

## Identification of Raman Defect Lines as Signatures of Ring Structures in Vitreous Silica

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By analyzing the vibrational eigenmodes of a model structure obtained previously by quantum molecular dynamics, the two sharp features appearing in the Raman spectrum of vitreous silica could conclusively be assigned to three- and four-membered ring structures embedded in the network. The projections of the eigenmodes onto oxygen breathing motions in these rings yield well defined peaks at frequencies in striking correspondence to the positions of the Raman lines. The good agreement between calculated and measured shifts upon isotopic substitution further confirms this assignment. [S0031-9007(98)06307-8]

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The presence of three- and four-membered ring structures [1] in vitreous silica has long been hypothesized [2–6]. Two unusually sharp features appearing in the Raman spectrum [7], which could not be explained [8] in terms of the vibrations of a continuous random network [9–11], are suspected to be experimental signatures of these rings [3–5]. The variety of alternative interpretations relying mostly on a defective network structure [12–18] and the difficulties encountered in realistically modeling the silica structure [4,5,19,20] have so far prevented a definitive assessment.

The Raman features at  $495$  and  $606\text{ cm}^{-1}$ , known as “defect” lines  $D_1$  and  $D_2$ , have full width at half maximum (FWHM) linewidths of only  $20$  and  $30\text{ cm}^{-1}$ , an order of magnitude narrower than the width of regular network bands [5]. The attribution to ring structures therefore requires that specific ring motions nearly decouple from the other network vibrations. Galeener suggested that in-phase breathing motions of oxygen atoms in planar three-membered rings or in regular four-membered rings could satisfy this condition [4,5]. Calculated frequencies of breathing modes in ring molecules provided support to this assignment [19], but a study based on empirical potentials in which the rings were embedded in a network was unable to reproduce the correct frequencies and widths of the  $D_1$  and  $D_2$  lines [20].

The model structure [21] used here was obtained previously using first-principles molecular dynamics [22,23]. After equilibration of the melt at  $3500\text{ K}$ , the structure was rapidly quenched to low temperatures, yielding a network of corner-sharing tetrahedra. The structure obtained in this way consists of  $72$  independent atoms in a periodically repeated cubic cell, at the experimental density ( $2.20\text{ g/cm}^3$ ). The structural and the vibrational properties of this model were found to be in excellent agreement with elastic and inelastic neutron data [21,24].

The connectivity of our vitreous sample can be characterized in terms of rings using the shortest path analysis [1,25]. For every silicon atom, we considered each

of the pairs of neighboring oxygen atoms in turn, and restricted the count to the shortest path connecting the oxygen atoms in each of the pairs. This limits the number of paths per Si site to six. Closed paths containing  $n$  Si-O segments are referred to as  $n$ -membered rings. Six-membered rings are found to be the most frequent, closely followed by five-membered rings (Fig. 1). Of interest to this study is the occurrence of smaller rings. We counted five three-membered and two four-membered ring structures in our sample. The three-membered rings do not share atoms among each other, and neither do the four-membered ones. Because the strain energy contained in three-membered rings is higher than in larger rings [4,26], the high concentration of such small rings indicates that the distribution in Fig. 1 does not correspond to thermal equilibrium and that it should be related to the thermal history of the sample [21]. Under the assumption that the  $D_2$  line can indeed be associated with three-membered rings, our findings are consistent with the experimental observations that the intensity of the  $D_2$  line increases considerably with increasing fictive temperature [27]. Thus, the formation of three-membered rings appears to be favored when the system rearranges from

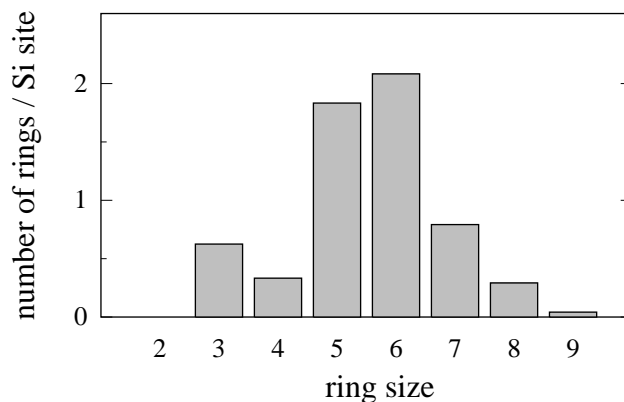


FIG. 1. Ring statistics according to the shortest path analysis [1] for the model studied here [21].

highly disordered configurations on short time scales, as also observed upon neutron irradiation [12].

Before addressing dynamical properties, we study the structural parameters of the three- and four-membered rings found in our sample. Whereas Si-O bond lengths in these rings do not differ significantly from the average value over the whole sample, bond angles in rings must be smaller than typical values to comply with the closure of the rings (see Table I). The high concentration of small rings in our sample directly affects the average Si-O-Si bond angle ( $136.9^\circ$ ), found to be slightly lower than typical experimental estimates which range between  $140^\circ$  and  $150^\circ$  (Ref. [28]). The deviations in the bond angles are smaller than on average, suggesting higher structural regularity in the rings [4,5]. The degree of planarity can be investigated by considering the sum of all the bond angles in the ring, which should give  $720^\circ$  and  $1080^\circ$  for planar three- and four-membered rings, respectively. We found that the five three-membered rings are close to being planar with a sum of  $702.5^\circ \pm 8.5^\circ$ . Deviations from planarity are more important for the two four-membered rings, for which we calculated  $978.7^\circ$  and  $980.2^\circ$ . Despite the closeness of these two values, we could not detect any other regularity shared by these two rings.

Since symmetric stretching motions such as the breathing motions in rings are recognized to be Raman active [5,29], a conclusive identification results from a correspondence between the distribution of breathing modes throughout the vibrational spectrum and the Raman defect lines. For every three- and four-membered ring, we thus projected the vibrational eigenmodes of our model [24] onto the coherent breathing motions of the oxygen atoms. Figure 2 illustrates these oxygen motions for one of the threefold rings in our model sample. The contributions corresponding to three- and four-membered rings were then added separately and represented as continuous curves using Gaussian broadening parameters  $\sigma$  (Fig. 3). By choosing  $\sigma = 12$  and  $6 \text{ cm}^{-1}$ , respectively, the broadening was large enough to yield single peaks in each of the projections shown in Fig. 3. The projections on three-membered and four-membered rings show peaks at  $609$  and  $497 \text{ cm}^{-1}$ , respectively, in impressive agreement with the positions of the  $D_2$  and  $D_1$  lines at  $606$  and  $495 \text{ cm}^{-1}$ , as shown in Fig. 3 where the experimental Raman spectrum [4] is reported for comparison. This remarkable match provides an unambiguous interpretation for the ori-

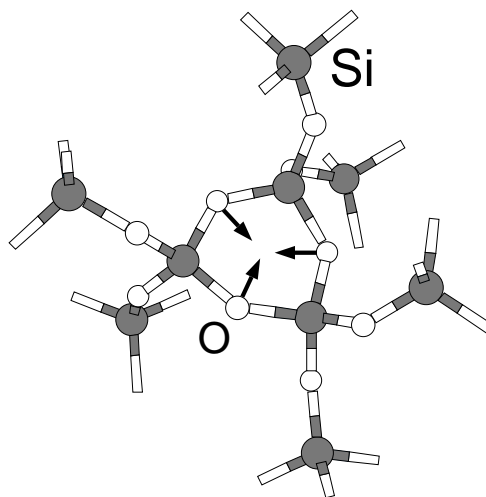


FIG. 2. Ball and stick model showing a threefold ring embedded in the structure of our sample of vitreous  $\text{SiO}_2$ . The arrows illustrate the motion of the oxygen atoms in the coherent breathing mode.

gin of the Raman lines. We obtained FWHM linewidths of  $62$  and  $21 \text{ cm}^{-1}$ , to be compared with the experimental widths of  $30$  and  $20 \text{ cm}^{-1}$ . The excellent agreement for the four-membered rings could be in part fortuitous and due to the limited statistics. A factor of 2 difference, such as for the three-membered rings, appears plausible in consideration of the limitations inherent to our model. These include the steric constraints induced by the limited size and the high concentration of small rings.

As a further confirmation, we verified that upon isotopic substitution the calculated positions of the oxygen breathing motions and the measured frequencies of the sharp Raman lines [30] shifted correspondingly. New eigenmodes were obtained by diagonalizing dynamic matrices in which the same force constants were combined with modified atomic masses. The  $^{16}\text{O} \rightarrow ^{18}\text{O}$  substitution yielded

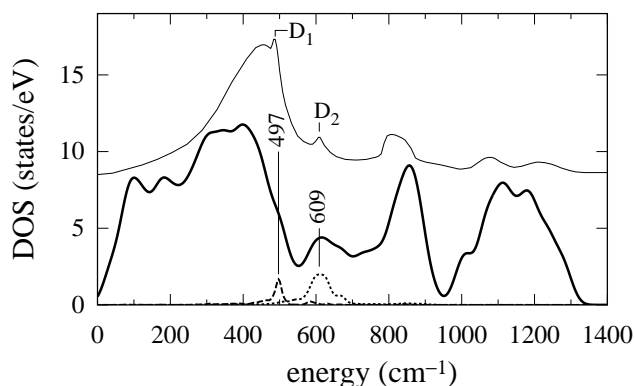


FIG. 3. Vibrational density of states of our silica model (solid) [24] and projections on the breathing modes of the three- (dotted) and the four-membered (dashed) rings. The amplitudes were broadened by  $12$  and  $6 \text{ cm}^{-1}$ , respectively. The experimental Raman spectrum (thin) is from Ref. [4].

TABLE I. Structural parameters in three- and four-membered rings compared to averages over the whole sample.

	Si-O bondlength (Å)	O-Si-O angle	Si-O-Si angle
3-memb.	$1.605 \pm 0.014$	$105.8^\circ \pm 2.4^\circ$	$128.4^\circ \pm 6.0^\circ$
4-memb.	$1.593 \pm 0.017$	$108.9^\circ \pm 1.9^\circ$	$135.9^\circ \pm 12.1^\circ$
Overall	$1.594 \pm 0.014$	$109.5^\circ \pm 5.3^\circ$	$136.9^\circ \pm 14.2^\circ$

TABLE II. Dependence of Raman lines on isotopic substitution. Experimental data are taken from Ref. [30].

	Natural SiO <sub>2</sub>		Shift in Si <sup>18</sup> O <sub>2</sub>		Shift in <sup>30</sup> SiO <sub>2</sub>	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
$D_1$ (cm <sup>-1</sup> )	495	497	-30	-27	-3	-1
$D_2$ (cm <sup>-1</sup> )	606	609	-31	-35	-1	0

shifts of approximately 30 cm<sup>-1</sup> to lower frequencies for both projections, while the <sup>28</sup>Si → <sup>30</sup>Si substitution hardly affected their positions (Table II), in very good agreement with the observed behavior of the  $D_1$  and  $D_2$  lines [30].

Note that the position of the peak in the vibrational density of states near 400 cm<sup>-1</sup> is in good agreement with neutron measurements [21]. Therefore the shift of about 50 cm<sup>-1</sup> to larger frequencies of the main Raman peak should be attributed to the frequency dependence of the Raman matrix elements. The concentration of small rings in vitreous silica is apparently too low to show features in the neutron spectrum [31]. The calculated vibrational density of states is indeed featureless at the  $D_1$  frequency. However, the density near 600 cm<sup>-1</sup> is overemphasized with respect to experiment and likely results from the too high concentration of three-membered rings in our model. In infrared experiments, the breathing ring motions are inactive, as confirmed by a recent calculation of the infrared spectrum for the same structural model as used in the present investigation [32].

This study unambiguously associates the Raman “defect” lines with three- and four-membered rings in the structure of vitreous silica, providing the first clear proof for the occurrence of such small rings. These lines therefore provide direct information on the concentration of these rings, opening the way to an unprecedented characterization of the random network of vitreous silica. A better understanding of small rings in silica is particularly important in view of the increased reactivity of the network at these sites [6].

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