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AB INITIO CALCULATIONS ON RING-SHAPED SILICA CLUSTERS

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Hartree–Fock SCF calculations have been performed on four ring-shaped clusters, $H_{2n}Si_nO_{3n}$, where n ranges from 3 to 6. These clusters consist of a number of n linked SiO_4 tetrahedra. with the dangling oxygen bonds saturated with hydrogen atoms. C_{nv} symmetry was imposed. For each cluster, first a geometry optimisation was performed using the STO3G basis set. This optimisation was followed by a single point calculation using the more flexible 6-31G split-valence basis set. Geometries and total energies of the clusters were compared.

Si–O bondlengths are found to decrease as the ringsize increases. The total energy per elementary building unit decreases similarly. The differences found between the rings for $n = 4$, 5 and 6 are very small. The 3-ring on the other hand is significantly different in both geometry (longer bondlengths, smaller bond angles) and total energy (less stable).

These results support the view that the relative stability of aluminium-free zeolite lattices, containing many rings of linked tetrahedra, is not determined by local bonding effects, and will be insensitive to the particular lattice structure.

1. Introduction

This study has been undertaken to determine whether particular lattice topologies are preferred in low-aluminium zeolites. Aluminium-free zeolites can be considered to be three-dimensional networks of vertex-connected SiO_4 tetrahedra. A detailed study of the stability of zeolite lattices is complicated by the large number of atoms in a unit cell, typically a few hundred. At present this number is still far too large to allow a complete description with *ab initio* methods. A number of other methods have previously been used to treat the problem of the stability of zeolite lattices, of which we mention in particular the cluster calculations using the semi-empirical extended Huckel method [1] and lattice relaxation techniques [2,3]. The present study uses an *ab initio* quantum chemical approach to compute geometries and energies of the ring systems from which zeolite lattices can be considered to be constructed.

Assuming that bonding in silica crystals is similar to bonding in appropriately chosen smaller clusters, as indeed has been shown in a number of cases, see e.g. [4,5], and assuming that local bonding effects provide the dominating stabilisation mechanism in alumina-free silica's, one expects differences in lattice energies to be reflected in smaller systems as well. For this purpose SCF calculations were performed on four ring-shaped clusters, containing 3, 4, 5 or 6 linked tetrahedra respectively.

2. Details of the calculations

The clusters we considered consist of a number of n SiO_4 tetrahedra, coordinated in such a way that a ring structure results. Each oxygen in the ring is shared by two tetrahedra. Hydrogen atoms were used to terminate the dangling oxygens. The fraction $SiO(OH)_2$ can be seen as the elementary building unit, occurring n times in the n-membered ring.

For practical considerations, since a full geometry optimisation (i.e. adjusting all internal coordinates) is rather costly for clusters of these sizes (notably for $n = 5$, 6), the constraint of C_{nv} symmetry was imposed, making the elementary units symmetry equivalent. This reduces the number of independent internal variables to 11, the most important ones being the Si–O bondlength and the Si–O–Si and O–Si–O bending angles within the ring.

The geometry optimisations were done using a STO3G minimal basis set. Although the variational flexibility of this basis set is limited, it is known that it often yields reliable geometries. After the geometry optimisation a single-point calculation was carried out using the 6-31G split valence basis [7] for the silicon and oxygen atoms, and the STO3G basis for the terminating hydrogens. The calculations were performed with the *ab initio* package GAMESS running on a Cray XMP/14 and a Cyber 205.

3. Geometries and total energies

Data for the optimised structures (STO3G basis) are presented in tables 1a, b and figs. 1a, b, c. Clear trends are visible in Si–O distances and Si–O–Si angles as a function of ring size. The Si–O distance shortens with growing ring size, whereas the Si–O–Si angle increases. This trend, which can be explained in terms of changes in the hybridisation of the oxygen orbitals, is in accordance with earlier results [6,8]. The differences in the geometric data rapidly diminish when we pass from the 3-ring to the 6-ring. For instance, the Si–O bondlength in the 3-ring is found to be more than 0.02 Å larger than those in the 4-ring, whereas the decrement is 0.007 and 0.003 Å for $n = 5$ and $n = 6$, respectively. A similar behaviour is seen for the Si–O–Si and O–Si–O angles. In particular, the O–Si–O angle in the 3-ring deviates considerably from the perfect tetrahedral angle of 109.5°. Bond angles and bond lengths not belonging to the ring frame, table 1b, are seen to be insensitive to the ringsize as can be expected.

Table 1a
STO3G equilibrium geometry of ring frame. Distances in Ångstrom, angles in degrees

	3	4	5	6
Si–O	1.622	1.602	1.595	1.592
Si–Si	2.942	3.042	3.063	3.067
Si–O–Si	130.2	143.5	147.5	148.8
O–Si–O	105.7	108.3	108.4	108.1

Table 1b
Equilibrium geometry of some other parameters

	3	4	5	6
Si–(OH)	1.647	1.648	1.649	1.648
	1.650	1.650	1.651	1.652
Si–O–H	109.3	109.3	109.3	109.3
	110.7	110.5	110.5	110.6
O–H	0.981	0.981	0.981	0.981
	0.981	0.981	0.981	0.981
O–Si–OH	111.3	111.0	111.2	111.4
	111.2	110.5	109.9	110.0

Table 2a gives the total energies (STO3G basis) in the optimised geometries. The relevant quantity of interest is the total energy $E_n = E/n$ per elementary unit $SiO(OH)_2$ in the n-membered ring. This energy is given in the second entry of the table. It is seen that E_n gradually decreases, implying greater stability, with increasing n. Table 2b shows the absolute value of their differences $E_m - E_n$, expressed in both kJ/mol and kcal/mol. The calculated differences between the 4-, 5- and 6-rings are very small, however, even less than 1 kJ/mol. The 3-ring, on the other hand, appears to be less stable, E_3 being some of 9 kJ/mol higher than E_4, E_5 and E_6.

This general picture remains the same when the 6-31G split valence basis set is employed (table 3): $E_3 > E_4 > E_5 > E_6$. Energy differences are more pronounced though: E_6 differs some 24–30 kJ/mol from E_4, E_5 and E_6. The difference of 0.9 kJ/mol between E_5 and E_6 still is very small. However, one should use these figures with some reserve, since they correspond to geometries which were optimised in the STO3G basis.

In order to investigate whether the conclusions would depend strongly on the particular choice of basis set we experimented with various other basis sets on the dimer $H_6Si_2O_7$. This cluster has also been studied by a number of other authors (e.g. [4] and references therein). Figures 2a to 2d show contour plots of the total energy versus Si–O bondlength and Si–O–Si bridging angle for this dimer, calculated from a number of SCF calculations with the following basis sets: STO3G (2a), the split valence basis set 3-21G (2b), 3-21G augmented with a

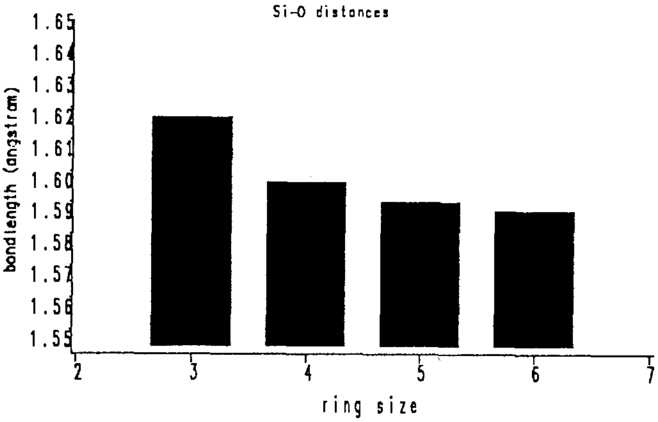

Fig. 1^a. Si-O bondlength in optimised geometries.

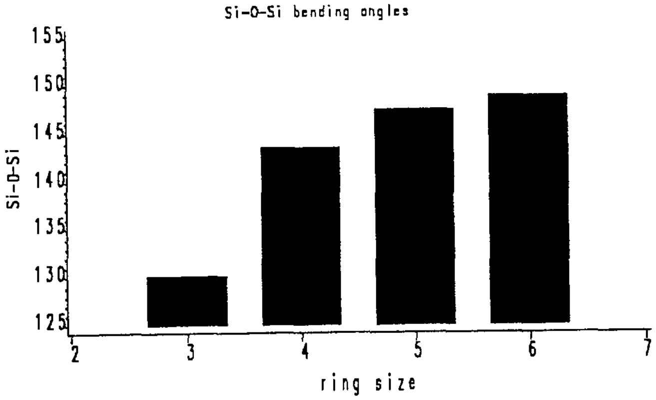

Fig. 1^b. Si-O-Si angle in optimised geometries.

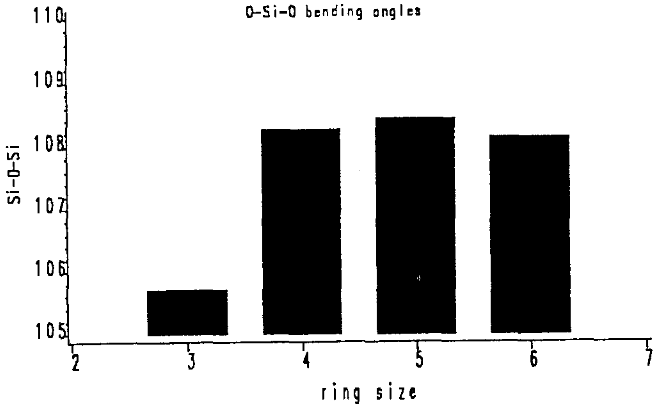

Fig. 1^c. O-Si-O angle in optimised geometries.

Table 2a
Total energies (STO3G basis) in a.u.

	3	4	5	6
E	−1525.236192	−2033.661883	−2542.078916	−3050.494793
$E_n = E/n$	−508.412064	−508.415471	−508.415783	−508.415799

Table 2b
Absolute differences $\lvert E_m - E_n \rvert$. Upper triangle: kcal/mol. Lower triangle: kJ/mol.

ΔE_n	3	4	5	6
3		2.14	2.33	2.34
4	8.94		0.20	0.21
5	9.77	0.82		0.01
6	9.81	0.86	0.04	

polarisation function on the bridging oxygen (2c) and 3-21G with polarisation functions added on both the silicon atoms and the bridging oxygen (2d). Energies are given in kJ/mol with respect to the global minimum as found for the used basis set. It is seen from these plots that the exact location of the global minimum depends rather strongly on the choice of basis set. Also, details of the curvature of the surface are seen to be basis dependent, implying that these basis sets are not suited for force constant calculations. For the purposes of comparing relative stabilities however, the plots are quite adequate. The energy surface near the minimum is very flat in the four figures. The spacing of the contour levels is rather similar in the figures, indicating that energy differences indeed will depend weakly on the particular basis set.

Table 3a
Total energies (6-31G basis) in a.u.

	3	4	5	6
E	−1544.031606	−2058.745817	−2573.442875	−3088.133435
E_n	−514.677202	−514.686454	−514.688575	−514.688906

Table 3b
Absolute differences $\lvert E_m - E_n \rvert$. Upper triangle: kcal/mol. Lower triangle: kJ/mol.

ΔE_n	3	4	5	6
3		5.8	7.1	7.3
4	24.3		1.3	1.5
5	29.9	5.6		0.2
6	30.7	6.4	0.9	

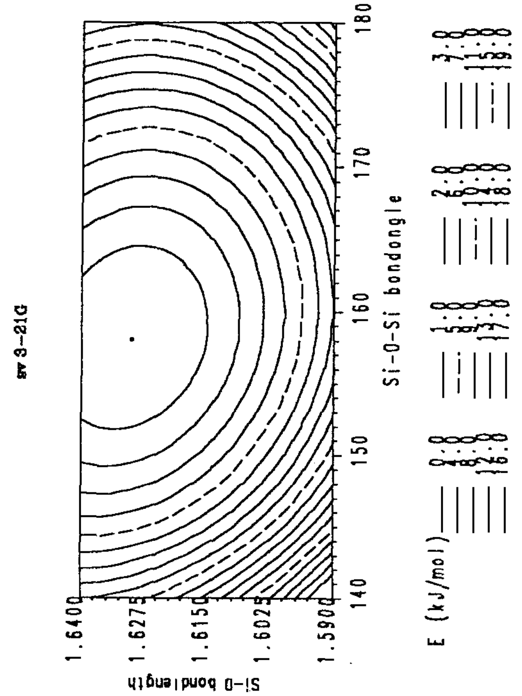
sv 3-21G
Si-O bondlength
1.6400
1.6275
1.6150
1.6025
1.5900
Si-O-Si bondangle
140
150
160
170
180
E (kJ/mol)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0

Fig. 2b.

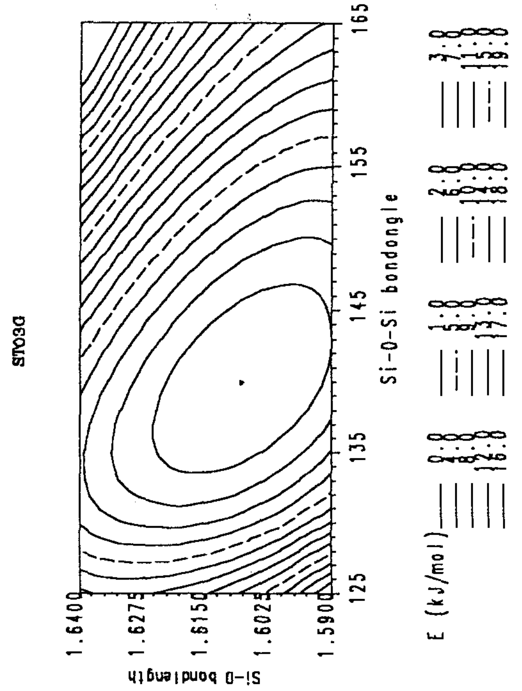
STO3G
Si-O bondlength
1.6400
1.6275
1.6150
1.6025
1.5900
Si-O-Si bondangle
125
135
145
155
165
E (kJ/mol)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0

Fig. 2a.

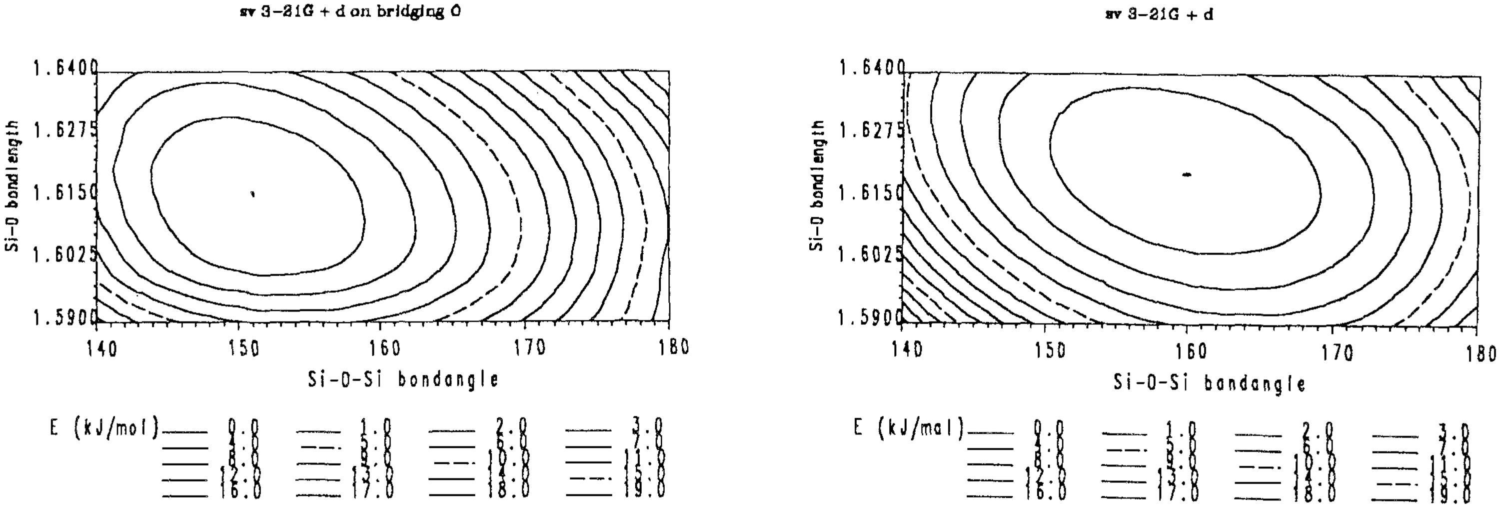

Fig. 2^c.

Fig. 2^d.

Fig. 2. Contour graphs of total energy as function of the Si-O-Si bending angle and Si-O bridging bondlength in the cluster $H_6Si_2O_7$, calculated for different basis sets. The contours correspond to increments of 1 kJ/mol relative to the minimum energy point.

4. Conclusion

It is found that the total energy per elementary unit decreases in the order $E_3 > E_4 > E_5 > E_6$, suggesting for instance that lattices containing many 5-rings will be more stable than lattices with many 4-rings. Networks containing many 3-rings, which are not found in nature, are unlikely to be formed in favour of systems with rings of higher order. However, the results obtained for the 4-, 5- and 6-rings indicate that only very small energy differences between silica networks with different tetrahedral ringsystems will be involved, implying that the stability of pure silica zeolites, in fact, is insensitive to the particular lattice topology. The recent finding [9] that with organic templates not only aluminium-free silicalite, which contains predominantly 5-rings, but also aluminium-free sodalite, which contains 4- as well as 6-rings are formed, appears to agree with these results.

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