

## Molecular orbital calculations on $H_6Si_2O_7$ with a variable Si-O-Si angle: Implications for the high-pressure vibrational spectra of silicate glasses

J. D. KUBICKI, DAN SYKES

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A.

### ABSTRACT

Two configurations of  $H_6Si_2O_7$  have been predicted from Hartree-Fock molecular orbital calculations with significantly different Si-O-Si angles (141.5 and 128.3°). OH dipolar attractions ( $OH \cdots OH$ ) between the tetrahedra are ascribed as responsible for creating a local minimum in the potential energy surface of the molecule at the smaller Si-O-Si angle. No minima were found for any other Si-O-Si angles. Vibrational analyses predict that the mode associated with the Si-O<sub>br</sub> stretch + Si-O-Si angle bend,  $\nu_s$ , increases from 709 to 755  $cm^{-1}$  as the Si-O-Si angle decreases from 141.5 to 128.3°. Theoretical frequency shifts of this mode with closure of the Si-O-Si angle are compatible with in situ, high-pressure vibrational spectra of silicate glasses. Predicted frequency shifts in the region from 800 to 1300  $cm^{-1}$  are mixed between positive and negative values that may complicate interpretations of silicate glass vibrational spectra. O-H stretching frequencies decrease by over 100  $cm^{-1}$  due to the formation of  $H \cdots O$  bridges. These next nearest neighbor effects may be responsible for observed O-H stretching peak shifts in the spectra of hydrous minerals.

### INTRODUCTION

The idea that melt and solid densities may cross over within the mantle (Stolper et al., 1981) has spurred research into the study of melt compressibility mechanisms. Some planetary accretion models predict the existence of a magma ocean early in Earth history (Matsui and Abe, 1986). Neutrally or negatively buoyant magmas at depth within the Earth during early planetary differentiation would have had significant consequences for the geochemistry of the Earth (Rigden et al., 1984). Hence, the relationship between melt structure and pressure is essential to our understanding of the chemical differentiation processes that have shaped the Earth.

One way of learning about high-pressure melts is to quench melts from high temperature under pressure in a piston-cylinder or multianvil apparatus. Studies of melts quenched at high pressure have shown that significant changes in coordination number occur under pressures relevant in geochemistry (Stebbins and McMillan, 1989). However, studies of glasses at ambient pressure may not quantitatively reflect the pressure-induced structural transformations in the melt phase because glass structures may relax from high pressure at room temperature (Hemley et al., 1986; Williams and Jeanloz, 1988; Kubicki et al., 1992). Another approach has been to compress glasses in a diamond-anvil cell and measure spectroscopic changes in situ under pressure. In situ vibrational spectroscopy of glasses in a diamond-anvil cell can shed light on the relationship between pressure and glass structure, but this type of study fails to account for differences between glass and melt compression mechanisms. Thus, al-

though recent work has shed some light onto the qualitative picture surrounding glass and melt compression, there have been no studies to determine melt structure at mantle temperatures and pressures for relevant compositions.

Molecular dynamics and Monte Carlo simulations have been used in an attempt to solve this problem by modeling melt structures at high pressures and temperatures (Rustad et al., 1991; Stixrude and Bukowinski, 1989). Kubicki and Lasaga (1991) have modeled the structures of  $MgSiO_3$  and  $Mg_2SiO_4$  melts over a range of pressure and temperature with molecular dynamics (MD) calculations, but the interatomic potentials employed in those simulations are not sufficiently accurate to predict reliably melt structure for a given temperature and pressure.

One common conclusion of all three types of studies (i.e., high  $P$  and  $T$  quenched, ambient-temperature diamond-anvil cell compression, and computer simulation) has been that a dominant compression mechanism in silicate glasses is the closure of Si-O-Si angles. This study of the siloxane dimer with variable intertetrahedral angles was undertaken to evaluate theoretically the relationships between Si-O-Si bond angles and vibrational frequencies. Similar work has been carried out by Lazarev (1972) and Furukawa et al. (1981) with empirical force constants that predicted an inverse relationship between Si-O-Si angle and the frequency of the Si-O<sub>br</sub> stretch + Si-O-Si angle bending mode. The calculations presented here are an attempt to improve on the earlier work by employing self-consistent, Hartree-Fock molecular orbital (MO) calculations instead of empirical force constants. MO calculations on small clusters have been used to

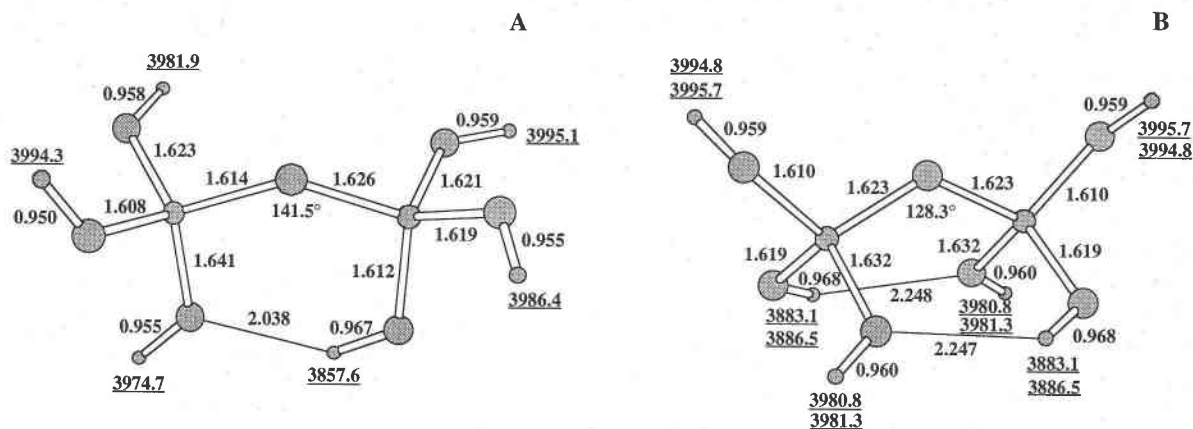


Fig. 1. The most stable configuration of  $H_6Si_2O_7$ , found has an Si-O-Si angle =  $141.5^\circ$  (A) with one H...O bridge between the tetrahedra at 2.038 Å. The configuration with two H...O bridges of  $\approx 2.25$  Å and an Si-O-Si angle =  $128.3^\circ$  (B) is metastable with respect to the more open intertetrahedral angle. Stretching frequencies (in  $cm^{-1}$ ) associated with each (O-H) group are marked by underlining. All other numbers refer to atomic distances in ångströms. Figures were generated using the program Atoms (Dowty, 1990).

model vibrations in condensed silicates by a number of authors (see Sauer, 1989, for a review). Hence, results of this study may be applied to studies of silicate glasses (Hemley et al., 1986; Kubicki et al., 1992) to estimate the changes in Si-O-Si angles with pressure based on frequency shifts of this vibrational mode.

### METHODS

The standard methods of Hartree-Fock, MO theory were applied with the program Gaussian 90 (Frisch et al., 1990). Slater-type orbital 3-21G\* basis sets were employed to model the electron charge density ( $G$  = Gaussian functions approximate atomic orbitals, 3-21 = 3 Gaussians per atomic orbital with the valence electrons represented with double-zeta Gaussians, and the asterisk indicates that d orbitals were used for second-row atoms as polarization functions).

In order to obtain meaningful vibrational analysis of a molecule, all structural parameters must be optimized to a minimum energy configuration. Molecular optimizations were carried out on  $H_6Si_2O_7$  with 39 (i.e.,  $3N - 6$  where  $N$  = the number of atoms in the molecule) independent parameters such that all bond lengths, bond angles, and dihedral angles within the cluster were unconstrained by symmetry. All parameters were varied until a minimum energy configuration was found within a tolerance of  $1 \times 10^{-7}$  H (H = Hartrees). Successive reoptimizations on these clusters indicate that the precision of these calculations is on the order of  $10^{-5}$  H. The potential energy changes calculated in this study are on the order of  $10^{-4}$  H, so the differences are significant. The accuracy of the calculations is undetermined because these molecules have not been synthesized. However, the basis set dependency of the results is on the order of 5 H (i.e., 0.5%) for a change of basis set from 3-21G\* to 6-31G\*.

At a minimum in the potential energy surface of a mol-

ecule, all first derivatives of atomic motion will be equal to zero [i.e.,  $(dV/dr) = 0$ ] and all second derivatives are positive [i.e.,  $(d^2V/dr^2) > 0$ ]. The molecule is in an equilibrium structure when the above criteria are met. Harmonic expansion of the interatomic potential then provides an estimate of vibrational frequencies. Frequency analyses of the optimized geometries based on diagonalization of the Hessian matrix (i.e., the second derivatives of the potential energy surface) were carried out for both clusters. This method is described in Lasaga and Gibbs (1988). No imaginary frequencies or negative eigenvalues of the Hessian matrix were calculated for the configurations in Figure 1. The frequencies are represented graphically in synthetic spectra in Figure 2.

Optimizations were also performed with the Si-O-Si angle initially constrained while all other parameters were optimized to obtain the energies in Figure 3. The Si-O-Si angle constraint was then removed, and the molecule allowed to optimize fully in order to search for possible stable configurations. Two local minima were found at  $128.3^\circ$  and  $141.5^\circ$ . Configurations constrained with Si-O-Si angles less than  $135^\circ$  optimized to the  $128.3^\circ$  configuration once this constraint was lifted. Configurations with Si-O-Si angles greater than  $135^\circ$  optimized to the  $141.5^\circ$  configuration. Attempts were also made to determine if another minimum for this molecule could be found with the H...O bridges between the tetrahedra. The Si-O-Si angle in  $H_6Si_2O_7$  tends toward  $180^\circ$  once there is no H...O attraction between tetrahedra. All configurations calculated with this geometry were found to be significantly higher in energy than the configurations in Figure 1 (i.e.,  $\Delta V > +0.03$  H). This does not preclude the possibility that another configuration of this molecule might be found with more stable energetics; but, at this time, the  $141.5^\circ$  configuration is the lowest energy structure that we have found.

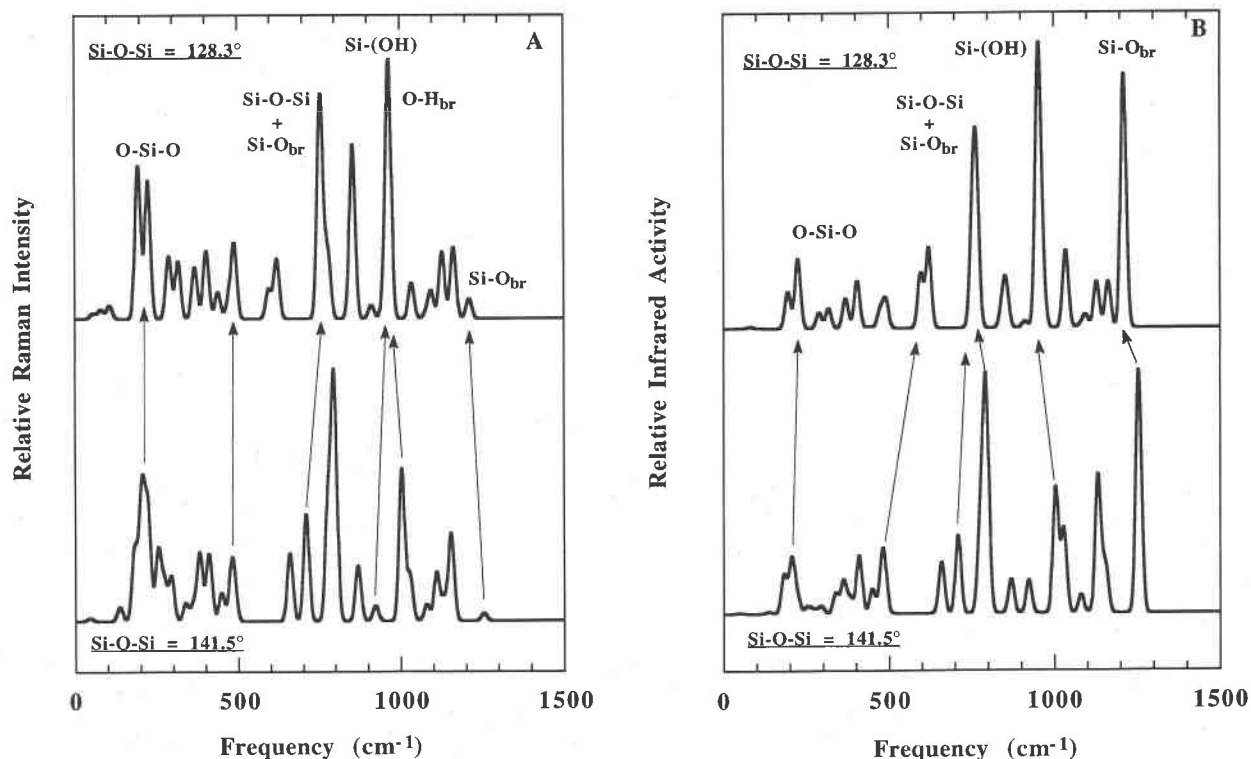


Fig. 2. Synthetic Raman (A) and infrared (B) spectra of the two configurations are plotted above. The line width is an arbitrary constant of  $25 \text{ cm}^{-1}$  for each peak; the frequencies and intensities are taken from the ab initio MO calculations. The frequency and intensity shifts are not simple functions of Si-O-Si angle. Complicated changes in vibrational modes associated with closure of the Si-O-Si angle make correlations of vibrational spectra with structural changes difficult. This is especially true for in situ, high-pressure glass spectroscopy when spectra are weak.

## RESULTS

### Structural

Optimized structural parameters for the configurations are outlined in Table 1, and the structures of both molecular configurations are pictured in Figure 1. The two configurations can be obtained reversibly from one another by changing the Si-O-Si angle and allowing all other parameters to optimize. No rotations of the tetrahedra are necessary to obtain the metastable configuration. The MO calculations predict an Si-O-Si angle of  $141.5^\circ$  for the stable configuration ( $-1100.16810 \text{ H}$ ) and  $128.3^\circ$  for the metastable configuration ( $-1100.16795 \text{ H}$ ). A decrease of  $13.2^\circ$  is a large change even in this relatively pliable structural parameter (Newton and Gibbs, 1980). A test of our results with polarization functions on all atoms (i.e., 3-21G\*\* basis set) gives the same relative order for the potential energies of the two species (Si-O-Si =  $141.8^\circ$ ,  $E = -1100.25957 \text{ H}$ ; Si-O-Si =  $128.4^\circ$ ,  $E = -1100.25899 \text{ H}$ ) with a higher potential energy at an intermediate Si-O-Si angle (Si-O-Si =  $135^\circ$ ;  $E = -1100.25878 \text{ H}$ ). The  $141.5^\circ$  configuration is similar to that reported for 6-31G\* calculations on  $H_6Si_2O_7$  by Lasaga and Gibbs (1991).

The  $H \cdots O$  bridge is  $2.04 \text{ \AA}$  in the stable species, and

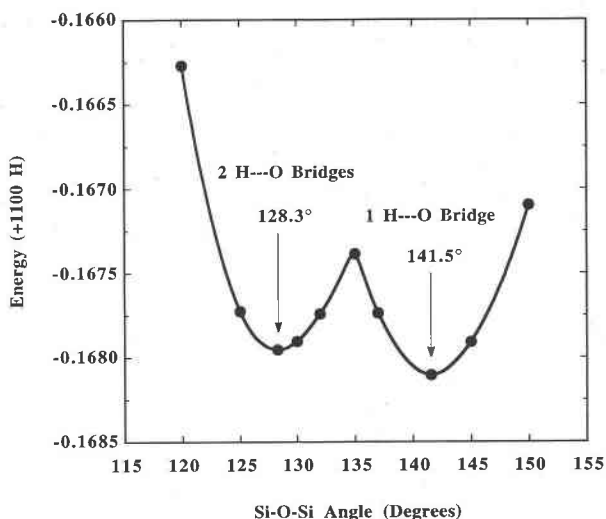


Fig. 3. Energy of the molecule  $H_6Si_2O_7$ , plotted as a function of Si-O-Si angle illustrates the metastability of the closed angle configuration. Note that only the  $128.3^\circ$  and  $141.5^\circ$  points are fully optimized stable structures. The other points in the diagram were calculated by constraining the intertetrahedral angle and optimizing all other parameters. A saddle point between the two stable configurations occurs at  $\approx 135^\circ$ .

TABLE 1. Energies and structures of  $H_6Si_2O_7$ 

Energy (H)	T-O (Å)	O-H (Å)	T-O-T (°)	O-T-O (°)	T-O-H (°)
-1100.168105	(1.620)*	(0.957)	141.5	(109.48)	(124.28)
	(1.620)**	0.950†		103.66†	119.18†
		0.967‡		114.06‡	126.98‡
		2.038§			
-1100.167953	(1.620)*	(0.962)	128.3	(109.45)	(123.71)
	(1.623)**	0.959†		103.54†	119.19†
		0.968‡		114.22‡	126.64‡
		(2.2473)§			

Note: Molecular orbital calculations at the 3-21G\* level predict that the stable configuration is at Si-O-Si = 141.5°. Energies are in Hartrees (1 H  $\approx 2.62546 \times 10^3$  kJ/mol). Note that there are two H $\cdots$ O bridges in the 128.3° configuration. Numbers in angle brackets represent average values.

\* Nonbridging O.

\*\* Bridging O.

† Minimum value.

‡ Maximum value.

§ H $\cdots$ O bridge distance.

the two H $\cdots$ O bridges are 2.25 Å in the metastable species. (Note that the same H $\cdots$ O bridge in the stable configuration exists in the metastable configuration, but it is lengthened by 0.2 Å.) Some of the Si-O<sub>nbr</sub> bonds in the molecules are lengthened by the presence of H $\cdots$ O bridges (Fig. 1). O atoms attracted to a H atom on the opposing tetrahedron are found at 1.63–1.64 Å from the bonded Si atom. The other Si-O bonds in the molecule are 1.61–1.62 Å. A similar effect is present in the O-H bond lengths as H $\cdots$ O bridges lengthen this bond from 0.96 to 0.97 Å. The bond distance differences are small, but they have significant effects on the vibrational spectrum of this molecule.

Another way of looking at the compression of silicates is to examine O-O distances (Levien et al., 1980). Calculation of the O-O distances in these two configurations reveals that the average distance between O atoms bonded to the same Si atom remains constant (within  $\pm 0.01$  Å) with closure of the Si-O-Si angle. The minimum O-O distance in the 128.3° configuration is only 0.0005 Å shorter than the minimum in the 141.5° configuration. On the other hand, the average nonbonded O-O distances (i.e., O atoms not bonded to the same Si atom) decrease linearly ( $R = 0.987$ ) from 4.6055 to 4.1929 Å as the Si-O-Si angles change from 150 to 120° (Fig. 4). Hence, because of the strong correlation between the two parameters, an increase in O-O repulsion can be equated with closure of the intertetrahedral angle in this molecule.

### Vibrational

Vibrational frequencies for each configuration are presented in Figure 2. In general, vibrational frequencies obtained from MO calculations on small clusters are 10% higher than those observed in solid silicates (Hess et al., 1986) because of the neglect of electron correlation (Andzelm and Wimmer, 1991). Although the absolute frequencies calculated without any configuration interaction to account for electron correlation have this 10% uncertainty, it has been demonstrated that the trends in vibra-

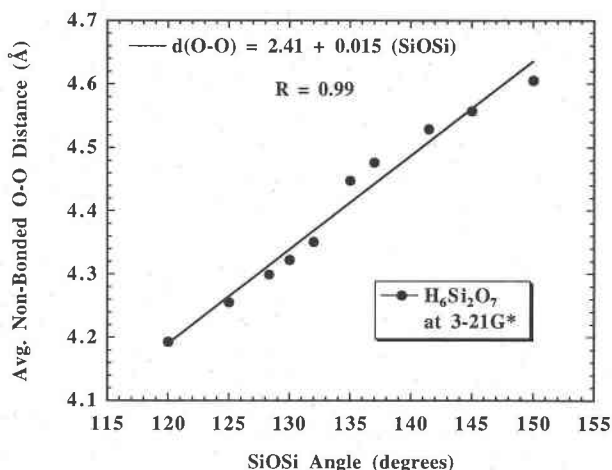


Fig. 4. Correlation of average nonbonded O-O (i.e., O atoms not bonded to the same Si atom) distances with the Si-O-Si angle in the  $H_6Si_2O_7$  molecule from optimized MO calculations. The strong linear correlation illustrates the equivalence of these two parameters in describing compression of the molecule.

tional spectra calculated with the smaller basis sets are similar to calculations with configuration interaction (Hermansson, 1991). It has been common practice to correct the molecular frequencies by the empirically determined error for comparison to condensed phases (Mortier et al., 1984). Furthermore, Dovesi et al. (1987) have determined that the structure and electron density of SiOSi linkages in  $\alpha$ -quartz are dominated by short-range forces, justifying the use of cluster calculations to study localized phenomena, such as Si-O vibrations, in condensed silicates (Lasaga and Gibbs, 1991).

The most relevant aspect of the calculated frequency shifts is the increase of the Si-O<sub>br</sub> stretch + Si-O-Si angle bending mode,  $\nu_s$ , with closure of the intertetrahedral angle from 709 to 755  $cm^{-1}$ . The calculated Raman intensity of this mode is the highest between 250 and 1000  $cm^{-1}$  in the molecule (neglecting the O-H + SiOH modes near 800  $cm^{-1}$ ). Raman peaks between 430 and 650  $cm^{-1}$  in silicate glass spectra (Brawer and White, 1975; McMillan, 1984; Sharma et al., 1988) have been assigned to mixed vibrational modes of T-O<sub>br</sub> stretching and T-O-T angle bending. Hence, we use the vibrational mode at 709  $cm^{-1}$  as an analogue for the  $\nu_s$  mode in silicate glasses. In  $H_6Si_2O_7$ , decreasing the Si-O-Si angle from 141.5 to 128.3° increases the frequency by 46  $cm^{-1}$  (Fig. 2). This shift is approximately equal to that observed for the Raman-active  $\nu_s$  bands in  $SiO_2$  glass from 0 to 4 GPa (Hemley et al., 1986) and in calcium magnesium metasilicate glass from 0 to 9 GPa (Kubicki et al., 1992).

O-H stretching frequencies in the region between 3800 and 4000  $cm^{-1}$  are divisible into three separate groups in the metastable configuration (Figs. 1, 2). The lowest frequency O-H stretches are associated with the H atoms that form the O-H (or O-H $\cdots$ O) bridges (i.e., 3883.1 and 3886.5  $cm^{-1}$ ). Higher frequencies are found for the O-H bonds where the O is involved in the H-O $\cdots$ H intertetra-

hedral bridge (i.e., 3980.8 and 3981.3  $cm^{-1}$ ). The highest frequencies arise from the O-H bonds where no bridging between tetrahedra takes place (i.e., 3994.8 and 3995.7  $cm^{-1}$ ). The splitting of these bands is significant: approximately 100  $cm^{-1}$  for the O-H with an O-H...O bridge and approximately 15  $cm^{-1}$  for the O-H with an H-O...H bridge relative to the unbridged O-H groups. These types of interactions could complicate the spectra of hydrous minerals and glasses as O-H groups with different next nearest-neighbor distances could give rise to separate peaks in infrared and Raman spectra (Mysen and Virgo, 1986; Skogby et al., 1990; Rossman and Aines, 1991).

## DISCUSSION

Changes in Si-O<sub>br</sub>, Si-O<sub>nbr</sub>, and O-H bond lengths and O-Si-O and Si-O-H bond angles between the two optimized structures are consistent with the results of Burkhard et al. (1991). However, Burkhard et al. (1991) have reported an inverse order of stability for these two configurations. We believe that our results are correct because the potential energies of the molecules in this study are lower than both of the configurations obtained by Burkhard et al. (1991). The Burkhard et al. (1991) results were reported for a 3-21G\* basis set with polarization added to the bridging O atom only, but we have used the 3-21G\*\* basis set with polarization functions on all atoms to test our results. Differences may also arise from different optimizations of the atomic basis sets. Burkhard et al. (1991) used the program Gamess (Dupres et al., 1980; Guest et al., 1987); whereas these calculations were performed with Gaussian 90 (Frisch et al., 1990). Frequency analyses of our optimized structures revealed no imaginary frequencies. Hence, the configurations in Figure 1 represent minima in the potential energy surface of the molecule. Burkhard et al. (1991) do not present vibrational analyses of their molecular configurations, so comparisons of vibrational spectra cannot be made at this time. Calculations with the Si-O-Si angle constrained to different values with all other parameters optimized reveal the metastable relationship of the 128.3° configuration relative to the 141.5° configuration (Fig. 3). A similar plot in Burkhard et al. (1991) did not show such a clear energy barrier or a well-defined maximum between the two structures.

In the region below 700  $cm^{-1}$ , the theoretical spectra are dominated by O-Si-O and Si-O-Si angle bending motions. Most of the shifts between the stable and metastable configurations are toward higher frequencies. Frequency shifts predicted with MO theory for the Si-O<sub>br</sub> stretching + Si-O-Si angle bending mode in  $H_6Si_2O_7$  qualitatively agree with the empirical calculations of Furukawa et al. (1981). The frequency of the vibration increases from 709 to 754  $cm^{-1}$  as the intertetrahedral angle closes. This behavior explains the positive trend of frequency vs. pressure of the midfrequency peak in calcium magnesium metasilicate glass Raman spectra (Kubicki et al., 1992). This prediction is also consistent with the observed Raman spectra of SiO<sub>2</sub> glass (Hemley et al.,

1986), where the bands between 300 and 600  $cm^{-1}$  move to higher frequency under pressure. The inverse correlation between Si-O-Si angle and frequency implies that the dominant motion in this mode is the angle bend. Decreasing the Si-O-Si angle increases the Si-O<sub>br</sub> bond distance, which could lower the vibrational frequency of this mode, if it were dominated by Si-O<sub>br</sub> stretching motions. Furthermore, the vibrational mode does not change significantly with closure of the intertetrahedral angle.

The opposite correlation, decreasing frequency of  $\nu_s$  with decreasing T-O-T angle, has also been observed in experimental Raman spectra (Sharma et al., 1988). Positive ( $d\nu_s/d\theta$ ) values result from compositional effects, however. For example, substitution of Al<sup>3+</sup> for Si<sup>4+</sup> in a dimer will decrease T-O-T, and the resulting  $\nu_s$  frequency will be lower (Sharma et al., 1988). This is due to the weaker character and increased length of the Al-O bond. The force constant for the  $\nu_s$  mode in a Si-O-Al bond is lower than the corresponding mode in an Si-O-Si linkage (Kubicki and Sykes, 1993). In a similar manner, increasing the ionic field strength of the network-modifying cations will have the same effect (Sharma et al., 1988).

The band widths of in situ, high-pressure Raman spectra of SiO<sub>2</sub> glass also narrow in this frequency region up to 8 GPa (Hemley et al., 1986). Decreasing band width is consistent with a decrease in the width of the Si-O-Si angle distribution present in the glass (Hemley et al., 1986). This explanation seems probable, based on Si-O-Si angle energetics. A decrease of T-O-T angle will lower the potential energy of the linkage if Si-O-Si is greater than the equilibrium value [i.e.,  $(dV/d\theta) > 0$  above 141.5° in Fig. 3]. On the other hand, closure of Si-O-Si angles less than 141.5° raises the potential energy of the linkage. It seems probable, therefore, that the Si-O-Si angle distribution will narrow with increasing pressure because larger angles will tend to close more readily than narrow angles. Increases in Raman intensities of vibrations at the higher frequency end of this region due to closure of the Si-O-Si angle (e.g., the peaks at 477.0 and 485.9  $cm^{-1}$  for  $H_6Si_2O_7$  at Si-O-Si = 141.5°) could also contribute to the narrowing of this band.

A decrease in the width of the Si-O-Si angle distribution with pressure has not been observed in theoretical simulations of glass structure (Kubicki and Lasaga, 1988; Murray and Ching, 1989; Rustad et al., 1991). An alternative explanation may be that narrower band widths result from strong positive frequency shifts in the low-frequency components of this band envelope combined with near-zero pressure-dependent shifts for the higher frequency components. The present results, however, do not support this interpretation. Failure of the theoretical simulations to produce a narrowing of the intertetrahedral angle distribution with compression are most likely the result of inadequate representation of the Si-O-Si angle in the interatomic potential.

In the Si-O stretch region (800–1200  $cm^{-1}$ ), there is a mixture between peaks increasing and decreasing in frequency with the closure of the Si-O-Si angle (Fig. 2).

Complex frequency shifts, combined with changes in the infrared and Raman activities of the modes, would make it difficult to tie changes in the vibrational spectra directly to structural changes in this molecule. The situation in the case of silicate glasses is more complicated because there are larger distributions of bond distances and bond angles to consider. Hence, it may be tenuous to correlate structural changes (e.g., coordination changes) in silicate glasses with changes in the relative intensity of the high-frequency envelope (Williams and Jeanloz, 1988). For example, within these calculations, the overall infrared activity between 1000 and 1200  $cm^{-1}$  decreases significantly between the 141.5 and 128.3° configurations, but this is not a reflection of a loss of tetrahedral coordination. Infrared activity is instead shifted toward the vibrations at 952.7 and 1211.0  $cm^{-1}$  (Fig. 2B), which would have the effect of flattening out the high-frequency envelope in the infrared spectrum. Exactly this type of intensity decrease is observed in calcium magnesium metasilicate glass infrared spectra up to 30 GPa (Williams and Jeanloz, 1988; Kubicki et al., 1992).

### CONCLUSIONS

In contrast to a previous study (Burkhard et al., 1991), these calculations predict that a more open configuration (Si-O-Si = 141.5°) with one H···O bridge between the tetrahedra is more stable than the closed configuration (Si-O-Si = 128.3°) with two H···O bridges. The second configuration is metastable (i.e., a local minimum in the potential energy surface) and allows for calculation of vibrational frequencies of the molecule at two different intertetrahedral angles. The reason for the discrepancy between the two calculations is uncertain at this time. However, the relative stability of the two structures has little bearing on the significance of the calculated changes in vibrational spectra between the two configurations.

Changes in the theoretical vibrational spectrum of  $H_6Si_2O_7$  with closure of the Si-O-Si angle are consistent with previous interpretations of in situ, high-pressure vibrational spectra of silicate glasses (Hemley et al., 1986; Kubicki et al., 1992). The 13° decrease of the Si-O-Si angle results in a frequency shift for  $\nu_5$  of 46  $cm^{-1}$ . This shift of the  $\nu_5$  mode correlates with observed changes of the  $\nu_5$  modes in  $SiO_2$  (Hemley et al., 1986) and calcium magnesium metasilicate glass Raman spectra under pressure (Kubicki et al., 1992). Hence, these calculations provide an estimate of the amount of Si-O-Si angle closure necessary to produce experimentally observed spectral shifts. Complex shifts in frequencies and intensities of individual vibrational modes within the molecule illustrate the difficulties in making simple correlations between observed differences in vibrational spectra and structural changes.

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