(bpy)$_3^{2+}$ can all be described as containing single-bpy-localized excited states but that in the last two complexes there is a weak bpy interligand interaction.

Introduction

The photophysical properties of transition-metal complexes continue to be extensively investigated for both theoretical reasons[4-6] and potential applications in the field of energy conversion.[7-16] In particular, much attention has been devoted to the

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