Journal of Molecular Modeling (2019) 25:161
https://doi.org/10.1007/s00894-019-4057-9

ORIGINAL PAPER

Quantum-chemical simulation of the adsorption-induced reduction of strength of siloxane bonds

Irina S. Flyagina[1] · Alexander I. Malkin[1] · Sergey P. Dolin[1,2]

Received: 12 March 2019 / Accepted: 29 April 2019

Abstract

Mechanical strength of silicate glasses is known to decrease markedly due to the adsorption of molecules from the environment, especially in aqueous alkali solutions. This effect, known as the adsorption-induced reduction of strength (AIRS), has not yet been fully understood. Here, the dependence on the chemical nature and electronic properties of adsorbates of the AIRS of siloxane bonds in silica was studied by means of quantum-chemical calculations at the wB97X-D3/def2-TZVP level of theory. A siloxane bond was modelled by $H_3Si\text{-}O\text{-}SiH_3$ and $(HO)_3Si\text{-}O\text{-}Si(OH)_3$ clusters, and the AIRS was simulated by a linear tensile deformation of the siloxane bond in the presence of the following adsorbates: OH^-, Cl^-, H_2O, H^+ and H_3O^+. Potential energy profiles and derivative force curves of the siloxane bond rupture were obtained. The varying effect of the adsorbates on the energy-force characteristics of the AIRS can be explained by changes in the bond lengths and electron occupancy. It is shown that the AIRS of the siloxane bonds increases with an increase in the nucleophilicity of the adsorbates, and correlates with an adsorbate-induced redistribution of electron density.

Keywords Siloxane bond · Tensile strain · Bond rupture · First principles · Adsorption induced reduction of strength

Introduction

It is well known that the strength of solids is sensitive to the influence of active environments during friction or wear and tear. This susceptibility can cause technological losses, related to destruction of construction materials such as cements and concretes, bearing beams of buildings, etc. [1, 2]. At the same time, the reduction in strength of solids is of great interest in the fields of grinding and milling of mineral ores and construction materials as well as drilling, tunnelling, materials processing, and so on. Some of the most important and widespread materials encountered in these processes are silicates, quartz and sandstone, and the milling of silicate-based materials is performed in an aqueous environment with the addition of detergents. Thus, investigation of the adsorption-induced reduction of strength (AIRS) of solids, in particular silicates, is an important problem.

The mechanical strength of silica in contact with aqueous solutions is often markedly lower than in an inert environment [3]. Experiments demonstrate that the activation energy of rupture of a silicate glass in humid conditions drops to ~92 kJ mol^{-1} compared to ~418 kJ mol^{-1} in vacuum [3, 4]. It is believed that the main reason of this is chemical affinity of the siloxane bond ≡Si-O-Si≡ to water, but the rate of the reaction between the siloxane bonds and water is very sluggish at moderate temperatures. However, the reaction rate is increased significantly by applying mechanical strain, leading to rupture of silica. It has been established that the siloxane bond rupture occurs in an autocatalytic process as follows [5]:

$$\underset{\text{deformed}}{\equiv Si-O-Si\equiv} + OH^- \rightarrow \equiv SiOH + \equiv SiO^- \quad (1)$$

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00894-019-4057-9) contains supplementary material, which is available to authorized users.

✉ Irina S. Flyagina
Irina.fliagina@gmail.com

Alexander I. Malkin
mlkn@list.ru

Sergey P. Dolin
dolin@igic.ras.ru

[1] A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, 31 Leninsky Prospect, Moscow 119071, Russian Federation

[2] N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninsky Prospect, Moscow 119991, Russian Federation

Published online: 15 May 2019

$$\equiv SiO^- + H_2O \rightarrow \equiv SiOH + OH^- \quad (2)$$

The rate of the first reaction depends on the degree of deformation of the siloxane bond, while the rate of the second reaction almost does not depend on it. Existing experimental data corroborates this mechanism [3, 6, 7].

In literature, the mechanism of the AIRS of the siloxane bond rupture is believed to be either nucleophilic or electrophilic substitution, as illustrated in Fig. 1. In the nucleophilic substution, a nucleophile, e.g., OH^- or Cl^-, attacks positively charged Si atoms, forming a five-fold coordination of the Si atoms [4, 8, 9]. In the electrophilic substitution, an electrophile, e.g., H^+, attacks negatively charged O atoms, resulting in a three-fold coordination of the Si atoms [10].

Computational chemistry tools such as molecular dynamics (MD) and quantum-chemical calculations provide an insight into processes that cannot be directly observed experimentally, e.g., enable atomistic investigations of surface reactions. There are several theoretical studies of the hydrolytic rupture of silica. The dissolution of a flat or concave surface of an amorphous SiO_2 under a 2 nm layer of water at 300 K was studied in an MD simulation [4], in which water molecules approached four common Si defect sites with different numbers of the Si–O–Si bridges. The activation energy of a rate-limiting step of the dissolution of the flat SiO_2 surface was found to be rather low, ~58–63 kJ mol^{-1}, while that of the concave SiO_2 surface ~92 kJ mol^{-1}. Another recent MD study combined with quantum-chemical calculations [11] is dedicated to the effect of deformation on hydrolysis of an amorphous silica. The calculated activation energy of the hydrolytic rupture was found to be 125 kJ mol^{-1} for undeformed siloxane bonds, modelled as a $H_6Si_2O_7$ dimer, consisting of two vertex-sharing SiO_4 tetrahedrons, and 84 kJ mol^{-1} for deformed siloxane bonds, modelled as a $Si_2O_2(OH)_4$ dimer with a strained $(SiO)_2$ cycle. The effect of strain on the hydrolysis of SiO_2 was also investigated in a plane wave density functional theory (DFT) study with periodic boundary conditions [12]. In this work, the activation energy of hydrolysis of a SiO_2 structure with wide distribution of the Si-O bond lengths and O-Si-O valence angles was found to be ~19 kJ mol^{-1}, and that of a more uniform SiO_2 structure ~63 kJ mol^{-1}. It can be argued that the activation energy values in [12] are substantially underestimated and imply that the siloxane bonds were strongly deformed prior to the hydrolysis.

The hydrolytic rupture of the siloxane bonds was also studied in a number of quantum-chemical works through characterization of transition states and reaction pathways, employing various cluster systems and model chemistries. In [13], the activation energy of the hydrolytic rupture of a strained siloxane bond, computed in B3LYP/6-31+G(d,p), was found to be ~104 kJ mol^{-1}, with the reactive centre of the model cluster consisting of two edge-sharing SiO_4 tetrahedrons that form a strained $(SiO)_2$ cycle. The authors of [14] pointed out that the structure of solid silica is sufficiently similar to the geometry of the disiloxane molecule H_6Si_2O as a non-strained siloxane bond model. The activation energy of the hydrolysis in [14] was found to be ~121 kJ mol^{-1} at the MP2/6-31G* level. In [15], small clusters Si_3O_3, Si_4O_3, Si_4O_4 or Si_5O_4, computed in B3LYP/6-31G*, were embedded in a larger a cluster, consisting of 50 to 70 Si and O atoms, computed in UHF/STO-3G. The activation energy was calculated to be 68–107 kJ mol^{-1} for a strained reaction centre and 96–123 kJ mol^{-1} for a non-strained one.

The theoretical activation energy of the hydrolytic rupture of silica reported in literature varies between 19 kJ mol^{-1} and 122 kJ mol^{-1} for the strained cyclic Si sites and 83–162 for the non-strained Si sites [2, 12, 16]. However, it is known that silicates possess high stability both in aqueous and alkaline environments, and, despite thermodynamic favorability of the hydrolysis, there must be kinetic hindrance [15]. In addition, the dissociation energy of a water molecule is as high as 492 kJ mol^{-1} [17], and it has been established that hydroxyl groups rather than water molecules play the key role in the rupture of silicates in humid conditions [1, 5].

Theoretical studies of the rupture of silica in the presence of OH^- groups are not abundant. The dissolution of quartz and amorphous silica in an NaOH solution has been studied in an MD simulation [18], where the activation energy of the

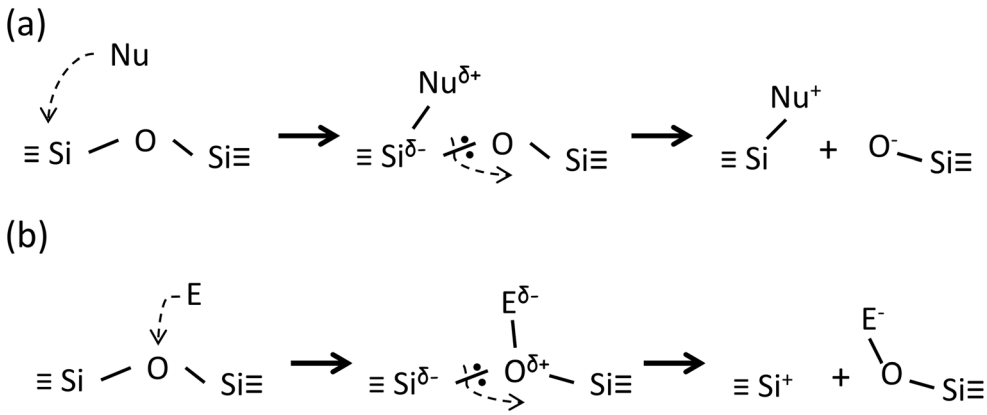

Fig. 1a,b The mechanisms of the adsorption-induced reduction of strength (AIRS) of siloxane bonds in silica. **a** the nucleophilic substitution, **b** the electrophilic substitution

hydroxyl-catalyzed rupture of the siloxane bonds was found to be 23 ± 5 kJ mol^{-1}per unit cell. A quantum-chemical study of hydrolysis of a $Si_4O_6(OH)_4$ cluster at the B3LYP/6-311G(2d,p) level [8] suggests that Na^+ ions play the main role in the formation of the five-fold coordinated Si atom and catalyse the siloxane bond rupture. The activation energy of hydrolysis in the presence of a NaOH molecule, not reacting with the model cluster directly, was calculated to be 82–88 kJ mol^{-1}, and 112–150 kJ mol^{-1} in the absence of NaOH.

Theoretical studies of the siloxane bond rupture in acidic media are few [2]. The activation energy of a non-strained siloxane bond rupture in the presence of $H^+(H_3O^+)$ for the disiloxane molecule H_6Si_2O was calculated to be 92–100 kJ mol^{-1} at the MP2/6-31G* level [14]. In another study at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level [19], the activation energy of H_3O^+-catalyzed rupture of the siloxane bond for a non-strained surface Si site, connected to three Si-O-Si bridges, was found to be 115–125 kJ mol^{-1}. However, another B3LYP/6-31+G(d,p) study [20] reports that the activation energy of H_3O^+-catalyzed hydrolysis of a non-strained siloxane bond in the $H_6Si_2O_7$ cluster is as low as ~69 kJ mol^{-1}, while the activation energy of H_2O- and OH^--catalyzed hydrolysis is calculated to be ~159 kJ mol^{-1} and ~110 kJ mol^{-1}, respectively. A combined MD, quantum-chemical and plane wave study [10] reports that atomic H can break strained S–O bonds in silica with energy barriers between 48 kJ mol^{-1} and 125 kJ mol^{-1}, averaging 96 kJ mol^{-1}.

To our knowledge, the effect of the electronic properties of adsorbates on the mechanism of rupture of silica has not been studied yet. Here, we attempt to gain a qualitative understanding of how the AIRS in silica depends on the electronic properties of adsorbates by means of quantum-chemical calculations. The AIRS was simulated by the tensile deformation of the siloxane bond in the presence of the following adsorbates: OH^-, Cl^-, H^+, H_3O^+ and H_2O. Potential energy profiles are obtained to estimate qualitative energy barriers of the siloxane bond rupture, and derivative stress–strain curves provide an estimation of mechanical properties. The varying influence of the adsorbates on the energetic and mechanical parameters of the AIRS in silica is explained through changes in Si–O bond lengths and electron occupancy analysis.

Molecular model and computational details

The siloxane bond was modelled using a $H_3Si–O–SiH_3$ cluster and a larger $(HO)_3Si–O–Si(OH)_3$ cluster for comparison. The AIRS was simulated by a stepwise increase in the distance between the Si atoms in the presence of adsorbed OH^-, Cl^-, H_2O, H^+ or H_3O^+. The structures of the model clusters, adsorption complexes and dissociation products were optimised to a minimum energy.

First, potential energy profiles of the siloxane bond rupture in the absence of adsorbates were obtained. Since this reaction is homolytic in vacuum [3], two series of calculations with fixed electronic states, singlet and triplet, were carried out. In the singlet state series, the Si···Si distance was increased from an optimised value to 7.00 Å with a step size of 0.1 Å, and in the triplet state series, the Si···Si distance was reduced from 6.00 Å. The interception of the curves resulted in the potential energy profile that provided an estimation of the activation energy of the siloxane bond rupture in the absence of adsorbates. Next were obtained potential energy profiles of rupture of the adsorption complexes. In contrast to the homolytic rupture of the siloxane bond in vacuum, the dissociation of the adsorption complexes is heterolytic and is calculated in the singlet electronic state.

The calculations were performed in ORCA 4.0.1.2 [21] using the hybrid functional wB97X-D3 method with the RIJCOSX approximation and the polarized valence triple-zeta basis set def2-TZVP with the auxiliary basis set def2/J. wB97X-D3 is one of the best performing double-hybrid functionals that is recommended for thermochemistry, kinetics and non-covalent calculations, while not being excessively heavy in terms of computational cost [22]. Electron occupancies were obtained from natural bond orbital (NBO) calculations in Gaussian 09 [23] using the NBO program [24] within the wB97X/def2-TZVP model chemistry. The molecular structures were visualised in Chemcraft 1.8 [25].

Results

Geometry optimized model structures

The optimized structures of the $H_3Si–O–SiH_3$ cluster and its adsorption complexes with OH^-, Cl^-, H_2O, H^+ and H_3O^+ are shown in Fig. 2. The adsorption of OH^- results in the formation of an additional covalent Si–O bond and the five-fold coordination of the Si atom. Due to the high affinity of OH^- to the siloxane bond, a number of adsorption complexes with slightly different geometry and local energy minima formed, with the lowest energy complex shown in Fig. 2. The interaction of Cl^- with a Si atom of the siloxane bond can be considered as a weak covalent bonding, given that the length of the Si–Cl bond in a geometry-optimized $SiCl_4$ molecule is approximately 2 Å. The interaction of the siloxane bond with H_2O is a van der Waals one, since the distance between the Si atom and H_2O is greater than 3 Å, and the changes in bond lengths in the adsorption complex are insignificant compared to the $H_3Si–O–SiH_3$ cluster. The adsorption of H^+ results in the formation of a three-coordinated O atom with a strong covalent O–H bond. Optimization of the adsorption complex with H_3O^+ results in the dissociation of the hydronium cation, with a proton binding to the O atom of the siloxane bridge and

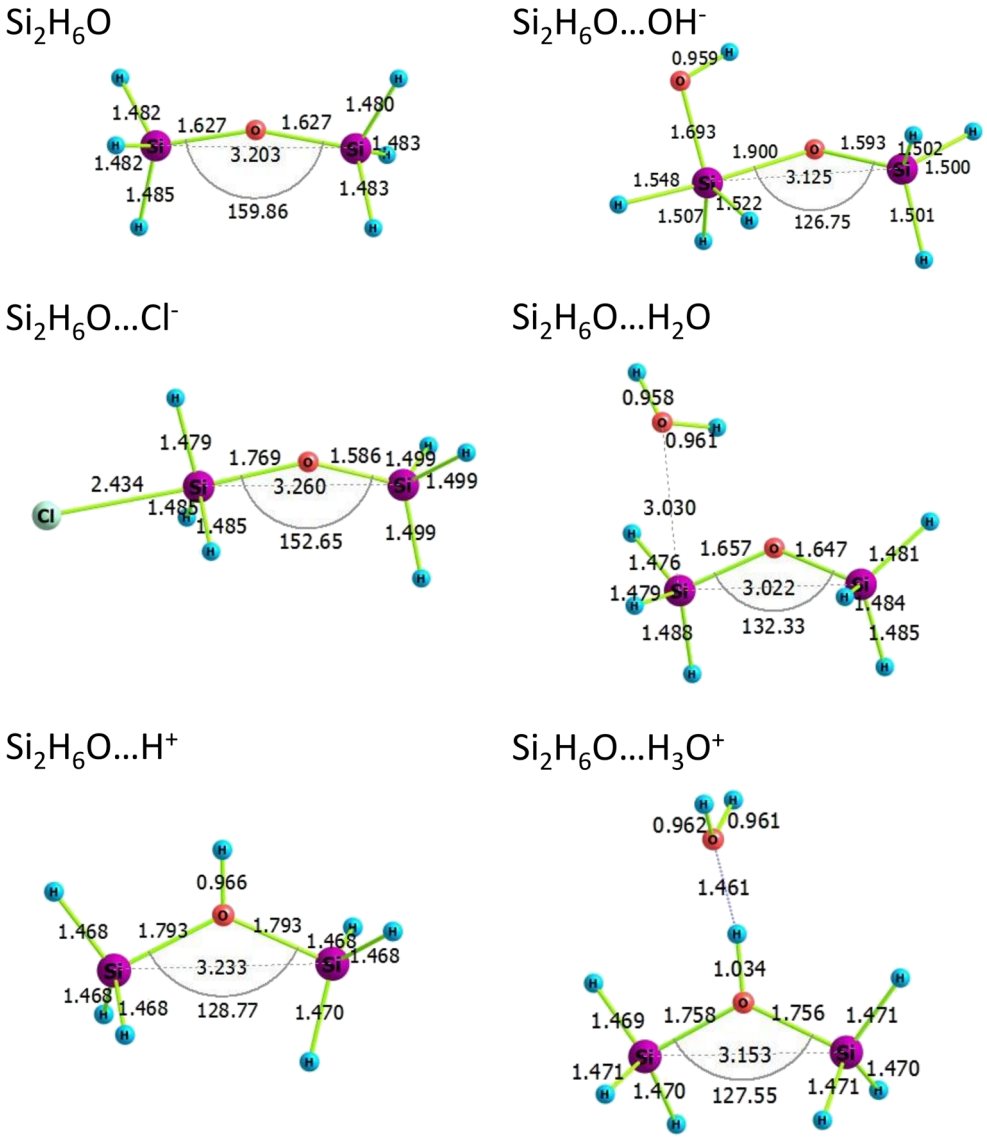

Fig. 2 The optimized structures of the $H_3Si–O–SiH_3$ (Si_2H_6O) model cluster and its adsorption complexes with OH^-, Cl^-, H_2O, H^+ and H_3O^+. Bond lengths and interatomic distances are shown in Å; bond angles are shown in degrees

forming a hydrogen bond with the forming H_2O molecule. The optimized structures of the $(HO)_3Si–O–Si(OH)_3$ adsorption complexes are essentially similar to those of the $H_3Si–O–SiH_3$ cluster (Supplementary Information, Fig.SI-1).

Potential energy profiles

Potential energy profiles (Fig. 3) have been obtained to estimate the upper limit of the activation energy E_a of the siloxane bond rupture, and the work of rupture W_r is estimated as the difference between the energy of products of the rupture and the energy of the optimized model cluster or adsorption complex. In the absence of adsorbates, the energy grows monotonously with the increasing Si···Si distance, and then forms a plateau, in which the lattermost point corresponds to the energy of isolated products of rupture, i.e., radicals $Si\ H_3^{\bullet}$ and $OSi\ H_3^{\bullet}$. The activation energy in this case is equal to the work of rupture. In the presence of the adsorbates, the potential energy profiles change markedly, with the work of rupture and activation energy becoming significantly lower than in vacuum. The energy of the ruptured Cl^- and H^+ adsorption complexes grows monotonously until reaching a plateau of products, which are SiH_3Cl and $OSiH_3^-$ for Cl^-, and SiH_3OH and SiH_3^+ for H^+. In the case of the OH^- adsorption complex, a small minimum in the energy profile at approximately 5.0 Å arises due to the formation of a hydrogen bond between the adsorbed OH group and the free-valence O atom of the model cluster, and the final products are SiH_3OH and $OSiH_3^-$. The potential energy profile of rupture of the H_2O adsorption complex has a pronounced peak at about 4.0 Å, or ~30% elongation of the siloxane bond. The peak and the subsequent energy drop are due to the dissociation of H_2O, followed by the formation of two SiH_3OH molecules. This result is consistent with the MD simulation [26], which

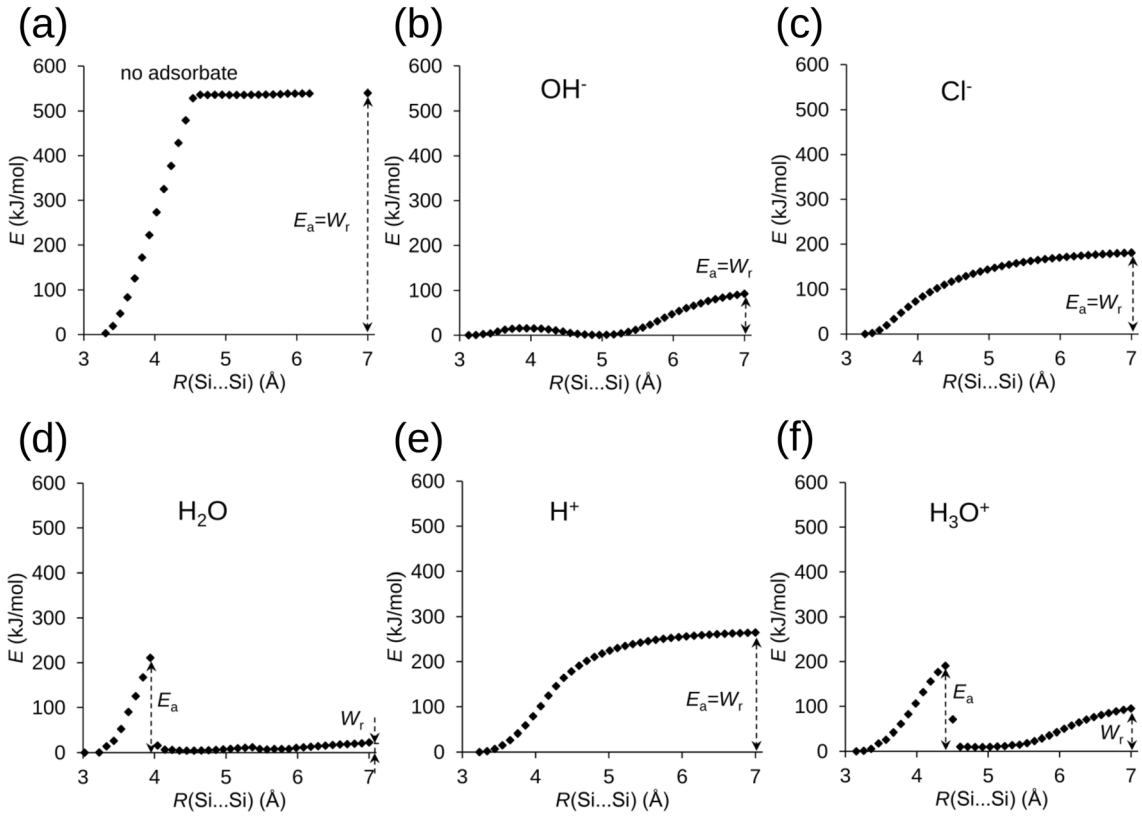

Fig. 3 The potential energy profiles of the siloxane bond rupture of **a** the H_3Si-O-SiH_3 model cluster and its adsorption complexes with **b** OH^-, **c** Cl^-, **d** H_2O, **e** H^+, and **f** H_3O^+

predicts dissociation of water when the stress reaches 30% of the strength of silica. The energy profile of rupture of the H_3O^+ adsorption complex also has a peak, followed by an energy drop at about 4.4 Å, or ~40% elongation of the siloxane bond, due to binding of the O atom of H_3O^+ to the free-valence Si atom and the formation an H_2O-SiH_3^+ ion and a SiH_3OH molecule as the products. Thus, in the case of the H_2O and H_3O^+ adsorption complexes, the estimated activation energy is considerably greater than the work of rupture.

The same set of calculations was performed for the $(HO)_3Si–O–Si(OH)_3$ model cluster (Supplementary Information, Fig.SI-2). Although the $(HO)_3Si–O–Si(OH)_3$ model may seem to be more realistic than $H_3Si–O–SiH_3$, it shows a significant drawback in the calculations. Namely, an increase in the Si⋯Si distance in the $(HO)_3Si–O–Si(OH)_3$ model leads to the formation of hydrogen bonds as a result of rotation of the OH groups, which is unlikely in a solid silicate.

Force curves

Mechanical properties of the siloxane bond can be assessed using force curves, obtained by differentiation of the potential energy profiles. The force curves for the $H_3Si–O–SiH_3$ cluster (Fig. 4) illustrate the effect of the adsorbates on the mechanical properties of the siloxane bond. The force curves for the $(HO)_3Si–OSi(OH)_3$ cluster are significantly noisy, and therefore are given in the Supplementary Information, Fig. SI-3. The force curves can be considered as molecular-scale stress-strain curves that provide information on such properties as

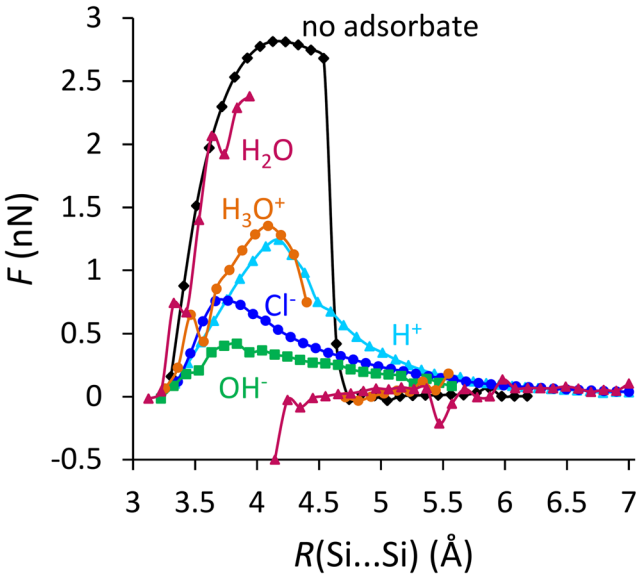

Fig. 4 The effect of the adsorbates on the mechanical properties of the siloxane bond rupture in the $H_3Si–O–SiH_3$ model cluster

mechanical strength and elastic modulus (Young's modulus). The slope of the initial linear section of the curves is the elastic modulus, and the magnitude of the maxima is the mechanical strength. The positions of the maxima correspond to the elongation at break and provide an indication to the "embrittlement" or "plasticization" of the siloxane bond.

Bond lengths

Fig. 5 shows the length of the non-breaking Si–O bond as a function of the Si···Si distance in the $H_3Si–O–SiH_3$ cluster and its adsorption complexes. Both the magnitudes and the positions of the maxima decrease in the sequence: no adsorbate > H^+ > H_3O^+ > H_2O > Cl^- > OH^-. This indicates that all the adsorbates cause an "embrittlement" of the siloxane bond, which increases when going from the acidic to the alkaline environment.

Discussion

Table 1 summarizes the calculated characteristics of the siloxane bond rupture in the $H_3Si–O–SiH_3$ cluster. OH^- exhibits the highest heat of adsorption, $\Delta E_{ads} \approx -282$ kJ mol^{-1}, followed by the acidic adsorbates: H^+ with $\Delta E_{ads} \approx -55$ kkJ mol^{-1}and H_3O^+ with $\Delta E_{ads} \approx -155$ kJ mol^{-1} , and this agrees well with the formation of the stable adsorption complexes with OH^-, H^+ and H_3O^+. The calculated heats of adsorption of Cl^- and H_2O are significantly lower than those of the acidic and alkaline adsorbates, which corresponds to the formation of the weakly bound complexes.

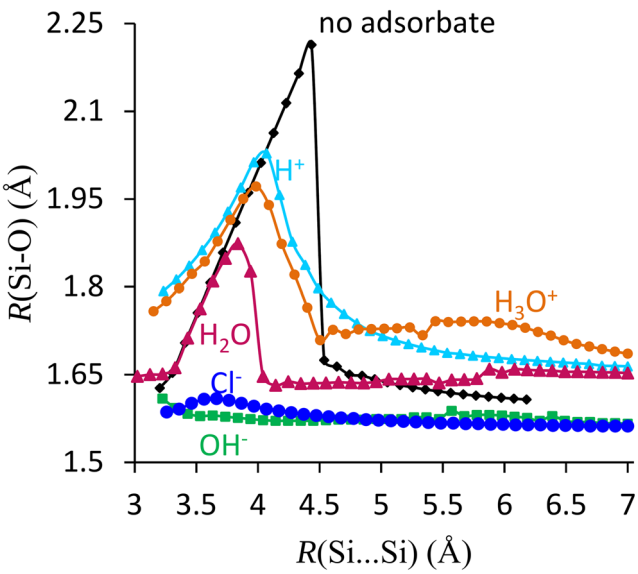

Fig. 5 The effect of the adsorbates on the elastic properties of the siloxane bridge in the $H_3Si-O-SiH_3$ cluster. The length of the non-breaking Si–O bond is shown as a function of the Si···Si distance

The calculated activation energy and work of rupture of the siloxane bond in the absence of adsorbates is $W_r = E_a \approx$ 540 kJ mol^{-1} for the $H_3Si–O–SiH_3$ model, and ~613 kJ mol^{-1} for the $(HO)_3Si–O–Si(OH)_3$ model. These estimations agree well enough with activation energies obtained in the quantum-chemical calculation at the B3LYP/6-311G** level (584 kJ mol^{-1}) and the ReaxFF MD simulation (514 kJ mol^{-1}) [27]. The experimental activation energy of rupture of silicate glass is ~418 kJ mol^{-1} [3], and the theoretical overestimation of this value can be explained by the fact that the bulk, and especially the surface, of a solid contain structural strains, stemming from geometric and energetic inequality of interatomic bonds and valence angles. These local structural defects play the role of additional stress, or strain concentrators, and reduce a material's strength compared to its theoretical value [3].

The presence of water vapors is known to lower the activation energy of rupture of the silicate glass to ~92 kJ mol^{-1}, and the catalyst of the AIRS in water is considered to be OH^- [3]. The activation energy and work of rupture of the siloxane bond in the OH^- adsorption complexes $W_r = E_a \approx$ 113 kJ mol^{-1}for $H_3Si–O–SiH_3$ and ~136 kJ mol^{-1} for $(HO)_3Si–O–Si(OH)_3$ are in reasonable agreement with the experimental strength of glass in a humid environment. The effect of chloride anions on the AIRS in silica has not been reported in literature so far. The estimated work of rupture and activation energy of Cl^--catalysed rupture of the siloxane bond $W_r = E_a \approx 194$ kJ mol^{-1} for $H_3Si–O–SiH_3$ and ~212 kJ mol^{-1} for $(HO)_3Si–O–Si(OH)_3$. Theoretical estimations of the activation energy of the hydrolitic rupture of the siloxane bond reported in literature are in the range of 19–122 kJ mol^{-1} for strained Si sites and 83–162 for non-strained Si sites [2, 12]. The higher values of the H_2O-catalysed rupture, obtained in this study, $E_a \approx 211$ kJ mol^{-1} for $H_3Si–O–SiH_3$ and ~289 kJ mol^{-1} for $(HO)_3Si–O–Si(OH)_3$, can be explained by the high strength of O–H bonds in water molecules, which is as high as 492.2 kJ mol^{-1} [17]. The H^+-catalyzed rupture of the siloxane bond yields $W_r = E_a \approx 277$ and ~248 kJ mol^{-1} for $H_3Si-O-SiH_3$ and $(HO)_3Si–O–Si(OH)_3$, respectively. In the case of H_3O^+, $E_a \approx 191$ and ~192 kJ mol^{-1} for $H_3Si–O–SiH_3$ and $(HO)_3Si–O–Si(OH)_3$, respectively. Expanding the acid-alkali properties of the adsorbates to the electrophilic-nucleophilic strength, it can be noted that the nucleophilic substitution in the siloxane bond rupture is kinetically more favorable than the electrophilic substitution. It can also be observed that there is a tendency of reduction in the activation energy and mechanical properties when going from the electrophilic to the nucleophilic adsorbates. This suggests that the AIRS of the siloxane bond increases with increasing nucleophilicity of the adsorbates.

In an attempt to explain this effect, we obtained electron occupancies of the bonding and anti-bonding natural bond orbitals (NBOs) of the breaking Si–O bond in the $H_3Si–O–SiH_3$ model cluster and its adsorption complexes. In the

Table 1 The calculated characteristics of the adsorption induced rupture of the siloxane bond in the $H_3Si–O–SiH_3$ cluster: the heat of adsorption $\Delta E_{ads.}$, the activation energy E_a, the work of rupture W_r, the maximum stress F_{max}, the siloxane bond length at break (R_{Fmax}), and theelectron occupancies of the natural bond orbitals of the breaking Si–O bond

Model system	Products of the siloxane bridge rupture	$\Delta E_{ads.}$, kJ mol^{-1}	E_a, kJ mol^{-1}	W_r, kJ mol^{-1}	F_{max}, nN	R_{Fmax}, Å	Occupancy of the breaking Si-O bond	
							Bonding NBO	Anti-bonding NBO
OSi_2H_6	$\cdot SiH_3 + \cdot SiH_3$	–	540	540	2.81	4.13	1.99249	0.02157
$OSi_2H_6...H^+$	$SiH_3OH + SiH_3^+$	−55	277	277	1.24	4.17	1.99020	0.03414
$OSi_2H_6...H_3O^+$	$SiH_3OH + H_2O\text{-}SiH_3^+$	−159	191	127	1.35	4.09	1.98835	0.03311
$OSi_2H_6...H_2O$	$SiH_3OH + SiH_3OH$	−12	211	28	2.38	3.94	1.98848	0.02379
$OSi_2H_6...Cl^-$	$SiH_3Cl + OSiH_3^-$	−90	194	194	0.76	3.76	1.93998	0.12843
$OSi_2H_6...OH^-$	$SiH_3OH + OSiH_3^-$	−282	113	113	0.42	3.84	1.92778	0.17574

absence of adsorbates, the occupancy of the bonding NBO is close to two electrons (~ 1.99), and that of the anti-bonding NBO is ~0.02. In the presence of the electrophilic adsorbates H^+ and H_3O^+, the occupancy of the bonding NBO decreases insignificantly, and the occupancy of the anti-bonding NBO increases to ~0.03 electrons, indicating a slight shift in the electron density to the anti-bonding orbital. In the H_2O adsorption complex, the occupancy of the anti-bonding NBO increases negligibly compared to the $H_3Si\text{-}O\text{-}SiH_3$ cluster, since the adsorption of H_2O is a weak van der Waals interaction. In contrast, in the presence of the nucleophilic adsorbates Cl^- and OH^-, the occupancy of the bonding NBO is reduced to ~1.94 and ~1.93 electrons, while the occupancy of the anti-bonding NBO increases up to ~0.13 and ~0.18 electrons, respectively. This indicates that Cl^-, and especially OH^-, induce a significant shift in the electron density from the bonding to the anti-bonding orbital of the ruptured Si–O bond. It should be emphasised that, although the electrophilic adsorbates can form strong covalent bonds with the siloxane bridge, the electron density redistribution is insignificant, while the nucleophilic adsorbates form strong covalent bonds as well, but induce a considerable shift in the electron density from the bonding to the anti-bonding orbital. Therefore, it can be speculated that the AIRS of the siloxane bond correlates with the magnitude of the electron density redistribution between the bonding and anti-bonding orbitals of the ruptured siloxane bond.

Conclusions

A quantum-chemical simulation of the effect of adsorption of OH^-, Cl^-, H^+, H_3O^+ and H_2O on the siloxane bond rupture was performed to explain the phenomenon of the adsorption induced reduction of strength in silicates. It was shown that, among the adsorbates studied, OH^- exhibits the greatest reduction in activation energy and work of rupture of the siloxane bond. A good agreement of the calculated activation energy of the OH^--induced rupture with the experimental value for humid conditions confirms the key role of OH^- groups in the reduction of strength in silicates. The estimated activation energies indicate that the mechanism of nucleophilic substitution is kinetically more favorable than the electrophilic substitution, and the strength of the siloxane bond decreases with increasing nucleophilicity of the adsorbates. Although both the electrophilic and nucleophilic adsorbates may bind strongly to the siloxane bridge, the electrophilic adsorbates induce insignificant changes in the distribution of the electron density of the ruptured siloxane bond compared to the nucleophilic adsorbates, that induce a substantial shift in the electron density from the bonding to the anti-bonding orbitals.

Acknowledgments The authors would like to thank Dr. Detlev C. Mielczarek for discussion of the computational methods, and Dr. Alexander A. Markov (N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences) for discussion of the electronic properties.

Compliance with ethical standards

Conflict of interests Irina S. Flyagina, Alexander I. Malkin, and Sergey P. Dolin declare that they have no conflict of interest.

References

1. Щукин ЕД, Савенко ВИ, Малкин АИ (2013) Влияние поверхностно-активной среды на механическую устойчивость и повреждаемость поверхности твёрдого тела. Обзор. Физикохимия поверхности и защита материалов 49: 44–61. https://doi.org/10.7868/S0023476113050081
2. Du J, Rimsza JM (2017) Atomistic computer simulations of water interactions and dissolution of inorganic glasses. NPJ Mater Degrad 1:16. https://doi.org/10.1038/s41529-017-0017-y
3. Берштейн ВА (1987) Механо-гидролитические процессы и прочность твёрдых тел. Наука, Ленинград

4. Kagan M, Lockwood GK, Garofalini SH (2014) Reactive simulations of the activation barrier to dissolution of amorphous silica in water. Phys Chem Chem Phys 16:25649–25649. https://doi.org/10.1039/c4cp90161d
5. Malkin AI (2012) Regularities and mechanisms of the Rehbinder's effect. Colloid J 74:223–238. https://doi.org/10.1134/S1061933X12020068
6. Malkin AI (2013) Adsorption-induced reduction of strength of solids (Rehbinder Effect). Encyclopedia of Surface and Colloid Science, 2nd edn. Taylor and Francis, London, pp 1–17.https://doi.org/10.1081/E-ESCS-120047359
7. Nikitina EA, Golubina TA, Malkin AI et al (1995) Computational investigation of the influence of the environment on mechanical properties of solids. Int J Quantum Chem 56:161–173
8. Tamada O, Gibbs GV, Boisen Jr MB, Rimstidt JD (2012) Silica dissolution catalyzed by NaOH: reaction kinetics and energy barriers simulated by quantum mechanical strategies. J Mineral Petrol Sci 107:87–98. https://doi.org/10.2465/jmps.110909
9. Mahadevan TS, Garofalini SH (2008) Dissociative chemisorption of water onto silica surfaces and formation of hydronium ions. J Phys Chem C 112:1507–1515. https://doi.org/10.1021/jp076936c
10. El-Sayed A-M, Watkins MB, Grasser T et al (2015) Hydrogen-induced rupture of strained Si─O bonds in amorphous silicon dioxide. Phys Rev Lett 114:115503–115508
11. Yeon J, Van Duin ACT (2016) ReaxFF molecular dynamics simulations of hydroxylation kinetics for amorphous and nano-silica structure, and its relations with atomic strain energy. J Phys Chem C 120:305–317. https://doi.org/10.1021/acs.jpcc.5b09784
12. Van Ginhoven RM, Jónsson H, Park B, Corrales LR (2005) Cleavage and recovery of molecular water in silica. J Phys Chem B 109:10936–10945. https://doi.org/10.1021/jp044973n
13. Rimola A, Ugliengo P (2008) A quantum mechanical study of the reactivity of (SiO)2-defective silica surfaces. J Chem Phys 128:204702. https://doi.org/10.1063/1.2929827
14. Xiao YT, Lasaga AC (1994) Ab-initio quantum-mechanical studies of the kinetics and mechanisms of silicate dissolution - H+(H3O+) catalysis. Geochim Cosmochim Acta 58:5379–5400. https://doi.org/10.1016/0016-7037(94)90237-2
15. Walsh TR, Wilson M, Sutton AP (2000) Hydrolysis of the amorphous silica surface. II. Calculation of activation barriers and mechanisms. J Chem Phys 113:9191–9201. https://doi.org/10.1063/1.1320057
16. Pelmenschikov A, Leszczynski J, Pettersson LGM (2001) Mechanism of dissolution of neutral silica surfaces: including effect of self-healing. J Phys Chem A 105:9528–9532
17. Maksyutenko P, Rizzo TR, Boyarkin OV (2006) A direct measurement of the dissociation energy of water. J Chem Phys 125:4–7. https://doi.org/10.1063/1.2387163
18. Oey T, Hsiao Y, Callagon E et al (2017) Rate controls on silicate dissolution in cementitious environments. RILEM Tech Lett 2:67–73. https://doi.org/10.21809/rilemtechlett.2017.35
19. Criscenti LJ, Kubicki JD, Brantley SL (2006) Silicate glass and mineral dissolution: calculated reaction paths and activation energies for hydrolysis of a Q3Si by H3O+using ab initio methods. J Phys Chem A 110:198–206. https://doi.org/10.1021/jp044360a
20. Nangia S, Garrison BJ (2008) Reaction rates and dissolution mechanisms of quartz as a function of pH. J Phys Chem A 112:2027–2033. https://doi.org/10.1021/jp076243w
21. Neese F (2017) Software update: the ORCA program system, version 4.0. Wiley Interdiscip Rev Comput Mol Sci 8:e1327. https://doi.org/10.1002/wcms.1327
22. Goerigk L, Hansen A, Bauer C, Ehrlich S, Najibi A, Grimme S (2017) A look at the density functional theory zoo with the advanced GMTKN55 database for general main group thermochemistry, kinetics and noncovalent interactions. Phys Chem Chem Phys 19(48):32184–32215. https://doi.org/10.1039/c7cp04913g
23. Frisch MJ, Trucks GW, Schlegel HB et al (2009) Gaussian 09, revision D.01. Gaussian Inc., Wallingford
24. Glendening ED, Reed AE, Carpenter JE, Weinhold F (2003) NBO version 3.1. Gaussian Inc., Pittsburgh
25. Andrienko GA. Chemcraft. https://www.chemcraftprog.com/
26. Hou D, Ma H, Li Z, Jin Z (2014) Molecular simulation of "hydrolytic weakening": a case study on silica. Acta Mater 80:264–277. https://doi.org/10.1016/j.actamat.2014.07.059
27. Yue D, Ma T, Hu Y et al (2015) Tribochemical mechanism of amorphous silica asperities in aqueous environment : a reactive molecular dynamics study. Langmuir 31:1429–1436. https://doi.org/10.1021/la5042663