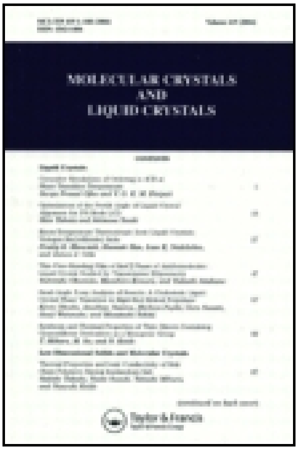

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Non-homogeneous Distribution of Organic Molecules Within Zeolites

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To cite this article: V. Ramamurthy (1994): Non-homogeneous Distribution of Organic Molecules Within Zeolites, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 240:1, 53-71

To link to this article: http://dx.doi.org/10.1080/10587259408029715

*Mol. Cryst. Liq. Cryst.* 1994, Vol. 240, pp. 53–71
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Printed in the United States of America

# NON - HOMOGENEOUS DISTRIBUTION OF ORGANIC MOLECULES WITHIN ZEOLITES

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*Abstract* Distribution of organic guest molecules within Na Y zeolites has been examined utilizing aromatic probe molecules such as pyrene, naphthalene and phenanthrene, and dyes such as thionin as photophysical probes. Results have been analyzed on the basis of three parameters, guest occupancy, families of sites and distribution of sites within a family. Distribution of guests, on all three counts, within zeolites has been shown to be non-uniform. Co-adsorbed molecules such as water and organic solvents, temperature and the nature of aromatics influence significantly the guest distribution within zeolites.

## INTRODUCTION

Photochemical studies within zeolites have attracted considerable attention over the last decade.[1] Most of the studies have been and continue to be "show and tell" variety. Most studies have been "set pieces" with little predictive value. The time has come to establish some ground rules so that predictability can become part of the field. One of the problems in carrying out studies of organic molecules within zeolites is the lack of knowledge concerning the location and distribution of molecules within these structures.[2] Since guest molecules within zeolites exert some motion, x-ray structural characterization has not been possible.[3] Further, single crystals of guest adsorbed zeolites are rarely available. However, recently attempts are being made to solve structures utilizing powder samples.[4] Information on the location and distribution of guest molecules within zeolites is becoming available utilizing solid state nmr techniques.[5] These studies, while provide a basic understanding of the location and distribution of organic molecules within zeolites, are less helpful to predict photochemical events since most of them occur on time scales much shorter than migration of molecules on surfaces; the distribution at the

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# Contribution number: 6622

steady state techniques or techniques such as nmr wherein time scales are much longer.[6] It is important to have a knowledge on the location and distribution of molecules on the time scale of photochemical events to be able to reliably predict the photobehavior of adsorbed guest molecules. Attempt has been made in this paper to focus on the above problem utilizing certain well characterized organic probes as guest molecules.

## STRUCTURE OF ZEOLITES

Zeolites may be regarded as open structures of silica in which aluminum has been substituted in a fraction of the tetrahedral sites.[7] The frameworks thus obtained contain pores, channels and cages. Substitution of trivalent aluminum ions for a fraction of the tetravalent silicon ions at lattice positions results in a network that bears a net negative charge which must be compensated by other counter ions. Such ions are mobile and may occupy various exchange sites depending on their radius, charge and degree of hydration. They can be replaced, to varying degrees, by exchange with other cations. If zeolite water is removed, many other organic and inorganic molecules can be accommodated in the intracrystalline cavities.

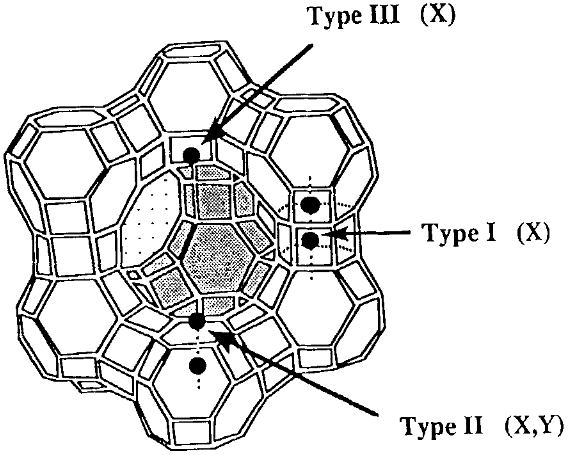


FIGURE 1. Structure of supercages of X and Y zeolites. Cation positions are shown as type I, type II and type III. In Y zeolites only sites I and II are occupied.

The topological structure of X- and Y-type zeolites (also known as faujasites) consists of an interconnected three dimensional network of relatively large spherical cavities termed supercages (diameter of about 13 Å; Figure 1). Each supercage is connected tetrahedrally to four other supercages through 8 Å windows or pores. The interior of zeolites X and Y also contains, in addition to supercages, smaller sodalite cages. The windows to the sodalite cages are too small to allow organic molecules access. Charge compensating cations present in the internal structure are known to occupy three different positions (Figure 1) in the zeolites X and Y. Only cations of sites II and III are expected to be readily accessible to the adsorbed organic molecule.

## GUEST OCCUPANCY WITHIN ZEOLITES

The term "occupancy" is used to indicate the aggregation status (monomer, dimer, microcrystals *etc.*) of guests within zeolites. As illustrated below with a number of examples, guests may exist within the internal structure of zeolites either as monomers or as aggregates such as dimers and microcrystals. As would become evident, the occupancy distribution is subjected to external factors especially the presence of co-adsorbents which can strongly interact with the internal structure of zeolites. Even at low loading levels the cages may not be uniformally occupied; *i.e.*, some may be singly occupied, some doubly occupied and some not occupied at all. A term average occupancy, represented by <S>, is used in the literature to indicate the loading levels in X and Y zeolites. The term <S> is defined as the number of guest molecules over the number of available supercages. Number of supercages in the amount taken can be calculated by knowing the average weight of a supercage assuming that there are eight supercages per unit cell .

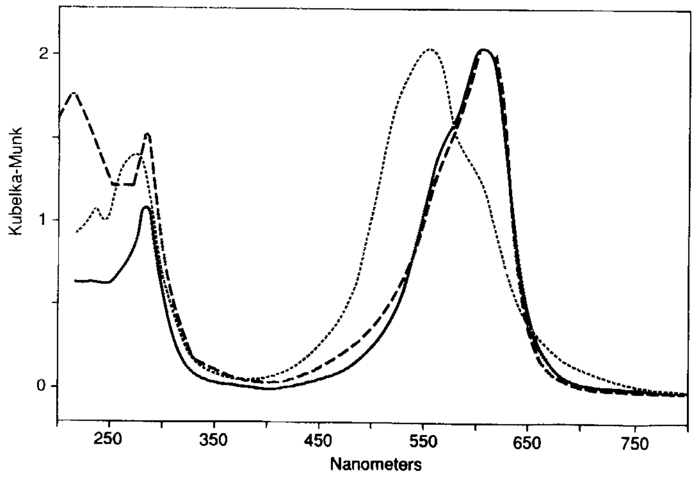


FIGURE 2. Diffuse reflectance spectra of thionin included within K L and NaY: (a) ········ Na Y, hydrated; (b) —— Na Y, anhydrous; (c) – – – – K L, hydrated or anhydrous.

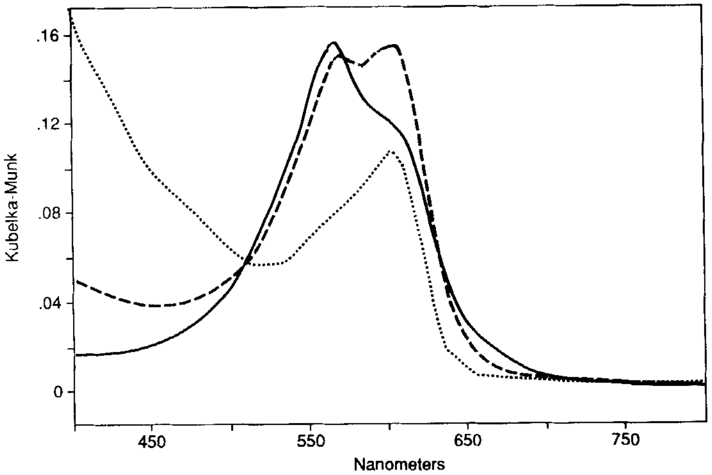


FIGURE 3. Diffuse reflectance spectra of thionin, at various loading levels, included within "wet" NaY:(a) ——, <S>: 0.02; (b) – – – , <S>: 0.002; (c) · · · · ·, <S>: 0.0004.

Dyes

Thinoin and related dye molecules (methylene blue, nile blue-A, acridine orange and cresyl violet) bearing a positive charge can be easily exchanged into zeolites such as Na X, Na Y, K L, Na M-5 and Na Ω–5.[8] Results obtained within Na Y are presented below. Exchange is achieved by stirring, for about two hours, known amounts of the dye and the zeolite in water. Anhydrous complexes were obtained by filtering the above slurry, washing the filtrate with excess water and drying the colored precipitate in a glassware oven. Comparison of the diffuse reflectance spectra of these anhydrous complexes with the absorption spectra of the dyes in aqueous solution revealed that dye molecules exist within zeolites in a monomeric form (Figure 2). Dramatic changes in color result when these anhydrous complexes were left open under normal laboratory conditions. According to thermogravimetric analysis, the complexes with a set of new colors contain about 15–20% of water; the main change that has occurred during the process of exposure to laboratory is the adsorption of water from the atmosphere. These hydrated complexes are termed "wet". The diffuse reflectance spectra of these "wet" complexes are distinctly different from those of "dry" ones (Figure 2).[9] Comparison of the above spectra with those of dyes in aqueous solution suggests that dye molecules are present as dimers within "wet" Na Y. The occupancy level of dyes within zeolites may not always be 100% of either monomer or dimer. Aggregation is believed to be a result of hydrophobic effects and the principles which govern this process in aqueous solution is expected to play a role here too. Indeed the factors those govern the aggregation process within Na Y are: (a) loading level of the dye (at low loadings dye molecules exist essentially as monomers within hydrated Na Y, Figure 3); (b) the inherent tendency of the dye to aggregate (*i.e.*, large equilibrium constant for dimer formation; for example oxazine-1 which has a low equilibrium constant for dimer formation did not dimerize within hydrated Na Y); (c) presence of large enough internal structure within the zeolite to accommodate the dimer (dyes exist only as monomers within narrow channel zeolites such as K L, Na M-5 and Na Ω–5, independent of whether zeolites are wet or dry). A photophysical consequence of the change in distribution is that the anhydrous complexes, wherein the dye exists as monomers, are highly fluorescent and wet complexes, where the dye exists as dimers, do not show any emission.

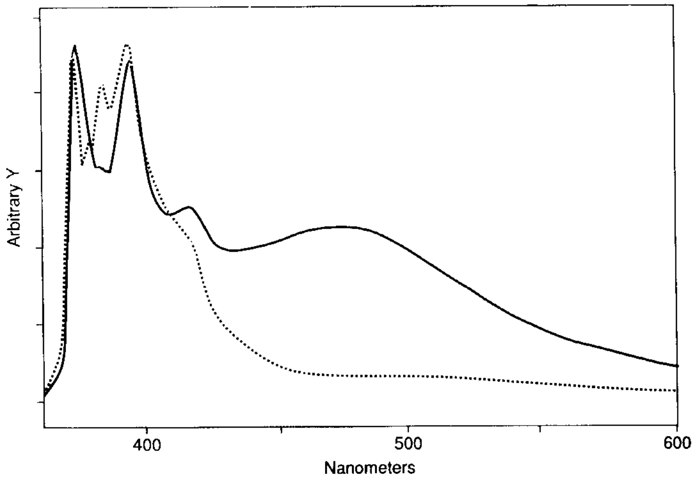


FIGURE 4. Emission spectra of pyrene, <S>: 0.2, included within Na Y under wet and dry conditions. (a) ———, "dry" Na Y; (b) ·········· , "wet" Na Y. Note the change in intensity of excimer emission and changes in vibronic pattern in the monomer emission.

## Pyrene

Inclusion of pyrene within Na Y is achieved by stirring known amounts of pyrene and Na Y in hexane for about 3 h, filtering and washing the white powder with excess hexane and drying it on a vacuum line. Excitation of pyrene included within anhydrous Na Y results in two emissions as shown in Figure 4, one from monomer and the other from excimer.[10] The so called excimer emission is definitely not an emission from typical dynamic excimer since the excitation spectra for the monomer and the excimer emissions are different (Figure 5). An obvious choice of the later emission being due to microcrystals was ruled out on the basis of following observations: (a) Both the wavelengths of emission and excitation were not identical to those of crystals reported in the literature. (b) Internal structure of Na Y is too small to accommodate microcrystals; however, if they are formed on the external surfaces they should be washable with excess hexane (see below). Hexane wash did not change the ratio of intensities of emission from monomer to excimer. These suggested that the excimer results from pre-aggregated dimers (static excimers) present within the supercages of Na Y. Such a conclusion is supported by the following observations: (a) No growing-in of the excimer in the nanosecond time scale was noticed when monomer and excimer decays were monitored by time resolved single photon counter. (b) No negative pre-exponential term for excimer decay was obtained. (c) The ratio of the intensities of excimer to monomer emission increased slightly upon lowering the temperature. (d) Variation of loading level between 0.002 and 0.2 (average number of molecules per supercage) did not alter pyrene monomer lifetime significantly.

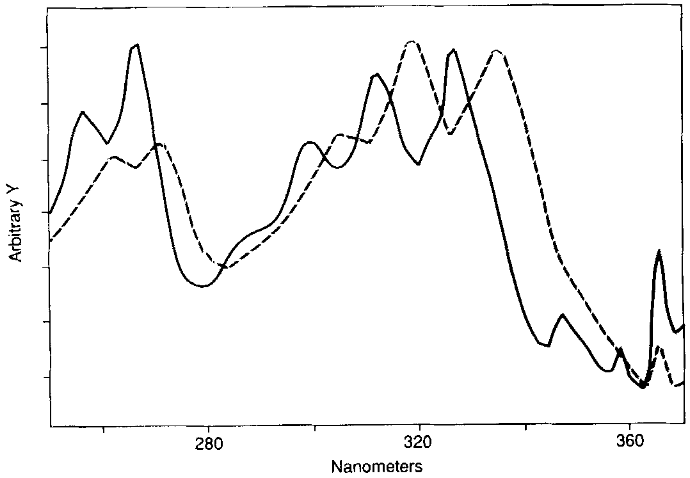


FIGURE 5. Excitation spectra for the monomer and excimer emissions of pyrene included within "dry" Na Y. (a) ——, monomer, em λ: 380 nm; (b) – – – , excimer, em λ: 480 nm.

There are certain similarities between pyrene and the dyes, discussed above, in terms of what factors influence the presence of monomer and dimer within zeolites. Co-adsorption of water has a striking influence on the nature of aggregation of pyrene within zeolites. As seen in Figure 4 the intensity of excimer emission from pyrene present within fully hydrated Na Y is fairly low. In fact, there is a correlation between the ratio of intensities of monomer to excimer emissions and the water content. Decrease in excimer emission with the increase in water content indicates that pre-aggregation is not favored within "wet" zeolites. As discussed in detail elsewhere,[10] such is the result of reduction in polarizing power of the cation; pre-aggregation is proposed to be a result of polarization of pyrene molecules by the cation. It is important to note that water has opposite effect on dyes to that on pyrene. While in the case of dyes it favors aggregation, in the case of pyrene it prohibits aggregation. However, the effect of loading level is the same in both cases. Higher loading of pyrene favors pre-aggregation as indicated by the increase in intensity of excimer emission (Figure 6).

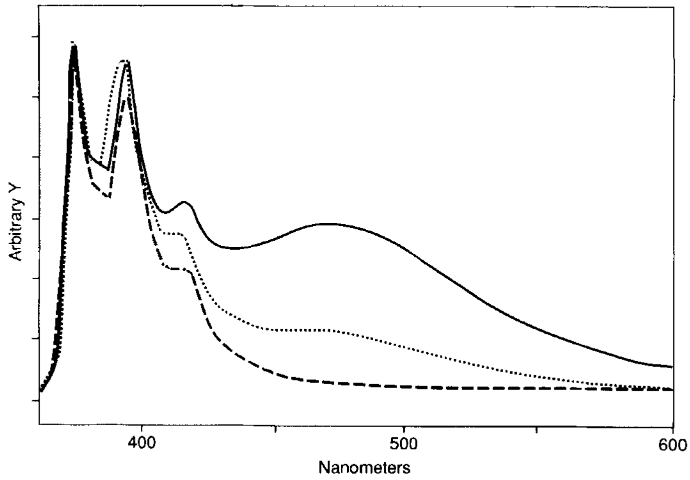


FIGURE 6. Emission spectra (excitation λ: 340 nm) of pyrene, at various loading levels, included within "dry" Na Y. Spectra at three loading levels (<S>) are presented: (a) – – –, <S>: 0.002; (b) · · · ·, <S>: 0.2 and (c) ——, <S>: 0.2. Note the changes in intensity of excimer emission.

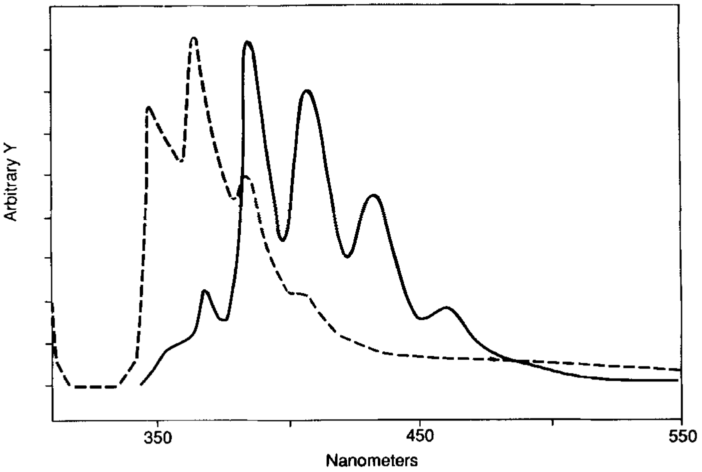


FIGURE 7. Emission spectra of phenanthrene, <S>: 0.4, included within "dry" and "wet" Na Y. (a) – – – –, "dry" Na Y, ex λ: 293 nm; (b) ———, "wet" Na Y, ex λ: 320 nm.

## Phenanthrene

Photophysics of phenanthrene brings out yet another unique characteristic of guest occupancy distribution within zeolites. Phenanthrene inclusion within zeolites can be achieved by following the procedure described above for pyrene. Emission spectra of phenanthrene (<S> varied between 0.002 to 0.4) included within anhydrous zeolite is non-unique; fluorescence from the monomer is detected and no excimer emission is seen (phenanthrene is known not to form excimer in solution). However, when the zeolite containing higher loadings of phenanthrene (<S> above 0.1) adsorbs water, in addition to the monomer emission, fluorescence from microcrystals is detected (Figure 7). A change in the occupancy status (monomer to microcrystals) is also reflected in diffuse reflectance spectra as shown in Figure 8. At lower loading levels (<S> lower than 0.1), independent of the hydration status emission spectra corresponded only to that of monomer and diffuse reflectance spectra of both wet and dry samples were nearly identical (Figure 9).

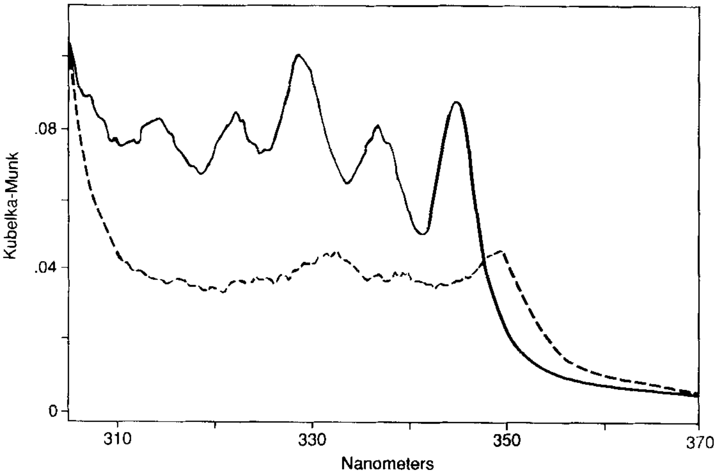


FIGURE 8. Diffuse reflectance spectra of phenanthrene, <S>: 0.4, included within "dry" and "wet" Na Y. (a) ———, "dry" Na Y; (b) – – – –, "wet" Na Y.

Association of phenanthrene to form micro-crystals at higher loadings is believed to be prompted by displacement of phenanthrene, by water, from the internal to external surface. At low loading levels of phenanthrene apparently both water and phenanthrene is able to co-exist within the internal surfaces of Na Y. Although, formation of microcrystals within the internal surfaces of zeolite would be extremely interesting, we were able to establish that micro-crystals are formed only on the external surfaces of Na Y. When the wet zeolite containing phenanthrene was washed with excess hexane, the hexane wash contained significant amounts of phenanthrene. However, similar wash of anhydrous zeolite containing phenanthrene did not result in phenanthrene loss into the hexane layer. This suggested that the location of phenanthrene under the two conditions (wet and dry) are different. Under anhydrous conditions phenanthrene is adsorbed onto the internal surfaces of zeolite (which are non-washable with hexane) whereas when the zeolite is hydrated, at least part of phenanthrene is adsorbed onto the outer surface (which are washable with hexane), *i.e.*, microcrystals are formed on the external surfaces of Na Y.

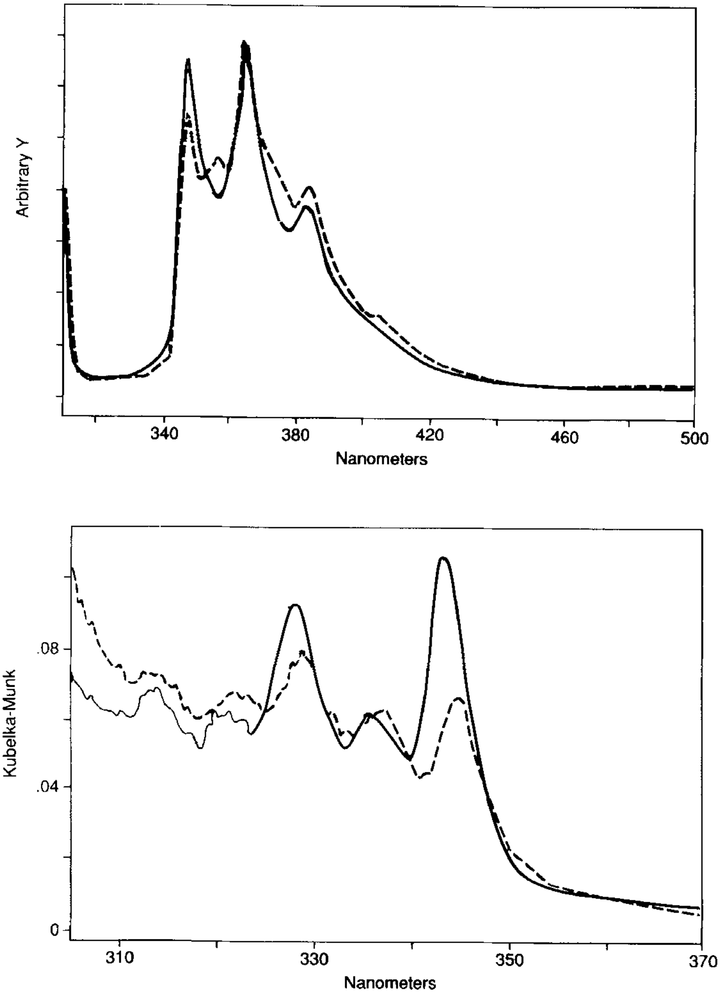


FIGURE 9. (Top): Emission spectra of phenanthrene, <S>: 0.001, included within "dry" and "wet" Na Y. (a) – – – –, "wet" Na Y, ex λ: 293 nm; (b) ———, "dry" Na Y, ex λ: 293 nm. Note the changes in vibronic pattern between dry and wet samples. (Bottom): Diffuse reflectance spectra of phenanthrene, <S>: 0.001, included within "dry" and "wet" Na Y. (a) ———, "dry" Na Y; (b) – – – –, "wet" Na Y.

When the above hexane washed wet phenanthrene–NaY complex was subjected to dehydration–hydration cycle, no micro-crystals were detected indicating that excess phenanthrene which could not be accommodated (at high loadings) in presence of co-adsorbed water has been removed by initial hexane wash. What was most unique was that when the unwashed hydrated sample was dehydrated, emission due to microcrystals completely disappeared and only monomer emission was detected. This suggests that dehydration of the hydrated zeolite leads to the migration of phenanthrene from external to internal surface of Na Y. Thus dehydration–hydration cycle promotes monomer–microcrystal cycle.

Above examples illustrate that distribution of guest occupancy within zeolites may not be homogeneous. Guests may be present either as monomers, dimers, microcrystals or as a combination of all. In general, occupancy re-distribution is brought forth by admittance of water into anhydrous zeolites. The occupancy distribution pattern, depending on the guest molecule, can be detected from their ground state spectra (*e.g.*, diffuse reflectance spectra) or from their excited state spectra (*e.g.*, fluorescence).

## FAMILIES OF SITES

By the term "family" we mean a group of sites which can be represented by a single primary characteristic. By the very term family, it is implied that there may be more than one site within a family. For example, a number of spectroscopic and x–ray studies have suggested that benzene molecules within the supercages of Na X and Na Y zeolites are located near the cation and at the window interconnecting two supercages (Figure 10).[11] We call these two sites–cationic and window–as two families of sites. Instead of calling simply as site, the adjective family is used to indicate that not all molecules at cationic or window sites need be identical. Small differences in guest molecules geometrical relationship with the cation or the window might exist which might become detectable under conditions wherein the time of exchange of molecules between sites within a family is longer than the duration of measurement. This aspect is discussed in the next section.

In homogeneous solution, one rarely discusses the possibility of more than one environment for the reacting solute. Fluid solutions allow reacting molecules experience an average microenvironment by virtue of fast relaxation time of the solvent and/or high mobility of reactant molecules. Important relaxation modes of low viscosity, non-polar solvents occur at rates near or greater than $10^{12}$ $s^{-1}$ at room temperature, *i.e.*, faster than the rates normally encountered for deactivation of $S_1$ and $T_1$ excited states. Under such conditions, temporal fluctuations in microscopic solvent structure may permit all molecules in the solution to be exposed to very similar environments during their excited state lifetimes. In essence all reactant molecules experience a 'single effective environment'. Unlike solvents, the zeolite structure is time independent. Guest molecules may experience identical environments within zeolites only if they can establish equilibrium, before they decay from the excited state, between various sites through fast migration. However, in zeolite media rates of guest diffusion may be slower than the time period of a photoreaction. These characteristics might lead to guest molecules residing at a number of different environments undergoing photochemical and photophysical changes. Thus on the time-scale of photochemical events guest molecules would be considered to have more than one families of sites.

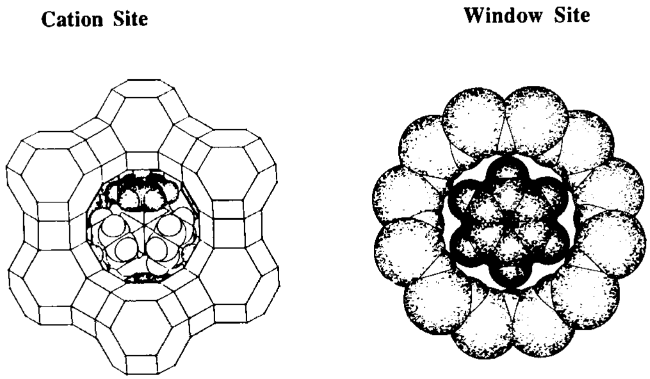
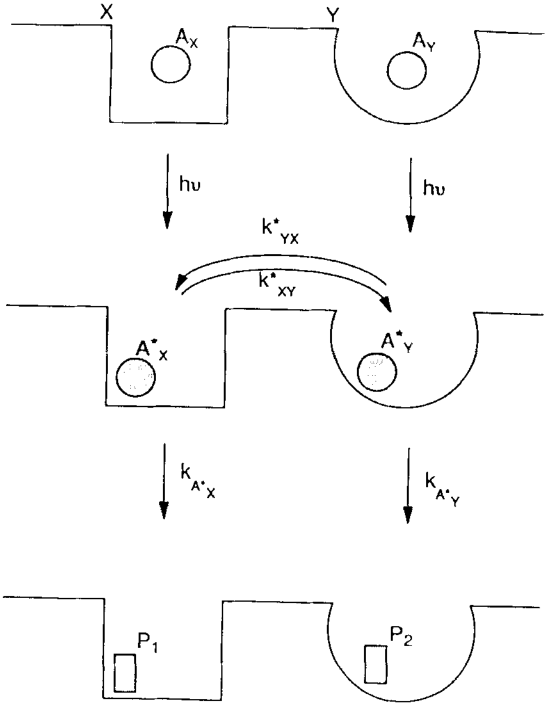


FIGURE 10. Two sites (cation and window sites) identified for benzene within the supercages of X and Y zeolites.

Above theme is briefly discussed below in terms of a two sites problem (Scheme).[6] In this scheme, two sites, square well type (X) and spherical well type (Y), are available for the residence of guest molecule (A). In the present context, these are equivalent to cationic and window sites in the supercages of Na Y. Molecules residing at sites X and Y are labeled $A_X$ and $A_Y$. Excitation of these molecules leads to $A_X^*$ and $A_Y^*$. Photobehavior of molecules excited in each site will be identical if they equilibrate between X and Y before becoming photoproducts. Two limiting dynamic situations can be envisioned: (1) The rates of excited state processes is slower than the rate of interconversion between $A_X^*$ and $A_Y^*$ (equilibrium is established between $A_X^*$ and $A_Y^*$ before decay; $k_{XY}^*$ and $k_{YX}^*$ >> $k_{A_X}^*$ and $k_{A_Y}^*$). This corresponds to the situation in a fluid isotropic solution where a single effective site should exist. Under such conditions a single exponential decay would be expected for the guest excited states and the photoreactivity would be predictable on the basis of a single effective site. (2) The rate of excited state process is faster than the rate of interconversion between $A_X^*$ and $A_Y^*$. As per this mechanism there should be two kinetically distinct $A^*$ in two non-interconverting sites. A double exponential decay would be predicted for the excited state of A. As illustrated below with aromatic molecules as probes, guest molecules adsorbed onto the interior of zeolites are best described by case 2 above.



SCHEME

Unlike in homogeneous solution media, fluorescence decay of pyrene, naphthalene and phenanthrene adsorbed onto Na Y does not follow single exponential decay. More than 95% of the fluorescence decay can be analyzed satisfactorily on the basis of two exponential decay indicating that primarily there are two families of sites in which these aromatic molecules are located (Table 1). Support for the independent nature of the two sites come from three different observations: (a) As shown in Figure 11, with increasing pressure of zenon, fluorescence of naphthalene is quenched and phosphorescence is enhanced;[12] zenon quenching of the excited singlet occurs through external heavy atom effect.[13] Surprisingly, only one of the two lifetimes depended on the pressure of zenon (Table 2). This suggests that among the two sites in which naphthalene is present only one is accessible to zenon. At this stage no knowledge on the nature of the two sites is available. (b) It has been established that the singlet lifetime of pyrene is related to the polarity of the medium; lifetime is fairly long in a non-polar medium (e.g., cyclohexane: 430 ns) and is relatively short in a polar medium (e.g., dimethylformamide: 280 ns).[14] When pyrene is included within Na Y two lifetimes, one short and one long, is measured. On the basis of the relationship between lifetime and polarity of the medium, it is likely that the one with shorter lifetime corresponds to pyrene closer to the cation (higher electric field/micropolarity) and the one with longer lifetime refers to the pyrene adsorbed onto the walls (lower electric field/micropolarity).[15] (c) Spectral features in the emission spectra of pyrene is found to be time dependent in the time range 1 to 900 ns (Figure 12). The intensity of the first band at 373 nm is fairly strong at early times and is weak at later times. It has been established in homogeneous solution that the intensity of this band is dependent on the polarity of the medium.[16] The intensity variation observed within Na Y is consistent with the proposal that pyrene molecules are present under two different micro-environments, one highly polar environment (cation site) and the other moderately polar (wall site).

TABLE 1: Excited state singlet lifetime of aromatics adsorbed within "dry" Na Y

| No. of molecules per supercage | Lifetime in ns (based on biexponential analysis) | | |
|---|---|---|---|
| | Pyrene | Phenanthrene | Naphthalene |
| 0.002 | 91.2, 29 | 33.5, 7.0 | 29.4, 1.5 |
| 0.02 | 84.7, 32.5 | 32.0, 7.3 | 26.3, 1.1 |
| 0.04 | 85.8, 25.3 | 32.1, 6.3 | 26.7, 1.5 |
| 0.08 | 86.5, 27.6 | 34.7, 6.7 | 26.3, 1.2 |
| 0.20 | 84.8, 38.4 | 32.1, 4.7 | 26.6, 1.1 |

TABLE 2: Quenching of the excited singlet state of naphthalene included within Na X by xenon

| Pressure of Xenon (mm) | lifetime in ns at 298K | lifetime in ns at 77K |
|---|---|---|
| 0 | 29.6, 14.2 | 67.8, 33.0 |
| 17 | 31.6, 13.0 | 64.0, 20.0 |
| 67 | 32.8, 9.9 | 63.3, 14.2 |
| 206 | 30.7, 6.1 | 61.2, 12.8 |
| 505 | 31.4, 5.3 | 61.9, 7.7 |
| 759 | 32.4, 3.4 | 58.5, 6.6 |

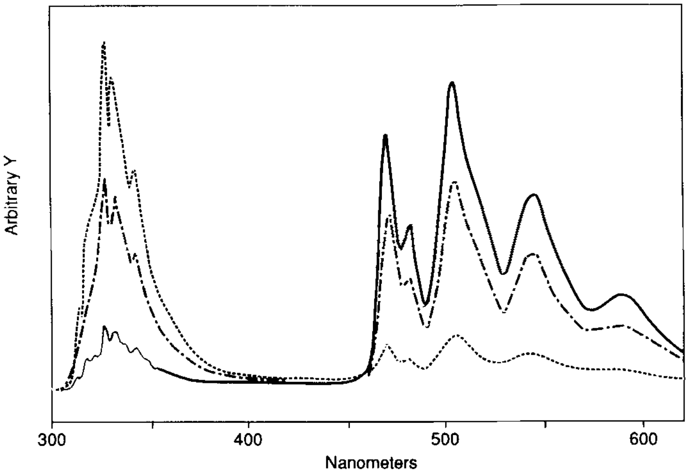


FIGURE 11. Emission spectra of naphthalene included within "dry" Na X in presence of xenon. Note that with increasing pressure of xenon, fluorescence decreases and phosphorescence increases. (a) ············ no xenon; (b) –. – . – . 75 mm pressure of xenon; (c) 200 mm pressure of xenon.

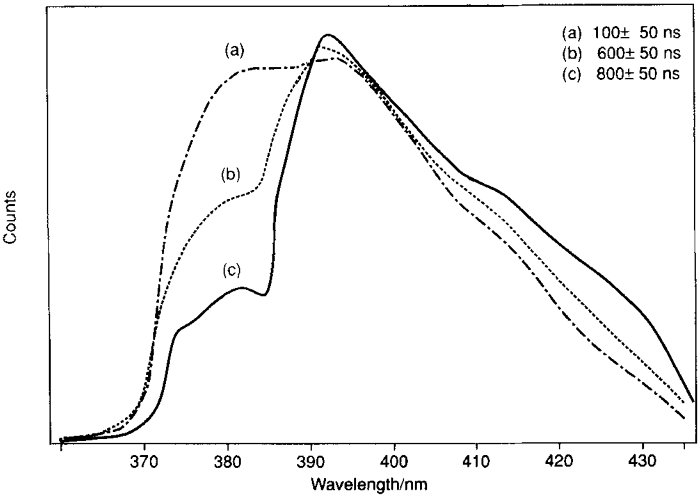


FIGURE 12. Time resolved emission spectra of pyrene within "dry" Na Y. Note that the intensity of the first band decreases with longer time.

## DISTRIBUTION OF SITES WITHIN A FAMILY

By the term "distribution" we mean that a site which is identified by a "family" in the above section (*e.g.*, cationic, window and wall sites) may consists of a number of sites which in their characteristics bear close resemblance to the primary site. For example, a cationic site while ideally can be defined by a unique arrangement between the cation and the guest molecule, may in fact consists of a number of closely related arrangements. Thus, while the principal characteristics of these closely related sites may be defined by the primary site, the individual sites belonging to the same family might show properties which are slightly different from each other. Whether these changes are detectable will depend upon the time the guest molecules take to migrate from one site to the other within the same family and the time involved in a particular measurement (Scheme).[6]

Analysis of fluorescence decay from pyrene, naphthalene and phenanthrene by a distribution analysis program (supplied with FL 900 single photon counter by Edinburgh Instruments)[17] provides an insight into the problem of distribution of sites within zeolites.[18] Distribution of lifetime obtained in the case of pyrene, naphthalene and phenanthrene within anhydrous Na Y are presented in Figure 13. It is quite clear from this figure that the distribution of lifetime, a reflection of the presence of distribution of sites (non-equilibriating sites), for naphthalene and phenanthrene within anhydrous Na Y is extremely narrow. Consistent with this, as pointed out in the previous section, the excited singlet decay can be analyzed by two exponentials. Essentially these molecules exist within two families of sites with very narrow distribution. However, such is not the case in the case of pyrene. In the case of pyrene, within anhydrous Na Y, the width of distribution centered around two families of sites is very broad. We believe that pyrene provides an ideal example wherein "distribution of sites" exists.

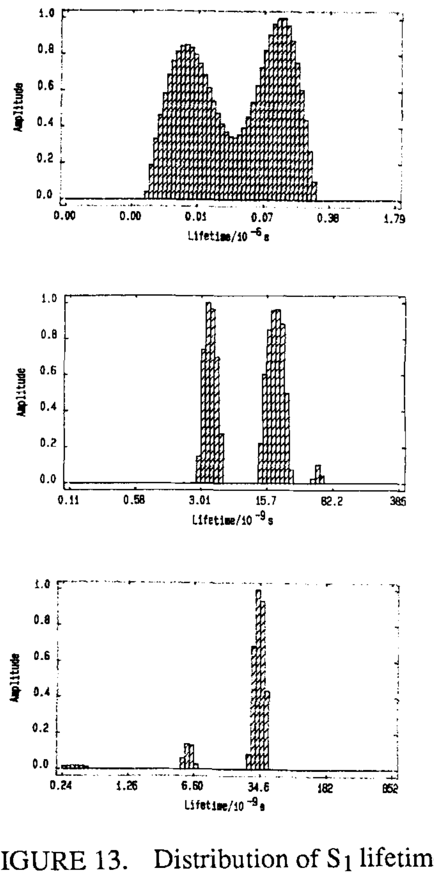


FIGURE 13. Distribution of $S_1$ lifetime of (a) pyrene, (b) naphthalene and (c) phenanthrene included within "dry" Na Y at room temperature.

Absence of a wide distribution in the case of naphthalene and phenanthrene may be due to either all molecules exist in an unique arrangement within two families of sites or the interchange of molecules between sites (within families) is fast on the time scale of fluorescence decay. Distribution seen at 77 K for naphthalene suggests that the second proposition may indeed be true. When the sample is cooled from room temperature to 77K within a few minutes the distribution at room temperature is expected to be frozen at 77K as the time required to attain equilibrium may be much longer. Thus cooled sample to 77K exhibited a wide distribution of lifetime (Figure 14). Similar, but not as striking, changes in the distribution is also seen in the case of pyrene. The increase in distribution at 77 K, we suggest, is due to reduction in mobility of molecules at this temperature. While at room temperature fast equilibrium is attained within the excited singlet lifetime (due to fast diffusion of probe molecules) between a number of sites within a family, such is prevented at 77 K. It is likely that the difference in site distribution seen between pyrene and the other two aromatics at room temperature also results from differences in mobility of these molecules within the supercages of Na Y.

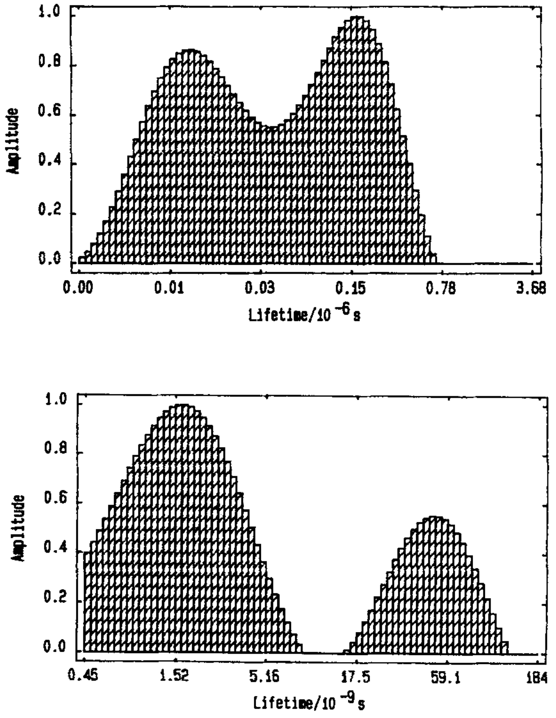


FIGURE 14. Distribution of lifetime of the excited monomer of (a) pyrene and (b) naphthalene included within "dry" Na Y at 77K. Compare with Figure 13 and note the changes in distribution width between room temperature and 77K.

The distribution is also affected by co-adsorbents present within Na Y along with the guest molecule. This is illustrated by the results obtained in the case of pyrene with water and other solvents as co-adsorbents. From Figure 15 it is evident that the lifetime distribution for pyrene within Na Y co-included with water is fairly narrow when compared to that in anhydrous Na Y. Similar decrease in distribution is obtained when organic solvents such as hexane, pentane, cyclohexane, acetonitrile, diethylether and methanol were used as co-adsorbents. Even, naphthalene and phenanthrene which have narrow distribution in anhydrous Na Y, possess much narrower distribution within hydrated Na Y. The narrow distribution most likely results from weakening of interaction between aromatics and the sites (cationic and wall) by co-adsorbents. Under such conditions fast migration of pyrene between sites within a family would be expected.

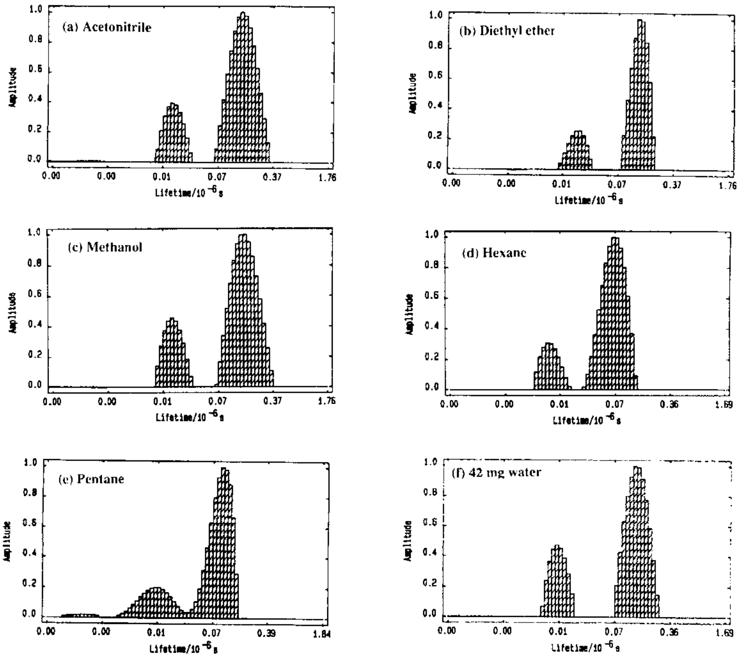


FIGURE 15. Distribution of lifetime of the excited monomer of pyrene within Na Y co-included with organic solvents and water. Compare with Figure 13a and note the changes in distribution width.

## FURTHER COMPLICATIONS

In environments such as zeolites where there are restrictions on molecular motions, the guest molecules may be forced to assume conformations atypical of homogeneous media. While in solution due to fast rotations an average shape of the molecule would be projected to the measurement, in media such as zeolites, complications might arise due to the presence of non-interconverting isomers. One such example has been presented in the literature.[19] Thus, one should note that a wider distribution of molecular sites than discussed above might result if rotational motions, in addition to diffusional motion, of guests are restricted by the zeolite matrix.

## CONCLUSIONS

Guest distribution within zeolites can be more complex than in homogeneous solution. Fast relaxation of solvent molecules and fast diffusional motion of solutes result in reactant molecules experiencing a single effective environment in homogeneous solution. Under such conditions predictions concerning the photobehavior of reactants can be made on the basis of a single reaction site. These need not be, and generally not, true in organized assemblies such as zeolites. Non-homogeneous site distributions is a general feature which lead to guest molecules reacting from a number of different environments. Non-homogeneity results from variation in guest occupancy between otherwise identical sites, from the presence of more than one families of sites possessing different micro-environments and from a distribution of sites within a family. A key controlling feature is the relationship between the time it takes for molecules to migrate from one site to the other and the lifetime of the excited state. Because of this, distribution of sites sensed by probes in their excited singlet and triplet states need not be identical. Rules governing the distribution of molecules within organized assemblies need to be established before these media can be reliably utilized to control photobehavior of guest molecules within these assemblies.

## ACKNOWLEDGEMENT

It is indeed a pleasure to thank D. R. Sanderson for superb technical assistance.

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