

Electronic Structure of Oxygen Dangling Bond in Glassy SiO₂: The Role of Hyperconjugation

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The electronic structure and the nature of optical transitions in oxygen dangling bond in silica glass, the nonbridging oxygen hole center (NBOHC), were calculated. The calculation reproduced well the peak positions and oscillator strengths of the well-known optical absorption bands at 2.0 and 4.8 eV, and of the recently discovered absorption band at 6.8 eV. The 2.0 eV band was attributed to transition from the σ bond between Si and dangling oxygen to nonbonding π orbital on the dangling oxygen. The uniquely small electron-phonon coupling associated with the 2.0 eV transition is explained by stabilization of Si-O bond in the excited state by hyperconjugation effects.

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Synthetic SiO₂ glass is a key optical material for deep ultraviolet and vacuum ultraviolet (VUV) lasers because of high optical transparency and resistance to laser damage. Optical lithography using an F₂ excimer laser ($\lambda = 157$ nm, $h\nu = 7.9$ eV) is now examined to achieve a design rule smaller than 70 nm. However, the cutoff wavelength of SiO₂ glass is close to 157 nm and its transmittance is affected both by photo-induced point defects [1–4] and by structural alternation of absorption edge induced by glassy disorder [5]. An oxygen dangling bond $\equiv \text{Si-O}\cdot$, which is illustrated in Fig. 1 and often denoted as nonbridging oxygen hole center (NBOHC), usually dominates the visible and near-UV absorption spectrum of irradiated silica by its two well-known optical absorption bands at ≈ 2.0 eV (1.97 eV at 295 K, 1.94 eV at 80 K) and at 4.8 eV [6]. Recently, it was found that NBOHC gives as well an intense vacuum UV (VUV) optical absorption band at ~ 6.8 eV [7], which together with the 4.8 eV band renders it a dominant cause of defect absorption in UV-VUV spectral regions.

Apart from its practical importance, NBOHC is of fundamental interest due to its uncommon spectroscopic properties. The electron-phonon coupling of its 2.0 eV absorption transition is unusually small: the associated photoluminescence (PL) band at 1.91 eV has a Stokes shift of merely ≈ 0.03 eV at 80 K and a strong resonance zero-phonon line is observed in site selective luminescence spectra [6]. This property makes NBOHC unique among point defects in light element oxides. To explain the small electron-phonon coupling, it was initially suggested [6] that the 2.0 eV absorption/1.9 eV PL transitions should occur between nonbonding states, namely, between the half-filled lone-pair orbital of the nonbridging oxygen $n(\text{O}_{nb})_y$ and the lone-pair orbitals $n(\text{O}_b)_\perp$ of the three oxygen atoms surrounding the central Si atom [Fig. 1]. The 4.8 eV absorption band was assigned to transition $\sigma(\text{Si-O}_{nb})_z \rightarrow n(\text{O}_{nb})_y$ involving σ -bonding orbital, expected to cause a strong relaxation, in accord with the

large half-width (1.05 eV) of this band. This scheme was supported as well by early calculations [8–10]. However, more recent calculations, performed by configuration interaction (CI) [11,12] and time-dependent density functional theory (DFT) techniques calculations [13]—favor a reverse scheme, with the 2.0 eV transition taking place between the Si-O_{nb} σ -bonding orbital and the half-filled lone-pair orbital of NBOHC (Fig. 1). This outcome is quite unusual by predicting almost a complete absence of relaxation of Si-O_{nb} bond after excitation of an electron from its σ -bonding orbital. The purposes of the present Letter were: (i) to provide an assignment for the recently discovered [7] NBOHC absorption band at 6.8 eV, (ii) to examine the nature of the Si-O bonding in NBOHC and to suggest that the “anomalous” properties of electronic structure of NBOHC and the small electron-phonon coupling of the 2.0 eV transition can be explained by hyperconjugation in Si-O bonding.

In our *ab initio* cluster calculation we used three hydrogen-terminated clusters to represent the local structure of SiO₂ glass with and without NBOHC: (i) (OH)₄Si

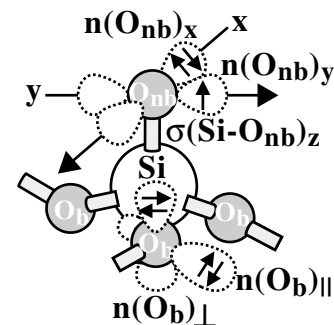


FIG. 1. Orbitals related to the optical transitions in dangling oxygen bond (NBOHC) in SiO₂ glass. Sticks show Si-O σ bonds. For cluster calculations, three or four dangling oxygen bonds were saturated with hydrogen atoms. Lone-pair electrons on the other two oxygens are omitted for simplicity.

(“ideal” cluster), (ii) paramagnetic $(\text{OH})_3\text{Si-O}\cdot$ (“NBOHC” cluster), and (iii) negatively charged $(\text{OH})_3\text{Si-O}^-$ (“negative NBOHC” cluster). Geometry optimization was performed without preassumed symmetry at the restricted open shell Hartree-Fock level using analytical gradients of the total energy [14,15]. The atoms were initially placed at their positions in α quartz. The hydrogen atoms were located at 98 pm from the bridging oxygen atoms to saturate the dangling bonds of the clusters. During the geometry optimization, the $\text{Si-O}_b\text{-H}$ angles and $\text{O}_{nb}\text{-Si-O}_b\text{-H}$ dihedral angles were fixed to the respective values of Si-O-Si angle and O-Si-O-Si dihedral angles in α quartz [16]. Split valence 6-31G basis sets [17] with d -type polarization functions were used for Si (exponent of the d -type function, $\alpha_p = 0.395$) and O_{nb} ($\alpha_p = 0.8$) atoms. MINI-1 [18] basis sets were used for the bridging oxygen and hydrogen atoms to reduce the load of calculations. The length of Si-O_b bonds was ~ 160 pm both in the optimized ideal and NBOHC clusters, close to the value of 160.8 ± 0.4 pm [19] reported for the normal silica glass network. The vibration frequency of the Si-O_{nb} stretching mode in the NBOHC cluster was estimated to be 916 cm^{-1} , in agreement with the observed value 890 cm^{-1} [6,20]. This gives some confidence to the results of the present calculations based on these cluster models.

Electron correlation effects were incorporated for precise calculation of transition energies (T_e) and oscillator strengths (f) using the optimized NBOHC cluster configuration. We adopted the multireference double electron excitation configuration interaction (MRD-CI) [21,22]. Nine roots were determined and 25 electrons were correlated in the MRD-CI calculation. About 1×10^4 configurations with the contribution to the CI energy larger than $10 \mu\text{Hartree}$ were included in the secular determinant while contribution of the other configurations (more than 1×10^6) was estimated through an extrapolation technique [21]. Full CI energies were extrapolated from the selected MRD-CI energies by the Davidson correction [23]. All calculations were performed using GAMESS-UK program [24]. The calculated molecular orbitals of the clusters were analyzed by natural bond orbital (NBO) techniques [25] in order to obtain the electron occupancies of σ and π orbitals.

Figure 2(a) illustrates the energy levels calculated for the ideal cluster. The highest occupied molecular orbital (HOMO) is a doubly occupied $n(\text{O}_b)_\perp$ state, consisting mainly of O_b lone-pair orbitals perpendicular to the $\text{Si-O}_b\text{-H}$ plane as illustrated in Fig. 1. The lowest unoccupied MO (LUMO) is made of the antibonding state of the bridging Si-O_b σ bonds [$\sigma^*(\text{Si-O}_b)$]. This result is consistent with a model that has been universally assumed. The bonding state of the bridging Si-O_b σ bond [$\sigma(\text{Si-O}_b)$] is located below the HOMO $n(\text{O}_b)_\perp$ and $n(\text{O}_b)_\parallel$ states, as usually expected. In the NBOHC clusters, additional states related to the nonbridging oxygen

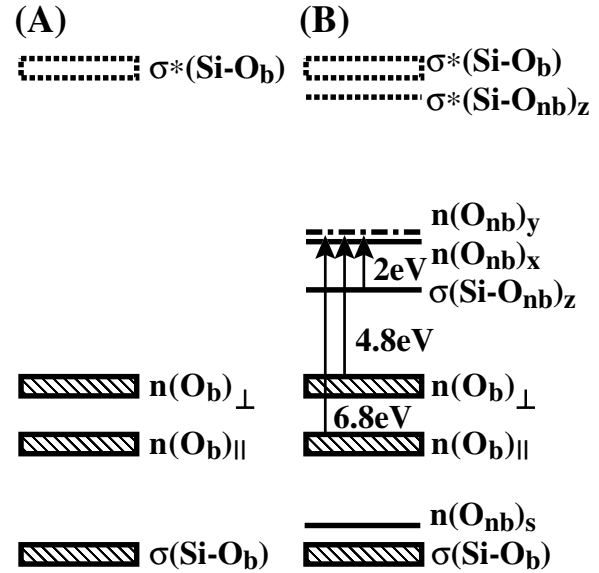


FIG. 2. Energy level diagrams of $(\text{OH})_4\text{Si}$ cluster (a) and the NBOHC cluster $(\text{OH})_3\text{Si-O}\cdot$ (b), showing the assignment of the observed optical absorption bands of NBOHC. Multiply degenerated levels are described as box-shape symbols for simplicity. The highest occupied MO in (b) is $n(\text{O}_{nb})_y$, which is the singly occupied level.

appear in the energy gap [Fig. 2(b)], forming new optical absorption bands. Table I shows the calculated transition energies and the oscillator strengths along with the experimental values.

In this scheme, the 2.0 eV absorption band ($X^2A \rightarrow 2^2A$ in Table I) is attributed to the transition from the $\sigma(\text{Si-O}_{nb})_z$ orbital to the half-filled $n(\text{O}_{nb})_y$ lone pair. The 4.8 eV absorption band (sum of $X^2A \rightarrow 3^2A$, $X^2A \rightarrow 4^2A$, and $X^2A \rightarrow 5^2A$ transitions) corresponds to the

TABLE I. Calculated electronic transition energies (T_e) and oscillator strength (f) for the $(\text{OH})_3\text{Si-O}\cdot$ cluster simulating the local structure of oxygen dangling bond (NBOHC).

State	T_e (eV)		f	
	Calculated/observed		Calculated/observed	
X^2A	-/-		-/-	
1^2A	0.20/-		$3.0 \times 10^{-6}/-$	
2^2A	2.02/2.0 ^a		$2.5 \times 10^{-5}/1.5 \times 10^{-4a}$	
3^2A	4.68		5.3×10^{-3}	
4^2A	4.86	4.8 ^b /4.8 ^a	0.022	0.038 ^c /0.05 ^a
5^2A	5.24		0.011	
6^2A	5.82		3.0×10^{-3}	
7^2A	6.15	6.2 ^d /6.8 ^e	5.3×10^{-3}	0.012 ^f /0.05 ^e
8^2A	6.52		4.0×10^{-3}	

^aIn Refs. [6,26,27].

^bAverage of $X^2A \rightarrow 3^2A$, $X^2A \rightarrow 4^2A$, and $X^2A \rightarrow 5^2A$.

^cSum of $X^2A \rightarrow 3^2A$, $X^2A \rightarrow 4^2A$, and $X^2A \rightarrow 5^2A$.

^dAverage of $X^2A \rightarrow 6^2A$, $X^2A \rightarrow 7^2A$, and $X^2A \rightarrow 8^2A$.

^eIn Ref. [7].

^fSum of $X^2A \rightarrow 6^2A$, $X^2A \rightarrow 7^2A$, and $X^2A \rightarrow 8^2A$.

transitions from the $n(O_b)_\perp$ to the $n(O_{nb})_y$ with the aggregate oscillator strength f of 0.038, which is close to the experimental value [26,27] of ≈ 0.05 . Low temperature measurements indicate that the 4.8 eV band is composed of several overlapping components [6], which together with its large observed half-width (FWHM = 1.07 eV) supports its assignment to three overlapping transitions. The levels of the other set of O_b lone-pair orbitals $n(O_b)_\parallel$, parallel to the corresponding Si- O_b -H planes, are located ~ 2 eV below the $n(O_b)_\perp$ levels. The transitions from these levels to the $n(O_{nb})_y$ level ($X^2A \rightarrow 6^2A$, $X^2A \rightarrow 7^2A$, and $X^2A \rightarrow 8^2A$) with calculated aggregate oscillator strength $f = 0.012$ and average transition energy of 6.2 eV may correspond to the recently found 6.8 eV absorption band (FWHM = ~ 1.8 eV, $f = 0.05$ [7]).

The present calculation provides a reasonable agreement with the measured peak positions and oscillator strengths for all three observed absorption bands of NBOHC. Additionally, it is in accord with the unexpected result of the previous calculations [11–13] assigning the nearly relaxation-free 2.0 eV absorption/luminescence transition to excitation of Si- O_{nb} σ bonding orbital. This result puts Si- O_{nb} σ orbital energetically higher than the lone-pair “nonbonding” orbitals of bridging oxygens, which form the top of the valence band. Notably, in the structurally similar methoxy radical $H_3C-O\cdot$, the lowest energy optical transition is also assigned to $\sigma \rightarrow$ oxygen $2p$ transition [28].

The assignment of the 2.0 eV transition (Refs. [11–13] and the present work) to $\sigma \rightarrow 2p$ transition challenges the conventional expectation that removing of an electron from σ orbital should weaken the bond and increase the bond length. This weakening happens, for example, in the methoxy radical, where the Stokes shift for $X^2E \rightarrow 2^2A$ transition is large (≈ 0.7 eV) and the oxygen stretching mode frequency in the excited state (676 cm^{-1}) is much smaller than in the ground state (1022 cm^{-1}) [28]. In contrast, Stokes shift for the 2.0 eV absorption transition in NBOHC is very small (≈ 0.06 eV). The partial Huang-Rhys factor for coupling of 2.0 eV transition to Si-O stretching vibration was measured to be as small as ≈ 0.1 [20], the frequency of this mode remains almost the same in the ground (890 cm^{-1}) and the excited state (860 cm^{-1}) [6]. This anomalous behavior of NBOHC can be explained only if one assumes that the weakening of $\sigma(\text{Si-O}_{nb})_z$ bond, caused by removal of an electron from bonding MO by 2.0 eV excitation, is compensated by some kind of an additional bonding, involving the electron transferred to the $2p$ -like $n(O_{nb})_y$ orbital in the excited 2^2A state.

To study the effects of an additional electron in lone-pair orbitals of NBOHC, a negatively charged NBOHC cluster was calculated. The optimized Si- O_{nb} bond length for a negative cluster was 155 pm, significantly shorter than Si- O_{nb} length in neutral NBOHC cluster, 169 pm. This result is consistent with the experimental observa-

tions, giving Si- O_{nb}^- bond length as 158 pm in alkali silicate glasses [29]. An important point for the present discussion on the nature of 2.0 eV transition in NBOHC is the shortening of the Si-O bond in negatively charged cluster. It shows that the additional electron on the $2p$ orbital of the nonbridging oxygen indeed enters a bonding state, evidently forming a π bond with the rest of the SiO_4 tetrahedron.

Our calculations show that the apparently bonding character of filled $2p$ orbitals of O_{nb} can be explained in the framework of hyperconjugation concept. Within the formalism classifying the bonds in σ and π types, hyperconjugation denotes interaction between π and σ bond subsystems. Such interactions are responsible, for example, for the lowering of energy in the staggered configuration of ethane molecule [30]. In NBOHC cluster, the filled $2p$ (π -type) MO primarily localized on O_{nb} (e -type symmetry in C_{3v} group) can interact with the appropriate e -type symmetry combinations of three empty Si- O_b antibonding σ^* orbitals (the case of “negative hyperconjugation”) as illustrated in Fig. 3(a) [31]. The associated changes of orbital densities are illustrated in Fig. 3(b) by considering the bonding of oxygen atom with $\text{Si}(\text{OH})_3$ unit to form a NBOHC cluster. As is evident from the lower part of Fig. 3(b), the hyperconjugation causes the transfer of some electron density from oxygen lone-pair orbital(s) towards the silicon atom. In the case of electronically excited NBOHC, this process partly delocalizes the excited state over the three Si- O_b bonds [Fig. 3(b)-iv].

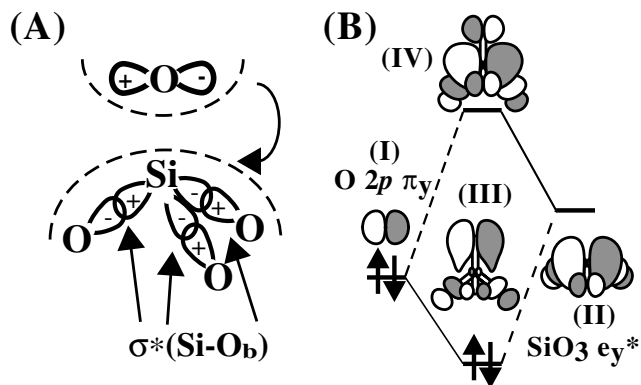


FIG. 3. Illustration of delocalization of O $2p$ lone-pair orbital due to hyperconjugation when O atom bonds to $\cdot\text{Si-O}_3$ cluster. (a) Scheme of hyperconjugation in the O + $\text{Si}(\text{OH})_3$ cluster by transferring electronic density from oxygen $2p$ lone-pair to e -symmetry combination of Si- O_b antibonding σ^* orbitals. (b) calculated changes of orbital amplitudes due to hyperconjugative interaction between the filled oxygen $2p$ orbital (i) and e -symmetry type combination of Si- O_b empty σ^* antibonding orbitals (ii) which occur on bonding of O to SiO_3 fragment to form NBOHC. The resulting bonding configuration (iii) shows transfer of electronic density from oxygen $2p$ closer to the Si atom in the center of the cluster.

TABLE II. Si- O_{nb} bond lengths and electron occupancies of the O $2p$ π orbitals and antibonding σ^* (Si- O_b) orbitals, which form the e_y^* group orbital [see Fig. 3(b)-ii] in the NBOHC cluster $(OH)_3Si-O^\cdot$ and in the negatively charged cluster $(OH)_3Si-O^-$.

		NBOHC	Negative NBOHC
Electron occupancies	$n(O_{nb})\pi_x$	0.987	1.885
	$n(O_{nb})\pi_y$	1.962	1.880
	$\sigma^*(Si-O_b)$	0.104 ^a	0.133 ^a
Si- O_{nb} bond length (pm)		169	155

^aAverage of three ligand (bridging) O_b s.

The suggested hyperconjugative interaction between the filled π orbitals of O_{nb} and the empty antibonding σ^* orbitals is supported by the results of natural bond orbital (NBO) [25] occupancy analysis. In Table II, the occupancies of O $2p$ nonbonding and $\sigma^*(Si-O_b)$ antibonding orbitals are compared for cases of neutral and negatively charged NBOHC clusters. A significant population of σ^* antibonding orbitals occurs at the expense of the occupancy of O $2p$ nonbonding orbitals. The transfer is stronger when both nonbonding orbitals are doubly occupied [this corresponds to $n(O_{nb})_y$ orbital in the excited 2^2A state of the NBOHC cluster], indicating an increase of hyperconjugation effects. It should be noted that this effect cannot be explained by electron correlation because the introduction of CI did not produce essential difference in the optimized structures and the electronic structures for all clusters examined in this study.

In this way, hyperconjugation can explain two experimentally observed properties of nonbridging oxygen in silica: the shortening of Si-O bond in the negatively charged nonbridging oxygen cluster [29], and the anomalously low electron-phonon coupling for the 2.0 eV electronic transition in oxygen dangling bond center (NBOHC) [6,20]. Both these cases involve completely filled $2p$ orbitals of the nonbridging oxygen, which maximizes the hyperconjugation effect.

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