

MOLECULAR DYNAMICS SIMULATIONS FOR Xe ABSORBED IN ZEOLITES

J.-H. KANTOLA, J. VAARA, T. T. RANTALA* and J. JOKISAARI

Dept. of Physical Sciences, University of Oulu, Oulu, Finland, *Tapio.Rantala@oulu.fi

ABSTRACT

We have carried out molecular dynamics simulations for Xe atoms absorbed in two different zeolites, NaA and AlPO-11. The main emphasis is in the distribution of Xe in the zeolites, Xe-Xe_n interactions in NaA, and structural data on Xe-zeolite cage interactions. We report single-particle and pair correlation data, along with diffusion constants of Xe at 300 K. NMR chemical shifts of Xe were estimated using *ab initio* parametrization.

INTRODUCTION

Noble gas atoms probe the local properties of their environment by showing a response in their NMR parameters [1,2]. ¹²⁹Xe (spin- $\frac{1}{2}$) has become the most popular nucleus, mainly due to the sensitivity of its chemical shift, δ_{Xe} , to the surroundings. δ_{Xe} is a sum of contributions from dynamical collisions and interactions with local electromagnetic fields, which cause deformations in the outer electronic shells.

Molecular dynamics (MD) simulations based on atomic level interactions can give a detailed picture of the mechanisms behind spectroscopic observables. The experimental temperature and loading dependencies of δ_{Xe} [3] were reproduced quantitatively in recent grand canonical Monte Carlo (MC) simulations of Xe in NaA [4], although the zeolite lattice was kept rigid. We have chosen that as a reference to our present MD work where, in addition to reproducing some of the MC and experimental data, we are able to see the effects of zeolite lattice dynamics and to directly evaluate quantities such as the Xe diffusion constant D_{Xe} . MD also provides statistical information on the Xe adsorption sites for *ab initio* work [5]. After testing our method against known data, we are able to study new zeolites like AlPO-11 and SAPO-11, which are also examined experimentally in our laboratory.

SIMULATIONS

The crystal structure of dehydrated zeolite A has been measured from a single crystal by x-ray diffraction [6]. The unit cell is cubic with the lattice constant of 24.56 Å and formula (Na₁₂Al₁₂Si₁₂O₄₈)₈. It consists of eight larger roughly spherical α -cages of a size about 12 Å with connecting necks. One of these is shown in Fig. 1 (a).

The 12 Na in an α -cage occupy three different sites. Eight Na(1) are near the center of 6-rings, three Na(2) in the plane of 8-rings and one Na(3) on a 4-ring. Experimentally only ca. 90 of the ideal 96 Na ions are contained in the unit cell of the dehydrated lattice.

We also consider AlPO₄-11, which forms 1-dimensional elliptical channels of stacked 10-rings of -Al-O-P-O- chains with the ideal formula (AlPO₄)₂₀ [7]. Fig. 1 (b) shows the body centered orthorhombic unit cell with the sides $a \times b \times c = 13.53 \times 18.48 \times 8.37$ Å³.

Models and potentials

The simulations were performed in the canonical (constant NVT) ensemble using the Nosé-Hoover MD algorithm [8] in conjunction with the Verlet stepping routine at $T = 300$ K.

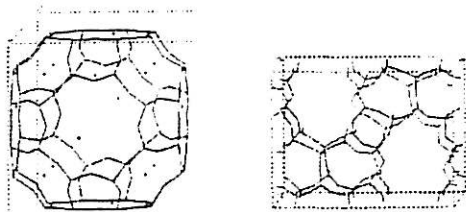


Fig. 1. (a) One α -cage of dehydrated zeolite NaA. (b) Unit cell of zeolite $\text{AlPO}_4\text{-11}$.

We chose the commercial simulation software Cerius² [9], which was run on SGI Indy and Power Onyx platforms for model building, simulations and analysis.

The systems considered were (I) a Xe atom and (II) eight Xe atoms distributed in the unit cell of NaA, and (III) a Xe atom in the unit cell of $\text{AlPO}_4\text{-11}$. The simulations (I) and (III) were aimed at investigating Xe distribution, adsorption sites and diffusion at low Xe-loading conditions. A lengthy enough MD simulation of type (II) should allow the cage occupancy statistics to reach the equilibrium distribution. This might require excessively long trajectories and in (II), we chose to distribute the number of Xe-atoms at different cages as 0, 0, 0, 1, 1, 1, 2 and 3 roughly according to the distribution obtained in ref. 4.

In all simulations the potentials were chosen to be very close to those in ref. 4 to preserve comparability. The software limits the functional forms of the interaction potentials, and fitting to the available forms was done. For the Xe-Xe potential, the exp-6 form

$$V_{\text{Xe-Xe}}(r) = D_0 \left[\frac{6}{\gamma-6} e^{\gamma(1-\frac{r}{r_0})} - \frac{\gamma}{\gamma-6} \left(\frac{r_0}{r} \right)^6 \right] \quad (1)$$

was fitted to the Maitland-Smith Xe-Xe potential [4] by weighting with the Boltzmann distribution at 300 K. The fit was very good around the potential minimum, r_0 , and deviates most (1.4×10^{-22} J) at about 6 ± 1 Å. The effective Xe-zeolite interaction [4] was described with Lennard-Jones (LJ) potentials

$$V_{\text{Xe-Na/O}}(r) = D_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right]. \quad (2)$$

The potentials and corresponding parameters for Xe-Xe and Xe-cage interactions are listed in Table I. The potential functions for interactions between the atoms in zeolite lattice were found from built-in libraries of Cerius², where we adopted the burchart1.01 [10] and UNIVERSAL1.01 [11] force fields. The former was used among the elements O, Al, Si and P of the cage, and the latter one was applied to interactions involving Na.

The charges of the exchange cations Na were assigned according to Kiselev [12], where the number of close oxygen atoms is the key factor. As the Na(2) at the 8-rings connecting adjacent α -cages are off-center, the coordination numbers for Na(1), Na(2) and Na(3) are six, three and four, respectively. The charges +1 and $+\frac{1}{2}$ were given for six- and three-coordinated cations, and $+\frac{2}{3}$ was interpolated for the four-coordinated ones. Neutrality of the unit cell was balanced by a slight collective adjustment of the charges -0.2 of all oxygen atoms. During the simulations some cations escape from their initial sites leading to a somewhat obscure situation with the coexistence of differently charged free Na ions.

Periodic boundary conditions were applied and both electrostatic and dispersion forces were calculated with the Ewald lattice summation method [13]. Neighbor lists for non-bonded interactions were used to reduce the simulation effort; the time interval between their updates was 100 fs in calculations (I) and (III), but was reduced to 25 fs in (II).

Table I. Interaction potentials and parameters for Xe used in the simulations.

pair	potential type	parameter	value	unit
Xe-Xe	exp-6	D_0	3.893×10^{-21}	J
		r_0	4.3563	Å
		γ	14.7304	-
Xe-O	LJ	D_0	2.996×10^{-21}	J
		r_0	3.7826	Å
Xe-Na	LJ	D_0	5.396×10^{-22}	J
		r_0	4.1262	Å

The chosen intrazeolite potentials were tested by performing energy minimizations of the two zeolites at different unit cell dimensions. Minimum energy configurations were reached with distortions smaller than 0.3% and 5% from the experimental unit cells (which were used during the actual simulations) in the cases of NaA and AlPO-11, respectively.

The time step Δt was calibrated by monitoring the total energy conservation of microcanonical test simulations. $\Delta t = 1$ fs was short enough to prevent any drift in E_{tot} over 2 ps for both zeolites. The coupling time τ_T between the studied system and the thermal bath of the actual canonical simulation was found by requiring the fluctuation pattern of the kinetic energy to match qualitatively with that observed in the microcanonical ensemble. This resulted in $\tau_T = 100$ and 30 fs for NaA and AlPO-11, respectively.

Analysis

Single-particle (SDF) and pair distribution (PDF) functions were calculated from the trajectories, the former for both Xe and Na, and the latter for the pairs Xe-O and Xe-Na. Diffusion constants were computed based on the RMS distances traversed by the atoms.

Following ref. 4, the NMR chemical shifts of Xe_n , i.e., n Xe atoms in an α -cage, were assumed to be pairwise additive with contributions from interactions with Na ions, Xe and O. As with the potentials, the last one can be taken as an effective shielding from the lattice. The chemical shift was calculated from the binary shielding curves $\sigma_{\text{Xe}}(r_{\text{Xe}-a})$ as $\delta_{\text{Xe}} = \sum_i (\sigma_{\text{ref}} - \sigma_{\text{Xe}}(r_{\text{Xe}-a_i}))$ where σ_{ref} corresponds to a free Xe atom, and i runs over all atoms of element a . The Xe-O shielding curve was obtained from *ab initio* calculations on the Xe-OH₂ system [14], the Xe-Na curve is from ref. 15, and Xe-Xe data from ref. 5.

RESULTS

MD requires more computer time than MC to sufficiently probe the available phase space. The present trajectories (I), (II) and (III) are 105, 80 and 149 ps, respectively, of which the first 40, 20 and 40 ps were used for thermalization and the remaining part for analysis. Quantitative conclusions will have to await for a forthcoming article [16], but some general properties and trends can already be seen from these trajectories.

Zeolite NaA

Xe atoms reside near the inner wall of the α -cage, as expected due to attractive Xe-wall interactions. The Xe SDF maxima, depicted in Fig. 2 (a), are on the average located about 4 Å from the centers of the O atoms that define the effective potential. The SDF of Na ions in Fig. 2 (b) shows that Na(1) sites remain mostly occupied, while the cations originally at Na(2) are more mobile.

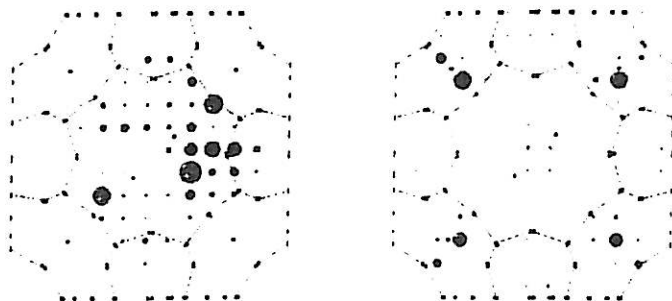


Fig. 2. Single-particle distribution (plane projection) of (a) Xe atoms and (b) Na ions in the α -cage of zeolite NaA. The relative size of the spheres here and in Fig. 4 encode the popularity of a given intracage $1 \text{ \AA}^3$ volume element in the trajectory.

It can be seen from the Xe SDFs calculated for clusters Xe_2 and particularly Xe_3 (not shown in the figures) that the adsorbant atoms are forced to sample the interior of the α -cage more evenly as the cage becomes crowded with more Xe atoms. This effect would obviously become more pronounced if clusters with $n > 3$ would be considered.

The calculated diffusion constants are shown in Table II. Intercage transport was not observed in the present simulations. Xe must approach at precisely right angles to the plane of the 8-ring to pass through. In addition, the Na ions may be blocking the path at some occasions. Comparison of D_{Xe} with (e.g., NMR) experiments is difficult because the experimental results contain also an interparticle contribution. However, the entries in Table II describe well the intracage mobility trend of Xe in NaA: the site-to-site diffusion is slower (ca. 40% for Xe_3) at higher loadings than for Xe that occupies its α -cage alone. The difference between Xe simulation (I) and the cluster Xe_1 of (II) may be in part due to the higher frequency of updates of the neighbor list in the latter.

Table II. Diffusion constants D_{Xe} (m^2/s) in the zeolites NaA and AlPO-11. Separate entries are given for NaA at different Xe loadings per α -cage. $D_{\text{Xe},\parallel}$ denotes diffusion along the channel in AlPO-11.

simulation	cluster	isotropic D_{Xe}	$D_{\text{Xe},\parallel}$
(I) 1 Xe@NaA	Xe_1	3.7×10^{-9}	
(II) 8 Xe@NaA	Xe_1	6.5×10^{-9}	
	Xe_2	5.9×10^{-9}	
	Xe_3	4.3×10^{-9}	
(III) 1 Xe@AlPO-11		6.2×10^{-9}	1.8×10^{-8}

Fig. 3 displays the Xe-O and Xe-Na PDFs for Xe_1 in simulation (II). The insets of the figure show how the PDFs change in the Xe_2 and Xe_3 clusters. There is depletion of the onset region to the left of the first peak of the Xe-O PDF, and accumulation at slightly higher interatomic distances. For the Xe-Na PDF the dominant feature is the increase of the first peak at the expense of depletion further out. The attractive Xe-Xe interaction increases the Xe-wall distance slightly from Xe_1 to Xe_2 , but the situation would reverse if still larger n were considered.

Jameson *et al.* found a very good agreement between their MC Xe_1 chemical shift, 77.2 ppm [4], and the experimental 74.8 ppm [3]. Our present result is 136 ppm, where

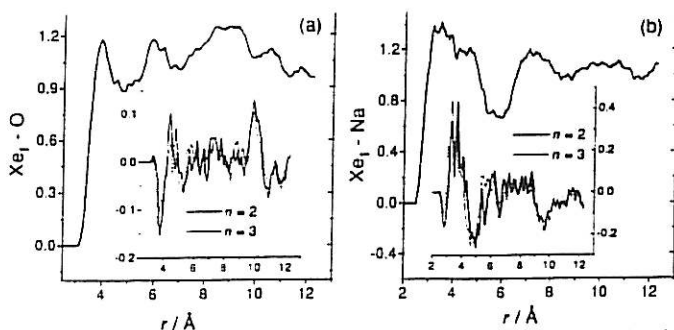


Fig. 3. Pair distribution between Xe_1 and (a) O atoms and (b) Na ions in the α -cage of zeolite NaA. The insets show the difference between Xe_n and Xe_1 for $n = 2, 3$.

60% comes from Xe-O and 40% from Xe-Na interactions. The value is very large, probably due to overestimating the Xe-Na contribution. The effective charge of the ions in a zeolite is lower than +1, for which the $\sigma_{\text{Xe}}(r_{\text{Xe-Na}})$ curve was calculated [15]. In addition, the Xe-Na potential may be too soft. Our results for the $n = 2, 3$ clusters show chemical shifts of 151 and 168 ppm, *i.e.*, the experimental shift increases induced by introducing additional Xe atoms to the α -cage, +17.5 and +19.4 ppm [3], are well reproduced by our respective +14.8 and +16.7 ppm. The intermolecular shielding functions $\sigma_{\text{Xe}}(r_{\text{Xe-O}})$ weigh the low separation limit of the PDFs. There is a decrease in the Xe-O contribution and an increase in the Xe-Na contribution to δ_{Xe} when Xe_3 is compared to Xe_1 , paralleling exactly the corresponding changes in the Xe-O and Xe-Na PDFs.

Zeolite AlPO-11

The motion of Xe in this zeolite is different from that in NaA; while the latter consists of large cages connected to form a three-dimensional network, there is freedom for adsorbants only in the direction of the channels in AlPO-11. D_{Xe} in AlPO-11 is given in Table II. The motion along a channel is at least three times faster than the intracage diffusion in NaA.

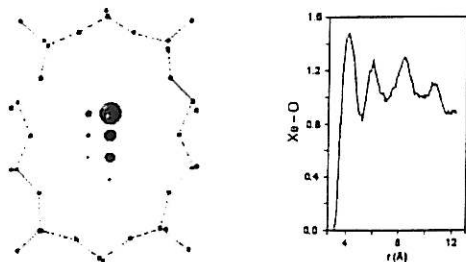


Fig. 4. (a) Single-particle distribution of Xe atoms and (b) Xe-O pair distribution function in the unit cell of zeolite AlPO-11.

Fig. 4 (a) shows the Xe SDF in a view along the channel of AlPO-11. The distribution is confined to a relatively small, asymmetrically shaped region along the long half-axis of the elliptical cross section. A view from a perpendicular direction (not shown) reveals that the channel consists of cells separated by successive 10-rings. Xe atom mainly resides in the cells from which it occasionally jumps to an adjacent free cell. The Xe-O PDF, Fig. 4 (b), shows a well-defined pattern reflecting the periodicity of the 10-ring network.

The calculated chemical shift in AlPO-11 is 150 ppm, which consists solely from Xe-O interactions. This value is in fair agreement with the experimental values [17] that range roughly from 120 to 140 ppm in the low loading limit.

Finally, to examine the validity of the effective Xe-O potential, local density (LDA) calculations were performed for the Xe atom in the plane of an AlPO-11 cluster consisting of a 10-ring with terminating hydrogens. It was found that the effective potential is a good approximation. Both the *ab initio* results and Eq. (2) predict a 2 Å wide, flat potential in the direction of the longer half-axis of the elliptical channel.

CONCLUSIONS

For NaA our results agree qualitatively with those of ref. 4: Xe atoms prefer contact with the cage walls and their mobility from one cage to another is low at 300 K. It is difficult to directly compare our parametrization of the chemical shift with that of the earlier work [4]. However, the loading trend of δ_{Xe} is well reproduced here and even the changes in the contributions of the cage walls are seen to be reflected in the structural data. In AlPO-11 the Xe atoms are mainly located in the cells between 10-rings, but move rapidly from one cell to another. The experimental δ_{Xe} is reproduced semi-quantitatively. The parametrization of the intrazeolite Xe chemical shift surface in terms of pair interaction contributions will be investigated later in a fuller account of the present simulations [16].

ACKNOWLEDGMENTS

We thank the Academy of Finland for financial support, Mr. M. Ylihautila for discussions, Dr. C.I. Ratcliffe for supplying the unit cell of AlPO-11 and Dr. L. Laaksonen for assistance with software. J.V. thanks also the Jenny and Antti Wihuri and Vilho, Yrjö and Kalle Väisälä Funds for grants. Computational resources were supplied by CSC, Espoo, Finland.

REFERENCES

1. P.J. Barrie and J.K. Klinowski, *Progr. NMR Spectr.* **24**, 91 (1992).
2. J. Jokisaari, *Progr. NMR Spectr.* **26**, 1 (1994).
3. C.J. Jameson *et al.*, *J. Chem. Phys.* **96**, 1676 (1992).
4. C.J. Jameson *et al.*, *J. Chem. Phys.* **100**, 5965 (1994); **100**, 5977 (1994).
5. J. Vaara, T. T. Rantala, J.-H. Kantola and J. Jokisaari, *to be published*.
6. J.J. Pluth and J.V. Smith, *J. Am. Chem. Soc.* **102**, 4704 (1980).
7. J.M. Bennet, J.W. Richardson, Jr, J.J. Pluth and J.V. Smith, *Zeolites* **7**, 160 (1987).
8. S. Nosé, *J. Chem. Phys.* **81**, 511 (1984); W.H. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
9. Cerius², Molecular Simulations Inc., Burlington, MA, (1994).
10. E. de Vos Burchart, Ph.D. Thesis, Technische Universiteit Delft (1992).
11. A.K. Rappé *et al.*, *J. Am. Chem. Soc.* **114**, 10024 (1992).
12. A.V. Kiselev and P.Q. Du, *J. Chem. Soc. Faraday Trans. 2* **77**, 1 (1981); A.G. Bezus, A.V. Kiselev, A.A. Lopatkin and P.Q. Du, *ibid.* **74**, 367 (1978).
13. N. Karasawa and W.A. Goddard III, *J. Phys. Chem.* **93**, 7320 (1989).
14. J. Lounila, J. Vaara, R. Seydoux, J. Jokisaari and P. Diehl, *to be published*.
15. A. Freitag, Ch. van Wüllen and V. Staemmler, *Chem. Phys.* **192**, 267 (1995).
16. J.-H. Kantola, J. Vaara, T.T. Rantala and J. Jokisaari, *to be published*.
17. J.A. Ripmeester and C.I. Ratcliffe, *J. Phys. Chem.* **99**, 619 (1995).