

^{129}Xe adsorbed in $\text{AlPO}_4\text{-11}$ molecular sieve: Molecular dynamics simulation of adsorbate dynamics and NMR chemical shift

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Molecular dynamics simulation of ^{129}Xe adsorbed in the $\text{AlPO}_4\text{-11}$ molecular sieve has been carried out in the constant NVT ensemble at $T = 300$ K. The host material was modeled as a fully dynamic framework. Single-particle and pair distribution functions of the adsorbed gas in the unidirectional channels of the material with different adsorbate loadings are presented. Self-diffusion coefficients, D_{Xe} , have been calculated for the dynamics of the adsorbates between the adsorption cells in $\text{AlPO}_4\text{-11}$. The dynamic framework is shown to decrease the effective potential barrier for intercellular jumps. An estimate is given for the jump frequency. The NMR chemical shifts of ^{129}Xe were evaluated using parametrizations based on first principles calculations of Xe-Xe and Xe-OH_2 model systems. No adjustable parameters were used to improve agreement with experimental results. The results of a phenomenological three-site dynamic averaging model proposed earlier by others were reproduced with a good accuracy using chemical shift parameters from gradient corrected density-functional theory. Finally, the approximations inherent to the present computational approach are discussed. © 1997 American Institute of Physics.
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I. INTRODUCTION

Microporous solids contain networks of interconnected channels and cavities of different shapes and sizes, and are thus capable of adsorbing guest atoms and molecules.¹ These materials are used in a variety of industrial applications such as molecular sieves, adsorbents, catalysts, and ion exchangers. Aluminophosphate molecular sieves consist of linked TO_4 tetrahedra, where aluminium and phosphorus alternate as T atoms.²

Noble gas atoms probe the local properties of their environment by showing a response in their nuclear magnetic resonance (NMR) parameters.³ ^{129}Xe (spin $\frac{1}{2}$) has become the most popular nucleus, mainly due to the sensitivity of the chemical shift, $\delta_{\text{Xe}} = \sigma_{\text{ref}} - \sigma_{\text{Xe}}$, of the shielding constant σ to the properties of the surroundings.⁴⁻⁶ The shift referenced to the free Xe atom is a sum of the medium-induced contributions from dynamical collisions and interactions with local electromagnetic fields, which cause deformations in the outer electronic shells. The application of ^{129}Xe NMR in the study of microporous solids, pioneered by Fraissard and Ito⁷ and Ripmeester,⁸ has lately been reviewed by Barrie and Klinowski.⁹

The pore space of the $\text{AlPO}_4\text{-11}$ molecular sieve consists of unidirectional, elliptically shaped channels. The basic structural units are stacked rings with ten oxygen and ten T atoms in each.¹⁰ These rings are rotated by 180° around the channel axis from one layer to the next. Two adjacent 10-rings enclose an adsorption cell of the size that allows the accommodation of only one Xe atom at a time. The ^{129}Xe chemical shift as a function of the adsorbate loading in

$\text{AlPO}_4\text{-11}$ has been measured by Springuel-Huet and Fraissard¹¹ and Ripmeester and Ratcliffe.¹² In these measurements a strong, loading-dependent anisotropy of the shielding tensor was found. The loading dependence has been interpreted by using a three-site dynamic averaging model.¹² The Xe exchange rate between the sites, i.e., cells with different occupation of the neighboring cells, is assumed to be fast at room temperature.

Detailed atomic level information of the structural and dynamic properties of adsorbates confined in microporous solids is available from computer simulations.¹³ Many simulations have been performed for different adsorbates in the variants of zeolite A (see Refs. 14 and 15 and references therein). On the contrary, we are not aware of any simulation studies of $\text{AlPO}_4\text{-11}$. Usually a rigid zeolite framework¹⁶ has been used, which very effectively reduces the simulation time necessary to obtain adequate sampling of the phase space available to the system.

Jameson *et al.*¹⁴ found a very good agreement of δ_{Xe} in the NaA zeolite between their experiments and grand canonical Monte Carlo simulations. In the latter the medium-induced δ_{Xe} was calculated using a parametrization based on pairwise additive shift contributions from interactions between the probe Xe atom and the other atoms in the system. The intermolecular binary chemical shift functions, $\delta_{\text{Xe}}^a(r) = \sigma_{\text{Xe}}(\infty) - \sigma_{\text{Xe}}(r_{\text{Xe}-a})$, i.e., the probe shift caused by another atom or molecule a at the distance r , were obtained from *ab initio* calculations^{17,18} for the Ar atom in the presence of either another Ar atom, sodium ion, or water molecule (with the direction of approach of the rare gas toward the oxygen atom in OH_2). The curves were scaled for the larger Xe atom based on the Drude model for intermolecular shielding effects¹⁹ and the observed empirical scaling trends

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of chemical shifts across the periodic table.¹⁷

Despite that pairwise additivity is known not to hold in high density media,^{4,5,20} it has often been applied for chemical shifts of adsorbed rare gas atoms in microporous solids^{14,17,21,22} and liquids.²³ This is justified, e.g., by the comparison of *ab initio* nuclear shielding calculations for the Ar_2 and Ar_3 systems¹⁷ and the results of the three-site model for δ_{Xe} in $\text{AlPO}_4\text{-11}$.¹²

The effect of the rigid framework approximation on the simulation results is still a partially open question. There is an increasing amount of evidence indicating that the framework dynamics is a significant factor in determining the adsorption properties.^{15,16,24–26} The effects of the dynamic cage on the NMR chemical shift of an adsorbate is, likewise, expected to be sizable, in particular for such tightly confined systems as Xe in $\text{AlPO}_4\text{-11}$.

We have performed a molecular dynamics²⁷ (MD) simulation of Xe atoms in the $\text{AlPO}_4\text{-11}$ molecular sieve. Different adsorbate loadings were studied by investigating channels with differing filling ratio. We employ a fully dynamic cage: The dynamics of the framework atoms and adsorbates are treated on an equal footing. The structures were simulated in the canonical ensemble (constant NVT) at $T=300$ K. We report data both on the structural and dynamical properties of the adsorbates. The single-particle distribution and pair distribution functions, self-diffusion coefficients (D_{Xe}) and cell-to-cell jump rates, along with the potential barrier for the cell-to-cell jump are examined.

The host-guest and guest-guest interactions are sensitively reflected by δ_{Xe} , which has been calculated here with no adjustable parameters, following the procedure of Jameson *et al.*¹⁴ To produce the binary shift curves, we carried out first principles electronic structure calculations for the ^{129}Xe chemical shift in Xe–Xe and Xe–OH₂ systems. By calculating the shifts directly for the target atoms (Xe) we avoid the need for the empirical scaling procedure,^{17,18} and consequently are able to test it. Parametrizations resulting from the Hartree–Fock (HF) and two exchange-correlation functionals of the density-functional theory (DFT)²⁸ are compared.

II. SIMULATION MODEL

The $(\text{AlPO}_4)_{20}$ unit cell is body-centered orthorhombic (space group $Icmm$) with $a=13.5348$ Å, $b=18.4807$ Å, and $c=8.3721$ Å. The simulation model consists of four $(2 \times 1 \times 2)$ unit cells and periodic boundary conditions. The primary simulation box contains four channels and four adsorption cells per channel. It is illustrated in Fig. 1. Initial atomic coordinates were obtained from Bennett *et al.*¹⁰ The adsorbate loading was chosen to be 0, 1, 2, and 3 Xe per channel, to simulate low, medium, and high loading situations. We adopt the notation $n\text{Xe}/\circ$, $n=0, 1, 2$, and 3 corresponding to the channel filling ratios of 0, 1/4, 1/2, and 3/4, respectively. For $3\text{Xe}/\circ$, only one cell in the channel direction is free at a given instant. The Xe atoms are not able to pass each other in the channels. The centers of the channels are 11–12 Å apart, a distance at which the guest-guest interaction is negligible.

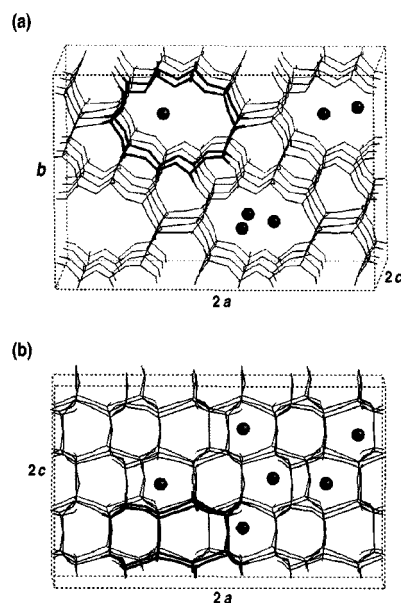


FIG. 1. The four unit cell simulation model of $\text{AlPO}_4\text{-11}$. (a) A view almost along the direction of the channel, and (b) perpendicular to the channel. One of the adsorption cells is emphasized with thick bonds. The depicted adsorbates identify some of the potential energy minima inside the adsorption cells.

The parameters for the interatomic potential were obtained from two sources. The framework (Al/P)–O parameter are due to Burchart²⁹ as implemented in the Cerius² software.³⁰ Bond, torsion, inversion, Urey–Bradley, electrostatic, and van der Waals interaction terms are included.

It has been customary to use an effective potential between the guest and the oxygen atoms of the host material to represent the guest-host interaction.^{14–16} Forces from other adsorbates are calculated separately, however. The interactions were taken to be the same used by Jameson *et al.*¹⁴ Their fitted form of the Xe–Xe potential (originally due to Aziz and Slaman³¹) was further fitted using Boltzmannian weighting to the exponential-6 form

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

available in the software. In Eq. (1), D_0 and r_0 are the well depth and distance parameters of the interaction. The parameter γ is a scaling factor that makes the exp-6 form more flexible than the Lennard-Jones potential. We have confirmed that our fit describes very well the original potential.³¹ For the Xe–O interaction we used potentials of the Lennard-Jones 12-6 form

$$V(r) = D_0 \left\{ \left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right\}, \quad (2)$$

with parameters giving the same potential as that used by Jameson *et al.*¹⁴ The final potential parameters are listed in Table I.

We used the Ewald summation method²⁷ for electrostatic and dispersion interactions. The integration time step Δt was chosen by requiring conservation of the total energy in a

TABLE I. Potential parameters used in the simulation.

Interaction	Potential form	D_0 (10^{-21} J)	r_0 (Å)	γ
Xe–Xe	exp-6	3.893	4.3563	14.7304
Xe–O	LJ 12-6	2.995	3.7826	

microcanonical (*NVE*) reference trajectory. The Nosé–Hoover heat-bath³² variable (called relaxation time in the software) τ_T was chosen by comparing the temperature fluctuations of a *NVE* trajectory and several *NVT* trajectories with varying values for τ_T . Relaxation time is a parameter that controls the strength of the coupling between the system and the thermal bath. We chose the values $\Delta t = 1$ fs and $\tau_T = 30$ fs. The summed Verlet algorithm^{30,33,34} was used for numerical integration. The potential cutoff radius of 12.2 Å was utilized, and snapshots of the trajectory were saved in intervals of 25 fs. The trajectory was first thermalized for 100 ps, followed by 390 ps of production run.

The Cerius² simulation software by Molecular Simulations, Inc.,³⁰ was used. The program was run on SGI Power Challenge and Indy platforms.

III. ^{129}Xe NMR CHEMICAL SHIFT

The nuclear shielding of a probe atom in a medium with density ρ is often expressed as a virial expansion^{17,35}

$$\sigma(\rho, T) = \sigma_0 + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \dots \quad (3)$$

The assumption of pairwise additivity corresponds to neglecting terms after the one linear in the density.^{36,37} The parameter σ_0 is the shielding constant of the atom *in vacuo* and the term involving σ_1 , the second virial coefficient of shielding^{17,35}

$$\sigma_1(T) = -4\pi \int_0^\infty dr r^2 \delta(r) \exp[-V(r)/kT], \quad (4)$$

arises from pair interactions (with the potential V) between the probe and a species in its surroundings. The form of Eq. (4) assumes interaction between two atoms as it specifies the chemical shift surface in terms of r only. For molecules, in general, both the interaction potential and the binary shift function are functions of more than one variable. In a multi-component system the generalization of Eq. (3) is straightforward: There will be a term linear in ρ_a for each species a present, multiplied by the corresponding $\sigma_1^a(T)$.

Effective interaction from the oxygen lattice sites and other adsorbate atoms only is adopted here for the ^{129}Xe NMR chemical shift. The present first principles calculations³⁸ of $\delta_{\text{Xe}}^a(r_{\text{Xe}-a}) = \sigma_{\text{Xe}}(\infty) - \sigma_{\text{Xe}}(r_{\text{Xe}-a})$ ($a = \text{Xe}$ and OH_2) were performed using GAUSSIAN 94 software^{39,40} with GIAO (gauge-including atomic orbital)^{41–43} HF and GIAO DFT methods (the use of DFT was already suggested in Ref. 36). In the latter, both local density (SVWN⁴⁴) and the gradient corrected BPW91 functional (exchange by Becke⁴⁵ and correlation by Perdew and Wang⁴⁶) were uti-

lized. The total of 11–12 distance values were used at the relevant separation range for each pair. The data were least-squares fitted to the functional form

$$\delta(r) = A/r^{p(r)}, \quad (5)$$

$$p(r) = c_0 + c_1 r + c_2 r^2 + c_3 r^3 + c_4 r^4 + c_5 r^5.$$

No physical interpretation of this form is being implied; it is rather used as an accurate and stable means of reproducing the calculated data numerically.

The average chemical shift of the ^{129}Xe probe species was determined from the MD trajectory as

$$\delta_{\text{Xe}} = \sum_{a,i} \langle \delta_{\text{Xe}}^a(r_{\text{Xe}-a_i}) \rangle, \quad (6)$$

where the summation runs over all neighbors a_i of the probe: We use i as the index of the atom of element a . The angular brackets denote time and ensemble averaging. The binary chemical shift curves were cut and shifted²⁷ at the distance of 8.3 Å. The method of group averages was used for estimating the errors of the chemical shifts. The analyzed trajectory was divided into k groups of m data. The standard deviations of the k group averages yield the standard errors of mean (SEM) of the groups, from which the SEM of the whole analyzed data can be calculated. Several values for k were tested and the value $k = 20$ giving the largest error was selected.

In a preliminary report of the present work²² we used chemical shift curves calculated using SVWN to obtain the Xe–Xe and Xe–OH₂ interaction contributions in a shorter and slightly different MD simulation.⁴⁷

IV. RESULTS AND DISCUSSION

A. Structure

Single-particle distribution functions (SDF) were obtained for Xe in a three-dimensional grid cast over the simulation cell. SDFs give the probability of finding the target atom in the volume $(0.33 \text{ Å})^3$ enclosed by each of the grid cells. They can be used to identify the Xe adsorption maxima. Contour plots of the Xe SDFs projected to the plane of the channels with different loadings are shown in Fig. 2. The free opening of the channel is shown by the width of the contours. The contours clearly show that Xe spends its time in the adsorption cells between the connecting 10-ring necks. Contrary to the case of solids with larger cavities, where adsorbates prefer to remain in the vicinity of the channel walls and leave the center of the cavity empty, the small cells of $\text{AlPO}_4\text{-11}$ represent a situation where the Xe occupation is maximal at the center of the cell.^{21,48}

Pair distribution functions (PDF) were calculated for the pairs Xe–O and Xe–Xe. They are shown in Fig. 3 for channels with different loadings. The well-defined pattern of the Xe–O PDF reflects the periodicity of the 10-ring network. As expected, Xe loading does not have an effect on the overall shape of the pair distribution function. Each Xe occupies its own cell regardless of channel loading. The three maxima of the PDFs in Fig. 3, as well as the shoulder between the

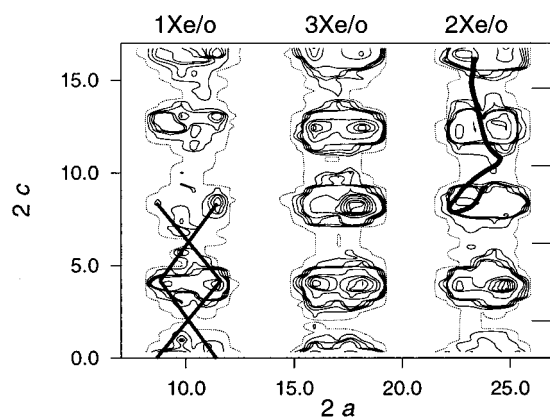


FIG. 2. Single particle distribution maps of ^{129}Xe in the channels of $\text{AlPO}_4\text{-11}$ at 300 K with different loadings, projected to the plane of the channels. The horizontal notches on the right denote the location of the 10-rings. Two zigzag paths between potential energy minima are visualized on top of the $1\text{Xe}/\text{o}$ distribution. An actual Xe trajectory during an intercellular jump in the $2\text{Xe}/\text{o}$ channel is also shown. The contour with the lowest density connects the grid cells that are visited once in the production trajectory, corresponding to the average density of $0.002 \text{ atoms}/\text{\AA}^3$. The next four lines correspond to $n \times 0.028 \text{ atoms}/\text{\AA}^3$, $n = 1, 2, 3$, and 4 , and the subsequent lines are $n \times 0.14 \text{ atoms}/\text{\AA}^3$, $n = 2, 3, \dots, 7$. Distances are measured in $\text{\AA}$.

second and the third one, can be attributed to oxygen atoms in different configurations with respect to a Xe atom lying in the potential energy minimum of an adsorption cell. The first PDF maximum is mainly due to the nearest oxygens in the two 10-rings forming the particular adsorption cell, whereas the rest of the oxygens in these rings (on the other side of the cell) contribute to separations between the first minimum and the second maximum. The atoms bridging the 10-rings that form the cell in question lie either at the area of the steepest ascent of the first maximum, and, across the cell, near the second minimum. The second maximum is caused by the bridge oxygens between adjacent channels, arranged diagonally and horizontally in Fig. 1. The main contribution to the shoulder comes from the next 10-ring layers along the channel. Finally, the third maximum is due to the oxygens in the 10-rings of the neighboring channel that is closest to the potential minimum in question, as well as ones that bridge to the next channel across the cell.

The Xe–Xe PDFs for the $2\text{Xe}/\text{o}$ and $3\text{Xe}/\text{o}$ channels appear very similar. However, the initial increase of the function towards its first maximum occurs slightly earlier in the more dense $3\text{Xe}/\text{o}$ channel. The beginning of the second maximum is, expectedly, more pronounced for $3\text{Xe}/\text{o}$ than $2\text{Xe}/\text{o}$.

B. Adsorbate dynamics

The motion of Xe between the adsorption cells can be characterized as jumps followed by longer periods of residence in the cell.¹² The activation energy, E_a , for the intercellular event, calculated as the potential experienced by the adsorbate, is ca. 1500 K estimated by keeping the framework atoms fixed in the experimental structure¹⁰ and moving the

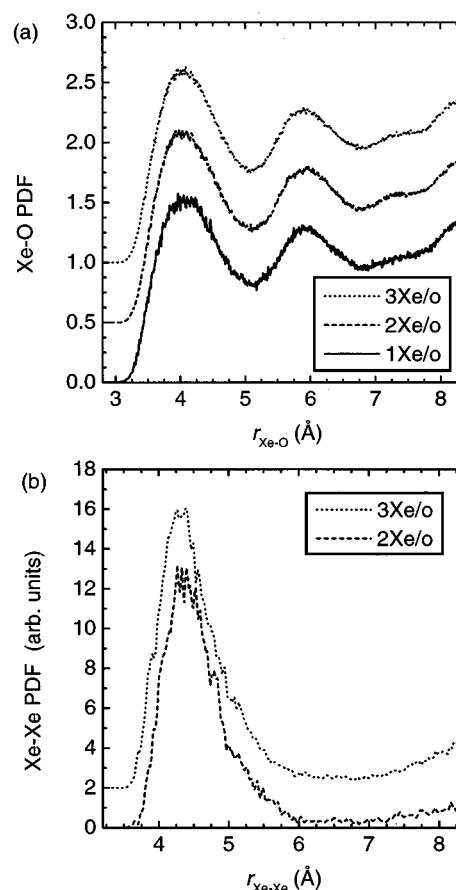


FIG. 3. (a) Xe–O and (b) Xe–Xe pair distribution functions in $\text{AlPO}_4\text{-11}$ at 300 K for Xe atoms occupying channels with different loadings, $n\text{Xe}/\text{o}$ ($n = 1, 2, 3$). The curves have been shifted vertically for clarity. Panel (b) in arbitrary units.

adsorbate along either of the two zigzag routes depicted in Fig. 2. For comparison, the energy barrier between the two potential minima within one adsorption cell is of the order of 500 K. The E_a estimated from the potential experienced by the Xe adsorbates in the actual simulation of the dynamic cage model is, taking an average over all occurrences in the trajectories, 490 K for the $1\text{Xe}/\text{o}$ loading, and ca. 620 K for $2\text{Xe}/\text{o}$ and $3\text{Xe}/\text{o}$ loadings. Thus a clear reduction in the barrier height appears to result from the use of the dynamical framework. The effective barrier increases with the channel filling ratio. An example of the Xe trajectory during an intercellular jump in the $2\text{Xe}/\text{o}$ channel is shown in Fig. 2.

The z-coordinates (along the channel) of the Xe atoms occupying the $2\text{Xe}/\text{o}$ channel are shown in Fig. 4 as functions of time.

The libration movement along the channel has a higher frequency as the Xe loading increases. A rough estimate for the frequency of cell-to-cell jumps can be obtained by counting the number of such events during the course of the trajectory. In our simulations, this frequency, ν_{jump} , is roughly 33 GHz for $1\text{Xe}/\text{o}$, 29 GHz for $2\text{Xe}/\text{o}$, and 13 GHz for $3\text{Xe}/\text{o}$, i.e., there is a decreasing trend as the Xe loading increases. There are only 3–13 jumps per atom per trajec-

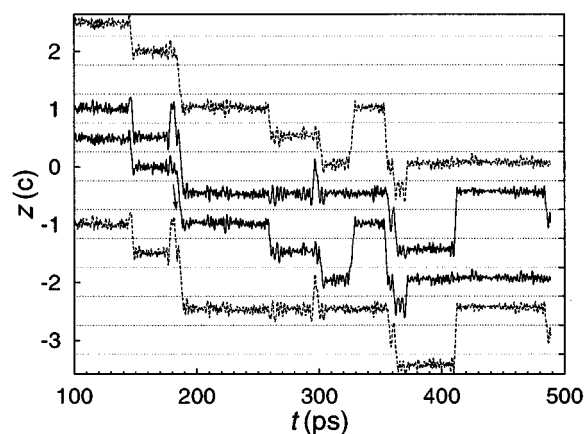


FIG. 4. The z -coordinates (along the channel in units of c) of the Xe adsorbates in the half-filled (two Xe atoms) channel of $\text{AlPO}_4\text{-11}$ as functions of time. The thinner curves represent the trajectories of the periodic images of the adsorbants. An arrow indicates the cell-to-cell jump illustrated in Fig. 2. The gridlines mark the approximate locations of the 10-rings.

tory, thus no reliable averages are available, however. In the case of $1\text{Xe}/\circ$, the duration of the intercellular jumps is 2.5–5 ps, whereas for channels with higher Xe loading the shortest duration decreases to 1.5 ps. The cell-to-cell transition rate is, of course, high compared to the intercrystallite exchange, the rate of which was eliminated by Ripmeester and Ratcliffe at 23 kHz.¹²

The frequency data above offer another, independent way to estimate E_a from the dynamics. The average libration frequencies ν_0 are approximately 410, 480, and 500–600 GHz for the loadings of $n\text{Xe}/\circ$, $n=1, 2$, and 3, respectively. With the observed cell-to-cell jump frequencies, the relation $\nu_{\text{jump}} = \nu_0 \exp(-E_a/T)$ at $T=300$ K yields the activation energies of 760, 840 and 1100 K for $n=1, 2$, and 3, respectively. These dynamical estimates are somewhat higher than those based on the channel structure, given above. In the $2\text{Xe}/\circ$ and $3\text{Xe}/\circ$ cases one likely reason for the lower structural estimates is the fact that jumps to occupied neighbor cells are hindered by the Xe–Xe interaction. Nevertheless, concerning the whole simulation we are able to conclude that the rigid host framework with its considerably higher E_a (by a factor 2–3) would definitely lead to qualitatively altered simulation data as compared with the present results.

The trajectories in Fig. 4 indicate that a cell-to-cell jump of one Xe may induce a jump of the neighboring Xe too, regardless of whether Xe moves toward the neighbor or away from it. By comparing similar plots of the $1\text{Xe}/\circ$ and $3\text{Xe}/\circ$ channels (not shown), it appears that this is true also for the neighboring channels: An intercellular event in one channel may induce a cell jump in the next channel, too. With the large distance between channel centers, it seems very unlikely that this phenomenon would be caused by direct interactions, i.e., the Xe–Xe potential. Hence, we presume that the vibrating lattice transfers indirect interactions between channels, and is most likely responsible for the observed effect. We have placed animations of the adsorbate dynamics and the effective potential barrier along the chan-

TABLE II. Simulated self-diffusion coefficients, $D_{\text{Xe}}(10^{-9} \text{ m}^2 \text{ s}^{-1})$, in the $\text{AlPO}_4\text{-11}$ molecular sieve at 300 K with different channel loadings.

Xe/ $\circ$	Channel filling ratio	D_{Xe}
1	$\frac{1}{4}$	6.5
2	$\frac{1}{2}$	2.6
3	$\frac{3}{4}$	0.9

nel direction for the $1\text{Xe}/\circ$ and $2\text{Xe}/\circ$ loadings available to a web page.⁴⁹

The self-diffusion coefficients, D_{Xe} , have been calculated from the mean square displacement (MSD) curve

$$2D_{\text{Xe}}t = \langle |z(t) - z(0)|^2 \rangle \quad (7)$$

appropriate for the unidimensional diffusion⁵⁰ of Xe in $\text{AlPO}_4\text{-11}$. The D_{Xe} along the channel direction for $n\text{Xe}/\circ$ ($n=1,2,3$) are listed in Table II. The D_{Xe} are obtained by fitting the slopes of the MSD curves for the time interval $t=5\text{--}20$ ps. They show expectedly a decreasing trend with loading.⁵¹ From purely structural considerations and also on the basis of our simulations, the Xe adsorbates are not likely to be able to pass each other, and the diffusion can be assumed to be of the single-file type.⁵⁰ The relative shortness of our trajectory (dictated by using the flexible framework model) precludes the identification of single-file behavior, however.⁵⁰ Single-file diffusion would require a modification of the left-hand side of Eq. (7) to $2F_{\text{Xe}}t^{1/2}$, where the factor F_{Xe} is termed the single-file mobility.

C. ^{129}Xe NMR chemical shift

The calculated parameters of the binary shift functions are available on request. The shift functions are illustrated in Fig. 5. Both the Xe–Xe and Xe–O curves [panels (a) and (b), respectively] display remarkably similar behavior among the different methods. The HF results are in both cases the lowest ones, while SVWN produces the largest shifts. The BPW91 results are located between the HF and local density ones. The empirically scaled curve for Xe–Xe by Jameson and de Dios¹⁷ resembles our HF results very much at the larger separations, while deviating slightly upwards only at the low end.

A further proof of the validity of the empirical scaling concept comes from the temperature dependence of σ_1^{Xe} [Eq. (3)], for which accurate experimental data is available.⁵ Figure 6 displays this dependence calculated using the Aziz-Slaman interatomic potential.³¹ Our fitted form of the Xe–Xe potential function results in numerical differences which would be unnoticeable in the scale of the figure—this displays the accuracy of our potential parameters. The scaled curve¹⁷ and our HF curve are almost exactly superimposed over the full temperature range. At the highest temperatures a slight deviation is noted, however. This reflects the deviation of the corresponding binary shielding curves at the low separation limit. These two curves are in excellent agreement with the experiment from about 275 K up, while at low temperatures DFT, particularly the BPW91 functional, is more

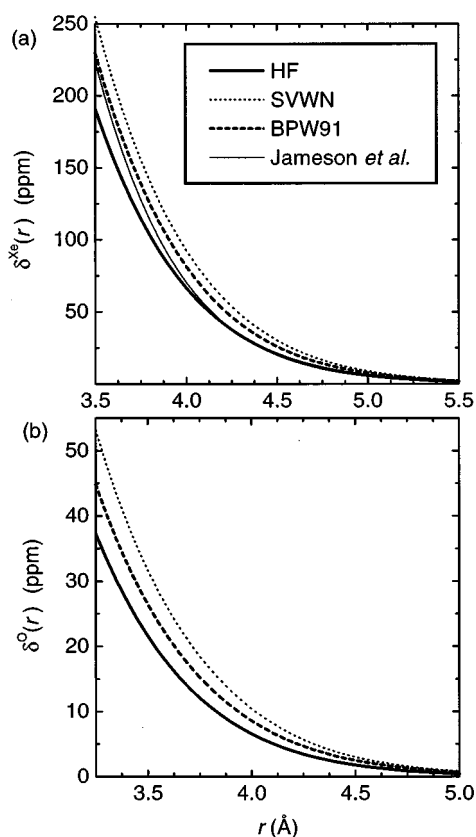


FIG. 5. The binary ^{129}Xe NMR chemical shift functions for the different interaction pairs: (a) Xe–Xe and (b) Xe–O. The empirically scaled Ar–Ar curve by Jameson and de Dios (Ref. 17) is also shown in (a). The curves in (b) have been obtained from calculations of the Xe–OH₂ system.

successful. As only the deepest well region of the Xe–Xe interatomic potential is sampled at low temperatures, the result may be interpreted so that BPW91 provides a better account for Xe shielding at the relevant pair separation range. Increasing the temperature causes sampling of a wider

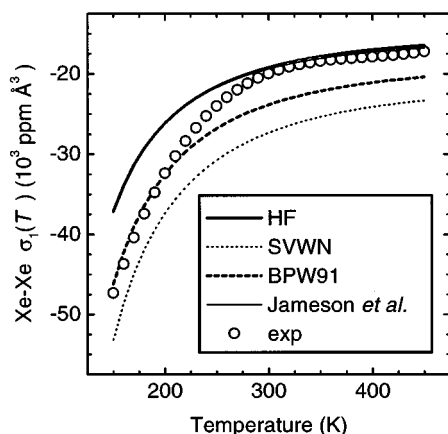


FIG. 6. The temperature dependence of the second virial coefficient of ^{129}Xe NMR shielding for the Xe–Xe interaction. The experimental (Ref. 5) and empirically scaled (Ref. 17) theoretical Ar–Ar curves by Jameson and co-workers are also shown.

distance range, both toward smaller distances where large shielding changes occur, and to larger ones where the chemical shift function has values close to zero. HF appears to be capable of better handling the shielding effects at the repulsive region of the pair potential.

We now turn to the analysis of the present molecular dynamics simulation trajectory in terms of Eq. (6) and the calculated binary shielding curves. We emphasize that there are no adjustable parameters in our approach.

The simulated trajectory can be partitioned in configurations of the adsorbates according to the number of nearest Xe neighbors of each of the Xe atoms. There are three possibilities.¹² A Xe atom adsorbed in one of the cells of $\text{AlPO}_4\text{-11}$ may have neither, one, or both two of the neighboring cells occupied by other Xe atoms. The distance between the adjacent channels is large enough to suppress any direct Xe–Xe interactions from affecting the chemical shift. Similarly, occupancy in the same channel but further than in the adjacent cells has very little influence. However, indirect interactions from distant adsorbates, mediated by the flexible cage, can be present in the data, as discussed already in the context of adsorbate dynamics.

We refer to the three configurations in the same manner as Ripmeester and Ratcliffe (RR),¹² thus $\text{O}^\circ\text{Xe}^\circ$ denotes a configuration where Xe has no near neighbors (no Xe atoms in adjacent cells), $\text{O}^\circ\text{XeXe}$ denotes a situation with one neighbor and XeXeXe refers to those occasions when Xe is in between two Xe atoms. The simulated chemical shifts for each of these configurations are listed in Table III and shown in Fig. 7. For comparison, the average chemical shifts of the Xe atoms residing in the three channels with different loadings ($n\text{Xe}^\circ$, $n=1,2,3$) are shown in Table III, too.⁵² The $\text{O}^\circ\text{Xe}^\circ$ “site” occurs in both the 1Xe° and 2Xe° channels: Although the former case is the dominating one, our simulation model with four successive cells along the channel direction allows the existence of a configuration where two $\text{O}^\circ\text{Xe}^\circ$ configurations arise in a channel with two adsorbates. Likewise, the 3Xe° channel contributes to the $\text{O}^\circ\text{XeXe}$ configurations (the more common character of the 2Xe° channel) twice in each simulation snapshot; there are two instances of a Xe atom with one Xe neighbor for each configuration of three atoms occupying four sites under periodic boundary conditions.

The Xe–O shift contributions can be assessed from the chemical shifts of the $\text{O}^\circ\text{Xe}^\circ$ instances. Among the present sets, the BPW91 seems to be the best suited one, $\delta_{\text{O}^\circ\text{Xe}^\circ}$ overestimating by 6% the result of the RR model for the experimental data, 114.4 ppm.¹² In contrast, the HF parametrization underestimates $\delta_{\text{O}^\circ\text{Xe}^\circ}$ by 18% and SVWN exaggerates it by no less than 28%. Looking at the trend when increasing the number of occupied neighbor sites, the absolute deviation from the RR model of the latter two parametrizations increases, while that of BPW91 remains almost constant. As expected from the similarity of the Xe–O PDFs with different channel filling ratios [Fig. 3(a)], the wall (Xe–O) contribution to δ_{Xe} remains constant as a function of the number of occupied neighbor sites. This implies little deformation of the lattice as a result of the additional adsor-

TABLE III. ^{129}Xe NMR chemical shifts (ppm) in $\text{AlPO}_4\text{-11}$ at 300 K simulated by different parametrizations of the binary shift functions. 3 SEM error limits are included. The relative contribution of the Xe–Xe interactions to the shifts is also shown for all methods (in %, the remaining contribution comes from the Xe–O interaction).

Site/loading ^a	RR ^b	HF	Xe–Xe	SVWN	Xe–Xe	BPW91	Xe–Xe
OXeO	114.4	93.9 ± 2.5	0.0	146.8 ± 3.6	0.0	121.3 ± 3.0	0.0
OXeXe	149.1	121.6 ± 1.7	21.5	186.5 ± 2.5	19.9	155.7 ± 2.1	20.7
XeXeXe	183.5	147.6 ± 3.3	35.6	223.3 ± 4.7	33.4	187.8 ± 3.9	34.6
$1\text{Xe}/\circ$		93.7 ± 2.9	0.0	146.6 ± 4.2	0.0	121.1 ± 3.5	0.0
$2\text{Xe}/\circ$		114.2 ± 6.3	17.2	176.0 ± 9.2	15.9	146.5 ± 7.8	16.6
$3\text{Xe}/\circ$		130.8 ± 1.4	26.7	199.4 ± 2.0	24.8	166.9 ± 1.7	25.9

^aThe OXeO , OXeXe , and XeXeXe refer to the three-site model (Ref. 12) in which adsorbate configurations are classified according to the number of occupied next neighbor adsorption cells. $n\text{Xe}/\circ$ ($n=1,2,3$) refer to average chemical shifts for different channel filling ratios (see Table II).

^bResults from the three-site dynamic averaging model proposed in Ref. 12.

bate(s). These findings further indicate that the Xe–Xe contributions are well described by BPW91; the error in this parametrization can be ascribed to the wall interactions. The BPW91 increments in δ_{Xe} from OXeO to OXeXe and further to XeXeXe are 32.3 and 32.6 ppm, respectively, while the increments in the RR model are ca. 2 ppm higher.

Equations (3) and (4) apply for homogeneous media only, and not to atoms confined in cavities where the range of distance sampling is limited.³⁶ This is reflected in the fact that the BPW91 parametrization (and not the HF one) is the most successful in reproducing the contribution of the Xe–Xe interaction to δ_{Xe} in our simulation. HF should be more accurate at the simulation temperature if judged on the basis of σ_1^{Xe} (Fig. 6), but the cellular structure of the $\text{AlPO}_4\text{-11}$ channels causes a Xe–Xe separation range different from that in the gas phase to be sampled. In contrast, HF may work better in a solid with large cavities (e.g., NaA) capable of accommodating multiple adsorbates simultaneously.

The almost quantitative agreement with the RR model reached by the simulation with the BPW91 parametrization is encouraging, particularly in view of the many approximations that have been made. The approximations of pairwise additivity of chemical shifts and the transferability of the

binary shift functions (calculated *in vacuo* for model systems and used for interactions in the condensed phase) are expected to work best for the interaction between the rare gas adsorbates. In the present chemical shift calculations, the Xe–OH₂ case is modeled as a function of $r_{\text{Xe-O}}$ only, despite the fact that there is more than one degree of freedom in this system. As the calculated curve is for the direct in-plane approach of Xe toward the oxygen atoms of the water molecule, we neglect the angular dependence of δ_{Xe} completely. This dependence is not only due to the hydrogens on the other side of the molecule (a situation not valid in the target solid material), but also due to the two oxygen lone pair orbitals which are present also in the material of interest here. We thus neglect of the immediate chemical neighborhood of the oxygen atom. The fact that the oxygen atoms usually stick inwards to the cavities in their –T–O–T– bonds makes them the principal sites of contact between the pore walls and the confined species. Consequently, defining the adsorbate potential energy and chemical shift surfaces in terms of oxygen only should be a reasonable approximation.

These approximations should be tested by first principles calculations of larger model systems, preferably with all atoms of the cavity housing the guest being explicitly quantum mechanically treated. Such an approach would also provide information about the transferability of the shift parameters for one material to another. Steps in this direction were taken in Ref. 53, which reported *ab initio* cluster calculations of δ_{Ar} in systems consisting of Ar and different ring fragments of type A zeolites.

V. CONCLUSIONS

We have carried out a canonical ensemble molecular dynamics simulation of ^{129}Xe adsorbants in the $\text{AlPO}_4\text{-11}$ molecular sieve at $T=300$ K using a fully dynamic model for the framework. The Xe single-particle distribution functions clearly show the cellular structure of the channels, with each cell capable of housing one guest Xe atom. The Xe–O pair distribution functions were given an interpretation in terms of the structure of the host material. The functions are found to be independent of the channel filling ratio.

The effective activation energy of jumps between successive cells is estimated at significantly lower value than what is calculated for a rigid system with atoms fixed to their experimental positions obtained from neutron scattering.

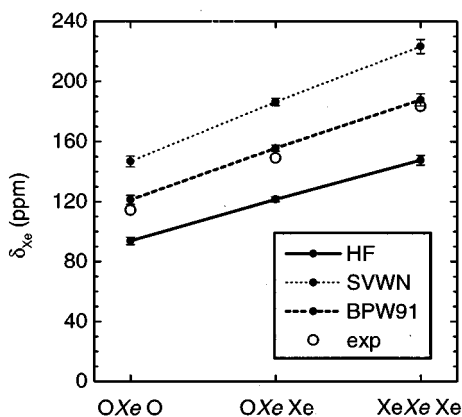


FIG. 7. Calculated and experimental (Ref. 12) ^{129}Xe NMR chemical shift in $\text{AlPO}_4\text{-11}$ at 300 K as a function of the number of occupied nearest neighbor adsorption cells. The 3 SEM error bars are shown.

This implies that it is necessary to treat the cage as a dynamical framework in microporous solids with cavities of similar size with the adsorbants. Increasing the loading causes a slight increase in the energy barrier. Accordingly, the frequency of the intercellular jumps of the adsorbants and their self-diffusion coefficients are found to decrease with increasing channel loading.

^{129}Xe NMR chemical shifts were calculated with no adjustable parameters using the approximation of pairwise additive interactions from the oxygen atoms of the host material and other adsorbates. The necessary binary chemical shift curves were obtained from first principles electronic structure calculations (using gauge-including atomic orbitals) carried out for the Xe–Xe and Xe–OH₂ model systems. The present chemical shift parametrizations based on Hartree–Fock and local density functional calculations result in under- and overestimation, respectively, of the ^{129}Xe chemical shifts as compared to experimental results in the $\text{O}\text{Xe}\text{O}$, OXeXe , and XeXeXe classification of adsorbate configurations (according to the number of occupied nearest neighbor cells of the Xe atom in question) proposed earlier. A gradient-corrected density functional method results in a good accuracy, however. Particularly, the Xe–Xe interaction contribution to the Xe chemical shift turns out to be best reproduced by this last method, despite that Hartree–Fock calculations perform best in comparison with the experimental second virial coefficient of Xe nuclear shielding at this temperature. This arises due to the limitations imposed on the Xe–Xe distance sampling by the confining framework of the host material. The nature of the many approximations in the present method of estimating the chemical shift of the adsorbate were given a brief discussion.

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³⁸TZ level Xe (18s15p9d) basis set (obtained from the same *ftp* distribution as the sets presented in Ref. 54) was used in a fully decontracted form. Two d -polarization exponents were taken from Ref. 55. One f -polarization primitive with the exponent 0.358, and s -, p -, and d -type diffuse functions (exponents 0.0394, 0.0315, and 0.0330, respectively) were added to the basis, giving the total of (19s16p12d1f). TZ2P bases (Ref. 54) were used in completely decontracted form for H and O [the exponents of the polarization functions were $\alpha_{p1}(\text{H})=1.30$, $\alpha_{p2}(\text{H})=0.33$, $\alpha_{d1}(\text{O})=2.704$, and $\alpha_{d2}(\text{O})=0.535$]. They were supplemented with diffuse s -[$\alpha_s(\text{H})=0.0344$, $\alpha_s(\text{O})=0.0798$] and p -type[$\alpha_p(\text{O})=0.0584$] primitives, giving the total sets of (6s2p) for hydrogen and (11s7p2d) for oxygen. The counterpoise correction (Ref. 56) of the basis set superposition error was applied for each point.

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