How Floppy Modes Give Rise to Adsorption Sites in Zeolites

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The question as to how zeolites are able to hold tightly bound ions is answered. We show that zeolite frameworks can support whole bands of rigid unit modes (floppy modes) in **k** space and hence show that localized rigid unit modes can form within such frameworks that do not distort the constituent tetrahedra to any significant degree. It is these local modes that enable cations at certain sites to pull the framework—with virtually zero cost in elastic energy—in such a way that oxygen-cation bonding distances become exactly optimal for the cation concerned. [S0031-9007(97)03174-8]

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Zeolites are an important class of technological and industrial materials. They have very complicated structures compared to other silicates (hundreds of atoms per unit cell), and hence some of our understanding of their behavior has remained somewhat qualitative—full *ab initio* calculations cannot be performed routinely on zeolites with large unit cells. However, we have discovered that some quite simple ideas allow us to gain a quantitative understanding of why zeolites have some of the unique properties that they do. In this Letter we focus on the ability of dehydrated zeolites to hold various concentrations of different metallic ions which can then in some cases act as catalysts, such as Ni^{2+} in dehydrated zeolite Y [1,2]. The question we address is exactly how these ions are held by the zeolite framework. Our answer, in brief, is that individual cations are able to rearrange the framework in a displacive fashion and pull framework oxygens around themselves. The resulting distorted framework is then nonperiodic in nature, and it might be thought that such an operation would cost a lot of energy since a large distortion of the framework would be required. However, this is not the case, since it is possible to achieve the necessary distortion of the structure *without* the SiO_4 and AlO_4 tetrahedra having to distort, and hence it costs very little energy. We show in this Letter that this possibility explains why ions sit at the particular sites that they do and not elsewhere.

Experiments have shown that Ni^{2+} ions in zeolites with the faujasite framework often sit at sites with a relatively low coordination number [1]. For example, the faujasite S_{II} site involves the ion coordinating with only three oxygens, but one might have thought that all ions would like to find sites with a coordination number of at least six. However, the framework is not infinitely flexible—far from it—but from our analysis we can now explain why it is flexible in the specific way needed to bring together three oxygens around a Ni^{2+} at the S_{II} site. Moreover, we explain how the flexibility is such that the Ni^{2+} ion can draw the oxygens toward it by an *adjustable* amount until a perfect coordination distance is achieved, giving the strong binding energy of this site.

The problem of the possible flexibility of framework aluminosilicate structures is a common problem within mineralogy, and arises, for example, when attempting to understand the origin of displacive phase transitions [3]. The main structural feature is the existence of SiO_4 and AlO_4 tetrahedra that are relatively stiff, which are each linked to four other tetrahedra through shared oxygen atoms, the link being very flexible in the subtended bond and torsional angles. Thus any low-energy deformation, whether a localized distortion around a cation site or a periodic distortion associated with a phase transition, will necessarily involve the tetrahedra moving without distortions. We are therefore first faced with the question of whether framework tetrahedral structures have this degree of flexibility. This is not a trivial issue, as we now demonstrate.

Last century, Maxwell showed that the stability or flexibility of a structure made up of discrete components (such as a bridge built from iron girders, or a crystalline silicate) is determined by the balance between the number of degrees of freedom of the components, F, and the constraints introduced when linking these components together, C. If $C \geq F$ the structure has no flexibility, but if $F > C$, there are $F - C$ possible low-energy modes of deformation. Indeed, if the only nonzero force is that associated with the stiffness of the components, these latter modes will have zero energy. For a structure formed by linking tetrahedra into an infinite framework, the balance between F and C is easy to evaluate. Each tetrahedron has $F = 6$. Each linkage involves three constraints associated with the x, y, and z coordinates. Since there are two linkages uniquely associated with each tetrahedron, we have $C = F = 6$ per tetrahedron. Thus the general case, called the “generic case” by Thorpe [4], has an exact balance between the degrees of freedom and the constraints, so that there will be no flexibility possible. However, we have shown elsewhere [3] that crystalline aluminosilicates are not covered by the generic case, because symmetry can make some of the constraints redundant. This then allows the possibility of some degree of flexibility. In the study of amorphous systems these modes are called "floppy modes," but in the atypical case of crystalline structures we have called these "rigid unit modes" (abbreviated as RUMs). The point is that they are not predicted by the generic theory.

The subsequent issue is that of determining the exact number of redundant constraints for any symmetric structure. We have solved this problem using a lattice dynamics approach, which allows us to calculate all the zero energy modes associated with any given wave vector of the system [5]. Our work on silicate minerals such as quartz, cristobalite, and feldspars showed that the action of symmetry allowed the existence of RUMs for lines and planes of wave vectors in reciprocal space. Although these RUMs can be observed experimentally and give rise to a number of consequences such as the existence of phase transitions, they still form an extremely small subset of the total number N of phonons, of order $N^{1/3}$ or $N^{2/3}$ for the cases of lines or planes, respectively. The big surprise, which underpins the results described in this Letter, is that open structures such as sodalite and zeolite structures can have one or more RUM *at each wave vector*. This means that the number of RUMs is now of order N, and the set of RUMs is a significant fraction of the total number of phonon modes.

The existence of RUMs at each wave vector has an important implication for the possibility of forming localized deformations of the crystal structure with no long-range correlations. Put another way, it is possible to form linear combinations of RUMs with different wave vectors to form *localized RUM deformations*. Our objective in this Letter is to quantify this idea, first by developing the computational methods required to construct local RUM distortions, and then to determine the degree of localization possible in a number of case examples.

We have looked for RUMs in several structures including sodalite, zeolite A, faujasite, and one form of the zeolite ZSM-5 [6]. Using our lattice dynamics approach we found that there is one complete band of RUMs throughout the Brillouin zone of the idealized high symmetry sodalite structure, space group $Im3m$ [7]. From the complete band of RUMs one can make a localized wave packet, i.e., a localized RUM, as discussed below. By imposing this local mode upon a structure and varying its amplitude, a ring or cluster of oxygens can be arranged around a metal ion of any radius at certain sites in the crystal, without costing any elastic energy in the framework. The nature of the local deformation is determined by the eigenvectors of the RUMs and is therefore not arbitrary. The zeolite A and faujasite frameworks both support four complete bands of RUMs. This gives a greater scope for several localized RUMs to form, so it is not surprising that several binding sites for ions that cost no elastic energy have been discovered in these structures [1].

To construct a localized RUM from a set of RUM eigenvectors calculated for a regular grid of N_k points evenly spaced in $\mathbf{k}$ space, we can use the formalism of Wannier functions. With a single RUM band, a localized RUM can be expressed as

$$|W\rangle = N_k^{-1/2} \sum_{\mathbf{k}} \exp(i\gamma_{\mathbf{k}})|R_{\mathbf{k}}\rangle \,, \tag{1}$$

where $|R_{\mathbf{k}}\rangle$ is the RUM eigenvector describing the displacements and rotations of the six tetrahedra per unit cell, extended throughout all space with Bloch phase factor $\exp(i\mathbf{k}\cdot\mathbf{l})$ in cell $\mathbf{l}$. The $\gamma_{\mathbf{k}}$ are arbitrary phase factors, which we can vary in order to localize the Wannier mode $|W\rangle$ as much as possible around the origin: These ensure constructive interference for the motion of the tetrahedra around the origin and destructive interference further away.

An even more localized RUM $|L\rangle$ can be constructed by writing

$$|L\rangle = \left(\sum_{\mathbf{k}} A_{\mathbf{k}}^2\right)^{-1/2} \sum_{\mathbf{k}} A_{\mathbf{k}} \exp(i\gamma_{\mathbf{k}})|R_{\mathbf{k}}\rangle \,, \tag{2}$$

where the $A_{\mathbf{k}}$ are arbitrary (real) amplitude factors. Unlike the Wannier modes, the $|L\rangle$ modes centered on different cells are not orthogonal, but this is of no concern when we describe one localized RUM around an isolated adsorbed ion. Of course, an infinite number of localized modes can be formed, but they are not arbitrary because their general character is contained in the eigenvectors $|R_{\mathbf{k}}\rangle$ which are never varied.

Initial values for the $\exp(i\gamma_{\mathbf{k}})$ and $A_{\mathbf{k}}$ are determined by projecting $|R_{\mathbf{k}}\rangle$ onto a "kernel" vector $|K\rangle$, which is an initial approximation of what we think the local RUM may look like within the central cell, and is set equal to zero in all outside unit cells. The chosen vector $|K\rangle$ is therefore perfectly localized. Thus initially $A_{\mathbf{k}} = |\langle R_k|K\rangle|$ and $\exp(i\gamma_{\mathbf{k}}) = A_{\mathbf{k}}^{-1}\langle R_k|K\rangle$ (where the quantity $\langle X|Y\rangle$ is the complex conjugate dot product $X^* \cdot Y$). It is also possible to choose an arbitrary kernel and use this as a starting point in a search for other local RUMs.

For sodalite, one kernel was suggested by the RUM eigenvector $|R_{\mathbf{k}}\rangle$ 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. We formed localized $|W\rangle$ and $|L\rangle$ and calculated new values for the $\gamma_{\mathbf{k}}$ and $A_{\mathbf{k}}$ by maximizing the total amplitude of the local RUM on a central ring of six tetrahedra. The degree of localization achieved is shown in Table I where it is shown that local RUM amplitudes can be concentrated onto small volumes of real space; if the local RUM were diffuse, then its amplitude in cell 0 would equal N_k^{-1}. For sodalite we give two alternative local RUMs. One was a purely rotational RUM of exactly the same form as the kernel described above, while the other was more general and consisted of all components of tetrahedral motion. We note that the

TABLE I. Degree of locality for some local RUMs in various materials. N_k and N_b are the numbers of k points and RUM bands used to make the local modes. % cell 0 is the percentage of local RUM amplitude that sits on the central cell, % n.n. denotes the average local RUM amplitude on each of the nearest neighbor cells, and n-n.n. similarly denotes that on next-nearest neighbor cells. Sodalite-R refers to a local mode of sodalite in which each tetrahedra was allowed to rotate only about one $\langle 100\rangle$ axis only. The other sodalite local RUM and those for zeolite-A, faujasite, and ZSM-5 involve all components of tetrahedral translation and rotation.

Description	N_k	N_b	Local RUM	% cell 0	% n.n.	% n-n.n
Sodalite	343	1	$\lvert W\rangle$	23.4	4.7	2.8
			$\lvert L\rangle$	28.1	5.1	2.7
Sodalite-R	343	1	$\lvert W\rangle$	12.5	5.3	2.3
			$\lvert L\rangle$	16.9	6.5	3.7
Zeolite A	125	4	$\lvert W\rangle$	61.9	1.5	0.4
			$\lvert L\rangle$	85.5	1.7	0.0
Faujasite	125	4	$\lvert W\rangle$	49.4	1.4	0.3
			$\lvert L\rangle$	73.4	1.4	0.1
ZSM-5	125	8	$\lvert W\rangle$	30.2	6.4	3.7
			$\lvert L\rangle$	37.5	9.6	4.8

more general RUM has a greater degree of localization but the framework distortions that result on the central cell are very similar when the local RUM is applied to the sodalite structure. Therefore, as expected, it is not possible to arrange the tetrahedra in an almost arbitrary fashion. The exact form of the distortion is shown in Fig. 1. To check that the resultant deformations of the tetrahedra are very small, we relaxed the size and shape of the tetrahedra while maintaining the local RUM distortion, using a straightforward energy minimization technique with a force constant model calibrated against other silicates. This gave an energy of 0.3 meV for the deformations of all the tetrahedra involved in the local RUM distortion. This is extremely low and supports our idea that local distortions within zeolite structures can form without significant energy cost associated with deformations of the tetrahedra.

For zeolite A and faujasite, with four bands of RUM phonons $|R_{\mathbf{k}}, n\rangle$ instead of the one for sodalite, we have to add an extra summation over bands n in Eqs. (1) and (2). In both cases we have found localized Wannier modes $|W\rangle$ and even more localized modes $|L\rangle$. Table I shows that for the zeolites, modes can be localized onto single unit cells quite effectively. Modes can be also be strongly localized onto particular fragments or subunits of a framework: One does not have to think in terms of whole units cells.

We have found that a local RUM can bring six oxygens around the S_{I} site in faujasite, and this explains why cations are bound there. This is the site in the hexagonal prism between two sodalite cages. Another of the modes we have found in faujasite gives rise to a distortion of the framework about the S_{II} site with three surrounding oxygens raised slightly above the center of a hexagonal ring inside the supercage, as found by Dooryhee *et al.* [1]. So again we can now understand how these binding sites come into being.

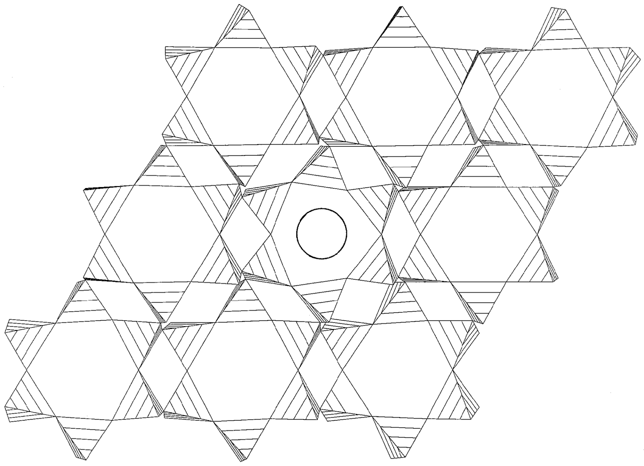

FIG. 1. Configuration of the sodalite structure with a local deformation about a Ni^{2+} ion. This was produced by projecting a local RUM eigenvector onto the structure as described in the text. Alternating rotations of the six tetrahedra in the central ring bring three oxygen atoms closer to a central ion while three others move further away. Neighboring rings are rather less distorted, showing the localization of the deformation. The three close oxygens sit in a smaller ring a little above the plane of the hexagon of Si (or Al) atoms. The center of the 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.

We have performed calculations on the high temperature *Pnma* form of ZSM-5 [6] using the eight lowest energy eigenvectors at points in **k** space. Table I shows that an appreciable degree of localization can be achieved in ZSM-5 and that this implied flexibility may significantly lower the energies of transition state complexes during chemical reactions. The larger value of the local-RUM amplitude in nearest neighbor cells for ZSM-5 is due to the lower symmetry of the unit cell. With cell lengths that are inequivalent the local RUM amplitude spreads unevenly over neighboring cells, an effect not noticed with cubic structures.

To show the nonarbitrary nature of the local RUM deformations, we have attempted to form local RUM deformations at two distinct parts of the framework of the zeolite UTD-1 [10]; see Fig. 2. We found that one part was distinctly more flexible than the other and enabled the formation of a more localized deformation. The RUM eigenvectors simply did not allow the formation of an arbitrary local deformation. We therefore predict that the more flexible part will more likely act as a binding or catalytic site in this zeolite. This highlights our point that these sorts of deformations cannot simply be predicted by inspection, but require the methods developed in this paper.

In conclusion, then, we have seen how localized RUMs can cause a group of framework oxygen atoms to cluster

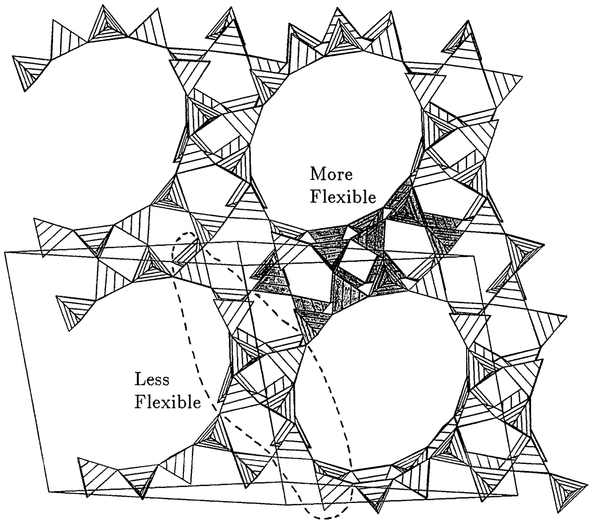

FIG. 2. The structure of the zeolite UTD-1. The flexible part of the framework is shaded while the less flexible part is enclosed within a dashed line. Both parts consist of 16 tetrahedra, there being 32 in the primitive unit cell.

around a metallic ion at certain sites and hence stabilize it there. The amplitude of framework distortion caused by a local RUM can freely adjust until the oxygens are at the optimum distance energetically from the cation. The required displacement in the structure consists entirely of rotations and translations of the tetrahedra as rigid units. The energy cost of the structural rearrangement is therefore very small—much less than the energy lowering from placing three or six highly polarizable oxygens about a charged ion. If the change in the local structure involved significant distortions of the tetrahedra it would cost so much energy that the ions would be unable to flex the framework to create high stability binding sites. The rigid unit character of any local displacement is therefore an essential ingredient in the working of a zeolite as a matrix for holding metallic ions.

Finally, we note that we are extending our application of these ideas. One example is to the catalysis of organic reactions, especially the specificity when framework oxygens and OH groups are involved, such as the decomposition of methanol within the zeolitic material chabazite [8]. Another role for local RUMs is their enhancement of molecular or ionic diffusion through zeolites. A local RUM has a large fluctuating amplitude because of its very low frequency. A local RUM that opens a ring in the structure will assist diffusion, but if it deforms the shape of the ring, then that will differentiate the diffusion abilities of molecules with different shapes. Also ions that are held at particular “storage” sites in a zeolite may need to travel to other “active” sites in order to act as catalysts [9]. This is the case for the cyclotrimerization of acetylene into benzene by Ni^{2+} within zeolite Y and thus a low energy pathway for the nickel ion to move along between these two sites will be required. We predict that rigid unit distortions of the framework will assist this.

It is important to realize that these calculations would be very difficult at a full *ab initio* level. To calculate a full set of frequencies and eigenvectors for a zeolite such as ZSM-5 at many different **k** points would require many thousands of hours of supercomputer time. Therefore an understanding of the contribution to zeolite behavior that local-RUMs provide remains currently outside the realm of accurate *ab initio* calculations. Approximate *ab initio* methods are more feasible, but they lack the simplicity of insight that our RUM approach gives.

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