Optical Absorption and Nonradiative Decay Mechanism of E' Center in Silica

Gianfranco Pacchioni* and Gianluigi Ieranò

Istituto Nazionale di Fisica della Materia, Dipartimento di Scienza dei Materiali, Università di Milano,
via Emanueli 15, 20126 Milano, Italy

Antonio M. Márquez

Departamento de Quimica Fisica, Facultad de Quimica, Universidad de Sevilla, 41012 Sevilla, Spain
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We report *ab initio* configuration interaction calculations on the optical transitions of the E' center, a hole trapped at an oxygen vacancy, $(—O)_3Si^\bullet \ ^+Si(O—)_3$, in silica. We found two competing excitation mechanisms: (1) promotion of one electron from an $O(2p)$ valence band orbital to the singly occupied Si dangling bond; (2) charge transfer (CT) transition from $(—O)_3Si^\bullet$ to $^+Si(O—)_3$. The two excitations occur at similar energies, $\approx 5.8-6$ eV (5.85 eV in the experiment), but only the CT has a strong intensity. The excitation is followed by a complex nonradiative decay process which may explain the absence of luminescence for this center. [S0031-9007(98)06572-7]

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Point defects in silica are of fundamental importance in metal-oxide semiconductor field effect transistors and fiber optics technology [1]. One of the most abundant and best characterized defects in SiO_2 is the E' center, a hole trapped at an oxygen vacancy, V_O^+. The E' center is a fundamental radiation-induced defect in amorphous silica, a-SiO_2 [1–6], and an important source of degradation in Si/SiO_2 based devices [4]. Several variants of the E' centers exist: E_1', and H-associated E_2', and E_4', in α-quartz; E_γ' and E_δ' centers in a-SiO_2. E_γ' is the closest analog to the E_1' in α-quartz [3]. Thanks to the combined use of optical absorption, OA [1], and electron paramagnetic resonance, EPR [1,6], spectroscopies, and theoretical calculations [7–11], the ground state structure of the E_1' and E_γ' centers is now quite well understood. The E' derives from the removal of a lattice oxygen to form a neutral oxygen vacancy, V_O, followed by hole trapping to give V_O^+. According to the first model proposed in 1974 by Feigl, Fowler, and Yip [7], FFY, the defect consists of a sp^3 hybridized $\equiv Si^\bullet$ dangling bond and of a nearly planar $\equiv Si^+$ unit, $\equiv Si^+ \ ^\bullet Si\equiv$ ($\equiv$ represents three Si-O bonds). The FFY model, however, does not account for the large hyperfine splitting, HFS, of ≈ 420 G of the unpaired electron with the ^{29}Si nuclide [6]. A refined model, suggested by Rudra and Fowler in 1985 [8], is based on an asymmetrical relaxation of the positively charged Si atom in a puckered position where it binds to a lattice oxygen which becomes three-coordinated. This structure was then confirmed by other studies including accurate first principle calculations [9–12]. The E_1' ground state structure, as obtained from the present cluster calculations, is illustrated in Fig. 1(a). It is generally accepted that the E_γ' in a-SiO_2 has a very similar structure.

Much less is known about the E' excited state properties. A typical OA band in bulk silica at 5.85 eV with an oscillator strength of 0.14 ± 0.04 has been assigned to

the E_γ' center by Weeks and Sonder based on a strong correlation with a characteristic EPR signal [2]. Two recent studies further reinforced the original assignment of the 5.85 eV band to E_γ' centers [13,14]. The nature of the transition, however, is still unclear. It could involve a charge transfer, CT, from $\equiv Si^\bullet$ to $\equiv Si^+$, as tentatively suggested back in 1980 by Griscom and Fowler [15], or simply a transition from the valence band to the partially filled Si sp^3 hybrid orbital. Furthermore, differently from many other defects in SiO_2 which exhibit typical photo-luminescence, PL, bands, emission upon exciting in the E_γ'-absorption band has never been observed. No mechanism has been proposed so far to elucidate this anomalous behavior. Another aspect which needs clarification is that on the surface of mechanically activated silica OA bands around 6.2 eV have been attributed to surface E_s' centers [16], consisting of a $\equiv Si^\bullet$ dangling bond. In this case the CT mechanism is not possible since there is no $\equiv Si^+$ unit in the vicinity of the $\equiv Si^\bullet$ groups.

The scope of this Letter is to present an accurate quantum-mechanical study of the absorption properties of the E' bulk and surface centers, and to provide a mechanism for the dissipation of the absorbed energy in the bulk through nonradiative decay. The computational approach is the same adopted recently to elucidate the OA and PL properties of V_O [17] and of other defects in silica [18].

We used SiO_2 clusters (with no symmetry) with the broken bonds saturated by H atoms placed along the O-Si directions of the crystal. The position of all the Si and O atoms, initially taken from α-quartz [19], has been reoptimized by computing analytical gradients of the total energy [20]. The H atoms were kept fixed to provide a representation of the mechanical embedding of the solid. A relatively large cluster $[Si_{14}O_{16}H_{26}]^+$ (Fig. 1) was used to determine the geometry of ground and excited states of V_O^+. All electron, AE, Hartee-Fock wave
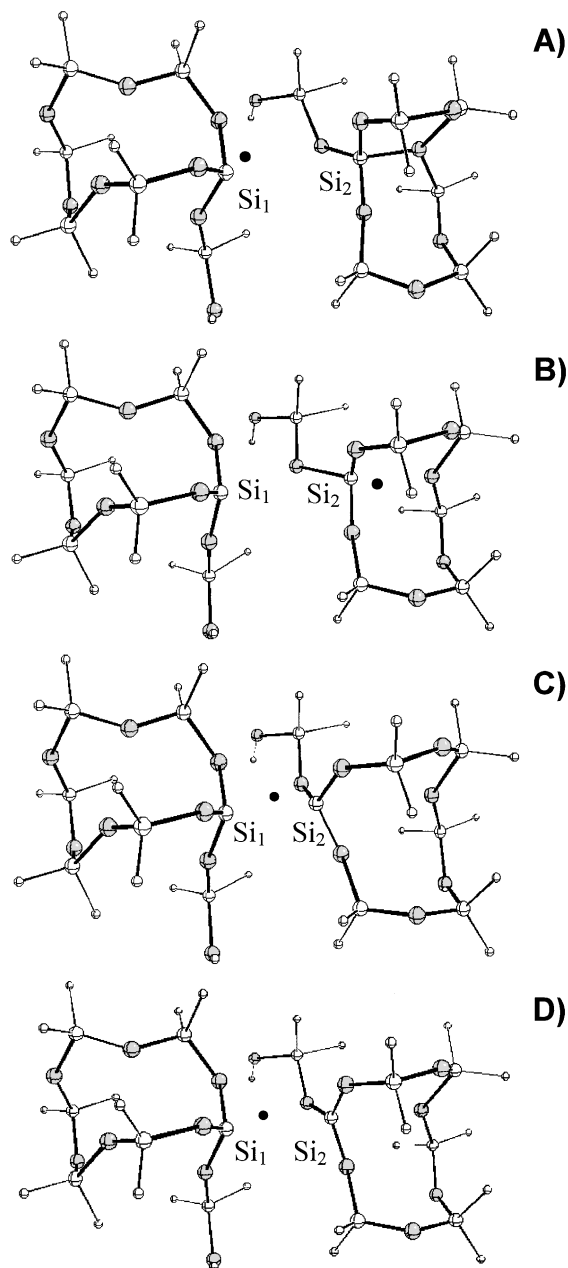
FIG. 1. $[Si_{14}O_{16}H_{26}]^+$ model of a E' center in a α-quartz. White spheres: Si; grey spheres: O; small white spheres: H. (a) Ground state minimum, E'_γ; (b) excited state minimum; (c) metastable E'_δ; (d) C → A transition state; see Fig. 3.

functions have been constructed using a 6-31G basis set on Si and O [21]. Smaller clusters were used to perform accurate calculations of the transition energies, T_e. On these smaller clusters we used an effective core potential [22], ECP, on Si to reduce the size of the configuration interaction (CI) calculations and a double-zeta, DZ, basis [22]. Diffuse s and p, plus one d, polarization functions have been added to Si. T_e's have been determined by performing multireference CI calculations, MRD CI [23,24]. Single and double excitations from the 12 highest occupied levels (24 electrons) have been generated with respect to

a set of main (M) configurations; for further details see Refs. [17] and [18]. Absorption intensities have been estimated by means of the oscillator strength, f, a dimensionless quantity, using the dipole-length operator formula, $f(\mathbf{r}) = \frac{2}{3}|\langle\Psi_0|e\mathbf{r}|\Psi_n\rangle|^2(E_n - E_0)$. Typical values of f for allowed transitions are between 0.1 and 1. Radiative lifetimes, τ, have also been determined. Both T_e's and intensities are determined with some uncertainty connected to the cluster and basis set size. These uncertainties are difficult to estimate: for the T_e's they are at least of the order of ±0.4 eV.

We start the discussion from the ground state structure of the E' center in bulk SiO_2 as obtained with the $[Si_{14}O_{16}H_{26}]^+$ cluster, Fig. 1(a). The defect is characterized by a rather long Si_1-Si_2 distance, 4.06 Å, and by a short distance, 1.81 Å, between the positively charged Si_2 and the three-coordinated oxygen. The isotropic HFS on Si_1, 364 G, is in reasonable agreement with the experimental value, 420 G [6]. These data are consistent with those reported in the literature for the E'_γ center [7–12]. To study the nature of the lowest excitations, we have considered two smaller models, one for the surface and one for the bulk. The model of a surface E'_s center is $(HO)_3Si^\bullet$, Fig. 2(a). For the bulk, we used a $(HO)_3Si^{\bullet\,+}Si(OH)_3$-$(OH_2)$ cluster; see Fig. 2(b), which includes also the three-coordinated oxygen of the E'_γ ground state structure. This latter cluster has been derived from the larger one, Fig. 1(a), but it has been fully reoptimized with the H atoms fixed. The optimal distances are similar to those obtained with the larger cluster. All the T_e are computed from minimum structures. The E'_s $(HO)_3Si^\bullet$ model allows us to analyze in detail the dependence of the T_e on the level of treatment. The lowest doublet-to-doublet transition corresponds to the excitation of one electron from a nonbonding O $2p$ valence band orbital to
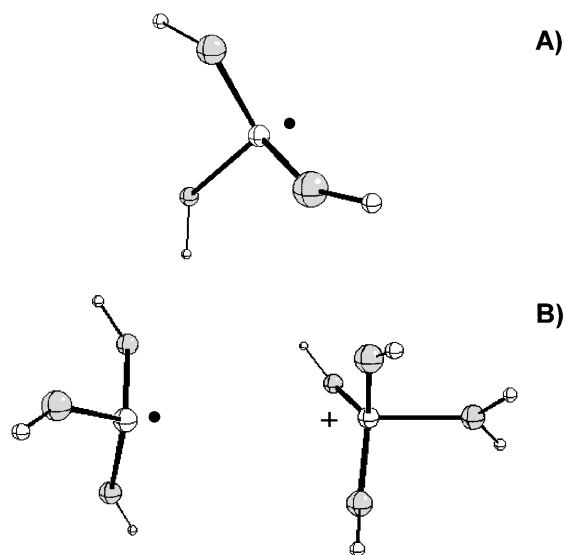

FIG. 2. Cluster models of surface (a) and bulk (b) E' centers used to compute T_e's.

the Si dangling bond. Using a 6-31G^* AE basis set on both O and Si plus diffuse s and p functions on Si, we obtain a T_e of 6.21 eV, in excellent agreement with the experiment [16]. Using an ECP on Si and a comparable basis, the T_e is slightly lower, 5.94 eV, Table I. The intensity of the transition is predicted to be low, $f(\mathbf{r}) \approx 10^{-2}$. The inclusion of a d function on O, cf. 6-31G and 6-31G^* basis sets in Table I, changes T_e by only ± 0.1 eV. In conclusion, an absorption band of weak intensity due to a transition from an O(2p) level to a Si dangling bond is expected around ≈ 6 eV for E_s' centers at the SiO$_2$ surface.

For the bulk E' center model we searched three roots in the CI secular problem: the ground state, the O (2p) $\rightarrow$ $\equiv$Si$^\bullet$ transition described above, and the CT transition where one electron is excited from Si$_1$ to Si$_2$. Strictly speaking, the O(2p) $\rightarrow$ $\equiv$Si$^\bullet$ is also a CT transition, but for clarity we refer only to the excitation from the two nonbonded Si atoms as CT. The CI results show that the two excited states have very small mixing and similar T_e, ≈ 5.7–5.8 eV; they are separated by ≈ 0.2 eV, but the relative ordering depends also on the details of the calculation, Table I. It is not possible to predict in a firm way which is the lowest transition in bulk E' based on the T_e's. However, the two transitions exhibit different intensities: the CT is about 10 times stronger than the O(2p) $\rightarrow$ $\equiv$Si$^\bullet$ transition. Experimentally, it has been observed that the transition at 5.85 eV associated with the E_γ' center has an oscillator strength of ≈ 0.14 eV [2]. Thus, both T_e and $f(\mathbf{r})$ are in agreement with the CT transition computed here while the predicted intensity of the valence band transition is too low. Consequently, the CT transition is expected to have a much shorter lifetime, $\tau \approx 10^{-9}$ sec, and to occur much more rapidly than the O(2p) $\rightarrow$ $\equiv$Si$^\bullet$ transition, $\tau \approx 10^{-8}$ sec. This latter transition, however, may dominate at the surface of the material.

Having established the nature of the 5.85 eV band in α-quartz and a-SiO$_2$, we consider now the decay mechanism. As we mentioned above, no luminescence is stimulated by the OA at 5.85 eV. In the bulk, the CT Franck-Condon excitation leads to a structure where one electron has been transferred from Si$_1$ to Si$_2$; see point A' in Fig. 3. The neutralization of Si$_2$ destabilizes the puckered structure, Fig. 1(a), because of the repulsion with the three-coordinated oxygen. The Si$_2$-O distance increases and the system undergoes a strong geometrical relaxation until it reaches a minimum; see Fig. 1(b) and point B in Fig. 3. In this minimum the unpaired electron is in a Si$_2$ sp^3 dangling bond, while Si$_1$ becomes almost flat because of the positive charge. Notice that no puckering of Si$_1$ occurs in this case because of the much longer distance with the lattice oxygen, Fig. 1(b). Starting the geometry optimization from a cluster where Si$_1$ has been inverted and puckered inside the ring results spontaneously in the structure shown in Fig. 1(b). In this respect the asymmetric nature of α-quartz is very important. From the excited state minimum, see Fig. 1(b) and point B in Fig. 3, the system could in principle decay radiatively. However, a barrier separates this minimum from another important reconstruction. This can be described as the inversion of Si$_2$ through the plane of the three O atoms with displacement of the unpaired electron toward the center of the cavity. It is reminiscent of the inversion doubling in a trigonal pyramidal molecule like NH$_3$. In an adiabatic picture, it is conceivable that the strong relaxation following the excitation provides enough vibrational energy to the system to overcome this barrier or that the electron can tunnel through the barrier and show up on the other side of Si$_2$. A more detailed analysis of the potential energy surface around this barrier shows that it actually originates from an avoided crossing of two states; see dotted lines in Fig. 3. In a diabatic picture the vertical CT transition from the E' ground state promotes one electron in a highly excited vibrational level; see $A \rightarrow A'$ in Fig. 3. The electron can then decay to lower vibration levels and, through an internal conversion, into the minimum of the upper state curve, Fig. 3, and from here can cross the narrow gap with emission of a low-frequency photon. Whatever description is used, adiabatic

TABLE I. Transition energies, T_e, and oscillator strength, $f(\mathbf{r})$, of E' centers at the surface and in the bulk of SiO$_2$.

Cluster	O basis	Si basis	O(2p) $\rightarrow$ $\equiv$Si$^\bullet$ transition T_e (eV)	$f(\mathbf{r})$	$\equiv$Si$^\bullet$ $\rightarrow$ $^+$Si$\equiv$ CT transition T_e (eV)	$f(\mathbf{r})$
(HO)$_3$Si$^\bullet$, surface E_s'						
	6-31G	6-31G^* + s + p	6.28	0.01	$\cdots$	$\cdots$
	6-31G^*	6-31G^* + s + p	6.21	0.01	$\cdots$	$\cdots$
	6-31G	ECP-DZ + s + d	5.81	0.01	$\cdots$	$\cdots$
	6-31G^*	ECP-DZ + s + d	5.94	0.03	$\cdots$	$\cdots$
Experiment [16]			6.2 $\pm$ 0.1		$\cdots$	$\cdots$
(HO)$_3$Si$^\bullet$ $^+$Si(OH)$_3$-(OH$_2$), bulk E'						
	6-31G	ECP-DZ + s + d	5.7^a	0.03	5.8^a	0.30
Experiment [2]			$\cdots$	$\cdots$	5.85	0.14 $\pm$ 0.04

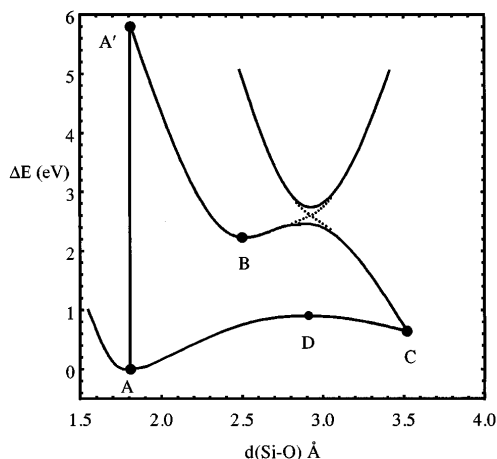^{a}Average value of different CI treatments.

FIG. 3. Schematic energy profile of the excitation-deexcitation mechanism of the E' center in bulk SiO_2. The energies are plotted versus the distance between Si_2 and the "three-coordinated" O. See Figs. 1(a), 1(b), 1(c), and 1(d) for the structure of the stationary points A, B, C, and D, respectively.

or diabatic, the system gains enough vibrational energy through the CT excitation to escape from the minimum of the excited state potential, Fig. 3.

Once the barrier is overcome, the system undergoes another important relaxation which leads to a metastable variant of the E' ground state structure. In this local minimum, point C in Fig. 3, the unpaired electron is shared among the two Si atoms of the vacancy, Fig. 1(c). The substantial delocalization of the spin is shown by the existence of two HFS's of 118 G (Si_1) and 62 G (Si_2). The electron remains trapped between the two Si atoms, a situation reminiscent of F centers in alkali halides; the Si-Si distance, 2.67 Å, is not too far from that of the regular lattice, 3.06 Å. This structure is not unprecedented and corresponds to the E'_δ described by Snyder and Fowler [10] and by Boero et al. [11] and probably observed in Cl-containing glasses by Griscom and Friebele [25]. The E'_δ is a metastable form of the E' ground state. In our approach it is 0.64 eV higher than the global minimum; the barrier separating the local, Fig. 1(c), and the global, Fig. 1(a), minima is 0.32 eV and corresponds, as shown by a full vibrational analysis, to a true transition state, Fig. 1(d), and point D in Fig. 3. The barrier is small enough that the lattice vibrations following the nonradiative decay will lead to a depopulation of the E'_δ structure in favor of the asymmetric E'_γ ground state, explaining why the E'_δ has not been clearly identified in EPR experiments so far. In this way, the system returns back to the original structure from which the CT transition has occurred and dissipates completely the absorbed energy through a nonradiative decay mechanism.

In conclusion, we have shown that E' centers at the surface and in the bulk of SiO_2 have similar absorption energies which, however, originate from different mechanisms. In bulk silica the excitation seems to have CT character; the absence of luminescence may be explained as due to a complex nonradiative decay mechanism which completely dissipates the energy of the adsorbed photon.

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*Electronic address: Gianfranco.Pacchioni@mater.unimi.it

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