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## Structure and Dynamics of Quasi-Ordered Systems

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### Abstract

The functionality of many materials of both fundamental and technological interest is often critically dependent on the nature and extent of any disorder that may be present. In addition, it is often difficult to understand the nature of disorder in quite well ordered systems. There is therefore an urgent need to develop better tools, both experimental and computational, for the study of such quasi-ordered systems. To this end, we have used neutron diffraction studies in an attempt to locate small metal clusters or molecules randomly distributed inside microporous catalytic materials. Specifically, we have used pair distribution function (PDF) analysis, as well as inelastic neutron scattering (INS) spectroscopy, to study interactions between adsorbate molecules and a microporous matrix. We have interfaced these experimental studies with computations of PDF analysis as well as modeling of the dynamics of adsorbates. These techniques will be invaluable in elucidating the local structure and function of many of these classes of materials.

### Background and Research Objectives

It is widely recognized that the presence of defects in crystals and other solid materials can have a profound effect upon their chemical and physical properties, and consequently that defects have a major impact on the practical utility of many technological materials. The reason is that the functionality of a material is often critically dependent on the nature and extent of any disorder that may be present, and it is often difficult to understand the nature of disorder in quite well ordered systems. There is also a great deal of current interest in complex, partially-ordered materials, such as the surfactant-mediated mesoporous silicas, biominerals, and hybrid organic-inorganic composites. Research on such materials has presented challenges that cannot easily be addressed by characterization

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tools that have been developed for well-ordered materials. The same situation is found in other areas, such as carbons (including nanotubes) and glassy metal oxides. There is therefore an urgent need to develop better tools, both experimental and computational, in this general area.

We have set two main objectives for this one-year effort: (a) to carry out neutron scattering experiments in zeolite systems where the partial disorder arises from randomly inserted molecules or clusters in a long-range ordered host, and (b) to develop computer codes for the analysis of INS vibrational spectra and for real-space analysis (PDF) of neutron and X-ray diffraction data on such systems. The results from these studies are expected to illustrate both the promise and possible limitations of our approach for the study of quasi-ordered systems.

### **Importance to LANL's Science and Technology Base and National R&D Needs**

Our effort is also closely connected with LANL core competencies in advanced materials as well as theory, modeling and high-performance computing. In addition, this development work utilizes unique LANL capabilities in computing, the neutron scattering facilities at the Lujan Center in LANSCE Division, and of the LANL Catalysis Initiative funded as Directed Research under the LDRD program. Because of the fundamental and technological importance of materials whose function depends critically on some partial structural disorder (for example, catalysts, battery materials, magnetoelectrics, and materials for gas separation and storage), this work is potentially of great importance to a number of DOE programs in ER, FE and others. For example, we expect that the tools developed under this program will be utilized in upcoming programs in Carbon Management. In addition, the P.I. of this project was commissioned by the DOE's Council on Chemical Sciences to organize a focused workshop on this topic (Partially Ordered Chemical Systems) which was held in Santa Fe NM, May 10-14, 1998. A report on this workshop was presented to the Council on August 3, 1998 and will be published as a review article.

### **Scientific Approach and Accomplishments**

Neutron scattering studies have the potential to help attain what may be considered the 'Holy Grail' of Catalysis Science, namely the identification and detailed local structure of the active site where the reaction(s) take place. In order to understand the action of catalysts, it is necessary to gain knowledge of this local structure of the active sites in addition to the long-range structure of the catalyst, preferably under reaction conditions. These systems are generally characterized by being locally disordered, and thus it is difficult to extract reliable structural information using conventional techniques. At present,

there is a significant amount of interest in using extended x-ray absorption fine structure (EXAFS) to determine the average nearest neighbor distances between heavy atoms in catalysts. EXAFS provides an incomplete model of the local structure because of the uncertainty inherent in the technique, largely due to the inability to accurately model multiple scattering processes and the lack of sensitivity to light elements. In situ EXAFS studies are also experimentally difficult because of the absorption of x-rays in the medium.

Neutron scattering has been underutilized for problems in catalysis despite its significant potential, which arises in part from the fact that it allows for in situ studies under realistic conditions. In addition to routine diffraction experiments, the potential of neutrons to provide information about the local structure at active sites represents a tremendous opportunity to advance catalysis science. The application of pair distribution function (PDF) analysis to determine the local structure has been highly successful in addressing questions on oxygen disorder in High- $T_C$  superconductors, and holds even more promise for the study of active sites in catalysts. While PDF analysis is complementary to EXAFS, it does not depend on physical models and yields results over much larger inter-atomic distances. Inelastic neutron scattering spectroscopy coupled with theoretical modeling studies is another powerful tool that allows us to probe the interactions between substrates and products and the catalyst surface. All of these techniques are readily amenable to in situ observation and allow for the elucidation of reaction mechanisms.

Recently, these methods have been applied to crystalline and partially ordered systems and have provided important new structural insights on the nanometer length scale including, for example, the arrangement of oxygen atoms in High- $T_C$  superconductors. The atomic pair-distribution function (PDF) [1] is the direct Fourier transform of the structure factor measured in a diffraction experiment and incorporates the diffuse scattering (from disorder) as well as the diffraction pattern. It is a three-dimensional generalization of the radial distribution function (RDF) used in the analysis of liquids and amorphous materials. The PDF gives accurate inter-atomic distances without underlying assumptions such as the *quasi-periodicity* that must be used to analyze disordered structures in the conventional way. PDF analysis requires the use of very short wavelengths (large  $Q$ ) in order to avoid termination errors in the Fourier transform – arising from pulsed neutron sources or synchrotron radiation facility diffractometers.

Several experiments were carried out to determine the effectiveness of PDF methods for the study of local structure in catalytic materials. The first of these was designed to obtain information on the location of small metal clusters within the large cages of faujasite zeolites. The two principal structural issues on these clusters that we hoped to

address by our diffraction studies are the geometry (size and coordination) of the cluster itself and its location within the zeolite cavities. We intend to combine X-ray and neutron diffraction studies using conventional as well as PDF analysis with theoretical modeling to obtain this information. First, good metal-metal correlations for the atoms in the cluster have previously been obtained from EXAFS studies [2]. In order to locate the clusters inside the zeolite cavities we planned to carry out both direct-space (PDF) and reciprocal-space joint Rietveld analysis of both X-ray and neutron diffraction patterns. Very high quality data was collected at the ISIS facility (UK) on six-atom Ir and Rh clusters in Faujasite at low temperatures. In addition, we obtained room-temperature X-ray diffraction data at LANL. Unfortunately, the samples that were provided contained only one metal cluster for every eleven supercages of the zeolite, and thus had too low a concentration to show unambiguous structure in the PDF. In addition, the X-ray data showed no evidence for the clusters at room temperature, which may be attributed to possible motion of the clusters. Low temperature X-ray diffraction data will be obtained in the near future. However, the neutron PDF structure could well be resolved with the neutron flux increase to be provided by the new diffractometer under construction at LANL's Lujan Center, or at the new high-intensity neutron scattering facility under construction at ORNL, the Spallation Neutron Source.

A second experiment was designed to determine the location of absorbed chloroform molecules relative to the framework in faujasites [3] by using a differential PDF with normal and deuterated chloroform. Guest/host systems such as molecules adsorbed in the cavities of zeolites are good examples of a quasi-ordered system. While the host in this case has long-range crystalline order, the guest molecule evidently can be absorbed at a variety of sites within the host with little or no correlation between the adsorbate molecules. Because of this, analysis of such a system in terms of an average structure often results in ambiguous information on the location of the adsorbate molecule, especially if the latter is small (such as chloroform in our case). In our previous work [3] we utilized computational studies as well as inelastic neutron scattering vibrational spectroscopy to determine that adsorption of chloroform in faujasites is governed by a weak hydrogen bonding interaction between the molecule's C-H group and framework O atoms. The H...O distance was found by the calculation to be 2.8Å. We were unable to locate the chloroform molecules by conventional analysis of neutron diffraction data, and thus collected new diffraction data suitable for real-space (PDF) analysis on the instrument GLAD at Argonne National Laboratory's Intense Pulsed Neutron Source. In this case the loading was two molecules for every large cage. Moreover, data was obtained for both CHCl<sub>3</sub> and CDCl<sub>3</sub> so that a differential PDF can be obtained between these data sets. In this case all pair correlations

that are the same in the two systems (such as O-O and Si-O) will subtract out and only those involving H and the other atoms will remain including, of course, the H to O distances. While data analysis is still in progress, this type of experiment appears to be promising for a variety of such disordered adsorption complexes.

We have developed computer codes to carry out pair distribution function analysis of partially ordered systems. The purpose of this effort was to evaluate the feasibility of using pair distribution function experiments to identify the local structure around disordered regions embedded in a periodic crystalline system. These systems are of great interest in catalysis and materials science where local disorder, usually in the form of defects, impurities, or adsorbates, is deliberately introduced into the system to achieve desired chemical and physical properties. Unfortunately, the local geometry around these imperfections is almost always unknown. The potential of pair distribution function analysis to elucidate the local structure was the focus of this part of our investigations.

To tackle the problem of how to use pair distribution function analysis for small disordered regions in an otherwise periodic matrix we needed to devise techniques to calculate these functions as accurately as possible. The main difficulty is that because we are interested in the local geometry of regions that may be only a small fraction of the whole system, the periodic matrix will dominate the pair distribution function. The question is how to identify the effects of small perturbations (the effect of the disordered region) on the perfect crystal pair distribution function.

In order to calculate the pair distribution function for the systems at hand we needed to be able to include the disordered region and a good portion of the surrounding areas. There are basically two approaches to solving this problem: (i) include the disordered region as part of a large unit cell (composed of several unit cells of the underlying crystalline matrix) and treat the system as a new crystal; (ii) treat the disordered region and its surroundings as a very large molecule. The main disadvantage of (i) is that the disordered region is periodically repeated leading to peaks in the pair distribution function that would not normally appear in the experiments. On the other hand, (ii) suffers from the potential problem that the number of atoms in the "molecule" is not necessarily large enough compared to what the experiments see. Both of these situations can be abated by making the unit cell in (i) and the "molecule" in (ii) larger and larger. In the results described below we employed method (ii) with several thousand atoms in the "molecule".

The pair distribution function for a simple, monoatomic system is given by [4]

$$g(r) = \frac{V}{N^2} \left\langle \sum_i \sum_{j(\neq i)} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle,$$

where  $V$  is the volume and  $N$  is the number of atoms;  $\mathbf{r}_{ij}$  is the difference between the position vectors of atoms  $i$  and  $j$ . The function  $g(r)$  gives the probability of finding a pair of atoms a distance  $r$  apart, relative to the probability expected for a completely random distribution at the same density. This pair distribution function can be directly compared with the pair distribution function measured from neutron scattering experiments [1]. We used a procedure similar to that of Allen and Tildesley [4] to calculate  $g(r)$  but taking into account that there are several kinds of atoms in our systems. We also had to develop accurate numerical techniques to be able to distinguish the perturbed from the unperturbed results.

To evaluate the feasibility of distinguishing the effect of small disordered regions in and otherwise periodic background we performed a series of calculations in a well defined model system. We chose rutile, a crystalline form of titanium oxide because it has been well studied experimentally and it is similar to some of the zeolitic systems that have been studied at Los Alamos. Our calculations compared the pair distribution functions of a perfectly periodic system with a series of distorted configurations where up to 10% of the atoms were displaced from their original positions. The amounts that these atoms were moved from their original positions were chosen in random directions by amounts of 5%, 10%, 15% and 20% of the nearest neighbor distance.

The main result from our calculations is that experimental detection of displaced atoms is very difficult unless the displaced atoms are moved by large amounts or if the fraction of displaced atoms is large. In other words, disorder regions that correspond to 10% or less of the atoms in the system lead to pair distribution functions whose difference from the perfect crystal results is very small, and may be experimentally indistinguishable from the perfect crystal pair distribution functions. Figure 1 shows that for a 10% displacement of about 8% of the atoms in the unit cell of rutile, the difference between the pair distribution function of the perfect and perturbed crystals is very small indeed. It should be noted, however, that for comparison with experiment the computed PDF's in Fig. 3 must be modified to include weighing of the partial PDF's by neutron scattering lengths and the peaks must be broadened by experimental thermal factors. Nonetheless, our results may suggest that it is necessary to utilize differential PDF's to extract local structural information when such defects are small in number.

Vibrational spectroscopy by INS on isolated molecules adsorbed in zeolites or other hosts has the potential of providing a great deal of detail on adsorption site geometry and guest/host interactions by virtue of the fact that in contrast to optical spectra full INS spectra can be calculated explicitly. The latter are extremely sensitive to the inter-atomic force field as the intensities are governed by the vibrational amplitudes of the atoms. A feedback loop between calculation and INS experiment can then be used to optimize the adsorption site geometry.

To this end we carried out experiments and calculations to analyze the sorption of organic molecules inside zeolites using inelastic neutron scattering. Here we illustrate the use of computer simulation to aid in the analysis and assignment of inelastic neutron scattering data for ethane and ethylene sorbed in Na-Y zeolite. The focus is on the investigation of the librational modes of the sorbate which correspond to (whole-body) librational modes for the isolated molecules.

The principal advantage of INS over related techniques such as Raman or infrared spectroscopies is the unique sensitivity of neutrons to vibrational modes involving hydrogen atoms on adsorbed molecules, while the framework motions give rise to much weaker scattering. INS spectra were recorded at 25 K on a sample of approximately 5g of dehydrated (at 500°C) NaY, and on NaY samples, which were loaded with one sorbate molecule per supercage. The data were collected using a closed-cycle He refrigerator on the Filter Difference Spectrometer [5] at the Manuel Lujan Jr. Neutron Scattering Center of Los Alamos National Laboratory and were treated [6] after background subtraction by deconvolution of the instrumental response function.

The technique of atomistic simulation was used in these calculations. A force field was taken from a previous simulation of aliphatic and aromatic hydrocarbons in Na-Y and the parameters adapted for use in this work [7]. A Monte Carlo docking procedure [8] was performed to obtain possible sorbate binding sites and then, using these sites, a force constant matrix was formed using a numerical Hessian. Diagonalisation of this matrix yielded eigenvalues and eigenvectors for comparison with the experimental spectra. Intensities were calculated from the eigenvectors and the neutron scattering factors of the atoms in the model.

The INS spectra for ethane in Na-Y show a broad band in the low-frequency region that is consistent with a large number of ill-defined sorption sites. The Monte Carlo docking calculation predicts a range of binding sites with energies spanning ca. 5 kJmol<sup>-1</sup>. For ethylene, the Monte Carlo docking calculation predicts two binding sites: one in the vicinity of the SII cation (Figure 2) and the other in window. The cation site is analogous to that for benzene in Na-Y, except that the molecule is bound off-center. The calculated

INS spectra in the librational region shows a good fit to the experimental data for the SII binding site (Figure 3). Examination of the eigenvectors for the low frequency modes reveals the three softest modes to be related to a combination of the rotational and translational motions of the molecule.

This work shows the value of using computational methods to provide an atomic level interpretation of INS spectra of sorbates in zeolites. Work in is progress to improve the quality of the calculations by using *ab initio* quantum mechanical methods as well as looking at systems of greater catalytic interest.

### Acknowledgments

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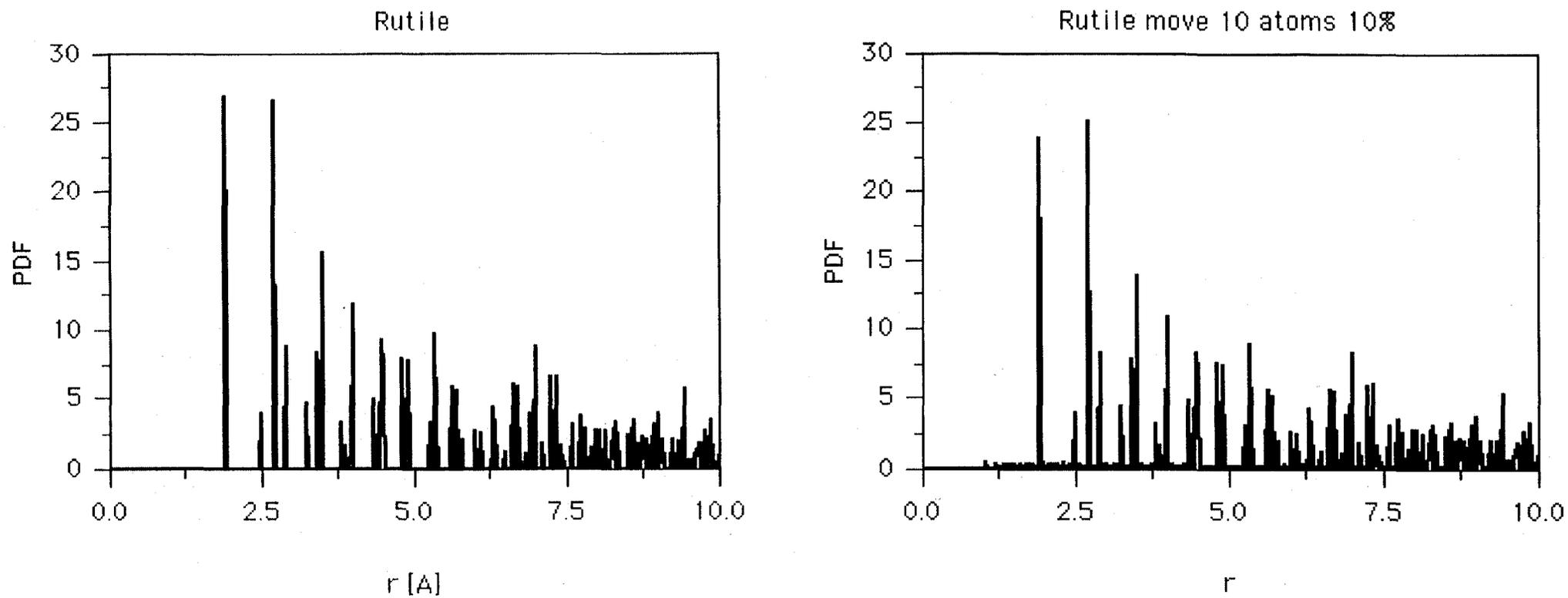


Figure 1: Pair distribution functions for rutile. (a) Perfect crystal; (b) when 8% of the atoms

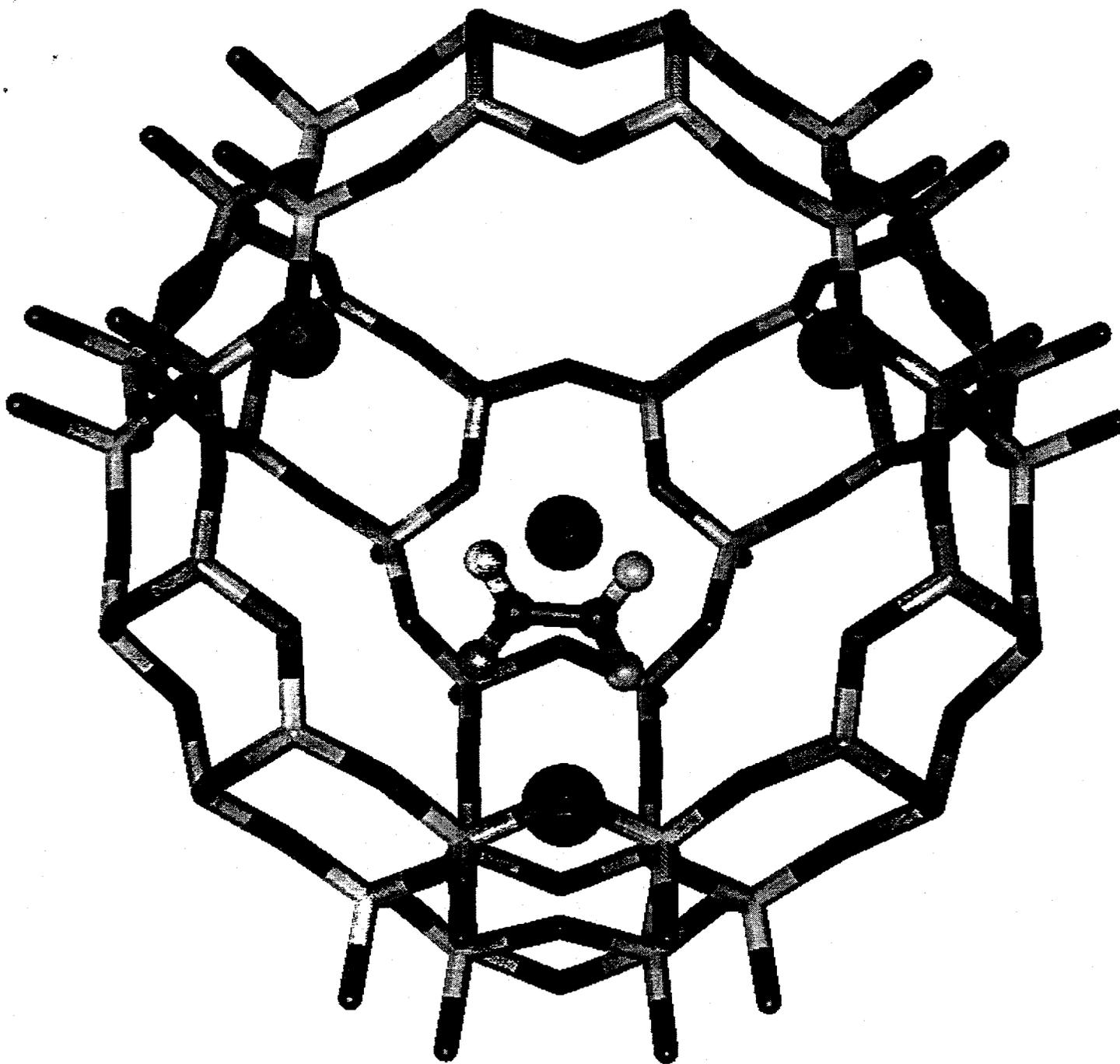


Figure 2: Binding site for ethylene in the faujasite zeolite Na-Y near the Na<sup>+</sup> cation.

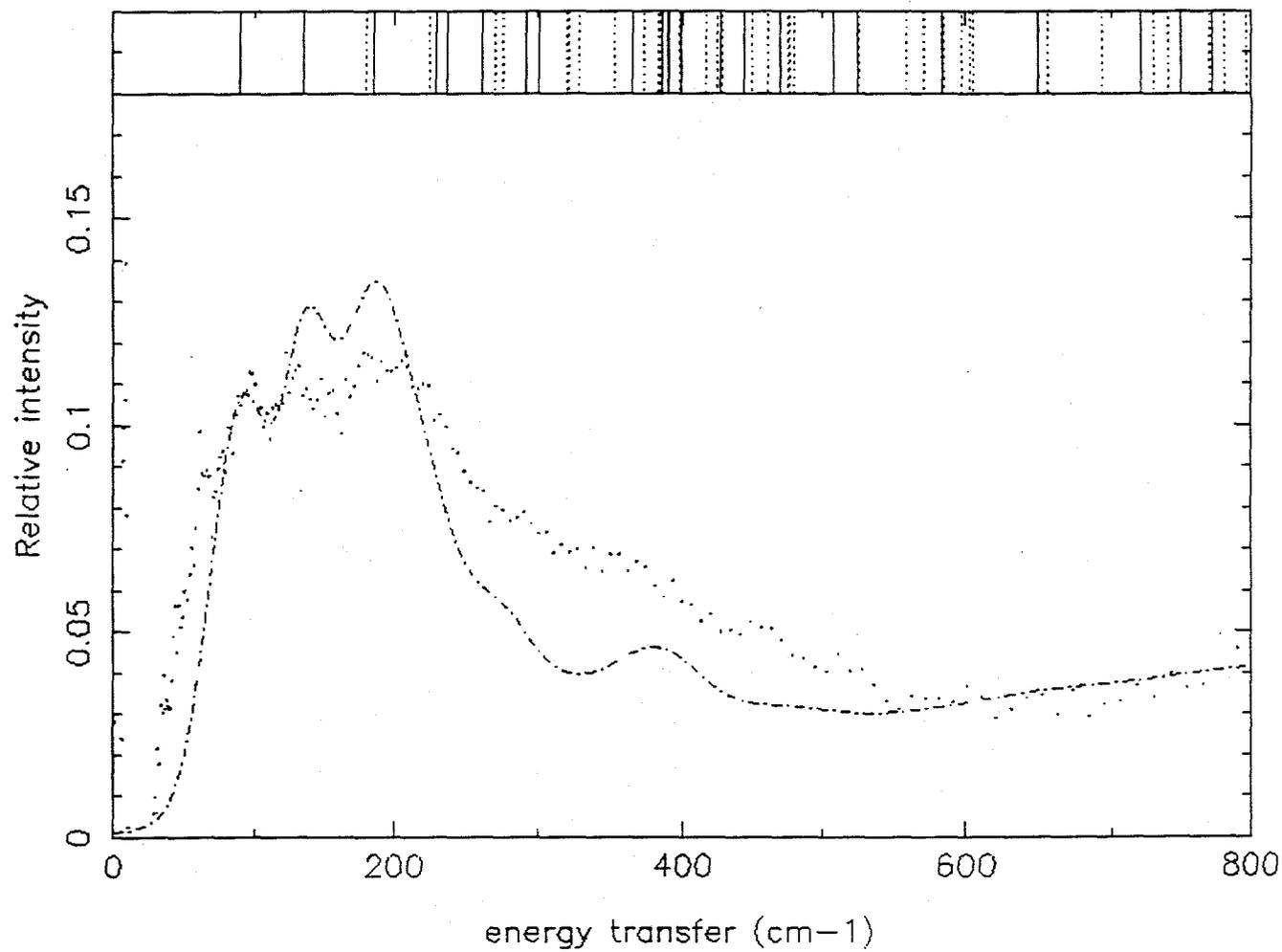


Figure 3: Comparison of calculated (---) and experimental (···) INS spectra for the librational modes of ethylene adsorbed in zeolite Na-Y.