

Physisorption of helium on a TiO₂(110) surface: periodic and finite clusters approaches

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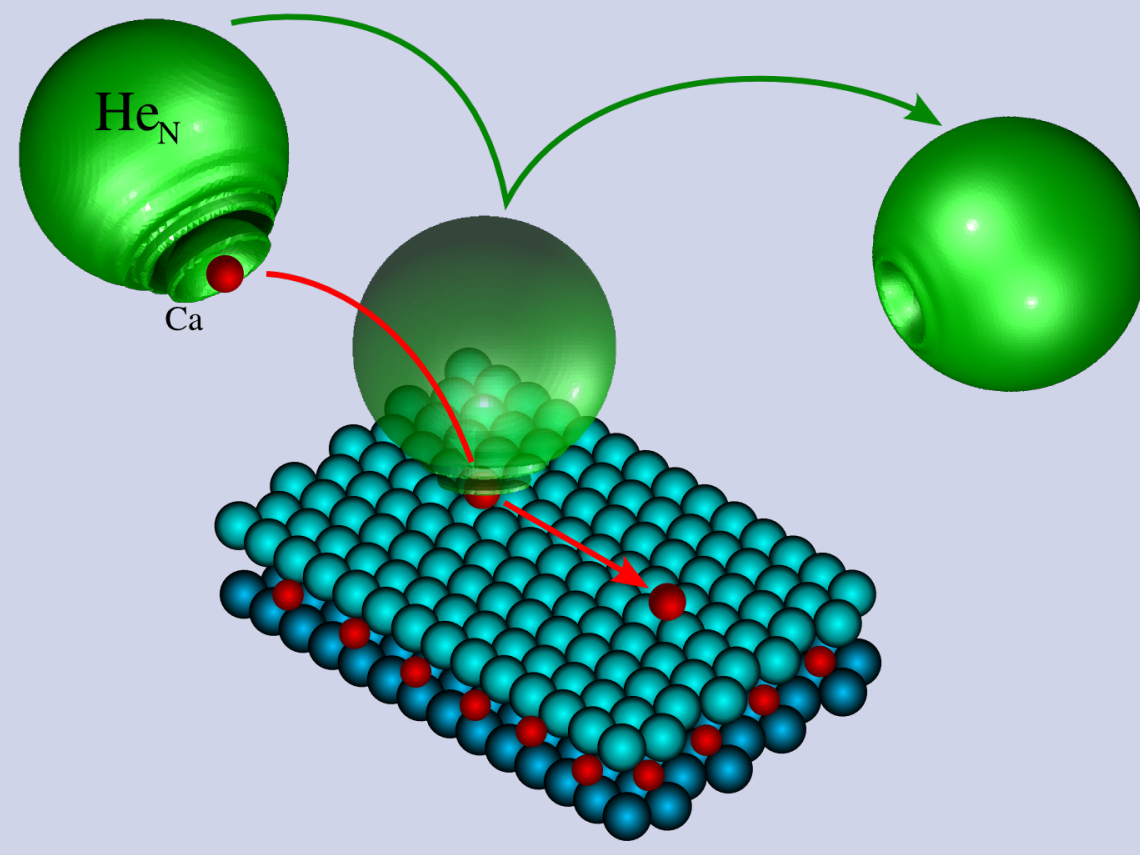
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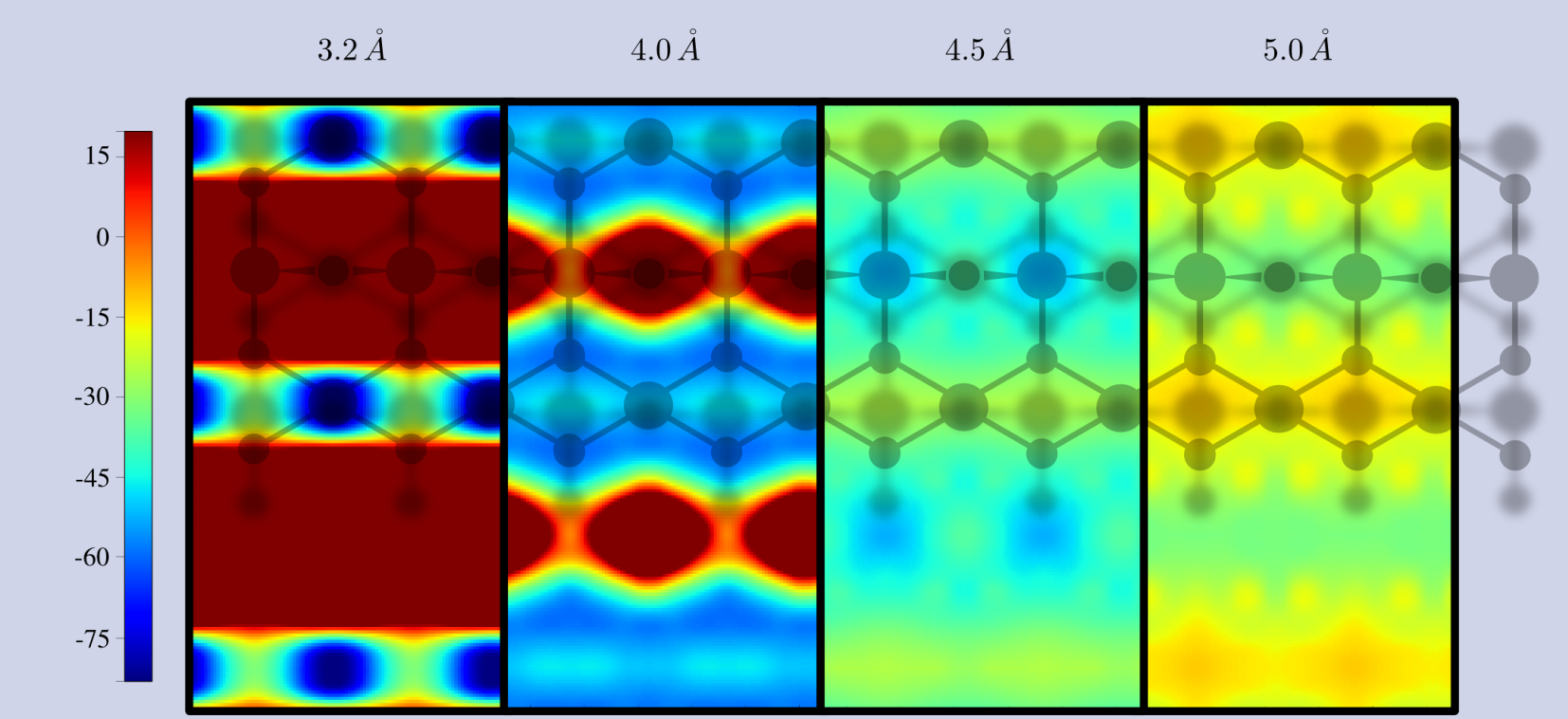


Introduction

As a proto-typical case of physisorption on an extended transition-metal oxide surface, the interaction of a helium atom with a TiO₂(110) surface is studied here by using finite cluster and periodic approaches and both wavefunction-based (post-Hartree-Fock) quantum chemistry methods, as well as density functional theory [1]. The finite cluster approach is applied to provide reference results at coupled-cluster and perturbative second-order Møller-Plesset levels of theory. It is shown that once the basis set is specifically tailored to minimize the basis set superposition error, periodic calculations using the Perdew-Burke-Ernzerhof functional yield short and medium-range interaction potentials in very reasonable agreement with those obtained using the correlated wave-function-based methods, while small long-range dispersion corrections are necessary to reproduce the correct asymptotic behavior. This study is aimed at the simulation of helium droplet-mediated deposition of metallic clusters on oxide surfaces.



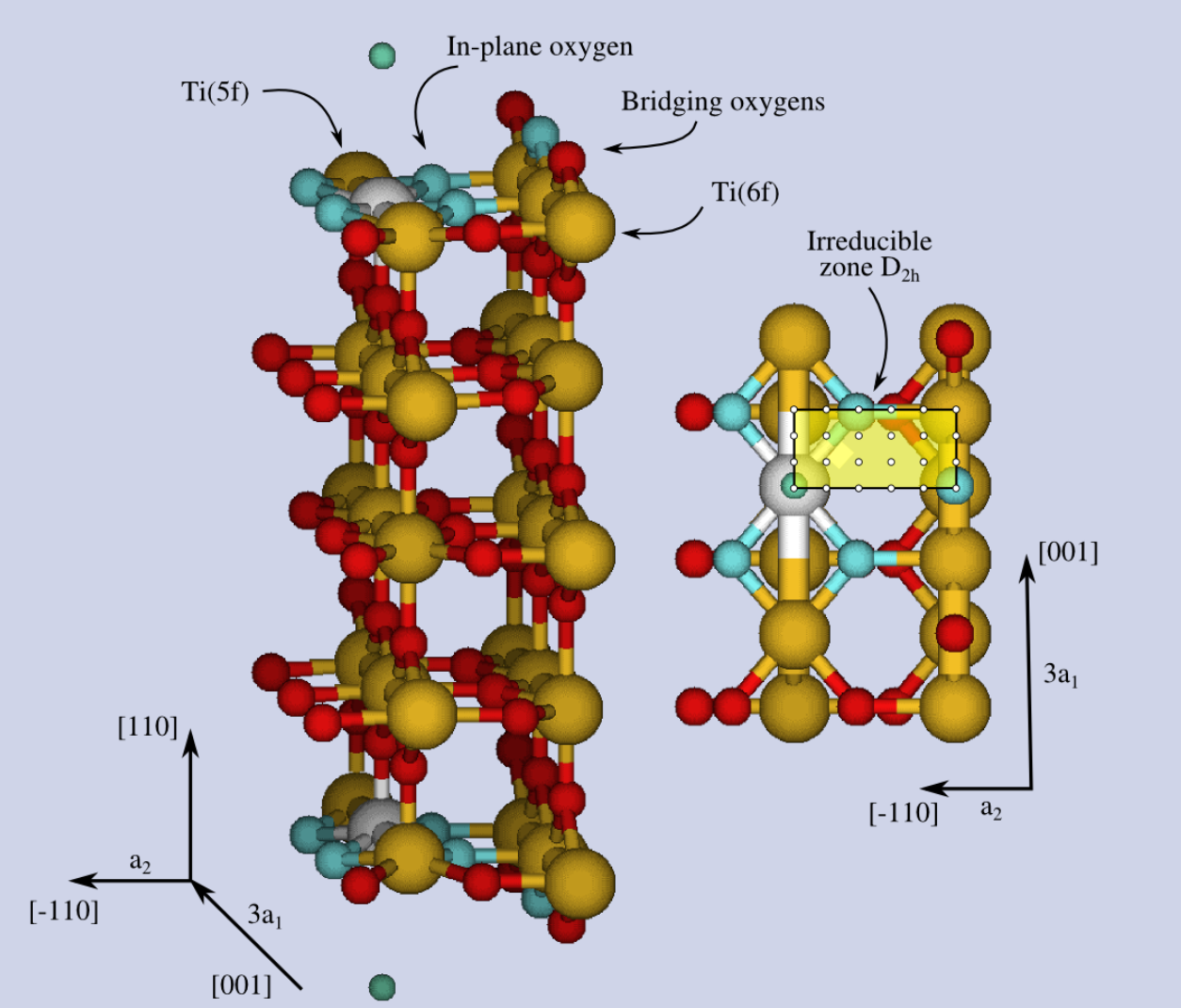
Potential energy surface (PES)



From the figures, it can be observed that the global minimum is located at the configuration atop the Ti(5f) sites, with an equilibrium distance of 3.2 Å and a physisorption energy of 83.6 cm⁻¹. The estimated energy for the lowest bound state is about 8 meV which can be compared with the value of ~10 meV attained for a helium atom adsorbed on a MgO(001) surface from high-resolution helium-scattering experimental measurements [3].

The least stable site is atop the bridging oxygen atoms. Thus, the interaction energy (~41 cm⁻¹) decreases by about a half value at the global minimum and the equilibrium distance elongates by ~1.5 Å (i.e. by about the distance between the bridging oxygen and the Ti(5f) atom). The locations of the saddle points on the PES are in configurations close to the two hollow sites (atop the Ti' and O' centers).

Calibration and test of the periodic calculations



The CRYSTAL09 code was used for the periodic calculations. To simulate the surface, a two-dimensional periodic slab model with a thickness of five molecular layers was used. To minimize the lateral interaction of the He atom with its periodic images, a supercell approach must be used. The final supercell was chosen to be of the 3x1 type. One helium atom is then added to both sides of the supercell to model the physisorption process. The physisorption energies are calculated as,

$$E_{\text{phys}} = (E[n\text{He}@\text{TiO}_2] - E[\text{TiO}_2] - nE[\text{He}]) / n$$

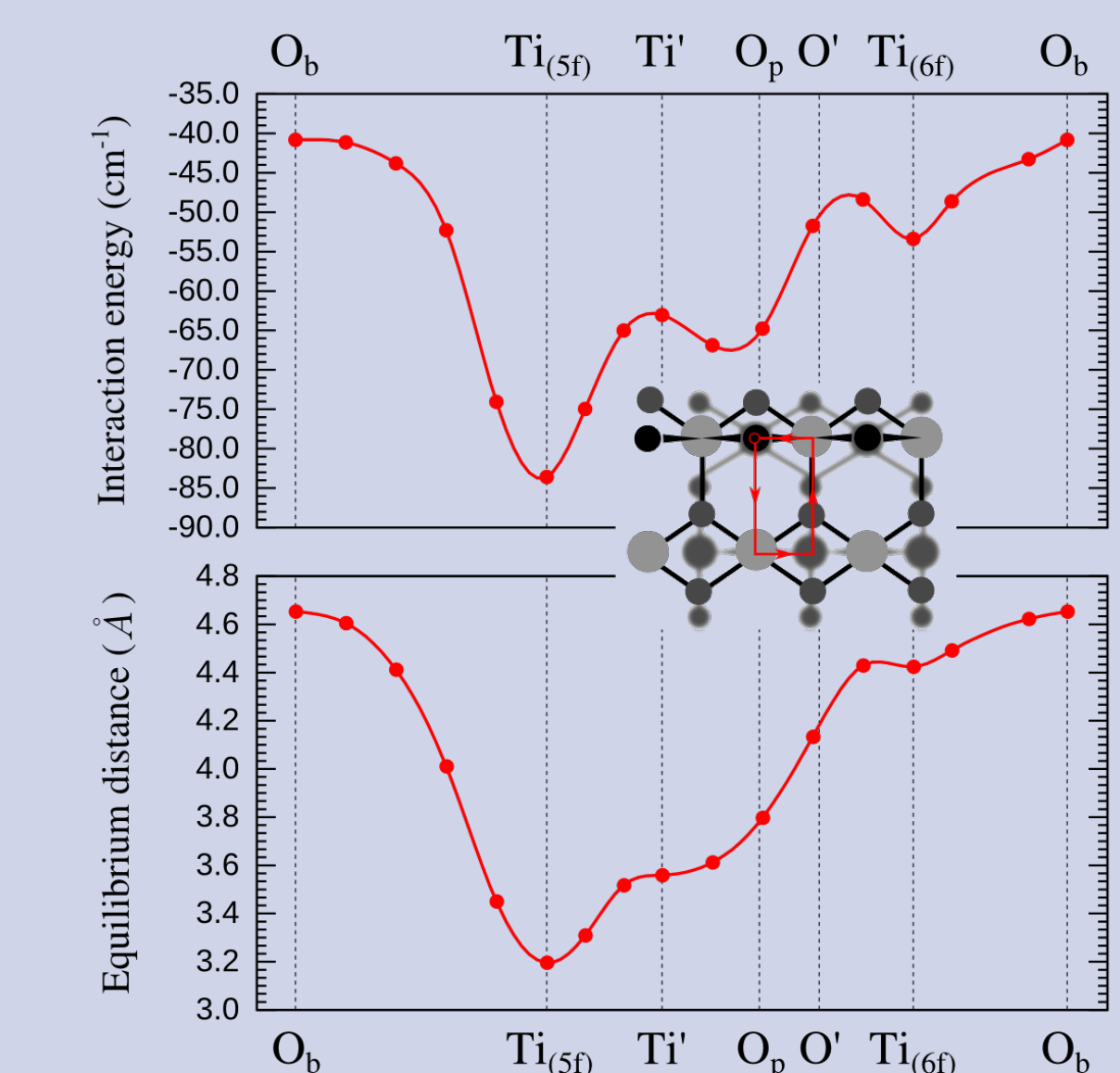
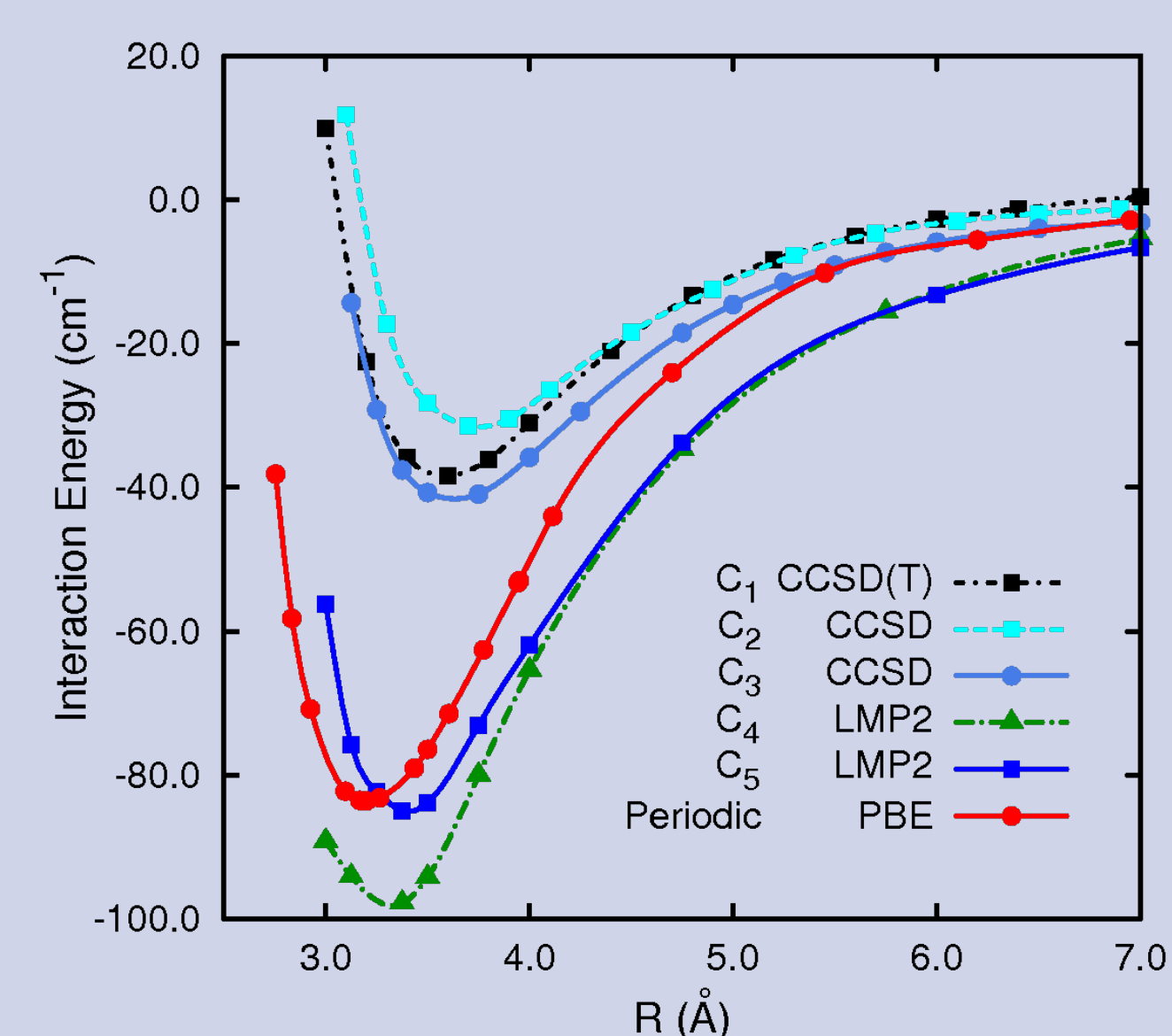
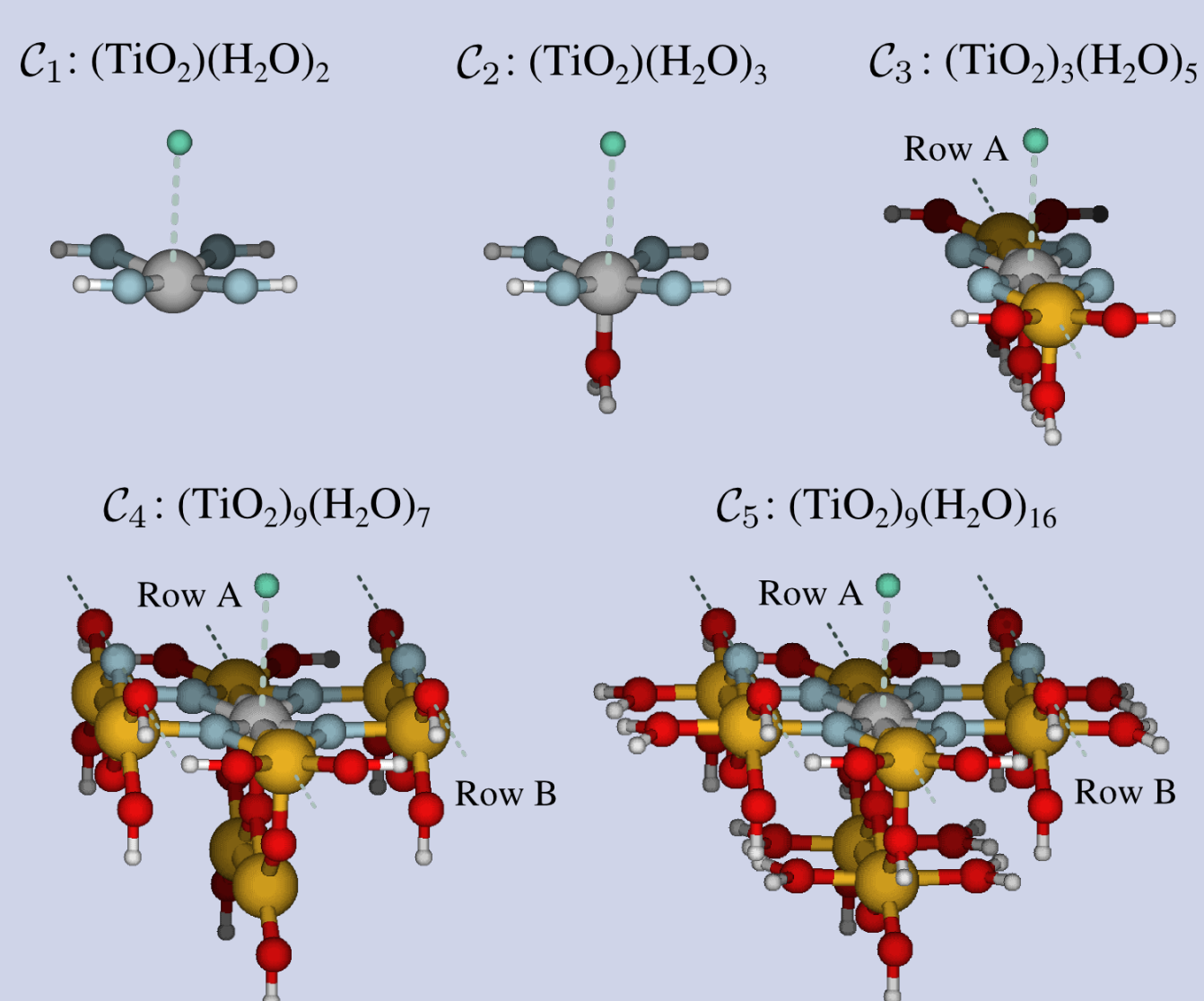
The structural parameters of the TiO₂(110) surface were fixed to their experimental values [2].

The PBE exchange correlation functional was chosen. Preliminary calculations proved that this functional performs better than other gradient-corrected functionals such as BLYP, PW91 over bound the He@TiO₂(110) interaction while BLYP functional did not predict a dwell, as it also occurred when the HF exchange was included.

The basis set calibration was carried out through the gradual addition and optimization of diffuse sp, d and f functions (basis ext-TVAE**) on oxygen and titanium atoms from the standard Muscat basis set TVAe**, so, the BSSE decreases from ~400 cm⁻¹ to ~5 cm⁻¹ (about 6% of the physisorption energy) which can be considered as acceptable. The He atoms are described with the aug-cc-pVTZ basis set.

In order to estimate the correlation effects and compare DFT with post-HF results, the most stable He@TiO₂(110) system was modeled with hydrogen-saturated clusters of stoichiometry (TiO₂)_n(H₂O)_m in which the number of hydrogen atoms are chosen so that the whole cluster is electrically neutral. The clusters were built by keeping the distance R(O-H) fixed to 1.0 Å and the atoms are added along the direction of the Ti-O bonds in the extended system. The basis set follows the same criteria applied for the periodic system and the H atoms are described with the aug-cc-pVTZ basis. The MOLPRO 2009.1 code was used for the cluster calculations.

BSSE-corrected CCSD(T), CCSD and LMP2 potential energy curves for five model clusters C are presented in the figure where the periodic DFT-PBE results are also shown. The clusters C₁, C₂ and C₃ provided an overly simplified picture of the He-substrate interaction with an apparently converged potential energy well of ~40 cm⁻¹. On other hand, the DFT-PBE and LMP2 potentials, calculated with clusters C₄ and C₅ are quite close. The agreement can be considered satisfactory, except for the long-range interaction which vanishes more rapidly when the DFT-PBE approach is used.



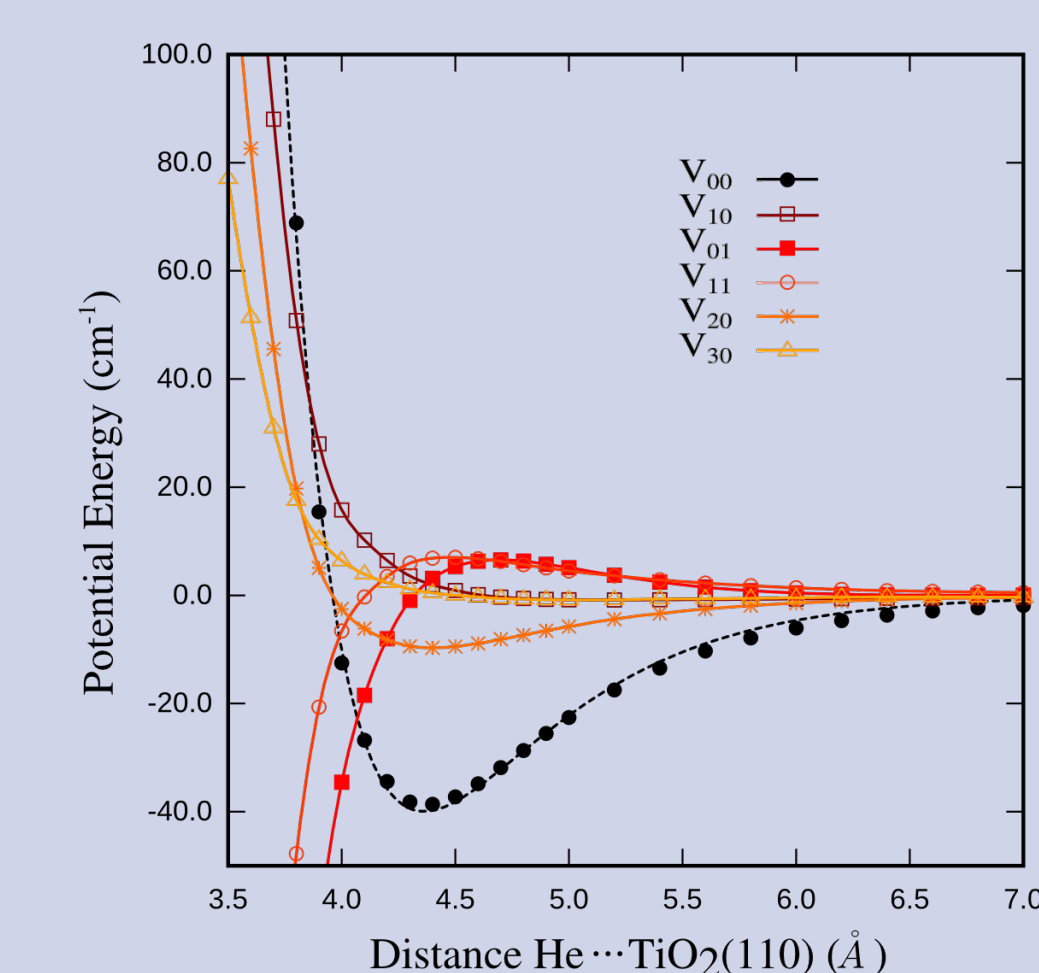
Towards the soft landing

As a preliminary step for the description of helium mediated deposition of metallic clusters on oxide surfaces, we studied the collision of a nanodroplet composed by 300 ⁴He atoms with the TiO₂(110) surface. The static and dynamical simulations were carried out in the framework of the Finite Range Density Functional (FDRF) theory, which is described in [4,5]. We used an "averaged potential" which corresponds to the first term of the Fourier expansion calculated as follows,

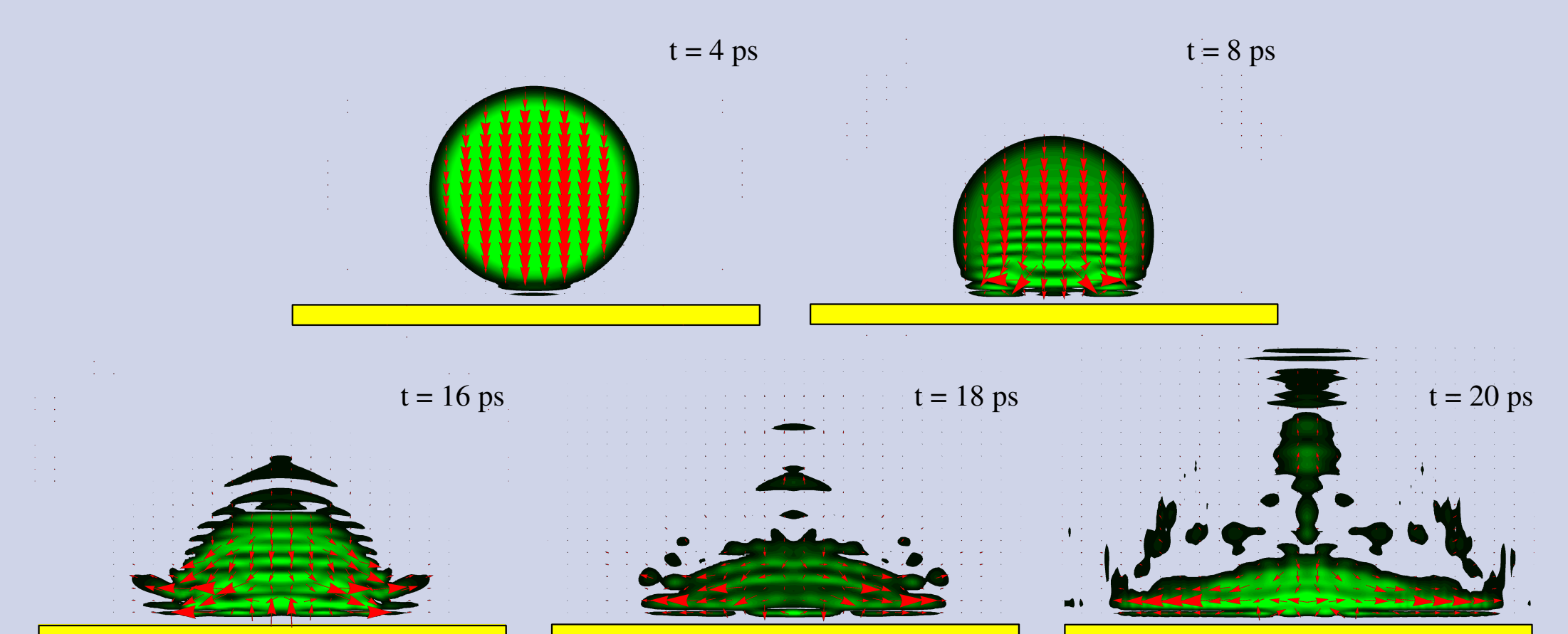
$$V(\mathbf{R}, z) = \sum_{\mathbf{g}=0} V_{\mathbf{g}}(z) \cos(\mathbf{g} \cdot \mathbf{R})$$

$$V_{\mathbf{g}}(z) = \frac{1}{S} \iint_{\mathcal{A}} V(x, y, z) \cos\left(\frac{2\pi g_1}{a_1} x + \frac{2\pi g_2}{a_2} y\right) dx dy$$

all the components are shown in the figure.



The initial state is represented by a spherical nanodroplet located close to the surface (15 Å from its center of mass). The one-particle density of this nanodroplet was calculated without accounting for the attractive He-surface potential. We selected an initial velocity of 200 m/s according to recent experimental measurements [6]. As shown in the figure the main process occurs in a time of 20 ps: the spreading of the ⁴He nanodroplet on the TiO₂(110) surface with a low fraction reflected. We are currently analyzing how the corrugation of the surface influences the results.



Conclusions

The very weak physisorption interaction of He atom on the TiO₂(110) surface has been analyzed by means of periodic DFT-PBE calculations. Correlated post-HF methods has been applied on model clusters to assess the accuracy of the DFT-PBE approximations. A good agreement between both approaches has been found. Moreover, a dual basis set has been developed in order to minimize the BSSE by two orders of magnitude. We also built a three-dimensional PES which was successfully applied to simulate the collision of a helium nanodroplet, as a first step towards the description of soft-landing processes.

Acknowledgments

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