Quantum chemical study of tobermorite surface

Marta M. Knitter, Valera Veryazov

Theoretical Chemistry, Lund University
Chemical Center, P.O.B. 124, Lund 22100, Sweden

Cement is a poorly crystalline structure, which is mainly built by C-S-H (CaO-SiO_2-H_2O) and a model of its formation includes a study of nucleation and growth of C-S-H nanoparticles. The first step in this investigation is to study the structure of cement-like materials, e.g. tobermorite 11Å. We used different kinds of tobermorite clusters: one represents a bulk ($Ca_4Si_{16}O_{46}(OH)_4(H_2O)_5$) and another represents a surface ($Ca_3Si_{11}O_{37}(OH)_3(H_2O)$) (Fig 1). Various types of embedding schemes were used: electrostatic potential, pseudoatoms, saturation by hydrogens. All calculations were made using Density Functional Theory (DFT/B3LYP).

Method

The calculations have been performed with Molcas *(www.teokem.lu.se/molcas)* using HF/DFT with Cholesky decomposition of integrals. ANO-RCC-VDZ, ECP.CaO and ECP.Quartz basis sets were used during the study. The electrostatic embedding (up to 11000 point charges), which provides electroneutrality of the system, has been used.

marta.knitter@teokem.lu.se

ZYX

Q: How to build a cluster from periodic crystal?

A: The selection of clusters and surrounding point charges was performed by a new tool – ZYX script. The script uses a new ZYX format, which describes an arbitrary cluster by a sequence of commands defining the shape and the size of a crystal region.

Water

Q: Where are water molecules inside the cluster?

A: The position of water molecule is determinated by a possibility to create extra hydrogen bonds inside the structure. The position of water molecule inside the tobermorite structure was obtained by the set of single point calculations (Fig 2).

Q: What is the difference between isolated water and water in tobermorite structure?

A: The difference in the electronic structure between isolated water and water in the tobermorite can be seen on Fig 3. It shows that the electron density moves to the H_2O oxygen due to the ionic interaction with Ca. Therefore water in the tobermorite structure becomes more ionic. Moreover the influence of hydrogen bonds can be seen for oxygens which belong to SiO_4.

Embedding

Q: Which kind of embedding scheme to choose?

A: The embedding scheme which has been created by pseudoatoms with electrostatic field gives the smallest border effect in the cluster. In this kind of embedding the transition subsystem (pseudoatoms) creates termination region for covalent Si-O bonds. The comparison of Mulliken charges in various embedding schemes is given in Fig 4.

Fig 1. The surface of tobermorite structure.

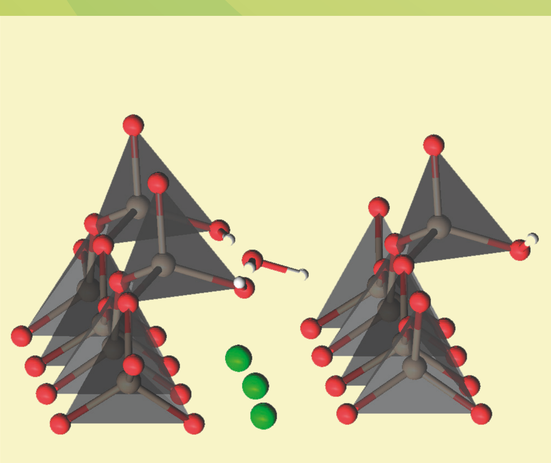


Fig 2. The potential curve of H_2O-Ca distance of surface structure.

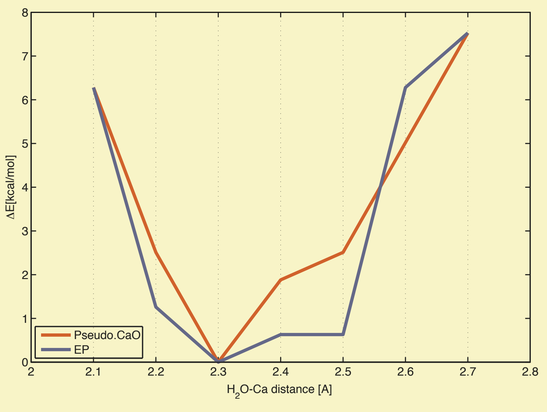


Fig 3. Density isosurface change of tobermorite bulk structure.

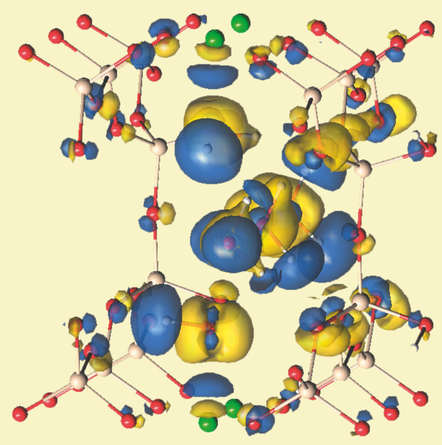
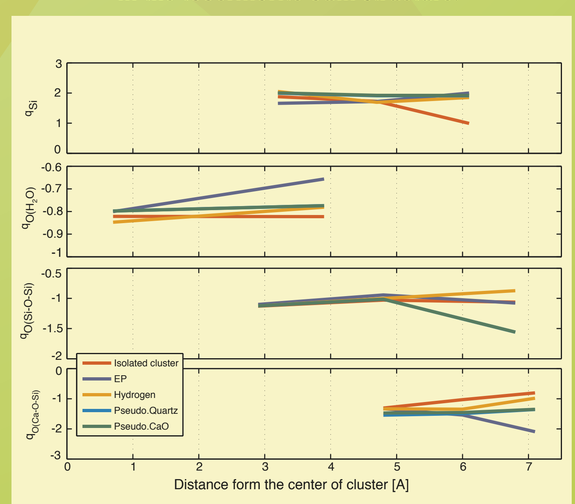


Fig 4. Change of Mulliken charges in the tobermorite bulk structure.



Conclusions

- Surrounding of the cluster by pseudoatoms with electrostatic field provides the best embedding.
- The interaction of water molecule with skeleton of tobermorite structure is relatively weak.
- The electron density of H_2O oxygen increases in tobermorite in comparison to isolated water molecule.

Acknowledgement

The work is founded by BASF – The Chemical Company. Thanks for scientific advice are addressed to Luis Seijo, André Nonat, Christophe Labbez and Luc Nicoleau. Thanks for computer support to Lunarc Team.