Toward a comprehensive understanding of solid-state core-level XPS linewidths: Experimental and theoretical studies on the Si 2p and O 1s linewidths in silicates

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High resolution X-ray Photoelectron Spectroscopy (XPS) core-level Si 2p and O 1s spectra of the nonconductors α-SiO2 (quartz) at 120 and 300 K and vitreous SiO2 at 300 K were obtained with a Kratos Axis Ultra XPS instrument (instrumental resolution of <0.4 eV) which incorporates a unique charge compensation system that minimizes differential charge broadening on nonconductors. The Si 2p and O 1s linewidths at 300 K (∼1.1 and ∼1.2 eV, respectively) are similar for all silicates (and similar to previous thin film SiO2 spectra obtained previously), showing that differential charging does not contribute significantly to our spectra. At 120 K, there is a small decrease (0.04 eV) in the Si 2p linewidth of α-SiO2, but no measurable decrease in O 1s linewidth. The O 1s lines are generally and distinctly asymmetric. We consider all possible sources of line broadening and show that final state vibrational broadening (FSVB) and phonon broadening are the major causes of the broad and asymmetric lines. Previous high resolution gas phase XPS studies have identified large FSVB contributions to the Si 2p spectra of SiCl4, SiF4, and Si(OCH3)4 molecules, and this vibrational structure leads to large Si 2p (p/2) linewidths of up to ∼0.5 eV, even with individual peak linewidths of <0.1 eV. The Si atom of Si(OCH3)4 is an excellent analog for Si in crystalline SiO2 because the Si-O bond lengths and symmetric stretch frequencies are similar in both compounds. Similar vibrational contributions to the Si 2p and O 1s spectra of solid silicates are anticipated if the Si 2p and O 1s core-hole states produce similar changes to the Si-O bond length in both phases. To investigate the possibility, Car-Parrinello molecular dynamics calculations were performed and show that changes to Si-O bond lengths between ion and ground states (∆r) for both Si 2p and O 1s hole states are similar for both crystalline SiO2 and gaseous Si(OCH3)4. ∆r are ∼0.04 Å for Si 2p and ∼0.05 Å for O 1s in both compounds. Indeed, the vibrational envelope from the Si 2p spectrum of Si(OCH3)4 broadened to our instrumental linewidth of 0.4 eV, accounts for the majority (∼0.8 eV) of the Si 2p (p/2) linewidth for crystalline SiO2 (∼1.1 eV) with phonon broadening accounting for the remainder. The results provide excellent support for the tenet that final state vibrational splitting, as seen in the gas phase molecules, similarly affects the solid-state spectra. The calculations also indicate that the O 1s linewidths should be larger than the Si 2p linewidths, as observed in our spectra. FSVB should also lead to small peak asymmetries, as seen in the O 1s spectra. The contribution of phonon broadening to the linewidth is also evaluated and shown to be comparable to the FSVB contribution at 120 and 300 K but considerably smaller at very low temperatures.

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I. INTRODUCTION

O 1s X-ray Photoelectron Spectroscopy (XPS) spectra and core-level spectra of many other elements in oxides are widely used to obtain chemical state information of oxygen and metal species in and on solids and surfaces before and after chemical reactions. With the advent of high resolution synchrotron x-ray sources, high resolution electron analyzers, and effective charge neutralization systems (e.g., Kratos Axis Ultra instrument) which dramatically decrease charge broadening for “rough” nonconductor surfaces, experimental core-level spectra are now highly reproducible for nearly all types of solid surfaces. Core-level XPS spectra and particularly O 1s spectra consequently have been used ever more widely to characterize bulk and thin film simple oxides (e.g., see very recent references to pristine, thin films, modified thin films, or reacted surfaces such as TiO2,1–7 SiO2 and silicates8–13 RuO2,14,15 MgO,16–18 CaO,19 ZnO,20 Fe3O4,21 Cu2O,22 and other transition metal oxides,23–25 also see a recent review of ambient pressure XPS on oxides26).

Recent XPS studies on nonconductor glasses,27–30 complex superconductor oxides,31–33 ceramics,34,35 and surface reactions of many oxygen-containing molecules on a wide variety of substances36–39 have also reported narrower O 1s and other core-level linewidths than previously collected. Because the majority of these substrates are nonconductors, many recent studies have been conducted using the Kratos instrument with its novel magnetic confinement charge compensation system. The instrument has yielded reproducible O 1s and other core-level spectral line shapes and linewidths on both atomically smooth and rough nonconductor surfaces: the O 1s linewidths, for example, are often much narrower8–11,27–29 than previously obtained with other instruments for bulk nonconductors. Moreover, nonconductor linewidths have been shown to be just as narrow as obtained for semiconductors8 or metals.40 For example,40 VO2 exhibits an insulator-metal transition above 300 K and the O 1s linewidth at 270 K of the insulator phase of VO2 (measured from Fig. 3 of Ref. 40 as 1.0 eV) is as narrow as (or slightly narrower than) the linewidth of the metallic phase at 320 K.
halides. The phonon contribution explained the temperature dependence of the linewidths, but the corrected experimental linewidths were, at all temperatures, larger than calculated, with no explanation provided. Furthermore, separate calculations yielded large differences (>0.2 eV) in the calculated linewidths. Finally, the linewidths extrapolated to 0 K [here referred to as $\Gamma_{\text{FSVB}}(0)$] have large uncertainties because extrapolations of experimental data extended over an ~300 °C range.

The extrapolations, nevertheless, indicate $\Gamma_{\text{FSVB}}(0)$ values much greater than inherent linewidths expected from final state lifetime contributions.

Another possible major contribution to solid-state line broadening is “final state” vibrational splitting and broadening which arise from the difference in bond lengths between the ground state and ion state. Siegbahn et al. first showed that final state vibrational broadening (FSVB) contributed to the Cs spectrum of CH$_4$ gas. Bancroft and co-workers later demonstrated the importance of this vibrational splitting on polyatomic gas phase Si compounds. Unlike PB, FSVB is temperature independent and can lead to asymmetric line profiles. In the last 10 years Thomas et al. obtained optimized spectra on the Cs 1s spectra of a host of gas phase C compounds as well as the Si 2p, P 2p, and B 1s spectra on Si, P, and B compounds. The vibrationally resolved 0 1s spectrum of gas phase H$_2$O has also been reported, yielding an inherent O 1s linewidth of 160 meV. These results demonstrated the following: (1) lifetime contributions to the overall band profile are small (e.g., in SiF$_4$, the inherent individual peak width is 79 meV compared to the overall Si 2p$_{3/2}$ profile width of ~0.5 eV); (2) FSVB is the controlling factor on the overall linewidth; (3) the symmetric $M-X$ stretching frequency dominates most spectra, although for the O 1s spectrum of H$_2$O the bending mode is dominant; (4) the total linewidth for a vibrational profile increases linearly with the symmetric stretch frequency [see Si 2p spectra of SiCl$_4$ and SiF$_4$ (Ref. 43)]; and (5) vibrational profiles are invariably asymmetric to higher binding energies.

For adsorbed molecules on surfaces, Martensson and Nilsson suggested that FSVB contributes to the overall widths of core-level spectra of adsorbed species (e.g., C 1s and O 1s of CO). Andersen et al. and Folisich et al., using high resolution synchrotron radiation, then resolved and characterized the C-H and C-O final state vibrational splittings (from the symmetric stretch) on the Cs 1s peaks of adsorbed ethylenes and CO, respectively. The resolved Cs 1s peaks were broadened somewhat relative to the gas phase spectra of C$_2$H$_4$ and CO because of low-energy “cooperative” vibrational modes, analogous to the phonon broadening in bulk solids. A large number of papers have reported both types of splitting and broadening to the core-level spectra of adsorbed species (for a recent paper see Ref. 60). Also, recently, Bergersen et al. observed both types of vibrational splitting and broadening in the C 1s spectra of CH$_4$ clusters of up to 1000 molecules.

To our knowledge, there has been only one mention in the literature of the importance of FSVB on the core-level XPS spectra of bulk solids. It was suggested that this final state vibrational splitting dominates the Si 2p linewidth in solid-state silicates such as Mg$_2$SiO$_4$, just as it dominates the over-
all Si 2p linewidth in the gas phase analog Si(OCH3)2. However, Andersen et al. reported resolved asymmetric vibrational structure (vibrational splitting of 58 meV) on the high resolution Be 1s XPS spectrum of Be metal. They attributed this structure to a resolved phonon effect. Because of the large calculated difference in Be-Be bond length between ground and ion state, it appears to us that the resolved vibrational profile in the Be 1s XPS of Be metal is more likely due to final state vibrational splitting. Coincidentally, the calculated Be 1s profile in molecular Be2 is very similar to that of Be metal.

It is important to show that both phonon broadening and final state vibrational contributions are the important contributors to the broad core-level spectra of solids (as for the above adsorbates and clusters) for at least two very practical reasons. First, it may be possible to obtain much narrower O 1s (and other core-level) linewidths on nonconductors in the future by cooling samples to low T and using synchrotron radiation to obtain the highest experimental resolution and second, many O 1s and other core-level spectra may be inherently asymmetric as expected when final state vibrational splitting is a dominant contribution to these core-level spectra. Recognition of asymmetry is especially important, otherwise small deviations from symmetric O 1s peaks may be interpreted as small additional peaks from moieties with unique chemical shifts.

In this paper, we present experimental and theoretical evidence for the importance of FSVB on the Si 2p and O 1s XPS spectra of silicates. High-level MD calculations are critical to show that the final state vibrational effects in a silicate should be very similar to those already observed on gas phase silicon analogs and that the broadening (and asymmetry) of the O 1s spectra should, if anything, be larger than for the Si 2p spectra. After addressing possible causes of line broadening (e.g., inherent linewidth differences, differential charging, inhomogeneous work functions, and surface chemical shifts), we show that the observed Si 2p and O 1s linewidths in silicates can be understood using the combination of FSVB and PB.

II. EXPERIMENTAL METHODS

A gem-quality α-quartz (SiO2) specimen (the same as used previously) was obtained from the UWO Dana collection, and pure vitreous SiO2 was obtained commercially. Their purity was characterized by broad scan XPS spectra that showed no impurities other than the usual small C 1s peak from ubiquitous carbon. Both samples were fractured in situ in the vacuum of the transfer chamber (low 10−9 Torr range) and immediately transferred to the analytical chamber where pressures were in the low 10−9 Torr range. Quartz has no cleavage so that its fracture exposes an irregular surface. Fracture of vitreous silica produces a conchoidal fracture surfaces. For the most general use of the XPS technique, it is important to be able to get the “minimal” linewidths on rough surfaces of nonconductors.

A Kratos Axis Ultra x-ray photoelectron spectrometer (with magnetic confinement charge compensation system) at Surface Science Western was used to collect the XPS spectra using Al Kα radiation at 1486.71 eV and a 300 μm2 spot size for all analyses. A sea of nondirectional low-energy electrons above the sample are trapped by a magnetic field and are available to compensate for different charge states on a sample surface. The take-off angle was 90°. Spectra were run at room temperature (295 K), but the sample surfaces heated up to about 300 K in the x-ray beam. The SiO2 was run at 120 K as well (100 K backing plate temperature) to observe the change in Si 2p and O 1s linewidths with temperature. A 10 eV pass energy was used to collect all core levels (Si 2p, S 2p, C 1s, Ti 2p, and O 1s). The instrumental resolution at 10 eV pass energy is <0.4 eV.8–11 The very small C 1s signal on all spectra indicated minimal C contamination. The charge compensation system was tested for effectiveness over a large range of settings with only very small changes (<0.03 eV) in linewidths. These widths were highly reproducible for all minerals over months of testing on different fractured samples. However, our experience with this instrument over several years has resulted in a slight improvement in linewidths—for example, we reported overall Si 2p linewidths of 3.16 eV for forsteritic olivine (Mg2SiO4) in 2004 (Ref. 8) and 1.26 eV in 2008. However, the Si 2p and O 1s linewidths for SiO2 at 300 K are identical to those reported 3 years ago (Table I). The linewidth can be slightly sensitive (less than 0.03 eV increase) if the surface carbon contamination is large or if the charge neutralizer plates become highly contaminated.

Core-level spectra were fitted with a 70% Gaussian–30% Lorentzian function as in previous papers. Slightly different functions (e.g., 50% Gaussian) sometimes gave slightly better fits with very small changes (<0.05 eV) in linewidth. Spin-orbit components were constrained to have the same linewidths. The Si 2p spin-orbit splitting was fixed to atomic values [0.617 eV (Ref. 56)], and the p3/2 peak was constrained to half the intensity of the p1/2 peak. Because of the constraints on the p1/2 position, linewidth, and intensity, just the p3/2 position and linewidth were iterated to minimize the root mean square deviations for a given spectrum. All spectra were corrected for the background using the Shirley approach. CASAXPS software was used to fit all the spectra. Thomas et al. kindly provided the raw data for their optimized high resolution gas phase spectra of SiF4 and SiCl4, for which the instrumental resolution was 30 meV and the inherent lifetime Si 2p widths were 79 and 54 meV respectively. The total observed individual linewidths of about 87 and 57 meV, respectively, made it possible to resolve completely a rich vibrational structure involving nine vibrational peaks separated by the symmetric stretching frequency in the ion state (about 10% larger than the measured ground state vibrational frequency). Our previous medium resolution Si 2p spectrum (instrumental resolution of 0.15 eV) of Si(OCH3)4 (a better analog to SiO2) showed a very similar vibrational envelope (ten peaks) to the above optimal spectra for SiF4 and SiCl4. To simulate the lower resolution Si 2p solid-state spectra (e.g., at our resolution of 0.4 eV) we used the raw spectra of SiF4, SiCl4, and Si(OCH3)4 and broadened the individual peak linewidths to a maximum value of 0.8 eV. The resulting broadened Si 2p spectra were then fit to a Si 2p doublet and the Si 2p3/2 linewidth obtained.
### III. COMPUTATIONAL METHODS

#### A. Structural models

Car-Parrinello molecular dynamics (CPMD)\(^6\) within the density functional theory formalism was used to obtain changes in Si-O bond lengths in solid-state SiO\(_2\) (\(\alpha\) quartz) and gas phase Si(OCH\(_3\))\(_4\) resulting from core ionization of Si (removal of a Si 2p or Si 1s electron) and O (removal of an O 1s electron). The Perdew-Burke-Enzerhof (PBE) exchange correlation functional\(^6\) was employed in the calculations. The core electrons were treated using a Troullier-Martins norm-conserving pseudopotential approach.\(^7\) Pseudopotentials for the ground state and partially screened O 1s and Si 1s and 2p cores were employed to investigate the effect of partial screening on the structure and dynamics of \(\alpha\) quartz. The ground state Si and O pseudopotentials were taken from the CPMD pseudopotential library. Previous work on silicate minerals has shown that these pseudopotentials yield satisfactory results for silicate compounds.\(^71\),\(^72\) Pseudopotentials for the (partially screened) half-core-hole (HCH) calculations were generated by removing half an electron from the relevant core levels. This half-core approximation, which originates from Slater’s transition state theory,\(^73\) is normally used to calculate core-level spectra such as the x-ray absorption near edge structure in SiO\(_2\) polymorphs,\(^74\) and in principle the relaxation energy is correct to second order via perturbation theory. A calculation was also performed after adding a full-core electron for comparison. Valence electrons were modeled using a plane wave basis with an energy cutoff of 90 Ry. Energy sampling was done for the \(\Gamma\) point only. As a test of the pseudopotentials for the ground state, the geometry of the initial quartz structure was optimized using the preconditioned conjugate gradient approach where convergence was achieved when the largest forces on the nuclei dropped below 0.0001 hartree/bohr.

#### B. Molecular dynamics

The initial structure for \(\alpha\) quartz was generated from known crystal coordinates obtained from the American Mineralogist crystal structure database.\(^76\) The unit cell had four SiO\(_2\) units in a hexagonal cell with cell parameters \(a=4.914\, \text{Å}\) and \(c=5.406\, \text{Å}\) in the P\(\bar{3}1\)2 space group.\(^76\) This cell was then transformed to the orthorhombic space group, yielding cell parameters \(a=4.914\, \text{Å}, b=8.511\, \text{Å}, c=5.406\, \text{Å}\). A \((2 \times 1 \times 2)\) supercell with 24 SiO\(_2\) units was then generated. Previous work on hydrous olivine\(^71\) and forsterite\(^72\) has shown that the \(k\)-point sampling and supercell size on silicate compounds are expected to yield satisfactory results. Indeed, the bond lengths reported here for the ground state structure are in very good agreement with the recent crystallographic data.

As a test of the quartz calculations, a similar set of runs was done for an isolated tetramethoxysilane molecule, Si(OCH\(_3\))\(_4\). This molecule gives a reasonable approximation to the SiO\(_4\) unit in \(\alpha\) quartz, and experimental data on the structure and vibrational dynamics\(^77\) are available. The Si(OCH\(_3\))\(_4\) input geometry was generated with Molden,\(^78\) and the geometry was optimized using the PBE functional and a 6-311++G** Pople basis set within the rational function optimization approach in GAUSSIAN\(_03\).\(^79\) The convergence was reached when the largest force on the atoms was less than 0.00045 hartree/bohr. An analysis of the harmonic frequencies indicated that a minimum had been reached. A check of the structure with the experimental geometry reported in Ref.\(^74\) indicated the structure was a good starting geometry to the CPMD calculations.

#### TABLE I. Si 2p\(_{3/2}\) and O 1s XPS linewidths (FWHM), Si-O symmetric stretching frequencies, and Debye Temperatures for solid silicates along with Si 2p\(_{3/2}\) linewidths for gaseous SiF\(_4\), SiCl\(_4\), and Si(OCH\(_3\))\(_4\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T) (K)</th>
<th>(\Delta E) (eV) (a)</th>
<th>Si 2p(_{3/2}) FWHM (eV)</th>
<th>O 1s FWHM (eV)</th>
<th>Si-O stretch (cm(^{-1}))</th>
<th>(\Theta_D) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-SiO(_2) (b)</td>
<td>120</td>
<td>0.4</td>
<td>1.09(0.01)</td>
<td>1.23(0.01)</td>
<td>1081(c,d)</td>
<td>528, 562(e)</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.4</td>
<td>1.13(0.01)</td>
<td>1.23(0.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_2) glass(b)</td>
<td>300</td>
<td>0.4</td>
<td>1.16(0.02)</td>
<td>1.27(0.02)</td>
<td>1095(e,g)</td>
<td>(\sim)645 (h)</td>
</tr>
<tr>
<td>SiO(_2) film(i)</td>
<td>300</td>
<td>0.2</td>
<td>1.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg(_2)SiO(_4)(j)</td>
<td>300</td>
<td>0.4</td>
<td>0.99(0.03)</td>
<td>1.24(0.03)</td>
<td>830(d,k)</td>
<td>763, 647(e)</td>
</tr>
<tr>
<td>SiF(_4) (m)</td>
<td>295</td>
<td>0.03</td>
<td>(-0.46)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>0.10</td>
<td>(-0.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiCl(_4) (m)</td>
<td>295</td>
<td>0.03</td>
<td>(-0.25)</td>
<td></td>
<td></td>
<td>423(o)</td>
</tr>
<tr>
<td>Si(OCH(_3))(_4) (p)</td>
<td>295</td>
<td>0.15</td>
<td>(-0.6)</td>
<td></td>
<td></td>
<td>840(p)</td>
</tr>
</tbody>
</table>

\(a\)Total instrumental resolution (photon plus electron) in eV.
\(b\)This work.
\(c\)Reference 98.
\(d\)Reference 82.
\(e\)Reference 99.
\(f\)Reference 100.
\(g\)Reference 83.
\(h\)This value is for the SiO\(_2\) polymorph coesite (from Ref. 5 above) which should be a good approximation for silica glass.

\(i\)Reference 98.
\(j\)Average from Refs. 8 and 10.
\(k\)Reference 93.
\(l\)Reference 82.
\(m\)Reference 43.
\(n\)Reference 41.
\(o\)Reference 101.
\(p\)Reference 55.
performed at 80 and 300 K using the Car-Parrinello approach for the electron dynamics and a classical approach for the nuclei. The molecular dynamics runs were performed in the microcanonical (NVE) ensemble. Identical pseudopotentials, functional, and energy sampling were employed for molecular dynamics runs as described above. The electron mass employed was 800 a.u. and a time step of 0.12 fs was used. Thermodynamic equilibrium was achieved in 1.8 ps and essential quantities (coordinates, velocities) were computed over an additional 1.2 ps. The temperature of the system for the equilibration runs was maintained by employing a simple velocity rescaling scheme. For the data collection runs, the temperature scaling was removed, though the temperature was monitored to ensure that it did not deviate from the equilibrium value. Molecular dynamics runs were generated for the ground state, O 1s, Si 1s, and Si 2p partially screened systems.

IV. RESULTS

A. Si 2p and O 1s XPSs of quartz and vitreous SiO2

Figure 1 illustrates the Si 2p and O 1s XPS spectra of α-SiO2 at 300 K [Figs. 1(a) and 1(d)], α-SiO2 at 120 K [Figs. 1(b) and 1(e)], and vitreous SiO2 at 300 K [Figs. 1(c) and 1(f)]. Linewidths are shown (with standard deviations) in Table I for these compounds, along with previously obtained linewidths for a thin SiO2 film on Si (Ref. 80) and for another silicate olivine (Mg2SiO4).9 The reproducibility of linewidths and peak shapes is excellent. For example, six separate spectra at 120 K and five separate spectra at 300 K for both Si 2p3/2 and O 1s of α-SiO2 (one spectrum at each T is shown in Fig. 1) yielded linewidths with a total range of 0.03 eV. Also, the linewidths at 300 K are identical to those previously reported for α-SiO2.9 The linewidths for the crystalline and vitreous phases of SiO2 are within 0.07 eV, and our Si 2p3/2 linewidths on α-SiO2 are within 0.07 eV of the Si 2p linewidth for a higher resolution (instrumental resolution of 0.2 eV compared to our resolution of 0.4 eV) spectrum of a thin ~30 Å film where charging is not a problem.80 An earlier high resolution XPS study of similar thin SiO2 films on Si gave a slightly larger high Si 2p3/2 linewidth [1.15–1.20 eV (Refs. 8 and 48)]. Also, Si 2p and O 1s linewidths for polycrystalline SiO2 suspensions41 and siloxane polymers containing SiO4 moieties39 yield very similar Si 2p and O 1s linewidths. These results (along with those reported in Refs. 8 and 40) provide confidence that reproducible minimal linewidths can be obtained on smooth and rough surfaces of nonconductors and even polycrystalline samples, using the Kratos charge compensation system. The results also show that the Si 2p3/2 and O 1s linewidths are similar in all compounds containing a SiO4 unit so far studied.

In addition, the Si 2p spectra of Si molecules41,43,55 have been collected at high instrumental resolution using synchrotron radiation (Table I), so that vibrational structure is readily resolved. The total width of the Si 2p3/2 vibrational envelopes for these gases (see Sec. IV B and Fig. 4 for the details) can be greater than 0.5 eV even with an instrumental resolution of 0.03 eV.41,43,55

FIG. 1. High resolution Si 2p and O 1s XPS spectra: (a) and (d) α quartz at 300 K; (b) and (e) α quartz at 120 K; and (c) and (f) SiO2 glass at 300 K.

Also reported in Table I are the symmetric Si-X (X=O, F, Cl) stretching frequencies along with the Debye temperatures for the bulk solids. The silicate species show quite a range of frequencies in Table I, 830 cm−1 for Mg2SiO4 with a Si-O unit with no Si-O-Si bonds to 1081 cm−1 for completely “condensed” SiO2 with all Si-O-Si bonds. These differences are used to assign the degree of Si-O-Si bonding in glasses from IR or Raman spectra.82,83 As mentioned above, it is the symmetric stretch in the core ionized state that dominates the XPS spectra of gas phase molecules, especially for the “central” atom in symmetric species such as Si in SiX4 (X=H, F, Cl, OCH3),41,43,55 B in BF3,44 P in PF3,45 or C in CH4.53,84 The Debye temperature is critical for the ensuing analysis of the phonon broadening.51–53 Note that the Debye temperature for Mg2SiO4 is substantially higher than that for α-SiO2.

Three general observations are apparent from the solid-state linewidths in Table I. First, the Si 2p and O 1s linewidths and line shapes for all the three SiO2 samples in Table I are within 0.1 eV at 300 K. In our recent studies of silicate minerals and glasses, the O 1s linewidths at 300 K for all samples (including minerals and glasses) are between 1.21 and 1.28 eV.9–11,27,28 Similarly, the O 1s linewidths are all very similar for TiO2 and amorphous and crystalline SrTiO3 and BaTiO3.5,29 Second, the Si 2p3/2 widths are always about
0.2 eV narrower than the O 1s linewidths. Third, there is a small increase in the Si 2p linewidth of SiO$_2$ with increase in $T$ from 120 to 300 K, but the O 1s linewidth does not change noticeably over this temperature range.

The fits to the Si 2p spectra are reasonable, giving no evidence for asymmetry in the peaks; but the spin-orbit doublet fits will tend to mask any peak asymmetry. In contrast, the one-peak fits to the O 1s spectra [Figs. 1(d)–1(f)] do not provide good fits to the “wings” of the spectra. We illustrate a one-peak fit to two of the O 1s spectra at 300 K in Fig. 2. The fits were optimized to reproduce the low binding energy part of the spectrum. Although a good fit is obtained to this part of the peak, the high binding energy side of the peak is very poorly fit. A second low intensity peak is needed to fit these O 1s peaks satisfactorily (see the residuals in Fig. 2).

For each fit, the second (minor) peak is about 0.9 eV above the main peak and has about 10% of the intensity of the main peak. These fits are similar to a recently published olivine and SiO$_2$ O 1s spectra.$^{13,28,81}$ These spectra provide evidence that the O 1s peaks from the bulk O are inherently asymmetric and that all have similar asymmetry. Because of the different O 1s binding energies for the three SiO$_2$ compounds and for Mg$_2$SiO$_4$ (e.g., close to a 2 eV difference between the O 1s binding energies in SiO$_2$ and Mg$_2$SiO$_4$), the similar degree of asymmetry makes unlikely the possibility that OH$^-$ or H$_2$O species$^{1,11}$ contribute to the O 1s asymmetry in any of these compounds. For example, the O 1s peak for OH$^-$ [at 532.0 eV (Ref. 11)] would be on the high binding energy side of the olivine O 1s peak at 531.0 eV (Ref. 11) but on the low binding energy side of the O 1s peak for quartz at 532.8 eV.

### B. Change in bond lengths in solid and gas phases after ionization

The vibrational splitting and broadening in the gas phase spectra arise because of bond length changes ($\Delta r$) accompanying the core-level transition from the ground to the ion state.$^{41–43,54}$ A Frank Condon analysis of the electronic transitions from ground state to ion state in the photoelectron process yields an XPS vibrational envelope with more vibrational peaks (and broader overall peak envelope) as $\Delta r$ and the magnitude of the vibrational splitting increases. In the case of Si, B, and P molecules,$^{41,43–45}$ $\Delta r$ is 0.06 Å. It is interesting to note that most recent theoretical calculations yield a $\Delta r$ value closer to 0.04 Å.$^{44}$ The core envelope model$^{55–88}$ (e.g., $\Delta r$ is the core envelope for $Si^{2+}$) suggests that $\Delta r$ should remain the same for a given element (e.g., Si) regardless of its bonding partner. The experimental Si 2p spectra indicate that $\Delta r$ for SiH$_2$, SiF$_2$, and SiCl$_2$ and their core equivalents are all 0.06 Å, a value consistent with a constant value expected from the core equivalent model. The actual difference in M-O bond lengths between silicates and their core equivalent phosphates is closer to 0.09 Å (Ref. 31 in Ref. 10), although a wide range (0.05 Å) of $\Delta r$ for the difference in Si-O and P-O bond lengths has been reported.$^{71,88,89}$

Accurate vibrational envelopes have been calculated for Si, P, As, Ge, and B molecules,$^{41,42,44,87}$ but the calculations are much more difficult for condensed solids and have not been performed except for adsorbed CO on Ni.$^{56}$

To more fully appreciate the effects of FSVB on solid-state XPS linewidths, $\Delta r$ values for the Si-O bond length in solid SiO$_2$ and the gas phase analog Si(OCH$_3$)$_2$ were calculated to determine the influence of three-dimensional network bonding in solid SiO$_2$ relative to gas phase analog Si(OCH$_3$)$_2$. The structures for $\alpha$-SiO$_2$ and Si(OCH$_3$)$_2$ are shown in Figs. 3(a) and 3(b). The calculated ground state Si-O bond lengths are (Table III) within 0.015 Å of the experimental values for both SiO$_2$ (Refs. 88 and 89) and Si(OCH$_3$)$_2$.$^{77}$ and these bond lengths are virtually identical at 80 and 300 K (within 0.003 Å). The changes to bond lengths after removal of a Si 2p and O 1s electron are listed in Tables II–IV. The change in Si-O bond lengths after Si 2p ionization for both SiO$_2$ and Si(OCH$_3$)$_2$ is similar, and the Si-O bond lengths [Si-O$_{1,2,3,4}$ for SiO$_2$ (Table II) and Si-O$_{1,2,3,4}$ (Table IV right column)] decrease by 0.04 Å in both compounds. The Si 2p vibrational envelopes (and overall broadening) in both gas phase and solid-state compounds are consequently expected to be similar, although the Si-O symmetric stretching frequency in SiO$_2$ is significantly larger than for Si(OCH$_3$)$_2$ (Table I). Our calculations yield $\Delta r$ values similar to values obtained previously using other theoretical methods on Si and B gas phase molecules,$^{43,44}$ so that our transition state method, with removal of half a Si 2p electron, gives reasonable results compared to other theoretical calculations on gas phase molecules. Note in Tables II and IV that the O-Si$_2$ bond lengths in SiO$_2$ (Table II) and O-C bond lengths in Si(OCH$_3$)$_2$ increase on Si 2p ionization by over 0.02 Å to compensate for the above decreases in the Si-O1 and Si-O bond lengths.

The changes in O-Si bond length after O 1s ionization for both SiO$_2$ and Si(OCH$_3$)$_2$ are also similar, with the O-Si bond length increasing by 0.05–0.06 Å in both compounds (Tables II–IV). Again, other bond lengths decrease to compensate. As for the Si 2p vibrational envelopes, the O 1s vibrational envelopes for the two compounds should be similar. Furthermore, a larger vibrational envelope and broader overall linewidth is expected for O 1s spectra compared to Si 2p spectra because of the larger $\Delta r$ on O 1s ionization. Similar $|\Delta r|$ values for the gas phase and solid-state comp-
TOWARD A COMPREHENSIVE UNDERSTANDING OF

pounds imply that relaxation upon ionization is similar in both states of matter, and the FSVB effects in solids consequently should be similar to gas phase analogs.

C. Simulation of the Si 2p solid-state spectra from the gas phase Si 2p spectra

Completely resolved Si 2p spectra have been published previously for SiH₄, SiF₄, and SiCl₄,⁴¹,⁴³ and vibrational structures are similar for SiF₄, SiCl₄, and Si(OCH₃)₄.⁴¹,⁵⁵

TABLE II. SiO₂ at 80 K: Si 2p ground state and HCH MD results from removal of a Si 2p electron (SiI⁺) [see Fig. 3].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Ground state (Å)</th>
<th>Si 2p HCH (Å)</th>
<th>Δr (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiI⁺-O1</td>
<td>1.6224</td>
<td>1.5846</td>
<td>-0.0378</td>
</tr>
<tr>
<td>SiI⁺-O2</td>
<td>1.6267</td>
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<td>-0.0379</td>
</tr>
<tr>
<td>SiI⁺-O3</td>
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<td>1.5890</td>
<td>-0.0374</td>
</tr>
<tr>
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<td>1.5845</td>
<td>-0.0379</td>
</tr>
<tr>
<td>O1-Si</td>
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<td>1.6559</td>
<td>0.0289</td>
</tr>
<tr>
<td>O2-Si</td>
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<td>1.6489</td>
<td>0.0266</td>
</tr>
<tr>
<td>O3-Si2</td>
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<td>1.6489</td>
<td>0.0270</td>
</tr>
<tr>
<td>O4-Si</td>
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<td>1.6558</td>
<td>0.0289</td>
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</table>

Δr=r_{HCH}-r_{ground state-}

FIG. 3. (Color online) (a) Atoms and their respective labels used in the reported parameters for the α-SiO₂ simulations; (b) atoms and their respective labels used in the reported parameters for the Si(OCH₃)₄ simulations.

There are nine vibrational peaks for the Si 2p₃/₂ and Si 2p₁/₂ peaks of SiF₄ [Fig. 4(a)] and SiCl₄ [Fig. 4(b)] (Ref. 43) and ten for Si(OCH₃)₄ (Ref. 55) (although the number may be nine because the individual peaks were not well resolved). Both the Si 2p₃/₂ and Si 2p₁/₂ peaks are asymmetric about the most intense peak, with the vibrational intensities being more intense on the high binding energy side of the most intense peak [i.e., Fig. 4 where peak 2 is larger than 2’ and 3 is larger than 3’]. These spectra show that the symmetric stretch in the ion state (v=0.111 eV or 895 cm⁻¹ for SiF₄ and v=0.058 eV or 470 cm⁻¹ for SiCl₄) dominates both spectra. There is no indication of a contribution from another vibrational mode, which is consistent with the expected symmetric relaxation about a tetrahedral Si atom when a Si 2p electron is removed. This vibrational pattern will be identical

TABLE III. SiO₂ at 80 K: O 1s ground state and HCH MD results from removal of an O 1s electron (O³⁺) [see Fig. 3] at 80 K.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Ground state (Å)</th>
<th>O 1s HCH (Å)</th>
<th>Δr (Å)</th>
</tr>
</thead>
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<tr>
<td>Si1-O1</td>
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<td>O7-Si</td>
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</tr>
</tbody>
</table>

Δr=r_{HCH}-r_{ground state-}
at 80 and 300 K, as indicated by the virtually identical calculated changes in bond length at the two temperatures. Also, the vibrational splittings in the ion state are consistently about 10% larger than in the ground state, e.g., 895 cm$^{-1}$ in the ion state versus 801 cm$^{-1}$ in the ground state of SiF$_4$.

Table I

<table>
<thead>
<tr>
<th>Ionization Energy (eV)</th>
<th>Intensity</th>
<th>Vib. Splitting</th>
<th>Exptl. Width</th>
<th>Fitted Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization Energy (eV)</td>
<td>Intensity</td>
<td>Vib. Splitting</td>
<td>Exptl. Width</td>
<td>Fitted Width</td>
</tr>
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<td>0.111eV</td>
<td>0.030eV</td>
<td>0.087eV</td>
</tr>
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<td></td>
<td>0.111eV</td>
<td>0.030eV</td>
<td>0.087eV</td>
</tr>
</tbody>
</table>

FIG. 4. The experimental high resolution Si 2$p$ spectra (instrumental resolution of 30 meV) of (a) SiF$_4$ and (b) SiCl$_4$ (Ref. 43) fit to nine vibrational peaks for both the Si 2$p$ spin-orbit components. Simulated spectra of SiF$_4$ and Si(OCH$_3$)$_4$ at our instrumental resolution of 0.4 eV are shown in (c) and (d), respectively.

The spectra for SiF$_4$ ($\nu$=895 cm$^{-1}$) and Si(OCH$_3$)$_4$ ($\nu$=992 cm$^{-1}$) have been simulated using our experimental (lower) resolution of 0.4 eV and are shown in Figs. 4(c) and 4(d), respectively, accompanied by a fit to a Si 2$p$ doublet. Changing the individual peak shapes from 85% Lorentzian (in the original spectrum) to 50% Lorentzian (because of the large expected Gaussian component from the 0.4 eV electron/photon contributions) at the lower resolution had little effect on the total Si 2$p_{3/2}$ linewidths. For example, the
lineweights in Fig. 4(c) decreased by less than 0.02 eV from the 85% case to the 50% Lorentzian case. The asymmetry in the high resolution spectrum [Fig. 4(a)] is not readily observed in the two doublet fits in Figs. 4(c) and 4(d) due primarily to the Si 2p1/2 peak accommodating much of the asymmetry.

As expected, the vibrational splittings are no longer resolved in Figs. 4(c) and 4(d), and even the spin-orbit splitting is indistinct. These two spectra are qualitatively similar to the solid-state SiO2 spectra in Figs. 1(a)–1(c). The linewidths in the simulated spectra of 0.68 eV [Fig. 4(c)] and 0.80 eV [Fig. 4(d)] with individual peak widths of 0.4 eV (instrumental resolution) already approach the observed Si 2p1/2 total linewidths observed for the solid-state SiO2 spectra [1.1 eV (Table I)].

Broadened Si 2p spectra were again simulated for all three gas phase species by varying the individual peak widths from 0.15 to 0.8 eV, and each spectrum was fit again to a spin-orbit doublet to obtain the Si 2p3/2 linewidth. The variation in Si 2p3/2 linewidths for the different individual peak widths is provided in Fig. 5 along with a linear best fit. Four observations are apparent. First, the overall linewidths vary linearly with the individual peak width (instrumental, phonon, etc.; see below) of each vibrational peak. Second, the Si 2p3/2 width increases markedly with the vibrational frequency for similar vibrational envelopes. Thus, the linewidths at individual peak width of 0.4 eV are 0.50, 0.68, and 0.80 eV for SiCl4, SiF4, and Si(OCH3)4, respectively. Third, the slopes of these lines (see equations in Fig. 5) decrease as the vibrational splitting increases from 0.82 for SiCl4 to 0.74 for SiF4 to 0.62 for Si(OCH3)4. Fourth, the Si 2p3/2 width approaches the individual peak width at large individual peak widths. At an individual peak width of 0.8 eV, for example, the Si 2p3/2 linewidth is 0.83 eV for SiCl4, SiF4, and Si(OCH3)4 respectively.

The XPS spectra taken with the Kratos instrument. The As 3d linewidths on a semiconductor (FeAsS) and a chemically similar nonconductor (As2S3) had identical and narrow linewidths of 0.51 eV. Many repeat spectra of the same material but from different surfaces (e.g., crystalline SiO2) give similar linewidths and shapes. Also, the similarity of linewidths for our SiO2 studies and for the noncharging thin film SiO2 (Refs. 48 and 80) shows that differential charge broadening in our spectra is significantly less than 0.1 eV. Second, surface core-level shifts and unique surface electronic states of polar compounds9,50,93–95 (Γsurf) may contribute an additional peak of up to about 10% of the intensity of the main peak with Al KE photons. Such surface contributions on an oxide, Cu2O, are very small22 and will not contribute significantly.
(<0.1 eV) to a one-peak width. A third contribution from inequivalent structural sites in crystals (ΓCS) does not apply to Si atoms in this study. In all samples studied here, the Si and other “central” atoms are in a unique position even though M-O bond lengths are not always equivalent. There are, for example, two pairs of Si-O bond lengths of 1.607 and 1.611 Å (Refs. 89 and 96) in α-SiO2 [about 0.015 Å smaller than our calculations (Table II)]. For Mg2SiO4, the Si-O bond lengths vary more than in quartz and lead to three chemically different oxygen atoms in each structure, but the central Si atoms are nevertheless restricted to one structural site. Thus, there can be no Si 2p chemical shift broadening for Si atoms in this study. The fourth contribution, inhomogeneous work functions, has been shown to shift peaks in thin film spectra up to ~0.1 eV (Ref. 48) and give measured linewidth differences of up to 0.09 eV on the Ti 2p level in semiconductor thin film TiO2 samples.7 However, the similarity of our Si 2p3/2 linewidths for α-SiO2 and with nonconducting thin film SiO2 samples48,60 shows that this effect should give linewidth broadening of less than 0.1 eV.

There remain only two sources of the large linewidth broadening in the materials here studied (in addition to the experimental broadening of ~0.4 eV for the Kratos instrument). These are final state vibrational broadening (ΓFSVB) and phonon broadening contributions (ΓPB)—the contributions that have been important for the adsorbed molecules and cluster species.63,64

The previously discussed theoretical calculations indicate that Si 2p vibrational profiles should be similar in solid silicates and in gaseous Si(OCH3)4, so that their Si 2p vibrational envelopes should also be similar. Figure 5 shows that the ion state vibrational splittings greatly increase the Si 2p3/2 “total” linewidth of Si(OCH3)4 to approximately 0.8 eV at our experimental resolution of 0.4 eV, accounting for much of the observed total Si 2p3/2 linewidth of 1.1 eV for α-SiO2. Because the ground state vibrational frequencies are even larger for SiO2 than for Si(OCH3)4 or for Mg2SiO4, this 0.8 eV should represent a minimum Si 2p3/2 linewidth for SiO2 at our experimental resolution of 0.4 eV. These arguments and observations demonstrate that ΓFSVB makes a significant contribution to the Si 2p linewidths of about 0.8 eV in all Si 2p solid-state spectra.

There remains the problem to determine the individual (vibrational) peak widths for the spectra here collected. These widths have to be appreciably greater than 0.4 eV because of the phonon broadening contribution ΓPB.

Figure 5 (and γ =0.62x+0.56) indicates that individual peak widths (Γip, x axis) are less than 0.92 and 0.84 eV for total observed Si 2p3/2 linewidths (y axis) of 1.13 eV (T =300 K) and 1.09 eV (T=120 K), respectively, because the vibrational splitting for SiO2 is larger than that for Si(OCH3)4. To calculate the approximate phonon contribution to these ~0.8–0.9 eV individual linewidths, we remove the experimental width of 0.4 eV from Γip using the quadratic formula in Eq. (1),

\[
Γ_{ip}^2 = Γ_{ex}^2 + Γ_{PB}^2.
\]  (2)

Substituting the above widths Γex and Γip, ΓPB’s of 0.83 and 0.74 eV are obtained at 300 and 120 K, respectively. We can then estimate the phonon linewidth ΓPB(0) (T=0 K) using the approximate formula,49,52

\[
Γ_{PB}^2(T_1) - Γ_{PB}^2(T_2) = (8/3)Γ_{PB}^2(0)(T_1 - T_2)/θ_D.
\]  (3)

Taking the θD=528 K (Table I) for α-SiO2 and substituting the above values into Eq. (3) yield

\[
Γ_{PB}^2(0) = 1.10[Γ_{PB}^2(T_1) - Γ_{PB}^2(T_2)].
\]  (4)

Substituting the two linewidths, ΓPB, calculated at T1 and T2 (the above two ΓPB values of 0.83 and 0.74 eV) yields ΓPB(0)=0.39 eV. This is an approximate value (probably good to no better than 30–40 %) and is probably an upper limit because the expected ΓFSVB for SiO2 should be larger than for Si(OCH3)4 as mentioned above. However, these very approximate calculations indicate that the final state vibrational contributions at 300 and 120 K are similar to the phonon contributions, and the estimated ΓFSVB of 0.58 eV [intercept in Fig. 5 for Si(OCH3)4 is larger than the estimated phonon width ΓPB (0) of 0.39 eV. The Si 2p3/2 linewidth for Mg2SiO4 (0.99 eV) is substantially narrower than for SiO2 (1.09 eV), as expected by the lower Si-O vibrational frequency in Mg2SiO4 compared to SiO2. Using the Si(OCH3)4 line (Fig. 5), one obtains Γip =0.69 eV and a ΓPB of 0.56 eV at 300 K. Because the Si-O vibrational splittings are similar for Si(OCH3)4 and Mg2SiO4, ΓPB is probably closer to the real value than the ~0.7–0.8 eV values for SiO2 calculated above. The temperature dependence of this linewidth would now have to be obtained to yield ΓPB(0), but it is likely to be greater than that for SiO2 because ΓD for Mg2SiO4 is substantially larger than for SiO2 (Table I). Additional low temperature studies of the linewidths for Mg2SiO4 are obviously required in the future.

B. Contributions to the O 1s linewidths

As previously emphasized, O 1s linewidths are appreciably larger than Si 2p linewidths for α-SiO2 and other silicates. They are also asymmetric (Figs. 2 and 3). The inherent linewidth (ΓH) for O 1s (0.16 eV (Ref. 56)) is larger than Si 2p inherent linewidths (<0.1 eV), but ΓH is still too small to make an appreciable contribution to the increased O 1s width. All O atoms are equivalent in α-SiO2, so there is no contribution from ΓCS. The O 1s linewidths in silicates and in siloxane polymers39 are consistently larger than the corresponding Si 2p3/2 widths indicating that the O 1s widths are also controlled by a large vibrational envelope. The O 1s vibrational envelope probably contains more than the nine peaks (as found in the Si 2p envelope). There are no high resolution gas phase O 1s data on a model compound such as Si(OCH3)4, so that it is not possible to estimate the number of peaks contributing to the O 1s envelope, the vibrational modes and splittings, or the relative intensities. For example, it is expected that the Si-O-Si bond angle of 144° in quartz66 will yield vibrational splitting from both symmetric Si-O modes and from asymmetric modes [as seen on the O 1s level in H2O (Ref. 56)].

The theoretical calculations strongly support the conclusion that the O 1s line in quartz should be broader than the
Si 2p$_{3/2}$ line from the FSVB mechanism. There are two differences between the Si*-O and O*-Si bond length changes on ionization. First, the O*-Si bond length increases on ionization, whereas the Si*-O bond length decreases on ionization. Second, the O*-Si bond length changes are larger than the Si*-O bond lengths for both gas and solid compounds, indicating that there should be more vibrational peaks for O 1s spectra compared to the Si 2p spectra. Also, an increase in bond length for the O 1s ionization should lead to a larger vibrational envelope than a decrease in bond length (for the same $\Delta r$ magnitude) because the slope of the low R part of the ion state potential curve is greater than the slope of the high R part of the potential curve.88

The lack of a measurable temperature dependence on the O 1s linewidths in SiO$_2$ is perhaps surprising. However, Fig. 5 shows that the slope of the FWHM line decreases with an increase in vibrational frequency [e.g., from SiCl$_4$ to Si(OCH$_3$)$_4$], and the slope should also decrease with an increase in the number of vibrational peaks from the Si 2p spectra to the O 1s spectra. Unfortunately, without measurable temperature dependence or a better knowledge of the O 1s vibrational structure, it is not possible to estimate the phonon broadening. There is no reason to suggest, however, that $\Gamma_{pp}(0)$ is any larger for O 1s than for the Si 2p$_{3/2}$ line (0.36 eV). For example, for the potassium halides, the anion and cation core levels have similar $\Gamma_{pp}(0)$ values.

VI. CONCLUSIONS

Our high resolution (0.4 eV instrumental resolution) Si 2p and O 1s XPS spectra of the nonconductor quartz ($\alpha$-SiO$_2$) and vitreous SiO$_2$ still yield relatively broad linewidths (1 eV or greater) compared to linewidths of most semiconductors. The Si 2p linewidths are similar to that obtained on a higher resolution spectrum of a thin conducting SiO$_2$ film, showing that differences in inherent linewidths, chemical shift broadening, differential charging, and nonuniform work functions are not a significant cause of the large linewidths. As suggested by the core equivalent model, high quality theoretical calculations on the ground state and Si 2p and O 1s ion states of quartz ($\alpha$-SiO$_2$) and the gas phase analog Si(OCH$_3$)$_4$ show that the bond length changes on ionization ($\Delta r$) are similar in both compounds. This suggests strongly that the Si 2p and O 1s vibrational splittings in both solid state and gas phase should be very similar. The high resolution gas phase Si 2p spectra of Si molecules, such as the analog Si(OCH$_3$)$_4$, show extensive vibrational structure and some asymmetry. Combined with the theoretical calculations, a large vibrational envelope should contribute to the Si 2p and O 1s linewidths of SiO$_2$. This conclusion is supported by the asymmetric linewidths of the observed O 1s peaks. Phonon broadening (PB) is shown to produce significant Si 2p line broadening, which leads to the temperature dependence of the Si 2p linewidths.

This study requires further research to confirm some of our assumptions and results. First, high resolution gas phase O 1s and metal 2p (and other central atom levels) spectra of oxygen-containing analogs such as the metal alkoxides [$M(OR)_3$]$_4$ ($M$=Si, Ti, etc.) need to be collected to confirm that the O 1s vibrational envelopes yield the predicted broad (and asymmetric) O 1s lines for these compounds. Vibrational structure will not be readily resolved in the O 1s spectra because the inherent O 1s linewidth of 0.16 eV is larger than the expected vibrational splittings. However, such spectra will confirm the overall large linewidth and asymmetry of the O 1s profile and probably the nature (the importance of symmetric and asymmetric O-Si contributions) of the vibrational splitting. Second, greater effort is required to collect high resolution spectra of solids using synchrotron radiation at a range of temperatures, particularly very low temperatures. These studies need to be performed on solids with large vibrational frequencies in an attempt to resolve vibrational effects in oxides and other solids such as polymers and to determine the phonon broadening effects in these samples over a wide temperature range. Third, there needs to be a detailed study, with the same high resolution, of a number of metal oxides (mostly nonconductors) with very different M-O stretching frequencies. Our analysis predicts that the metal and O 1s linewidths (and asymmetry) should increase as the M-O frequencies increase. Already, the literature indicates that the light metal oxides such as MgO (Ref. 18) have much larger linewidths than the heavier metal oxides such as TiO$_2$ (Refs. 1–7) and RuO$_2$. Also, the O 1s spectra for TiO$_2$ show no significant asymmetry.

Numerous theoretical aspects need to be addressed. Molecular dynamics calculations are required on other solids to determine the $\Delta r$ values after ionization. Complete vibrational calculations on the Si 2p and O 1s vibrational profiles for solids such as SiO$_2$ are required. A re-examination of the phonon broadening calculations is warranted with particular emphasis on values of $\Gamma_{pp}(0)$ and the contribution of ion state profiles to these values. The $\Gamma_{pp}(0)$ values obtained by extrapolation of results in the literature typically yield rather large values for nonconductors. The large values are unexplained but may well result from final state vibrational splitting. Apart from the probable example of the Be 1s XPS of Be metal mentioned earlier, this contribution has not been included in previous theoretical treatments of core-level XPS spectra of solids.

Predictions from this study should extend the scope of nonconductor XPS studies. If there is a small M-X stretching frequency (such as in metal halides), linewidths for many compounds may approach 0.5 eV at room temperature (as observed previously for As$_2$S$_3$ (Ref. 8)). Such linewidths (and well-behaved line shapes) are much narrower than obtained in earlier studies and should make an appreciable difference to the chemical sensitivity of XPS studies of many nonconductors. Already, McIntyre and co-workers have used the increased chemical sensitivity of the Kratos instrument to study multiplet effects in transition-metal oxide compounds at much better resolution than previously obtained, and we have used the increased chemical sensitivity to study leaching and the structure of silicate glasses. Second, the inherent asymmetry of the O 1s (and other peaks) must be taken into account for analysis of broad XPS spectra. A unique asymmetric O 1s peak shape needs to be agreed on to fit all the spectra of silicates and other oxides with large vibrational frequencies.
ACKNOWLEDGMENTS

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