Computed Optical Absorption and Photoluminescence Spectra of Neutral Oxygen Vacancies in α-Quartz

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We report *ab initio* configuration interaction calculations of the optical transitions of a SiO_2 neutral oxygen vacancy (V_O) using cluster models. The transition from the V_O ground state and the consequent radiative decay explain the 7.6 eV absorption and the 4.4 eV photoluminescence bands reported in the literature. We suggest that the transition from a metastable structure of V_O is responsible for the 5.0 eV absorption band. The model accounts for the fact that the 4.4 eV fluorescence is stimulated by excitations in both UV and vacuum UV regions with different decay kinetics. [S0031-9007(97)03629-6]

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A major motivation for the investigation of the optical properties of point defects in silica is their role in the degradation of SiO_2-based electronic devices. Structural imperfections created during fabrication or generated by heat treatments or irradiation determine the optical absorption (OA) and photoluminescence (PL) properties of crystalline and amorphous silica [1–6]. In particular, oxygen deficient centers (ODC) give rise to an OA at 5.0 eV (B_2 band, more pronounced in amorphous silica) and at 7.6 eV (E band) with a typical PL band at 4.3–4.4 eV. Excitation in both B_2 and E bands absorption regions induces the 4.4 eV fluorescence [2–6]. Recent studies have shown that the 5.0 eV OA and the 4.4 eV PL bands are actually envelopes of several bands probably due to different relaxation of the crystal around the defect responsible [6]. In spite of the large number of studies, structural models of point defects responsible for the optical transitions in silica are still controversial. According to Thomon *et al.* [3] the neutral oxygen vacancy, V_O, has a singlet-triplet transition at 5.0 eV (B_2) and a singlet-singlet transition at 7.6 eV (E). Imai *et al.* [2] and Nishikawa *et al.* [4] suggested that the B_2 and E bands involve transitions from two distinct configurations of the same center, the relaxed and unrelaxed oxygen vacancy, ODC(I) and ODC(II), respectively. Skuja [7] proposed that a twofold coordinated Si, $=$Si$:$, gives two singlet-singlet transitions at 5.0 and 7.0 eV, both effective in pumping the PL emission at 4.4 eV.

Several theoretical studies have addressed the ground state (gs) properties of V_O centers in α-quartz and amorphous SiO_2 showing that the removal of an oxygen atom from the lattice leads to the formation of a $\equiv$Si—Si$\equiv$ bond [8–11] with a decrease of d(Si-Si) from 3.06 Å in α-quartz to $\approx$2.5 Å in V_O. On the other hand, very few studies have addressed the problem of the optical transitions [3,10,12,13]; the majority are based on approximate treatments with a limited representation (if any) of the structural relaxation. A quantitative description of OA and PL bands requires flexible models and an extensive inclusion of correlation effects. This is hardly feasible within approximate quantum-chemical schemes or band structure approaches and implies the use of cluster models, a technique justified for the investigation of localized phenomena in solids.

In this work we study the optical transitions of a V_O center in α-quartz with *ab initio* cluster model Hartree-Fock (HF) and configuration interaction (CI) wave functions. We find that the V_O center exists in two configurations, one of which is metastable. A singlet-singlet transition occurs at 7.6 eV from the gs, $\equiv$Si—Si$\equiv$, to an excited state characterized by a singly occupied dangling bond on each Si, $\equiv$Si$^\bullet$ $^\bullet$Si$\equiv$. The transition is followed by a rapid vibrational relaxation to the minimum of the excited state where the Si atoms moved apart because of the occupation of an antibonding state. The radiative $S_1 \rightarrow S_0$ decay from this minimum is the origin of the 4.3–4.4 PL band. We suggest that the 5.0 eV OA is due to the vertical transition from the metastable form of the V_O center to the $\equiv$Si$^\bullet$ $^\bullet$Si$\equiv$ excited state. Through a different vibrational channel, the system relaxes to the same S_1 minimum excited by the 7.6 eV absorption. This explains why the PL at 4.4 eV is stimulated by absorption in both UV and vacuum UV regions but with different kinetics.

We modeled α-quartz by means of SiO_2 clusters (with no symmetry) with the dangling bonds saturated by H atoms placed along the O-Si directions of the crystal. The position of all the Si and O atoms has been reoptimized by computing analytical gradients of the total energy [14]. The H atoms were kept fixed to provide a representation of the mechanical embedding of the solid matrix. Relatively large clusters, $Si_{14}O_{16}H_{26}$ (Fig. 1), $Si_8O_{24}H_{18}$, $Si_8O_{23}H_{16}$, and $Si_5O_{14}H_{12}$, representing different sections of the crystal, were used to determine the geometry of ground and excited states of V_O. Smaller clusters, e.g., $(OH)_3Si$—$Si(OH)_3$, were used to perform highly accurate calculations of the transition energies, T_e. All electron HF-SCF wave functions have been constructed using a 6-31G double zeta (DZ) basis set [15] augmented by a d function on Si and a MINI-1 basis set [16] on H and O. The computed bond distances agree with the experimental values of

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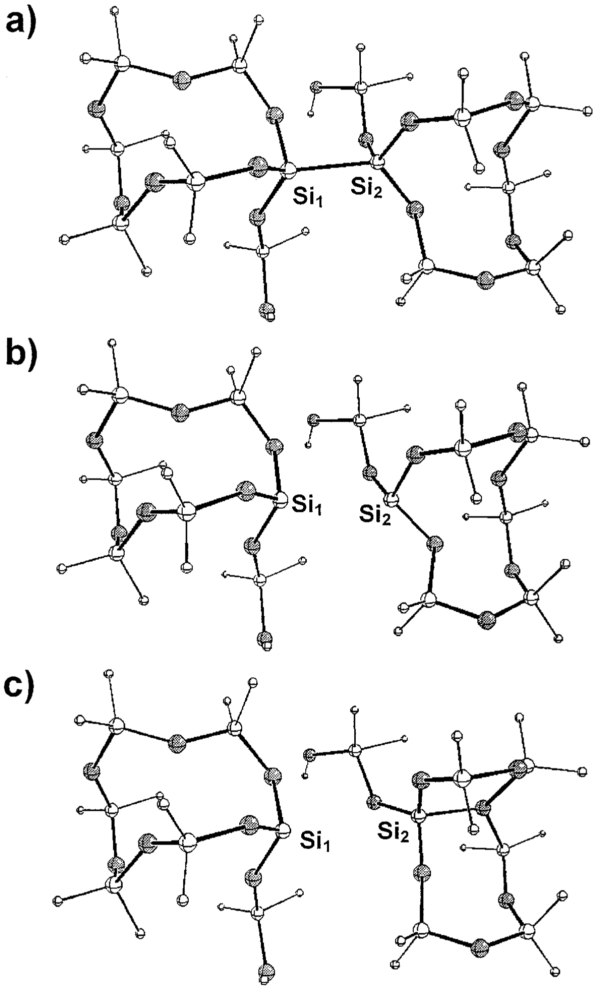

FIG. 1. $Si_{14}O_{16}H_{26}$ model of a neutral oxygen vacancy in α-quartz. Grey spheres, O, large white spheres, Si; small white spheres, H. (a) Ground state minimum structure, S_0, ≡Si—Si≡; (b) excited state minimum structure, S_1, ≡Si$^\bullet$ $^\bullet$Si≡; (c) metastable puckered structure, S_0', ≡Si$^-$ ≡Si$^+$—O═.

α-quartz [17] within 0.02 Å. Larger basis sets do not alter the results. Diffuse *s* and *p* functions have been added on Si to describe high excited states with Rydberg character. T_e's have been determined by performing multireference CI calculations, MRD CI [18,19]. Single and double excitations from the 12 highest occupied levels (24 electrons) to all virtual orbitals have been generated with respect to a set of main (*M*) configurations; in this way higher excitation classes are included in the final CI wave function [18]. The configurations with an estimated contribution to the CI energy larger than 10 μHartree (about 10.000) are included in the secular determinant; the contribution of the remaining configurations (more than 1×10^6) is estimated through an extrapolation technique [18]. The reported CI energies refer to the larger CI space. 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.

The formation of a V_O center results in a short d(Si-Si) = 2.55 ± 0.05 Å, due to the formation of a two-center two-electron bond. From the combination of the sp^3 hybrids on each Si, a doubly occupied σ bonding and an empty σ^* antibonding state appear in the band gap [12]. The gs, S_0, is therefore $(\sigma)^2(\sigma^*)^0$. The first excited state is a triplet, T_1 $(\sigma)^1(\sigma^*)^1$, with a MRD CI T_e of 6.3 eV; see Table I (see also Fig. 2). $S_0 \rightarrow T_1$ transitions, however, are forbidden and can carry sufficient intensity only through spin-orbit coupling. Therefore, our calculations do not support the assignment of Thomon *et al.* [3] of a $S_0 \rightarrow T_1$ transition at 5.0 eV due to a neutral V_O center. This assignment has also been seriously questioned because of recent experimental measurements of the radiative lifetimes [4]. The first allowed transition is S_0 $(\sigma)^2(\sigma^*)^0 \rightarrow S_1(\sigma)^1(\sigma^*)^1$ with formation of two singly occupied dangling bonds, coupled singlet, on the adjacent Si atoms. The vertical T_e computed with the Si DZ + *d* basis set is 8.8 eV. This is 1.2 eV higher than the 7.6 eV *E* band in SiO_2. High excited states have often Rydberg character. For example, the first allowed transition in the Si_2H_6 molecule occurs at 7.6 eV and is a $(2a_{1g})^2 \rightarrow 4s$ Rydberg excitation [20]. We compute this transition in Si_2H_6 at 8.7 eV, i.e., ≈1.1 eV larger than in the experiment. This is the same error found on V_O. Including a diffuse *s* and *p* function on Si, we obtain a T_e of 8.1 eV for Si_2H_6 and of 7.5 eV for V_O (Table I). Both these values are in much better agreement with the experiment, and for V_O the T_e is almost exact; however, this is partly fortuitous since small structural changes in the model can

TABLE I. Computed optical properties of a neutral oxygen vacancy in α-quartz.

Defect	Cluster	Transition	nM/nR[a]	T_e, eV	*f*	τ, ns	Expt. band
≡Si—Si≡	$Si_2O_6H_6$	$S_0 \rightarrow S_1$	$11M/2R$	8.79 (7.47)[b]	0.33	1	7.6 eV [2–4]
	$Si_2O_6H_6$	$S_0 \rightarrow T_1$	$1M/1R$	6.31 (6.21)[b]	forbidden	⋯	not obs.
≡Si$^\bullet$ $^\bullet$Si≡	$Si_2O_6H_6$	$S_1 \rightarrow S_0$	$14M/2R$	4.96 (4.31)[b]	0.40	3	4.4 eV [4]
≡Si$^-$ ≡Si$^+$—O═	$Si_2O_6H_6$-OH_2	$S_0' \rightarrow S_1$	$24M/3R$	3.31	0.09	21	not obs.
	$Si_2O_6H_6$-OH_2	$S_0' \rightarrow S_2$	$24M/3R$	5.26	0.21	4	5.0 eV [2–4]
═Si:	$(OH)_2Si$	$S_0 \rightarrow S_1$	$12M/2R$	5.79 (5.59)[b]	0.06	12	5.8 eV [22]

[a] Number of main configurations, *M*, and of roots, *R*, for each CI calculation.

[b] With Rydberg functions on the Si basis set.

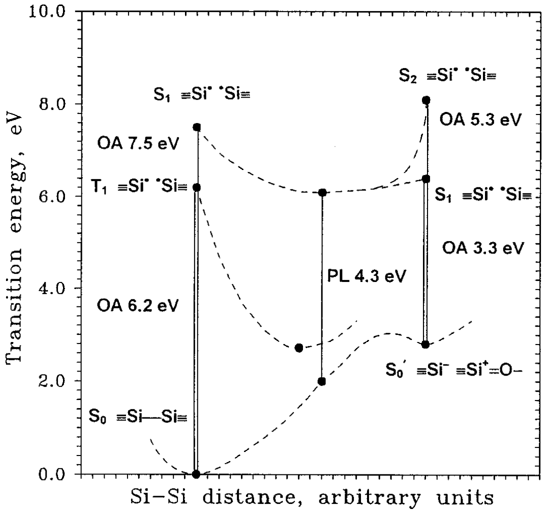

FIG. 2. Schematic energy diagram of computed optical transitions in a SiO_2 oxygen vacancy. Solid lines indicate optical absorption (OA) or photoluminescence (PL). The dotted curves represent nonradiative processes but have no quantitative meaning. The data are reported as a function of increasing Si-Si distance, in arbitrary units.

easily result in ±0.3 eV shifts in T_e. Notice that with the Rydberg functions the $S_0 \rightarrow T_1 T_e$ changes only slightly, from 6.3 to 6.2 eV (Table I). The oscillator strength of the $S_0 \rightarrow S_1$ transition, $f = 0.3$, indicates a strong absorption intensity, the computed radiative lifetime is 1 ns. These results strongly support the assignment of the E band to a $S_0 \rightarrow S_1$ transition in a neutral oxygen vacancy, ODC(I).

The two-coordinated Si proposed by Skuja *et al.* [7], $=\!Si\!:$, was studied using a $(OH)_2Si\!:$ model derived from α-quartz. The cluster gs is singlet, and the lowest transition, $S_0 \rightarrow S_1$, has a $T_e = 5.8$ eV (5.6 eV with Rydberg functions, Table I). The excitation occurs from a Si sp^2-like hybrid to a Si 3*p* orbital normal to the O-Si-O plane. MRD CI calculations on the isovalent SiF_2 molecule give a $X^1A_1 \rightarrow {}^1B_1 T_e$ of 5.7 eV, in excellent agreement with the experimental T_e of 5.5–5.7 eV [21]. Thus, for molecular systems the method produces T_e's with estimated errors which do not exceed ±5%. Our results do not support the two-coordinated Si as the origin of the 5.0 eV (B_2) or 7.6 eV (E) bands. On the other hand, this defect could be the cause of the 5.8 eV OA band attributed to a diamagnetic center [22]. It is not excluded that strong geometrical distortions in amorphous silica can lead the two-coordinated Si to absorb in the 5.0 eV region. Recent studies clearly indicate that the B_2 band is actually a complex superposition of different transitions [6,23].

The rupture of the Si-Si bond due to the absorption of a 7.6 eV photon causes a substantial geometrical relaxation of the excited state. Using a generalized valence bond wave function and analytical gradients we found that in the minimum configuration of the S_1 state the Si atoms move ≈3.6 Å apart [Fig. 1(b)]. A similar relaxation is found for the T_1 excited state. From the minimum of the S_1 excited state the system decays to S_0 (Fig. 2). The computed energy of the emitted photon, 4.3 eV with Rydberg functions and 5.0 eV without (Table I), is consistent with the observed PL band at 4.3–4.4 eV. The Stokes shift is therefore more than 3 eV. The lifetime, 3 ns, is extremely close to the experimental one, $\tau = 2.1$ ns [4]. Thus we can conclude that the 4.4 eV emission is due to a radiative $(\sigma)^1(\sigma^*)^1 \rightarrow (\sigma)^2$ decay from the minimum of the $\equiv\!Si^{\bullet}\ {}^{\bullet}Si\!\equiv$ S_1 excited state.

The calculations described above unambiguously assign the 7.6 eV band and the corresponding 4.4 eV PL to a neutral oxygen vacancy, but the origin of the 5.0 eV band is still unclear. Experimentally the following observations have been made: (1) the B_2 and E bands always appear together suggesting that the same defect is responsible for the two transitions [2,3]; (2) both bands are reduced by heat treatment in O_2 atmosphere clearly identifying an ODC as the origin of the transitions [2]; (3) the B_2 band is ≈4 orders of magnitude less intense than the E band [2]; (4) both OA's lead to an emission at 4.4 eV with different radiative lifetimes indicating different channels for the decay [4]; (5) irradiation with an excimer laser decreases the intensity of the B_2 band but not that of the E band suggesting a transformation of ODC(II) into ODC(I) [2]. Starting from these observations, we suggest a tentative assignment for the 5.0 eV transition. As mentioned previously, a metastable ODC(II) state is found in our models of a neutral V_O center, Fig. 1(c). This is reminiscent of the structure of the positively charged oxygen vacancy, $V_O{}^+$ (or E'). The $V_O{}^+$ center undergoes an asymmetrical relaxation which leaves a singly occupied dangling bond on one Si, hereafter referred to as Si(1), and a net positive charge on Si(2) [24]. According to a more refined model [25] the asymmetric relaxation is stabilized by the formation of a "puckered" configuration where Si(2) is bound to a lattice oxygen by electrostatic forces, $\equiv\!Si^{\bullet}\ \equiv\!Si^+\!-\!O\!=$. This structure, characterized by the presence of a three-coordinated oxygen [25], is found also in our calculations on $V_O{}^+$. Adding one electron to puckered $V_O{}^+$ can result in two V_O structures. If the electron goes into the empty sp^3 hybrid of Si(2) the loss of electrostatic interaction with the lattice oxygen breaks the $\equiv\!Si^+\!-\!O\!=$ bond. The ensuing coupling of the dangling bonds on the neighboring Si atoms restores the $\equiv\!Si\!-\!Si\!\equiv$ gs structure of V_O, Fig. 1(a). If the electron goes into the partially filled sp^3 hybrid of Si(1) one is left with a singlet state which can be schematically represented as $\equiv\!Si^-\ \equiv\!Si^+\!-\!O\!=$, Fig. 1(c). A doubly occupied dangling bond forms on Si(1) while Si(2) is still positively charged and electrostatically bonded to the lattice oxygen. The structure is very close to that of the $V_O{}^+$ gs [25] with the Si atoms ≈4 Å apart [Fig. 1(c)] and a $\equiv\!Si^+\!-\!O\!=$ distance of ≈2 Å and is closely related to the valence alternation pair defect described by Luckovsky [26]. Puckered V_O is a local minimum on the S_0 potential energy surface and, at the HF level, is about 2.7 eV higher in energy than the gs. The charges on Si(1) and Si(2) are

+0.5 and +1.7, respectively. Thus, Si(2) has a net charge not too different from that of the other Si atoms of the cluster, while Si(1) is almost neutral; the classification as $\equiv$Si$^-$ $\equiv$Si$^+$—O$=$ is purely conventional. It is not the first time that the bistable nature of the V_O center is observed. Snyder and Fowler [27] found a puckered closed shell configuration $\approx$2.6 eV higher than the $\equiv$Si—Si$\equiv$ dimer and estimated a barrier of only 0.2 eV for the interconversion of the puckered into the stable structure. Very recently, Boero *et al.* confirmed the existence of the puckered structure and of the small barrier, 0.3 eV, using the Car-Parrinello approach [11]. The reported barriers for α-quartz [11,27] are too small to justify the thermal stability of ODC(II), but it is possible that a higher barrier separates the two minima in amorphous silica where the B_2 band is much more intense than in quartz. The importance of the puckered structure for the interpretation of the optical properties of ODC in silica is stressed here for the first time.

To compute the ODC(II) T_e we constructed a small model, (OH)$_3$Si—Si(OH$_3$)-OH$_2$, with a water molecule added at 2 Å from Si(2) to represent the $\equiv$Si$^+$—O$=$ bond. Two singlet-singlet excitations are computed at 3.3 and 5.3 eV, respectively; see Table I and Fig. 2. The $S_0' \rightarrow S_1$ transition has a relatively low intensity and a long lifetime, 20 ns, and corresponds to the excitation of one electron from Si(1) to a 3*s* level of Si(2); the $S_0' \rightarrow S_2$ transition occurs at 5.3 eV and has a strong intensity and a short lifetime, $\tau = 3.9$ ns. It corresponds to the excitation from a sp^3 hybrid on Si(1) to a corresponding sp^3 level on Si(2), with formation of a $\equiv$Si$^\bullet$ $^\bullet$Si$\equiv$ diradical structure. The most rapid process following excitation to any state higher than S_1 is nonradiative internal conversion down to S_1. The structural relaxation leads to the same minimum of the S_1 state excited at 7.6 eV, but through a different channel for the nonradiative decay, Fig. 2. A 4.4 eV PL occurs from the minimum of S_1. This is consistent with the different kinetics of the 4.4 eV PL stimulated by 5.0 and 7.6 eV OA's [4]. The about 4 orders of magnitude smaller intensity of the 5.0 eV band [2] are consistent with a much lower thermal population of puckered V_O and are not due to a reduced cross section of this transition, in agreement with Imai *et al.* [2]. Furthermore, the identification of the puckered structure as the origin of one component of the B_2 band is consistent with the observed bleaching of this band by irradiation with excimer laser due to the conversion of ODC(II) in ODC(I) [2].

To summarize, we have shown that the 7.6 eV *E* band is unambiguously due to a $S_0 \rightarrow S_1$ transition from the $\equiv$Si—Si$\equiv$ gs configuration of the V_O center. The spin forbidden $S_0 \rightarrow T_1$ transition is predicted to occur at 6.2 eV. The radiative $S_1 \rightarrow S_0$ decay from the minimum of the S_1 excited state, $\equiv$Si$^\bullet$ $^\bullet$Si$\equiv$, is the origin of the 4.4 eV PL band. Both absorption and emission have very short lifetimes of 1 and 3 ns, respectively. A metastable configuration of the V_O center exists; it is a puckered configuration reminiscent of that of the paramagnetic E' center and can be schematically represented as $\equiv$Si$^-$ $\equiv$Si$^+$—O$=$. From this metastable structure an intense $S_0' \rightarrow S_2$ transition occurs at 5.3 eV. The nonradiative decay leads to the minimum of the S_1 state, $\equiv$Si$^\bullet$ $^\bullet$Si$\equiv$, through a different channel. From this minimum the same 4.3–4.4 eV emission excited in the vacuum UV region occurs. We suggest that the metastable V_O structure is responsible for the 5.0 eV B_2 band.

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