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Vibrational properties of the surface-nonbridging oxygen in silica nanoparticles

L. Vaccaro,[1,2] M. Cannas,[1] and V. Radzig[3]
[1]*Dipartimento di Scienze Fisiche ed Astronomiche, Università di Palermo, Via Archirafi 36, I-90123 Palermo, Italy*
[2]*Istituto di Biofisica CNR, Area della Ricerca di Palermo, Via Ugo La Malfa 153, I-90146 Palermo, Italy*
[3]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russia*

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By studying the site-selective luminescence spectra of oxidized silica nanoparticles we identify the electronic and the vibrational lines associated with the surface nonbridging oxygen, $\equiv$Si-O$^\bullet$. This defect emits a zero-phonon line inhomogeneously distributed around 2.0 eV with full width at half maximum of 0.04 eV, weakly coupled with the local Si-O$^\bullet$ stretching mode whose frequency is measured to be 920 cm^{-1}. These findings are different from those of the well-characterized defect in the bulk silica thus evidencing structural peculiarities of the surface defect that is characterized by a nearly unperturbed nonbridging oxygen and of the nanoparticles that induce a narrower inhomogeneous broadening of the electronic transition.

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Study of nanometer sized silica particles (nanosilica) is nowadays an important issue for the nanoscale physics and technology.[1] Because of the large specific surface area, point defects at surfaces have a crucial role in determining and probing the nanosilica properties and are therefore the subject of ongoing investigations.[2–5] The generation of defects is strongly conditioned by the accessibility of surface sites for molecules of the environment; one of dominant processes is the surface oxidation that produces oxygen radicals or nonbridging oxygen (NBO) centers, $\equiv$Si-O$^\bullet$.[6–8]

NBO is of fundamental interest for the study of the optical properties of defects in oxides due to the uncommon feature related to the weak coupling between its nearly coincident transitions, optical absorption (OA), and photoluminescence (PL) around 2 eV, and the local phonon mode associated with the Si-O$^\bullet$ stretching.[9,10] Nevertheless, the surface-NBO center is still poorly investigated in comparison with the bulk counterpart (see review papers[11,12] and references therein). The properties of the surface NBO remain unclear partly because the analogies with the bulk defect are not obvious as a consequence of the different defect interaction with the surface or the bulk network. At silica surfaces the defect structure is, in fact, determined by its generation occurring by the chemical reaction of an axially symmetric surface-E' center, $\equiv$Si$^\bullet$,[13] with an oxygen destined to become the NBO interacting effectively only with the atoms of its own tetrahedron thus resulting in a defect with symmetry close to C_{3v}.[7] This is potentially advantageous to find out the electronic and vibrational properties of the nearly unperturbed NBO, differently from the bulk where the defect, generated by the radiolysis of O-H (Ref. 14) or strained O-Si bonds,[15] also experiences the interaction with neighboring atoms or ions. In the present work we therefore report spectral PL features associated with the single surface-NBO center site-selectively excited by a tunable laser radiation. In particular, from the detection of the purely electronic transition, zero-phonon line (ZPL), and of the vibronic side bands are derived: (i) the measure of the stretching frequency of the Si-O$^\bullet$ bond in the ground and in the excited electronic state; (ii) the inhomogeneous distribution of the ZPL. The relevance of these results is really provided by the comparison with earlier studies on NBO centers in bulk silica that point out the structural properties distinctive of both the surface defect and of the nanosilica.

The sample used was a porous film obtained by pressing a highly dispersed Aerosil® −300, a hydrophilic fumed silica with an average particle size of 7 nm, a pore size of 3–6 nm, and a specific surface of $\sim 10^6$ cm^2/g. In agreement with the procedure described in Ref. 7, a multistep thermochemical method was applied to stabilize NBO centers at the sites of surface hydroxyl groups ($\equiv$Si-O-H). Methoxy groups Si-OCH$_3$ are generated after treatment in methanol vapor at $T=700$ K and undergo a pyrolysis reaction at $T \geq 1050$ K Si-OCH$_3 \Rightarrow$ Si-H+O=CH$_2$. Subsequent pyrolysis of Si-H causes the generation of surface E' centers and eventually the thermal oxidation treatment in N$_2$O atmosphere above 750 K leads to the oxygen chemisorptions thus producing the NBO center. To avoid any reaction of the surface centers with molecular species, the sample is placed in a pure silica container with residual He atmosphere of 3–4 mbar.

Time-resolved luminescence was excited by a VIBRANT OPOTEK optical parametric oscillator laser system, pumped by the third harmonic (3.55 eV) of a Nd doped yttrium aluminum garnet (YAG) laser (pulse width of ~ 5 ns, repetition rate of 10 Hz). Laser photon energy was varied from 1.887 to 2.156 eV with a minimum step of 3 meV, the linewidth being ~ 1 meV. The beam intensity was monitored by a pyroelectric detector and was kept sufficiently low, 1.0 ± 0.1 mJ/pulse, to avoid saturation of the PL intensity. The emitted light was spectrally resolved by a monochromator equipped with two gratings with 300 and 1200 grooves mm^{-1}, the spectral slit resolution was set to be 0.05 nm corresponding to ~ 0.15 meV in the investigated range. Detection used a gated intensified charge coupled device camera (PIMAX Princeton instruments); the gate window and the delay with respect to the arrival of laser pulse were set to be $W_T = 40$ μs and $T_D = 1$ μs, respectively, so that any scattered laser light was completely suppressed in the emission spectra reported in the following. Preliminary detection of the scattered laser line was performed to locate the excitation energy. Temperature was varied in the range of 290–8 K by using an Oxford-OptistatCF continuous-flow helium cryostat, equipped with four optical windows and controlled by an Oxford-ITC503 instrument.

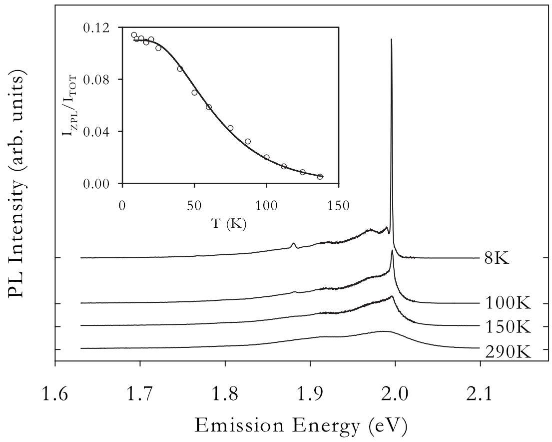

FIG. 1. Time-resolved PL spectra of surface-NBO centers under pulsed laser excitation at $E_{ex}=1.997$ eV measured on decreasing temperature from 290 to 8 K. The inset shows the temperature dependence of the Debye-Waller factor; solid line is the best-fit curve of Eq. (1).

Figure 1 shows the effects of temperature on time resolved PL spectra of surface-NBO centers measured with $E_{ex}=1.997$ eV. At $T=290$ K the emission is characterized by two subbands peaked at 1.92 ± 0.01 and 1.99 ± 0.01 eV,[16] and it extends over the anti-Stokes region. On lowering T, the PL amplitude increases, the anti-Stokes part vanishes and, below 150 K, the ZPL resonant with the excitation is increasingly evident together with vibrational structures. The temperature dependence of the ratio between the intensities of ZPL and the whole band, I_{0L}/I_{tot}, also known as Debye-Waller factor $\alpha(T)$, is shown in the inset and allows to quantify the thermal deactivation of the environment vibrational modes the PL transition is coupled to. The expression of $\alpha(T)$ is derived under straightforward approximations (homogeneous system of defects characterized by an electronic transition linearly coupled to a single mode of mean effective frequency ϖ, so that all defects are selectively excited, namely, ZPL is in resonance with the laser light),[17,18]

$$\alpha(T)=\exp\left[-S_{tot}\times\coth\left(\frac{\hbar\varpi}{2k_BT}\right)\right], \qquad (1)$$

where S_{tot}, the total Huang-Rhys factor, is the coupling strength averaged over the totality of phonons. Experimental results and the curve of Eq. (1) are in good agreement and the best-fit parameters result to be $S_{tot}=2.2\pm0.1$ and $\varpi=89\pm7$ cm^{-1}. However, as we will demonstrate in the following, the optical line shape of surface-NBO center has an inhomogeneous component. This implies that a fraction of NBO is not selectively excited (the ZPL is not in resonance with the laser light) so as to give a contribution to the spectrum independent of temperature; for this reason, $S_{tot}=2.2$ represents an upper limit of the actual value. We also note that the calculated values lead to a Stokes shift smaller than $2S_{tot}\times\hbar\varpi\approx0.05$ eV in good agreement with the experimental results on the emission/excitation spectra of the surface-NBO center.[16]

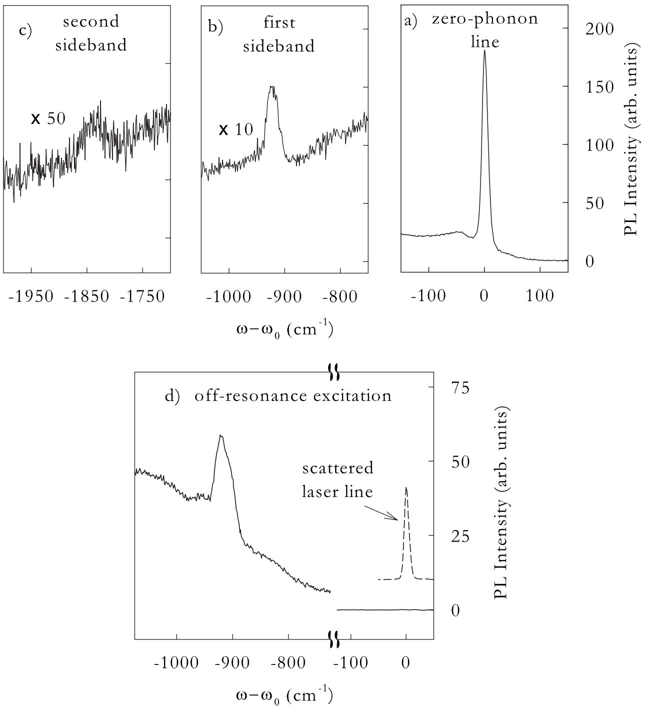

FIG. 2. Emission spectra, detected at 8 K, plotted as a function of distance from the laser line ω_0. The upper part shows (a) the ZPL, (b) the first, and (c) the second sidebands detected under excitation at $E_{ex}=\hbar\omega_0=1.997$ eV. The lower part displays (d) the ZPL detected under excitation at $E_{ex}=\hbar\omega_0=2.112$ eV; the laser line shape, acquired by the scattered light, is also shown arbitrarily scaled respect to the emission spectrum.

The most significant features of the local vibrations coupled to the electronic transition around 2 eV are derived by the emission spectra reported in the upper and lower sides of Fig. 2. The emission excited at 1.997 eV shows the ZPL, whose full width at half maximum (FWHM) is 11 cm^{-1}, coincident with the laser line; that is, the ZPL originates from those centers located within the laser spectral linewidth in a much larger inhomogeneous distribution. At lower energies one observes two sidebands centered at 923 ± 3 and 1840 ± 10 cm^{-1} apart from the ZPL that identify the fundamental, ω_g, and the overtone, $2\omega_g$, frequencies of the nearly equally spaced vibrational levels of the surface-NBO in the electronic ground state. We note that these sidebands are more and more wider than the ZPL: FWHMs being ~20 and 40 cm^{-1} for the first and the second lines, respectively; this spreading is due to an inhomogeneous distribution of the vibrational frequency of centers having the same ZPL.[9,17] From these emission spectra we also measure the ratio between the integrated intensities of ZPL and the first and second vibrational lines: $I_{0L}/I_{1L}=13.5\pm0.5$, $I_{0L}/I_{2L}=160\pm30$, the error being mainly due to the inaccuracy in the reference line subtraction to account for the overlapping nonselectively excited luminescence. Basing on the linear electron-phonon coupling, subsequently evidenced by the equal values of vibration frequency both in the ground and in the excited state, we compare these values with Poisson's distribution, $I_{kL}=\exp(-S)\times S^k/k!$ and extract the partial Huang-Rhys factor S: $I_{0L}/I_{1L}=1/S$ yields $S=0.074\pm0.003$ and $I_{0L}/I_{2L}=2/S^2$ yields $S=0.11\pm0.01$. We note that the difference between the values of S is larger than the experimental uncertainty and admit that we have no valid interpretation to explain this finding. Despite this incongruence, our result quantifies the low coupling of the electronic transition with the local mode of Si-O$^\bullet$ stretching, namely, the nearly free relaxation of the Si-O$^\bullet$ bond after excitation. Under excitation at higher energies ($E_{ex}=2.112$ eV) an off-resonance ZPL is detected as well, shifted by 920 ± 3 cm^{-1} from the laser line [Fig. 2(d)]; this difference is the measure of the frequency ω_e of the surface-NBO stretching in the electronic excited state. The acquisition of a series of emission spectra on varying the laser excitation energy both around 2.0 and around 2.1 eV has confirmed that both ω_g and ω_e have an average value of 920 cm^{-1} with a spread of 10 cm^{-1}.

These results demonstrate that the surface-NBO oscillates with the same frequency both in the ground and in the excited electronic states: $(\omega_g)_{\text{surf}} \approx (\omega_e)_{\text{surf}} = (\omega)_{\text{surf}} \approx 920$ cm^{-1}. On the basis of the reduced mass of the Si-O molecule ($m^* = 1.692 \times 10^{-26}$ kg), we calculate the force constant of Si-O$^\bullet$ bond at the surface: $k = (\omega_{\text{surf}})^2 m^* \approx 508$ N/m. We note that these vibrational features related to the surface NBO differ from the bulk where the stretching frequency is measured to be $(\omega_g)_{\text{bulk}} \approx 890$ cm^{-1}, $(\omega_e)_{\text{bulk}} \approx 860$ cm^{-1}.[11] In retrospective, we argue that the NBO is almost unperturbed when located at the silica surface. In contrast, NBO embedded in the bulk experiences an electrostatic interaction with atoms or ions nearby that causes the reduction in the Si-O$^\bullet$ force constant and consequently the stretching frequency, this perturbation being more effective in the excited electronic state. Our measure of the stretching frequency, $(\omega)_{\text{surf}} \approx 920$ cm^{-1}, is therefore a valid reference for those computational works dealing with the vibrational properties localized in the Si-NBO bond.[7,10,19] In particular it corroborates previous calculations performed on the radical F$_3$Si-O$^\bullet$ (Ref. 7): $\omega_g \approx 960$ cm^{-1} in the electronic ground state and $\omega_e \approx 970$ cm^{-1} in the excited state that is associated with a lone pair in both nonbonding $2p$ orbitals of the dangling oxygen, following a charge transfer from the Si-O$^\bullet$ σ bonding orbital, accompanied by a slight shortening (~ 0.005 nm) of the bond.

Finally, in Fig. 3 we report the ZPL intensity distribution function. The low energy curve derives from the detection of the ZPL resonant with the laser line and it is best fitted by a Gaussian curve centered at 1.995 ± 0.003 eV with FWHM of 0.042 ± 0.005 eV (340 ± 40 cm^{-1}) that represents the inhomogeneous distribution $w(E)$ of the electronic transitions due to the different local environment surrounding the surface-NBO centers. A replica of $w(E)$ appears at higher excitation energies; each point is obtained by the ZPL excited by the promotion to the second vibrational level in the excited electronic state, the shift between laser line and ZPL being 920 cm^{-1}.

It is worth noting that $w(E)$ of the surface NBO is narrower than that measured in the bulk defect (FWHM ~ 0.08 eV),[9,20] as if the defect might experience a smaller inhomogeneity from the host network. These findings could be caused by the unperturbed nature of the surface defect that reduces the sources of inhomogeneity. A relevant analogy is provided by the vibrational features of silanol (SiOH) groups in porous silica: their spectrum exhibits a sharp peak at 3750 cm^{-1} due to isolated noninteracting surface SiOH, and a broad composite band at lower energies associated with hydrogen-bonding interacting SiOH and adsorbed water molecules.[21,22] A further cause of the observed inhomogeneous broadening could be related to the structure of the matrix adjacent to the Si coordination sphere. This hypothesis is supported by electron paramagnetic resonance (EPR) studies on the E' centers in ^{29}Si enriched samples; in fact, strong and weak hyperfine interactions of the unpaired electron with ^{29}Si atoms account for the distribution of the dihedral angle (namely, the torsion angle between two tetrahedra).[13,23] In accordance with the inhomogeneous broadening of EPR spectra, the variation in the dihedral angle at the surface is lower than in the case of bulk defects. Differences between the structure of high surface nanosilica and bulk silica have been also reported in recent studies pointing out that nanosilica favors the formation of more low ($n=3$ and 4) membered rings.[3,5]

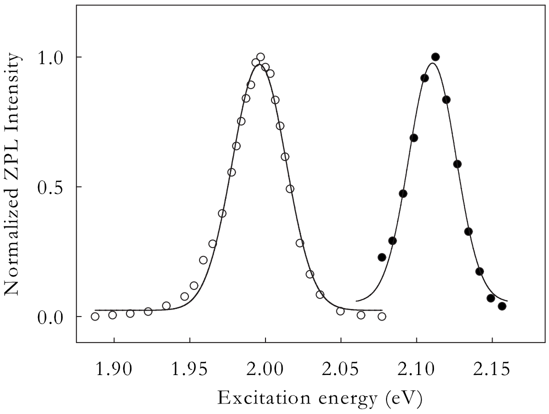

FIG. 3. Dependence of the zero-phonon line intensities on the excitation photon energy. The emission is resonant (open symbols in the lower energy band) and off resonance (full symbols in the higher energy band) with the laser line; solid lines are the best-fit Gaussian curves.

In conclusion, the ZPL and the phonon sidebands of the surface-NBO center in a porous film of nanosilica single out the defect coupling with vibrational modes: (i) due to the environment that contributes with an effective phonon frequency $\varpi \approx 90$ cm^{-1}; (ii) associated with the stretching of the Si-O$^\bullet$ bond, whose frequency is $(\omega)_{\text{surf}} \approx 920$ cm^{-1} regardless the electronic state. Moreover, the detection of ZPL is also relevant to measure the inhomogeneous broadening (0.04 eV) due to the statistical disorder of the environment. These findings are related to the specific properties of the unperturbed NBO peculiar to the silica surface and are a probe to find out the different structure of the silica nanoparticles in comparison with the bulk.

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