Ab Initio Simulations of Photoinduced Interconversions of Oxygen Deficient Centers in Amorphous Silica

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We have studied by *ab initio* molecular dynamics the interconversion between oxygen deficient centers (Si—Si bond, dicoordinated silicon ═Si:, and E' centers) induced by UV irradiation in a-SiO$_2$. By dynamical simulations in the excited state of a periodic model of a-SiO$_2$ we have identified the reaction path and activation barrier for the Si—Si → ═Si: interconversion. A new competitive transformation of the excited, neutral Si—Si bond into two E' centers has been identified. Our results provide strong theoretical support to the viability of these processes, proposed experimentally on the basis of optical data only.

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Although photoinduced Bragg gratings are widely used in optical fiber technology [1], a detailed description of the microscopic processes which stand behind silica glass photosensitivity has not yet been fully achieved. Two different mechanisms have been called upon to explain the change of refractive index in silica glass induced by UV illumination: transformation of preexisting point defects [2,3] and matrix densification [3,4]. Oxygen deficient centers (ODC) are the main defects expected to play a role in these processes. Recently a possible photoinduced interconversion mechanism was proposed [5]: it involves the two main diamagnetic ODC defects, i.e., the Si—Si bond [≡Si—Si≡, named ODC(I)] and the dicoordinated silicon [═Si:, ODC(II)]. The photoinduced transformation of ODC(I) into ODC(II) would rationalize a huge amount of spectroscopic data which show the appearance of luminescence lines (at 4.4 and 2.7 eV) attributed to ODC(II) [6], when amorphous silica is illuminated with light in resonance with the absorption line (7.6 eV) attributed to ODC(I) [7]. Upon ionizing irradiation a correlation has been experimentally found between the bleaching of the optical absorption band at 5 eV, assigned to ODC(II) in a-SiO$_2$ [6], and the appearance of the electron paramagnetic resonance (EPR) signal assigned to the E' center. The latter center is a threefold coordinated silicon atom with an unpaired electron (≡Si·) [5]. These results lead us to assume that the photoionized ODC(II) transforms into the E' center. The flexibility of the glassy network has been advocated to make these transformations possible. As appealing as it may appear, this picture still lacks a compelling verification. Few calculations [8,9] have been performed so far which aim at validating the interconversion models of ODCs. In particular, Uchino *et al.* [8] proposed a mechanism for the ODC(I) → ODC(II) transformation based on photoionization of ODC(I). However, the use of simple cluster models did not reliably describe the strain energy of the glassy network surrounding the transforming defect and prevented so far a reliable calculation of the activation barriers.

In this work we have simulated, by Car-Parrinello molecular dynamics (MD) [10,11], the ODC(I) → ODC(II) photoinduced transformations in a periodic model of bulk a-SiO$_2$. This work represents the first attempt to model the ODC(I) → ODC(II) interconversion in the neutral excited state, as proposed experimentally [5]. The transformation into ODC(II) was simulated by adiabatic Born-Oppenheimer MD on the lowest triplet (T_1) excited state energy surface, within density functional theory (DFT) in the local spin density approximation (LSDA). A norm-conserving and an ultrasoft pseudopotential [12] are used for silicon and oxygen, respectively. Kohn-Sham orbitals are expanded in a plane wave basis set with a kinetic energy cutoff of 27 Ry. Although the photoinduced reaction would occur on the singlet excited state, MD on the T_1 excited energy surface is more easily affordable within our framework and would provide a transformation path that also sheds light on the interconversion induced by the singlet exciton.

A periodic model of a-SiO$_2$ at density of 2.2 g/cm^3 has been generated by quenching from the melt in classical MD, adopting the empirical pair potential by van Beest *et al.* [13], which is known to provide a reliable description of bulk a-SiO$_2$ [14]. In the quenching process an oxygen vacancy has been introduced in a periodic supercell containing 32 formula units. The distance of the as-produced Si—Si bond was constrained to 2.5 Å such a way as to generate an ODC(I) defect with a low-strain environment [15]. We checked that our model accounts well for the structural properties of a-SiO$_2$ as it does not contain any coordination defect but the ODC(I) we have introduced (Fig. 1). The constraint on the geometry of the Si—Si bond was then relaxed and the system annealed at 500 K by *ab initio* MD. The ground state configuration of the ODC(I) ($d_{\text{Si-Si}}$ = 2.46 Å) embedded in the amorphous matrix is in good

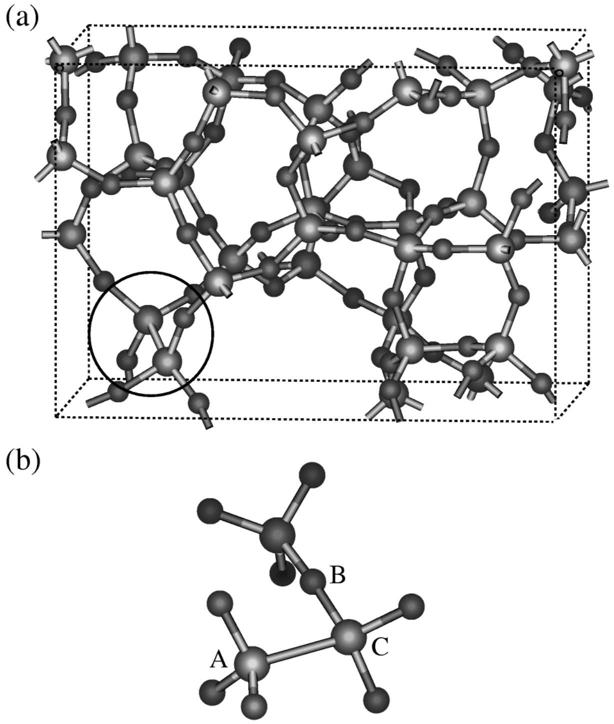

FIG. 1. (a) The simulation cell of the amorphous silica model with the Si—Si bond enclosed by a circle [ODC(I)]. Cell dimensions are 10.08, 10.08, and 14.26 Å. It contains 95 atoms with periodic boundary conditions. The small dark spheres are oxygen atoms and the large light-gray spheres are silicon atoms. (b) The local environment of the Si—Si bond. For the labels see the text and Figs. 2 and 3.

agreement with previous Hartree-Fock and DFT calculations on cluster [16,17] and periodic [18,19] models.

Starting from the ground state geometry of ODC(I), we have excited the system into the T_1 state which is 4.1 eV higher in energy [20]. The atoms relax under the modified potential energy surface, the Si—Si cleaves and expands up to 3.2 Å (Fig. 2a), thus inducing a large distortion in the amorphous network surrounding the defect. The computed relaxation energy is 1.8 eV.

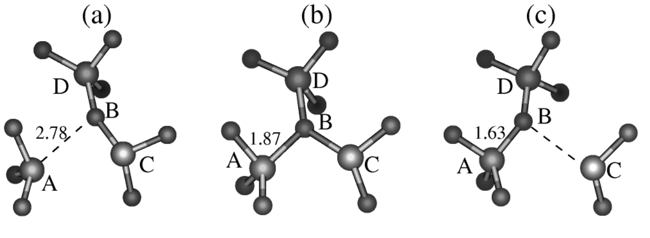

FIG. 2. The interconversion path of ODC(I) into ODC(II) in the lowest triplet (T_1) excited state. Panels (a) and (c) show the local relaxed configuration of ODC(I) and ODC(II) embedded in the amorphous sample of Fig. 1, respectively. Panel (b) shows the transition state. The reaction coordinate in the constrained *ab initio* molecular dynamics simulations (see text) is the distance (here shown in Å) between atoms A and B. The labels on atoms are the same as in Fig. 1. In panel (b) the BD and BC bond lengths are 1.89 and 1.95 Å, respectively.

We have then followed the path toward the ODC(II) (Fig. 2c) within constrained *ab initio* MD [21], i.e., we sampled the reaction path by performing MD simulations at different values of the reaction coordinate, chosen as the distance between the silicon atom labeled as A and the oxygen atom labeled as B in Fig. 2a. The transition state is shown in Fig. 2b and corresponds to an activation energy of 0.72 eV. By further decreasing the reaction coordinate the system transforms spontaneously into the ODC(II) configuration in Fig. 2c. The geometries of the final ODC(II) in the T_1 and S_0 states and the lowest excitation energies are very close to the results of previous CI calculations [22] (see Table I). The use of gradient corrected energy functionals [23] does not change the activation energy within 0.1 eV. Among the many possible local configurations of the ODC(I) defect in a-SiO$_2$, only a small fraction is expected to transform into the ODC(II) upon excitation, as deduced from the experimental report of separate photobleachable components of the 7.6 absorption [5]. Although our calculated value for the activation energy is still relatively high, other local configurations different from ours may be more favorable for the interconversion [24]. A possible overestimation of the activation energy may also come from the limitations of the LSDA. In fact, the excitation energy of ODC(I) is largely underestimated [20] while the excitation energy of ODC(II) is fairly well reproduced by LSDA. Based on the analysis of the degree of localization of the T_1 state (details will be given elsewhere), we expect the error in the excitation energy of the transition state to be intermediate between those of ODC(I) and ODC(II), which implies an overestimation of the activation energy.

Experimentally, both of the photoluminescence lines at 4.4 eV ($S_1 \rightarrow S_0$) and 2.7 eV ($T_1 \rightarrow S_0$) produced by excitation at 7.6 eV, decrease in intensity by increasing temperature (from 10 to 300 K) [25,26] which might seem in contrast with our finding of an activated ODC(I) → ODC(II) transformation. However, the experimental data can be rationalized by assuming the presence of another competitive nonradiative channel for the ODC(I) deexcitation, as argued hereafter. In fact in our MD simulation on the T_1 excited energy surface we have found a second reaction path which leads to the formation of two threefold

TABLE I. Structural properties of the ODC(II) in the ground state and in the lowest triplet excited state plus vertical excitation and recombination energies.

		This work	Zhang *et al.* [22]
Ground state S_0	Si—O (Å)	1.65	1.65
	O—Si—O	103°	101°
Excited state T_1	Si—O (Å)	1.64	1.64
	O—Si—O	114°	117°
Transition energies	$S_0 \rightarrow T_1$ (eV)	2.96	3.06
	$T_1 \rightarrow S_0$ (eV)	2.62	2.48

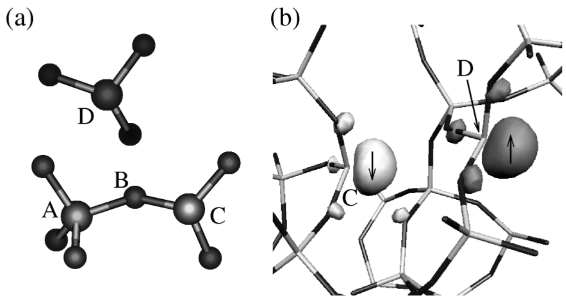

FIG. 3. (a) The final configuration of the two E' centers obtained by the exited ODC(I) configuration in Fig. 2a. The two unpaired electrons are localized on atoms C and D. (b) Spin densities of the relaxed E' centers in the singlet electronic state. The labels on atoms are the same as in Fig. 2.

coordinated silicon atoms with two unpaired electrons, i.e., two E' centers ($2E'$), as shown in Fig. 3. The transition state for this process is very close to the configuration in Fig. 2b from which the two E' centers can be generated by breaking the bond between atoms B and D (cf. Figs. 2b and 3a). The resulting threefold coordinated silicon atoms (D and C in Fig. 4) are 4.35 Å apart and host two unpaired electrons weakly interacting, the singlet-triplet splitting being as low as 0.09 eV in the configuration of Fig. 3. This transformation is therefore a nonradiative channel for the ODC(I) deexcitation. The spin densities of the relaxed configuration of the two E' centers in the singlet electronic state is shown in Fig. 3b. The activation barrier for the ODC(I) $\rightarrow 2E'$ interconversion on the T_1 excited energy surface is 0.6 eV, close to the value obtained for the ODC(I) → ODC(II) transformation. However, the activation energy (2.2 eV) for the backward reaction $2E' \rightarrow$ ODC(I) is much larger than the energy barrier (0.4 eV) for the ODC(II) → ODC(I) backward conversion. By increasing the temperature the excited ODC(II) may revert to the saddle point configuration in Fig. 2b and then undergo an irreversible transformation into the $2E'$ center. This might explain the bleaching of the ODC(II) photoluminescence lines observed at higher temperatures. Furthermore, our results support the recent experimental data [27], interpreted as the formation of E' centers via single photon absorption at 7.6 eV. To make contact with EPR data we calculated the isotropic part of the hyperfine tensor a_{iso} on the Si atoms of our system, using the scheme proposed by Van de Walle and Blöchl [28]. We obtained two different values of a_{iso} for the two inequivalent E' centers in Fig. 3, namely, 461 and 339 G. These values are in good agreement with those computed for the single E' center in α quartz (467 G) within this same framework [18,29].

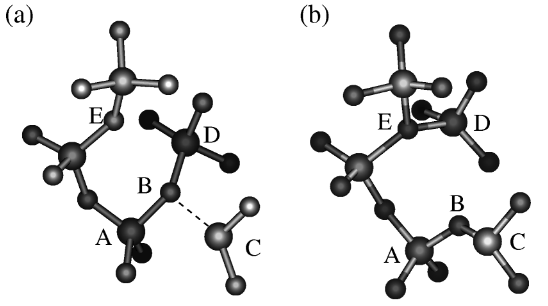

FIG. 4. The transformation of the ionized ODC(II) [panel (a)] into the E' center [panel (b)]. The unpaired electron is located on the silicon atom C of the former ODC(II). The three Si—O bonds formed by the threefold coordinated oxygen atom (E) are 1.83, 1.82, and 1.85 Å long and trap the hole produced by the ionization of ODC(II) (see text). The labels on atoms are the same as in previous figures.

Finally, we have examined yet another viable route for the formation of E' centers: the ODC(II) $\rightarrow E'$ interconversion upon ionization of the ODC(II) defect. This would explain the simultaneous bleaching of the 5 eV absorption line assigned to ODC(II) and the appearance of the EPR signal assigned to the E' center [7,30]. By removing an electron from the final configuration of the ODC(II) obtained in the previous simulation (in the electronic ground state) we have identified a nearly barrierless (the activation energy is as low as 0.04 eV) transformation of the ionized ODC(II) into the E' center along the path depicted in Fig. 4. The E' center is localized on the silicon atom of the former ODC(II) (atom C in Fig. 4), the positive charge being transferred to another silicon atom (D in Fig. 4) which in turn forms a bond with a threefold coordinated oxygen atom in a puckered configuration (oxygen atom E in Fig. 4). This geometry is similar to the puckered E' center produced by hole trapping on the ODC(I) in a-SiO$_2$ [18,31]. The isotropic hyperfine parameter of the E' center produced from ODC(II)$^+$ is $a_{\mathrm{iso}} = 384$ G [32].

In conclusion, we performed *ab initio* MD simulations of the interconversion among ODCs in a-SiO$_2$ which provided us with the path and energy barrier for the ODC(I) → ODC(II) interconversion on the T_1 excited state, and for the ODC(II)$^+ \rightarrow E'$ transformation. The simulations provide strong theoretical support for the viability of these interconversions proposed experimentally on the only basis of spectroscopic data [5]. Moreover, we also identified a competitive nonradiative deexcitation of the excited ODC(I) leading to the formation of a couple of E' centers. This process can rationalize both the temperature dependence of the photoluminescence spectra [25,26] and the formation of E' centers via single photon excitations at 7.6 eV [27].

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