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Comparative *ab initio* study of the structure and stability of H^- and Li^- anions in silica networks

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The existence of alkali metal anions in interstitial cavities of crystalline silica and microporous materials (e.g., zeolites) has been suggested based on NMR and EPR measurements but has never been studied theoretically. In this work we report results of density functional theory calculations on the interaction of a Li^- anion with cluster models of α quartz containing up to ≈ 100 Si and O atoms. We also consider the interaction of Li^- with orthosilicic acid, $Si(OH)_4$. The properties of Li^- incorporated in a silica structure have been compared with those of the hydride anion, H^-. We found that, in agreement with previous theoretical studies, H^- forms stable structures where a Si atom becomes penta-coordinated with a bipyramidal trigonal structure. Li^- behaves completely differently. Because of its larger size, Li^- does not come close enough to the tetracoordinated Si atom to induce the structural distortion observed for H^-. On the contrary, the Li atom becomes incorporated into the silica structure, with formation of a $\equiv$Si-$O^{\delta-}$-$Li^{\delta+}$ linkage. The negative charge is transferred to the host silica structure where becomes trapped at pre-existing defects or induces additional structural changes in the network.

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I. INTRODUCTION

The role of impurity atoms in insulators is of great importance for a number of processes, like ion conductivity, dielectric breakdown of oxide thin films in microelectronic devices, transport phenomena, etc.[1] In general, extrinsic defects are present in the form of substitutional neutral atoms or as cation interstitials, less frequently in form of interstitial anions. Very rare is the case of the presence of alkali metal anions, a chemical entity which is hardly found because of the strong tendency of alkali metals to ionize and chemically reduce other substrates. Nevertheless, the presence of alkali metal anions (Na, K, Rb) has been suggested to interpret NMR spectra of alkali metal loaded zeolites.[2–4] Very recently, the formation of Li anionic species has been invoked on the basis of EPR spectra of paramagnetic AlO_4 centers in α quartz.[5] The possibility to stabilize alkali metal anions in microporous silicate structures would be of great interest in view of the high reactivity expected for these species and of their potential role as charge traps.

Differently from alkali metal anions, for which theoretical studies do not seem to exist, several theoretical investigations point to a significant stability of the hydride anion, H^-, in solid materials and in particular in SiO_2.[6–9] Hydrides are known to form on the surface of ionic materials like MgO as a consequence of the heterolytic breaking of the H_2 molecule; this results in the formation of a proton, H^+, bound at a surface oxide anion and an hydride, H^-, stabilized at one or more surface cations.[10] Atomic hydrogen in insulators can introduce energy levels in the gap which can act as an electron trap, with formation of H^-. Neutral hydrogen is in fact a negative U defect as the reaction $2H^0 \rightarrow H^+ + H^-$ in silica is exothermic.[6,9] First principles theoretical studies have shown that the hydride anion binds to a Si atom in SiO_2 with formation of a distorted penta-coordinated Si with bipyramidal trigonal structure.[6–9] Apparently, this distortion is very important for the stabilization of the hydride species. Penta-coordinated Si molecular anions have been widely studied in the past both theoretically and experimentally.[11–14] The field was reviewed in 1990.[15] Despite the stability of a simple penta-coordinated complex like $[Si(OH)_5]^-$ has been predicted some time ago,[16] this has never been isolated and characterized. It has been argued that such species are stable only in the gas phase but not in aqueous solution or at mineral interfaces.[17] However, compounds with a SiO_5 skeleton have been synthesized and structurally characterized recently.[13] Moreover, penta-coordinated silicon units, resulting from coordination of F^- anions, $[SiO_4F]^-$, have been detected in various high silica zeolites by solid-state NMR experiments[18] and their trigonal bipyramidal structure has been determined by density functional theory calculations.[19] These results are of particular interest, since it was believed for a long time that penta-coordinated Si in zeolite did not exist.

This brief discussion shows that there are some open questions about the possible existence and the mechanism of stabilization of alkali metal anions in the cavities or interstitials of an insulator. In particular, one aspect which has not been investigated in detail so far is the possibility for alkali metal anions to bind to a silicate structure with a similar mechanism of that of the hydride ion, i.e., a nucleophilic attack at Si atom of a $[SiO_4]$ unit by an anionic species. The aim of this paper is to evaluate the possible existence and stability of a Li^- anion in SiO_2. In the following we will compare the results of *ab initio* density functional theory (DFT) calculations on the interaction of H^- and Li^- anions with a silica network. To this end cluster models of increasing size of crystalline SiO_2 have been generated and the interaction of H^- and Li^- with the lattice has been simulated. We show that the H and the Li anions behave very differently, and that they give rise to completely different structures. In particular, while we find a significant stabilization of the H^- species in SiO_2, there is no tendency of Li^- to be stabilized in the same way, except perhaps for the formation of metastable structures. Li^- tends to react and incorporate into the silica structure with formation of a $\equiv$Si-O-Li chain structure. The reasons for the completely different behavior of H and Li anions are discussed.

II. COMPUTATIONAL DETAILS

Different strategies are usually adopted to "embed" cluster models of solid materials depending on the more or less ionic nature of the material. The most common simplified embedding for SiO_2 and other systems dominated by covalent bonds is the saturation of the cluster dangling bonds by H atoms.[20–30] The positions of the cluster atoms can be taken initially from those of a crystalline phase of the material; the H atoms are then fixed at a given distance from the O and Si atoms at the cluster border and the positions of all the heavy atoms of the cluster are reoptimized. The clusters are derived from α quartz.[31] The fixed H atoms provide a simple representation of the mechanical embedding of the crystalline matrix. This approach has been successfully adopted for the study of the ground and excited state properties of a series of point defects in silicon dioxide.[1,21–30] Clusters of increasing size have been considered: the smallest one, $Si(OH)_4$, actually corresponds to the orthosilicic acid and is not representative of the quartz structure. The larger clusters are $Si_2O_7H_6$, $Si_8O_{25}H_{18}$, and $Si_{40}O_{57}H_{46}$. This latter cluster consists of a portion of the solid of about 15 Å of diameter and allows to properly include the local geometrical relaxation in this region. On $Si(OH)_4$ and $Si_2O_7H_6$ we used a 6-311+G* basis set[32,33] on all atoms; on $Si_8O_{25}H_{18}$ we used the 6-311+G* basis on the central Si_2O_7 part of the cluster, and the 6-31G basis set on the rest. Finally, for the large $Si_{40}O_{57}H_{46}$ model we used three basis sets: 6-311+G* (Refs. 32 and 33) on the central Si_2O_7 unit, 6-31G on the surrounding Si_6O_{18} atoms, and 3-21G (Ref. 34) on the rest. The reaction of the orthosilicic acid with the following anions has been considered to study the possible formation of a five-coordinated Si: H^-, OH^-, F^-, CN^-, Cl^-, and Li^-. For H and Li anions the calculations have been performed also with the cluster models of SiO_2.

The calculations have been done at the DFT level using the nonlocal, gradient corrected, B3LYP functional. This is a hybrid density functional (containing some Hartree-Fock exchange) that combines the Becke-3 (Ref. 35) and the Lee-Yang-Parr[36] forms of the exchange and correlation functionals, respectively.

The importance of the long range electronic polarization in the presence of an adsorbed ion has been estimated by means of the isodensity polarizable continuum model (IPCM) approach,[37] a recently proposed variant of the PCM method.[38–40] The solid lattice is described as a continuous unstructured dielectric with a given dielectric constant surrounding a cavity where the charge is localized. The charge distribution of the cavity interacts with the surrounding medium to create a reflection dipole which acts electrostatically to stabilize the defect region. The procedure is repeated self-consistently, and in this way an estimate of the long-range polarization induced in the lattice by a charged defect is obtained. This is equivalent to carrying out the dipole expansion to infinite order. In a recently proposed modification of this approach by Foresman *et al.*[37] the electric field normal to the cavity is evaluated analytically, thus improving the efficiency of the calculation. The cavity containing the impurity atom (or the solute in the original idea) is defined in terms of an isosurface of the total electron density calculated at the DFT level. A typical value for the isosurface is $0.0004|e|/\text{a.u.}^3$. This approach removes the approximations inherent to the choice of the size of the overlapping spheres.

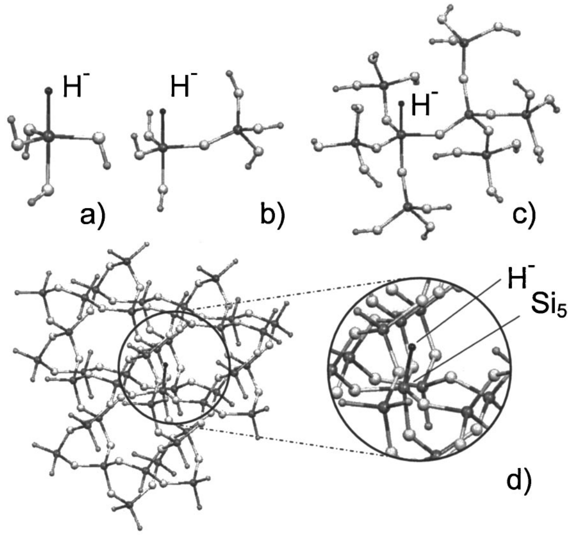

FIG. 1. Structures of penta-coordinated Si with the H^- anion in axial position: (a) $Si(OH)_4H^-$, (b) $Si_2O_7H_6$–H^-, (c) $Si_8O_{25}H_{18}$–H^-, and (d) $Si_{40}O_{57}H_{46}$–H^- (the inset shows the internal region of the cluster enlarged).

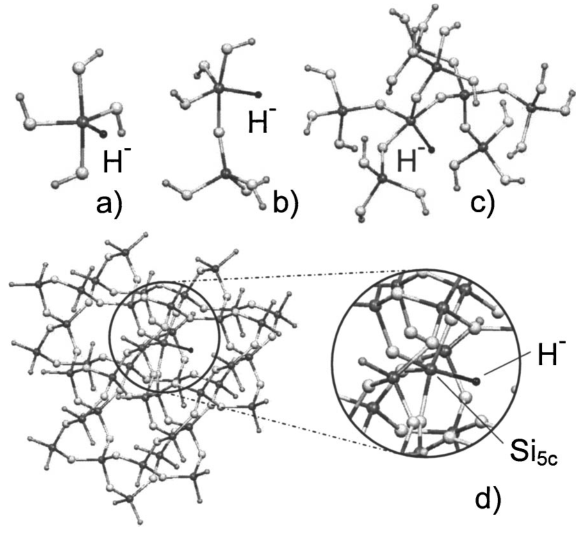

FIG. 2. Structures of penta-coordinated Si with the H^- anion in equatorial positions: (a) $Si(OH)_4H^-$, (b) $Si_2O_7H_6$–H^-, (c) $Si_8O_{25}H_{18}$–H^-, and (d) $Si_{40}O_{57}H_{46}$–H^- (the inset shows the internal region of the cluster enlarged).

TABLE I. Computed properties of axial H^- in SiO_2.

Cluster	r(Si-H) Å	E_{int} eV	E_p(Born) eV	E_P(IPCM) (neutral) eV	E_P(IPCM) (charged) eV	ΔE_P(IPCM) eV
$Si(OH)_4$	1.53	−2.59	-	-	-	-
$Si_2O_7H_6$	1.59	−2.29	−1.76	−0.48	−1.99	−1.51
$Si_8O_{25}H_{18}$	1.53	−2.47	−1.09	−1.57	-	-
$Si_{40}O_{57}H_{46}$	1.50	−2.02	−0.78	-	-	-

For a recent review on this topic see Ref. 41. The method has been recently applied to the study of charged defects in insulators.[6,42,43]

The results of the IPCM approach have been compared with those of the classical Born's equation[44] for the estimate of the polarization contribution of a charge in a solid. If a charge q, spread over a sphere of radius R, is moved from the vacuum into the solid the energy change due to the electronic polarization is given by

$$E_p(\mathrm{Born}) = -(1-1/\varepsilon)q^2/2R, \tag{1}$$

where ε is the dielectric constant. Here we defined R as the average distance of the external H atoms from the center of mass of the cluster. In both IPCM and Born models, we used the dielectric constant 4.4 for SiO_2. For some systems we have computed two polarization terms, E_p(IPCM) and E_p(Born); on the larger clusters we have found problems in converging the IPCM calculations so that only the Born estimate is available. All the calculations have been performed with the GAUSSIAN98 program package.[45]

III. RESULTS AND DISCUSSION

A. Formation of five-coordinated silicon

The possible formation of a stable complex between an anion and a SiO_4 tetrahedral unit has been studied by considering the following reaction:

$$Si(OH)_4 + X^- \rightarrow [Si(OH)_4X]^-, \tag{2}$$

where X=H and Li. The structure of the resulting complex has been fully optimized without any constraint. The anionic species, with an unshared pair of electrons, act as nucleophiles towards the Si center, which presents outer empty d orbitals available to expand the valence shell. In the case of H^- the resulting structure is more stable than the separated fragments by ≈2.6 eV; the complex corresponds to a trigonal bipyramid where Si is effectively five-coordinated [Figs. 1(a) and 2(a)] The short Si-H bond length, ≈1.5 Å, is indicative of the strong interaction. Two possible isomers can form with the H atom in axial [Fig. 1(a)] or equatorial [Fig. 2(a)] positions but they are iso-energetic, see Tables I and II. No bond is broken upon formation of the $[Si(OH)_4H]^-$ complex.

Things are completely different when one considers the same reaction with the Li^- anion. In fact, Li^- reacts with $Si(OH)_4$, induces the breaking of a Si-OH bond and the insertion of Li into the structure [Fig. 3(a)]. The resulting complex can be described as a $Li^{\delta+}OH^{\delta-}$ unit interacting electrostatically with a $[Si(OH)_3]^-$ fragment [Fig. 3(a)] (the Si-Li bond distance is 2.63 Å). In fact, the analysis of the charge distribution in the complex shows the accumulation of charge on the three-coordinated Si, and a residual positive charge on Li. The structure is energetically more stable than Li^- and $Si(OH)_4$ by 1.42 eV. Thus, a completely different behavior is found for H and Li. This cannot be attributed to a different electron affinity (EA) of the two atoms: Li has an experimental EA of 0.62 eV (Ref. 46) (0.56 eV with the present method and basis set), similar to that of H, 0.75 eV (Ref. 46) (0.21 eV in our approach). Other reasons must be at the basis of the different behavior of the two anions.

In order to better understand the mechanism of formation of a penta-coordinated Si we have constructed a potential energy curve for reaction (2) where the hydride anion approaches the $Si(OH)_4$ molecule (Fig. 4). The Si-H distance has been taken as the reaction coordinate, and for each fixed Si-H distance the structure of the complex has been reoptimized (some selected structures are shown in the inset of Fig. 4). At a Si-H distance of 2.2 Å the interaction is already attractive by more than 1 eV and the $Si(OH)_4$ unit is considerably distorted from the initial tetrahedral structure (the O-Si-O angle goes from 116° to 162°). As the Si-H distance further decreases the bonding becomes stronger and the structure becomes even more distorted, with a O-Si-O angle of 190° in the minimum configuration. The key aspect of the entire process is that the energy gain due to the addition of

TABLE II. Computed properties of equatorial H^- in SiO_2.

Cluster	r(Si-H) Å	E_{int} eV	E_p(Born) eV	E_P(IPCM) (neutral) eV	E_P(IPCM) (charged) eV	ΔE_P(IPCM) eV
$Si(OH)_4$	1.50	−2.61	-	-	-	-
$Si_2O_7H_6$	1.52	−2.40	−1.73	−0.48	−1.89	−1.41
$Si_8O_{25}H_{18}$	1.49	−2.65	−1.10	−1.57	−2.54	−0.97
$Si_{40}O_{57}H_{46}$	1.49	−2.19	−0.77	-	-	-

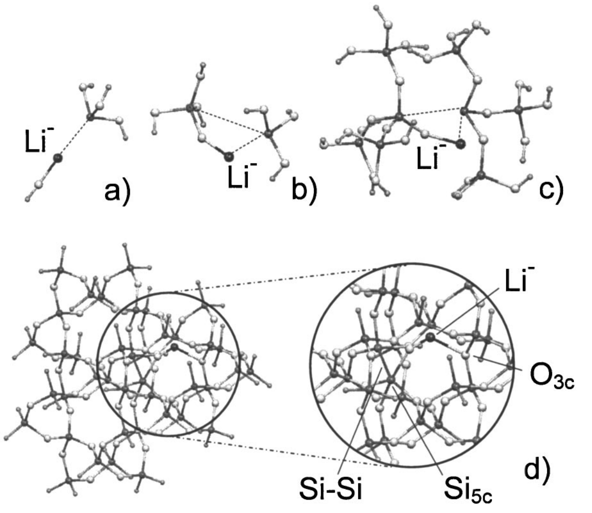

FIG. 3. Silica clusters with the Li^- anion inserted into the structures: (a) $Si(OH)_4Li^-$, (b) $Si_2O_7H_6$–Li^-, (c) $Si_8O_{25}H_{18}$–Li^-, and (d) $Si_{40}O_{57}H_{46}$–Li^- (the inset shows the internal region of the cluster enlarged).

the H^- ion overcompensates for the large cost of the distortion of the $Si(OH)_4$ unit. The energy of the distorted $Si(OH)_4$ unit, as obtained in the minimum of the $[Si(OH)_4H]^-$ complex, lies 2.99 eV above that of the tetrahedral configuration. Since the final interaction energy for reaction (2) is of 2.6 eV, this means that the binding energy of H^- to the distorted $Si(OH)_4$ unit is of about 5.6 eV. This bonding arises from the donation of charge from the H^- ion (a strong base and a very good nucleophile in gas phase and in a solid matrix, where it is not surrounded by solvent molecules) to the empty levels of the $Si(OH)_4$ unit. In the distorted form these are hybrid orbitals resulting from the combination of the Si $3s$, $3p$, and $3d$ levels. The efficient overlap of the H^- $1s$ orbital to the acceptor orbital on Si is the key aspect of the interaction. We now consider the case of Li^- and the reasons why this anion does not form a stable five-coordinated Si complex.

In Fig. 5 we report the interaction energy curves of a distorted $Si(OH)_4$ unit (the structure has been idealized with a O-Si-O angle of 180°) with a series of atomic and molecular anions: H^-, OH^-, F^-, CN^-, Cl^-, and Li^-. The interaction energy curves have been determined as a function of the distance of the anion from the Si atom of the rigid $Si(OH)_4$ group so as to form a trigonal bipyramidal coordination (with the anion in equatorial position). With respect to this distorted $Si(OH)_4$ structure all the interactions are attractive, with the largest energy found for H^- to be -5.8 eV, and the smallest for Li^- to be about -2.4 eV. The other anions exhibit interaction energies which are between these two extremes. At the same time, the minimum distance of the anions from Si increases from 1.5 Å for H^- to 2.7 Å for Li^-. This turns out to be the decisive factor in determining the stability of the five-coordinated complex. The energy required to distort the $Si(OH)_4$ structure from the initial tetrahedral form to the idealized one used in the calculations is 3.7 eV. This means that if the interaction energy of the anion with this distorted structure exceeds the distortion energy the complex will form, while in the other cases the energy gained through the interaction is not sufficient to compensate the high cost for the deformation. This is indeed the case of Li^-: its dimension prevents the ion from approaching closely the Si atom, so that the overlap and the interaction remain weak and insufficient to cause the distortion. The Li^- ion results to be a very poor nucleophile due to steric hindrance. The fact that the dimension of the anion is the key factor is shown by the interaction energy curves of the other anions considered, (Fig. 5). OH^- and F^- anions form a strong bond, >5 eV, and a short distance, 1.7 Å; CN^- is borderline with an interaction energy, -3.91 eV, slightly higher than the cost for the distortion and a Si-C distance of 1.9 Å; Cl^- cannot go closer than 2.2 Å and the interaction energy, -3.1 eV, is too low to induce the distortion. The main difference between F^- and Cl^- is the ionic dimension, but this is sufficient to lead to a stable five-coordinated complex in case of F^- but not in case of Cl^-. It is interesting to note that so far examples of penta-coordinated Si in zeolites have been reported for the case of F^- but do not seem to exists with Cl^-.[18,19]

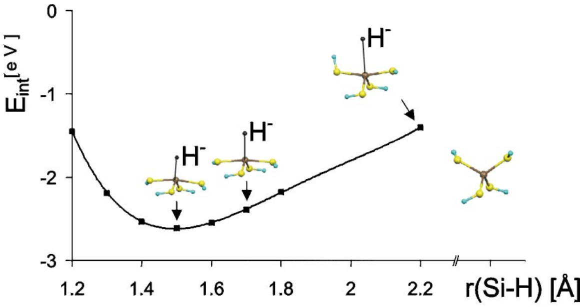

FIG. 4. Potential energy curve for the interaction of the H^- anion with orthosilicic acid (equatorial position) as a function of the Si-H distance. In the inset are shown the optimal structures of the complex for a given Si-H distance.

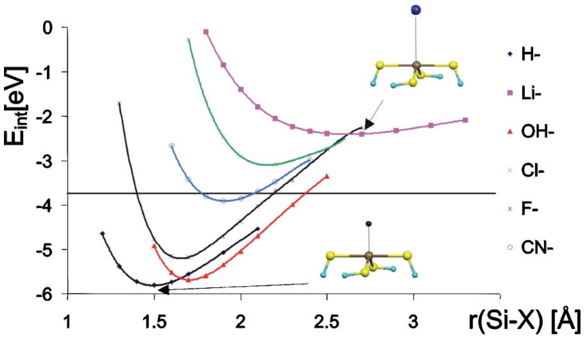

FIG. 5. Potential energy curves for the interaction of H^-, OH^-, F^-, CN^-, Cl^-, and Li^- anions with a rigid distorted $Si(OH)_4$ unit as a function of the Si-anion distance.

B. H^- anion in SiO_2

The mechanism of stabilization of an H^- anion in SiO_2 has been considered by adsorbing the hydride on three cluster models of SiO_2 of increasing size: $Si_2O_7H_6$, $Si_8O_{25}H_{18}$,

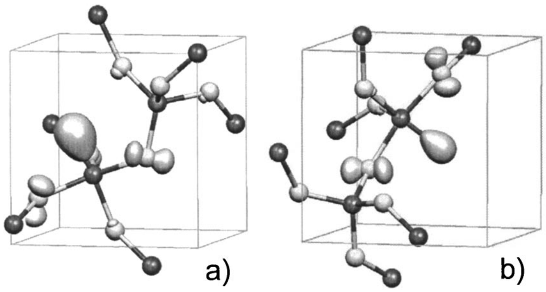

FIG. 6. Charge density difference maps obtained as $\Delta\rho = \rho(Si_8O_{25}H_{18}\text{-}H^-) - \rho(Si_8O_{25}H_{18})$. (a) H^- anion in axial position. (b) H^- anion in equatorial position.

TABLE III. Computed properties of Li^- in SiO_2.

Cluster	E_{int} eV	E_p(Born) eV
$Si(OH)_4$	-1.42	-
$Si_2O_7H_6$	-1.09	-1.52
$Si_8O_{25}H_{18}$	-1.52	-1.01
$Si_{40}O_{57}H_{46}$[a]	-0.32	-0.74
$Si_{40}O_{57}H_{46}$[b]	-1.97	-0.74

[a] Li^- in a SiO_2 cavity (Fig. 7).

[b] Structure corresponding to the insertion of the Li atom into the lattice [Fig. 3(d)].

and $Si_{40}O_{57}H_{46}$ (Fig. 1) (axial position) and (Fig. 2) (equatorial position). In all cases we observe the formation of the five-coordinated Si with a trigonal bipyramidal structure. Thus, the constraint introduced by the extended SiO_2 lattice does not affect the formation of this peculiar conformation. The binding energy of H^- shows an oscillatory behavior with cluster size, being 2.2–2.3 eV with the minimum $Si_2O_7H_6$ cluster, 2.5–2.6 eV with the medium $Si_8O_{25}H_{18}$ cluster, and 2.0–2.2 eV with the largest $Si_{40}O_{57}H_{46}$ model (Tables I and II). The structures with the hydride anion in equatorial position are always slightly preferred over the axial ones (Tables I and II). The contribution of the long-range polarization has been estimated in two ways, either using the IPCM approach or the simple Born formula. In the IPCM the net polarization contribution due to the presence of the trapped ion, $\Delta E_P(\text{IPCM})$, has been computed as the difference of the polarization induced by the neutral cluster, $E_P(\text{IPCM; neutral})$, minus the corresponding polarization in the charged system, $E_P(\text{IPCM; charged})$. For the larger clusters we have found difficulties in converging the self-consistent field procedure with the IPCM method and only the Born estimate is available. When a direct comparison of the two approaches is possible the results are comparable. With the $Si_8O_{25}H_{18}$ cluster (equatorial configuration) $\Delta E_P(\text{IPCM}) = -0.97$ eV is close to $E_P(\text{Born}) = -1.10$ eV (Table II). With the large $Si_{40}O_{57}H_{46}$ model the long-range polarization estimated with the Born formula is -0.8 eV, which brings the total interaction energy to nearly -3 eV.

The negative charge is largely localized on the H atom, with some tails extending on the neighboring O atoms. This is shown by the density difference maps obtained as $\Delta\rho = \rho(Si_8O_{25}H_{18};H^-) - \rho(Si_8O_{25}H_{18})$; see Fig. 6. These results are in line with those obtained by other authors on periodic models of α cristobalite[9] and α quartz[7,8] and further show the ability of the silica network to stabilize H^- anions through the formation of five-coordinated Si atoms.

C. Li^- anion in SiO_2

The addition of Li^- to a SiO_2 cluster model has been done following the same strategy adopted for H^-. The Li^- anion has been positioned at various distances from a Si atom and a full geometry optimization has been performed. In no case (except for a situation that will be described below) we found evidence of the formation of a Li^- ion coordinated to the network. As for the case of orthosilicic acid, we always observe the breaking of a Si-O bond and the insertion of the Li anion in the lattice. With the smaller $Si_2O_7H_6$ and $Si_8O_{25}H_{18}$ clusters there is an opening of a Si-O-Si bond with the formation of a $\equiv$Si-O-Li---Si$\equiv$ linkage (Fig. 3). The Li atom actually forms a sort of $\equiv \text{Si-O}^{\delta-}\text{-Li}^{\delta+}$ complex which interacts electrostatically with the three-coordinated $\equiv \text{Si}^{\delta-}$ unit (Fig. 3) where the negative charge is accumulated. Notice that the insertion of Li^- is exothermic and the final structure is more than 1 eV more stable than the separated fragments (Table III) even before including the contribution of the long-range polarization.

In principle one could think that the insertion of the Li anion in the lattice is the consequence of using small clusters that do not properly represent the cavities of the SiO_2 network. The larger $Si_{40}O_{57}H_{46}$ cluster provides a representation of the ring structure and contains cavities where the Li anion is completely surrounded by the SiO_2 matrix (Fig. 7). The geometry optimization has been started in two ways, either placing Li^- near a Si atom or in the center of a cavity (Fig. 7). Unfortunately, it was not possible to include the long-range polarization self-consistently in the calculations because of convergence problems. The final result of the geom-

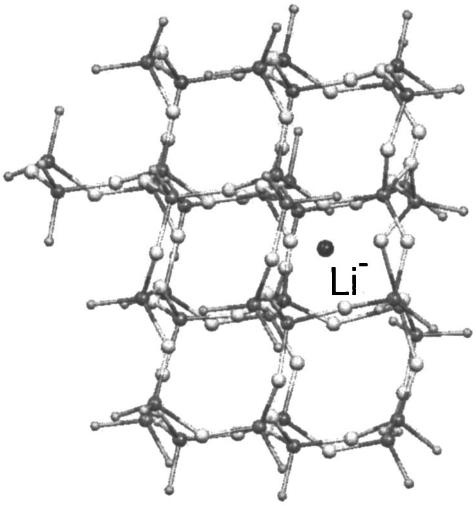

FIG. 7. Side view of the $Si_{40}O_{57}H_{46}$ cluster showing one cavity where the Li^- ion can exist in a metastable configuration.

etry optimization is, independent of the starting point, a complex reconstruction of the structure with insertion of Li^- into a Si-O bond. However, when the optimization is done starting with Li at the center of the cavity we found a very shallow region in the potential energy surface where the Li^- ion exists as such in the silica framework with a stabilization energy of -0.32 eV compared to Li^- and SiO_2 (Table III). After a considerable number of optimization steps the system evolves towards the new complex structure where bonds are broken and formed [Fig. 3(d)]. We cannot exclude that with larger clusters and with direct inclusion of long-range polarization effects one could find a real local minimum for the Li^- ion in a cavity; however, it is likely that this will correspond to a metastable structure which can easily evolve into a deeper minimum by overcoming a presumably small energy barrier.

In the heavily reconstructed structure [Fig. 3(d)], a Si-O-Si bond breaks with formation of a $\equiv$Si-O-Li unit; the negative charge is transferred to the three-coordinated Si atom which then binds through a dative bond to another Si atom which becomes penta-coordinated (Si_{5c}) with the formation of a direct Si-Si bond. The Li atom binds electrostatically to a two-coordinated oxygen which becomes effectively three-coordinated (O_{3c}). The final structure is 1.97 eV lower than the separated fragments (Table III). It is difficult to establish if such a complex reconstruction does really occur. The entire complex is diamagnetic and there are no paramagnetic centers to detect and identify by means of the EPR spectroscopy. However, the point here is not to establish if the insertion mechanism is correct in every detail but rather that the Li^- ion in silica is unstable, loses the extra electron, transforms into a Li atom which becomes coordinated to a Si-O bond with formation of a $\equiv$Si-$O^{\delta-}$-$Li^{\delta+}$ linkage. The extra negative charge introduced in the lattice can be stabilized at a pre-existing defect or can induce an additional reconstruction, as found in our model.

IV. CONCLUSIONS

The possible existence of negative alkali metal anions has been suggested in zeolites[2–4] and in crystalline silica.[5] In a similar way hydride ions, H^-, are predicted to be stable species in insulating materials.[6–9] In this study we have analyzed by means of DFT cluster model calculations the mechanism of stabilization of Li^-, the smallest alkali metal anion, and H^- in the SiO_2 lattice. We have shown that the two anions give rise to completely different structures. H^- binds strongly to a four-coordinated Si atom with the formation of a stable penta-coordinated Si species with a bipyramidal-trigonal structure. This is possible thanks to the small dimension of H^- and to the strong overlap with the Si empty states. Similar structures are expected in the presence of other small anions like OH^- ($r_{ion}=1.37$ Å) or F^- ($r_{ion}=1.33$ Å).[46] The small dimensions allow the anion to approach the Si atom and to induce the strong distortion from tetrahedral to bipyramidal-trigonal coordination. The energy gained in the interaction largely overcomes the price paid to distort the structure. Anions with larger dimensions, as is the case of Li^- or Cl^- ($r_{ion}=1.81$ Å),[46] do not gain enough energy to induce the distortion, and do not become coordinated to the Si atom. The small electron affinity of Li is not significantly enhanced when the Li^- anion is placed at the center of a cavity in the silica network. This causes the transfer of the electron to the silica lattice (or to an acceptor level associated to a point defect if this is present) and to the formation of a reactive Li atom which breaks a Si-O-Si bond with formation of a polar $\equiv$Si-$O^{\delta-}$-$Li^{\delta+}$ bond. In this way the Li ion finally becomes incorporated into the structure. On the basis of our results we cannot exclude that in certain situations a Li^- anion can become stabilized inside the cavity of a zeolite or of SiO_2, but this could correspond to a metastable situation which can easily evolve towards the Li insertion by moderate increase of the temperature. In this respect it is worth noting that also the assignment of the NMR signal to alkali metal anions like Rb^- is not completely unambiguous and one should not discount the possibility that it actually arises from the central atom of a highly symmetric metal cluster.[2]

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