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Ab initio calculation of the mechanical strength of the Si–O–Si bond

V. S. YUSHCHENKO, E. D. SHCHUKIN[§]
Institute for Physical Chemistry of the Academy of Sciences of Russia, Leninsky prospect, 31 Moscow, 117915, Russia, [§]and also Department of Material Science and Engineering, John Hopkins University, 34th and Charles Street, Baltimore, MD 21218, USA
M. HOTOKKA
Department of Physical Chemistry, Åbo Akademi University, SF-20500 Åbo, Finland

The theoretical mechanical strength of the Si–O–Si bond has been evaluated by means of *ab initio* RHF/3-21G* calculations on the $Si_2O_7H_6$ molecule simulating the structure of the α-cristobalite crystal. Deformation was applied by increasing the distance between the silicon atoms from equilibrium up to the distance of maximum force. The position of the bridging oxygen has been optimized at each step of deformation. The interatomic force, the total energy, atom charges and overlap population have been calculated as functions of the Si–Si separation. The strength of the structure appears to be equal to 1.1 mdyn, i.e. the theoretical strength of the crystal for fracture along the [0 1 1] plane is equal to 64 GPa. The model used has been found to overestimate strongly the rigidity of the Si–O–Si angle and therefore the elasticity of silica. Nevertheless, the value of the ideal strength (that is determined by the strength of the Si–O bond) may be considered as a reasonable approximation.

1. Introduction

The main purpose of this series is to elucidate the most obvious and "direct" atomic scale mechanism of the Rehbinder effect – the weakening of the mechanical strength of the chemical bond in the surface layer of a solid caused by its interaction with an active environment. The extent of this influence is evaluated by means of an *ab initio* calculation of the force that should be applied to the structure element of the crystal in order to rupture the bond in the presence and in the absence of a molecule of the medium i.e. unlike the usual quantum chemical definition of the bond strength as the *energy* of the interaction, we use this term for the *force* characteristics.

In our previous study [1] we investigated the most important chemical bond in organic nature, the C–C bond. For the present study we choose the most abundant chemical bond in inorganic nature, the Si–O bond that determines the strength of silica and various minerals. The mechanical properties of silica are in themselves interesting even without influence of the environment. Therefore, we have separated these results into individual papers.

In spite of the fact that various properties of silica were studied by means of *ab initio* calculations (the review of these works is far beyond the scope of the present paper and may be found in recent books [2, 3], and references therein) we could not find any investigation of large deformations of the Si–O bond in the silica structure up to its rupture. Thus, for our purposes, the most interesting previous studies in the literature are the calculations of the interatomic potential [2–9], but these studies are performed in a relatively narrow range of Si–O distances, especially in tension deformation. (Compression of silica has been studied to a greater extent owing to its importance in geology. For example the Si–O potential curve calculated by Silvi and Bernard [9] includes the range of bond stretching from – 0.05–0.02 nm). The second point is that while the word "force" is used widely in these papers, we could not find any example of calculation of forces for deformed silica structure, only the energy and force constants (derivatives of forces in equilibrium or the metastable state when forces themselves are equal to zero) in spite of the significance of forces for prediction of the mechanical properties. The forces are also important for the *ab initio* potentials in molecular dynamics calculations (unlike lattice dynamic calculations of vibrations frequencies, MD simulations, especially those of the liquid and amorphous state, demand the force curve for all interatomic distances). Even in materials science where *ab initio* calculations are usually performed for metallic systems (see the paper by Eberhart *et al.* [10] for a review) direct calculations of forces are scarce. An example and a discussion of such calculations are presented in the articles by Painter and Averill [11, 12].

The strength of a real soild material depends on its real defect structure and such conditions of fracture as the temperature, the type of the stressed state, velocity of deformation, etc. It may be evaluated from the data on the strength of the individual interatomic bonds by means of the mechanics of fracture (recent reviews on its application to brittle solids are collected in the books edited by Attkinson [13] and Barber and Meredith [14]). It may also be evaluated by simulation of fracture on a more macroscopic level by the molecular dynamics method as an intermediate step between ultra-microscopic and macroscopic approaches. The material science applications of simulations is now a fast-increasing field (see reviews [15–17], an application to sodium glass [18], and our study of the environmental effect on the fracture [19]. We will not discuss this problem in this article. Only three points should be noted here.

1. Modern approaches relate the fracture with the critical value of the stress intensity factor or the strain energy release rate instead of the ideal strength of the material and stress concentration at the crack tip. Such methods are very convenient and useful because they exclude the unknown and difficult-to-study conditions in the tip of the crack, but they hide the physical nature of the fracture. For prediction of mechanical properties of materials starting from their physical characteristics atomistic approaches (e.g. [20]) should be used.

2. Depending on the material and conditions, the process of fracture may be controlled either by critical stress in the crack tip or by the energy required to perform the single step of fracture. In the latter case the role of the mechanical stresses is (a) to make crack propagation preferable (the Griffith criterion should be fulfilled to ensure that the strain energy release rate exceeds the fracture surface energy) and (b) to facilitate the process that controls the rate of fracture by reducing its activation energy. While analysis of the first item may be done without considering the tip of the crack, the second one demands knowledge of the strain and stress distribution in this region.

3. The ideal strength of a solid is usually evaluated as a portion of its elasticity modulus, usually between $\sim E/10$ and $\sim G/30$, where E and G are the Young's and shear moduli; the latter expression emerges from an analysis of the lattice stability with respect to long-wave shear oscillations. (This approach may fail when dealing with the strength of a real solid because the high stresses are present only in a small zone around the crack tip and the infinite increase of the oscillation amplitude demands a large volume of correlated oscillations). This approach is possible for metals and other crystals with a compact lattice but the elasticity and strength of silica are determined by quite different properties. The initial deformation of silica crystals and glass is related to the changes in Si–O–Si angle while the length of the Si–O bond is almost constant; for example, compression of α-quartz at a pressure 20.7 kbar causes the Si–Si distance to decrease by about 1.3%, but the length of the Si–O bond decreases by less than 0.1% [23]. Therefore the ideal strength of silica (which is determined by the strength of the Si–O bond) is not related directly to its elastic properties and may be much more than $E/10$.

2. Model and methods

The Hartree–Fock method and the 3-21G* basis set are used because a preliminary study [21] has shown that they are suitable for calculation of interatomic forces. Calculations were performed on a VAX-6510 computer using the Gaussian-86 program [22].

The $Si_2O_7H_6$ molecule was chosen as a model of silica. It has the Si–O–Si bond which is the main object of the study and the same nearest neighbours to the silicon atoms as in silica. The rest of the bonds are saturated by the simplest atoms.

In accordance with the suggestion of O'Keeffe and McMillan [23] we have used the Si–Si distance to describe the molecular geometry instead of the Si–O–Si angle. The objective of this study was to chart the dependence of the molecule's properties on this parameter.

The configuration of the molecule was selected to reproduce the structure of the α-cristobalite crystal. This model was chosen owing to its high symmetry. The position of the central oxygen atom was optimized completely at each step of the deformation and the non-bridging oxygens were fixed relative to the Si–Si bond. The Si–O–H bond angles and the torsion angles of the O–H bonds were also set to the values of the corresponding parameters in the cristobalite crystal. These parameters do not undergo optimization. The length of each O–H bond was assumed to be equal and was optimized as a single parameter.

The molecule was deformed by changing the distance between the silicon atoms under the restrictions mentioned above.

Formally, the structure of silica crystals and glass may be considered as consisting of formal Si–Si bonds (realized as two Si–O bonds). The precise properties of these Si–O bonds and the Si–O–Si angle are less important for the analysis of mechanical properties than the Si–Si distance and they are not independent. At least for slow deformations, the oxygen atoms find positions of local minima for any Si–Si bond length which is determined by an external strain. Therefore, in some studies the oxygen atoms may be excluded from the explicit consideration by introducing formal Si–Si bonds which include them implicitly. For example, in molecular dynamics calculations (especially in static ones) this approach may reduce the number of atoms by a factor of three times and/or allow the size of the system to be increased.

3. Results and discussion

3.1. Optimization of the unstrained molecule

The geometrical parameters from optimization of the structure of the unstrained molecule are listed in Table I together with the experimental values for α-cristobalite [24] and α-quartz [25]. The results of a full optimization of the $Si_2O_7H_6$ molecule at RHF/6-31G* level [5] are also given in Table I. It is interesting to note that the present values for both Si–O distances and for the Si–O–Si angle are in better agreement with the experiment for α-quartz than the

TABLE I Optimized parameters of the non-strained $Si_2O_7H_6$ molecule in comparison with results of complete optimization in 6-31G* basis set [5] and experimental data for α-quartz [25] and α-cristobalite [23].

	RHF/3-21G* this work	RHF/6-31G* [5]	α-quartz [25]	α-cristobalite [23]
Si–Si (nm)	0.31102	0.30230	0.3059	0.3072
Si1–O br. (nm)	0.16085	0.16159	0.1605	0.1604
Si2–O br. (nm)	0.16196	0.16265	0.1614	0.1604
nbr.O–H (nm)	0.09481	0.0945–0.095	–	–
Si–O–Si (deg.)	148.9	137.6	147.3	146.4

TABLE II Results of Mulliken population analysis: charges of heavy atoms and Si–O bond overlap populations

Atom	Charge	Bond	Overlap
nbr.O1	− 0.8295	nbr.O1–Si1	0.3503
nbr.O2	− 0.8214	nbr.O2–Si1	0.3678
nbr.O3	− 0.8173	nbr.O3–Si1	0.3721
nbr.O4	− 0.8149	nbr.O4–Si2	0.3711
nbr.O5	− 0.8234	nbr.O5–Si2	0.3616
nbr.O6	− 0.8200	nbr.O6–Si2	0.3667
⟨nbr.O⟩	− 0.8216	⟨nbr.O–Si⟩	0.3646
Si1	1.5786	br.O–Si1	0.3380
Si2	1.5879	br.O–Si2	0.3222
br.O	− 0.8446		

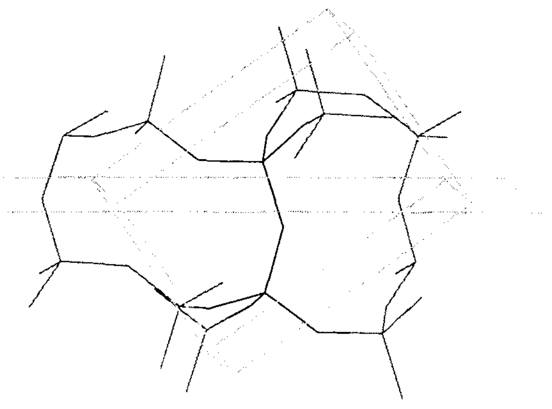

Figure 1 The structure of the α-cristobalite crystal. The unit cell and the [0 1 1] plane are also shown. The molecule under investigation is outlined by solid lines.

RHF/6-31G* results, but the error in the Si–Si distance is larger in the present calculations than in the RHF/6-31G* ones [5] because of mutual compensation of errors in the latter.

The Mulliken populations are very sensitive to the basis set (see [6] for comparison of the performance of the 6-21G, 6-21G* and 6-21G** basis sets in silica) but for a single system it will supply useful information about the nature of the bond. The results in Table II show some minor differences in the charges of the bridging and non-bridging oxygen atoms and in the overlap populations of the Si–O bonds. These differences reflect both the role of the neighbours and the known difference in the properties of the Si–O bonds in the α-quartz crystal. The last effect is quite visible both in bond orders and in lengths of the Si–O distances to the bridging oxygen. The difference between the lengths of two Si–O bonds agrees quite well with the experiment [25].

3.2. Deformation of the molecule

Deformation of the molecule causes simultaneous changes in both Si–O distances and in the Si–O–Si angle. Optimization of the position of the bridging oxygen allows one to estimate all components of the deformation in a self-consistent manner. The changes in the Si–O bonds lengths and in the Si–O–Si angle when the Si–Si distance is varied are shown in Fig. 2. The deformation caused by changing the angle, i.e. $(r_1^2 + r_2^2 - 2r_1r_2\cos\varphi)^{1/2} - R_0$ (r_1, r_2 and R_0 being the initial lengths of the two Si–O bonds and the Si–Si distance, respectively, and φ the Si–O–Si angle in the deformed molecule) is also shown. In the present model the total deformation is, at least for small changes, the sum of almost equal contributions from the elongation of both Si–O bonds and increase of the angle between them. The larger deformations occur mostly due to elongation of the Si–O bonds while the angle between them does not exceed 165°. The length of the two Si–O bonds becomes more different, the initially longer bond is deformed more while the rate of deformation of the second bond becomes slower.

The critical elongation corresponding to maximum force appeared to be equal to 26% of the equilibrium Si–Si distance, i.e. 0.080 nm. Further deformation causes contraction of the shorter bond and additional elongation of the longer one.

Changes in the energy and the force are shown in Fig. 3. The shape of the energy and the force curves may be quite well approximated by equations $\Delta E = 3.0380\varepsilon^2 - 3.9280\varepsilon^3$ a.u. and $F = 8.515\varepsilon - 16.518\varepsilon^2$ mdyn where ε is the relative elongation of the Si–Si distance. The error of approximation is less than 2% at any elongation but is increased to 10% at a contraction of 0.01 nm (~ 3%). The value of critical force is equal to 1.10 mdyn that corresponds to the ideal strength of the α-cristobalite crystal along the [0 1 1] plane equal to 64 GPa.

The results for the small deformations may be compared with other calculations. The force constants obtained separately for both Si–O bonds and the Si–O–Si angle by O'Keeffe and McMillan [8] were used to evaluate the changes in total energy and the force of elongation of the Si–Si distance with values of changes of these parameters obtained in the present study. Results shown in Fig. 3 are in excellent agreement with calculated values.

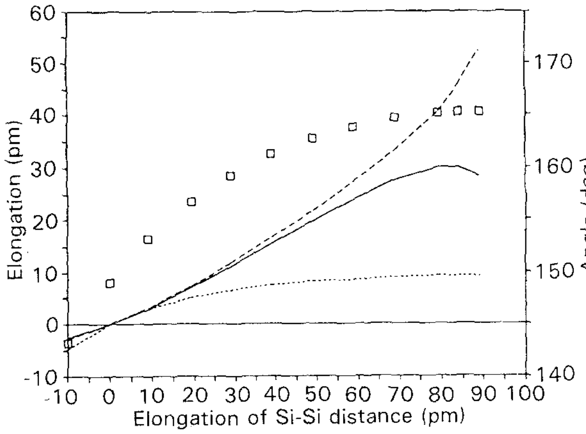

Figure 2 Changes in geometry parameters of strained molecule: (——, – – –) elongation of the Si–O bonds, (· · ·) elongation, caused by increase of the Si–O–Si angle (see text) and (□) values of Si–O–Si angle versus elongation of Si–Si distance. (——) O/Si1, (– – –) O/Si2, (· · ·) due to angle.

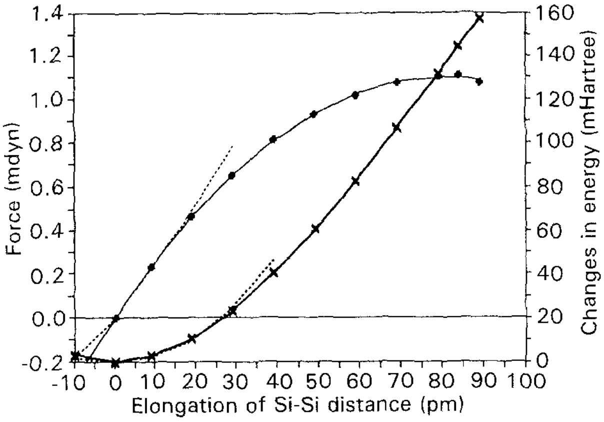

Figure 3 (——) Force applied to the molecule and (——) increase of total energy due to elongation of the Si–Si distance. Results of RHF/3-21G* calculations (points), approximation by 2nd and 3rd power polynoms, respectively (solid lines) and evaluation using the force constants [8] (dotted lines, lines are drawn much beyond the range implied by authors [8] to show where visible difference appears). Energy (×) calculated: (——) approximation, (– – –) literature data. Force (+) calculated: (——) approximation, (– – –) literature data.

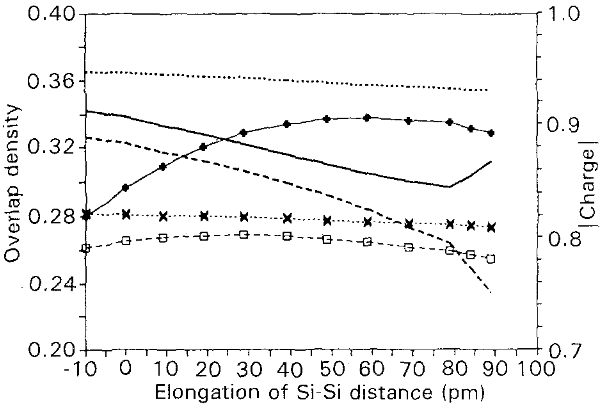

Figure 4 Results of Mulliken population analysis: (——, □) charges of the atoms and (——) overlap population of the Si–O bonds in the strained molecule: (+), (×) absolute values of the charge of the bridging oxygen of the average charge of the non-bridging oxygens and (□) half of the average charge of the silicon atoms; (——, – – –) the overlap population of two Si–O bonds with bridging oxygen and the average overlap population of the bonds between non-bridging oxygens and silicon atoms. (□) Si–O–Si, (——) Si1–O, (– – –) Si2–O, (- - -) angle.

The deformation mode of the molecule under investigation is in contradiction with both the experimental data and the results of previous *ab initio* calculations (see discussion in [7] and [26]). The present calculations overestimate the rigidity of the Si–O–Si angle and, consequently, underestimate its deformation. The small deformations should be caused almost exclusively by the increase of the angle between the Si–O bonds. Evaluation of the relative deformations based on the force constants [8] have shown that elongation caused by increase of the angle should be about 60 times greater than the contribution from the Si–O bond elongation instead of the ratio 1 : 1 found in the present calculations (note, however, that in our calculations these deformations were not set separately but were obtained as the result of the optimization of the position of the bridging oxygen atom). Therefore, the elasticity of the silica could not be evaluated from the data obtained in the present calculations. However, the ideal strength of the crystal depends on the strength of the Si–O bonds and a comparison of the various approximations in the previous part of this series [21] confirms that the obtained value is a reasonable approximation.

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