Two-Membered Silicon Rings on the Dehydroxylated Surface of Silica

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We present extensive modeling of the amorphous silica surface, aimed at connecting its structural and chemical features. β-cristobalite surfaces are initially studied to model the hydroxylated surfaces. A model reconstruction of the (111) surface is used to define a path leading to the formation of two-membered silicon rings upon dehydroxylation. Subsequently, a realistic model of the amorphous dehydroxylated (dry) surface is produced, by full *ab initio* annealing of an initial model generated by classical simulation. The presence of surface two-membered silicon rings emerges naturally. A calculation of IR activity yields an associated peak doublet in agreement with experimental data.

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The presence of amorphous silica is pervasive in everyday life and technology, ranging from window glass to toothpaste, to optical fibers, and even to car tires. While bulk silica are reasonably well understood, many important applications rely on very specific *surface* properties [1], whose microscopic underpinnings are still very uncertain. Understanding the amorphous silica surface is thus a challenge of both principle and practical importance. To quote just one example, the precise nature of surface reactive sites is still vastly a subject of speculation. Yet, these sites control very crucial processes such as the wetting of the silica surface, or the adhesion to silica of organosilanes—the typical silica-polymer coupling agents in the coating of the optical fibers.

In the current literature, it is customarily, even if rather tentatively, proposed [2–4] that strongly metastable two-membered (2M) silicon rings could constitute the main reactive sites on the surface of dehydroxylated (i.e., dry) silica. Supporting evidence consists in a similarity between the IR spectra [2–5] of dehydroxylated silica, exhibiting two strong bands at 888 and 908 cm^{-1} (where bulk silica is transparent) and that of cyclodisiloxane molecules which also display in the spectral region 800–900 cm^{-1} two strong peaks due precisely to vibrations of the 2M ring. The silica IR peaks appear upon dehydroxylation above 500°, and disappear upon adsorption of ammonia, water, methanol, and organosilanes [2–5]. It is therefore conceivable that the surface structures responsible for the new IR bands could arise by condensation of neighboring silanols (Si-OH) on the hydroxylated surface. However, this kind of evidence is so indirect (and the alleged 2M ring so unusually strained, the required OŜiO angle being ~90°) that it raises legitimate concern about the validity of this overall picture of the reactive sites on the dry silica surface.

A crucial piece of additional evidence, either in favor of or against the existence of 2M rings, could come from the assessment of the viability of their formation mechanism upon dehydroxylation. In this perspective, we first simulated by *ab initio* molecular dynamics (MD) [6,7] the dehydroxylation reactions of the crystalline surfaces of β cristobalite, often used to model the hydroxylated surface of amorphous silica. The information gained guided us in the generation of a model of the dehydroxylated amorphous surface. As it turns out, the simulations do support the existence of 2M rings on the dehydroxylated surface, and lead to the identification of a simple and plausible path for the formation of 2M rings whose fingerprint in the calculated IR spectra matches the experimental IR bands at 908 and 888 cm^{-1}.

We first studied the hydroxylated silica surface. Existing data (IR [4,5,8,9], Raman [10,11], and NMR [8,12]) on the amorphous hydroxylated surface are often rationalized by modeling the surface as an alternation of patches of the hydroxylated (100) and (111) surfaces of β cristobalite which is the crystalline phase of silica with density and refractive index closest to those of amorphous silica [1,8]. Moreover, the two main faces of β cristobalite can sustain the two types of silanol groups identified experimentally on the amorphous silica surface, namely, the single silanols (a single hydroxyl attached to a surface Si) typical of the (111) surface, and the "geminal" silanols (two hydroxyls attached to the same surface Si), which are typical of the (100) surface. We modeled the surfaces of β cristobalite by periodically repeated slabs containing 18 formula units in the $I\bar{4}2d$ geometry at the experimental bulk density [13]. We used a gradient corrected density-functional approach [14]. Only valence electrons are treated explicitly and core-valence interactions are described by norm-conserving pseudopotentials [15]. Kohn-Sham orbitals are

expanded in plane waves up to a kinetic energy cutoff of 70 Ry, and 3D periodic boundary conditions are imposed. Brillouin zone (BZ) integration was restricted to the supercell Γ point in geometry optimizations, but relevant energies were then computed by using two special points [16] in the surface BZ. This framework has already been shown to correctly reproduce the properties of bulk amorphous silica [17,18].

As could be expected on simple geometrical arguments, we found that the vicinal, geminal silanols on the (100) [19] surface are H bonded while the single, isolated silanols on the ideal (111) surface are not (Fig. 1). This is in contrast with the experimental evidence [8] that nearly half of the single silanols on hydroxylated amorphous silica surfaces are engaged in H bonding. Therefore we sought possible reconstructions of the (111) surface which might display H-bonded silanols on that face too. A plausible reconstruction emerged naturally by analogy between the silicon sublattice in β cristobalite and crystalline silicon. One of the reconstructions of Si(111) is the so-called π-bonded chain model of Pandey [20]. In fact, we found that the (111) surface of β cristobalite is locally stable in the geometry shown in Fig. 2 which is topologically equivalent to the Pandey reconstruction model. The π-bonded chain of Si(111) is here replaced by a chain
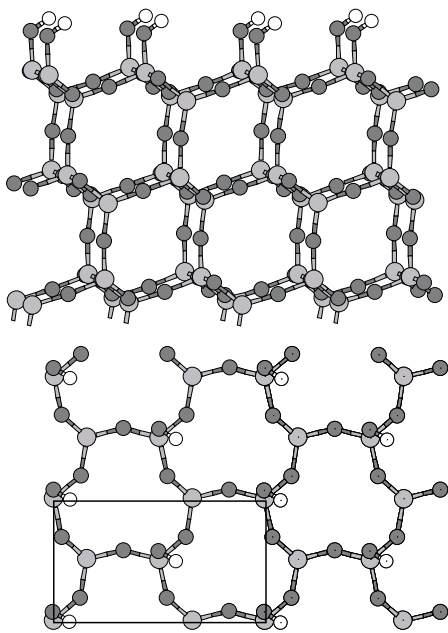
of vicinal silanols. The six-membered ring below the ideal β-cristobalite surface is replaced by five- and seven-membered rings. The rotation of surface tetrahedra induces a dimerization of the silanols chain and the formation of a weak H bond 2.22 Å long and 10 kJ/mol strong. The surface energy of the reconstructed hydroxylated (111) surface thus obtained is only slightly higher (by 0.1 eV/ silanol) than the ideal surface, and it is thus likely that this reconstruction occurs locally on the amorphous surface.

More importantly, besides reproducing single H-bonded silanols at a surface density (4.55 OH/nm^2) close to the experimental one on amorphous surface (4.9 OH/nm^2) [8], this model directly provides a simple path for the formation of 2M silicon rings upon dehydroxylation by condensation of H-bonded silanols. The optimized structure resulting from this condensation reaction is shown in Fig. 3. A 2M silicon ring per unit cell is formed. The condensation energy is 127 kJ/mol, slightly higher than the experimental value of 81 kJ/mol [10] which, however, should correspond to an average over different processes including the formation of less strained five-, four-, and three-membered rings. The dehydroxylated reconstructed surface is now 85 meV/Å^2 lower in surface energy than the ideal unsaturated surface with one undercoordinated Si atom and one undercoordinated O atom. Therefore a cleaved (111) surface should spontaneously transform into the reconstructed structure and form 2M silicon rings as in Fig. 3 [21]. Subsequent hydroxylation in air would thus first produce the reconstructed hydroxylated surface
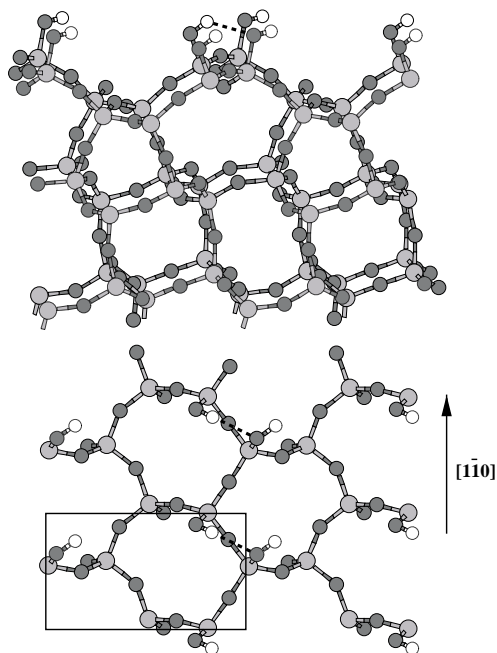

FIG. 1. Optimized geometry of the ideal (111) surface of β cristobalite. Top panel: side view. Bottom panel: top view. The periodically repeated slabs are separated along the [111] direction by a vacuum 6 Å wide. The slab contains three additional silicon layers, not shown. The surface supercell (44 Å^2), shown in the bottom panel, contains two silanols ~5 Å far apart where the O-H bond forms an angle of 17° with the surface normal. The simulation cell contains 54 atoms. Oxygen, silicon, and hydrogen atoms are represented by dark, gray, and white spheres, respectively.

FIG. 2. Optimized reconstructed (111) β-cristobalite surface. Top panel: side view. The bottom surface (not shown) is unreconstructed as in Fig. 1. Bottom panel: top view of reconstructed surface. The silanols chain along $[1\bar{1}0]$ are dimerized forming a weak H bond 2.22 Å long (dashed line).
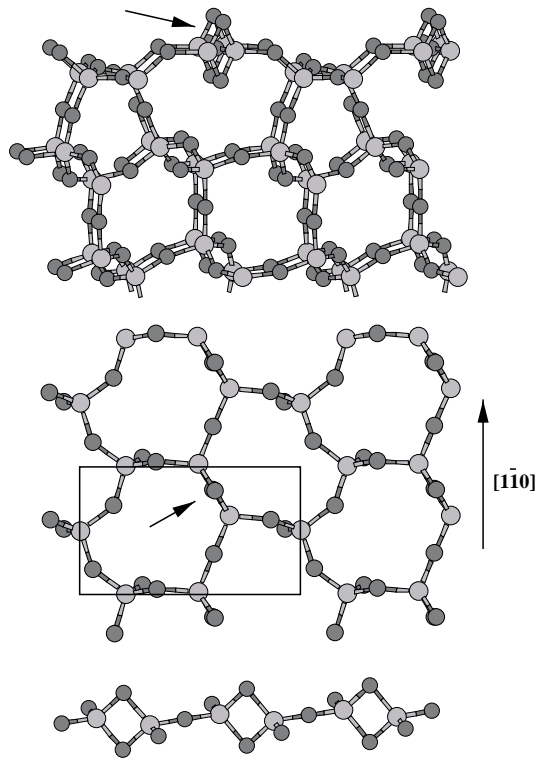
FIG. 3.   Optimized structure of the dehydroxylated reconstructed (111) surface. Top panel: side view. Central panel: top view. A single two-membered ring is present in the unit cell. The ring lies is a plane perpendicular to the surface as indicated by the arrow. The two OŜiO angles are 90°. The four Si-O bonds are equal and 1.70 Å long (the theoretical bulk value in β cristobalite is 1.628 Å). Bottom panel: the chain of two-membered rings along the [1$\bar{1}$0] direction.

FIG. 4.   Calculated IR spectrum of the β-cristobalite slab in Fig. 3. The displacement patterns of the two strongest peaks are sketched. The peak at 870 cm^{-1} is mostly localized on the siloxane bond between two neighboring two-membered rings (see Fig. 3).   It disappears in the IR spectrum projected on the atoms of the two-membered ring. Inset: experimental IR spectrum of amorphous silica [4].

(Fig. 2).   Although higher in energy, the reconstruction might survive as metastable also in crystalline β cristobalite, since kinetic barriers could prevent its transformation into the ideal geometry.   No experimental data are available on the β-cristobalite surfaces and our predicted 2 × 1 reconstruction is open to experimental verification.

In order to identify a distinctive spectroscopic fingerprint, shared between our model and the experiment, we computed the IR vibrational spectrum (Fig. 4) of the dehydroxylated surface (Fig. 3) from phonons and effective charges in the harmonic approximation as done for bulk amorphous silica [18]. Gratifyingly, we found a very good fingerprint, namely, two strong peaks at 791 and 841 cm^{-1} due to modes localized on the 2M ring. The degree of localization on the ring is 74% and 45% for the 791 and 841 cm^{-1} modes, respectively. Identification of these peaks with the pair of experimental peaks at 888 and 901 cm^{-1} on the amorphous surface seems compelling. First, there are no other strong peaks in this frequency region but for the weaker peak at 870 cm^{-1} which is, however, mostly localized on the siloxane bond between two neighboring 2M rings and thus an artifact of the particular geometry of Fig. 3. Second, in the real surface the local
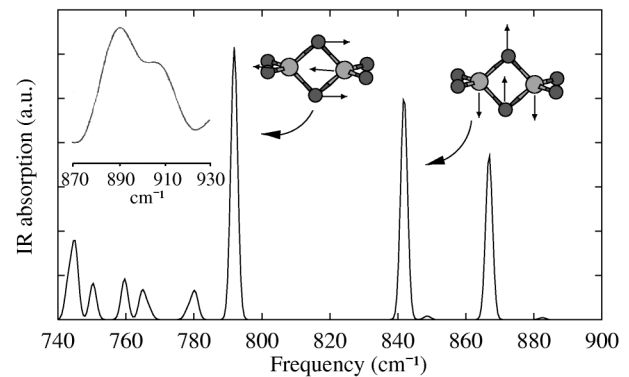
strains responsible for the large inhomogeneous broadening (see inset of Fig. 4) might shift the peaks position toward even closer agreement.

In order to obtain a better description of the local environment of the 2M ring on the real surface, and coming to the central result of our modeling effort, we generated a large model of the amorphous silica surface. Because of the impossibility of doing that *ab initio* all the way, this goal was achieved in steps. The starting point was a classical MD simulation of amorphous silica based on the empirical potential by van Beest *et al.* [22], known to describe reasonably well bulk silica [23]. Unfortunately, the surface is not equally well described by that classical model, which generates far too many under- and over-coordinated surface atoms.   We succeeded nevertheless in providing a reasonable model of the amorphous silica surface by adopting the following strategy: (i) a sample of bulk amorphous silica was generated by quenching from the melt in classical MD; (ii) the bulk sample was cut in such a way as to reproduce a charge compensated surface with the minimum number of undercoordinated Si and O atoms; (iii) the nearest neighbor undercoordinated atoms were forced to bond together by constraining their distance in classical MD. New closed rings are formed. Occasionally, a deeper reconstruction with surface migration of the undercoordinated atom turned out to be necessary in order to minimize the stress and avoid bonds breaking in the constrained MD; (iv) finally the structure was annealed in *ab initio* MD. The final model of the fully dehydroxylated amorphous silica surface is free of under- and overcoordinated atoms, as shown in Fig. 5. A single 2M ring is present in an area of 1.8 nm^2, or a density of 0.5 nm^{-2}, not too far from the experimental estimate on dehydroxylated amorphous surface (0.2–0.4 nm^{-2}, Ref. [3]). The 2M ring appeared naturally as a result of step (ii). Moreover, underneath the 2M ring, a seven- and a five-membered ring,
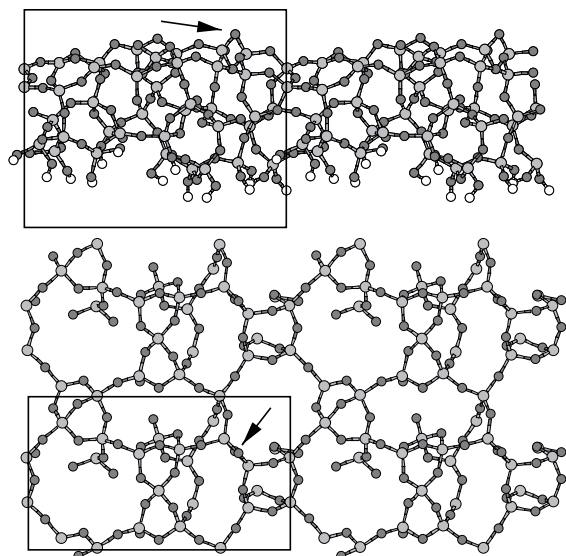
FIG. 5. Model of dehydroxylated amorphous surface. Top panel: side view of the slab. The bottom surface is the fully hydroxylated termination of the bulk. Bottom panel: top view. Only surface atoms are shown. The simulation cell containing 135 atoms is indicated in both panels. The top surface contains one two-membered ring per unit cell indicated by the arrow, lying in a plane perpendicular to the surface.

reminiscent of the reconstructed (111) surface of β cristobalite, were produced spontaneously during the constrained dynamics of step (iii). The IR spectra of this model amorphous surface shows two peaks at 849 and 856 cm^{-1}, due to the 2M ring. They match the experimental doublet even somewhat better than the β-cristobalite calculation does [24]. As expected, the peak at 870 cm^{-1} in Fig. 4 is absent in the calculated spectrum of the amorphous surface.

In summary, we have modeled both crystalline and amorphous silica surfaces, both hydroxylated and dry, with a wealth of results. On the β-cristobalite surfaces, hydroxylation is accompanied by weak H bonding between adjacent hydroxyls, which is directly possible on the (100) face, but requires a surface reconstruction on the (111) face. Dehydroxylation of that face is demonstrated as a route that naturally yields 2M silicon rings. The same 2M rings emerge spontaneously in our final model of the dry amorphous silica surface of Fig. 5. The IR doublet associated with these rings is confirmed by *ab initio* calculation. The calculated strain energy of the 2M ring in Fig. 2 is as large as 1.38 eV/Si_2O_4 (with respect to β cristobalite) which is probably closer to the strain energy of 2M rings on the amorphous surface than previous estimates coming from calculations on clusters or W silica [25]. Ring opening by chemical reactions with adsorbing molecules, triggered by the large strain energy, is currently being pursued in our groups.

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