Diffusion of Molecular Hydrogen through Porous Materials: The Importance of Framework Flexibility

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The importance of framework flexibility in facilitating the passage of molecules through confining framework materials is probed via both periodic energy minimizations using dedicated force fields and embedded quantum mechanical/semiempirical cluster calculations. Specifically, molecular hydrogen transport through an all-silica zeolitic structure is investigated. Particular attention is given to the comparison of the two modeling methodologies used and the effect of their corresponding approximations. Regardless of methodological differences, the quantitative and qualitative agreement between the different techniques is surprisingly good, tending to confirm the quality and suitability of each respective method. The choice of rigid framework reference structure is shown in both modeling methodologies to strongly affect the predicted influence of the lattice flexibility on the size of the molecular transport barrier, helping to resolve the differing results of previous studies. In all of our calculations, we find the energetics of molecular transport through a confining porous environment to be strongly dependent on the flexibility of the framework.

Introduction

Atomistic computer simulations are often employed for predicting diffusion rates and adsorption properties of gaseous species in solid porous frameworks.[1] Frequently in such studies, the framework structure is taken to be rigid, which has proven in several studies to be a suitably accurate assumption for molecules that are considerably smaller than the smallest pore aperture.[2–5] Such rigid-framework simulations also have the additional benefit of a great reduction in computer calculation time over simulations using fully flexible frameworks and, thus, have been utilized often. For molecules that are relatively more confined by the surrounding framework, having effective diameters of a similar size to that of the largest framework pore, the approximation of an unresponsive inflexible framework can introduce significant errors.[6–9] In numerous simulations, the influence of the framework flexibility on the ease of diffusion has been indicated clearly,[10–12] although with different conclusions as to its extent.

As a model system for investigating the influence of framework rigidity on diffusion, several authors have investigated the passage of inert gases through the zeolite sodalite, which has a rather small largest pore aperture. Kopelevich[13] investigated the influence of incorporating framework flexibility in the calculation of diffusion of Ne, Ar, and Kr in all-silica sodalite by performing calculations using force field energy minimizations combined with transition-state theory, finding a small difference in the predicted diffusion barrier for Ne, and larger differences for Ar and Kr. Murphy[14] used a comparable calculation method to determine the diffusion of He, Ne, and

Ar in an all-silica sodalite structure assuming the lattice to be rigid. Finally, Nada[15] calculated the diffusion of He, Ne, and Ar in an all-silica sodalite structure with symmetry-simplified periodic Hartree–Fock calculations using a rigid framework. When comparing the corresponding activation energies predicted by this series of computational investigations,[13–15] large discrepancies between the results are observed.

Experimentally, although all-silica sodalite can be synthesized, an organic template is employed (which resides in the pores of the framework) which can only be removed by destroying the surrounding silicate structure.[16] The template-free siliceous form of sodalite is thus, presently at least, an idealized structure for which consequently no experimental data exists regarding the diffusion of guest molecules. Therefore, currently the above-mentioned literature results cannot be compared directly with experimental data to test their accuracy. In calculations employing the empty all-silica sodalite framework, one must be careful, therefore, to use computational methods known to accurately reproduce all-silica structures when preparing an appropriate reference rigid framework structure. In this study, we demonstrate that the choice of reference structure is particularly important in assessing the influence of flexibility on the transport of small molecules.

Herein, we report on the first study of the energetics of a diatomic molecule passing through the sodalite framework. Specifically, we calculate the energy barrier for the diffusion of molecular hydrogen through the Si_6O_6 pores (or six rings) of all-silica sodalite both by means of (i) periodic framework energy minimizations employing a dedicated force field and by (ii) embedded quantum mechanical ONIOM[17] calculations employing a large terminated silica cluster of 90 atoms cut from the sodalite crystal structure. By comparing the respective rigid and flexible framework calculations for both calculation types, a strong dependence of the energy barrier height for hopping between cages on the framework flexibility is observed.

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TABLE 1: Descriptive Overview of All Potentials Used in the Force Field Calculations

potential	formula	description	parameters
Buckingham	$E_{\text{buck}} = A \cdot e^{-r/\rho} - C \cdot r^{-6}$	the covalent or ion bonding energy between two atoms	A, ρ, C = empirical parameters [eV], [Å], [eV*Å]; r = distance between the two bonded atoms [Å]
core/shell	$E_{\text{spring}} = \frac{1}{2} \cdot k2 \cdot r^2$	the energy due to the polarization of the oxygen atoms	$k2$ = spring constant = 74.92 eV*Å^{-2}; r = distance between core and shell [Å]
three-body	$E_{\text{three}} = \frac{1}{2} \cdot k2 \cdot (q - q_0)^2$	the angular energy of the O–T–O angles	$k2$ = three-body constant [eV*rad^{-2}]; q_0 = optimal bending angle of O–T–O [°]; q = angle of O–T–O [°]
Lennard-Jones	$E_{\text{LJ}} = 4\epsilon \cdot \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right)$	the nonbonding energy between two interacting atoms	ϵ = minimum energy of the potential curve [eV]; σ = atom–atom distance at zero energy [Å]; r = atom–atom distance [Å]

TABLE 2: Parameter Values for the Buckingham Potentials

bonding atoms	A [eV]	ρ [Å]	C [eV*Å^6]	cutoff distance [Å]	reference
O–Si	1283.907	0.32052	10.66	10.0	21
O–O	22764.000	0.14900	27.88	10.0	21

TABLE 3: Parameter Values for the Three-Body Potential

atoms in angle	$k2$ [eV*rad^{-2}]	q_0 [°]	cutoff distances [Å]	reference
O–Si–O	2.09724	109.47	1.8, 1.8, 3.2	21

TABLE 4: Parameter Values for the Lennard-Jones Potentials

interacting species	ϵ [eV]	σ [Å]	cutoff distance [Å]	reference
Si–H$_2$	0.002254531	1.8175	15.0	29
O–H$_2$	0.005270509	2.8330	15.0	29

Furthermore, a comparison of the barrier heights using both methods shows that, considering the large difference in calculation type, each approach gives remarkably comparable results with respect to both absolute barrier magnitudes and predicted relative effects of framework flexibility.

The importance of modeling the barrier for molecular hydrogen hopping through the confined environment of a porous structure is of immediate relevance to questions relating to materials for hydrogen storage. As with other molecular modeling studies on hydrogen storage and diffusion,[18,19] in our force field energy minimizations we employ the approximation that the diatomic hydrogen molecule is represented as a single-centered Lennard-Jones (LJ) particle. By examining our quantum mechanical embedded calculations, which make no approximations as to the molecular nature of hydrogen, the suitability of this single center approximation for H$_2$ is also assessed for the relatively extreme case of passage though a confined pore.

Computational Methodology

Force Field Energy Minimizations. The force field calculations were performed using the computer code GULP[20] together with the force field parameters given in Tables 1–4.

The force field employed to calculate the interatomic interactions between the framework atoms of the zeolite was developed by Sanders.[21] This force field has been proven to reproduce very accurately various zeolite structures,[22-25] their relative energies,[22] and zeolite vibrational properties[26] in energy minimization calculations. Additionally, it has been shown to be suitable for the molecular dynamics simulation of diffusion along inner and outer zeolite surfaces and pores.[27,28] Thus, this force field was judged to be suitable to accurately represent the change in energy and structure of a sodalite pore induced by the passage of a hydrogen molecule. The LJ parameters for the interaction between H$_2$ and the atoms of the zeolite framework are taken from Watanabe.[29] These parameters are derived from

experimental data of gas adsorption on zeolites. Hydrogen is considered here as a single-centered particle which has been shown in other computational studies to be an accurate approximation.[18,19] Indeed, perhaps somewhat unintuitively, this approximation is known to work very accurately for H$_2$ under a wide range of conditions.[30] The sodalite framework is modeled as a $2 \times 2 \times 2$ supercell (see Figure 1) to avoid boundary cutoff problems (vide infra). To obtain a suitable starting all-silica sodalite framework structure, the isomorphic (template-free) aluminosilicate sodalite structure was first taken from the IZA database[31] and then energy-minimized at a constant pressure of 1 bar using the BFGS algorithm[32] and using the Sanders[21] silica force field.

The previously mentioned studies[13,14] on diffusion in all-silica sodalite used crystal structure data based on a single-crystal X-ray diffraction analysis of an all-silica sodalite crystal.[33] We decided not to use these data because the crystal from which it was obtained contained the organic template, ethylene glycol, in every cage of the framework. Because of this template, the sodalite cages are artificially expanded, which is not their energetically most favorable state when empty. We found that performing an energy minimization calculation on this structure, without the organic template inside, employing the RFO algorithm[34] in GULP[20] causes the cages to relax to a less expanded state while the total system energy per supercell decreases ($-1.19 \cdot 10^6$ kJ/mol), giving exactly the same all-silica sodalite structure as the one we employ throughout. Since the force field we employ is proven to be accurate in reproducing other all-silica zeolite structures, this effect is not artificial and, therefore, we regard it more appropriate to use the energy-minimized lower energy structure as a more realistic all-silica sodalite reference structure.

Embedded ONIOM Calculations. The embedded quantum mechanical calculations were performed using the ONIOM[17] methodology employing a Si$_{18}$O$_{48}$H$_{24}$ cluster (see Figure 1) cut from the force field energy-minimized all-silica sodalite unit cell. Hydrogen atoms were used to terminate the silica cluster with their positions determined by taking the direction of the Si-atoms that were in the original periodic framework and reducing the bond to that of a typical O–H bond (0.98 Å). Throughout the optimizations, the terminating hydrogen atom positions were fixed and all other atom positions were variable unless stated otherwise. The Si$_6$O$_6$ pore opening and its nearest oxygen atoms together with the hydrogen molecule were modeled using density functional theory (DFT) employing the hybrid exchange-correlation functional B3LYP[35,36] with a double-ζ basis set, 6-31G(d,p),[37,38] including polarization functions on both framework atoms and the hydrogen molecule. The remaining peripheral atoms of the cluster (see Figure 1) were modeled using the semiempirical method MNDO. The ONIOM methodology provides a physical link between the embedded DFT-treated region and the semiempirical-treated environment.[17] In the calculations, both of these regions are relaxed self-
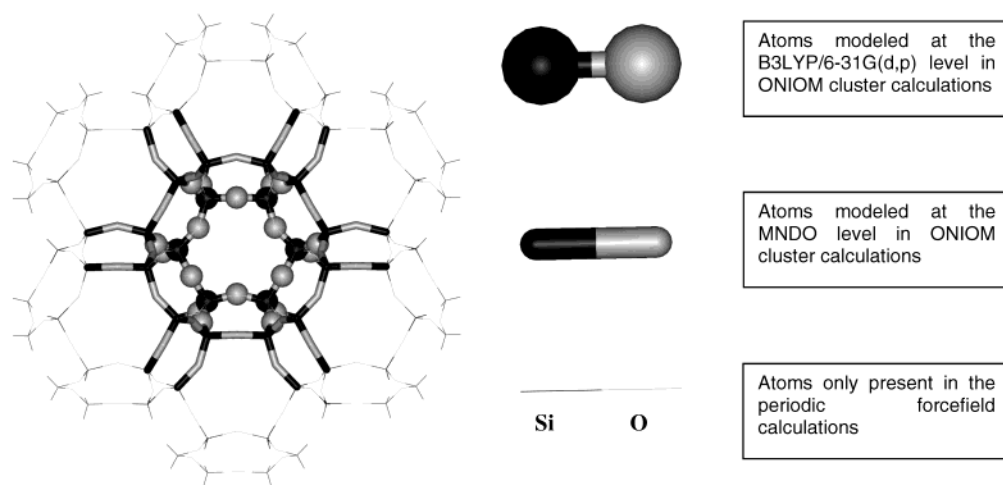
Figure 1. Schematic representations of the sodalite systems employed in the calculations. The total system depicted is the $2 \times 2 \times 2$ supercell ($Si_{96}O_{192}$) employed in periodic force field calculations. The highlighted part is the cluster ($Si_{18}O_{48}H_{24}$) used in the ONIOM calculations with the boundary silicon atoms representing the terminating H-atoms. Atoms represented as balls are modeled at the B3LYP/6-31G(d,p) level and the atoms represented as sticks at the MNDO level.
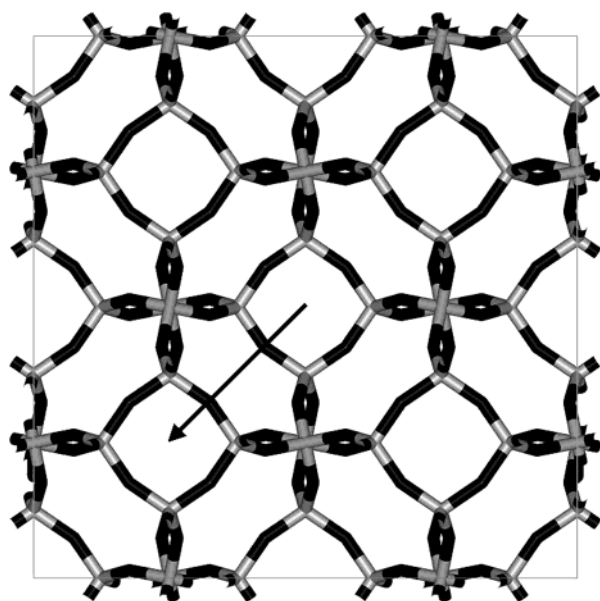
Figure 2. Schematic representation of the trajectory, the black arrow, of a hydrogen molecule from the central sodalite cage to an adjacent cage through a six-ring. Black represents the position of the oxygen atoms and gray represents the position of the silicon atoms.

consistently until there are only negligible differences in forces across the boundary between the two regions. Within the explicitly calculated DFT region, the hydrogen molecule has a direct interaction with all other atoms. The combination of the basis set and the functional used here has been used numerous times successfully for calculations regarding other silica cluster systems[39–41] and also has been employed for the modeling of molecular adsorption in cluster models of zeolites.[42,43] The embedding region of the cluster does not directly interact with the hydrogen molecule but provides a representation of the bulk environmental forces on the central six-ring. The use of MNDO has proven to provide a good representation of the mechanically responsive silica environment[44–47] in other embedded ONIOM silica calculations. The dependency of our choices of basis set and semiempirical method on the barriers obtained was further tested by sampling a few points along the trajectory employing an extended 6-311+G(d,p) basis set in combination with MNDO and the 6-31G(d,p) basis set together with both the PM3 and AM1 semiempirical methods. These changes made differences

in the magnitude of the total barrier height of only 2−4% and, thus, only results using the 6-31G(d,p) basis with MNDO are reported. The effects of basis set superposition error (BSSE) on the hydrogen interaction energies is likely to be about 1 kcal/mol, on the basis of our own calculations and other studies of H_2 physisorption over zeolite clusters using a similar level of theory.[43,48] The overall tendency of these offsets would be to shift the calculated barrier as a whole, having relatively less effect on the energy differences which are used to calculate the barrier heights. As we were primarily interested in comparing energy barrier heights and not absolute interaction energies (and further because of the large number of energies sampled), we did not attempt to correct for BSSE in our calculations. Gaussian 98[49] was used for all the ONIOM calculations.

In both the force field and ONIOM calculations, a trajectory was taken as a straight line from the coordinates of the center of one sodalite cage through the middle of the six-ring in the direction of the center of the neighboring sodalite cage (see Figure 2). To obtain the energy barrier graph, the energies at 30−40 points on this trajectory were calculated. No framework symmetry was employed. The barrier heights were taken to be the differences between the points of maximum and minimum total system energy along this trajectory (cf. Figure 3).

Results and Discussion

Table 5 gives an overview of the energy barriers calculated for the passage of a hydrogen molecule through an all-silica sodalite six-ring using both the periodic force field and ONIOM optimizations. To illustrate how large an influence the choice of the reference sodalite geometry has on the outcome of an energy barrier calculation in a rigid structure, the energy barriers calculated for the rigid Richardson structure[33] are also added to this table.

For both our force field and ONIOM calculations, using the optimized all-silica reference structure, we find the difference in energy barrier between a rigid and a flexible framework to be significant (7.1 and 6.7 kcal/mol, respectively, see Table 5). These differences correspond to increased barrier heights of 127% and 93% (cf. Figure 3). On the other hand, if the crystallographic data of Richardson[33] is used as the reference rigid structure, the calculated energy barriers are almost identical to the barriers calculated with a flexible framework.

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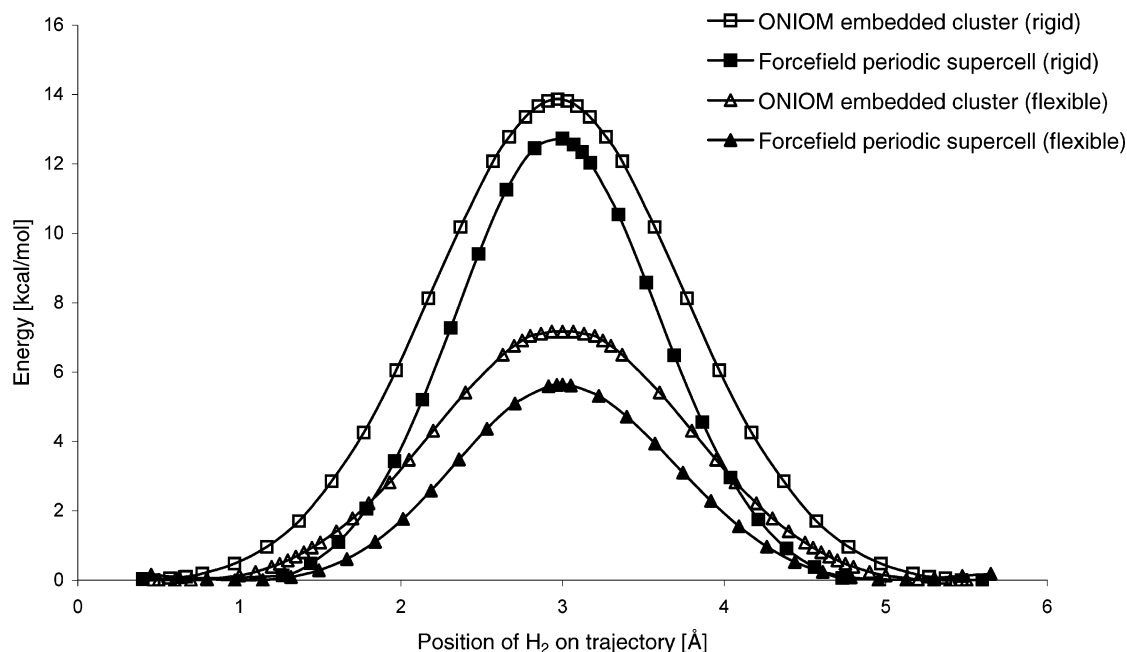
Figure 3. Total system energy versus H_2 position for hydrogen passage through rigid and flexible all-silica sodalite six-rings in the ONIOM cluster and periodic force field calculations.

TABLE 5: Energy Barriers Calculated for the Passage of H_2 through an All-Silica Sodalite Six-Ring

geometry source	framework status	periodic force field energy barrier [kcal/mol]	ONIOM energy barrier [kcal/mol]
IZA[a]	flexible	5.6	7.2
IZA[a]	rigid	12.7	13.9
Richardson[b]	rigid	5.4	8.7

[a] Reference 31. [b] Reference 33.

This small difference in energy barrier between rigid and flexible calculations was already observed before by Kopelevich[13] for the diffusion barrier of neon in the Richardson structure (5.5 and 4.8 kcal/mol, respectively). As discussed before, the Richardson structure data is based on a single-crystal X-ray diffraction analysis of a crystal that still contains an organic template, forcing the cages into an energetically unfavourable expanded state and, thus, causing the pore window to be unrealistically expanded as well. The larger the pore window openings are, the smaller the energy barrier for the passage of atoms/molecules tends to be. Coincidentally, in this case the reduction in energy barrier because of this artificial pore opening in this expanded sodalite system happens to be comparable to the barrier in the flexible system hiding the true effect of lattice flexibility. The energy values in Table 5 explicitly show this effect, confirming the importance of the choice of rigid input reference structure. In another study, calculating the diffusion of methane in zeolite LTA,[50] a similar observation was also noted. Since it cannot be predicted beforehand if the chosen rigid structure will give reliable results, it is strongly advocated that a flexible framework approach should always be used when doing calculations on diffusion in systems of which the diameter of the largest openings and of the diffusing molecules lie within the same order of magnitude.

The diffusion barriers calculated for the flexible system with GULP and ONIOM differ by 1.6 kcal/mol (cf. Figure 3). Thus, the ONIOM barrier is approximately 20% larger than the GULP barrier. Although this calculated difference is remarkably small considering the large dissimilarity in the corresponding methodologies employed, it is instructive to try to establish the

underlying reasons for the modest disparity to gauge which factors are important in the hydrogen diffusion process. One reason for the difference could be the fact that a cluster is used for the ONIOM calculations, while a periodic system is employed in the force field calculations. The cluster inherently does not take long-range effects into account, for example, interactions of the hydrogen molecule with the distant framework atoms or long-range framework relaxations. To test the effect of such long-range effects, additional force field calculations employing only the atoms of the ONIOM cluster were performed, showing that the energy barriers through a fixed and a rigid cluster increase only by 0.01 and 0.18 kcal/mol over the periodic calculations, respectively. Both contributions are too small to be considered as important factors for constrained molecular transport in our system. However, these calculations, by showing the small dependence of the energy barrier on long-range effects, justify the use of the cluster size employed in the ONIOM calculations.

A further justification of the cluster approach can also be gained from examining the displacements of the sodalite framework atoms because of the passage of hydrogen through the six-ring (see Figure 4). It can be observed that the magnitude of the atomic displacements effectively tends toward zero at a distance of about 6 Å. A similar picture of the decay of framework displacements was also obtained by Kopelevich[13] for the passage of Neon through a six-ring of all-silica sodalite. The cluster we employed is about 12 Å in diameter and, thus, large enough to incorporate most of the framework relaxation. In Figure 4, the displacement of the oxygen atoms provides the main contribution to the framework relaxation.

One other possible source of error is the treatment of hydrogen in the force field calculations. Although confident in the adequacy of the silica framework force field employed, the description of the interaction of the H_2 molecule with the framework and the treatment of molecular hydrogen as a single-centered entity may be cause for concern.

The structural and, in part, electronic changes in the diatomic hydrogen molecule during movement through the silica six-ring of sodalite are given in Figure 5, showing that the hydrogen
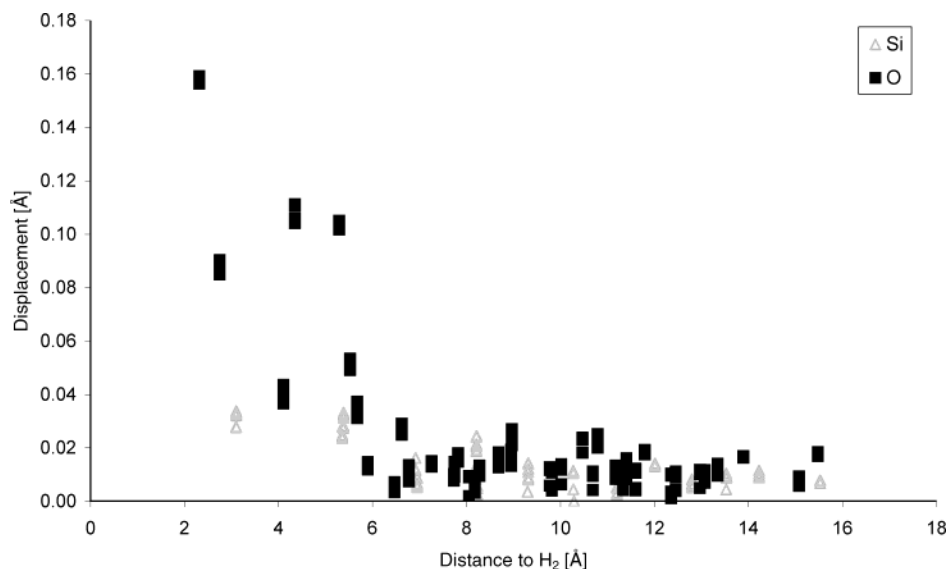
Figure 4. The displacements of the sodalite framework atoms because of the presence of a hydrogen molecule in the most confined location of the framework, the six-ring center (as determined from the force field calculations). The displacement is defined as the distance between the position of the framework atom in the fully relaxed empty sodalite system and its position in the sodalite system with a hydrogen molecule in the center of a six-ring. The distance to H_2 is defined as the distance between H_2, located in the six-ring center, and a framework atom in the force field energy-minimized system.
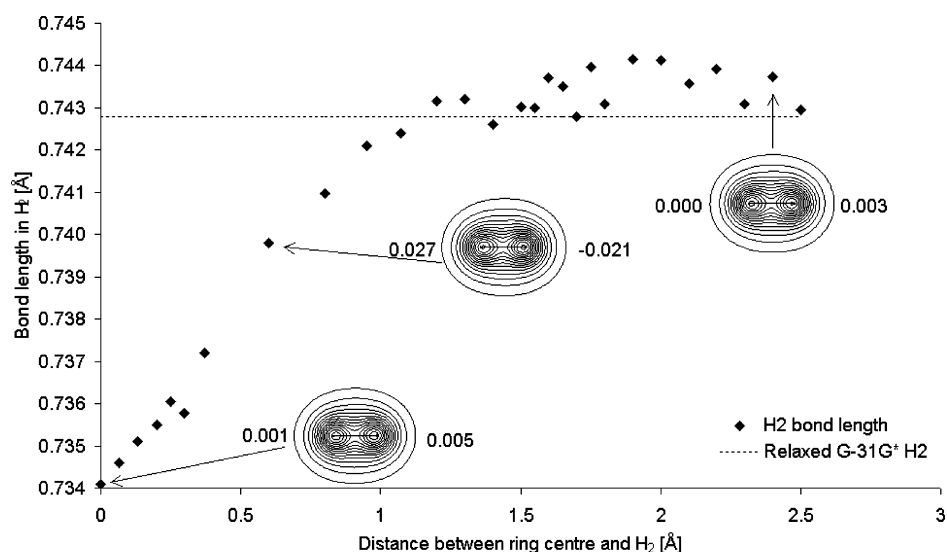
Figure 5. The changes in bond length and polarity of the hydrogen molecule on its path through the six-ring center of the cluster represented in Figure 1 as determined from the ONIOM optimizations. For each depicted hydrogen molecule (the H-atom on the left is the one closest to the six-ring center), the Mulliken partitioned charges [e^-] are given on each side. Note the small induced repulsive dipole in the intermediate case.

molecule is slightly contracted when moving through the six-ring. However, at most this contraction is only 1%, thus causing a negligibly small change in internal molecular structure. Furthermore, the inset charge density contour plots in Figure 5 show that the polarization of the hydrogen molecule is virtually unaffected during its passage through the confining pore. Thus, the hydrogen molecule can be considered as a rigid body when moving through the narrow six-ring. These results further confirm the validity of the single-center approximation made for H_2 in the force field calculations.

The LJ interaction between hydrogen and the sodalite framework is derived from the experimental data of hydrogen adsorption on purely siliceous zeolites.[29] Although the parameters of this force field can be altered straightforwardly to increase or decrease the calculated barrier, it is unclear that it is desirable to do so to match the ONIOM results, since they are based on the reliability of the nonempirically parametrized DFT method to accurately reproduce the relatively weak H_2-

framework interaction. Although improving the basis set of the framework and the H_2 molecule has little effect on the predicted barrier heights (approximately 2%), in line with the expected small effect on energy differences for BSSE, it is known that DFT is often not the perfect method to model systems for which dispersive interactions are dominant.[51] This may be of some concern for the H_2 molecule when relatively far from the pore, near to its energetically most favored position (approximately 2.4 Å from the pore in all cases, see Figure 3), but, in our confined scenario, when H_2 is passing through the pore, the barrier energetics are almost solely due to the short-range, hard-core repulsive interactions between H_2 and the framework atoms. In such cases, the DFT calculations should give a relatively better representation of the interactions, and we rely on the fitted R^{-12} terms in the H_2 LJ potentials to adequately reproduce such interactions. The R^{-12} term is often inferior to other representations of repulsion such as the exponential form $e^{-R/\sigma}$, but, in the absence of other specifically fitted potentials to describe

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the hydrogen interactions in our system, it is difficult to assess the suitability and likely error involved in the use of the R^{-12} form. The fact that we observe a reasonable quantitative agreement between the ONIOM calculations and our periodic force field calculations tends to support the quality of the parametrization, which appears to capture the essential character of the hopping process.

In the absence of other likely significant errors due to methodological approximations, the main result, that the energy barrier for hydrogen passage with a flexible framework is substantially lower than with a rigid framework, is clearly supported by both sets of calculations pointing to the local response of the silica framework being the general overriding influence on barrier height. We feel that in the case of sodalite, particular emphasis should be placed on the six oxygen atoms in the pore aperture. From our displacement analysis, it can be seen that the main mechanical distortions to the six-ring involve the oxygen atoms in closest proximity to the hydrogen molecule. From previous works,[10,11] it is further known that the sodalite framework has one local special mode of distortion or vibration, termed a "rigid unit mode" involving these very atoms. This particular mode allows three of the oxygen atoms in each six-ring to move more closely to each other, while the other three in a natural cooperative manner move further away from each other. This six-ring pore response has been noted to occur in the sodalite framework which, when doped with aluminum atoms, enables it to adsorb charge-compensating cations more firmly to each six-ring. When a hydrogen molecule passes through the all-silica six-ring, we find that the same response of the oxygen atoms effectively enlarges the pore window area. In the cation case, the ring mode enhances the interaction of the oxygen atoms with the cation, whereas in our barrier calculations the same mode allows for the flexible response of the ring atoms to the passage of an obstructing molecule. Although the periodic force field energy minimizations demonstrate this six-ring response, the cluster approach does not reproduce the mode very well. In the force field calculations, the distortions in the ring as the hydrogen passes through are very clear; three oxygen atoms move closer while the other three move away from each other. However, in the ONIOM calculation all oxygen atoms move away from each other in a similar concerted response and the ring behaves more rigidly. This, we feel, provides much of the reason for the relatively small differences in molecular transport energy barriers found between our ONIOM and force field calculations.

Conclusion

The importance of framework flexibility for the diffusion of guest molecules through framework materials, when the size of the guests is comparable to the largest pore window opening, has been demonstrated by two complementary modeling methods using the model system of H_2 in all-silica sodalite. Both sets of calculations clearly show that the molecular transport energy barrier is increased considerably (approximately 100%) when the sodalite is modeled as a rigid framework as compared to its natural responsive flexible state. The periodic force field calculations give energy barrier magnitudes that correspond within an error of 20% to the results obtained for the same system with the embedded ONIOM cluster method. Furthermore, the ONIOM results show that the hydrogen molecule is almost unaltered when moving through the energy barrier, confirming that modeling molecular hydrogen as a single-centered particle is a reliable approach for the force field calculations. The demonstrated acceptability of the force field

calculations indicates their suitability for further calculations of hydrogen diffusion in confining all-silica framework materials. As a follow-up study to this work, molecular dynamics simulations are currently in progress to estimate the diffusion rate of hydrogen throughout all-silica sodalite as a function of temperature.

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