for isozyme III, very strong anion binding is reported. Isozyme
III has a much more positive potential in the active site region
that would enhance anion binding. The model is so simple that
it is easy to suggest that water or other nearby ionic residues or
couples such as the Thr–Glu will alter details. It does show the
need for the more complete treatment exists and that all of the
studies of CA have not properly considered the problem of the
ionicity of the metal active site.

Registry No. Carbonic anhydrase, 9001-03-0.

Zeolites versus Aluminosilicate Clusters: The Validity of a
Local Description

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5600 MB Eindhoven, The Netherlands. Received December 7, 1990

Abstract: A comparison of force field calculations on extended systems and ab initio quantum chemical calculations on ring
structures reveals that the relative energy content of neutral-framework silicas and aluminophosphates is determined by that
of the smallest substructures. Energy-minimized structures containing only four, five, and six rings have the same energy
content to within 10 kJ/mol. Hypothetical three-ring-containing structures have considerably higher energy content, which
may well inhibit their synthesis in the pure SiO2 modification. The results accord with sparse experimental information. Using
the same combination of techniques, we demonstrate that substitution of aluminum in silica causes an appreciable, albeit local,
distortion of the lattice. The relaxation energy for such a substitution amounts to 100-200 kJ/mol, depending on the way
charge compensation is accomplished.

1. Introduction

Secondary building units (SBU) play an important role in the
structural study of zeolites and aluminophosphates. The SBUs are small composite entities like rings or double rings, built from
corner sharing TO4 (T = Si, Al, P) tetrahedrons, which can be
used to formally describe the framework topology. Thus, they
provide a useful tool for classifying the large number of known
zeolite networks as well as for systematically enumerating the
endless number of hypothetical four-connected networks. At a
less abstract level, their proven existence in silica synthesis
endless number of hypothetical four-connected networks. At
a less abstract level, their proven existence in silica synthesis
has led to speculations concerning their role in steering the still
poorly understood process of zeolite synthesis. Lastly, SBUs are very similar to the clusters that are used by
theoretical chemists as model systems for zeolites, in studies on
zeolite stability, acidity, water coordination, and framework
substitutions. The use of ab initio quantum chemical calculations on these small clusters contrasts with the other approach
of zeolite theoretical chemistry: the classical modeling of extended systems, using force fields to describe the interatomic interactions. So far it has been difficult to reconcile the two theoretical
approaches.

For some time, force fields have been used in the scientific community to deal with calculated structures. However, since they are based on effective, classical potentials, they are not able to handle electronic effects that control the chemical reactivity of isomorphously
substituted zeolites. The classical study of the acidity of protons
attached to a zeolite lattice provides an example of such a problem. This kind of subject can at present only be approached by application of quantum chemical calculi to small clusters. The
variational character of the ab initio SCF scheme of quantum chemistry implies that the results are unambiguous only for
gometry-optimized clusters. The question that emerges is whether
or not, or to what extent, the results on geometry-optimized (free)
clusters still have any bearing on the chemically reactive sites
embedded in extended systems (zeolites), where the geometric

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†Eindhoven University of Technology.

the energy surface of small zeolitic clusters, determined from ab initio calculations. At the same time, we have ascertained that it accurately describes the structure and properties of extended systems. This force field and the philosophy behind it have been elaborated in two previous papers.\(^{21,22}\)

This dual approach will be used to study two types of systems. Firstly, we will study the relative energies of all-silica zeolites and all-silica clusters. It appears that the energy of a zeolitic SiO\(_2\) polymorph can be considered to be the sum of the energies of clusters (specifically rings), indicating that the strain that arises from the embedding of free ring structures into the infinite lattice is small (less than 10 kJ/mol SiO\(_2\)). The small energy differences found between SiO\(_2\) systems with different network topologies is in quantitative agreement with the sparse experimental information about this subject.\(^{23}\) Also, we find that three-ring molecular sieves have a considerably higher energy content, which may prohibit their synthesis (at least in the purely siliceous form). The same invariance of the energy for differences in network topology is found for AlPO\(_4\) polymorphs. Here three-ring structures are forbidden because of the alternation of Al and P within the framework.

In a second series of calculations, we will extend the scope to aluminosilicates, focusing on the local properties of an isolated aluminum substituted into the framework of a SO\(_2\) zeolite. The local environment of such a substitution is of particular interest, since it is thought responsible for the catalytic behavior of aluminosilicate in heterogeneous catalysts. For this system, as for the all-silica system, the strain that results from replacement of silicon by aluminum (having a 0.1 Å longer bond to oxygen) is removed by structure relaxation in zeolites and clusters alike. This provides support for the idea that small geometry-optimized clusters are suited for studying the acidic properties of extended zeolites.

In the next section, we will present the details of both the quantum chemical calculations and the lattice energy minimization calculations. Also, we point out how an effective interaction potential for an acidic OH group was derived from ab initio calculations on a small cluster. Finally, a scheme is presented for the correction of force field energies for a spurious density dependence. An analysis and a detailed comparison of ab initio and force field results are reserved for the Discussion. In the Conclusion, results and their implications are summarized.

2. Computational Details and Results

2.1. Quantum Chemical Calculations. Quantum chemical calculations were performed with the GAMESS ab initio package,\(^{24}\) using either STO3G or 3-21G basis sets.

### Table I. Total Energies (hartrees/Si) and Energy Differences (kJ/mol Si) of Optimized Silica Clusters as Obtained from ab Initio Quantum Chemistry

<table>
<thead>
<tr>
<th>SBU symm</th>
<th>STO3G E</th>
<th>STO3G (\delta E)</th>
<th>3-21G E</th>
<th>3-21G (\delta E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 (C_6)</td>
<td>-508.415 799(^a)</td>
<td>0</td>
<td>-512.157 759</td>
<td>0</td>
</tr>
<tr>
<td>5 (C_5)</td>
<td>-508.415 783(^a)</td>
<td>0.0</td>
<td>-512.156 219</td>
<td>4.0</td>
</tr>
<tr>
<td>4 (C_4)</td>
<td>-508.412 064(^a)</td>
<td>9.8</td>
<td>-512.146 269</td>
<td>29.2</td>
</tr>
<tr>
<td>3 (T_3)</td>
<td>-470.900 205</td>
<td>37.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)SBU\(\)s are denoted by their Schläfli symbols (e.g., \(46^3\) is a double-six-ring structure). \(^b\)From ref 11. \(^c\)From ref 26.

The energy of a zeolitic SiO\(_2\) polymorph can be considered to be the sum of the energies of clusters (specifically rings), indicating that the strain that arises from the embedding of free ring structures into the infinite lattice is small (less than 10 kJ/mol SiO\(_2\)). The small energy differences found between SiO\(_2\) systems with different network topologies is in quantitative agreement with the sparse experimental information about this subject.\(^{23}\) Also, we find that three-ring molecular sieves have a considerably higher energy content, which may prohibit their synthesis (at least in the purely siliceous form). The same invariance of the energy for differences in network topology is found for AlPO\(_4\) polymorphs. Here three-ring structures are forbidden because of the alternation of Al and P within the framework.

In a second series of calculations, we will extend the scope to aluminosilicates, focusing on the local properties of an isolated aluminum substituted into the framework of a SO\(_2\) zeolite. The local environment of such a substitution is of particular interest, since it is thought responsible for the catalytic behavior of aluminosilicate in heterogeneous catalysts. For this system, as for the all-silica system, the strain that results from replacement of silicon by aluminum (having a 0.1 Å longer bond to oxygen) is removed by structure relaxation in zeolites and clusters alike. This provides support for the idea that small geometry-optimized clusters are suited for studying the acidic properties of extended zeolites.

In the next section, we will present the details of both the quantum chemical calculations and the lattice energy minimization calculations. Also, we point out how an effective interaction potential for an acidic OH group was derived from ab initio calculations on a small cluster. Finally, a scheme is presented for the correction of force field energies for a spurious density dependence. An analysis and a detailed comparison of ab initio and force field results are reserved for the Discussion. In the Conclusion, results and their implications are summarized.

2. Computational Details and Results

2.1. Quantum Chemical Calculations. Quantum chemical calculations were performed with the GAMESS ab initio package,\(^{24}\) using either STO3G or 3-21G basis sets.

### Table II. Total Energies (hartrees) of Ring-Shaped Aluminosilicate Clusters at the 3-21G SCF Level in the All-Silica Geometry and Geometry-Optimized

<table>
<thead>
<tr>
<th>SBU symm</th>
<th>all-Si geometry</th>
<th>optimized geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>4R-Si</td>
<td>(D_{4h})</td>
<td>-2048.60311</td>
</tr>
<tr>
<td>4R-Al</td>
<td>(D_{4h})</td>
<td>-2001.80712</td>
</tr>
<tr>
<td>4R-Al(_{0.1})</td>
<td>(D_{2d})</td>
<td>-2162.74818</td>
</tr>
<tr>
<td>4R-Al(_{0.1})</td>
<td>(C_s)</td>
<td>-2002.29379</td>
</tr>
</tbody>
</table>

\(^a\)The point group symmetry of the clusters is also indicated. \(^b\)Na\(^+\) position optimized. \(^c\)Proton position optimized.

### Table III. Bonding Distances (Å) and Angles of the (OH\(_3\)Si\(_2\))(OH\(_2\))\(_4\)-AI(OH\(_2\))\(_4\) Dimer, Found from ab Initio Calculations, Compared with the Averaged Distances and Angles Found in Force Field Calculations on a Single Al/OH\(_2\) Substitution in Faujasite

<table>
<thead>
<tr>
<th>bond</th>
<th>(\text{ab initio})</th>
<th>force field</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO</td>
<td>4R-Si</td>
<td>FAU-Si</td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO</td>
<td>4R-Al</td>
<td>FAU-Al</td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO</td>
<td>4R-Al(_{0.1})</td>
<td>FAU-Al(_{0.1})</td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
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<tr>
<td>SiO(_i)</td>
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<td>SiO(_i)</td>
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<td>SiO(_i)</td>
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<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_i)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The latter figures are averages over all possible O\(_{2}\) substitution sites. The subscript NN denotes nearest neighbor to the Al substituent; SiO\(_i\) denotes Si atoms connected to an OH group.
Zeolites versus Aluminosilicate Clusters

Table IV. Force Field Parameters for Si, Al, P, O, Na, and O₆

<table>
<thead>
<tr>
<th>species</th>
<th>( \alpha \rightarrow \alpha )</th>
<th>( A_{\alpha \alpha} ) (eV)</th>
<th>( b_{\alpha} ) ((^A))</th>
<th>( C_{\alpha \alpha} ) (eV (^B))</th>
<th>charges ( q_\alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>1388.7730</td>
<td>2.7600</td>
<td>175.0000</td>
<td>-1.20</td>
<td>q₉ = -1.20</td>
</tr>
<tr>
<td>O-P</td>
<td>9747.0105</td>
<td>3.8799</td>
<td>175.0000</td>
<td>-0.20</td>
<td>q₉ = -0.20</td>
</tr>
<tr>
<td>Na-O</td>
<td>18003.7572</td>
<td>4.8733</td>
<td>133.5381</td>
<td>2.80</td>
<td>q₉ = 2.40</td>
</tr>
<tr>
<td>Si-Si</td>
<td>26949.7285</td>
<td>5.0388</td>
<td>176.6941</td>
<td>1.40</td>
<td>q₉ = 1.40</td>
</tr>
<tr>
<td>Al-Al</td>
<td>1434.0434</td>
<td>4.8156</td>
<td>190.5516</td>
<td>1.46</td>
<td>q₉ = 1.46</td>
</tr>
<tr>
<td>Al-O</td>
<td>9419.8558</td>
<td>5.4150</td>
<td>120.5589</td>
<td>2.40</td>
<td>q₉ = 2.40</td>
</tr>
<tr>
<td>P-O</td>
<td>9034.2080</td>
<td>5.1909</td>
<td>19.8793</td>
<td>1.35</td>
<td>q₉ = 1.35</td>
</tr>
<tr>
<td>Na-O</td>
<td>3542.2072</td>
<td>4.1345</td>
<td>0.0000</td>
<td>1.00</td>
<td>q₉ = 1.00</td>
</tr>
<tr>
<td>Si-O-Al</td>
<td>( k = 0.5334 ) (eV rad⁻¹)</td>
<td>( \phi_\theta = 82.86 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-O</td>
<td>1388.7730</td>
<td>2.7600</td>
<td>175.0000</td>
<td>-1.20</td>
<td>q₉ = -1.20</td>
</tr>
<tr>
<td>Si-Si</td>
<td>37139.8950</td>
<td>6.6553</td>
<td>175.0000</td>
<td>-0.70</td>
<td>q₉ = -0.70</td>
</tr>
<tr>
<td>Al-Al</td>
<td>18003.7572</td>
<td>4.8733</td>
<td>133.5381</td>
<td>2.40</td>
<td>q₉ = 2.40</td>
</tr>
<tr>
<td>Si-O</td>
<td>14031.8388</td>
<td>4.7900</td>
<td>101.0583</td>
<td>1.35</td>
<td>q₉ = 1.35</td>
</tr>
<tr>
<td>Al-O</td>
<td>8566.5434</td>
<td>4.6622</td>
<td>73.0913</td>
<td>1.35</td>
<td>q₉ = 1.35</td>
</tr>
<tr>
<td>Al-O</td>
<td>3237.5079</td>
<td>4.0360</td>
<td>32.2857</td>
<td>1.46</td>
<td>q₉ = 1.46</td>
</tr>
<tr>
<td>Si-O-Al</td>
<td>( k = 0.7099 ) (eV rad⁻¹)</td>
<td>( \phi_\theta = 82.86 )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The symbol O₆ refers to an effective atom representing a protonated oxygen. The force fields between blank lines form internally consistent sets. The first uses a formal charge difference (\( \phi_\alpha = 1.00 \)). The subsequent sets are for \( \phi_\alpha = 0.50, 0.96, \) and 0.48. Fixed during optimization.

Table V. Bond Distances (\( A \)) and Bond Angles (degrees) of the Geometry-Optimized \((\text{OH})_3\text{Si-(OH)}-\text{Al(OH)}_2\) Dimer

<table>
<thead>
<tr>
<th>bond</th>
<th>distance/angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO</td>
<td>1.611</td>
</tr>
<tr>
<td>SiOH</td>
<td>1.670</td>
</tr>
<tr>
<td>AlO</td>
<td>1.714</td>
</tr>
<tr>
<td>AlOH</td>
<td>1.995</td>
</tr>
<tr>
<td>OHO</td>
<td>0.960</td>
</tr>
<tr>
<td>SiOHAl</td>
<td>138.8</td>
</tr>
<tr>
<td>OSiOH</td>
<td>106.6</td>
</tr>
<tr>
<td>OAIH</td>
<td>99.4</td>
</tr>
</tbody>
</table>

The potential energy surface of a \((\text{OH})_3\text{Si-(OH)}-\text{Al(OH)}_2\) dimer (Figure 1). This potential energy surface was calculated at the RHF-SCF level, using the valence part of the 6-31G* basis and employing effective core potentials for the core electrons. Relevant distances, angles, and Mulliken populations of the geometry-optimized dimer are given in Table V. Note that the Al-O distances. This is accompanied by a significant reduction of the O-H-Al angle with respect to the tetrahedral angle. Similar distortions are reported in the literature.

Starting from the geometry-optimized structure (see Table III), the potential energy surface was sampled for four different distortion modes drawn in Figure 1. The Si-O and Al-O bond lengths were varied from 1.35 to 1.95 \( A \) and from 1.55 to 2.15 \( A \), respectively. The O-Si-OH and O-Al-OH angles between 70 and 130°, and the Si-O-Al angle between 120 and 160°. For each configuration of the \((\text{OH})_3\text{Si-(O)-Al(OH)}_2\), the hydrogen position within the bridging hydroxyl group was optimized. The optimized of the hydrogen position is imposed by the effective atom approach. We implicitly assume that the proton position is always ideal, i.e., not hindered by geometrical constraints of, e.g., the zeolite lattice. The O-O interaction was determined from the O-T-O bending modes. Subsequently, the Si-OH and Al-OH interaction could be determined from the stretching modes.

It appeared to be necessary to include a bond bending term to account for the rigidity of the Si-OH-Al angle. The 3-coordination of oxygen in a bridging hydroxyl group results in an increased stiffness of this bending mode by a factor of 10 with respect to the Si-O-Si and Si-O-Al bending modes. This makes it necessary to include a bond bending term to account for the rigidity of the Si-OH-Al angle. The form chosen here is quadratic:

\[
\phi_{\theta}(\theta_{\phi}) = \frac{1}{2}(\theta_{\phi} - \theta_{0})^2
\]

The \( \phi_\theta \) force field parameters are given in Table IV, together with the previously published parameters.

The first set of parameters that was determined was based on the use of formal charge differences (\( \phi_\alpha = 1.00 \)), between Al and Si, and between O and O₆. As the Mulliken charge analysis of electron distribution in clusters indicates that the actual charge separation between Si and Al is much less pronounced, we derived an additional force field which assumes charge differences that have half the formal values. This is the second force field in Table IV.

Finally, a set of force fields has been developed that may be used for a "bare" aluminosilicate, i.e., without external compensating charge. In this case, we assume that the negative charge that is introduced by the aluminum atom is compensated by a slight increase in the silicon charge. Two consistent Si/Al force fields have been derived for charge separations of 0.48 and 0.96 between aluminum and silicon. All force fields, given in Table IV, have been fit to the same ab initio potential energy surface as the one used to determine the generic (\( \phi_\alpha = 1.00 \)) force field. Unless mentioned otherwise, the results presented were obtained with the \( \phi_\alpha = 1.00 \) force field.

2.3. Lattice Energy Minimization Calculations. Rigid-ion lattice energy minimization results were obtained by constant-pressure energy minimization. In this method, both atomic positions and unit cell parameters are varied till the net force on all atoms is zero. The long-range Coulomb interaction is evaluated via the Ewald summation; the short-range interactions are truncated at a cutoff radius of 10 Å. The Si-O-Al bond valence term is evaluated only for the two T atoms nearest to the O. In all cases, the experimental structure was used as a starting point. Care is taken to ensure that optimized structures correspond to energy minima by checking that all vibrational frequencies are positive. Therefore, the minimum-energy structures correspond to stable (global) minima. This is confirmed by a molecular dynamics study by Tsuneyuki et al., who show that a force field of the type used here produces thermodynamically stable SiO2 polymorphs.

For the twenty-four SiO2 polymorphs listed in Table VI and the seven AlPO4 polymorphs listed in Table VII, an energy minimization has been performed, starting from the experimental crystal geometries. The term 3+ sodalite refers to a hypothetical structure (supersodalite), obtained by replacing the Si atoms by SiO2 tetrahedra consisting of four fused three-ring structures (hence, 3+). For the SiO2 systems, additional calculations were performed with a 3-Å cutoff radius, to probe the effect of truncation of the short-range potential. For all structures, we have tabulated the smallest ring(s) that can be identified, the framework density, following a scheme that will be presented in section 2.4. Additionally, the relative energy with respect to a-quartz (Em) is given. These numbers have been corrected for a spurious dependence on the framework density, following a scheme that will be presented in section 2.4. As indicated in the Introduction, acid zeolites that are of catalytic interest have part of the silicon atoms replaced by aluminum or other trivalent cations. We will consider here the isomorphic substitution of silicon by aluminum. The framework of the resulting aluminosilicate becomes negatively charged. Replacement of silicon by aluminum in a free cluster induces considerable changes in the interatomic distances and angles, as can be seen from the data on geometry-optimized small clusters shown in Table VII.

With a view to probing the structural relaxation of an aluminum substitution in a silica four ring (ab Initio, 3-21G) and in Faujasite (Molecular Mechanics)* as a starting point. Care is taken to ensure that optimized structures correspond to energy minima by checking that all vibrational frequencies are positive. Therefore, the minimum-energy structures correspond to stable (global) minima. This is confirmed by a molecular dynamics study by Tsuneyuki et al., who show that a force field of the type used here produces thermodynamically stable SiO2 polymorphs. For the twenty-four SiO2 polymorphs listed in Table VI and the seven AlPO4 polymorphs listed in Table VII, an energy minimization has been performed, starting from the experimental crystal geometries. The term 3+ sodalite refers to a hypothetical structure (supersodalite), obtained by replacing the Si atoms by SiO2 tetrahedra consisting of four fused three-ring structures (hence, 3+). For the SiO2 systems, additional calculations were performed with a 3-Å cutoff radius, to probe the effect of truncation of the short-range potential. For all structures, we have tabulated the smallest ring(s) that can be identified, the framework density, following a scheme that will be presented in section 2.4. As indicated in the Introduction, acid zeolites that are of catalytic interest have part of the silicon atoms replaced by aluminum or other trivalent cations. We will consider here the isomorphic substitution of silicon by aluminum. The framework of the resulting aluminosilicate becomes negatively charged. Replacement of silicon by aluminum in a free cluster induces considerable changes in the interatomic distances and angles, as can be seen from the data on geometry-optimized small clusters shown in Table VII.

With a view to probing the structural relaxation of an aluminum substitution in a silica four ring (ab Initio, 3-21G) and in Faujasite (Molecular Mechanics)*

Table VII. Energy Content of Different AlPO4 Polymorphs, Using a 10-Å Cutoff a

<table>
<thead>
<tr>
<th>framework</th>
<th>C.O. = 10 Å</th>
<th>type</th>
<th>rings</th>
<th>E</th>
<th>Em</th>
</tr>
</thead>
<tbody>
<tr>
<td>berlinite 41</td>
<td>6</td>
<td>24.52</td>
<td>-5716.59</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>AEL</td>
<td>4, 6</td>
<td>18.35</td>
<td>-5693.12</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>AI</td>
<td>4, 6</td>
<td>15.87</td>
<td>-5688.74</td>
<td>-5.0</td>
<td></td>
</tr>
<tr>
<td>SOD</td>
<td>4, 6</td>
<td>15.84</td>
<td>-5683.20</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>ERI</td>
<td>4, 6</td>
<td>14.95</td>
<td>-5676.27</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>VPI-5</td>
<td>4, 6</td>
<td>13.49</td>
<td>-5667.71</td>
<td>-1.9</td>
<td></td>
</tr>
<tr>
<td>FAU</td>
<td>4, 6</td>
<td>12.11</td>
<td>-5668.97</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

**Symbols and units are the same as in Table II.**

Table VIII. Relaxation Energy (kJ/mol) of an Aluminum Substitution in a Silica Four Ring (ab Initio, 3-21G) and in Faujasite (Molecular Mechanics)*

<table>
<thead>
<tr>
<th>system</th>
<th>δE</th>
<th>system</th>
<th>δQ</th>
<th>δE</th>
</tr>
</thead>
<tbody>
<tr>
<td>4R-Al</td>
<td>114.3</td>
<td>FAU-Al</td>
<td>0.96</td>
<td>107.0</td>
</tr>
<tr>
<td>4R-AlNa</td>
<td>129.2</td>
<td>FAU-AlNa</td>
<td>1.00</td>
<td>119.3</td>
</tr>
<tr>
<td>4R-AlOAl</td>
<td>211.4</td>
<td>FAU-AlOAl</td>
<td>1.00</td>
<td>304 ± 9</td>
</tr>
</tbody>
</table>

*For FAU-AlOAl, the numbers are averaged over all possible Ox substitution sites.
were performed on faujasite with one aluminum substitution per unit cell of 48 T atoms.\textsuperscript{42} The reference structure was all-silica faujasite (FAU-Si) as determined by lattice energy minimization with the force field of Table IV. The difference in formal charge between 4-coordinated silicon and aluminum renders the framework negatively charged. To compensate for this charge, we will consider three models that are analogous to the three quantum chemical models.

In the first model (FAU-Al), the compensating charge is distributed over all remaining silicon atoms. This corresponds to the physical situation where the compensating charge is spread out evenly over space. This makes the model insensitive to the precise location of the compensating charge. Two calculations have been performed with different charge separations between Si and Al ($Q = 0.48$ and 0.96). This allows us to check the sensitivity of our answers with respect to variations in the degree of covalency or ionicity of the system. The force fields, discussed in the previous section, are given in Table IV. Table VIII lists the relaxation energies for each of these force fields. The relaxation energy is defined as the energy difference between the aluminum substitution in the FAU-Si structure and that in the fully relaxed structure.

The second model (FAU-AlNa) has a sodium ion to compensate for the negative framework charge. In a first calculation, the Na$^+$ position is optimized with respect to the framework that has the FAU-Si geometry. This calculation provides the energy reference value of the unrelaxed structure. Subsequently, the structure is fully optimized to obtain the energy of the relaxed system.

Finally, in the third model, we consider substitution of aluminum combined with the attachment of a proton to a neighboring oxygen atom. The model (FAU-AlO$_3$) has four realizations, because of the four different oxygen atoms with the asymmetric unit of faujasite. The results on relaxation energy and relaxed structure are averaged over the four substituted configurations.

The resulting relaxation energies ($6E$) are given in Table VIII; structural parameters, such as bond distances and angles, for the various models are given in Table III. Figure 2 shows a graphic representation of the framework relaxation around one of the AI/OH substitutions in faujasite. Note that the lattice distortion is very localized, i.e., confined almost to nearest neighbors of Al and O$_2$H. As seen from Table III, the local geometry resembles very closely the optimized geometry of the FAU-Si structure and that in the fully relaxed structure.

The potential energy function. As discussed in a previous paper,\textsuperscript{22} this term is defined as the energy difference between the aluminum substitution in the FAU-Si structure and that in the fully relaxed structure.

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Values of 6.6, 41, 33, and 25 eV Å² result for the O-O, Al-O, Si-O, and P-O interactions, respectively; up to 30 times less than those used in the force field (Table IV).

It is this overestimation of the \( r^4 \) term that leads to a spurious density dependence of the total energy. Figure 4 shows the atom-atom pair correlation function, \( G(r) \), for \( \alpha \)-quartz and zeolites MOR and FAU. We have defined \( G(r) \) as

\[
G(r) = \frac{1}{4\pi r^2 N} \sum_{i<j} \delta(|\mathbf{r}_i - \mathbf{r}_j| - r)
\]

where \( i \) runs over all \( N \) atoms in a unit cell. Note that the first coordination shells are identical for all systems. Beyond 4 Å, \( G(r) \) is system-dependent and rapidly converges to the bulk density \( \rho_{\text{B}} \). As a consequence, the lattice energy contains a contribution, \( \Phi_2(\mathbf{R}) \), which is linearly dependent on the framework density:

\[
\Phi_2(\mathbf{R}) = \Phi_2^{\text{ph}}(\mathbf{R}) = \sum_{i,j} c_{i,j} r_{ij}^6 + \sum_{i,j,k} c_{i,j,k} r_{ij}^{12} + \sum_{i,j,k,l} c_{i,j,k,l} r_{ij}^{18}
\]

\[
\Phi_2(\mathbf{R}) = \int_{R_{CO}}^{\infty} \frac{R_{CO}}{r^5 \rho_{\text{B}}} \left\{ \frac{1}{r^2} - \frac{1}{R_{CO}^2} \right\} d\mathbf{r} = \Phi_2(\mathbf{R}) - \frac{4\pi}{3} (2c_{\text{COO}} + c_{\text{SO}_2}) \int_{R_{CO}}^{\infty} \frac{R_{CO}}{r^5 \rho_{\text{B}}} d\mathbf{r}
\]

\[
\Phi_2(\mathbf{R}) = \Phi_2(\mathbf{R}) - \frac{4\pi}{3} (2c_{\text{COO}} + c_{\text{SO}_2}) \left\{ \frac{1}{R_{CO}^2} \right\}
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\]

\[
G_2(\mathbf{R}) \text{ is the type-selective pair correlation function, defined as in eq 4, and } \mathbf{R} \text{ runs over all atom types; } R_{CO} \text{ and } R \text{ denote the cut-off radius and the physically relevant range of the } r^4 \text{ term, respectively.}
\]

The relation between framework density and lattice energy as found in the energy minimizations of the 21 "regular" SiO₂ frameworks is accurately described by the relation

\[
E = -5509.612 - 4.55639\rho_{\text{B}}
\]

for the calculations with a cutoff radius of 10 Å and by the relation

\[
E = -5502.218 - 3.34876\rho_{\text{B}}
\]

when a 5-Å cutoff radius is used. Energies are in kilojoules per mole of SiO₂, and the framework density is in Si atoms per 1000 Å³. The difference between the 10 and 5 Å slopes (1.20 Å²/mole) should be accounted for by \( r^4 \) contributions from pairs of atoms that are between 5 and 10 Å apart. Using eq 5 with \( R = 5 \) Å, we calculate 1.37 Å²/mole, thus corroborating the idea that the density dependence stems from the \( r^4 \) term. Taking this idea one step further, we may calculate the value for \( R \) that would eliminate the density dependence completely. One finds that \( R = 3.45 \) and 3.41 Å for the data sets obtained by using \( R_{CO} = 10 \) and 5 Å, respectively. This value for \( R \) corresponds with the next-nearest-neighbor distance. If one subtracts this spurious contribution to the energy, the total energy content for all silicon networks is the same to within 10 kJ/mol and essentially independent of framework density.

The data for a series of AlPO₄ polymorphs show exactly the same trend. Energy contents for benilite and six microporous AlPO₄ networks are given in Table VII. The optimal relation between energy content and framework density is

\[
E = -5623.860 - 3.79207\rho_{\text{B}}
\]

for \( R_{CO} = 10 \) Å. The slope can be correlated with the slope of the SiO₂ networks: Their ratio should, according to eq 5, be given by

\[
\frac{4c_{\text{COO}} + 2c_{\text{SO}_2}}{4c_{\text{COO}} + c_{\text{AlO}} + c_{\text{PO}}} = 1.14
\]

in reasonable agreement with the ratio between the slopes in eq 6 and 8 (4.56/3.79 = 1.20). The remaining differences in lattice energies between the polymorphs are less than 10 kJ/mol TO₂, identical with the spread in the SiO₂ energies.

The theoretical predictions for SiO₂ polymorphs are compiled in Figure 5, where a comparison is made with experimental data of Johnson et al.\(^{43}\) It is gratifying that the prediction for "spiro-five-ring" correlates so well with experiment. As argued in a previous paper,\(^{49}\) the accuracy with which our force field models this compound, which has Si coordinated

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(46) Since the force field parameterization was done on the basis of ab initio results using a 6-31G basis, it is fair to make the quantitative comparison with the 3-21G results, rather than with the STO3G results.
The magnitude of the excess energy associated with three-ring structures is such that it seems highly unlikely, if not impossible, that SiO₂ polymorphs can be synthesized with a large number of three-ring units in the structure. Incorporation of other framework elements may lift this prohibition, as indicated by the presence of beryllium in the spinel-like structure of luzodarite and by the 3⁴ units found in germanium sulfides.²⁵

The other question that can be answered on the basis of a comparison of ab initio and force field results relates to the geometric relaxation around an aluminum substitution in an all-silica lattice. Resolving the local structure around such a substitution is of great importance for our understanding of the acidity of zeolites. A recent paper by Corbin et al.⁴⁷ provides experimental evidence for the extreme flexibility of the zeolite lattice (in that case, zeolite RHO). In their work, the researchers are not able to discriminate between silicon and aluminum atoms. Instead, they work with effective T atoms. Only in the case of zeolites with a 1:1 Si:Al ratio, does the Si/Al ordering induced by Löwenstein's avoidance rule enable a structure refinement where one can discriminate between Al and Si. For low aluminum loadings, such structural refinement is impossible. It is here that accurate theoretical modeling can be of help.

In nature, charge compensation comes either from protons, attached to (neighboring) oxygen atoms, or from cations (e.g., Na⁺) in the pores of the zeolites. In our calculations, these possibilities are covered by the model systems 4R-AlOH and FAU-AlOH, respectively, 4R-AlNa and FAU-AlNa. Additionally, we have considered the case where charge compensation is completely delocalized (4R-Al and FAU-Al). A study of Table III reveals a remarkable feature of all models. The local geometry changes that occur near an aluminum substitution are virtually the same in the cluster models as in the extended models. In spite of the long-range electrostatic forces within zeolites, which we explicitly account for in our force field model, the reconstruction of the lattice is a purely local phenomenon. This spatial confinement is also illustrated by Figure 2.

A rationale for the above lies in the order of magnitude difference between the bond stretching and bond bending of the Si-O-Si and Si-O-Al angles. Whereas the Si-O distances are invariant from one zeolite to the next, the Si-O-Si angle varies between 130 and 180°, to allow vastly different network topologies and structures. Just as the angles change from one zeolite to the next, so do they upon substitution of a framework atom. The distance differences are accommodated in the infinite network by a slight adjustment of the next angle on oxygen.

The coupling between the locality of distortions and the weakness of the Si-O-Si bond bending implies that the reliability of the results depends primarily on the accuracy with which this bond bending is accounted for in the force field. Previous work²² indicates that the vibrational frequencies that correspond to bond bending are predicted slightly too high by the force field. This would imply that, in reality, the above-described effect of accommodation of distance differences by bond bending is even stronger.

Apart from insight into the geometry of a framework substitution, we have obtained information on the relaxation energy of substitutions. The data of Table VIII show the same ordering of relaxation energies for different models of charge compensation within the ab initio and the force field approach. Perhaps the most striking thing about the relaxation energies is their similarity in the cluster models and extended structures. The predicted relaxation energies of the 4R-Al and FAU-Al, as well as the 4R-AlNa and FAU-AlNa models, are mutually the same to within 10 kJ/mol. This points (i) to the reliability of the force field and (ii) to the freedom of the embedded cluster. For the models that have an acidic proton as the charge-compensating entity, the correspondence is somewhat less, but the discrepancy is significantly reduced if one lowers the charge separation δQ between Al and O₆ from 1.0 to 0.5. The latter value is in better agreement with the Mulliken charges found in the ab initio calculations on the 4R-AlOH model. The difference by a factor of 2 in relaxation energies between Al and AlNa models on the one hand (δE ≈ 100 kJ/mol) and the AlOH models on the other (δE ≈ 200 kJ/mol) can be correlated with the number of T centers that are distorted: one (the Al center) in the case of Al and AlNa and two (Al and SiOH) in the AlOH case.

In conclusion, just as in all-silica zeolites, Al-containing zeolites can accommodate ring structures virtually without strain. The structural relaxation induced by the appreciable bond length differences remain local; the relaxation energy involved is approximately 100 kJ/mol per distorted T site.

The evidence compiled in this paper for the comparative "freedom" of embedded aluminosilicate clusters has important consequences for the value that can be attached to various quantum chemical results on aluminosilicate clusters. The foremost conclusion is that quantum chemical calculations on small, geometry-optimized clusters provide a good basis for the study of electronic properties of zeolites, attachment of acid protons, etc. As shown in this paper, it is essential to include relaxation effects when isomorphous framework substitution or proton attachment is studied. The very presence of relaxation causes the site of disturbance to behave as in isolated geometry-optimized clusters.

This idea is completely opposite to the reasoning behind the calculations on substitutional energy by Derouane and others,¹⁵-¹⁷ who calculate differences in substitution energy from quantum chemical calculations on clusters with the "experimental" geometry. This implies a complete neglect of the relaxability of the zeolite lattice, which we have shown to be overriding important.

4. Conclusion

A combination of quantum chemical calculations on aluminosilicate clusters and force field calculations on extended systems reveals that small clusters are virtually strainlessly embedded within an extended system, which justifies their use as model systems for the theoretical study of zeolites.⁴⁸

In the case of all-silica systems, we have shown that all experimentally known four-connected silica polymorphs have lattice energies that are the same to within 10 kJ/mol, not much different from the energy differences found between four-, five-, and six-ring clusters, and in accordance with the few experimental data. All-silica three-ring clusters are energetically less favorable, which might explain their absence in nature.

The freedom of substructures was shown to have important consequences for the deformation of the silica lattice around an aluminum substitution. This work is a first attempt to give a realistic theoretical description of these distortions. It was found that the relaxation is very local. Locally, the Al-O bonds adopt the same length as in a cluster, due to the flexibility of the Si-O-Si and Si-O-Al angles.
