Multiconfigurational study of dissociation of water molecule on the surfaces of ionic oxides

Valera Veryazov, Takashi Tsuchiya, and Victor P. Vysotskiy

Theoretical Chemistry, Chemical Center, P.O.B. 124, Lund 22100, Sweden,
E-mail: valera.veryazov@teokem.lu.se

Game-changing development

The electron correlation is important for describing chemistry. The correlation effects can be treated in an approximate way using the density functional theory (DFT). The results obtained by DFT depend on the choice of the functional, and often fail for the description of the systems with localized electron density: charge transfer, bond creation, etc. Multiconfigurational methods, in particular, complete active space CASSCF/RASSCF followed by second order perturbation theory correction CASPT2/RASPT2, are known to be very accurate and reliable *ab initio* technique. The selection of the active space, where all possible excitations are treated explicitly, requires a manual set up for each calculation. Also, the computational costs can become prohibitively large especially when applied to large systems.

MOLCAS computational package (http://www.molcas.org)

Recent improvements include:

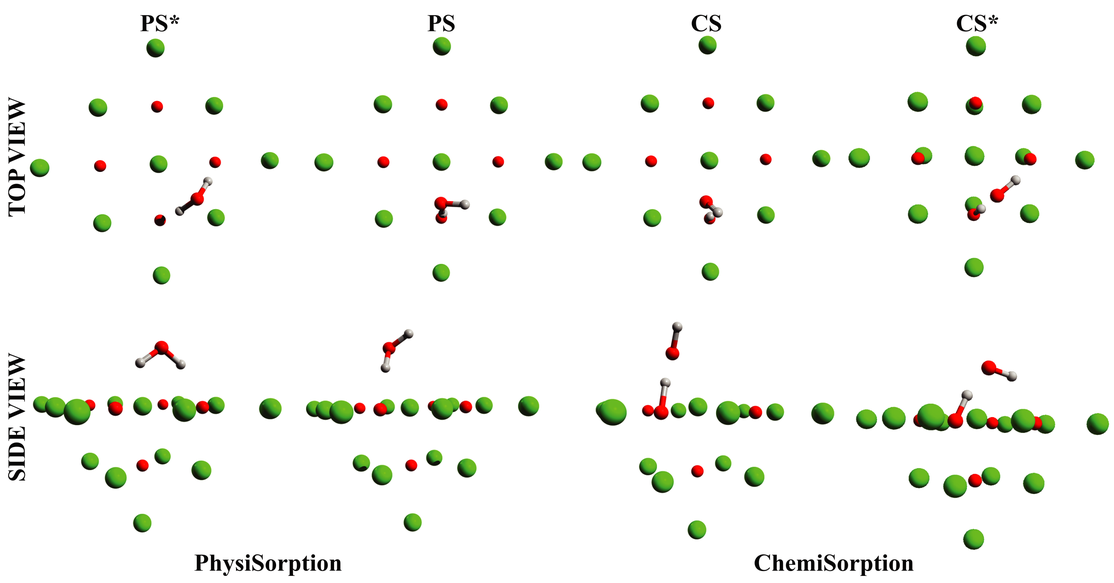
1. Development of multiconfigurational methods, including RASPT2
2. A semiautomatic procedure for the selection of the active space
3. Resolution of Identity and Cholesky Decomposition for two-electron integrals
4. New embedding techniques
5. Fragment based optimization code
6. Adjustment to modern hardware (parallelization, efficient memory use)

CaO and MgO surface

To model the CaO or MgO surface we constructed several clusters, the smallest one: $Me_{14}O_6$ has been used for all calculations, including DFT, CASSCF/CASPT2, CCSD and CCSD(T). The remaining crystal has been modelled by 3354 atomic charges. Ca/Mg atoms on the border of the cluster have AIMP (Ab Initio model potential) basis set. For other atoms SVP basis set has been used.

Physi- and Chemi-sorption of water

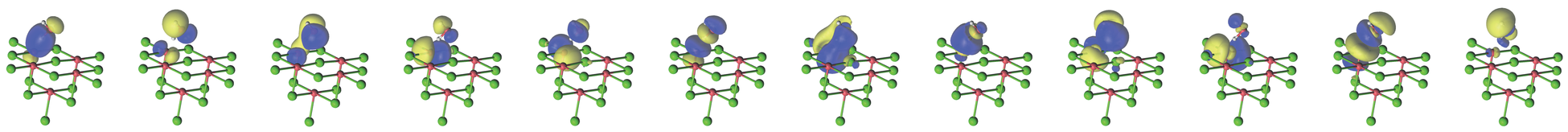
Physical sorption (no structural changes neither at surface or at adsorbed molecule) of water leads to two geometries: symmetric with two hydrogen bonds (PS*), or asymetric with one hydrogen bond (PS).



Method	PS		PS*
	Physi/Chemi-sorption E,eV		
B3LYP//B3LYP	-0.907	-1.097	-1.018
CCSD//B3LYP	-0.936	-1.066	-1.034
CCSD(T)//B3LYP	-0.971	-1.109	-1.082
CASPT2//B3LYP	-0.963	-1.319	

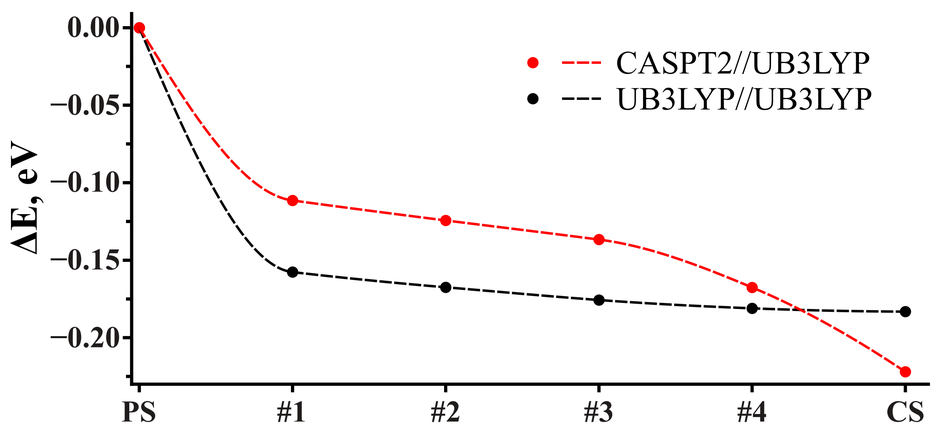
For intermediate structures, obtianed with DFT/B3LYP, we performed CCSD(T) and CASSCF/CASPT2 single point energy calculations. In case of multiconfigurational calculations the selection of the active space for dissociation process is a challenging task since the same set of active orbitals should be used for all intermediate structures.

Active space (12,12) for PS⇨CS

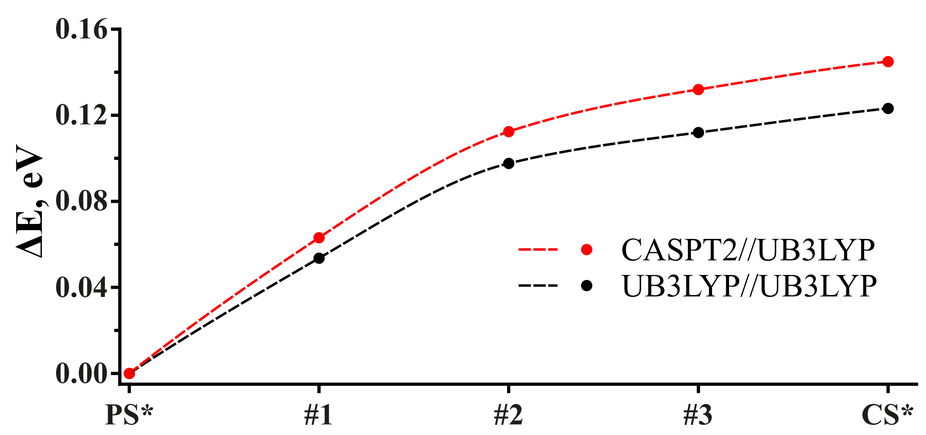


Dissociation of water molecule on MgO and CaO surfaces

For MgO surface we did not find any barrier-free dissociation of single water molecule. In contrary, for CaO surface the dissociation depends on the reaction path. The asymetric PS structure posses a barrier-free dissociation pathway while the activation barrier for the symmetric dissociation pathway is about 0.12 eV. The surface relaxation play an important role. In the particular case of the symmetric structure PS, the barrier-free dissociation never occurs if all atoms on the surface are fixed.



Asymmetric (C_s) reaction path for dissociation of absorbed H_2O on CaO



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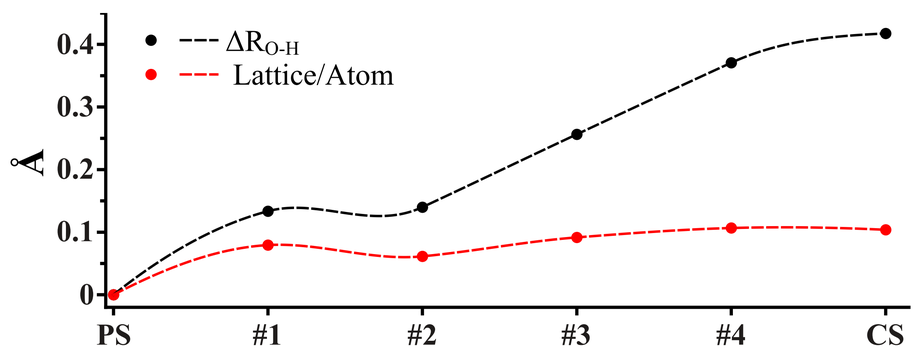
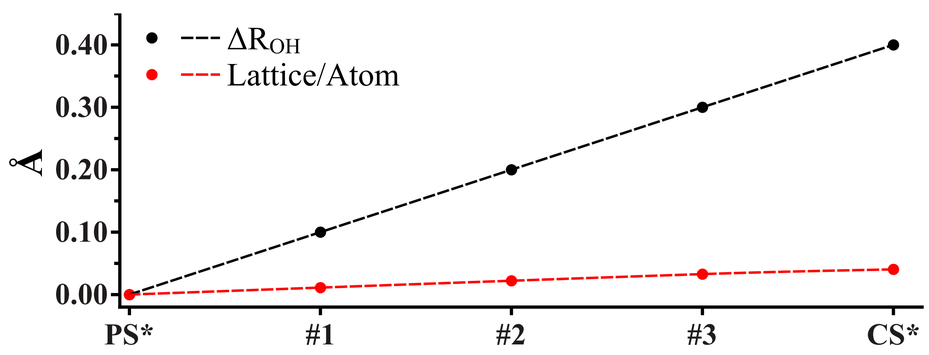


Geometry changes occuring along the asymmetric pathway



Geometry changes occuring along the symmetric pathway