

# Ab initio many-body investigation of structure and stability of two-fold rings in silicates.

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## Abstract

In this paper we present *ab initio* many-body calculations on the strain energy of W-silica, taken as a model system for edge-sharing tetrahedral SiO<sub>2</sub>-systems with respect to corner-sharing ones as in  $\alpha$ -quartz. The mean-field results were obtained using the restricted Hartree-Fock approach, while the many-body effects were taken into account by the second-order Møller-Plesset perturbation theory and the coupled-cluster approach. Correlation contributions are found to play an important role to determine the stability of edge-sharing units. The most sophisticated method used in our calculation, i.e., the coupled-cluster approach with single and double excitations, yields a strain energy of 0.0427 a.u. per Si<sub>2</sub>O<sub>4</sub> unit with respect to  $\alpha$ -quartz, which is even smaller than the value obtained by a previous DFT calculation.

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## I. INTRODUCTION

Most polymorphs of silicates are formed by corner-sharing of the  $\text{SiO}_4$  tetrahedra with differing topology of the networks. However, there also exist structures like stishovite [1] and W-silica [2] containing  $\text{SiO}_6$  octahedra and edge-sharing tetrahedra, respectively. The edge-sharing tetrahedral structures are quite rare in nature, which is usually explained by Pauling's third rule in terms of Coulombic repulsion between the cations sharing the polyhedral units. Violation of the rule suggests a covalent nature of the structures. Recently, Car-Parrinello molecular dynamics simulations of a dehydroxylated silica surface showed the presence of edge-sharing tetrahedra [3]. We also obtained a small percentage of edge-sharing tetrahedra in molecular dynamics simulations of amorphous forms derived from zeolite ZSM-5 [4].

Considerable interest has been focused on the study of edge-sharing  $\text{SiO}_4$  tetrahedra as defective centers in vitreous silica, which act as sites of high chemical reactivity [5–8]. The occurrence of these edge-sharing units makes structures geometrically constrained and result in an energy penalty. The lack of experimental insight into the stability of these unusual features makes theoretical methods important tools to investigate these strained systems. The knowledge of the energy penalty presently rests on theoretical studies of mainly small clusters using the techniques of quantum chemistry [9–11] and classical force field models based on quantum chemical reference data [12]. Such calculations neglect the effect of the condensed environment in which the strained part of the system actually resides. Calculations on other solids showed the importance of electron correlation to allow a meaningful comparison of calculated quantities like cohesive energy etc. with experimental data [13, 14]. The most widely used approach is density-functional theory (DFT) [15–17]. Recently, Hamann used DFT based on the generalized gradient approximation (GGA) to extract the strained energies of two- and three- membered rings in models of a  $\text{SiO}_2$  network [15]. The calculations gave much smaller strain energies than previously estimated from Hartree-Fock (HF) calculations applied to small hydrogen-terminated molecular models [9–11]. However despite the large success in electronic structure theory DFT has the drawback that the results are highly dependent on the chosen functional and cannot be improved in a systematic way. As an alternative one can use wave-function based quantum chemical *ab initio* techniques, which are free from these flaws and provide a large array of methods of

different accuracy and computational cost.

In this paper we present HF self-consistent field (SCF) calculations and subsequent correlation calculations of the energy of edge-sharing tetrahedra and provide a comparison to the usual corner-sharing tetrahedral system. We choose W-silica and  $\alpha$ -quartz as the model systems for edge-sharing and corner-sharing silicate systems, respectively. The total and correlation energy per unit cell of W-silica and  $\alpha$ -quartz were obtained using a finite cluster and an incremental approach. Various non-metallic polymeric systems have been studied previously using the finite-cluster approach, which yielded accurate results for geometries and energies [14, 18]. The incremental scheme has been used to explore cohesive and geometrical properties of covalent solids [19, 20], semiconductors [13, 21] and ionic solids [22, 23]. Within the incremental approach, starting from HF data obtained with a standard solid state program package as CRYSTAL [24], the necessary correlation corrections to the total energy per unit cell of a periodic system can be obtained as a sum over increments defined in terms of localized orbitals. The correlation energy increments of well localized orbitals may be derived from quantum chemical calculations on finite model systems.

The remainder of the paper is organized as follows. In Sec. II the computational details are described. The results and discussions are presented in Sec. III. Finally a summary is given in Sec. IV.

## II. COMPUTATIONAL DETAILS

### A. Finite-Cluster Approach/A Simple Approach

W-silica as shown in Fig. 1 has a body-centered orthorhombic crystal structure with  $Ibam$  space-group, characterized by chains of edge-sharing  $\text{SiO}_4$  tetrahedra. Since, these chains are interacting only by weak van der Waals forces, the geometry is mainly determined by the lattice parameter  $c$  in the chain direction, i.e., the Si-Si distances. We have carried out series of all electron atom calculations using DFT based on the generalized gradient approximation (GGA) of Perdew and Wang (PW91) varying  $c$  over a range 4.2 Å to 5.2 Å.  $a$  and  $b$  were varied with fixed  $a/b$  ratio to change the  $a$ - $b$  plane area by  $\pm 5\%$ . These calculations were performed using new version of CRYSTAL code, i.e., CRYSTAL2003 which can optimize the fractional coordinates implicitly [25]. These calculations are analogous to the one by

Hamann in Ref. 15 where Si and O ion cores were represented by pseudopotential. One can easily see in Fig. 2 that the potential energy surface is considerably flatter with respect to  $a, b$  variations. This is conclusive that no significant change of energy and ring geometry could be obtained by optimizing  $a$  and  $b$  parameter as shown by Hamann [15]. Calculations with and without chain interaction at the minima shows a small energy difference of  $\approx 0.005$  a.u. Hence one can neglect the weak inter-chain interactions and consider only single-chain for the calculations of geometries and energies.

In principle, the total energy  $E$  per  $[\text{Si}_2\text{O}_4]$  unit cell of a single chain of W-silica may be obtained as the limit

$$E = \lim_{n \rightarrow \infty} \frac{E(\text{Si}_{2n}\text{O}_{4n+2}\text{H}_4)}{n}, \quad (1)$$

i.e., by performing calculations for increasingly long oligomers  $(\text{OH})_2(\text{Si}_2\text{O}_4)_n\text{H}_2$ . In order to reduce the finite-size effects due to the termination of the oligomers by two OH and H groups saturating the dangling bonds of  $(\text{Si}_2\text{O}_4)_n$ , one may consider instead

$$\begin{aligned} E &= \lim_{n \rightarrow \infty} \Delta E_n \\ &= \lim_{n \rightarrow \infty} [E(\text{Si}_{2n+2}\text{O}_{4n+6}\text{H}_4) - E(\text{Si}_{2n}\text{O}_{4n+2}\text{H}_4)], \end{aligned} \quad (2)$$

i.e., the energy change between the subsequent oligomers differing by a single unit cell. Therefore, identical unit cells were used as building blocks for both oligomers, i.e., the geometrical optimization was restricted only to the parameters relevant for the polymer. Eq. (2) was used for computing the energy per unit cell employing HF, Møller-Plesset second-order perturbation (MP2) and coupled cluster (CC) levels of theory.

## B. Incremental Approach

The simple approach outlined in the previous section relies on the correlated calculations for the whole finite model system, i.e., all the valence electrons have to be correlated at a time. For larger basis sets or more complex systems (as in the case of  $\alpha$ -quartz) this approach may become computationally too expensive. Therefore we used an incremental approach based on localized orbitals. One of the prerequisites for the electron correlation treatment within the incremental approach is a reliable HF ground state calculation. We performed such a calculation using the periodic HF code CRYSTAL 98 [24]. Starting from the occupied canonical orbitals of a standard SCF calculation localized bond orbitals are generated using

a suitable criterion, e.g., the Foster-Boys localization. The correlation energy per unit cell is expanded as

$$E_{corr} = \sum_i \epsilon_i + \sum_{i<j} \Delta\epsilon_{ij} + \sum_{i<j<k} \Delta\epsilon_{ijk} + \dots, \quad (3)$$

where the summation over  $i$  involves localized orbitals in the reference cell, while those over  $j$  and  $k$  include all the localized orbitals of the crystal. The "one-body" increments  $\epsilon_i = \Delta\epsilon_i$  are calculated by correlating each of the localized orbitals in turn, while others are kept frozen at the HF level. The "two-body" increments are determined by considering pair of bonds and performing correlated calculations for each chosen pair. Excitations are allowed only from the orbitals belonging to this pair, keeping the rest of the orbitals frozen. Hence the "two-body" increments  $\Delta\epsilon_{ij}$  are defined as  $\Delta\epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j)$ , where  $\epsilon_{ij}$  is the correlation energy obtained by correlating orbitals  $i$  and  $j$ . Higher-order increments are defined in an analogous way. Finally, adding all increments, with the proper weight factors determined by the occurrence in the unit cell, one obtains the exact correlation energy per unit cell of the infinite system as given in Eq. (3). In order to get reliable results a size-extensive correlation method should be used, although non-size-extensive schemes also may provide a reasonable estimate. We used MP2 and CCSD for this approach for both the systems.

### III. RESULTS AND DISCUSSIONS

Calculations on both the systems, i.e., W-silica and  $\alpha$ -quartz were performed with 6-31G\*\* basis sets [26, 27]. Usually for polar polymeric systems, calculations using the finite-cluster approach at the HF level may not be applicable due to the long-range of Coulomb interactions. Nevertheless in case of W-silica the finite-cluster approach seems to be accurate enough. For  $n = 4$ , the HF energy per  $\text{Si}_2\text{O}_4$  unit is found to be -877.6282 a.u. at the optimized geometry (cf. below). The Bloch-type function based periodic HF code CRYSTAL 98 uses five parameters (ITOL1 to ITOL5) to determine the accuracy of the integral evaluation with respect to the Coulomb and exchange series. For the default combination (6, 6, 6, 6, 12) the HF energy per  $\text{Si}_2\text{O}_4$  unit is found to be -877.6268 a.u. and for an even tighter threshold (10, 10, 10, 12, 26) a value of -877.6278 a.u. in excellent agreement with the finite-cluster value is obtained. For the HF calculations on the infinite system, using CRYSTAL, the most diffuse  $sp$  Gaussian exponents of the original basis sets had to

be increased due to linear dependency problems. This led to exponents of 0.28 for oxygen (original 0.27) and 0.21 for silicon (original 0.0778). We want to mention that the energy obtained using CRYSTAL, shows a drastic dependence on the  $d$  Gaussian exponents. For the optimized geometry and the tighter threshold the HF energy per  $\text{Si}_2\text{O}_4$  unit is found to be -877.6513 a.u. with optimized  $d$  exponents of 0.48 for oxygen and 0.72 for silicon. However for the correlated calculations and for the comparison with  $\alpha$ -quartz, we used the original basis set as a lower value of the total energy per unit cell is obtained.

The correlation energy was calculated by subtracting from the MP2, CCSD and CCSD(T) values the corresponding HF energy/cell. In this manner we ensured that no spurious contributions to the correlation energy arose due to the use of two different basis sets. The cohesive energies were obtained by subtracting the corresponding energies of the free ground state atoms from the energy per unit cell. These calculations were performed using the MOLPRO molecular orbital *ab initio* program package [28–30]. The energy per unit cell and the cohesive energy converge rapidly with respect to the cluster size (cf. Fig. 3). One finds  $\Delta E_4 - \Delta E_3 \approx 10^{-5}$  a.u. (see Eq. (2) for definition of  $\Delta E_n$ ). An all-electron CCSD(T) (CCSD with a perturbative contribution of triples) approach could not be used to compute  $\Delta E_4$  due to the large system size. The optimized geometry reported in Fig. 4(a) and (b) and in Table I was obtained by performing in turn several total energy calculations for various values of each geometric parameter and fitting the results by a least-squares procedure to polynomials of suitable degrees. The computed lattice parameter  $c$  of 4.75 Å is in good agreement with the experimental value of 4.72 Å. However, the Si-O bond length of 1.844 Å determined in Ref. 2 appears to be un-physically large. This bond length is even larger than those of three-fold coordinated O in stishovite [31] as was pointed out also in other theoretical studies [9, 15]. Generally, our MP2, CCSD and CCSD(T) structural values agree with those of a previous gradient-corrected DFT study within 0.02 Å and 1°.

In order to perform a comparison of the stability of W-silica with respect to  $\alpha$ -quartz, we performed correlated calculations for both systems on the same footing, i.e., by using the incremental approach truncated at the same level of correlation increments. The experimental geometry [32] was used for  $\alpha$ -quartz, whereas the optimized geometry at the CCSD level was used for W-silica (cf. above). The HF ground state calculations were done using the CRYSTAL code. In order to overcome the convergence problems due to too diffuse exponents and the resulting near-linear dependencies we optimized the exponents of the most

diffuse *sp* Gaussians of a 6-31G\*\* basis set also for  $\alpha$ -quartz as performed in Ref. 33. For O and Si values of 0.28 and 0.21, respectively, were obtained. The exponents of the single *d* shell of O and Si were optimized to be 0.45 and 0.72 respectively. These *d* exponents led to a lower total HF energy compared to the original basis sets. The exact equation for the infinite system, i.e., Eq. (3) is of little use in practice. However, since electron correlation is a local phenomenon one may derive  $E_{corr}$  from a finite model system. Thereby changing the infinite sums in Eq. (3) to finite sums up to a maximum order of increments given by the number of bonds *n* in the finite system. It has been shown by previous calculations that usually there is a rapid convergence of the many-body expansion with respect to the number of atoms included and the integration error decreases with  $r^{-3}$  [13, 34]. Therefore, we restricted the expansion of the correlation energy per unit cell to one- and two-body increments, and included the interaction between up to second-nearest neighbor unit cells. The resulting finite clusters as shown in Fig. 5 (a) and (b), contain 30 and 57 atoms with dangling bonds saturated by hydrogens for W-silica and  $\alpha$ -quartz, respectively. We performed standard SCF calculations on the clusters in  $C_1$  symmetry and localized the bonds according to the Foster-Boys criterion [35] within the occupied valence space. Following the procedure described above we calculated the correlation energy increments at the MP2 and CCSD level using the MOLPRO molecular orbital *ab initio* program package [28–30]. Computed increments to the correlation energy are summarized in Table II. It is interesting to note that for  $\alpha$ -quartz the two-body increments amount to 69% and 65 % of the correlation energy computed by the MP2 and CCSD methods, respectively.

The correlation contributions to the cohesive energies for  $\alpha$ -quartz were obtained as  $E_{coh}^{corr} = E_{solid}^{corr} - \sum_i E_{atom,i}^{corr}$  per  $\text{SiO}_2$  unit. The results are shown in Table III for different theoretical methods. For the best method, i.e., CCSD, we obtain 88% of the experimental cohesive energy, which amounts to  $\approx 57\%$  of the "experimental" correlation contribution to the cohesive energies (defined as the difference between the experimental cohesive energy and the SCF value). DFT using the local density approximation (LDA) overestimates the cohesive energy by 18%.

In Table IV we present the relative energy per  $\text{Si}_2\text{O}_4$  unit for two-fold rings with respect to  $\alpha$ -quartz. Our HF value seems to be much higher compared to the values in References 9, 10, 16. These calculations were done on small clusters which lack the strain effect of the environment due to successive edge sharing units. Correlation also seems to play an

important role for the stability of these edge-sharing systems. A DFT study using a GGA functional gave a much lower relative energy [15]. In our calculations, by considering MP2 correlation contributions the stability increased by 65%, whereas upon inclusion of CCSD correlation increments the stability increased by 73%. The most sophisticated correlation approach used in our study based on CCSD gave a strain energy of 0.0427 a.u., even less compared to the one of 0.0452 a.u. obtained by a previous DFT calculation [15].

#### IV. CONCLUSION

We have performed a comparative study on periodic W-silica and  $\alpha$ -quartz based on correlated *ab initio* electronic structure calculations. The former compound is considered as a model system for edge-sharing  $\text{SiO}_4$  tetrahedra silicates and the latter for corner-sharing ones. Periodic HF theory was used to obtain the mean-field results. The finite-cluster and the incremental approach were used to determine correlation effects in W-silica and  $\alpha$ -quartz. For the finite-cluster approach, the geometry as well as the energy per unit cell seem to converge rapidly. Our optimized geometry supports the claim of a previous DFT study that the experimentally available  $\text{Si} - \text{O}$  distance is abnormally large and might be incorrect. For  $\alpha$ -quartz we have obtained at the CCSD level around 88% of the experimental cohesive energy using a 6-31G\*\* basis set. The remaining error may be partly due to the lack of higher polarization functions in our one-particle basis set as well as the absence of triple excitations.

Our results and those available from literature predict the strain energy associated with the two-fold rings to depend highly on the chosen model system as well as on the method. Correlation contributions seem to play an important role for the relative stability of the edge-sharing units with respect to corner-sharing ones. HF calculations done solely on the infinite W-silica system gave a strain energy of 0.156 a.u. much higher than the relaxed finite-cluster calculations. Correlation contributions reduce this result by about a factor of three. The most sophisticated method, i.e., CCSD, gave a strain energy of 0.0427 a.u., even slightly lower than the value of 0.0452 a.u. obtained by a previous DFT calculation. We conclude that edge-sharing  $\text{SiO}_4$  tetrahedra in (partially) amorphous  $\text{SiO}_4$  systems are possible at a modest energetic expense.

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TABLE I: Geometries of two-membered rings in W-silica.

Method	$c$ (Å)	Si-O (Å)	Si-O-Si (°)	O-Si-O (°)
CRYSTAL SCF	4.680	1.643	90.86	89.13
Finite cluster SCF	4.717	1.650	91.28	88.72
MP2	4.744	1.683	89.62	90.38
CCSD	4.744	1.676	90.09	89.91
CCSD(T)	4.745	1.680	89.81	90.19
GGA <sup>a</sup>	4.757	1.678	90.3	89.7
Expt. <sup>b</sup>	4.720	1.844	79.6	100.4

<sup>a</sup>Reference [15].

<sup>b</sup>Reference [2].

TABLE II: Various increments to the correlation energy per unit cell (in Hartrees) for W-silica and  $\alpha$ -quartz. 1NN and 2NN stand for nearest and next-nearest neighbors, respectively.

Correlation treatment	W-silica		$\alpha$ -quartz	
	MP2	CCSD	MP2	CCSD
One-body	-0.261366	-0.336929	-0.327725	-0.419682
Two-body (1NN)	-0.535584	-0.565459	-0.692420	-0.738037
Two-body (2NN)	-0.016056	-0.019333	-0.037162	-0.044587

TABLE III: Cohesive energies per  $\text{SiO}_2$  unit (in a.u) in  $\alpha$ -quartz at different theoretical levels. The percentage of the experimental value is given in parentheses.

HF	HF+MP2	HF+CCSD	LDA <sup>a</sup>	Expt. <sup>b</sup>
.507 (72%)	.598 (85%)	.618 (88% )	.824 (118%)	.706

<sup>a</sup>Reference [36].

<sup>b</sup>Reference [37].

TABLE IV: Relative energy of a  $\text{Si}_2\text{O}_4$  unit for various systems with respect to  $\alpha$ -quartz (in a.u.).

Method	System	$\Delta E$
HF <sup>a</sup>	W-silica	.156
MP2 <sup>a</sup>	W-silica	.0547
CCSD <sup>a</sup>	W-silica	.0427
GGA <sup>b</sup>	W-silica	.0452
HF <sup>c</sup>	$\text{H}_4\text{Si}_2\text{O}_6$ ( $C_{2h}$ )	.0849
HF <sup>d</sup>	$\text{H}_4\text{Si}_2\text{O}_6$ ( $C_{2h}$ )	.0673
HF <sup>e</sup>	$\text{H}_4\text{Si}_2\text{O}_2$ ( $D_{2h}$ )	>.1058
HF <sup>f</sup>	$\text{H}_{14}\text{Si}_9\text{O}_{25}$	.0680

<sup>a</sup>This work.

<sup>b</sup>Reference [15].

<sup>c</sup>Reference [9].

<sup>d</sup>Reference [10].

<sup>e</sup>Reference [11] (Relative to  $\text{H}_8\text{Si}_4\text{O}_4$  ( $D_{4h}$ )).

<sup>f</sup>Reference [16].

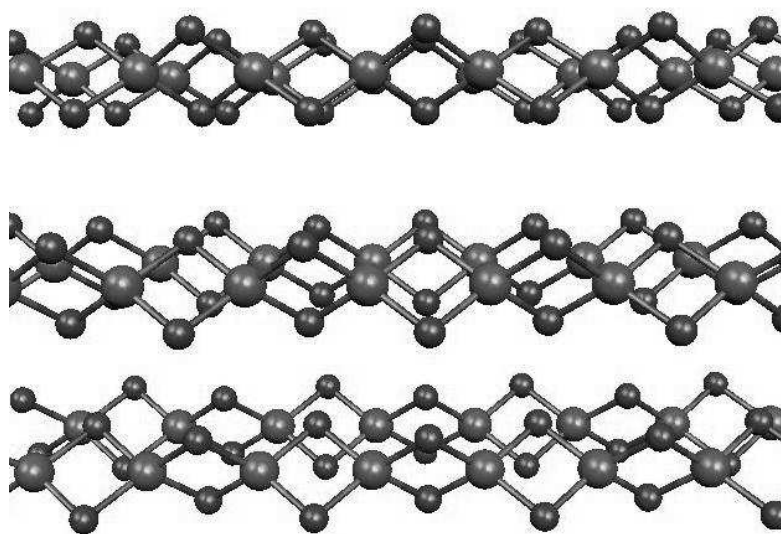


FIG. 1: Mukhopadhyay et al, Journal of Chemical Physics.

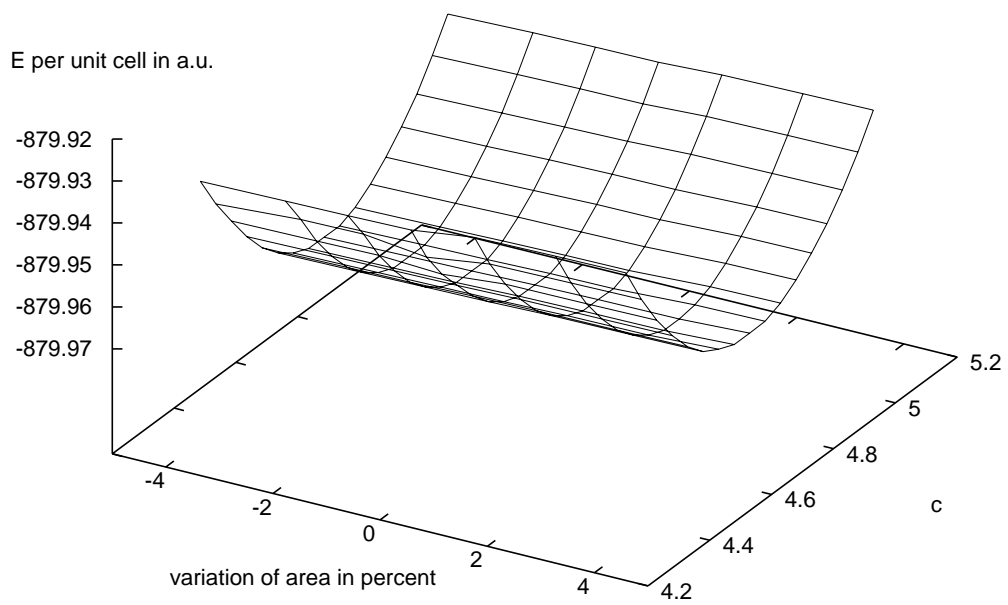


FIG. 2: Mukhopadhyay et al, Journal of Chemical Physics.

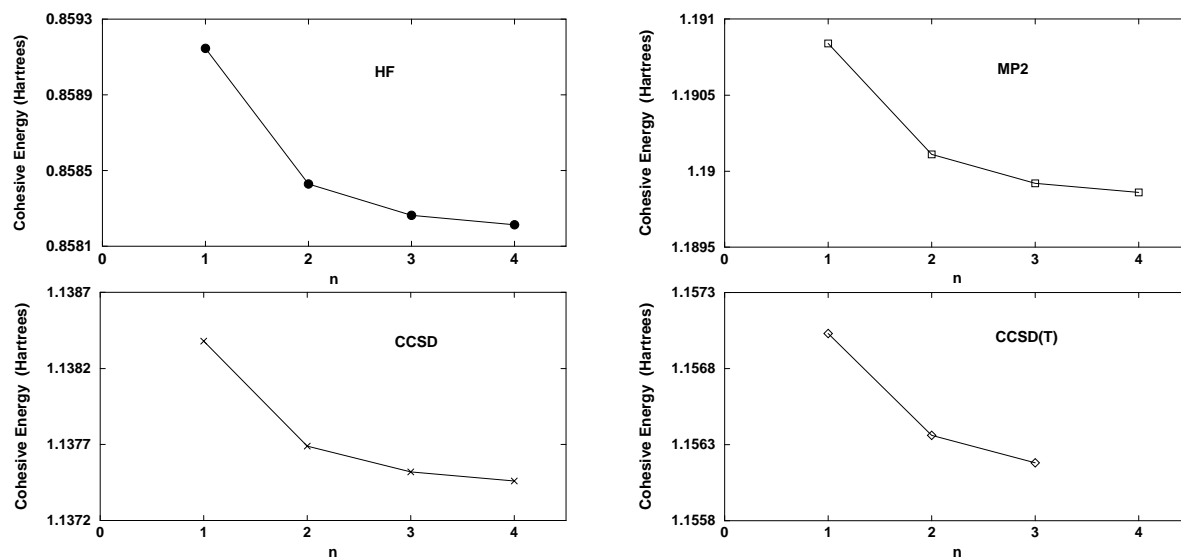


FIG. 3: Mukhopadhyay et al, Journal of Chemical Physics.

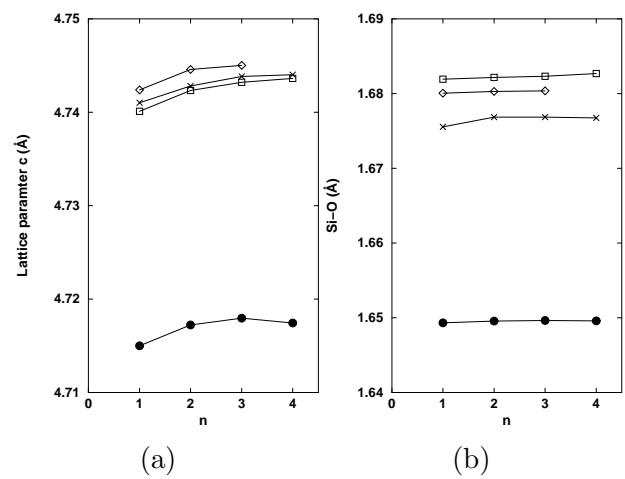
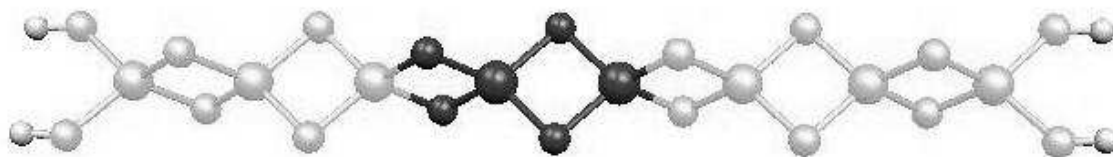
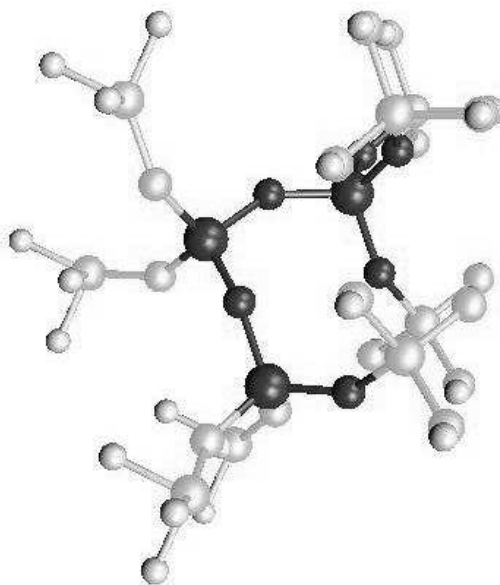


FIG. 4: Mukhopadhyay et al, Journal of Chemical Physics.



(a)



(b)

FIG. 5: Mukhopadhyay et al, Journal of Chemical Physics.

### List of figure captions

Figure 1. Model of W-silica which are characterized by weakly interacting chains of edge-sharing  $\text{SiO}_4$  tetrahedral units. Small and large spheres represent O and Si atoms, respectively.

Figure 2. Potential energy surface plotted with respect to the variations of the area of  $a$ - $b$  plane, where the ratio  $a/b$  is constant and the lattice parameter  $c$  in Å.

Figure 3. Cohesive energy per  $\text{Si}_2\text{O}_4$  unit of W-silica computed by the finite-cluster approach, plotted as a function of the number unit cells  $n$ .

Figure 4. (a) Lattice parameter  $c$  and (b) Si-O distance of W-silica computed using the finite-cluster approach, plotted as a function of the number unit cells  $n$  (filled circles, squares, crosses and diamonds represent HF, MP2, CCSD and CCSD(T) results, respectively).

Figure 5. Finite clusters of 30 and 57 atoms of (a) a chain of W-silica and (b)  $\alpha$ -quartz, respectively, which are used for the incremental approach. The reference cell is represented by dark-colored spheres and the environment by light ones. Here the small-, medium- and large-sized spheres represent H, O and Si atoms, respectively.