

## **Absorbed Molecules in Microporous Hosts - Computational Aspects**

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### **1. Introduction**

During the last decade, the use of computational methods to study microscopic processes has grown significantly. This is especially noticeable in the field of molecular biology [1], where pharmaceutical companies have a considerable investment in computational resources. In the area of materials science, important advances in the development of computational techniques have also been made in the simulation of materials themselves to both reproduce experimental data and to make predictions [2]. The application of computational methods to zeolitic systems is becoming an increasingly important tool in studying the relation between microscopic properties and their relation to both sorption and catalytic applications [3]. A detailed understanding of important processes at the microscopic level is an essential prerequisite in providing a rational method for computer-aided catalyst and molecular sieve design. The routine application of such methodologies would allow candidate zeolite structures to be screened prior to experimental study, their catalytic activity assessed using a computational algorithm, and the most promising candidates selected for experimental trials. Although the development of such screening techniques still lies in the future, the wide range of computational methods that are currently available can provide a useful insight into the interpretation of both experimental data and the identification of the important fundamental processes at the microscopic level. In this chapter, we will review current progress in this field, with illustrations of recent work and examples in the modeling of sorbates in zeolites of catalytic interest.

### **2. Theoretical Techniques**

Many detailed reviews of the computational techniques available to the solid-state chemist have been written [3,4,5]. In this section, we provide only a short description of each method and highlight the analogous experimental data that is relevant for comparative and predictive purposes. The theoretical approaches can be divided into two main areas. Firstly, there are those methods having a quantum mechanical basis that consider the electronic structure of the atoms in the system explicitly by solving the Schrödinger equation. In addition, there are those methods which make use of

interatomic potentials to represent the energies and forces acting with the systems in question.

## 2.1 QUANTUM MECHANICAL METHODS

Quantum mechanical methods have the advantage that they allow the calculation of properties which directly depend on the electronic configuration of a system such as the bond-breaking and bond-making that occurs during a chemical reaction. However, such calculations tend to be computationally expensive, and the approach is mainly limited to clusters with fewer than 200 atoms. Quantum mechanical calculations have been performed by a number of workers both at the semi-empirical [6] and the *ab initio* Hartree-Fock level [7,8,9]. The calculations have focused on the structure and properties of the zeolite acid site and its interaction with molecules of catalytic interest. The results of calculations can be usefully compared with crystal structure determinations, infra-red spectra, and acidity measurements of protonated zeolites [10]. One of the problems with cluster calculations is the question of how the cluster is terminated so as to create the correct electrostatic potential in the region of the acid site. This effect was recently investigated by Brand and co-workers [11]. Several methods have been proposed to circumvent this problem. One approach is to embed the quantum mechanical cluster in an infinite array of point charges [12,13], whereas perhaps a more rigorous approach is to use periodic Hartree-Fock techniques. To date, periodic calculations have been performed on several zeolite crystal structures including silicalite [14], mordenite [15], and chabazite [16]. Although these studies do not include guest molecules directly, by means of analyzing of the electrostatic potential, the most favorable binding sites for sorbed species can be postulated. Recently, Nicholas and Hess have performed a periodic Hartree-Fock calculation on the acid sites in sodalite [17] looking at cases in which there are both one and two acid sites in the same  $\beta$ -cage. They found considerable differences between periodic and cluster calculations on the same system.

## 2.2 FORCEFIELD METHODS

There are several simulation methods that employ interatomic potentials. However, before employing these methods, an accurate set of forcefield parameters must be defined to correctly represent the interactions of interest. Historically, there have been several approaches to forcefield development. The first method uses an empirical procedure to fit the forcefield parameters to experimental data [18,19]. In cases where experimental data are not available, electron gas calculations can be performed to obtain parameters [20]. However, the most promising method is to fit the forcefield to high quality, quantum-mechanically determined *ab initio* potential energy surface derived calculations on either clusters or a periodic system. Forcefields for both silicates [21] and aluminophosphates [22] have recently been derived by this method.

The numerous forcefields that have been developed to model zeolite structures can be divided into two general categories. Firstly, there are those relying on Born-model type potentials [23]. In this form, the system is presumed to be predominantly ionic with the ions carrying either formal or partial charges interacting via a Coulombic potential, combined with pair potentials (usually of Lennard-Jones or Buckingham form) representing the dispersive interaction. The periodic nature of the system requires a systematic method such as the Ewald summation [24] for dealing with the long range Coulombic interactions. Often, three-body terms are added to correctly represent the bond angles about the tetrahedral atoms. An additional refinement to the forcefield may be provided by the inclusion of shell-model potentials to treat atomic polarizability [25]. In addition, there are forcefields that take a more covalent approach involving potential functions representing the bonding directly with harmonic functions for bonds, angles and torsional terms [26,27]. The interactions between the zeolite lattice and intercalated molecules are presented using similar potential functions as for the zeolite, with some degree of Coulombic and dispersive interaction included in the forcefield. Lennard-Jones functions are often used for the dispersive contribution :

$$E_{ij} = \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6}$$

where  $E_{ij}$  is the interaction energy between species  $i$  and  $j$  separated by the distance  $r_{ij}$ , and  $A_{ij}$  and  $B_{ij}$  are fitted parameters. Early work by Kiselev and co-workers [28] derived interactions parameters from expressions such as the Slater-Kirkwood formula [29] relating quantities for the polarizabilities and van der Waals radii to the Lennard-Jones parameters :

$$B_{ij} = \frac{3}{2} e^2 \sqrt{a_0} \frac{\alpha_i \alpha_j}{\left(\frac{\alpha_i}{n_i}\right)^2 + \left(\frac{\alpha_j}{n_j}\right)^2}$$

where  $\alpha_i$  and  $\alpha_j$  are polarizabilities,  $e$  is the electronic charge,  $a_0$  is the Bohr radius, and  $n_i$  and  $n_j$  are the effective number of electrons in atoms  $i$  and  $j$ . Since values of polarizabilities of ions inside a zeolite lattice are not directly measurable by experimental methods and there is some ambiguity over the choice of  $n$ , various assumptions must be made. A better method, which is similar to that described above, is to fit parameters to experimental data. We note that although more accurate quantum mechanical calculations would be desirable, system size and the often considerable effects of long-range Coulombic interaction on the sorption characteristics of the system generally make the calculation of ab initio potential energy surfaces intractable. Suitable experimental data include structural information from crystallographic studies of zeolites with sorbed guest molecules, thermochemical data, and sorption isotherms. This approach was recently applied to the simulation of benzene in silicalite [30] and in siliceous faujasite [31].

Once a forcefield has been derived that can reproduce the experimental quantities of interest to the desired accuracy, a number of different types of calculations can be considered [32]. The simplest experimentally interesting calculation that can be performed is the determination of the most favorable binding sites for sorption in a zeolite. In early work, this was carried out by manually moving the guest molecule of interest through the zeolite [33]. This methodology has been replaced by static-lattice energy minimization techniques, which are now quite efficient for periodic systems consisting of several hundred atoms. In this approach, all structural degrees of freedom of the system are allowed to relax under the influence of the forcefield until an energy minimum has been located. With suitable potential energy functions for the zeolite, the importance of lattice relaxation on the sorption energetics can also be assessed. One disadvantage of this approach is that, for systems of this complexity, local minima are often a problem, and the final minimized system configuration is strongly dependent on the initial state. Methods to overcome such difficulties, such as simulated annealing techniques, will be discussed later in this section. Another important consideration when comparing sorption energies derived from this method is that they represent determinations at zero Kelvin. Although there are several ways to include the effects of temperature into these methods, for example, via the quasi-harmonic approximation or by the inclusion of lattice dynamical theory, these have not generally been applied to studies of guest-host interactions.

A much simpler method to obtain temperature dependent properties is to use techniques derived from statistical mechanical approaches to the problem. Molecular dynamics (MD) has been widely used in zeolite problems to study the transport properties of molecules through zeolite pores. In this method, Newton's equations are solved by iterative procedures in order to propagate the system through time. A fundamental component of the iterative procedure is the MD time step, which is usually chosen to be smaller than the fastest important process in the system (for example, a bond vibration) so as to give the correct energy conservation properties. A popular method of integration is the velocity modification [34] of the Verlet method [35], which is based on a Taylor series expansion. The positions are advanced in one step by:

$$r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2}\delta t^2\frac{F(t)}{M}$$

where  $r(t)$  is the position at time  $t$ ,  $v(t)$  is the velocity,  $F(t)$  is the force acting on the particle as computed from the forcefield,  $M$  is the particle mass, and  $\delta t$  is the MD time-step. The velocities are advanced to the mid-time step position:

$$v(t + \frac{1}{2}\delta t) = v(t) + \frac{1}{2}\delta t\frac{F(t)}{M}$$

The forces are then computed at the new position and the velocities updated to the full-time step position:

$$v(t + \delta t) = v(t + \frac{1}{2}\delta t) + \frac{1}{2}\delta t \frac{F(t + \delta t)}{M}$$

The simplest MD simulation that can be performed is in the *NVE* ensemble (constant number of particles, volume, and energy), although it is often more useful for comparison with experiment to run a simulation at constant temperature (*NVT* ensemble). In the limit of an infinitely large system, the two ensembles are equivalent; however, in order to study constant temperature dynamics in commonly sized systems, a number of suitable thermostating algorithms have been developed to obtain the *NVT* ensemble [36,37]. Constant temperature MD offers the opportunity of studying the behavior of the system as a function of temperature and deriving activation energies for the transport process.

Early MD studies in zeolites focused on the study of simple sorbates such as xenon [38,39,40]. For example, Pickett and co-workers examined the diffusion of xenon in silicalite with the zeolite lattice held rigid [38]. This is a particularly interesting sorbate since self-diffusivities can now be measured routinely with  $^{129}\text{Xe}$  pulsed-field gradient NMR [41] and directly compared with values obtained from the simulations. Yashonath and Santikary have also recently looked at the effect of varying both the size of a spherical sorbate and its interaction strength with the zeolite on the mechanism of diffusion in zeolite Y and zeolite A [42]. They found a strong correlation between the sorbate diameter and the rate of intercage diffusion. There have also been several studies which considered molecules of more catalytic interest such as small hydrocarbons [43-47] and benzene [48,49]. Demontis and co-workers have made an extensive study of methane in silicalite and have also looked at the effect of adding zeolite lattice dynamics into the model on the transport behavior. They conclude that allowing the lattice to flex not only affects the mobility of the sorbate but also more subtle properties such as the distribution and clustering of the sorbate in the pore structure.

There are, however, cases in which the application of molecular dynamics can be impractical, since the simulation needs to sample sufficient time to obtain statistically meaningful results. This is particularly apparent for systems in which the diffusivities of interest are less than  $10^{-10} \text{ m}^2\text{s}^{-1}$  [44]. Indeed, June and co-workers have estimated that, to study a slow moving molecule such as n-hexane in silicalite by MD, a simulation run of at least 300 ns would have to be performed requiring approximately 4000 CPU hours on a large-scale supercomputer [50]. In addition, the inclusion of lattice dynamics can often cause similar problems due the small time steps required to correctly handle lattice vibrations in the numerical integration of Newton's equations of motion. Possible solutions to this problem will be discussed later in this section.

The final statistical mechanical technique that can usefully be applied to zeolite-guest problems is that of Monte Carlo (MC) simulation. The Monte Carlo method provides a further technique for generating an ensemble of system configurations which can be used to calculate averages and correlation functions that can be compared with experimental data. The widely used algorithm of Metropolis and co-workers [51] uses random

numbers to create new configurations based on Boltzmann probabilities. Monte Carlo methods tend to be faster than MD simulations, since the calculation of energy derivatives is not required; however, in most traditional MC methods, there is no relation between a single MC step and a time-scale, so dynamical information is not readily accessible. Several studies have been made investigating the sorption of xenon in zeolites using standard Monte Carlo methods [52,53]. If this approach is extended to more complicated molecules, the internal degrees of freedom of the guest molecule must also be varied, which increases the computational cost to obtain statistically meaningful ensemble averages. June and co-workers studied the sorptive properties of linear alkanes in silicalite and found that the molecules locate preferentially in the main body of the channels rather than at channel intersections [54]. Recently, Smit and Siepmann have developed a configurational-bias Monte Carlo methodology for zeolites which greatly improves the efficiency of such simulations for chain molecules [55].

The method of Grand Canonical Monte Carlo (GCMC) [32] allows, in addition to the standard random moves provided by the Metropolis method, the possibility of creating and destroying particles. One useful application of this method is to fix the chemical potential of the system (and thus the pressure) and use several different GCMC simulations to calculate a sorption isotherm that can be compared directly with experimental sorption data. Woods and Rowlinson used this technique to study the sorption of Xe in faujasite [56] whereas two more recent studies have looked at the behavior of Xe in Na-A [57,58]. Cracknell and Gubbins have also investigated the sorption of Ar in the aluminophosphates  $\text{AlPO}_4\text{-5}$ ,  $\text{AlPO}_4\text{-8}$ , and VPI-5 [59].

The development of hybrid methods which combine two or more of these techniques in a single calculation provides the most promising and powerful tools in forcefield methods. For example, the problem of local minima in static-lattice energy minimizations can be approached by the method of simulated annealing in which the system is subjected to a period of molecular dynamics prior to the minimization stage. The goal here is for the MD phase to perturb the system sufficiently to escape the local minima. The technique tends to produce a series of different minima of which one is the true global minimum on the potential energy surface. Deem and Newsam used this method to generate possible zeolite crystal structures given limited information on structural composition [60]. Another method of dealing with this problem is provided by the docking protocol first demonstrated for zeolites by Freeman and co-workers [61]. Using this approach, the zeolite-guest potential energy surface is probed by first carrying out high temperature dynamics on the guest molecule itself to generate a series of thermally accessible conformations. The guest molecule is then inserted into the zeolite at random locations and each zeolite-guest configuration energy minimized. As with simulated annealing, this technique generates a series of energy minima which can be analyzed to determine the preferred binding sites. This method has been applied by a number of groups to the study of zeolite-template interactions. Santilli and co-workers have used this method to study the effect of *inverse shape selectivity* [62]. They concluded that the selectivity of, for example, a hydrocracking reaction can be predicted by calculating the binding energies of the various products in the cavity of the zeolite

pores. Cox and co-workers [63] have also extended the docking approach to assess the importance in template-template interactions on the binding energy.

Several methods have been demonstrated to probe the diffusion of molecules through zeolites that occurs too slowly for conventional MD methods. The general principles combine techniques in reaction rate theory with conventional forcefield methods. We can use the docking protocol detailed above to probe the zeolite pores for favorable binding sites and then postulate diffusion as occurring via a series of hopping events. By performing a series of energy minimizations along the hopping path, the transition state and thus the activation energy for the hop can be identified. June and co-workers used a transition-state theory approach similar to this to calculate rate constants for the hopping processes and thus diffusion coefficients for the diffusion of Xe and SF<sub>6</sub> in silicalite [50]. An alternative to using transition state theory is to calculate the rate constants directly from the activation energy making realistic estimates for the pre-exponential factor from the reaction rate expression:

$$v = v_0 \exp\left(\frac{-E_a}{kT}\right)$$

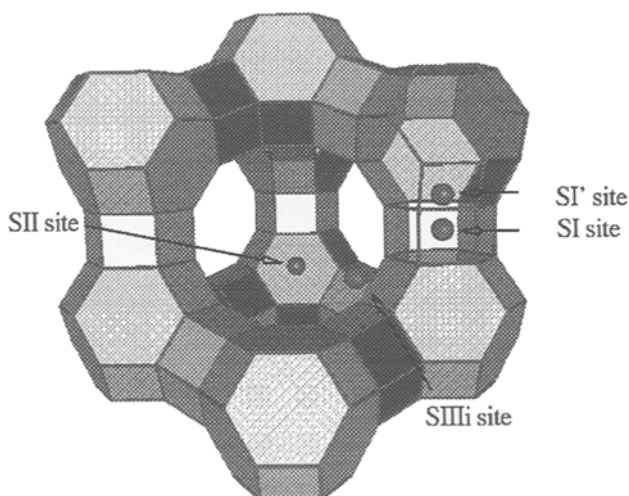
where  $v$  is the reaction rate,  $v_0$  is the pre-factor,  $E_a$  is the activation energy,  $k$  is the Boltzmann constant, and  $T$  is the temperature. The rate constants can then be used in a *kinetic* Monte Carlo simulation. The most widely used algorithm is based on the Metropolis method. For each kinetic Monte Carlo step, an attempted hop is either rejected or accepted based on Arrhenius-Boltzmann statistics. A system clock can be updated based on the shortest time-scale process in the system. Standard analysis techniques can be applied to determine the diffusion coefficient. This method was recently applied by Auerbach and co-workers to investigate the transport of benzene in Na-Y [64].

### 3. Examples

Rare-earth and high silica faujasites are widely used as catalysts in the fluid catalytic cracking process [65], showing both good selectivity and high conversion rates. The development of computational models to study the behavior of aromatic molecules, which are important products of this reaction, is an interesting challenge in this area. In the following examples, we will show how we can use experimental data to derive a forcefield for this system and how it can be applied to rationalize experimental data on this system.

The faujasite framework has two main structural features (Figure 1). There are large spherical supercages which are about 13 Å in diameter. Access to the supercages is afforded by four 12-ring windows about 10 Å in diameter which are tetrahedrally distributed about the center of the supercage.

This work was motivated by recent  $^2\text{H}$  spin-lattice relaxation NMR measurements on the transport of benzene in faujasite samples of varying Si/Al ratio [48]. The NMR results are summarized in Table 1. It can be seen that diffusion is quite facile in the purely siliceous system, but once we introduce cations into the zeolite, the diffusivity is reduced by about two orders of magnitude due to the benzene molecule's preferred, strong interaction with the  $\text{Na}^+$  cations. However, this effect does not have a simple dependence on sodium ion concentration; since when we move to a system with a lower Si/Al ratio (and hence more cations), the diffusion is found to be enhanced. Clearly, a microscopic picture of the important processes in this system would be of value in rationalizing these experimental trends.



**Figure 1.** The structure of faujasite showing cation positions.

**Table 1.** Diffusion coefficients ( $D$ ) and activation energies ( $E_a$ ) for benzene absorbed in various faujasite structures (taken from Bull et al. [48]).

	$D$ (298 K) ( $\text{m}^2\text{s}^{-1}$ )	$E_a$ ( $\text{kJmol}^{-1}$ )
siliceous faujasite	$5 \times 10^{-10}$	10
Na-Y (Si/Al = 1.2)	$4 \times 10^{-11}$	14
Na-X (Si/Al = 1.7)	$2 \times 10^{-13}$	24



### 3.1 DEVELOPMENT OF A ZEOLITE-AROMATIC FORCEFIELD

The first step in this work is the development of a forcefield that can be used to calculate the experimental properties of interest. We begin by considering the simplest system, that of the siliceous zeolite and its interaction with benzene. There are two main experimental measurements which have been made on this system that are relevant to our work. Firstly, a low-temperature neutron diffraction study failed to locate a benzene sorption site [66]. This indicates that although the benzene is indeed sorbed, there are a large number of similar binding sites in the structure of similar energy, and a number of them are low-symmetry sites. Also, a recent thermochemical study of this system shows the heat of sorption to be approximately 55 kJmol<sup>-1</sup> [31].

Since there are a number of forcefields that have been already developed for zeolites, we chose simply to adopt one of these and concentrate on fitting realistic parameters for the zeolite-benzene interaction. We decided to employ the silicate potential derived by Kramer and co-workers [67], since it uses partial charges ( $q_{Si} = 2.4$ ,  $q_{Al} = 1.4$ ,  $q_{Na} = 1.0$ ,  $q_O = -0.7$ ) which numerous ab initio quantum mechanical calculations on clusters have shown to be more realistic than the formal values. In addition, the Kramer forcefield provides parameters for Al and Na which will be important in looking at the cation-containing faujasites. For our model of siliceous faujasite, we took the structure determination of Hriljac and co-workers [66]. A point-charge model for benzene was obtained from a semi-empirical quantum mechanics calculation (MNDO) using a Mulliken charge population analysis ( $q_C = -0.153$ ,  $q_H = 0.153$ ) and has been shown to approximately reproduce the quadrupole moment of benzene [30].

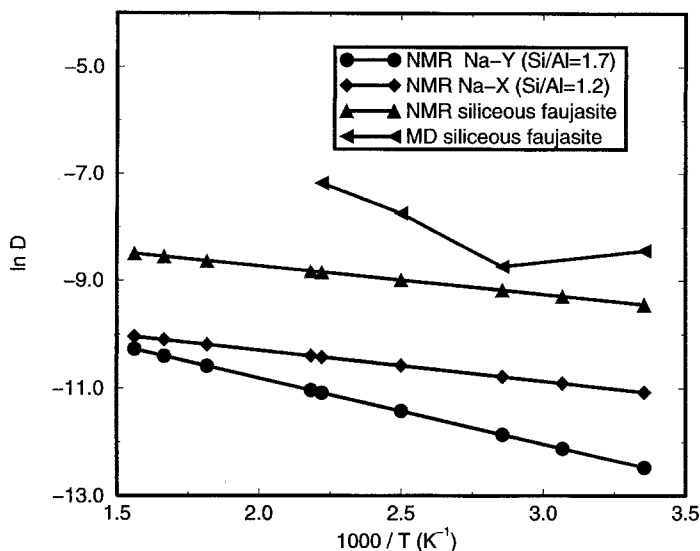
To obtain reasonable parameters for the zeolite-benzene interactions, we carried out a docking calculation as detailed in the previous section. This located a number of binding sites in the siliceous system, of which a site lying above the four rings on the wall of the supercage was the most favorable. Given this, we made the approximation that this site dominates the heat of sorption. With the Coulombic interactions already fixed by the choice of partial charges on benzene and on the zeolite lattice, we fitted the O-C and O-H dispersive parameters to reproduce the experimental heat of sorption at this site.

In the case of the cation-containing faujasite models, we used the experimental heat of sorption from the measurement of Barthomeuf and Ha [68] (75 kJmol<sup>-1</sup>) as the first parameter in our fit. The crystal structure of Fitch and co-workers [69] determined by low-temperature neutron diffraction shows two sites: the first with the benzene molecule bound facially through its  $\pi$ -electron cloud to the SII cation lying in center of the six-ring in the wall of the supercage; at higher coverages, a window site is also found to be occupied. Taking the parameters fitted to the siliceous system as our basis, we adjusted the C-Na, and C-H dispersive parameters to reproduce the correct minimum at the SII site, and give an interaction energy at this site approximately equal to the experimental heat of sorption. This rather simplified fitting method takes no account of the temperature variation of the heat of sorption and can be considered to be a first approximation to the interactions present in the experimental system.

### 3.2 DYNAMICS OF BENZENE IN SILICEOUS FAUJASITE

Since the value of the diffusivity for benzene in siliceous faujasite as measured in the NMR experiment is  $4.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , our first attempt to investigate this system was using a traditional molecular dynamics simulation.

As an initial test of our potential, we performed a static-lattice energy minimization on the structure of siliceous faujasite itself, removing strains on the cell by optimizing the lattice vectors as well as the atomic positions. The cell parameters are reproduced to within 2% of the experimental values. Although a better representation of siliceous faujasite could be obtained by using a more sophisticated potential model such as one of the several shell model potentials available for silicates [21,70], the high frequency of oscillation of the core-shell pairs would require the use of such a small time-step in the MD simulation that the total time spanned by the simulation would be vastly reduced. To improve further the validity of the siliceous faujasite model, we fixed the cell parameters at their experimental values using the *NVT* ensemble. An Ewald summation was used to sum the electrostatic interactions, whereas a cutoff of 12 Å was used for the short-range terms. A time-step of 1 fs was used and Newton's equations solved by the velocity Verlet algorithm. The temperature was constrained by the Nosé algorithm [37]. The system was equilibrated for a period of 25 ps and data collected over a time-scale of 100 ps. A series of molecular dynamics simulations were performed at 298 K, 350 K, 400 K, and 450 K. Diffusion coefficients were calculated from the Einstein relation using a multiple time-origin analysis on the center of mass of the benzene molecule as a function of time.



**Figure 2.** Comparison of the temperature dependence of the diffusion coefficients obtained for Na-Y and siliceous faujasite from the NMR experiments and MD simulations.

An activation energy and pre-exponential factor were determined from fitting the temperature dependence of the diffusion coefficients to an Arrhenius equation. The results are compared to NMR data in Figure 2.

The results are in reasonable agreement with experiment. The molecular dynamics calculation also provides information on possible trajectories. For example, by the use of animation, it can be seen that the benzene molecule spends a large proportion of its time close to the wall of the supercage and little time in the energetically less favorable supercage center. We find that the cage-to-cage hopping process is highly improbable at the temperatures studied and during the limited time-scales of the simulations. Indeed, we observe this process only to occur at the highest temperature studied (450 K).

### 3.3 DOCKING OF BENZENE IN FAUJASITES

Since the NMR experiment measures the diffusivity in both Na-Y and Na-X to be at least two orders of magnitude lower than in the siliceous system, neither of these systems are accessible to study by a conventional molecular dynamics simulation. With this in mind, we decided to investigate the cation-containing systems by an examination of the zeolite-benzene potential energy surface for possible binding sites. For completeness, the first system studied was that of siliceous faujasite. The docking methodology developed by Freeman and co-workers for zeolites was employed, as detailed in the last section. The initial docking minimizations were performed using a fixed zeolite lattice, which was then allowed to relax once the benzene minimum was located. Several binding sites were located in the siliceous structure, which could be divided into the following broad categories:

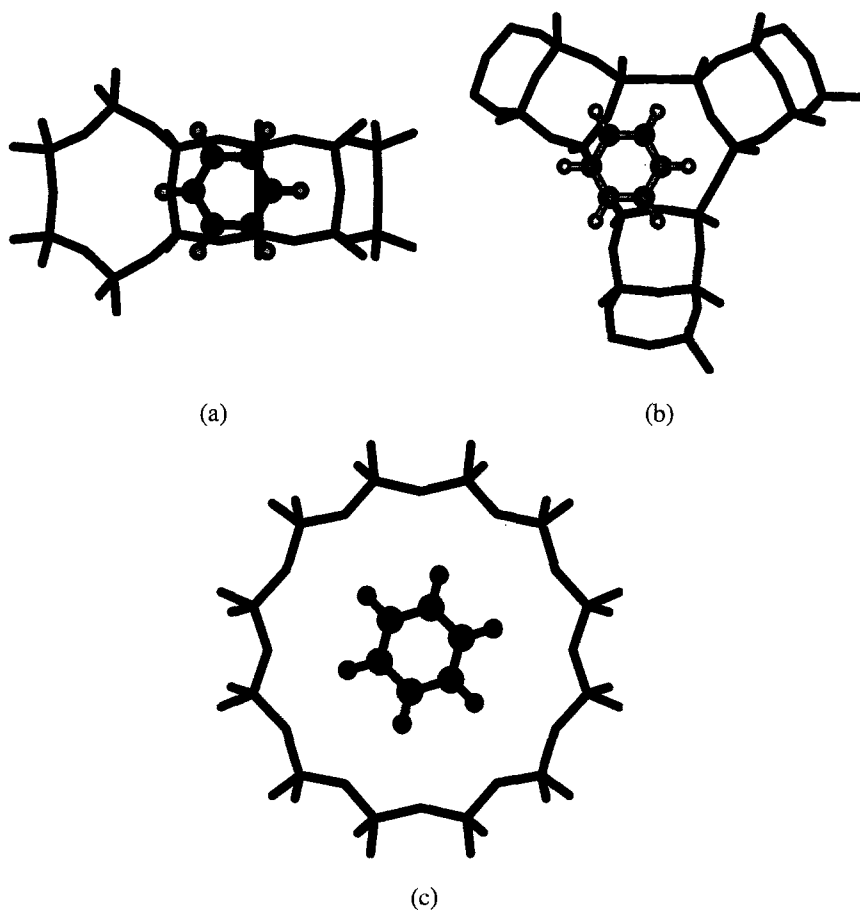
- (i) sites in the region of the 4-ring on the wall of the supercage;
- (ii) sites in the region of the 6-ring in the wall of the supercage;
- (iii) 12-ring window site.

The geometry of these binding sites is shown in Figure 3. The relative energetics of the various sites indicate that the potential energy surface around the walls of the supercage is relatively flat, and consists of a number of low symmetry sites; this is consistent with the diffraction data. The effect of lattice relaxation on these binding sites is shown in Table 2 and is most pronounced for the sites lying close to the supercage walls, reflecting the more intimate coordination afforded by those sites.

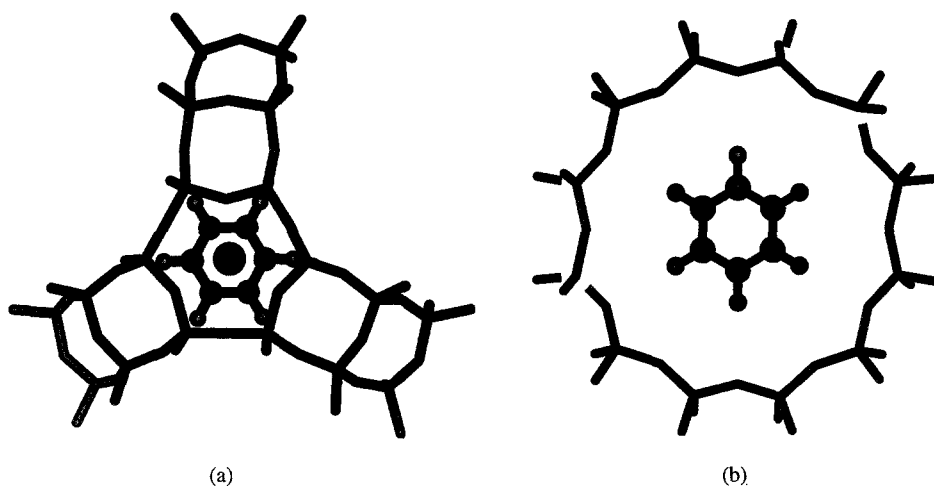
This procedure was then repeated for the cation-containing systems. Firstly, a model for Na-Y was constructed using the structure of Fitch and co-workers as a basis. There are three cation sites in this structure which are of relevance to our modeling (see Figure 1). The SI cation site is located in the center of the double 6-ring, whereas the SI' cation site is located in the wall of the sodalite cage above the 6-ring window. The separation between these sites is such that they cannot be occupied simultaneously. The final site, which is the most important for its interaction with benzene, is the SII site which is

**Table 2.** Effect of lattice relaxation on the docked sorption energies for benzene in siliceous faujasite.

site	binding energy (fixed zeolite) (kJmol <sup>-1</sup> )	binding energy (flexible lattice) (kJmol <sup>-1</sup> )
4-ring	55.8	58.4
6-ring	42.9	43.7
window	48.2	50.6

**Figure 3.** Docked sorption sites for benzene in siliceous faujasite: (a) 4-ring site, (b) 6-ring site, and (c) window site.

located in the wall of the supercage at the center of the 6-ring. To create an ordered model for Na-Y, we filled all the SI' and SII sites to give a Si/Al ratio of 2.0. Since at this Si/Al ratio the Si-Al substitution is known to be disordered, we made no attempt in this initial study to include Al explicitly. Instead, we used an average T-site model in which the charge on Si is reduced to balance the effect of the Na<sup>+</sup> cations. The results of the docking calculation on this system are shown in Figure 4. We locate only two binding sites in this system, both of which are observed in the diffraction experiment; the SII

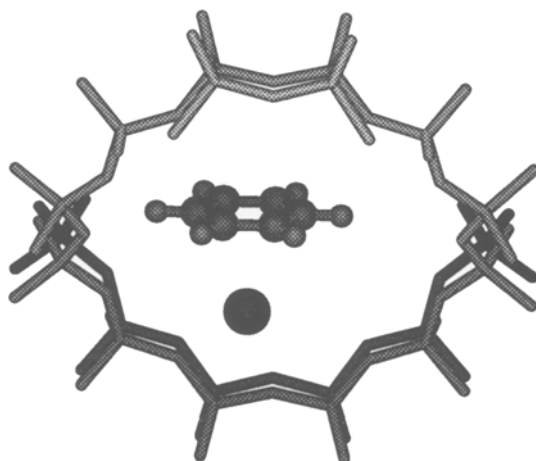


**Figure 4.** Docked sorption sites for benzene in Na-Y: (a) SII cation binding site ( $74.7 \text{ kJmol}^{-1}$ ) and (b) window site ( $50.2 \text{ kJmol}^{-1}$ ).

binding site is the most favorable by about  $25 \text{ kJmol}^{-1}$ . It can be noted that the presence of cations in the supercage has greatly enhanced the preference of binding in the supercage as compared to the window. Interestingly, the window site is shown to be a stable binding site, even at low dilution, since our docking calculation corresponds to a loading of one benzene molecule per unit cell. Although the presence of nearby benzene cations bound at the SII site undoubtedly perturbs the energetics of the window site, it is not a necessary prerequisite for its stability.

In order to construct models having Si/Al ratios lower than 2.0, further cation sites must be filled. Diffraction studies suggest that these cation sites are located in the region of the 4-rings in the wall of the supercage near to the 12-ring windows. In the absence of any diffraction for benzene in a Na-X sample, we used the crystal structure determination of Hseu [71] as a basis for our Na-X models. In this study, Hseu identifies the SIIIi cation

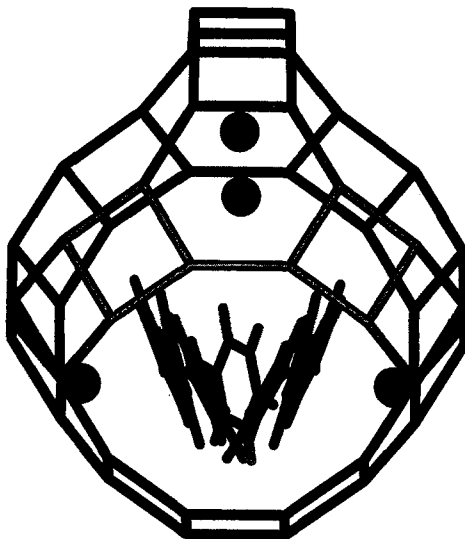
site as the repository for extra  $\text{Na}^+$  cations, of which there are 96 per unit cell (see Figure 1). These occur in pairs which are related by a mirror plane, lying above the 4-rings. There are two constraints on the occupation of the SIII sites. Firstly, the separation of these pairs of cations precludes the simultaneous occupancy of both sites; this reduces the maximum number of cation sites to 48. Secondly, Löwenstein's rule for this system limits the Si/Al to 1.0 (the structure of this system is referred to Na low-silica X or Na-LSX), which corresponds to 32 SIII cation sites filled. With this in mind, we constructed two models, one with 16 cation sites filled (Si/Al =1.4), and a second with 32 cation sites filled (Si/Al =1.0). For the Na-X models, we find the binding sites that occur for Na-Y are also sites in which the benzene is bound directly to the SIII cation (Figure 5). The energy of this site is found to be very similar to that of the SII cation site. The SII site is slightly perturbed due to the close contact of the hydrogens with the SIII cation.



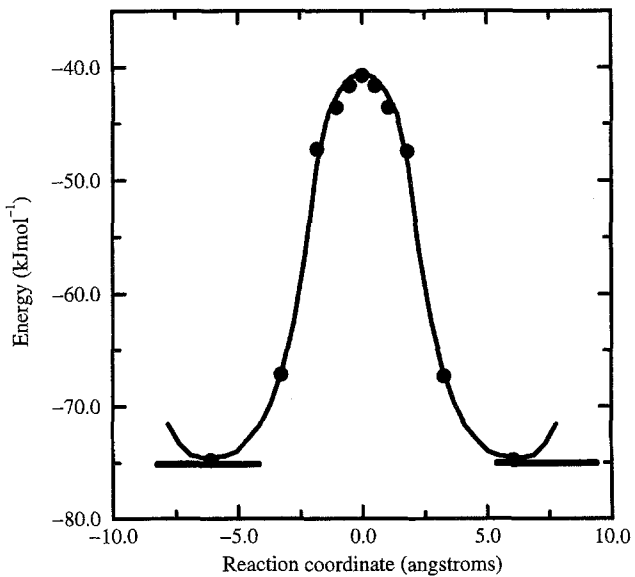
**Figure 5.** Docked sorption site for benzene at the SIII cation in Na-X (68.5 kJmol<sup>-1</sup>).

### 3.4 DIFFUSION OF BENZENE IN CATION-CONTAINING FAUJASITES

In the previous section, we determined possible binding sites for benzene in various cation-containing faujasite models. While the depth and location give little insight into the diffusion mechanism in these structures, they do provide a basis from which we can determine possible trajectories. If we assume that the transport occurs by hopping between adjacent energy minima, we can analyze the potential energy surface along such pathways. Since the forcefield was fitted to the equilibrium properties of the experimental system, we are making the assumption that the same parameters are also valid close to transition states. Considering the structure of Na-Y which has two binding

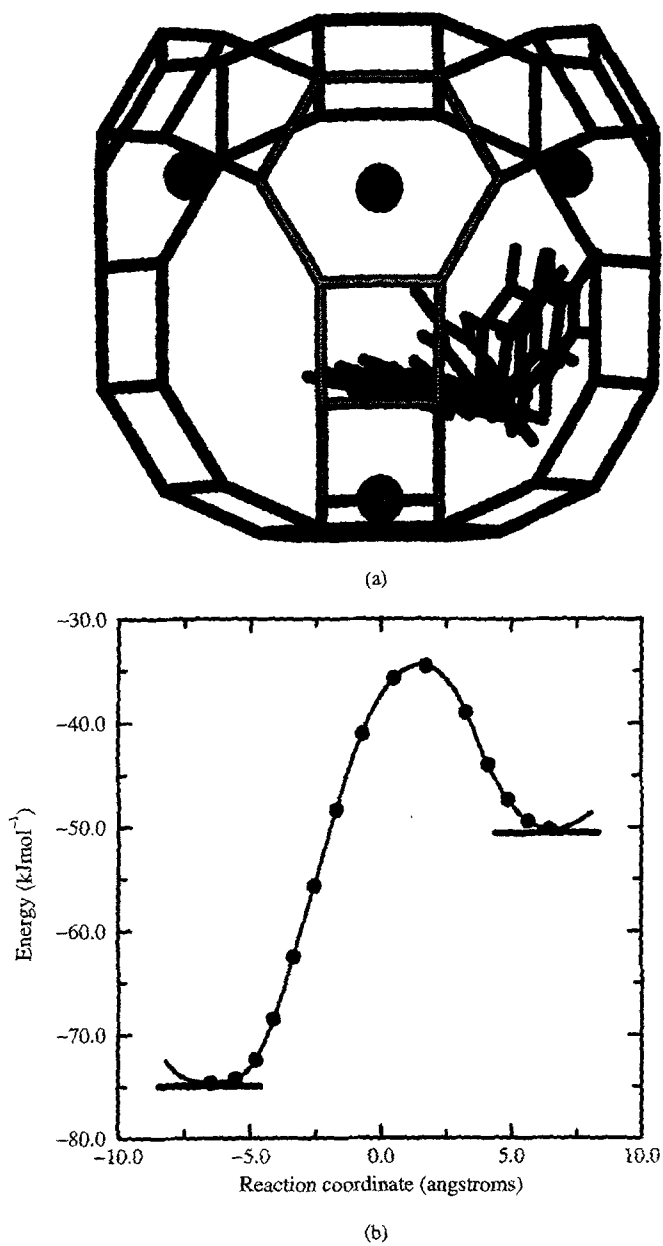


(a)



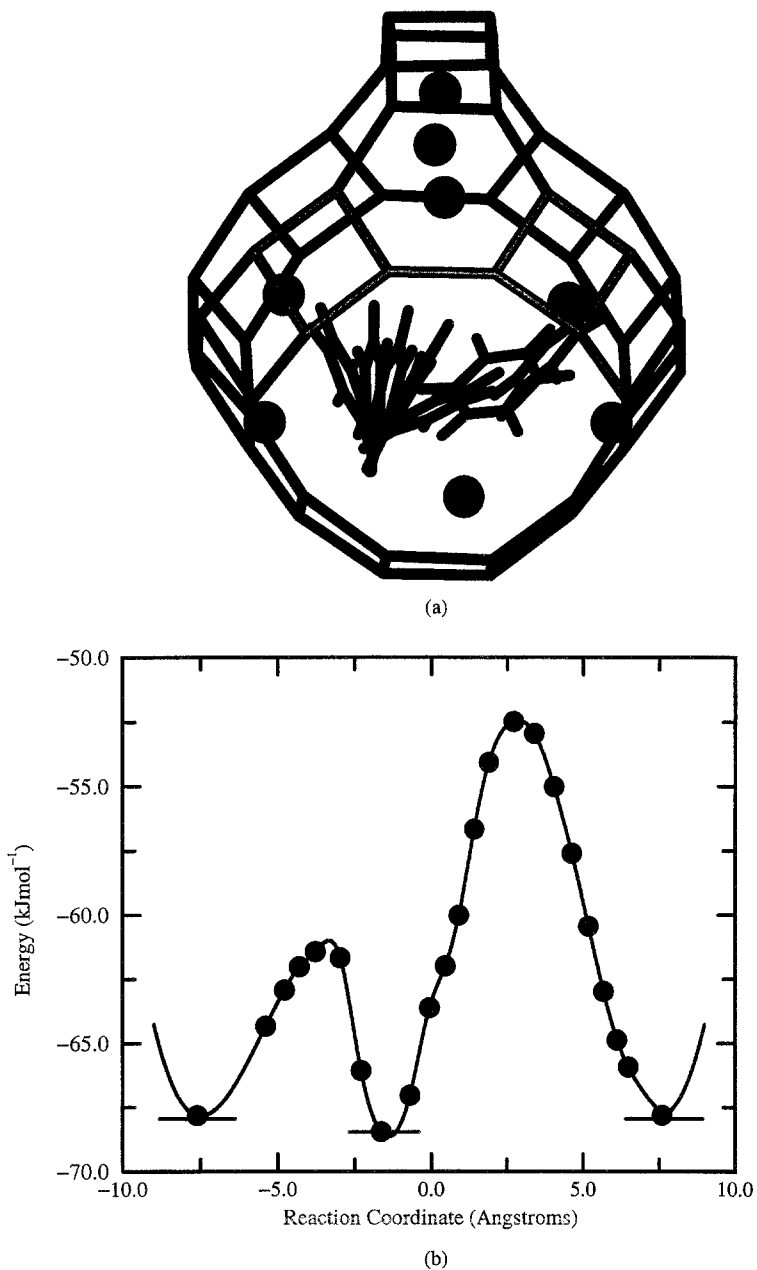
(b)

**Figure 6.** Calculated hopping trajectories for benzene in Na-Y: (a) SII  $\rightarrow$  SII site and (b) energetics.



**Figure 7.** Calculated hopping trajectories for benzene in Na-Y: (a) SII  $\rightarrow$  window site and (b) energetics.





**Figure 8.** Calculated hopping trajectory for benzene in Na-X: (a) SII → SII site and (b) energetics.

sites of interest, the SII cation site and the window site, we can propose three possible hopping processes: SII site  $\rightarrow$  SII site, SII site  $\rightarrow$  window site, and window site  $\rightarrow$  window site. As the energy difference between the window and SII sites is significant, we can neglect the window to window process since the molecule will spend little time at the window site.

Firstly, we can construct the potential energy profile for a jump between two SII sites by performing a series of energy minimizations along a line joining two SII cations, as detailed in the last section. The results of such a calculation are shown in Figure 6. The activation barrier for this process is 34.0 kJmol<sup>-1</sup>; the transition state is above the four rings joining the two 6-rings with the benzene plane lying at roughly 90 degrees to the 4-rings. A similar analysis for the SII site to window hopping process is shown in Figure 7. The energy barrier for this process is 40.2 kJmol<sup>-1</sup>, slightly higher than the SII  $\rightarrow$  SII hop. This hopping process is also essential for long range diffusion to occur, since it is the only fundamental hopping process that allows a benzene molecule to move between supercages. The activation energy for this process is in reasonable agreement with the NMR measurement with possible deviations being caused by the forcefield fit being performed at absolute zero rather than at the temperature of the NMR experiment. The transition state lies close to the window site, in close analogy with Hammond's postulate in reaction dynamics. We also considered the Na-LSX model to estimate the effect that SIIIi cations have on the SII  $\rightarrow$  SII hopping process, to rationalize the enhancement in diffusivity that is observed experimentally. The results of this calculation are shown in Figure 8. It can be seen that the presence of the SIIIi cation provides an additional strong binding site on the hopping pathway between adjacent SII cations. This acts as a "stepping-stone" which lowers the activation energy for hopping between adjacent SII sites. Work is currently in progress to fully investigate this effect by probing the SII  $\rightarrow$  window hopping process in Na-X and the possible enhancement of the hopping rate due to lattice relaxation at the SIIIi site.

#### 4. Conclusions

Modeling the behavior of aromatic molecules absorbed in zeolitic cavities represents a daunting challenge. For example, the development of a guest-host forcefield that is both transferable and reasonably accurate might appear to be out-of-reach. However, the results presented above would argue that this problem is not intractable, but that, with sufficient attention to detail, it is possible to predict the geometrical placement, the binding energies, and the dynamics of absorbed molecules, even in systems that require a treatment of cation-benzene interactions. Further work is still required, especially in relation to refinement of the forcefield, where we are still using formal charges for the cations, and long time-scale molecular motion, where a more rigorous evaluation of the pre-exponential terms is needed. Other exciting challenges include the development of a forcefield to describe the interactions in the groundstate between sorbates and acid sites.

This will begin to impact our understanding of catalysis at the atomic level, and will lead, in the future, to detailed quantum mechanical treatments of reactivity.

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**Abstract.** This review examines the computational tools that are available for modeling the behavior of absorbed molecules in microporous hosts such as the aluminosilicate zeolites. The role of quantum mechanical methods is briefly discussed, followed by a more detailed examination of approaches that utilize forcefields for both the zeolite host, itself, and the host-guest interactions. These approaches include molecular dynamics and Monte Carlo simulations. Several examples are presented, focusing on the behavior of benzene absorbed in zeolites belonging to the faujasite family. The development of an appropriate forcefield is described, and the utilization of this forcefield to study the structure, energetics, and dynamics of benzene in siliceous faujasite, Na-Y and sodium Na-X is explored. The results are compared with the available experimental data.