

## LETTER

### Coordination changes and the vibrational spectrum of SiO<sub>2</sub> glass at high pressure

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#### ABSTRACT

We investigated the persistence of tetrahedral coordination in SiO<sub>2</sub> glass under high pressures by comparing experimental infrared spectra with the calculated spectra of Monte Carlo simulations of SiO<sub>2</sub> glass. The calculations are self-consistent: we used the same potential model, which prevents bonded Si-O coordinations higher than four, to generate the simulated structures and to calculate the eigenfrequencies and eigenvectors. The simulated, tetrahedrally coordinated structures agree well with available structure and equation-of-state data and, at higher pressures, are expected to differ from the real glass only if the latter undergoes coordination changes. The calculated vibrational density of states and infrared spectrum at zero pressure agree well with the data. The calculations reproduce most of the important features of the observed high-pressure infrared spectrum, including the features thought to be indicative of the onset of octahedrally coordinated Si at high pressures. We therefore suggest that the infrared spectra do not yield a unique structural interpretation and leave open the possibility that SiO<sub>2</sub> glass preserves its tetrahedral coordination to at least 40 GPa.

#### INTRODUCTION

Igneous processes in the Earth's interior are ultimately controlled by the physical properties and the atomic structure of silicate liquids. To the extent that glasses are faithful analogues of their molten counterparts, investigation of their high-pressure structure can provide important constraints on magma genesis and transport. Characterizing the gradual change in coordination of Si-O from four to six as a result of increased pressure in amorphous silicates is of central importance since this structural change will substantially increase magma densities, perhaps beyond those of coexisting solids, thereby preventing the magma's ascent.

Analogies with SiO<sub>2</sub> crystals and NMR experiments on a variety of quenched, high-pressure silicate liquids (Xue et al., 1991) indicate that SiO<sub>2</sub> liquid may become octahedrally coordinated by approximately 20 GPa. However, kinetic hindrances are likely to play a significant role in the compression of SiO<sub>2</sub> glass and may delay the four- to sixfold coordination change to much higher pressures. Monte Carlo simulations show that kinetic hindrances cause SiO<sub>2</sub> glass at room temperature to compress less efficiently than SiO<sub>2</sub> liquid at 2000 K, making

the glass less dense at high pressure, despite the competing effects of thermal expansion (Stixrude and Bukowinski, 1991). Further, although SiO<sub>2</sub> crystals readily convert to octahedral coordination near 10 GPa if the temperature is greater than several hundred kelvins, at room temperature four-coordinated quartz and coesite survive compression to roughly three times the equilibrium transition pressure to octahedral stishovite (Hemley et al., 1988). Thus, the structure of SiO<sub>2</sub> glass compressed at room temperature may be very different from the liquid at the same pressure.

Vibrational spectroscopy provides the only in situ high-pressure constraints on glass structure (Hemley et al., 1986; Williams and Jeanloz, 1988; Wolf et al., 1990). Because the atomic structure and the form of the vibrational eigenmodes in glasses are complex, quantitative interpretation of these data demands comparison with precise theoretical calculations, based on realistic structural models. At zero pressure, this approach is well established, beginning with the pioneering work of Bell and Dean (see Bell, 1976), who used a continuous random network and a force constant model to predict zero pressure spectra. It is difficult to extend such work to higher pressures because of the lack of independent structural information from, for instance, X-ray diffraction. Murray and Ching (1989) treated pressure as a perturbation by assuming that the bonding topology of their continuous random network was independent of volume. They used a force constant model to predict the response of bond lengths and the Raman spectrum to compression. The

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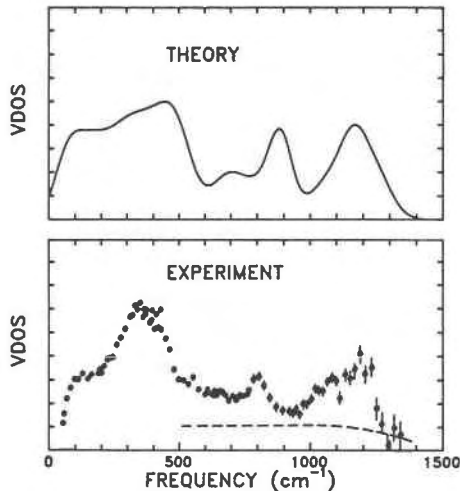


Fig. 1. Comparison of calculated and experimental (Galeener et al., 1983) vibrational density of states at zero pressure. The dashed line is the estimated two-phonon contribution (Galeener et al., 1983).

resulting structures are probably inaccurate above approximately 8 GPa, where network rearrangement begins to contribute substantially to compression (Hemley et al., 1986; Stixrude and Bukowinski, 1991). Although computer simulations can overcome these limitations by simultaneously predicting high-pressure structure and spectra, their accuracy depends critically on the assumed form of the interatomic forces. The simple ionic models used so far have not reached the level of agreement typical of the Bell and Dean approach (Garofalini, 1982; Rustad et al., 1991 and references therein).

To investigate the persistence of tetrahedral coordination in SiO<sub>2</sub> glass under compression, we compare results of Monte Carlo simulations with measured, high-pressure vibrational spectra. Simulated structures and vibrational spectra are based on an empirical covalent model of bonding in four-coordinate SiO<sub>2</sub>, which prevents bonded Si-O coordinations greater than four. Within this context, the model has proved successful in matching a wide variety of data and is the first to reproduce the structure and equations of state of tetrahedral crystalline, liquid, and vitreous SiO<sub>2</sub>, including irreversible compaction of the latter above 10 GPa (Stixrude and Bukowinski, 1989, 1991). We therefore expect the simulations and spectral calculations to mimic closely the real glass and to deviate substantially only if the latter develops a significant population of Si-O coordinations that exceed four.

### METHODOLOGY

These are the first self-consistent calculations of the vibrational density of states and infrared spectra of SiO<sub>2</sub> glass: we use the same model to generate simulated structures and to solve the vibrational eigenvalue problem. Glass structures are taken from the final configurations of equilibrated room-temperature Monte Carlo simula-

tions (Stixrude and Bukowinski, 1991). These structures are quenched to the local energy minimum at zero temperature to eliminate residual forces on the atoms.

Vibrational frequencies and modes at the Brillouin zone center are determined by solving the eigenvalue problem:  $Wa = \lambda a$ , where  $a$  and  $\lambda$  are the eigenvectors and eigenvalues, respectively, and the elements of  $W$  are given by

$$W_{i\alpha,j\beta} = (m_i m_j)^{-1/2} \left( \frac{\partial^2 U}{\partial x_{i\alpha} \partial x_{j\beta}} \right)_0 \quad i, j = \{1, \dots, N\};$$

$$\alpha, \beta = \{1, 2, 3\} \quad (1)$$

where  $U$  is the total energy,  $m_i$  is the mass of atom  $i$ , the  $x_{i\alpha}$  are its Cartesian coordinates, the subscript 0 indicates equilibrium, and  $N$  is the total number of atoms in the unit cell of the simulated structure ( $N = 192$ ). The IR intensity of eigenmode  $\xi$  is given by

$$I(\xi) \propto \sum_{\alpha=1}^3 \left( \sum_{i\beta} Q_i A_{i\beta}^{\xi} \frac{\partial \mu_{\alpha}}{\partial x_{i\beta}} \right)^2 \quad (2)$$

where  $A_{i\alpha} = m_i^{-1/2} a_{i\alpha}$  and  $\mu_{\alpha}$  is the  $\alpha$  Cartesian component of the dipole moment, calculated by assuming effective charges,  $Q_i$ , equal to formal ionic charges (Bell, 1976). Vibrational mode assignments, rocking, bending, stretching, and cation contributions to an eigenmode, are based on the Bell and Dean decomposition method (Bell, 1976).

### RESULTS

Figure 1 shows the calculated and experimental vibrational density of states. The three main peaks of the experimentally determined profile are reproduced, as well as the smaller peak near 600 cm<sup>-1</sup> and the broad low-frequency shoulder on the 400 cm<sup>-1</sup> peak. The experimental high-frequency peak may be divided by LO-TO splitting, although the neutron diffraction data do not demonstrate this conclusively. Because the model contains no long-range coulomb forces, this effect is absent in the calculations. Our calculations match the data significantly better than ionic molecular dynamics simulations (Garofalini, 1982; Rustad et al., 1991) or the results of Bell and Dean (Bell, 1976). Murray and Ching (1989) achieve comparable agreement by optimizing potential parameters to minimize disagreement with experiment.

Calculated and experimental IR spectra are compared in Figure 2. At zero pressure the locations and relative heights of the four main peaks agree well with the measured spectrum. Although discrepancies must be caused in part by the simple point-charge model used to calculate intensities, certain differences are attributable to deficiencies in the simulated structures and the potential model. Analysis of compression mechanisms in SiO<sub>2</sub> crystals suggests that the Si-O stretching force constant predicted by our interatomic force model is too large (Stixrude and Bukowinski, 1988), probably accounting for the overestimated frequency of the peak at 1080 cm<sup>-1</sup>. An underestimated intertetrahedral Si-O-Si angle in the simulated structures (Stixrude and Bukowinski, 1991) probably explains the overestimated frequency of the experimental

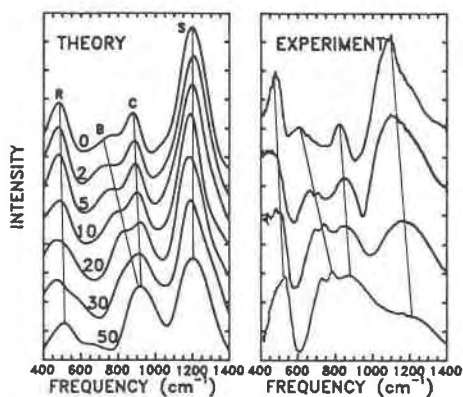


Fig. 2. Comparison of calculated and experimental (Williams and Jeanloz, 1988) infrared absorbance. The calculated spectra are labeled by the appropriate pressure in GPa. From top to bottom, the experimental spectra were taken at 2.2, 17.2, 27.5, and 38.9 GPa. By comparing with our calculated spectra, we assign the four measured peaks, in order of increasing frequency, to rocking (R), bending (B), cation (C), and stretching (S) motions (see Fig. 3). The bending and cation peaks converge at high pressures in both calculated and experimental spectra. The straight lines are guides to the eye.

peak at 600 cm<sup>-1</sup>. This band is due mostly to bending motion of bridging oxygens, which involves increasing amounts of Si-O bond length variation as the Si-O-Si angle closes. Although the model was constrained independently of structural or vibrational data on glass, our calculations match the IR data somewhat better than the results of Bell and Dean (Bell, 1976) and at least as well as those of Murray and Ching (1989), who used an optimized potential function.

At higher pressures, though the agreement is not fully quantitative, the calculations reproduce most of the important pressure-induced trends in the experimental IR spectra (Fig. 2). In calculations and experiments, the positions of the lowest and highest frequency bands change little with pressure, whereas at midfrequencies the two peaks present at low pressure merge to form a single high-pressure peak. The increase in midfrequency intensity and the insensitivity of low-frequency intensity to pressure are also reproduced by the calculations. The calculations' inability to reproduce the observed decrease in intensity of the high-frequency peak may be due to underestimated distortion of the SiO<sub>4</sub> tetrahedra at high pressure as a result of an overly strong Si-O bond (Stixrude and Bukowski, 1988). The necessary distortion need not be large enough to compromise tetrahedral coordination: elimination of the O-Si-O force constant yields almost vanishing intensities of this peak at pressures above 30 GPa while retaining well-defined fourfold Si-O coordination with an O-Si-O angular variance of 22° from the ideal tetrahedral value (Oshagan, 1990). Significantly larger distortions are needed to produce pseudo-octahedral coordinations.

Analysis of the eigenvectors shows that four types of atomic motion readily account for the IR peaks at all

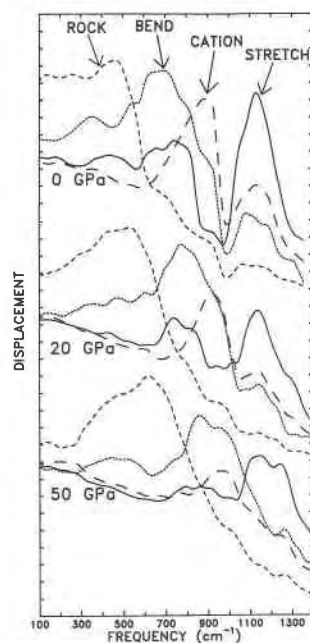


Fig. 3. Bell and Dean type decomposition of predicted normal modes of SiO<sub>2</sub> glass, showing the total contribution of rocking, bending, stretching, and cation motions (3) at each eigenfrequency.

pressures (Fig. 3). At low pressures the four IR peaks coincide with maxima in rocking, bending, cation, and stretching motion in order of increasing frequency. This pattern agrees well with the results of Bell and Dean (Bell, 1976). No new types of atomic motion are needed to explain the high-pressure spectrum. Rocking and stretching still account for the relatively isolated lowest and highest frequency peaks, respectively, whereas maxima in bending and cation motions merge with increasing pressure, accounting for the single, greatly amplified mid-frequency peak.

The effect of pressure on the basic bitetrahedral unit readily explains the frequency shifts of the various modes. Bending is most strongly affected since closing the Si-O-Si angle increases the participation of Si-O bond length variation in this motion. A competition between Si-O bond compression, which raises stretching frequencies, and Si-O-Si angle bending, which lowers them through decreased participation of Si-O bond length variation, probably accounts for the small effect of pressure on the high-frequency peak. Rocking and cation motions are less directly affected by angle bending or bond compression and change little with pressure.

Based on a comparison with our results, we have identified rocking, bending, cation, and stretching peaks in the high-pressure experimental spectra (Fig. 2). The pressure shifts of the experimental modes share important features with the calculated ones. The strongest measured pressure shift, that of the bending mode, agrees very well with the calculated value, as does the pressure shift of the

cation mode. Measured rocking and stretching modes, like the calculated ones, are relatively insensitive to pressure.

### DISCUSSION

The calculated vibrational spectrum of a tetrahedrally coordinated glass accounts for most of the features of the observed IR spectrum. In particular, the dramatic pressure-induced increase in midfrequency absorption, previously attributed by analogy with crystals to the appearance of SiO<sub>6</sub> octahedra (Williams and Jeanloz, 1988), is readily explained by the combination and intensification of tetrahedral bending and cation modes. A four-coordinated high-pressure structure also readily accounts for the tetrahedral rocking mode (500 cm<sup>-1</sup>). Its nearly constant shape and intensity in both experimental and calculated spectra are difficult to reconcile with the pressure-induced disappearance of SiO<sub>4</sub> tetrahedra proposed by Williams and Jeanloz. We suggest that comparatively minor structural changes, tetrahedral distortions somewhat greater than those predicted by our model, may account for the observed pressure-induced decrease in intensity of the tetrahedral stretching mode.

The survival of fourfold coordination in SiO<sub>2</sub> glass to at least 40 GPa is also consistent with Raman spectroscopy of SiO<sub>2</sub> and GeO<sub>2</sub> glasses. Raman spectra of SiO<sub>2</sub> glass show significant broadening and weakening of bands at high pressure but no evidence of new bands up to 40 GPa (Hemley et al., 1986). In contrast, GeO<sub>2</sub> glass, for which there is independent evidence of a four- to sixfold coordination change from 8 to 13 GPa (Itie et al., 1989), develops a new low-frequency Raman band over the same pressure interval, which has been attributed to GeO<sub>6</sub> octahedral modes (Durben and Wolf, 1991).

Larger populations of nonbridging O atoms or the presence of Al in more complex silicates may alleviate kinetic hindrances somewhat and allow glasses to undergo coordination changes at lower pressures more typical of the liquid (sodium tetrasilicate may be an example, Wolf et al., 1990). However, experiments on anorthite and diopside glasses (Williams and Jeanloz, 1988), like measurements of SiO<sub>2</sub> glass, show low-frequency (500 cm<sup>-1</sup>) peaks whose shape and intensity are virtually unaffected by pressure, and neither glass shows distinct high-pressure bands that would require the appearance of new structural units such as AlO<sub>6</sub> or SiO<sub>6</sub> octahedra. Thus, these glasses may also be tetrahedrally coordinated throughout the experimental pressure range. Our results emphasize the importance, for geophysical applications, of studying liquids directly or liquids quenched in situ at high pressure.

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