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Letter to the Editor

NMR CONFIRMATION OF STRAINED "DEFECTS" IN AMORPHOUS SILICA

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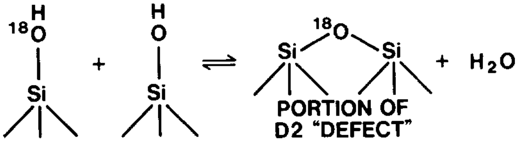
Solid state ^{29}Si magic angle sample spinning nuclear magnetic resonance spectroscopy and Raman spectroscopy were used to investigate the local silicon environment and siloxane ring vibrations in amorphous silica gels. Our results unambiguously relate the 608 cm^{-1} Raman "defect" in a-SiO_2 with reduced Si–O–Si bond angles indicative of strained 3-membered rings of silicate tetrahedra.

The controversy surrounding the structure of amorphous silica (a-SiO_2) is germane to many areas of science and technology. For example, thermally grown a-SiO_2 is essential to all metal–oxide–silicon (MOS) transistors, a-SiO_2 "soot" formed by the pyrolysis of $SiCl_4$ is used in the fabrication of fiber optics, and porous, a-SiO_2 substrates are used in supported metal catalysis. This paper presents the results of solid state ^{29}Si NMR and Raman Spectroscopy experiments performed on amorphous silicate gels which unambiguously relate reduced Si–O–Si bond angles (ϕ) with the silicate structure responsible for the 608 cm^{-1} Raman "defect" in a-SiO_2. In establishing this relationship, we unify the structural understanding of a-SiO_2 in such diverse topical areas as the Si–SiO_2 interface, neutron compacted and high pressure a-SiO_2, and photophysics and chemistry on silicate surfaces.

Raman spectra of amorphous silicates prepared by sol–gel methods are shown in fig. 1 (p. 420) for four different thermal treatments (dried at 50 °C, and heated to 200, 600, and 1100 °C). The narrow bands at about 490 and 608 cm^{-1} have not been explained by continuous random network (CRN) models [1] for conventionally prepared a-SiO_2 (fig. 1d) and have been ascribed to defects [2] (labeled in fig. 1 as D1 and D2, respectively). The evidence concerning the structural origins of these Raman-active defects is summarized as follows: 1) The vibrations responsible for both the D1 and D2 Raman bands are highly symmetric and involve nearly pure oxygen motion, as confirmed by ^{18}O and ^{29}Si isotopic enrichment studies [3,4]. 2) D1 and D2 result from two different structural species as evidenced by their different variations in intensity with thermal history. For conventional a-SiO_2 cooled from well above the glass transition temperature, T_g, the intensity of D2 increases with increasing fictive temperature and obeys an Arrhenius relationship with an activation energy of 0.44 eV/defect [5], whereas the intensity of D1 varies with a substantially lower activation energy [5]. In sol–gel prepared silicates, D2 is absent after drying to 50 ° C (fig 1a). It appears after heating to about 200 ° C, becomes quite intense at intermediate temperatures (fig. 1c), and is reduced in relative intensity in the final densified gel (fig. 1d) where its intensity is similar to that in conventional a-SiO$_2$ (fig. 1e). By comparison, D1 is present in the spectrum of the 50 ° C dried gel (fig. 1a), and its relative intensity decreases only slightly with subsequent heating. 3) The D2 defect structure forms preferentially on the silica surface by condensation reactions involving isolated vicinal silanol groups as confirmed by ^{18}O isotopic enrichment studies [4] illustrated by the following reaction:



(1)

This explains the high concentrations of D2 species observed in silica gels and other high surface area, amorphous silicates [6]. 4) The formation of the D2 species is a significantly endothermic process. In addition to the estimate of the activation energy, 0.44 eV/defect, which Geissberger and Galeener equated to the heat of formation of the defect [5], differential scanning calorimetry (DSC) results provide an estimate of 0.88 eV for the heat of formation of the D2 species formed by dehydroxylation according to eq. 1 [4]. 4) The D2 species is metastable with respect to surface silanol groups and to the silica CRN as evidenced by its enhanced reactivity with water (fig. 2) and its substantial removal at elevated temperature in the vicinity of T_g (fig. 1d) [4]. By comparison the D1 species is relatively inert (figs. 1 and 2).

Galeener has assigned the D1 and D2 bands in conventional a-SiO$_2$ to symmetric oxygen ring breathing vibrations of regular cyclic tetra and trisiloxanes (4-membered and 3-membered rings), respectively, partly on the basis of close agreement with the respective oxygen ring breathing frequencies in isolated cyclosiloxane ring molecules [7]. Galeener et al. later established the force constants required to vibrationally decouple the oxygen ring breathing modes of regular rings from the surrounding CRN, thereby explaining the narrowness of the bandwidths and how the vibrations could involve nearly pure oxygen motion [8].

These assignments have been criticized because the planarity and regularity of small rings embedded in a CRN are expected to be destroyed [9], whereas theoretical density-of-states calculations of oxygen ring breathing require the rings to be very homogeneous in shape in order to produce the narrow bandwidths observed for D1 and D2 [10].

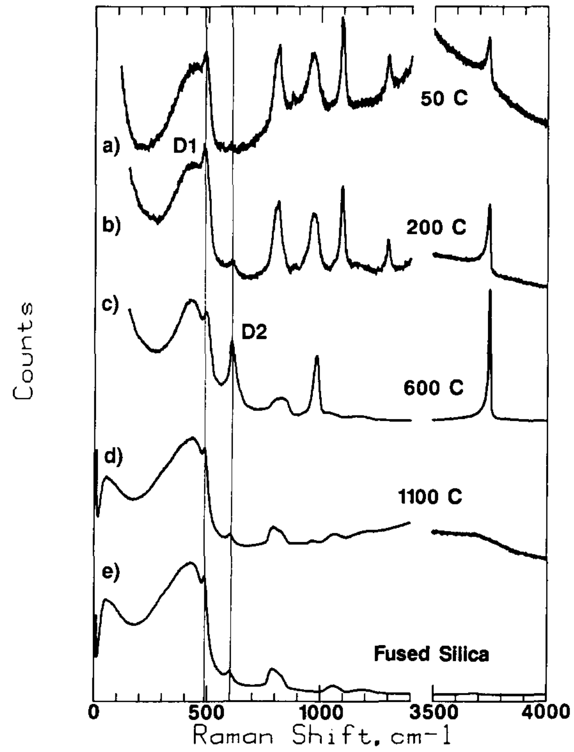


Fig. 1. Raman spectra of amorphous silicates: a) silica gel dried at 50 ° C; b) silica gel after heating to 200 ° C; c) silica gel after heating to 600 ° C; d) silica gel consolidated at 1100 ° C; and e) conventionally prepared a-SiO$_2$. The 50, 200, and 600 ° C samples are both high surface area materials ($S > 500$ m^2/g), whereas the consolidated gel and conventionally prepared silica contain no external surface area.

Phillips has assigned the defect bands in a-SiO$_2$ to the vibrations of bonds in a ⟨100⟩ cristobalite surface planar overlayer [11]. He uses the high concentrations of defects observed in gels to justify his model which locates the defects on surfaces [9]. The specific model for the D1 band is the bending mode of a Si–O–O–Si intrasurface chain segment [11]. The D2 band is associated with intercluster crosslinking perhaps involving 4-membered rings [11].

An important distinguishing difference between these two structural models is that Galeener's model associates D2 with a strained ring and D1 with an unstrained ring (fig. 3), whereas Phillips' model involves no strained species. Molecular orbital (MO) calculations have established that the optimized geometry for the cyclic trisiloxane molecule, $H_6Si_3O_3$, is planar with D_{3h} symmetry and a Si–O–Si bond angle, ϕ, equal to 136.7° [12]. This ϕ is significantly less than the most common ϕ in conventional a-SiO$_2$ (average $\phi = 151°$) and in cyclic ring molecules which comprise four or more silicons

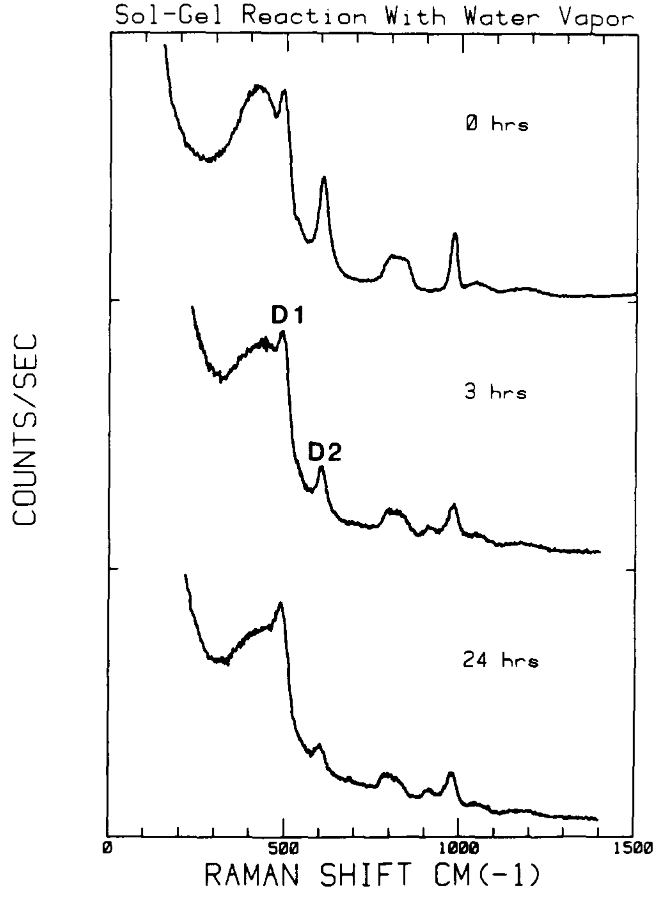


Fig. 2. Raman spectra of an a-SiO$_2$ gel initially heated to 600 °C and subsequently exposed to 100% RH water vapor for the times indicated.

[13], e.g., $\phi = 144°$ in hexamethylcyclotetrasiloxane [13]. MO calculations indicate that the strain energy per molecule of cyclic trisiloxanes is 1.06 eV [12], whereas cyclic tetrasiloxanes are predicted to be relatively unstrained [12].

The recent development of high-resolution solid state nuclear magnetic resonance spectroscopy employing magic angle sample spinning (MASS NMR) has provided an important new tool for the in situ investigations of the local environment of silicon in condensed systems [14]. ^{29}Si MASS NMR data for a variety of crystalline phases with known structures has established a linear correlation of the ^{29}Si chemical shift (δ) of Q^4 * resonances with ϕ: δ(ppm) =

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* In Q terminology the superscript (0–4) is the number of oxygens surrounding the nucleus which are bonded to two silicons (bridging oxygens). For example, the monomer Si(OH)$_4$ represents a Q^0 species, whereas the silicon atoms in a continuous, ideal 4–2 CRN are by definition Q^4 species.

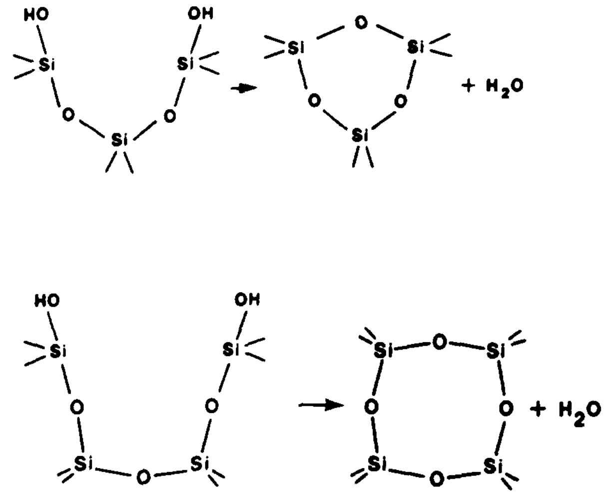


Fig. 3. Three-membered and four-membered rings proposed by Galeener to be the structural origins of the D2 and D1 Raman bands in conventional a-SiO_2. Both species may form by dehydroxylation on the silica surface.

-0.59 (ϕ)–23.21 (correlation coefficient = 0.982) where ϕ is the average of the four Si–O–Si angles per Q^4 site [15], providing a powerful method of directly determining ϕ.

We have performed ^{29}Si MASS NMR and cross polarization (CP)MASS NMR [16] experiments and have obtained Raman spectra (fig. 1) on porous, amorphous silicates produced by sol–gel methods after drying at 50 °C and after heat treatments between 200 and 1100 °C, at which temperature the porous gel is consolidated to a dense glass. After heating in dry O_2 the gels were cooled to room temperature, evacuated, and sealed in glass ampules under vacuum. Thereafter the gels were maintained under rigorously dry conditions for the initial set of MASS and CPMASS experiments. A second set of MASS NMR spectra were collected after exposure of the gels to 100% RH for 24 h.

The NMR spectra were obtained at an H_0 field strength of 8.45 T (^{29}Si frequency of 71.49 MHz) using the spectrometer described in ref. [15]. The sample probe was built by Doty Scientific. The samples were spun with dry nitrogen, and the standard was external tetramethylsilane (TMS). ^{29}Si–^{1}H CPMASS spectra were obtained with the same instrument using contact times of 7.5 ms. Figure 4 shows the ^{29}Si MASS and CPMASS spectra obtained for the heated samples and ^{29}Si MASS spectra collected after exposure of the gels to water vapor. The three prominent peaks at chemical shifts of about -91, -101, and -110 ppm in the MASS and CPMASS spectra of the 50 and 200 °C gels and in the rehydrated 200 and 600 °C gels correspond to Q^2, Q^3, and Q^4 silicon sites, respectively [17]. Terminal oxygens associated with Q^2 and Q^3 silicons are bonded to hydrogen (OH groups) as evidenced by the ^{1}H CPMASS spectra in which the intensities of silicon resonances of the Q^2 and

Q^3 sites are enhanced relative to those associated only with bridging oxygens (Q^4 sites) [16,17]. According to the regression equation cited above, the -110 to -111 ppm chemical shift for Q^4 sites corresponds to an average ϕ of 147–149° which is quite close to the average ϕ in conventional a-SiO_2, 151° [15]. Thus we infer that to a first-order approximation the average environments of Q^4 silicons in the 50 and 200 ° C gels and all the rehydrated samples are similar to those in conventional a-SiO_2.

The MASS spectrum of the 600 ° C sample is quite different. The Q^3 and Q^4 peaks are not resolved and there is a broad band of intensity centered at

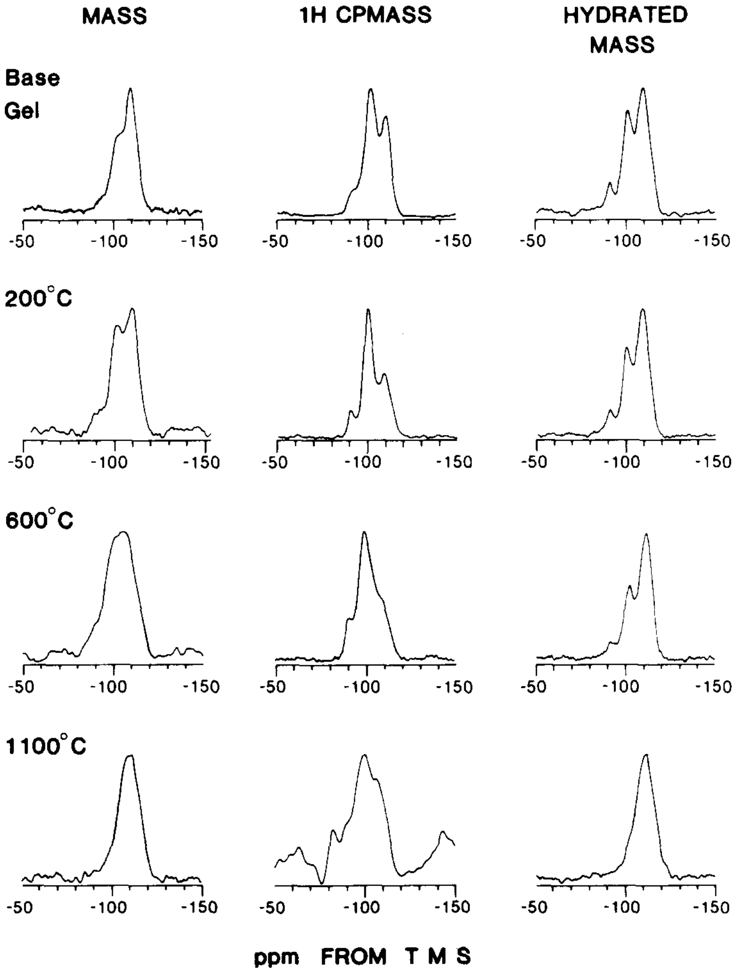


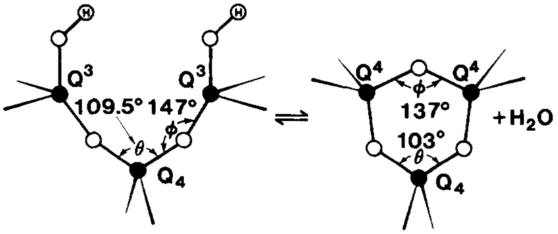
Fig. 4. ^{29}Si MASS and CPMASS spectra of silica gels after heat treatments between 50 and 1100 ° C. Hydrated MASS spectra were collected after exposure of the original samples to 100% RH for 24 h at 25 ° C. The ^1H CPMASS spectrum of the 1100 ° C sample is greatly scale-expanded in order to reveal the Q^2 and Q^3 resonances.

about −107 ppm corresponding to an average ϕ of 142° for Q^4 sites. Statistically acceptable deconvolution [15] of this spectrum, using peak positions of −91 and −101 ppm for Q^2 and Q^3 sites can be performed with various combinations of numbers of peaks, peak intensities, and peak breadths. All of these deconvolutions, however, require a peak at about −105 ppm. Because Q^2 and Q^3 sites containing OH^- groups are not known to resonate in this chemical shift range, the additional peak must be due to a Q^4 site with a small ϕ value. −105 ppm corresponds to $\phi = 138°$. The lack of preferential enhancement in this chemical shift range in the ^1H CPMASS spectrum of the 600 °C sample confirms this assignment to a Q^4 species. Exposure of the 600 °C sample to water vapor causes a narrowing and shift of the Q^4 peak position back to its original value in the 50 and 200 °C samples.

Heating to 1100 °C consolidates the gel reducing its surface area and causing loss of most of the silanol groups. The ^{29}Si NMR spectrum of this sample consists of a Q^4 peak at about −111 ppm corresponding to $\phi = 149°$. ^1H CPMASS yields very little signal (fig. 4) for Q^2 and Q^3 sites, consistent with a very low proton (OH^-) content. The spectrum of the 1100 °C sample exposed to 100% RH is unchanged, indicating the lack of exposed surface available for rehydration.

The relative intensity of the D2 Raman peak correlates well with the NMR data. D2 is practically absent in the 50 and 200 °C samples, intense in the 600 °C sample, and quite low in relative intensity after heating to 1100 °C. The relative intensity of D2 is also quite low for the 600 °C sample after exposure to water vapor at 25 °C and 100% RH (fig. 2). In contrast to this behavior, the D1 Raman band is present in all samples and its relative intensity changes little with heating or exposure to water vapor.

The NMR data thus unambiguously associate the formation of the species responsible for D2 with the presence of Q^4 silicon sites with reduced values of ϕ and conversely the elimination of this species with an increase in ϕ. These observations combined with our previous results on gels [4] uniquely identify the D2 species as a cyclic trisiloxane (3-membered ring) as originally proposed by Galeener [7]. 3-Membered rings are absent at low temperatures. They form at intermediate temperatures, predominately on the silica surface, by the condensation of isolated vicinal silanol groups located on unstrained precursors via the following reaction:

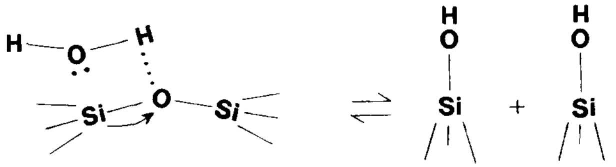


(2)

We previously eliminated strained 2-fold rings (edge-sharing tetrahedra) as being responsible for D2 by showing that the oxygen ring breathing vibrations occur at a much higher frequency, 873 cm^{-1}, than observed experimentally, 608 cm^{-1} [4].

For the 350–650 ° C temperature interval in which the D2 species primarily form, we calculate [4] the average heat of formation of a siloxane bond to be 0.88 eV, which is close to the calculated strain energy of 3-membered rings [12]. Because the heat of formation of unstrained siloxane bonds by the condensation of silanols is close to zero [18], we conclude that all of the associated strain energy is a result of ring closure, i.e., the precursor structure (left side of eq. (2)) is unstrained. Eq. (2) is consistent with the NMR results in which strain is associated only with D2 formation, and all strained species are Q^4 silicons as evidenced by the fact that Q^3 and Q^2 peak positions, clearly shown in the CPMASS spectra, are unaffected by the formation or elimination of D2 species.

The dramatic reduction in the concentration of 3-membered rings upon exposure to water vapor is due to ring hydrolysis (the reverse of eq. (2)). The population of 3-membered rings decreases relative to the populations of higher-order rings for two reasons: 1) Most of the 3-membered rings are present in surface sites which have direct access to water, and 2) strain in the 3-membered rings makes them more susceptible to hydrolysis than unstrained, higher-order rings (see kinetics results below). From a mechanistic standpoint, the enhancement in ring reactivity with ring strain can be understood by considering the change in the acid/base properties of the Si–O bond associated with bond angle changes required to make strained rings. Normal unstrained Si–O–Si bonds are hydrophobic [19] and resistant to hydrolysis [18]. Silicon atoms which are tetrahedrally coordinated by oxygens lack the acidity to interact with the basic lone-pair electrons on the oxygen in water. The lone-pair electrons in the Si–O–Si bridge lack the basicity to interact with the protons in water. However, reaction studies on strained model compounds (1-silaadamantanes) [20] suggest that changes in the tetrahedral geometry around Si activate empty d-acceptor orbitals, making the Si more acidic. MO calculations [21] suggest that decreasing the Si–O–Si angle transfers electron density into the lone pair orbitals of the bridging oxygen, making the oxygen more basic and the Si more acidic. The increased polarity and enhanced acid/base properties of strained Si–O bonds promote the absorption of water on the bond and the subsequent bond hydrolysis reaction [22]:



(3)

The deshielding at silicon with decreasing ϕ is also consistent with electron transfer from silicon to oxygen [16].

The fact that the D1 species is relatively unaffected by exposure to water vapor (fig. 2) also appears consistent with the NMR results in which D1 is associated with unstrained structures.

The behavior of D1 and D2 upon exposure to water vapor closely parallels that of the cyclic molecules octamethylcyclo*tetra*siloxane (OMCT) and hexamethylcyclo*tri*siloxane (HMCT). OMCT is stable in aqueous environments, whereas HMCT hydrolyzes with a pseudo-first order rate constant 3.8 $(\pm 0.4) \times 10^{-3}$ min^{-1} $(t_{1/2} = 3.0$ h) [23]. This latter value is comparable to the rate constant for D2 hydrolysis, 5.2 $(\pm 0.5) \times 10^{-3}$ min^{-1} $(t_{1/2} = 2.2$ h) [6] and is 75 × greater than the rate constant describing hydrolysis of unstrained, conventional a-SiO_2 (as estimated by extrapolation of the data in ref. [24]).

The reduction of 3-membered rings at elevated temperatures (fig. 1c) indicates that as the viscosity decreases the surface undergoes reconstruction to form a lower energy, unstrained configuration, as is evident from the NMR results. Thus, at intermediate temperatures, we infer that strained 3-membered rings are kinetically stabilized by the exceedingly high matrix viscosity.

Mulder and co-workers [25,26] have proposed an alternate structural model for the D1 band in "wet" gels and in high surface area gels prior to consolidation, namely the symmetric localized vibrations of O atoms bonded to network terminating Q^3 silicon sites. This assignment is based on an analogy with PCVD F-doped SiO_2, in which a sharp band at 487 cm^{-1} is observed to increase in relative intensity with $[F^-]$, and the general observation that the intensities of the D1 band and the SiO–H and Si–OH bands at 3740 and 980 cm^{-1}, respectively, all decrease as the gels are heated above 400 °C. Lippert et al. [27] have combined ^{29}Si NMR and Raman results to show that the intensity of a band at 487 cm^{-1} observed in solution during the latter stages of polymerization and in "wet" gels is proportional to the concentration of Q^3 silanols consistent with the Mulder model. Because Q^3 silicons bonded to one hydroxyl are not involved in altered Si–O–Si bond angles, they cannot be distinguished on the basis of ^{29}Si chemical shift. Furthermore these species are not expected to exhibit greatly enhanced depolymerization kinetics, they have small (negative) heats of formation as products of condensation, and they could become ^{18}O-enriched upon exposure of a siloxane surface to $H_2{}^{18}O$ vapor, consistent with our experimental results. However, based on the results of published spectra and our own results we do not currently support the Mulder model due to the following observations: 1) The Raman band associated with Q^3 silanols in solution is much broader (~ 100 cm^{-1}) than the D1 band observed in high surface area gels and in conventional a-SiO_2 (~ 50 cm^{-1}). The sharpness of the D1 band is more consistent with a discrete 4-membered ring structure which is decoupled from its surroundings than a Q^3 silanol in an amorphous (random) matrix. 2) Although the D1 and silanol bands all decrease in relative intensity as the temperature is increased, they exhibit a different temperature dependence. For example in a Raman study by Krol and van Lierop [28], the relative intensity of the 980 cm^{-1} band decreases continuously between 400 and 800 ° C, whereas in this same temperature interval the relative intensity of D1 appears to actually increase and then decrease suddenly at 800 ° C (fig. 5 in ref. [28]). 800 ° C is the same temperature at which D2 anneals, which suggests that structural relaxations rather than silanol removal are responsible for the decrease in D1. 3) The relative intensity ratio of D1 to the silanol bands (normalized to the ~ 800 cm^{-1} band) appears to vary greatly depending on the sample preparation procedure. For example Raman spectra of three different high surface area silicates (sol–gel silica, leached silicate glass and colloidal silica, fig. 1 in ref. [6]) show substantially different relative intensity ratios of D1 to the ~ 980 cm^{-1} Si–OH vibration. For the Q^3 silanol model to be correct this ratio should remain constant. Therefore we feel that although Q^3 silanols may make a contribution to the intensity at 490 cm^{-1} (especially in gels which have not been heat-treated), the sharp feature denoted D1 exhibits a behavior which is more consistent with 4-membered rings.

Having associated the D2 Raman band with reduced values of ϕ and in turn reduced values of ϕ with enhanced chemical reactivity, we can provide insight into several topical areas involving a-SiO$_2$. First, we evaluate the structure-induced charge transfer (SICT) model [29], used to describe the Si–SiO$_2$ interface. In this model electron density is transferred from silicon to oxygen with *increasing* Si–O–Si angles. In fact, the opposite occurs, as is evident from the enhanced reactivity of strained siloxane bonds toward water (eq. 3). Thus, we must reconsider structural interpretations of the Si–SiO$_2$ interface which are based on the SICT model. Secondly, we can corroborate the hypothesis proposed by Hemley et al. [30] concerning the structure of a-SiO$_2$ at high pressure, i.e., both the D1 and D2 defects are high-density structures with the density of the D2 structure greater than that of D1. A similar enhancement of D1 and D2 in neutron-compacted a-SiO$_2$ [2] can also be explained by a shift in ring statistics toward smaller 3- and 4-membered rings at the expense of larger rings.

Our NMR results indicate that after heating at intermediate temperatures, e.g. 600 ° C, the silica surface is composed primarily of OH terminated Q^3 sites and two different Q^4 sites with quite different Lewis acid-base character. This may explain recent surface photochemistry results in which the most inhomogeneous silica surface, as judged by multiple exponential decay of pyrene probe molecules [31], is that which results after heating to 700 ° C. Subsequent adsorption of water (which we know eliminates strained Q^4 sites) renders the surface much more homogeneous.

What remains to be answered regarding "defect" formation in a-SiO$_2$ is why 3-membered rings form in such high concentrations on silica surfaces. Estimates of the maximum percentage of silicons incorporated in 3-membered rings exceed 20% (based on deconvolution of the NMR results and estimates of the extent of dehydroxylation according to eq. (2)). High concentrations of 3-membered rings in a-SiO$_2$ are not limited to so-called sol–gel SiO$_2$. The D2

Raman band is prominent in all high surface area amorphous silicates dehydroxylated at intermediate temperatures [6] (e.g. Cab-O-Sil and LUDOX). Thus, previous studies of high surface area a-SiO_2 should be reevaluated in the light of the present results.

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