

# AB INITIO INVESTIGATION OF STRUCTURE AND STABILITY OF TWO-FOLD RINGS IN SILICATES

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## Motivation

W-silica has a body-centered orthorhombic crystal structure characterized by chains of edge sharing  $\text{SiO}_4$  tetrahedra interacting only by **weak van der Waals forces**. The occurrence of edge-sharing units also in silicates makes structures geometrically constrained and results in an energy penalty. The lack of experimental insight into the stability of these strained systems makes theoretical methods important tools. The knowledge of the **energy penalty** presently rests on theoretical studies of mainly small clusters which neglect the effect of the condensed environment. We choose **W-silica** and  **$\alpha$ -quartz** as model systems for a calculation of geometries and strain energy using wavefunction based quantum chemical *ab initio* techniques.

## Methods

• **Finite-Cluster Approach:** The total energy per  $[\text{Si}_2\text{O}_4]$  unit cell of a single chain of W-silica can be considered as the energy change between the subsequent oligomers (the dangling bonds saturated by two OH and H groups) differing by a single unit cell:

$$E = \lim_{n \rightarrow \infty} \Delta E_n$$

$$= \lim_{n \rightarrow \infty} [E(\text{Si}_{2n+2}\text{O}_{4n+6}\text{H}_4) - E(\text{Si}_{2n}\text{O}_{4n+2}\text{H}_4)]. \quad (1)$$

Identical unit cells were used as building blocks for both oligomers and the geometrical optimization was restricted to the parameters relevant for the polymers. Eq. (1) was used for computing the energy per unit cell employing the HF, MP2, CC levels of theory.

• **Incremental Approach:** HF ground state calculations were performed using the periodic code CRYSTAL 98. Starting from the occupied canonical orbitals of a SCF calculation **localized orbitals** are generated using the **Foster-Boys criterion**. The correlation per unit cell is expanded as

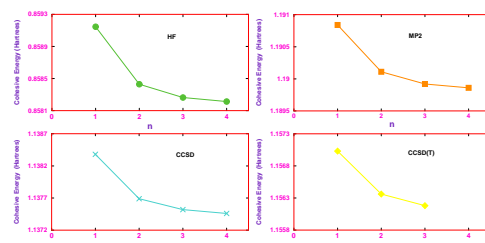
$$E_{\text{corr}} = \sum_i \epsilon_i + \sum_{i < j} \Delta \epsilon_{ij} + \sum_{i < j < k} \Delta \epsilon_{ijk} + \dots, \quad (2)$$

where  $i$  runs over localized orbitals in the reference cell and  $j$  and  $k$  involves all localized orbitals of the crystal.  $\epsilon_i$  are calculated by correlating each of the localized orbitals in turn, while others are kept frozen at the HF level. The  $\Delta \epsilon_{ij}$  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  $j$  keeping the rest of the orbitals frozen. We used MP2 and CCSD for this approach for both systems.

## Results

• Calculations on both systems were performed with **631G\*\*** basis sets.

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

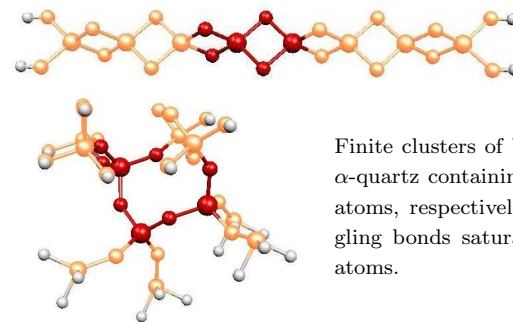


• Geometries of the two-membered rings.

Method	c (Å)	Si-O (Å)	Si-O-Si (°)	O-Si-O (°)
SCF <sup>1</sup>	4.717	1.650	91.28	88.72
MP2 <sup>1</sup>	4.744	1.683	89.62	90.38
CCSD <sup>1</sup>	4.744	1.676	90.09	89.91
CCSD(T) <sup>1</sup>	4.745	1.680	89.81	90.19
GGA <sup>2</sup>	4.757	1.678	90.3	89.7
Expt. <sup>3</sup>	4.720	1.844	79.6	100.4

• In order to **compare 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 was used for  $\alpha$ -quartz, whereas the optimized geometry at the CCSD level was used for W-silica. Since **electron correlation** is a **local phenomenon** one may derive  $E_{\text{corr}}$  from a **finite model** system. 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  $r^{-3}$ . 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.



Finite clusters of W-silica and  $\alpha$ -quartz containing 30 and 57 atoms, respectively, with dangling bonds saturated with H atoms.

• Increments to the correlation energy\*\*\*:

Correlation treatment	W-silica		$\alpha$ -quartz	
	MP2	CCSD	MP2	CCSD
1-body	-.261366	-.336929	-.327725	-.419682
2-body (1NN)	-.535584	-.565459	-.692420	-.738037
2-body (2NN)	-.016056	-.019333	-.037162	-.044587

• The two-body increments amount to 69% and 65 % of the correlation energy computed by the MP2 and CCSD methods, respectively.

• **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>1</sup>	W-silica	.156
MP2 <sup>1</sup>	W-silica	.0547
CCSD <sup>1</sup>	W-silica	.0427
GGA <sup>2</sup>	W-silica	.0452
HF <sup>4</sup>	$\text{H}_4\text{Si}_2\text{O}_6$ ( $C_{2h}$ )	.0849
HF <sup>5</sup>	$\text{H}_4\text{Si}_2\text{O}_6$ ( $C_{2h}$ )	.0673
HF <sup>6</sup>	$\text{H}_4\text{Si}_2\text{O}_2$ ( $D_{2h}$ )	>.1058
	(Relative to $\text{H}_8\text{Si}_4\text{O}_4$ )	
HF <sup>7</sup>	$\text{H}_{14}\text{Si}_9\text{O}_{25}$	.0680

## Conclusions

• Our HF value seems to be much higher compared to the other HF results. 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**. 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.

• **Edge-sharing  $\text{SiO}_4$  tetrahedra in (partially) amorphous silicates systems are possible at a modest energetic expense.**

## References

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- \*\*\* Using the MOLPRO program package.