

This article was downloaded by:

On: 14 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713644482>

Cation distribution in faujasite-type zeolites: A test of semi-empirical force fields for Na cations

S  verine Buttefey^a; Anne Boutin^a; Alain H. Fuchs^a

^a Laboratoire de Chimie Physique, UMR 8000 CNRS, Universit   Paris-Sud, Orsay, France

Online publication date: 26 October 2010

To cite this Article Buttefey, S  verine , Boutin, Anne and Fuchs, Alain H.(2002) 'Cation distribution in faujasite-type zeolites: A test of semi-empirical force fields for Na cations', *Molecular Simulation*, 28: 12, 1049 – 1062

To link to this Article: DOI: 10.1080/0892702021000011070

URL: <http://dx.doi.org/10.1080/0892702021000011070>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

CATION DISTRIBUTION IN FAUJASITE-TYPE ZEOLITES: A TEST OF SEMI-EMPIRICAL FORCE FIELDS FOR NA CATIONS

SÉVERINE BUTTEFEY, ANNE BOUTIN and ALAIN H. FUCHS*

Laboratoire de Chimie Physique, UMR 8000 CNRS, Université Paris-Sud, 91405 Orsay, France

(Received April 2001; In final form May 2001)

(N,V,T) Monte Carlo (MC) simulations have been performed in order to test three available force fields for sodium cations in faujasite-type zeolites. A rigid framework faujasite model, using an average T atom scheme and the cation force field proposed by [Jaramillo, E. and Auerbach, S.M. *J. Phys. Chem.* **103** (1999) 9589] was found to reproduce quite well the experimentally observed cation location in NaY and could thus be used in future works for predicting cation distributions and possible cation migration upon adsorption in faujasites.

Keywords: Faujasite; Force fields; Cations; Zeolites

INTRODUCTION

Understanding the factors that control separation properties in zeolites requires a detailed knowledge of the structure of the host materials. In aluminosilicate zeolites the presence of aluminum atoms introduces charge defects, which are compensated with some non-framework cations (sodium, potassium, barium, etc.). Zeolites are characterized by the fact that the number of crystallographic cation sites observed in the structure usually exceeds the number of cations needed to ensure electroneutrality of the material. The need exists for a method that could predict the way the extraframework cations are distributed among the

*Corresponding author.

available sites, since this is known to play a crucial role on the adsorption and transport behavior of guest species in the host framework. Migration of cations into the aluminosilicate framework is also suspected to occur upon adsorption of water and other highly polar molecules. To perform computer simulations one needs a reliable, yet simple, potential for the cation-framework interaction. We have tested here three available force fields for sodium in faujasite-type zeolites, using (NVT) Monte Carlo (MC) simulations. One of these models was found to reproduce quite well the experimentally observed-cation location and could thus be used in future work for predicting cation distribution and mobility data in faujasites.

A substantial number of experimental [1], theoretical [2–5] and computational [6–10] studies have examined the cation distribution in the industrially important faujasite-type zeolites. NaX and NaY are distinguished by their Si:Al ratio [$\text{Si} : \text{Al}(\text{X}) < 1.5$, $\text{Si} : \text{Al}(\text{Y}) > 1.5$]. Cations can occupy different types of sites in faujasite (Fig. 1). Sites I are located in the hexagonal prism, which connects sodalite cages. Sites I' are inside the sodalite cage facing site I. Sites II are in front of the 6-rings inside the supercage. Sites III are also in the supercage, near the 4-rings of the sodalite cage. Site I has a multiplicity of 16 per unit cell, sites I' and II have a multiplicity of 32 and site III of 64 per unit cell. Some cations have also been found (in the case of NaX) in the 12-ring window [9,11]. These are called sites III'. Sites III and III' are believed to be of higher potential energy than sites I, I' and II. At low occupancy ($\text{Si} : \text{Al} \geq 2$) cations are known to occupy sites I, I' and II only.

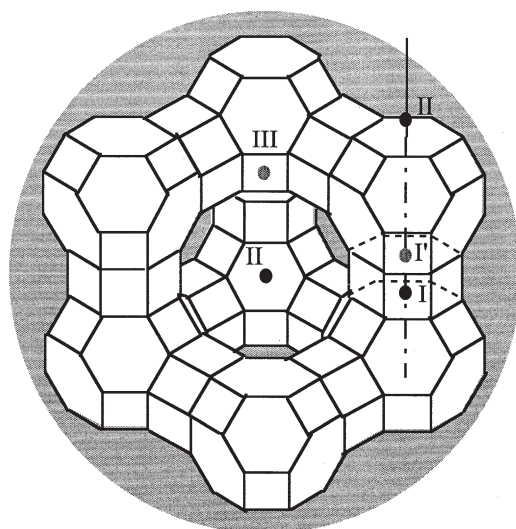


FIGURE 1 Schematic view of a faujasite supercage.

TABLE I Cation distributions observed in NaY (experiments in bold, simulations in italic)

<i>Si/Al ratio</i>	<i>Cation number/unit cell</i>	<i>Experiments/Simulation</i>				<i>Reference</i>
		<i>I</i>	<i>I'</i>	<i>II</i>	<i>Other site</i>	
2.7	52	9.3	13.7	25.3	3.5	[17]
2.55	54	7.04	13.76	29.44	3.76	[22]
2.5	55	4.0	17.6	32.0	1.4	[14]
2.4	56	7	17	25	7	[10]
2.35	57	8.0	18.88	30.08	0.04	[13]
2.3	58	7.1	18.6	32.2	–	[15]

Even in prototypical systems such as dehydrated NaX [9,11,12] or NaY [13–17] the precise location of some of the cations remains uncertain (see Table I), even though diffraction methods have greatly improved in the past few years. This is particularly true for cations occupying low-symmetry sites with low occupancy factors. The variety of cation positions reported in the literature for the same systems might also arise from genuine differences among the samples [9] (inhomogeneous aluminum distribution in an overall identical nominal composition, small amount of residual water molecules in the sample). Although theory and computer simulations have helped in corroborating the experimental findings, a general understanding of cation occupancy in faujasite, taking into account the nature of the cation and the Si:Al ratio, is still lacking.

The remainder of the paper is organized as follows. In “Computational methodology section” we discuss the computational methodology and describe the cation force field models that we have tested in this work. In “Results and discussion section” we present the results of the MC simulations for NaY (having an Si:Al ratio of 3), and the comparison with available experiments. Concluding remarks are given in “Conclusion section”.

COMPUTATIONAL METHODOLOGY

We have used a simple structural model in which the framework atoms are fixed and only the cations are allowed to move. Several MC simulations with a fixed number of cations have been performed. Long enough MC runs enable, in principle, to perform a proper averaging of the different instantaneous cation arrangements; thus allowing a direct comparison between the simulation averaged quantity and the corresponding experimental observable. In aluminosilicate zeolites however the thermodynamic averaging problem is getting somewhat more complicated because of the existence of two tetrahedrally

coordinated atoms (T atom: Si or Al) in the framework. In all but the Si : Al = 1 case, aluminum atoms will be asymmetrically arranged in the simulation box (one unit cell in our case). The use of periodic boundary conditions leads to a replication of this arrangement in all three directions of space. This is unphysical, since in a real crystal the asymmetry would be averaged over space. Thus, in order to compute a reliable quantity in thermodynamic limit, one would also have to perform an average over a large number of different aluminum atom arrangements in the simulation cell. This double averaging (over cation and aluminum atom arrangements) is a tedious task. A way to overcome this problem is to consider a unique average T atom in the simulations. This has been done quite often in previous studies of adsorption in zeolites [18–20], and we have used this assumption again here. By doing this we are aware that our model will miss some of the details of the cation-framework interaction.

Faujasite Model

The framework structure of dehydrated faujasite was taken from the experimental neutron diffraction studies of Fitch *et al.* [15]. The crystalline structure is described in the $Fd3m$ space group and the cubic lattice parameter is 24.8536 Å. The structural parameters of the model are given in Table II. One unit cell of faujasite was used as the simulation box, with periodic boundary conditions in all three directions. Most of the simulations were performed with Si : Al = 3, the corresponding number of sodium cations per unit cell being 48 (this we call the Na₄₈Ysystem). Some simulations have also been carried out in a Na₅₆Ymodel (Si : Al = 2.4). Partial charges on the oxygen and T atoms have been taken from the work of Mortier and coworkers [21], using the electronegativity equalization method. We assigned $q_{\text{Na}} = +1$.

TABLE II Framework structure of dehydrated faujasite obtained by neutron diffraction experiments[15]

Atom	Position	x/a	y/a	z/a
Si/Al	192i	−0.0543	0.0354	0.1247
O(1)	96h	0	−0.1061	0.1061
O(2)	96h	−0.0021	−0.0021	0.1418
O(3)	96h	−0.1764	0.1764	−0.0335
O(4)	96h	0.1786	0.1786	0.3182
Na(II)	32e	0.2345	0.2345	0.2345
Na(I')	32e	0.0507	0.0507	0.0507
Na(I)	16c	0	0	0

Cation Force Fields

The total potential energy U of the system is calculated as a sum of a cation-framework (CF) term and a cation–cation (CC) term:

$$U = U_{\text{CF}} + U_{\text{CC}} \quad (1)$$

Three different force fields have been proposed in the literature. Jaramillo and Auerbach (JA) [10] have used the following form for U_{CF} :

$$U_{\text{CF}}^{\text{JA}} = \sum_{\text{C}, \text{F}=\text{O}} \left[a_{\text{CO}} \exp(-b_{\text{CO}} r_{\text{CO}}) - \left(\frac{c_{\text{CO}}}{r_{\text{CO}}} \right)^6 \right] + \sum_{\text{C}, \text{F} \in \text{T}, \text{O}} \frac{q_{\text{C}} q_{\text{F}}}{r_{\text{CF}}} \quad (2)$$

in which an exp-6 repulsion–dispersion term acts between the cations (C) and the oxygen (O) atoms of the framework, and a coulombic term acts between the cations and all the framework atoms. The cation-T atom repulsion–dispersion interaction is not taken into account here. The JA sodium–oxygen a , b and c parameter values are given in Table III. In the JA potential, the cation–cation energy U_{CC} contains a coulombic term only:

$$U_{\text{CC}}^{\text{JA}} = \sum_{\text{C}, \text{C}'} \frac{q_{\text{C}} q_{\text{C}'}}{r_{\text{CC}'}} \quad (3)$$

Henson *et al.* [23] and Bandyopadhyay and Yashonath (BY) [24] have proposed a Lennard–Jones form to model the repulsion–dispersion terms in U_{CF}

$$U_{\text{CF}}^{\text{Henson, MS}} = \sum_{\text{C}, \text{F}=\text{O}} -4\epsilon_{\text{CO}} \left(\frac{\sigma_{\text{CO}}^6}{r_{\text{CO}}^6} - \frac{\sigma_{\text{CO}}^{12}}{r_{\text{CO}}^{12}} \right) + \sum_{\text{C}, \text{F} \in \text{T}, \text{O}} \frac{q_{\text{C}} q_{\text{F}}}{r_{\text{CF}}} \quad (4)$$

TABLE III Parameter values for the JA [10], Henson *et al.* [23] and BY [24] cation force field models

Model of potential	Potential	Parameters
JA[10]	$a_{\text{ij}} \exp(-b_{\text{ij}} r_{\text{ij}}) - \frac{c_{\text{ij}}^6}{r_{\text{ij}}^6}$	$a_{\text{ONa}} = 61 \times 10^6 \text{ K}$, $b_{\text{ONa}} = 4.05 \text{ \AA}^{-1}$, $c_{\text{ONa}} = 76.52 \text{ K}^{-6} \text{ \AA}^6$
Henson <i>et al.</i> [23]	$-4\epsilon_{\text{ij}} \left(\frac{\sigma_{\text{ij}}^6}{r^6} - \frac{\sigma_{\text{ij}}^{12}}{r^{12}} \right)$	$\sigma_{\text{NaNa}} = 1.29 \text{ \AA}$, $\sigma_{\text{ONa}} = 1.78 \text{ \AA}$, $\epsilon_{\text{NaNa}} = 8186.5 \text{ K}$, $\epsilon_{\text{ONa}} = 1949.3 \text{ K}$
BY [24]	$-4\epsilon_{\text{ij}} \left(\frac{\sigma_{\text{ij}}^6}{r^6} - \frac{\sigma_{\text{ij}}^{12}}{r^{12}} \right)$	$\sigma_{\text{NaNa}} = 3.26 \text{ \AA}$, $\sigma_{\text{ONa}} = 3.025 \text{ \AA}$, $\epsilon_{\text{NaNa}} = 10.7 \text{ K}$, $\epsilon_{\text{ONa}} = 47.6 \text{ K}$

In both Henson and BY force fields U_{CC} contains coulombic as well as Lennard–Jones terms

$$U_{CC}^{\text{Henson,BY}} = \sum_{C,C'} -4\epsilon_{CC'} \left(\frac{\sigma_{CC'}^6}{r_{CC'}^6} - \frac{\sigma_{CC'}^{12}}{r_{CC'}^{12}} \right) + \sum_{C,C'} \frac{q_C q_{C'}}{r_{CC'}} \quad (5)$$

The Henson and BY σ and ϵ parameter values for the sodium–oxygen and sodium–sodium interactions are given in Table III.

The repulsion–dispersion part of the sodium–oxygen interaction is sketched in Fig. 2 for each force field model. The Henson *et al.*'s force field is characterized by a deep potential minimum and a small cation radius. The BY potential displays a very shallow minimum and a large cation radius. The JA potential lies in between the Henson and the BY cases.

In all cases, Ewald sums were used to calculate the long range coulombic terms. The Ewald parameter α was equal to 0.19\AA^{-1} and the \mathbf{k} vectors were such that $\mathbf{k} \in [-3, 3]$.

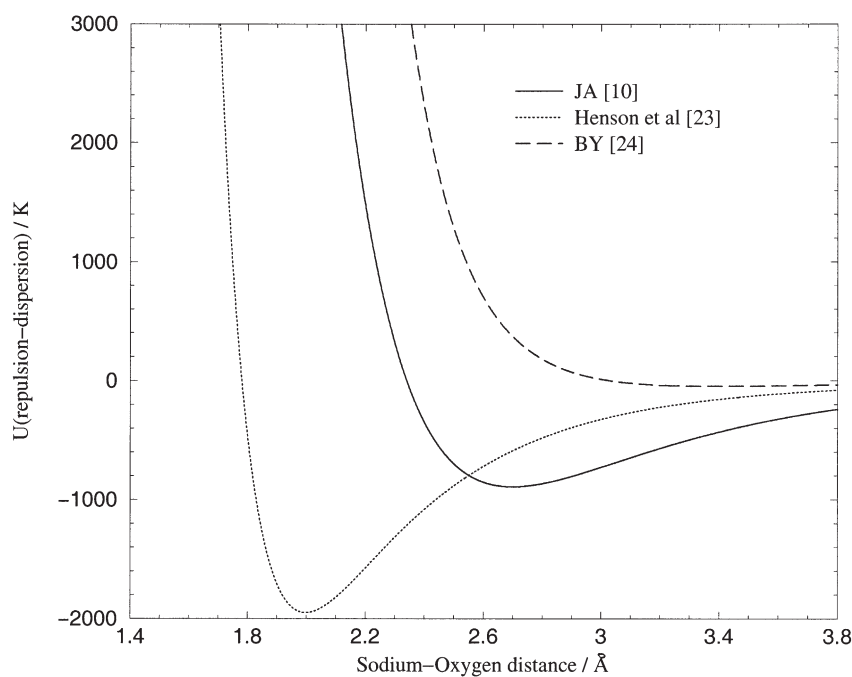


FIGURE 2 Repulsion–dispersion part of the sodium–oxygen interaction for the JA [10], Henson *et al.* [23] and BY [24] force field models.

Monte Carlo Simulations

Several NVT simulations were performed ($T = 298$ K, or otherwise mentioned). Random translational displacement of cations were adjusted so to obtain an acceptance rate of $\sim 50\%$ (maximum displacement of 0.3 \AA). Equilibrium was typically reached after 10^5 moves. A further 10^6 production steps were performed to average quantities.

Metastable cation distributions have been obtained in the simulations. Depending on the initial configuration, standard NVT simulation at $T = 298$ K will or will not converge spontaneously, in a finite MC run, to the most stable configuration. This kind of problem is often encountered in the simulation of particles with strong ($\gg kT$) interaction energy. This is why a standard MC simulated annealing procedure was used to search for the global minimum, starting from configurations at high temperature (1500 K) and progressively cooling down the system to 298 K. Each cation distribution annealing consisted of at least 100 independent energy minimization.

RESULTS AND DISCUSSION

The distance distributions between the cation locations observed in the simulations of Na_{48}Y , using the JA force field, and the known crystallographic sites I, I' and II are shown in Fig. 3A. In the most stable distribution, a full occupancy of sites I (16 cations) and II (32 cations) was found. As seen in Figs. 3Aa and 3Ac, the observed average locations in the simulation closely correspond to the experimental crystallographic sites I and II [15]. Cations were found not to occupy sites I' in this system (the peak observed in Fig. 3Ab corresponds to the cations in site I). In the Na_{56}Y system, a partial occupancy of sites I and I' was found (Fig. 3B). As seen in Fig. 3Bc, the average cation location found in the simulation agrees rather well with the crystallographic site I'. We report in Table IV several computed interatomic average distances. Computed and experimental data are in fair agreement, although the JA potential slightly underestimates the sodium–oxygen distances. It should be pointed out that the potential used here is not strictly equivalent to JA's since we are using an average T-atom while JA have distinguished Si and Al atoms in their molecular dynamics simulation [10]. Thus the partial charges borne by the framework atoms are slightly different from one work to the other. We will show, in the second part of this work, that the initial and modified JA forcefields yield much the same results for cation location in NaY [28].

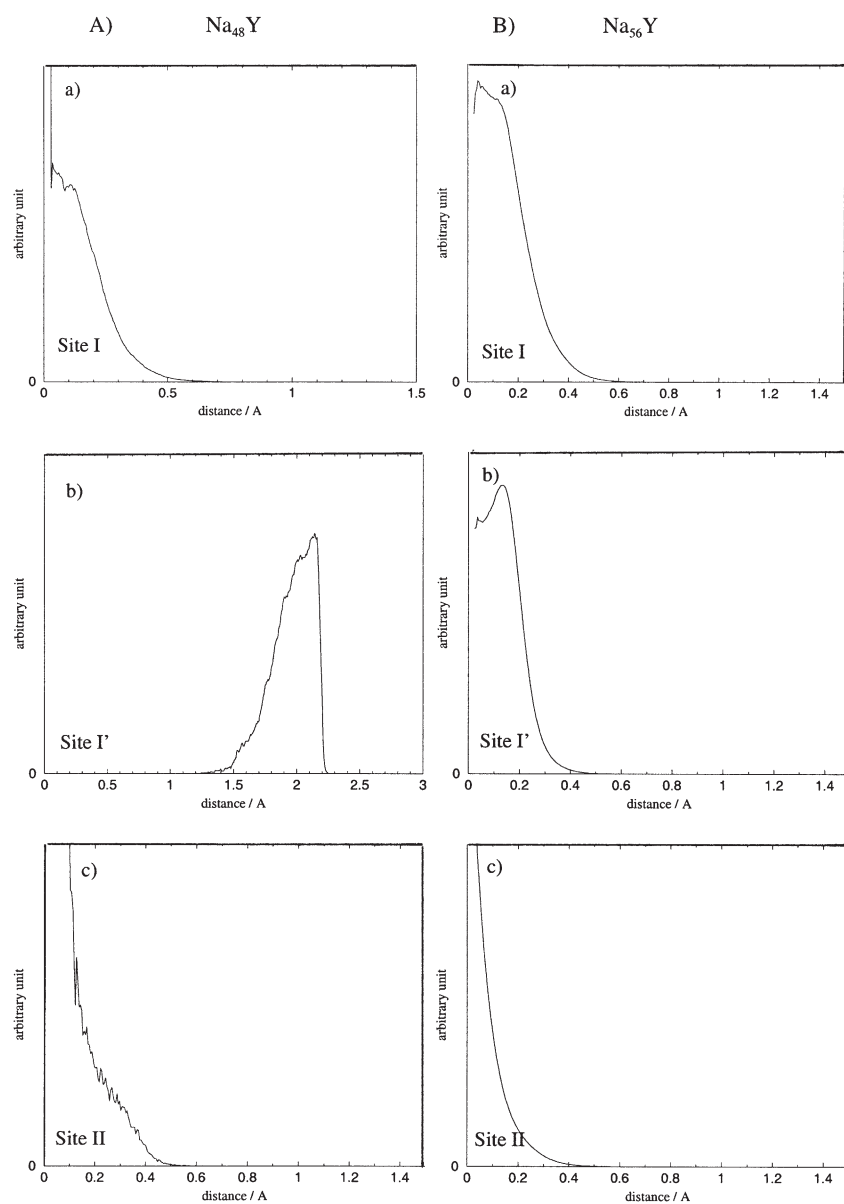


FIGURE 3 Computed distance distributions between the observed cation locations and the known crystallographic sites I, I' and II in Na_{48}X (A) and Na_{56}X (B) using the JA [10] cation force field.

The distance distributions in the Na_{48}Y model using Henson *et al.*'s cation force field are shown in Fig. 4. Sixteen cations occupy a site which is located in between site I and site I' in the sodalite cage (1.5 Å away from site I and 0.7 Å away from site I'). 32 cations are found in a site which is 0.2 Å away from the crystallographic site II. The agreement between computed and experimental interatomic distances (Table IV) is also less satisfactory than in the case of the JA potential.

Simulating the Na_{48}Y model system using the BY cation potential is rather more complicated since the energy barrier separating the sites I and I' is insurmountable in a finite MC time scale. This is due to the unphysical size of the sodium cation used in the BY potential. Thus, two types of distance distributions (shown in Fig. 5A and 5B) are found, depending on the initial cation distribution. The most stable configuration corresponds to the distributions shown in Fig. 5A. This distribution is very similar to the one described above in the case of the JA force field. The situation in which the cations in sites I' are unable to escape from the sodalite cage through an hexagonal ring corresponds to the distribution shown in Fig. 5B. Two pseudo-I' sites are found in this latter case. Many other metastable distributions can be found in which the cations are partially occupying sites I and pseudo sites I'.

CONCLUSION

From the results presented above we conclude that a simple, rigid framework faujasite model, using an average T atom scheme and the cation force field proposed by Jaramillo and Auerbach [10] enables to reproduce quite well the experimentally observed cation locations in NaY.

The Henson *et al.*'s cation force field yields to less satisfactory results and the BY force field suffers from an unphysical sodium cation size. It is interesting to

TABLE IV Interatomic distances obtained in this work as compared to experimental and to other simulation results

Distance (Å)	This work			Simulation [10]	Experiments				
	JA	Henson	BY		[13]	[15]	[25]	[26]	[27]
Na(I)–O	2.4	–	2.6	2.11–2.29	2.71	2.71	2.71	2.71	2.3
Na(I')–O	2.2	2.0	2.3	2.07–2.27	2.44	2.24	2.32	2.25	
Na(II)–O	2.3	2.1	2.5	2.15–2.36	2.33	2.39	2.34	2.39	
Na(I')–Na(I)	2.2	–	2.6	1.73–1.84	2.61	2.18		2.42	1.58
Na(I')–Na(II)	4.6	4.1	4.5	4.21–4.63	4.48				

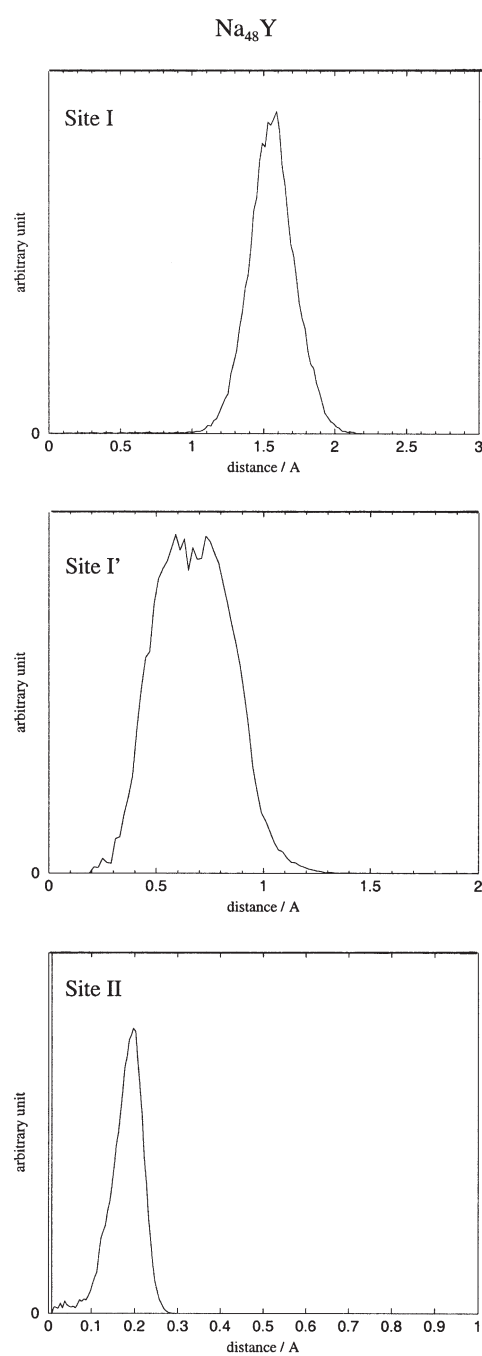
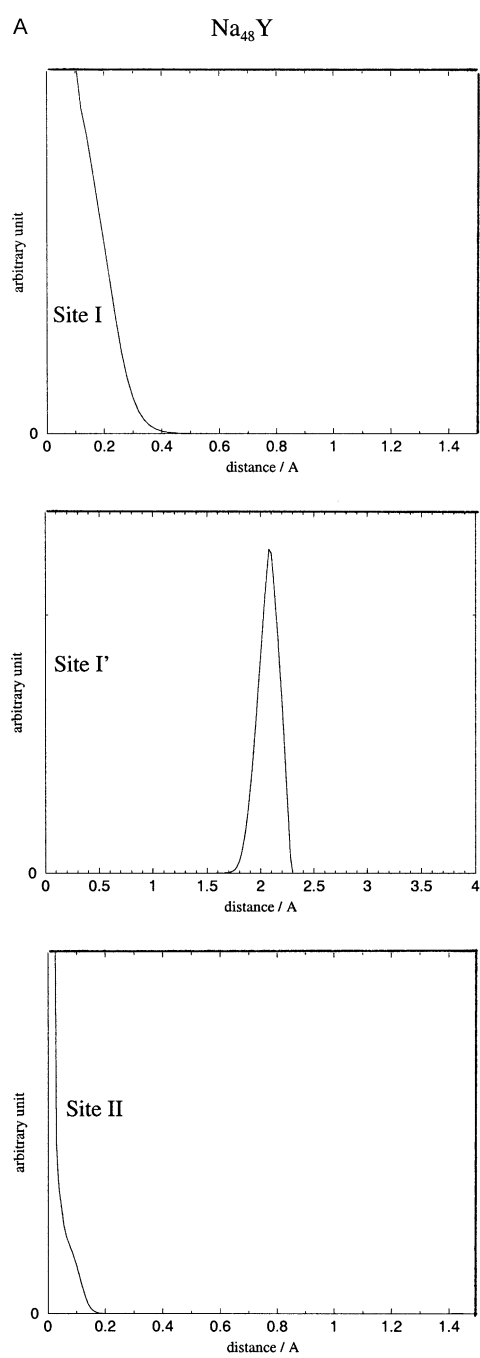


FIGURE 4 Computed distance distributions between the observed cation locations and the known crystallographic sites I, I' and II in Na_{48}X using Henson *et al.*'s cation force field [23].



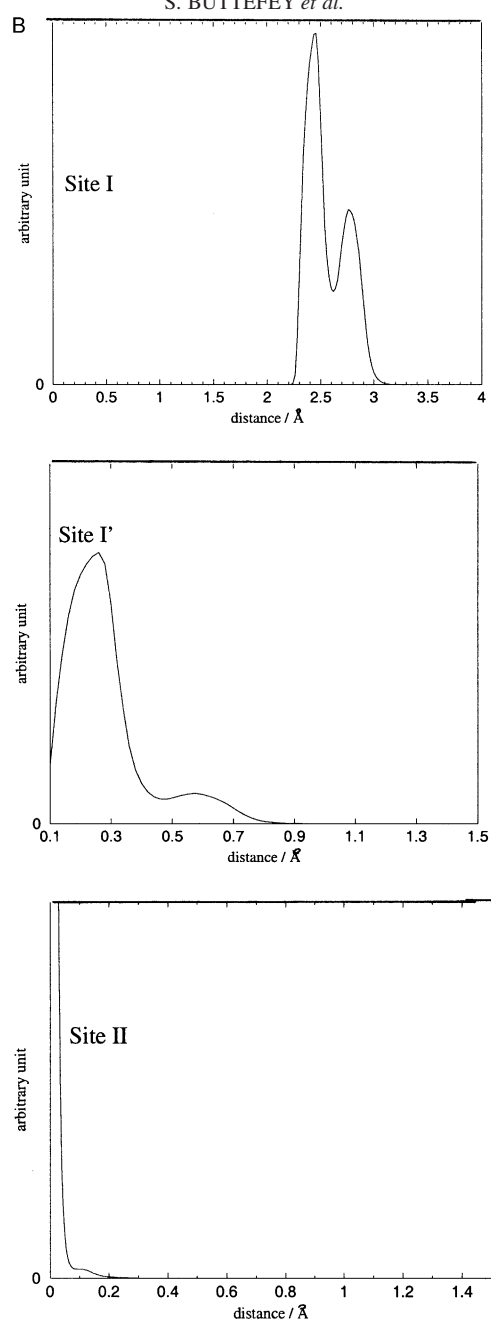


FIGURE 5 Computed distance distributions between the observed cation locations and the known crystallographic sites I, I' and II in Na_{48}X using the BY cation force field [24]. (A) Distributions obtained when starting from cations placed in sites I and II. (B) Distributions obtained when starting from cations placed in sites I' and II.

point out, however, that interatomic distances are fairly well reproduced in all cases (Table IV), although the repulsion–dispersion part of the Na–O interaction is strikingly different from one potential to the other (Fig. 2). This is presumably due to the fact that the cation distribution and location is dominated by the coulombic interactions.

In the second part of this work [28] Monte Carlo simulation of cation distributions have been performed in NaY and NaX, using the zeolite model described above together with the JA cation force field. The aim is to be able to predict cation distributions in dehydrated NaY and NaX whatever the Si:Al ratio is.

Acknowledgements

Caroline Mellot and Tony Cheetham are gratefully acknowledged for fruitful discussions. We wish to thank the Institut Français du Pétrole for financial support through a BDI/CNRS grant for S.B. and for a generous allocation of computer time.

References

- [1] Mortier, W.J. (1982) *Compilation of Extra-Framework sites in Zeolites* (Butterworth, Guildford, UK).
- [2] Dempsey, E. (1969) "Variation of the lattice parameter with aluminium content in synthetic sodium faujasites. Evidence for ordering of the framework", *J. Phys Chem.* **73**, 3660.
- [3] Sanders, M.J., Catlow, C.R.A. and Smith, J.V. (1984) "Crystal energy calculation for strontium ions in zeolite A", *J. Phys Chem.* **88**, 2796.
- [4] Barrer, R.M. (1984) "Cation partitioning among sub-lattices in zeolites", *Zeolites* **4**, 361.
- [5] Smolders, E., Van Dun, J.J. and Mortier, W.J. (1991) "A statistical thermodynamical description of the cation distribution and ion exchange in zeolites", *J. Phys Chem.* **95**, 9908.
- [6] Newsam, J.M., Freeman, C.M., Gorman, A.M. and Vessal, B. (1996) "Simulating non-framework cation location in aluminosilicate zeolites", *Chem. Commun.* **16**, 1945.
- [7] Gorman, A.M., Freeman, C.M., Kolmel, C.M. and Newsam, J.M. (1997) "Accelerated approach to non-framework cation placement in crystalline materials", *Faraday Discuss* **106**, 489.
- [8] Herrero, C.P. and Ramirez, R. (1992) "Energetics of cation ordering in the faujasite framework: MC simulation", *J. Phys Chem.* **96**, 2246.
- [9] Vitale, G., Mellot, C.F., Bull, L.M. and Cheetham, A.K. (1997) "Neutron diffraction and computational study of zeolite NaX: influence of Si^{IV} cations on its complex with benzene", *J. Phys Chem.* **101**, 4559.
- [10] Jaramillo, E. and Auerbach, S.M. (1999) "New force field for Na cations in faujasite-type zeolites", *J. Phys Chem.* **103**, 9589.
- [11] Olson, D.H. (1995) "The crystal structure of dehydrated NaX", *Zeolites* **15**, 439.
- [12] Zhu, L. and Seff, K.J. (1999) "Reinvestigation of the crystal structure of dehydrated sodium zeolite X", *J. Phys Chem. B.* **103**, 9512.
- [13] Eulenberger, G.R., Shoemaker, D.P. and Keil, J.G. (1967) "The crystal structure of hydrated and dehydrated synthetic zeolites with faujasite aluminosilicate framework", *J. Chem. Soc.* **71**, 1812.
- [14] Jirák, Z., Vratislav, S. and Bosáček, V. (1980) "A neutron diffraction study of Na-Y zeolites", *J. Phys. Chem. Solids* **41**, 1089.

- [15] Fitch, A.N., Jobic, H. and Renouprez, A. (1986) "Localization of benzene in sodium-Y zeolite by powder neutron diffraction", *J. Phys Chem.* **90**, 1311.
- [16] Van Dun, J.J., Dhaze, K. and Mortier, W.J. (1988) "Temperature-Dependent cation distribution in zeolites. 2. dehydrated Na_xHY ($x = 13, 23, 42, 54$), Ca₁₅HX and Sr₂₇Y", *J. Phys Chem.* **92**, 6747.
- [17] Marra, G.L., Fitch, A.N., Zecchina, A., Ricchiardi, G., Salalaggio, M., Bordera, S. and Lamberti, C. (1997) "Cation location in dehydrated Na-Rb-Y Zeolite: an XRD and IR study", *J. Phys Chem. B.* **101**, 10653.
- [18] Mellot, C.F., Davidson, A.M., Eckert, J. and Cheetham, A.K. (1998) "Absorption of chloroform in NaY zeolites: a computational and vibrational spectroscopy study", *J. Phys Chem. B* **102**, 2530.
- [19] Demontis, P., Yashonath, S. and Klein, M.L. (1989) "Localization and mobility of benzene in sodium-Y zeolite by MD calculations", *J. Phys Chem.* **93**, 5016.
- [20] Lachet, V., Butterfey, S., Boutin, A. and Fuchs, A.H. (2001) "Molecular simulation of adsorption equilibria of xylene isomers mixtures in faujasite zeolites. A study of the cation exchange effect on adsorption selectivity", *PCCP* **3**, 80.
- [21] Uytterhoeven, L., Dompas, D. and Mortier, W.J. (1992) "Theoretical investigations of the interaction of benzene with faujasite", *J. Chem. Soc. Farad. Trans.* **88**, 2753.
- [22] Van Dun, J.J. and Mortier, W.J. (1988) "Temperature-dependent cation distribution in zeolites.1. A statistical thermodynamical model", *J. Phys Chem.* **92**, 6740.
- [23] Henson, N.J., Cheetham, A.K., Redondo, A., Levine, S.M. and Newsam, J.M. (1994) "Computer simulations of benzene in faujasite-type zeolites", *Stud. Surf. Sci. Catal.* **84**, 2059.
- [24] Bandyopadhyay, S. and Yashonath, S. (1997) "Conformational analysis of *n*-butane in zeolite NaCaA: temperature and concentration dependence", *J. Phys Chem. B* **101**, 5675.
- [25] Grey, C.P., Poshni, F.I., Gualtieri, A.F., Norby, P., Hanson, J.C. and Corbin, D.R. (1997) "Combined MAS NMR and X-ray powder diffraction structural characterization of hydrofluorocarbon-134 absorbed on zeolite NaY: observation of cation migration and strong sorbate-cation interactions", *J. Am. Chem. Soc.* **119**, 1981.
- [26] Lievens, J.L., Mortier, W.J. and Verduijn, J.P. (1992) "Influence of the framework composition on the cation-site energy: the structures of dehydrated Na_xHgaY ($x = 54, 36$, and 21) zeolites", *J. Phys Chem.* **96**, 5473.
- [27] Engelhardt, G. (1997) "Cation location in dehydrated zeolite NaY revisited: SI position is displaced from the center of the hexagonal prism", *Microporous Mater.* **12**, 369.
- [28] Buttefey, S., Boutin, A. and Fuchs, A.H. (2001) "A simple model for predicting cation distribution in NaY and NaX zeolites", *J. Phys Chem.*, in press.