

Rigid-Unit Modes and the Quantitative Determination of the Flexibility Possessed by Zeolite Frameworks

Kenton D. Hammonds,^{*,†} Volker Heine,[‡] and Martin T. Dove[†]

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom, and Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom

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This paper is concerned with the way in which the flexibility of zeolite frameworks can be calculated and expressed in an exact and quantitative manner. It is found that zeolites modeled as frameworks of tetrahedra are extremely flexible but only as a few very specific modes in specific places. These modes give specificity in the action of a zeolite: in lining up of Brønsted acid sites to fit reacting molecules, in adapting the shapes of channel windows to the shapes of certain diffusing molecules, and in attaching catalytically active cations to the framework. These floppy modes or “rigid-unit modes” (RUMs) can be very localized, and we show how local RUMs may be calculated precisely as wave packets of standard RUM phonon modes for any given zeolite. Applications to six zeolites are given. Local modes may be static deformations costing virtually no energy as in holding cations, or fluctuating as in facilitating the diffusion of certain molecules, or quasi-static as in catalyzing a reaction with acidic sites. In addition, it is possible to attempt to create local RUMs with eigenvectors that have a desired form. This means that the presence of any kind of specific flexibility within a zeolite can be tested for. Thus it becomes possible to determine the exact nature of the flexibility present within any aluminosilicate zeolite. In particular, local RUMs enable one to determine which parts of a framework are most flexible and hence more likely to be catalytically active.

Introduction. Flexibility and RUMs

The flexibility of zeolites is chemically important in three respects. First, zeolite frameworks host many acidic defect sites along channels and within cages, and these allow chemical reactions to occur readily involving adsorbed molecular species. However, the presence of the framework implies that the acidic sites are more or less fixed in position, and so reactions are determined by the possible interaction between the geometry of molecular species and the geometry of the framework. If these geometries are incompatible, then no possibility exists for reactions to occur unless a molecular species happens to possess the shape required to utilize the acidic sites. Therefore it is vital to know whether the framework contains the specific flexibility or not needed to match the positions and orientations of the Brønsted acid sites to the geometry of the molecule. Second, holding a catalytically active cation such as Ni^{2+} requires a flexing of the framework to bring together a cluster of oxygen atoms around the cation. Third, kinetic processes such as molecular or ionic diffusion and the reorientation of molecular species are also key to the operation of zeolites as catalysts. Molecules and ions must be able to diffuse into zeolites, move to reaction sites, change orientation so that energy barriers to reaction are lowered, and finally react. The new molecules must then be able to diffuse out of the zeolite so that they can be collected and utilized. Again, a nonrigid framework will greatly assist all of these processes and a specific type of floppiness in a channel window will assist the diffusion of a specifically shaped type of molecule.

It is therefore very important that the inherent flexibility of a zeolite framework can be understood in a quantitative fashion. Knowing in general terms that a zeolite has a certain amount of flexibility does not provide much scientific understanding. We need to know the specific ways in which a zeolite framework can flex, and we need to be able to calculate these in a simple and direct manner. For example, we may wish to know whether it is possible for a cage within a particular zeolite to contract along a particular crystal axis, or we may simply wish to know all of the possible ways in which a zeolite structure can deform. All the applications described above imply a local flexibility, not just in a global manner as in a structural phase transition, and we want to show that it costs negligible energy. This paper outlines the ideas, methods, and concepts that we have been using for some time to solve these precise problems—ideas that are collectively known as the rigid-unit mode (RUM) theory. Some of the advantages of RUM theory are that it is based on simple ideas, needs relatively little computing power, but is able to yield quantitative answers to questions such as “In what way are those channels able to display flexibility in that particular zeolite?”

Zeolites are by many standards very complicated materials that have large unit cells containing hundreds of atoms and this complexity has resulted in a lot of our understanding of them being qualitative or empirical in nature. In particular, the computing revolution of the last 20 years has not previously enabled a clear understanding of zeolite flexibility to be achieved. Computer simulations using empirical potentials have been performed, but results concerning the flexibility of frameworks cannot be easily expressed or used in a precise way—framework deformations that occur during molecular dynamics runs can be observed by visualising the data, but the

* Corresponding author. Email: kenton@minp.esc.cam.ac.uk. FAX: +44 (0)1223 333450.

[†] Department of Earth Sciences.

[‡] Cavendish Laboratory.

complete nature of the floppiness possessed by a zeolite framework cannot be understood from such simulations. Electronic structure calculations on zeolites with large unit cells are not yet routine, being possible only on the most powerful of current supercomputers, and even then many zeolites remain currently out of reach. In any case, these do not enable a clear understanding of the flexibility of a structure to be readily achieved although they have many other uses.

By contrast, the rigid-unit mode theory has proven itself to be a very powerful tool for understanding the behavior of aluminosilicates and other materials made up of XO_4 tetrahedra and XO_6 octahedra that are linked into three-dimensional frameworks. Using the RUM model it is possible to explain a large range of phenomena including displacive phase transitions,¹ negative thermal expansion,² cation-ordering schemes, negative Poisson ratios, diffuse scattering from X-ray and electron diffraction experiments,³ low material compressibilities and amorphization.

The Basis of the Rigid-Unit Mode Model

X-ray structure analysis has shown that many silicates including zeolites are what are termed "tetrahedral framework structures". In these the Si/Al ions are surrounded by four oxygens in a tetrahedral arrangement with each of the oxygens being shared between two Al/Si atoms. The bonding inside the tetrahedra is very strong, and they remain intact under very many displacive and atomic ordering phase transitions.⁴ On the other hand, the bond angle at the oxygen atom joining two tetrahedra is rather flexible. From the phonon spectra of several silicates and electronic structure calculations,⁵ we can infer that the linkages between tetrahedra are about 100 times more flexible than the tetrahedra themselves. Therefore we say that these materials possess a "floppy/stiff duality"—stiff tetrahedra with floppy linkages between them.

However, that still leaves as an open question the degree and type of flexibility of the structure as a whole, because the framework contains three-dimensional cross-bracing. The crux of the problem that the present work addresses is the type of flexibility allowed by the geometry of the framework.

In view of the floppy/stiff duality at the tetrahedron level, it is an excellent approximation to model a zeolite framework as a set of very stiff tetrahedra that are completely flexible about their oxygen hinges.^{6,7} The modes we are particularly interested in are those that leave the stiff tetrahedra undistorted. They have been termed rigid-unit modes (RUMs) because they remain geometrically allowed motions even when the tetrahedra are made infinitely rigid. The key point is that the motions of the five atoms that make up a tetrahedron are correlated under these phonon modes so that their relative positions remain constant. They can be looked for computationally by the methods of molecular lattice dynamics,⁸ because they have exactly zero frequency if the force constant at the hinges (*i.e.*, the T–O–T angle force constant) between the tetrahedra is set equal to zero. Thus RUMs in this approximation have zero restoring force when considered as oscillations, and cost zero energy as static displacements. In practice we shall use the term "floppy modes" to include not only the RUMs but all vibrations up to 1 THz (the range for which floppy modes are observed in silica glass⁹). These vibrations with a small but nonzero frequency are referred to as quasi-RUMs or QRUMs. They are also of interest since they are modes that barely deform the tetrahedra as they propagate and so also have a very low energy associated with them—they have a force constant in their potential energy term less than 0.1% of that of an average lattice vibration in a

framework silicate. (The force constant varies as the square of the frequency, and the lattice vibrations range up to about 20 THz excluding the optic modes of the Si/Al atoms inside their tetrahedra).

Computer codes to study RUMs and floppy modes have been written using the theory of molecular lattice dynamics. There are several papers that discuss this.^{1,2,3,6–8,10,11} Molecular lattice dynamics is an extension of atomic lattice dynamics and in particular takes into account the rotational degrees of freedom that molecules have. The calculations have been based on a one-parameter model called the split-atom model in which the stiffness of the tetrahedra is represented by one parameter without distinguishing between the different inequivalent ways of deforming a tetrahedron. The model is incorporated in the CRUSH code,^{10,11} which works as follows: first imagine some silicate framework made up of SiO_4 molecular units. Then at every oxygen position there are going to be two oxygen atoms, one belonging to each silicon. If one creates an arbitrary set of displacements and rotations of these strictly rigid tetrahedra starting from a perfect framework structure, then the corners of the tetrahedra would in general have to move apart instead of remaining joined. The distance that two corners would move apart is a measure of the amount that the tetrahedra will have to distort in reality for their corners to remain joined. Thus a stiff spring is inserted at each corner with an ideal length of zero and a force constant of about 245 N m^{-1} . This gives a moderately good representation of the whole phonon spectrum as well as allowing us to identify all the floppy modes. A point to note is that pure RUMs would continue to have a frequency of zero even if an infinite stiffness is used, while the frequencies of other floppy modes rise as the force constant rises.

Modelling a zeolite as a set of rigid tetrahedral SiO_4 units with springs connected between all oxygens that are superpositioned in space may seem to be a very simplistic way of doing things. However the essential physics of the situation is captured by such an approach, especially in the low-energy regime. If a complex empirical potential were used, then the same low-energy deformations will result since we know that the tetrahedra retain their shape under all but the most extreme conditions and would rotate in whatever way was required to achieve this. So the Si–O–Si angle-bending potential is effectively flat compared to all other terms in such a potential model. Therefore our one-parameter model with no Si–O–Si angle-bending term at all can be seen to be a good approximation of reality, and the eigenvectors obtained from it will also be trustworthy.

Our codes allow one to calculate the phonon eigenvectors (*i.e.*, associated displacement patterns), their symmetries, and ways of combining them into local RUMs. More information concerning the computer programs used for these calculations, such as CRUSH, can be obtained from the web-site http://www.esc.cam.ac.uk/mineral_sciences/crush.

A plot of the density of phonon modes for a typical silicate and a typical zeolite are shown in Figure 1. These were calculated with the CRUSH code and hence omit the bands of very high-frequency modes that result from the internal vibrations of the Si/Al atoms inside the tetrahedron. The two plots are similar except in the low-frequency region where zeolites have a very large peak while other minerals do not. Many nonzeolitic minerals are known to have lines and planes and curved surfaces of RUMs and floppy modes in \mathbf{k} -space.^{1,12} These may give rise to a small peak near zero frequency for many minerals in a density-of-states plot, but zeolites are different because they can support a certain number of RUMs and floppy

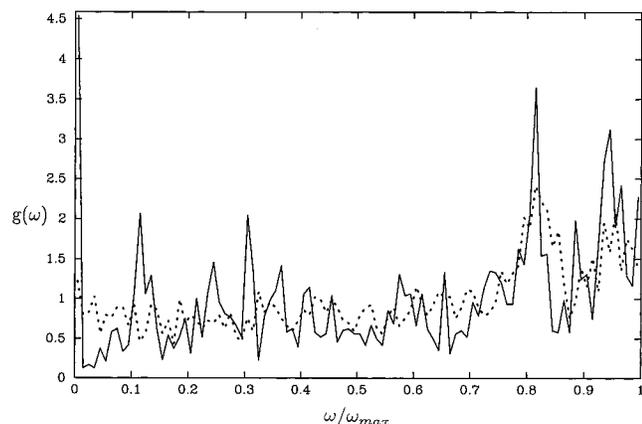


Figure 1. Density of phonon modes calculated from the one-parameter model. The dotted line represents a typical silicate such as a feldspar, while the solid line is for faujasite, a typical zeolite. The important difference between the two plots is the large peak at nearly zero frequency for the zeolites, containing about 5% of all its phonon modes. The quantity ω_{\max} is about 20 THz.

TABLE 1: Numbers of Pure, i.e., Exactly Zero Frequency, RUMs Observed in Various Body-Centered Cubic Materials^a

k-point	Z-rho	Z-rho	Sod	Sod	Leu	Pau
	$Im\bar{3}m$	$I\bar{4}3m$	$Im\bar{3}m$	$I\bar{4}3m$	$Ia3d$	$Im\bar{3}m$
$\Gamma(0, 0, 0)$	10	4	7	3	8	44
$H(0, 0, 1)$	10	4	3	3	0	44
$N(\frac{1}{2}, \frac{1}{2}, 0)$	6	2	3	2	4	24
$P(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	4	4	3	3	0	24
$\Delta(\alpha, 0, 0)$	4	2	3	2	0	24
$\Lambda(\alpha, \alpha, \alpha)$	2	2	1	1	0	14
$\Sigma(\alpha, \alpha, 0)$	5	2	3	1	4	24
$D(\frac{1}{2}, \frac{1}{2}, \alpha)$	4	2	2	2	0	14
$F(\alpha, 1 - \alpha, \alpha)$	2	2	1	1	0	14
$G(\alpha, 1 - \alpha, 0)$	5	2	2	1	0	24
(α, α, β)	2	2	1	1	0	13
$(\alpha, \beta, 0)$	4	1	2	0	0	24
(α, β, γ)	2	1	1	0	0	13

^a The points, lines, and planes in \mathbf{k} -space are labeled by their position and denoted by Roman and Greek letters. In particular note that RUMs can occur at general points (α, β, γ) in \mathbf{k} -space for many of these materials. sod is sodalite, Z-rho is zeolite-RHO, Leu is leucite, and Pau is paulingite. At Γ we have also included the three acoustic modes among the RUMs. The total number of frequencies for the structures in the table are 144, 144, 36, 36, 144, and 2016, respectively, excluding internal motions of si and al atoms inside the tetrahedra. We generally find that about 5% of all modes can be considered to be floppy in many zeolites.

modes at all possible values of \mathbf{k} in reciprocal space. Therefore we say they have one or more complete bands of RUMs or floppy modes in \mathbf{k} -space.¹³ This means that a finite fraction of all modes in a zeolite are RUMs or floppy and hence you get the very large peak at zero frequency shown in Figure 1.

To exemplify the above ideas consider, Table 1. This shows the number of RUMs observed at special symmetry \mathbf{k} -points in the Brillouin zone for some body-centered cubic zeolites. Note that there are many RUMs along lines and within planes of \mathbf{k} -space. Also we can see that at any arbitrary \mathbf{k} -point there are still some RUMs observed for some of the structures and these are the RUMs that form the bands discussed earlier. The zeolite paulingite is particularly interesting because it has 13 RUMs at any general \mathbf{k} -point. The faujasite (face-centered cubic) and zeolite LTA (simple cubic) structures both have four RUMs at general \mathbf{k} -points, while the numbers at other symmetry points have already been given in ref 13. The (α, β, γ) row of Table 1 effectively shows the number of RUMs per unit cell that a crystal has. To be totally floppy, all the normal-mode

motion of a crystal would have to be RUMs, but it is clear from Table 1 that this is not the case for the zeolites shown; hence, we say that zeolites are flexible in only a few specific ways. For example the $Im\bar{3}m$ phase of sodalite has one RUM per six tetrahedra, so $1/36$ or 2.8% of all modes are RUMs. If a band of floppy modes is included as well then the number of floppy or RUM modes rises to 5.6%, a lot less than 100%. Sodalite in the $I\bar{4}3m$ structure does not have a complete band of RUMs but does have a complete band of floppy modes in the more general sense defined above. The same applies to the $Ia3d$ phase of leucite. The possible deformations that a zeolite can undergo are held within the RUM eigenvectors. These contain the displacement patterns of oxygens and Al/Si atoms under mode propagation, and so all the allowed flexibility of a zeolite is described within them.

The Nature of Local RUMs

It is from bands of RUMs, and particularly the information held within the eigenvectors Φ_{nk} (where n is the band number), that the flexibility of a framework can be examined in great detail. At any point in \mathbf{k} -space there are $6N_T$ lattice modes, each with its own eigenvector, where N_T is the number of tetrahedra in the primitive unit cell. The motions of atoms in a crystal are equal to a superposition of all the eigenvectors of all the allowed lattice vibrations. We can therefore consider what would happen if the eigenvectors of just the RUMs and other very low-frequency modes were to be superposed, without mixing in the higher frequency modes. The answer is that the bands of RUMs and floppy modes can combine to form what we call "local RUMs" or "local floppy modes". If the RUMs combine with suitable phases and amplitudes, then the resulting local RUM may have a large intensity over a very small region of real space, often just a few tetrahedra, and negligible intensity elsewhere. The frequency of such a local RUM is very low since its constituent modes have very low frequency. Therefore such a mode could "condense" out in the zeolite structure (to use the language of soft-mode-phase transition theory) and give rise to a local static deformation in the framework. The presence of a single molecule within an empty zeolite crystal could cause this to occur by pulling oxygens toward itself (or $-\text{OH}$ groups in the case of Brønsted acid sites), and a significant change in the local environment will result while the rest of the crystal remains unaffected. With several molecules, each one could change its local environment with the areas of crystal between them again remaining unaffected. The important point is that since only RUM modes are involved these distortions cost negligible energy to create—a point shown in a previous paper.¹³

The precise nature of possible distortions is determined by the nature of the eigenvectors of the RUMs. If many RUM eigenvectors exist within a zeolite, then there is the possibility of a large variety of deformations. However, the exact character of the eigenvectors limits the possibilities. This gives rise to the important point that zeolites have frameworks that are flexible but only in certain specific ways; they are not flexible in a completely general sense. Another important point is that since the eigenvector of a local RUM can be explicitly calculated, we know exactly what any local distortion will look like. In addition one can attempt to create a local RUM with an eigenvector that has a specific wanted form. The degree to which such an eigenvector can be formed will then tell you whether that particular distortion is possible or not. Therefore the existence of any form of flexibility within any zeolite structure can be explicitly tested for.

The Calculation of Local RUMs

To form a local mode one must superpose phonons from the whole of reciprocal space (\mathbf{k} -space), and hence to form a local RUM (or local floppy mode in the more general sense defined above), we require one or more whole bands of RUMs or floppy modes. To calculate local RUM eigenvectors, one therefore first calculates all the RUM eigenvectors for a particular zeolite structure over an entire grid of N_k points evenly spaced in \mathbf{k} -space using the CRUSH code. This can be viewed as a discrete sampling for computational purposes of the continuous \mathbf{k} -space. Alternatively it is equivalent to a superlattice structure with supercell dimension $N_k^{1/3} \times N_k^{1/3} \times N_k^{1/3}$, and any local RUMs that are made are then defined in this supercell and so are repeated periodically on the scale of the supercell. This paper uses the supercell viewpoint of sampling \mathbf{k} -space. Since a RUM eigenvector Φ_{nk} is just the complex conjugate of the eigenvector at $-\mathbf{k}$, we only need to consider half of all the \mathbf{k} -points across the Brillouin zone. Since RUM eigenvectors all have zero frequency, they will generally mix up, and in some cases one may want to separate them: a way must then be found to break the degeneracy and so produce pure eigenvectors. For example, some points in the Brillouin zone have extra RUMs that are specific to that point as well as those that are part of RUM bands. One way to separate the two is to use \mathbf{k} -points that are very slightly off position whenever this occurs. RUMs that are not part of RUM bands will increase in frequency as one moves away from a special point in a general direction, and this will cause the eigenvectors to unmix. Other ways of separating eigenvectors include the use of minor extensions to the split-atom model such as an extra but very weak harmonic potential that acts between the centers of tetrahedra. Once the N bands of RUM eigenvectors Φ_{nk} have been obtained then a local RUM, \mathbf{L} can be generated as below

$$\mathbf{L} = \frac{1}{N_k N (\sum_{\mathbf{k}} \sum_n A_{nk}^2)^{1/2}} \sum_{\mathbf{k}} \sum_n A_{nk} \exp(i\gamma_{nk}) \Phi_{nk} \quad (1)$$

where Φ_{nk} is a RUM eigenvector describing the displacements and rotations of all the tetrahedra within some central reference cell within the supercell. This RUM eigenvector extends throughout all space with Bloch phase factor $\exp(i\mathbf{k}\cdot\mathbf{l})$ in a cell \mathbf{l} that has a position vector \mathbf{l} relative to the central reference cell. It should be noted that \mathbf{L} is defined over the whole of a supercell and is different in every cell of that supercell. Care is needed here since the CRUSH code only gives the eigenvector Φ_{nk} in one cell of the parent structure. The factors of $\exp(i\mathbf{k}\cdot\mathbf{l})$ have to be factored in to get the values of Φ_{nk} in different cells, so that \mathbf{L} can be calculated over the whole of the superlattice. The γ_{nk} and A_{nk} are arbitrary phase factors and amplitudes, which we can vary in order to localize \mathbf{L} as much as possible around the area of interest: these ensure constructive interference for the motion of the tetrahedra in that area and destructive interference further away. Of course an infinite number of localized modes with eigenvectors \mathbf{L} can be formed depending on the choice of A_{nk} and γ_{nk} , but as mentioned before they cannot be arbitrary because their general character is contained in the eigenvectors Φ_{nk} , which are never varied.

Suitable values for γ_{nk} and A_{nk} can be determined by a maximization program where the objective is to vary the A_{nk} and γ_{nk} to produce a local RUM that has the maximum possible intensity within a central reference cell. This then gives the eigenvector \mathbf{L} of the most localized mode that is possible within this zeolite. The intensity of a local RUM is defined as

$$I = \sum_{ij} |L_{ij}|^2 \quad (2)$$

where the sum is over all components i of motion for all the tetrahedra j of interest. If the local RUM eigenvector has been correctly normalized, then a sum over all components for all tetrahedra over the whole of the supercell will equal unity. Usually we consider the intensity over just the central unit cell or even over a particular structural fragment within that cell.

More selective calculations require the concept of a “kernel” eigenvector \mathbf{K} . This is an initial approximation of what we may want a local RUM to look like within the central cell. The eigenvector has six components for each tetrahedron in the whole supercell—three for translations in orthogonal directions x , y , and z and three for rotations of the tetrahedron about these directions. Often all components of \mathbf{K} outside the central cell are set to zero, but this need not be so. Once \mathbf{K} has been set up then initial values for the $\exp(i\gamma_{nk})$ and A_{nk} are determined by projecting the Φ_{nk} onto the kernel vector \mathbf{K} giving

$$A_{nk}(\text{initial}) = |\Phi_{nk}^* \cdot \mathbf{K}| \quad (3)$$

$$\exp(i\gamma_{nk})(\text{initial}) = (\Phi_{nk}^* \cdot \mathbf{K}) / A_{nk} \quad (4)$$

where the quantity $\mathbf{X}^* \cdot \mathbf{Y}$ is the complex dot product between vectors \mathbf{X} and \mathbf{Y} and all vectors have the length of six times the number of tetrahedra in the supercell.

Starting with the initial values (3, 4), the $\exp(i\gamma_{nk})$ and A_{nk} are refined to achieve the maximum possible value of some quantity by an iterative procedure, for example the projection of \mathbf{L} onto \mathbf{K} so that the quantity $\mathbf{L} \cdot \mathbf{K}$ is maximized. This will then give the most local RUM possible that resembles the form required. If the resulting local RUM has rather small intensity in the region of interest or the resulting \mathbf{L} no longer resembles \mathbf{K} sufficiently, then one can be certain that the type of flexibility being sought after is not possible in this particular zeolite.

The kernel can be chosen in many ways; for example, one could select only certain tetrahedra or only certain components of their motion, the other components being set to zero. As with any maximization method, the starting point can influence the final result so that several different kernels should be tried for each calculation of a local RUM to make sure that a real optimization has been achieved. A kernel composed of random numbers inside the central cell and zero outside can be used equally well, this implying that the computer should simply search for high-intensity local RUMs of any form. One of the examples below shows how a particularly interesting result was obtained from a calculation that started with a random kernel. Many refinements can be made to these calculations such as having weighting functions dependent on the energy of particular eigenvectors if one wants to include floppy modes that are not strictly RUMs, etc., but the results of the calculations in this paper have used eq 1 in a straightforward manner.

Determining the Localization of Local RUMs

Table 2 gives details concerning some local RUMs that were produced in a number of zeolites. N_k is the number of points used in the \mathbf{k} -point grid, and N_r and N_f are the number of pure RUM bands and floppy bands, respectively, used to make the local modes. The “% cell 0” column is the percentage of local RUM intensity that sits within the central unit cell, while “% n.n.” denotes the average percentage of local RUM intensity on each nearest-neighbor unit cell. On more distance unit cells the intensity is very low. As can be seen from Table 2, modes can be localized onto single unit cells quite effectively for

TABLE 2: Local RUM Details for Several Materials^a

description	N_k	N_r	N_f	% cell 0	% n.n.	% flex
sodalite-R	343	1	0	16.9	6.5	
sodalite-RT	343	1	0	28.1	5.1	
sodalite	343	1	1	37.4	3.6	
zeolite LTA	125	4	0	85.5	1.7	
D4R unit only	125	4	0	80.5	1.6	99.9
UTD-1	125	0	4	38.1	3.3	
more flexible part	125	0	4	35.1	2.6	95.1
less flexible part	125	0	4	32.4	3.5	62.6
chabazite	125	0	4	72.1	3.0	
faujasite	125	4	0	73.4	1.4	
faujasite S _I	125	4	0	27.9	0.4	73.9
faujasite S _I	125	4	0	19.8	0.3	48.5
faujasite S _{II} + S _{II}	125	4	0	19.0	0.3	42.9
faujasite S _{III}	125	4	0	28.7	0.5	73.6
ZSM-5	125	0	8	37.4	4.8	

^a The “sodalite-R” data refer to a local mode of sodalite in which each tetrahedra was only allowed to rotate about one $\langle 100 \rangle$ axis only. All the other local RUMs involve all six components of tetrahedral motion.

zeolites. A nonlocal mode would have a “% cell 0” intensity of $1/N_k$, i.e., less than 1% and much less than the values shown.

The “flex” column of Table 2 shows the percentage of the intensity within the central cell that sits on a particular fragment of structure (so this value is a percentage of a percentage). If this value is nearly 100%, then that fragment can flex in isolation to all other parts of the framework within the same unit cell. This is the case for the D4R units in zeolite LTA (see below). A lower value indicates that other parts of the framework within the central cell must flex to compensate for the motion of that fragment. Thus one can gain a quantitative measure of how independently flexible various structural units are. Hence one can see whether the flexibility of the framework allows a particular deformation to occur in isolation or not. If not, then we know what doesn’t happen in that particular zeolite—which is frequently as important as knowing what does happen. The columns where the flex number is not present refer to calculations involving every component of every tetrahedron in the unit cell so %flex would always be 100%.

Another way of quantifying the degree to which a local RUM is localized is to calculate its participation coefficient. This gives a measure of how many tetrahedra are involved in a local RUM vibration. It is defined as

$$P = \left(\sum_{j=1}^{N_T} \left(\sum_{i=1}^6 |L_{ij}|^2 \right) \right)^{-1} \quad (5)$$

where i is the sum over the complex components of the eigenvector that relate to tetrahedron j and N_T is the number of tetrahedra in the supercell. Each tetrahedron contributes six complex components L_{ij} to the local RUM eigenvector \mathbf{L} , and \mathbf{L} should be normalized so that the sum of the squares of all components is equal to unity. The value of the participation coefficient as defined in (5) is then the number of tetrahedra that effectively take part in the local RUM distortion and will range between 1 and N_T (again the total number of tetrahedra in the supercell). If \mathbf{L} is evenly distributed over the supercell, then all the L_{ij} will equal $(6N_T)^{-1/2}$. Feeding this into (5) gives $P = N_T$, so all the tetrahedra are participating in the local RUM. If \mathbf{L} is located on just one tetrahedron, then it has six components (the squares of which will sum to 1) and all the other components of \mathbf{L} will be zero, so from (5) $P = 1$. For a

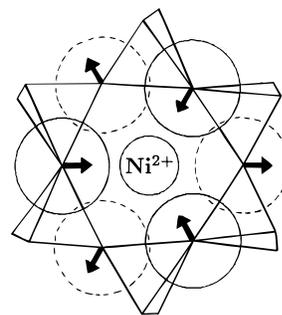


Figure 2. Alternating translations and rotations of six tetrahedra in sodalite bring three oxygen atoms (large solid circles) closer together, while three others (large dashed circles) move further away. The three close oxygens then sit in a ring a little above the plane of the hexagon of Si/Al atoms, and this ring is then a strong binding site for a cation such as Ni^{2+} . The S_{II} binding site in faujasite is also of this form. This figure also emphasizes the point that the oxygens occupy a large volume: structural diagrams composed entirely of lines or tetrahedra can be misleading when thinking about adsorption sites.

well-localized deformation, P is several tens or even a hundred tetrahedra. This may seem a lot: the intensity of the local RUM decays rapidly as you move away from the center of the deformation, but the small contributions to other tetrahedra will add up and contribute to P . A poorly localized deformation will have P equal to several hundred or even a thousand. Thus it is easy to determine how localized a local RUM really is. One advantage of using this as a measure of locality is that the whole of the local RUM over the whole of the supercell being used is considered, not just the effect on the central cell where the deformation of interest usually lies.

Applications of Local RUM Calculations

We now apply the ideas discussed above to a variety of zeolites and show how different aspects of the behavior of zeolites can be affected by local RUMs.

(1) Example Calculation on Sodalite. Sodalite may not be a particularly interesting zeolite, but the very high symmetry $Im\bar{3}m$ structure does have a single complete band of RUMs and a cation can be adsorbed onto one of the hexagonal faces in an interesting way, as shown in Figure 2. A kernel \mathbf{K} for sodalite was suggested to us by an optic RUM eigenvector Φ_{nk} very near $\mathbf{k} = 0$. This denoted alternating rotations of the six tetrahedra in a hexagonal ring about $\langle 100 \rangle$ -type axes. These rotations bring three oxygen atoms nearer to the center of the ring and three further away, with some displacement above and below the plane of the ring, respectively, as indicated in Figure 2. We therefore formed a localized eigenvector \mathbf{L} by varying the γ_{nk} and A_{nk} in order to maximize the total intensity of \mathbf{L} on a central ring of six tetrahedra. The results in Table 2 (labeled sodalite-R) show that this did not give a particularly localized mode, when rotations only were included. If a more general local mode consisting of all components of tetrahedral motion is produced (by starting with a kernel that included translational as well as rotational components), then a greater degree of localization is achieved as shown by the sodalite-RT results in Table 2. It is interesting to note that the resultant framework distortions on the central cell are very similar if either of these two local RUMs is condensed onto the $Im\bar{3}m$ sodalite structure. Therefore, as expected, it is not possible for the structure to flex in an almost arbitrary fashion. The exact form of the sodalite-RT local RUM deformation is shown in Figure 3, where nine unit cells of the sodalite supercell are displayed and it is clear that the central cell is much more deformed than those around it.

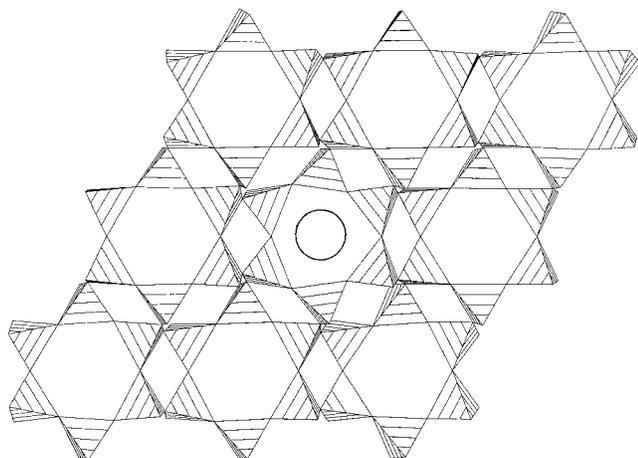


Figure 3. Configuration of the sodalite structure with a local RUM deformation present. This was produced by projecting the local RUM eigenvector corresponding to the sodalite-RT entry in Table 2 onto the original $Im\bar{3}m$ structure. The central cell is quite deformed, while neighboring rings are rather less distorted, showing the degree of localization. The circle represents a possible binding site for a adsorbed ion.

The local RUM deformation of sodalite now represents a near-perfect adsorption site for an ion since three oxygens move toward one another and lift up out of the plane of the hexagon providing a very good binding site. It should be noted that since the overall amplitude of a local RUM is almost arbitrary, oxygens can move freely until they are at optimum bonding distances from cations. Hence the best possible binding site is produced, regardless of the size of the ion. This continuous flexibility that local RUMs give to zeolite frameworks is one of the prime reasons that they are able to manipulate molecules in the precise way that they do. Optimal distances for all sorts of contacts can be achieved for very little cost in energy. If in addition to the band of RUMs the lowest frequency band of floppy modes is also included for sodalite, then an even more localized local RUM can be made as shown by the sodalite entry in Table 2 with $N_f = 1$. With a greater number of bands, the possibility of better localization usually increases. The number of bands N_f cannot be increased without limit however since their energy increases and then the deformations become high-energy ones and cease to be of interest.

(2) Diffusion and Local RUMs. Localized distortions enable molecules to diffuse through a framework more easily: if a large molecule approaches a small aperture between two zeolite cages, then diffusion will proceed more readily if a local distortion centered on the aperture causes it to open up in a temporary fashion. This can be seen quite well in Figure 4, where the ring of six tetrahedra that comprise the S_{II} site in faujasite are shown opening and closing under the influence of a local RUM. Note that in Figure 4B,C one can see the tetrahedra that make up the D6R at the back of the sodalite cage are still in the same position; the local deformation opens only one aperture at a time. A 6-fold ring is not a particularly large pore, but the effect on larger pores will be similar if suitable local RUMs can be formed from the eigenvectors of the relevant frameworks.

Molecules and molecular ions have shape, and in fact it may be more important that the pores within a zeolite can change shape rather than change their total area to allow molecules of different form to diffuse. It should be remembered that diffusion constants are proportional to the exponentials of jump activation energies, and therefore even a small local RUM effect could change diffusion coefficients considerably.

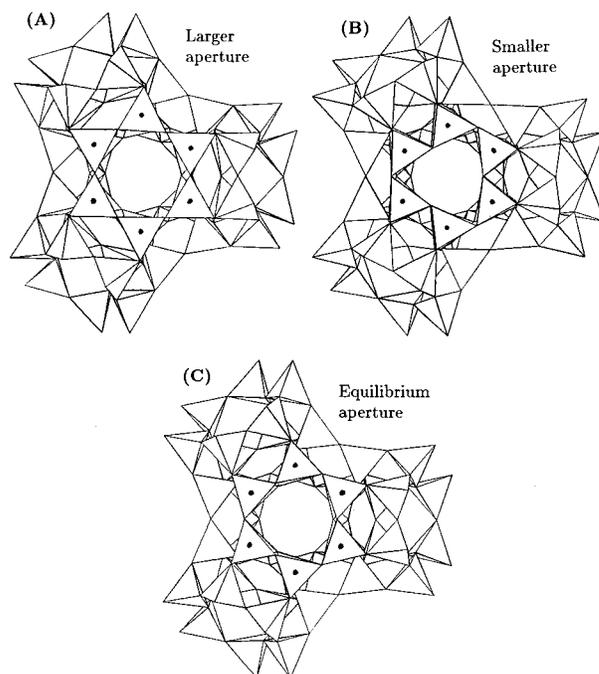


Figure 4. Opening and closing of a ring aperture due to local RUM deformations. The aperture, shown by the dotted tetrahedra, connects the supercage with the interior of a smaller sodalite cage in faujasite. (A) The aperture in a more open position; (B) a more tightly closed position; (C) the equilibrium structure observed via X-ray diffraction. Note that the D6R aperture behind the one of interest remains in an equilibrium position, so that we see that only one aperture is changing at a time, not every aperture within the crystal.

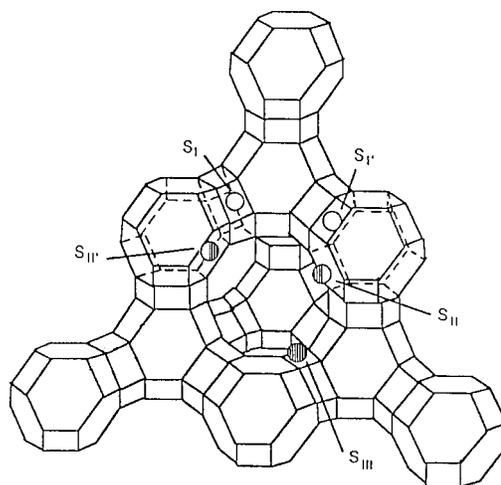


Figure 5. Experimentally determined positions for adsorbed ions within the faujasite framework. Note that the framework can be considered to be made up solely of D6Rs (or hexagonal prisms). Alternatively the D6Rs can be considered to connect sodalite cages together to give the overall framework.

Diffusion can also have a more direct effect on catalysis. Ions often have to move from one site to another to find molecular fragments. This is known to be the case in faujasite where Ni^{2+} ions move from S_I sites (see Figure 5), where they are tightly bound by the framework, out into the supercages where they can catalyze the cyclotrimerization of acetylene into benzene.¹⁴ This motion is assisted by interactions between the Ni^{2+} and acetylene molecules. However, if the framework itself can flex sufficiently to provide a low-energy diffusion pathway from the S_I sites into the supercages, then reactions will occur at a faster rate. Figure 4 has already shown that the aperture into the



Figure 6. Framework structure of zeolite LTA. The shaded region is a D4R unit, and these form the connections between the sodalite cages. The heavily outlined tetrahedra form a single 8-fold ring (S8R). Note that every tetrahedron is simultaneously part of a D4R and a S8R.

faujasite supercage, through which the Ni^{2+} must pass, can indeed flex in the continuous manner required.

A point to note concerning diffusion is the fact that the larger the extent of a deformation to a ring, etc., the smaller is the probability of large-amplitude fluctuations of that deformation. Hence, only if very localized deformations can form are we likely to see them contribute to the diffusion process. If a deformation extended over a large volume of real space (many hundreds of tetrahedra), then it is less likely that it would gain sufficient amplitude to have any effect, even if it cost zero energy, due to the large degree of cooperative motion required. Another point concerns the fact that in some cases the amplitude of a local RUM cannot be arbitrarily large. If a local RUM gives rise to a deformation with amplitude B , then although the tetrahedra remain joined and undistorted to lowest order in B , this may not be true to order B^2 or higher, in which case the distortion ceases to be exactly a RUM at large amplitude and starts to cost a significant amount of energy. Once this occurs, the amplitude of the local RUM will no longer increase and no increased effects concerning diffusion will occur.

(3) Calculations on Zeolite LTA. Zeolite LTA is interesting since this example shows how local RUMs can be concentrated onto particular structural fragments rather than sitting equally over a whole unit cell of the parent zeolite. The structure is composed of sodalite cages joined across their square faces in a simple cubic fashion. These joins consist of eight tetrahedra and form square prisms or double-four-rings (D4Rs) as in Figure 6. A local RUM can sit on one of these and deform it in almost complete isolation to everything else, so the participation coefficient has a very low value, $P = 11$. Eight of these tetrahedra make up the D4R, while the rest of the local RUM, which is spread over 3000 tetrahedra, only amounts to the equivalent of three tetrahedra participating. We have formed many local RUMs on zeolite LTA, but it appears that the D4Rs are the only parts of the framework that are individually flexible. Therefore, to deform other structural fragments such as a large eight-membered ring, one must form a local RUM that is distributed across all the 32 tetrahedra in the four D4Rs that border the eight-membered ring in question. Then the entire ring can be deformed in shape. It is not possible to deform the eight tetrahedra that the large ring is composed of in isolation. The four D4Rs that border the ring mean that it can be effectively thought of as a square, and this means that one can work out all the possible deformations that can occur. We make

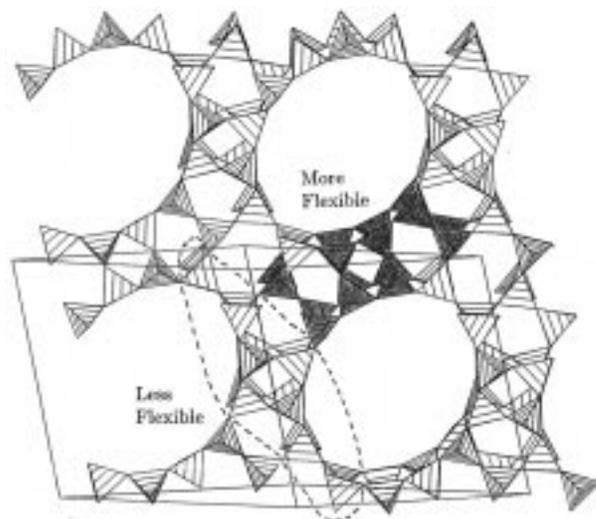


Figure 7. Framework structure of zeolite UTD-1. The shaded region is the part of the framework that is predicted to be flexible on the basis of the local RUMs that can be imposed upon it. The other, less flexible, part is that enclosed within the dashed line. Each part composes 16 tetrahedra, there being a total of 32 in the primitive unit cell.

the point that the circular ring can become oval, one diameter increasing, the other perpendicular diameter decreasing. This would then enable flat molecules, like benzene and its derivatives, to diffuse if they pass through the eight-ring parallel to the long axis. Similarly, for a hexagonal ring in LTA; one can have the same pattern as in Figures 2 and 3 but the local RUM must be distributed across the three D4Rs that share tetrahedra with it to achieve the same effect. We have therefore discovered the nature of the geometric flexibility of the zeolite LTA framework. From the point of view of flexibility, it is better to think of the structure as being made up of D4Rs rather than sodalite cages or eight-membered rings. Local RUMs will tend to sit on the flexible parts of a framework and avoid the nonflexible parts, making it very easy to differentiate between them.

(4) Stiff and Flexible Structural Fragments in UTD-1. Zeolite UTD-1 was the first aluminosilicate framework produced that has 14-membered rings.¹⁵ These are oval in shape and will allow large molecules of a certain form to diffuse through the structure. UTD-1 does not have complete bands of pure RUMs but does have planes in \mathbf{k} -space with four RUMs apiece at every \mathbf{k} -point on them. Not surprisingly then the lowest four bands are very floppy over the whole of the Brillouin zone and were used to construct local RUMs. Interestingly, we find that the framework can be considered as two separate parts. There are stiffer sections composed of 16 tetrahedra, while the other 16 tetrahedra in each unit cell are much more flexible and can move independently of the rest of the structure, see Figure 7 and the last column in Table 2 where the “% flex” value is very high, 95.3%, for this section of the UTD-1 framework. If four RUM bands are used then a local RUM with a participation coefficient of $P = 122$ can be created on the flexible part, this being quite low and showing how localized the mode is. On the nonflexible part a value of $P = 221$ is the lowest yet calculated, almost double the previous value. Also note that the percentage of intensity on the nearest-neighbor cells (the % n.n. column in Table 2) is higher for the nonflexible part, again showing that this local RUM is less localized. We therefore conclude that this more flexible part is more likely to be the center of any catalytic activity that may occur in this zeolite. It should be noted that these results were found by

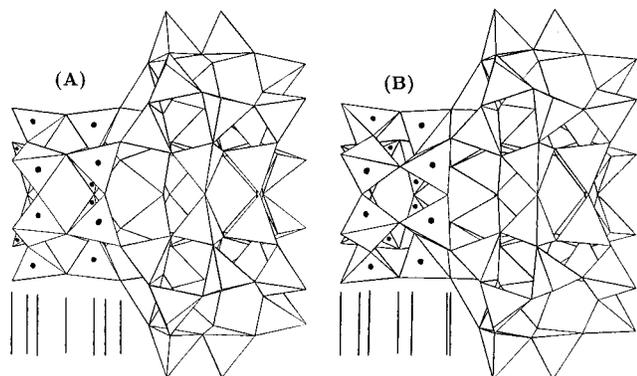


Figure 8. Effect of a local RUM on a D6R unit in faujasite whose tetrahedra are marked by dots. (A) The original structure; (B) the structure after the local RUM has been applied with a certain amplitude. Note changes in the orientations of tetrahedra between the two figures and the changes in the positions of the planes of oxygen atoms marked by lines below the D6R unit.

starting off with a random kernel \mathbf{K} inside the central cell and then finding that the resulting local RUM was localized onto only half of the tetrahedra within the central unit cell. Therefore searching for flexibility in a general way while making no previous assumptions can yield valuable results.

(5) Binding of Ions in Faujasite. Faujasite is composed of sodalite cages joined in a diamond arrangement across their hexagonal faces, as are zeolites X and Y. These hexagonal prisms or double-six-rings (D6Rs) between sodalite cages are particularly flexible parts of the framework. So again, as for zeolite LTA, it seems that the joins between sodalite cages are quite flexible whereas sodalite cages as a whole are not. Experiments have shown that adsorbed ions sit at particular sites within the framework,^{16,17} as shown in Figure 5 where all except site S_{III} lie near hexagonal rings in a manner similar to Figures 2 and 3. We find that local RUMs can be concentrated onto the parts of the framework that correspond to these sites as discussed below. With the extra flexibility that these fragments of the framework possess, it is no surprise that adsorbed ions are observed to sit where they do. Participation coefficients as low as $P = 87$ can be achieved for this zeolite. This is higher than for zeolite LTA but is still quite a low value and represents a well-localized distortion.

First consider the S_I site within the hexagonal prism. Here a local RUM can sit on the 12 tetrahedra that compose this, deforming it so that six cation–oxygen distances are reduced, increasing coordination stability. Table 2 shows that the D6R unit can flex with little movement required from the rest of the tetrahedra in the same unit cell, so this is an ideal site for ions to be adsorbed. Figure 8 shows a D6R before and after a local RUM has been imposed onto it. The local RUM changes the position of the oxygen planes within the D6R as shown by the vertical lines below the D6Rs in Figure 8. Since the local RUM can be imposed with any amplitude, the shape of the cation coordination cage within the D6R unit could change in a continuously variable manner.

An ion at the S'_I site sits inside a sodalite cage against one of the hexagonal faces of a hexagonal prism. The part of the framework that flexes is that hexagonal face and the three single square rings that lead off the hexagonal face upon which the ion sits. This enhances the flexibility of the face so that three oxygens can move in a fashion similar to that shown in Figure 2. Most of the local RUM intensity is on the face where the ion sits, as expected. This site has a lower independent flexibility, only 48% since the far face of the hexagonal prism,

away from the ion, has to move somewhat when the near face moves. The S_{II} and S'_{II} sites are based on hexagonal faces of the sodalite cages that are not part of the hexagonal prisms. Here a local RUM sits on the three four-membered square rings about the hexagon in question. So again 12 tetrahedra are involved. To favor an S_{II} site (i.e. inside the supercage) as opposed to an S'_{II} site (inside a sodalite cage, not the supercage), the sign of the overall amplitude of the local RUM must reverse. One amplitude will bring three oxygens closer together inside the supercage (S_{II} site), while changing the sign of the amplitude will bring the other three oxygens closer together inside the sodalite cage (S'_{II} site).

For the S_{III} site, an ion sits on one of the six outer square faces of a prism. The flexible part is the prism and the two other tetrahedra of the square adjacent to that on which the ion sits, a total of 14 tetrahedra. The deformation is therefore similar to that for the S_I site.

To summarize our calculations on faujasite, we have been able to select whatever parts of the framework interest us, i.e., the cation sites, and have been able to calculate local RUMs \mathbf{L} and so determine the nature of the flexibility and whether this can occur in isolation or not.

(6) Methanol Dissociation in Chabazite. The zeolite chabazite has quite a small unit cell, only 12 tetrahedra, and has been used to study the break up of methanol molecules within its eight-membered rings. Various electronic structure calculations have suggested several ways in which this process may occur. In some a methanol molecule can attach itself to an acidic site on one side of the eight-membered rings via two hydrogen bonds and then go on to be chemisorbed to the framework,^{18–20} and this is then thought to be a precursor to dissociation. Other calculations indicate that the minimum-energy configuration has the methanol physisorbed onto the chabazite framework.²¹ Still other calculations indicate that the framework acts more as a solvent rather than as a nucleophile,^{22,23} so the nature of the methanol dissociation is still somewhat unclear.

The important point from our point of view is that the flexibility of the framework will play an important role regardless of the exact mechanism involved. One question is whether the ring can deform in reality via a local RUM so that both sides of the ring can attach to the molecule simultaneously. This is important since dissociation may then be helped if both sides of the ring can grab hold of the two ends of the molecule, helping it to dissociate by keeping hold of the two molecular fragments that result. One will be a water molecule and the other a CH_3 unit. In particular, the CH_3 unit will need to be stabilized by hydrogen bonding on the other side of the ring away from the water molecule.

Our calculations show that there are four bands of floppy modes from which to make local RUMs. The local RUM we seek is one in which the tetrahedra on opposite sides of the ring move toward the ring's center to reduce its diameter in one direction. This is in fact possible, and the resulting deformed ring is shown in Figure 9B, where it can be seen that the distance $\text{X}-\text{X}$ is reduced compared to the undistorted ring, Figure 9A. In addition, that extra flexibility afforded by local RUMs will improve the strength of the hydrogen bonds by providing a more perfect fit for the methanol molecule and any molecular fragments that may result after dissociation. We also show the same ring with the amplitude of the local RUM reversed, see Figure 9C. This causes the ring to increase in size, and while this is may be of little value for helping reaction processes it will greatly assist diffusion. The ring area is now

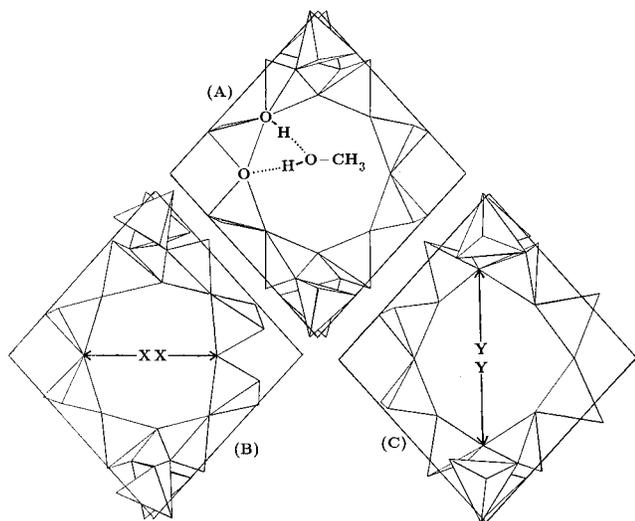


Figure 9. Unit cells of chabazite showing (A) an undistorted cell containing a methanol molecule that is doubly hydrogen-bonded (dotted lines) to the cage side; (B) a ring on which a local RUM distortion has caused the distance X–X to contract, this possibly helping the process of decomposing methanol molecules; (C) a ring on which a local RUM distortion has increased the overall ring area, particularly the diameter Y–Y, thus assisting the diffusion of a flat molecule oriented parallel to Y–Y.

larger, and in particular the distance Y–Y has increased so any molecule that orients parallel to Y–Y will be more likely to diffuse through the eight-ring aperture.

It should be noted that local RUM influences cannot be incorporated into standard electronic structure calculations because many unit cells are required. Calculations on even a single unit cell of chabazite require substantially more than a single workstation sized computer if a reasonable study (a number of calculations) is to be performed in a reasonable time. Since around 100 unit cells (many thousands of atoms) are required for the local RUM effect to become readily apparent, then electronic structure calculations that implicitly incorporate these effects are not going to be possible on any present computers. However, it may be possible to combine the ideas in this paper with empirical simulations of zeolites since large simulations based on simple empirical potential models are easy to perform. It may be thought that cluster calculations would have an advantage over periodic calculations since these would allow a great deal more flexibility and allow local distortions to occur. However, the big problem with cluster calculations for these purposes is that the flexibility of zeolites is very specific and only by having periodic boundary conditions can you be certain that you get the geometrically allowed flexibility and no other. Low-energy deformations allowed in clusters may be very high energy ones in a periodic system.

(7) Application to ZSM-5. The zeolite ZSM-5 is used extensively in industry in the production of gasoline: hence it is well-studied. The orthorhombic $Pnma$ phase of ZSM-5²⁴ has no pure bands of RUMs in k -space, but there are planes that contain eight pure RUMs so the lowest eight bands of modes across the whole of the Brillouin zone were determined. From these we have calculated the form of the most localized mode that includes the whole of the central unit cell and find it has a participation coefficient of $P = 377$ tetrahedra out of the 12 000 contained within the $5 \times 5 \times 5$ supercell used for this calculation. In fractional terms P is equal to 0.03 for this deformation. This is low, so we know that local RUMs do have a role to play in this larger zeolite. Any molecule at any possible defect site will be able to utilize local RUMs to some degree in

order to lower energy barriers to reaction. Hence, any research into the catalytic behavior of molecular fragments within this zeolite should take the possibility of local RUMs into account. Similar calculations could be applied to the rest of the ZSM family as well as to the $AlPO_4$ family of zeolites.

Summary

In summary, we have seen that the low-frequency floppy modes that are so prevalent in zeolites can combine to give superpositions of modes that we call local RUMs. Since the frequencies of the floppy modes are so low, then the motions associated with a local RUM will be very long-lived, even stationary. The enhanced flexibility provided by local RUMs will enable ions and molecules to change the environment of their cages to give more favorable conditions for effective catalysis to occur. For example, a flexing of a cage along some particular axis may give rise to better hydrogen bonding between molecules and framework oxygens. The important point is that since local RUMs can be explicitly calculated from the original RUM eigenvectors of a particular structure, it is possible to see exactly what kind of flexibility a structure may possess.

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