

A molecular orbital study of $H_6Si_2O_7$ under simulated compression

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Abstract

Ab initio SCF molecular orbital calculations (STO-3G approximation) have been used to compute equilibrium Si–O bridging bond lengths and SiOSi angles as well as stretching and bending force constants in the $H_6Si_2O_7$ molecule under confined compression. Compression on the Si–O bridging bond is simulated by placing He atoms along the Si–O bridging vectors and symmetrically stepping the He atoms toward the silicon.

The major effect of compression applied to $H_6Si_2O_7$ is to close down the SiOSi angle while $d(\text{Si–O}_b)$ decreases slightly. The linear correlation between $d(\text{Si–O}_b)$ and $-\sec(\text{SiOSi})$ observed at 1 bar appears to hold at higher pressure. Both the Si–O stretching and SiOSi bending force constants increase with higher compression.

Introduction

In the past decade, there has been a concerted effort to study silicate stereochemistry using molecular orbital (MO) formalisms. Although the MO calculations in these investigations have been completed for small molecular groups, their agreement with experimental observations support the view that isolated molecules possess local bonding forces similar to those found in crystals (cf. Newton and Gibbs, 1980; Gibbs, 1982). Molecular orbital calculations on simple molecular fragments such as $(H_3Si)_2O$ have therefore been useful in the study of bonding in silicates.

The equilibrium geometry and interatomic force constants of the pyrosilicic acid molecule, $H_6Si_2O_7$, have recently been determined through *ab initio* MO calculations (Newton and Gibbs, 1980; Newton et al., 1980). Optimization of Si–O bond lengths as a function of SiOSi angle in the molecule reproduces trends observed in the silica polymorphs (Newton and Gibbs, 1980) and *ab initio* force constants calculated for Si–O stretch and Si...Si non-bonded interactions in $H_6Si_2O_7$ are comparable with experimental values derived from the lattice dynamics of α -quartz (Newton et al., 1980). In addition, Meagher et al. (1980) and Gibbs et al. (1981) found in *ab initio* calculations on pyrosilicic acid that the minimum energy values of $d(\text{Si–O})$ and SiOSi were in close agreement with those observed for α -quartz.

To date, these investigations have been limited to zero pressure. With the ever increasing interest in high pressure phases and mantle mineralogy, bonding studies of

molecular groups at simulated high pressure can be an invaluable aid to understanding high pressure crystal chemistry. In addition, such studies will enable us to simulate pressures beyond the limits of current experimental technology. Meagher and Ross (1982) have completed an MO study on symmetric tetrahedral and octahedral clusters of Mg, Al and Si under simulated high pressure. In this investigation (Ross and Meagher, 1981) we are concerned with the relationship between the bridging bond lengths, $d(\text{Si–O}_b)$, and SiOSi angles, $\angle\text{SiOSi}$, in addition to symmetric stretching, k_s , and bending, k_δ , force constants in the pyrosilicic acid molecule under simulated compression.

Computational procedure

In this study, we have utilized the *ab initio* self consistent field molecular orbital (SCF MO) method. Basically, the method evaluates electron–electron, electron–nuclear and nuclear–nuclear energies as well as electron kinetic energies in computing a total energy. All MO calculations were completed with a minimal basis set of Slater type orbitals approximated by an expansion of three Gaussian functions (STO-3G) with the Gaussian 76 computer program (Binkley et al., 1978).

Molecular orbital calculations lend themselves readily to the evaluation of force constants (Newton et al., 1970). The total potential energy can be expanded in terms of q ,

$$E = E + (\partial E/\partial q)q + 0.5(\partial^2 E/\partial q^2)q^2 + \dots$$

Where q is a displacement from either the equilibrium bond length or the angle depending on whether a stretching force constant, k_s , or bending force constant, k_δ , is

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being calculated. By definition, the quadratic force constant is twice the coefficient of the quadratic term:

$$k_s = (\partial^2 E / \partial q^2) \text{ Nm}^{-1}$$

$$k_\delta = (\partial^2 E / \partial q^2) / r^2 \text{ Nm}^{-1}$$

where r is the bridging Si–O bond length. Thus the force constants are found directly by fitting a parabola to the potential energy curve. Increments of 0.01 \AA about the equilibrium bond length and 2° about the equilibrium bridging angle were used for determination of k_s and k_δ , respectively. A minimum of four data points were then used in least squares fitting of the quadratic function. With ranges of 0.05 \AA and 8° about the equilibrium bond length and bridging angle, higher order terms in the expansion of the potential energy were found to be insignificant. The definition of the bending force constant given above is preferred because it yields the same dimension (force/length) as the stretching force constant.

Throughout this investigation the $H_6Si_2O_7$ dimer (Fig. 1) has been fixed in a staggered conformation with O–H distances, $d(\text{O–H})$, and Si–O nonbridging bond lengths, $d(\text{Si–O}_{nb})$, of 0.96 \AA and 1.65 \AA , respectively. The OSiO and SiOH angles were maintained at 109.47° and 180° , respectively. The 180° SiOH angle was chosen in order to minimize He–H interactions in simulation of compression.

In asymmetric polyhedra, such as $H_6Si_2O_7$, one cannot simulate application of hydrostatic pressure. Rather, a confined compression can be simulated by placing helium atoms along the Si–O bridging bond (Fig. 1) and symmetrically stepping the two heliums toward the Si, keeping $d(\text{Si–O}_b)$ constant. At a particular He–Si distance, the He is locked in position and the Si and three nonbridging O–H are stepped in along the Si–O direction with the total energy calculated at each step. The equilibrium distance and force constant is then determined by least squares fitting a quadratic function. At a fixed $d(\text{Si–O}_b)$ the equilibrium SiOSi and bending force constant is similarly determined by “rocking” the $\text{Si}(\text{OH})_3$ group through a series of closely spaced angles. The one difference is that the He is “rocked” along with the $\text{Si}(\text{OH})_3$ group.

Since $d(\text{Si–O}_b)$ increases as the SiOSi angle narrows

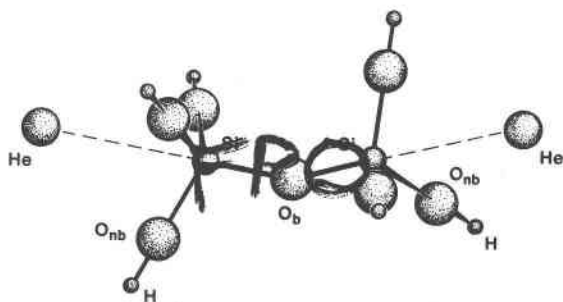


Fig. 1. Molecule $\text{He}_2\text{H}_6\text{Si}_2\text{O}_7$ in a staggered conformation showing the position of the He atoms (point symmetry C_2).

(Newton and Gibbs, 1980), the same He–Si distance used over a range of SiOSi would not impose the same amount of compression at each angle. To simulate an equivalent compression over the range of SiOSi angles, Hooke's law was employed along with the fact that the compression will be directly proportional to the applied force represented as $k\Delta x$. To compute $k\Delta x$ an equilibrium $d(\text{Si–O}_b)$ and stretching force constant is calculated at a given SiOSi. At the same angle $d(\text{He–Si})$ is then decreased a small amount thereby simulating increased compression and a new equilibrium $d(\text{Si–O}_b)$ and force constant is calculated. The average of these force constants times the difference in the equilibrium $d(\text{Si–O}_b)$ values gives the relative force being applied to the Si–O bond. At different SiOSi, $d(\text{He–Si})$ is adjusted until an equal $k\Delta x$ value is obtained. This provides a reasonable means of assuring that the force being applied at different SiOSi is equivalent as long as the interval Δx is small. Since $k\Delta x$ is proportional to compression on the Si–O bond, we have chosen to label the compressions associated with a “low” and “high” value of $k\Delta x$ as C1 and C2, respectively.

Results and discussion

Using the method outlined above, a potential energy surface for $\text{He}_2\text{H}_6\text{Si}_2\text{O}_7$ was constructed as a function of $d(\text{Si–O}_b)$ and $\angle\text{SiOSi}$ at 0 bar and C2 (Fig. 2). The topology of the energy surface changes notably from a long, narrow valley surrounded on three sides by steep energy barriers at 0 bar to one with a distinct minimum surrounded by steeper energy barriers at C2. Comparing the minimum of the energy trough at the two states, SiOSi narrows from 142° to 132° and $d(\text{Si–O}_b)$ decreases from 1.585 \AA to 1.565 \AA . A steepening of the sides of the energy surface is reflected by an increase in k_s from 743 Nm^{-1} at

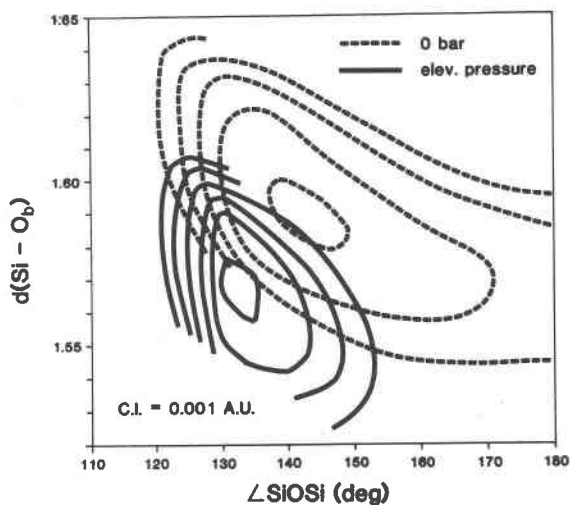


Fig. 2. The calculated total potential energy surface for $\text{He}_2\text{H}_6\text{Si}_2\text{O}_7$ at 0 bar (Meagher et al., 1980) and at C2 (this study) plotted as a function of the bridging Si–O distance and $\angle\text{SiOSi}$. (1 a.u. = 2.625×10^3 kJ per mole.)

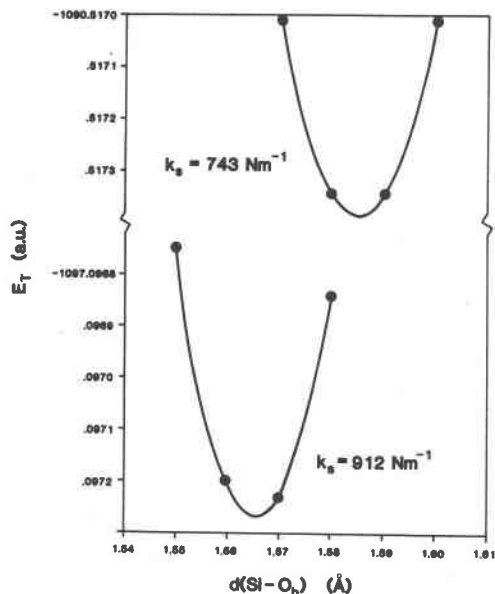


Fig. 3. Potential energy curve as a function of the bridging Si-O distance for $H_6Si_2O_7$ (upper curve) at 0 bar and $He_2H_6Si_6O_7$ (lower curve) at C2. The latter curve is lower in energy because of the additional He atoms. Note the increased stretching force constant, k_s , at the higher compression.

0 bar to 912 Nm^{-1} at C2 (Fig. 3) and an almost tripling of k_s from 8.2 Nm^{-1} at 0 bar to 20.6 Nm^{-1} at C2 (Fig. 4). The increase in k_s with compression is in agreement with infrared spectroscopic studies of Ferraro and Manghni (1972) and Ferraro et al. (1972) on α -quartz and silicate glasses at pressures up to 58.8 kbar.

A decrease in the SiOSi angle is the most prominent affect of compression in our calculations, narrowing 7.0% from 0 bar to C2 while $d(\text{Si}-\text{O}_b)$ decreases 1.3%. Recent

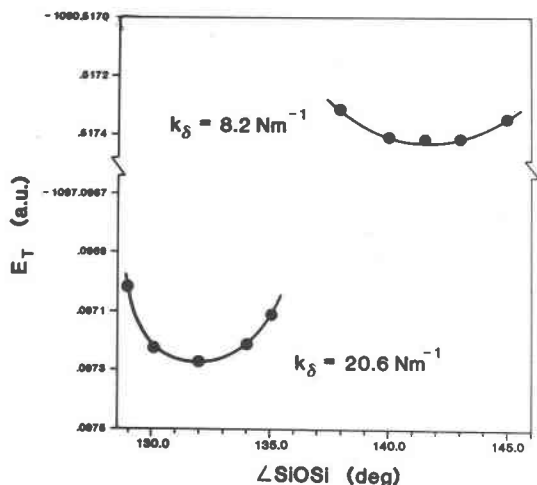


Fig. 4. Potential energy curve as a function of the bridging SiOSi angle in $H_6Si_2O_7$ (upper curve at 0 bar and $He_2H_6Si_6O_7$ (lower curve) at C2. The latter curve is lower in energy because of the additional He atoms.

Table 1. Mulliken bond overlap populations, $n(\text{Si}-\text{O})$ and $n(\text{Si}\dots\text{Si})$ along with atomic charges on the bridging oxygen, $Q(\text{O}_b)$, and silicon, $Q(\text{Si})$, for $H_6Si_2O_7$ at 0 bar, C1 and C2. The bridging Si-O bond length and SiOSi angle are optimized.

	$n(\text{Si}-\text{O}_b)$	$n(\text{Si}\dots\text{Si})$	$Q(\text{O}_b)$	$Q(\text{Si})$	$d(\text{Si}-\text{O}_b)$	$\angle\text{SiOSi}$
0 bar	+0.50	-0.058	-0.70	1.57	1.585Å	142°
C1	+0.50	-0.060	-0.70	1.58	1.580	136°
C2	+0.50	-0.062	-0.71	1.59	1.565	132°

high-pressure crystallographic studies of α -quartz (Jorgensen, 1978; Levien et al., 1980) have also shown that the major effect of pressure on the structure is to close down the SiOSi angle. With an increase in pressure, the framework of corner-linked tetrahedra can be collapsed ideally (thereby reducing molar volume) by a cooperative tilting of the rigid tetrahedra in such a way that the tetrahedra remain undistorted while the SiOSi angle is significantly reduced. In our calculations, a confining compression is imposed by helium atoms placed along the Si-O_b vectors which results in a similar decrease in $\angle\text{SiOSi}$. The reason for this intrinsic preference for a smaller SiOSi angle with increased compression in the $He_2H_6Si_6O_7$ molecule is not apparent. The electronic adjustments with increasing compression are minimal as can be seen in Table 1. There is essentially no change in the Mulliken bond overlap population $n(\text{Si}-\text{O}_b)$ and in the net charges on the bridging oxygen and silicons. Likewise gross charges on the valence orbitals of silicon and oxygen show no significant variation. The increasing negative values of $n(\text{Si}-\text{Si})$ (Table 1) would tend to favor a wider SiOSi angle with increasing compression. It is of interest, however, that although volume considerations are not explicitly included in the calculation the corner-shared tetrahedral group realizes an energy minimization at a smaller $\angle\text{SiOSi}$ with increasing compression similar to observed responses in α -quartz and coesite. It should be noted that even at the highest simulated compression we found the Mulliken bond overlap populations between He and the nonbridging oxygens, $n(\text{He}-\text{O}_{nb})$, and the $n(\text{He}-\text{Si})$ were never greater than 0.007 and the net charge on He to be nil. This indicates that a minimum of charge transfer is occurring between He and the neighboring atoms.

Newton and Gibbs (1980) have demonstrated at 0 bar that $n(\text{Si}-\text{O}_b)$ shows a curvilinear trend when plotted against SiOSi but is linearly correlated with $-\sec(\text{SiOSi})$. The latter correlation can be related to hybridization of the valence orbitals on the bridging oxygen of $H_6Si_2O_7$. If the hybrid orbitals on the bridging oxygen are expressed in the form $s + \lambda p$ where λ is the $s-p$ mixing coefficient, it can be shown that $\lambda^2 = -\sec(\text{SiOSi})$; furthermore, the SiOSi angle determines the percentage s -character, $100/(1 + \lambda^2)$, of each hybrid (McWeeney, 1979). To investigate how compression affects this relationship, $n(\text{Si}-\text{O}_b)$ values were plotted against the bridging angle at 0 bar and C2

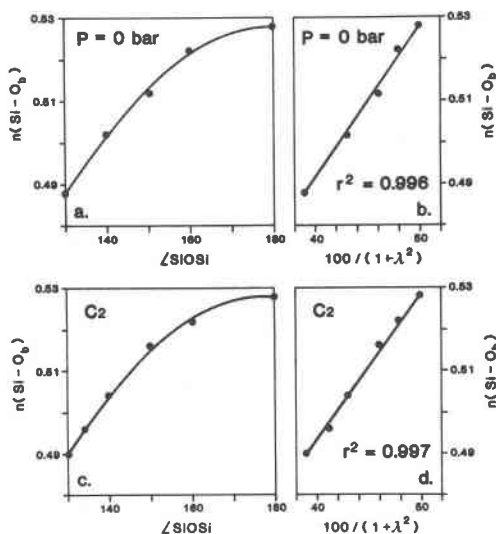


Fig. 5. The Mulliken bond overlap population, $n(\text{Si}-\text{O}_b)$, versus bridging angle, $\angle\text{SiOSi}$, and the percent s -character of the hybrid orbital on the bridging oxygen, $100/(1 + \lambda^2)$, at 0 bar (a,b) and C2 (c,d). The straight lines are regressed with r^2 values indicated.

(Figs. 5a,c). The trends at both states of compression are curvilinear; however, when $n(\text{Si}-\text{O}_b)$ is plotted against the percentage s -character of the bridging oxygen at 0 bar and C2 (Figs. 8b,d), well-developed linear correlations are obtained.

Newton and Gibbs (1980) have also discussed the linear correlation between $d(\text{Si}-\text{O}_b)$ and $-\sec(\text{SiOSi})$ and suggested that with increasing SiOSi , the s -character of the hybrid orbitals on the bridging oxygen increases thereby decreasing $d(\text{Si}-\text{O}_b)$. When observed $\text{Si}-\text{O}$ bridging bond lengths in coesite are plotted against $-\sec(\text{SiOSi})$ at 1 bar (Gibbs et al., 1977), a well-developed linear correlation ($r^2 = 0.96$) results with short bonds involving wide angles. Levien et al. (1980) and Levien and Prewitt (1981) suggest that this relationship fails to hold with increasing pressure. They drew this conclusion by plotting an SiOSi angle against its included average $d(\text{Si}-\text{O})$ at several pressures. However, one would not expect the relation to hold for a single bond angle in a structure with changing

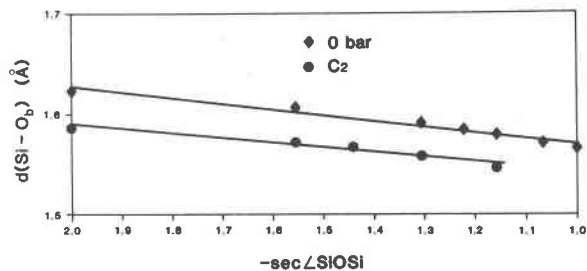


Fig. 6. Calculated equilibrium bridging bond lengths, $d(\text{Si}-\text{O}_b)$, versus $-\sec(\text{SiOSi})$ at 0 bar and C2. The straight lines are regressed with r^2 values indicated.

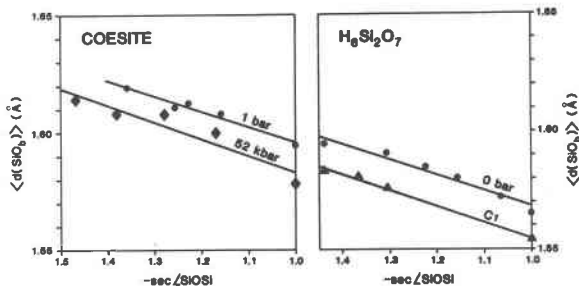


Fig. 7. Plots of average included $d(\text{Si}-\text{O}_b)$ versus $-\sec(\text{SiOSi})$ from observed data for coesite and calculated values for $H_6Si_2O_7$ suggesting that the linear relationship known to occur at 1 bar holds at elevated pressure. Regressed lines are drawn with r^2 values of 0.97 and 0.90 for coesite at 1-bar and 52 kbar, respectively and values of 0.97 and 0.98 for $H_6Si_2O_7$ at 0 bar and C1, respectively.

pressure; rather, one would expect the relation to hold for all bond angles and their included bond lengths in a structure at a constant pressure whether it be 1 bar or an elevated pressure. To verify this, we undertook a study of the relationship between $d(\text{Si}-\text{O}_b)$ and $-\sec(\text{SiOSi})$ at an elevated compression. The results, illustrated in Figure 6, support our assertion that this linear correlation holds at high pressure as well as at 1 bar.

Recent work on the structure and compressibility of coesite at high pressure (Levien and Prewitt, 1981) also supports this assertion. When the average observed $\text{Si}-\text{O}$ bridging bond lengths are plotted against $-\sec(\text{SiOSi})$ at 51.9 kbar, a significant linear correlation ($r^2 = 0.90$) is found. Figure 7 compares the experimental data for coesite at 1 bar and 51.9 kbar with calculated data for $H_6Si_2O_7$ at 0 bar and C1. The agreement between experiment and theory is encouraging.

This investigation demonstrates the promise of using He-atoms as a "pressure medium" in *ab initio* MO calculations. Although in asymmetric molecules such as pyrosilicic acid one is limited to simulation of a confined compression rather than a hydrostatic pressure, it appears that calculated trends in interatomic distances and angles as well as atomic force constants are consistent with observed trends at elevated hydrostatic pressures.

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