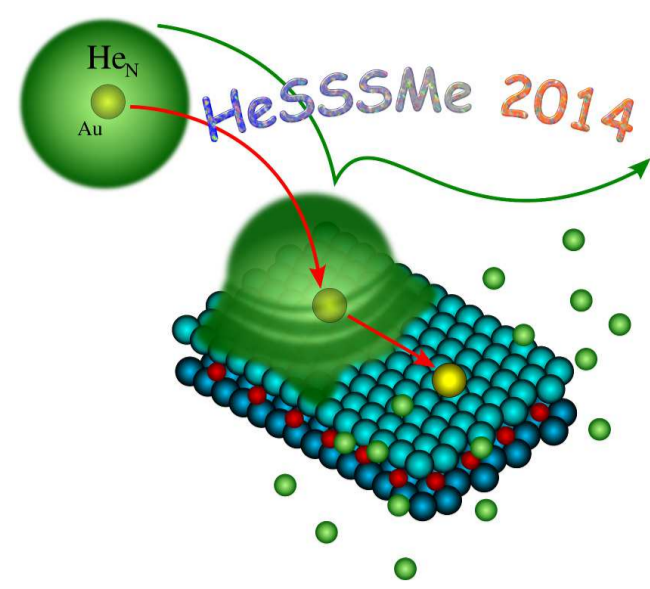


ASSESSING THE PERFORMANCE OF DISPERSIONLESS AND DISPERSION-ACCOUNTING METHODS: HE/TiO₂(110)



María Pilar de Lara-Castells,⁽¹⁾ Hermann Stoll,⁽²⁾ and Alexander O. Mitrushchenkov⁽³⁾

⁽¹⁾Instituto de Física Fundamental, C.S.I.C., Serrano 123, E-28006 Madrid, Spain

⁽²⁾Institut für Theoretische Chemie, Universität Stuttgart, D-70550 Stuttgart, Germany

⁽³⁾Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, France

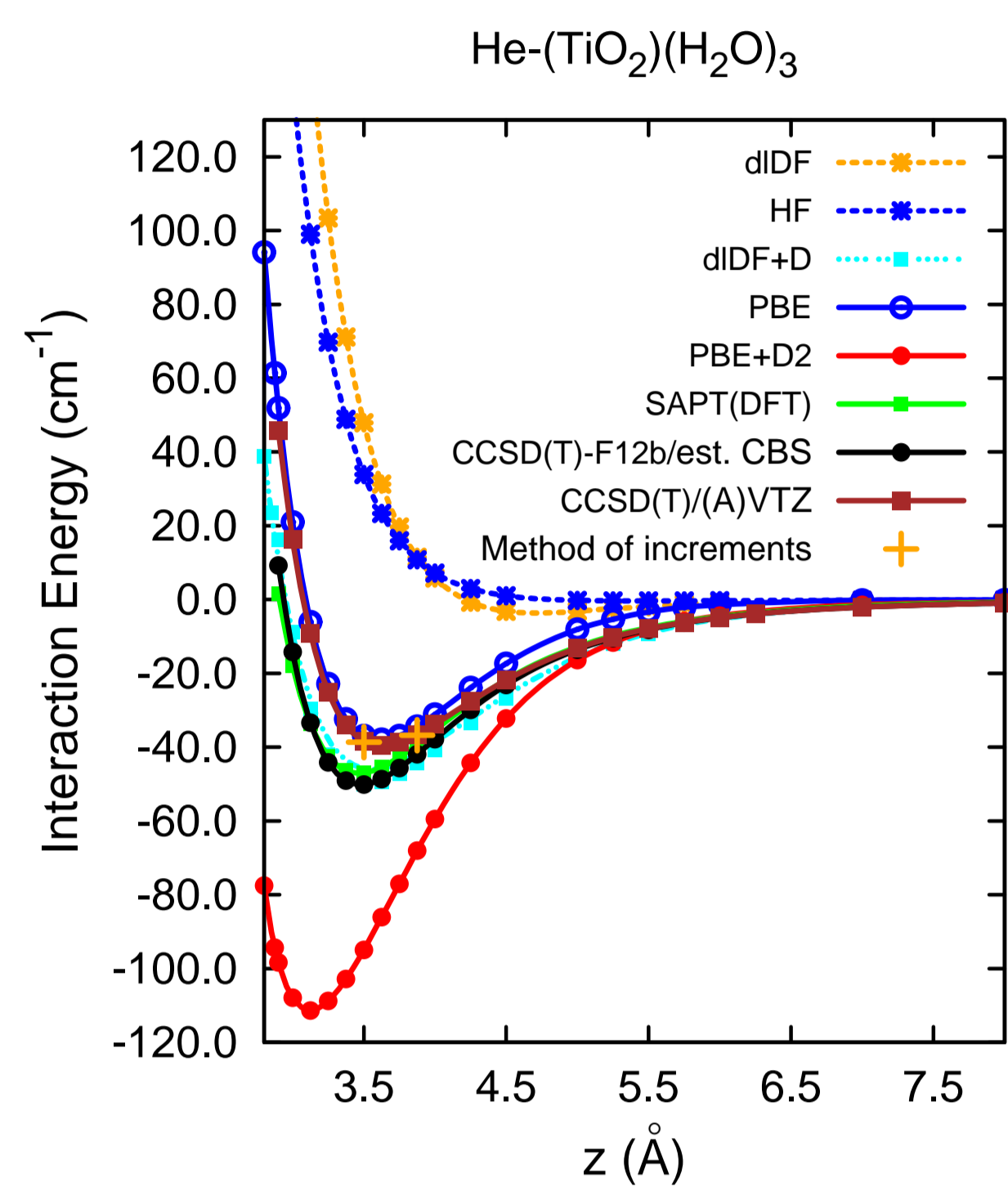
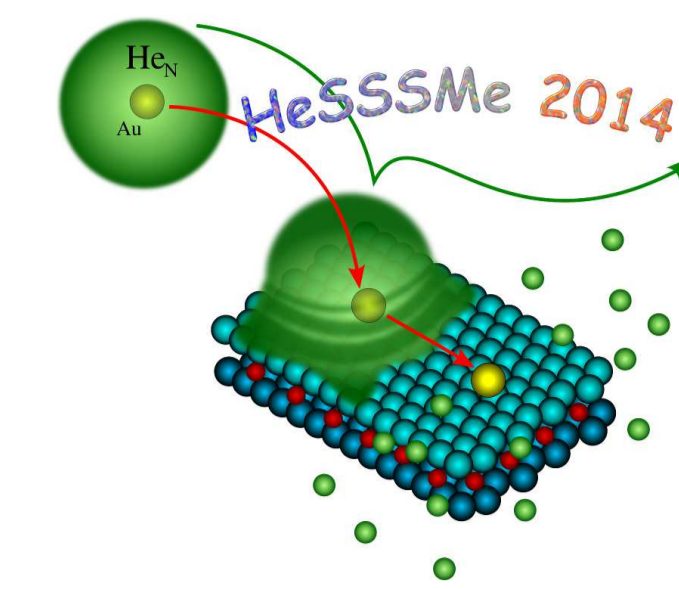


FIGURE 1: He-C₁ interaction energies as a function of the He-Ti(5f) distance (z) using different methodologies. The dIDF functional has been used for both the total SAPT(DFT) interaction energies and the dispersion energy component within the dIDF+ D construction.

Overview

As a prototypical dispersion-dominated physisorption problem, we analyze here the performance of dispersionless and dispersion-accounting methodologies on the helium interaction with cluster models of the TiO₂(110) surface [1]. A special focus has been given to the dispersionless density functional dIDF and the dIDF+ D_{as} construction for the total interaction energy [2], where D_{as} is an effective inter-atomic pairwise functional form for the dispersion. Intra- and inter-monomer correlation contributions to the physisorption interaction are analyzed through the method of increments [3] at CCSD(T) level of theory. This method is further applied in conjunction with a partitioning of the Hartree-Fock interaction energy to estimate individual interaction energy components, comparing them with those obtained using the different SAPT(DFT) approaches.

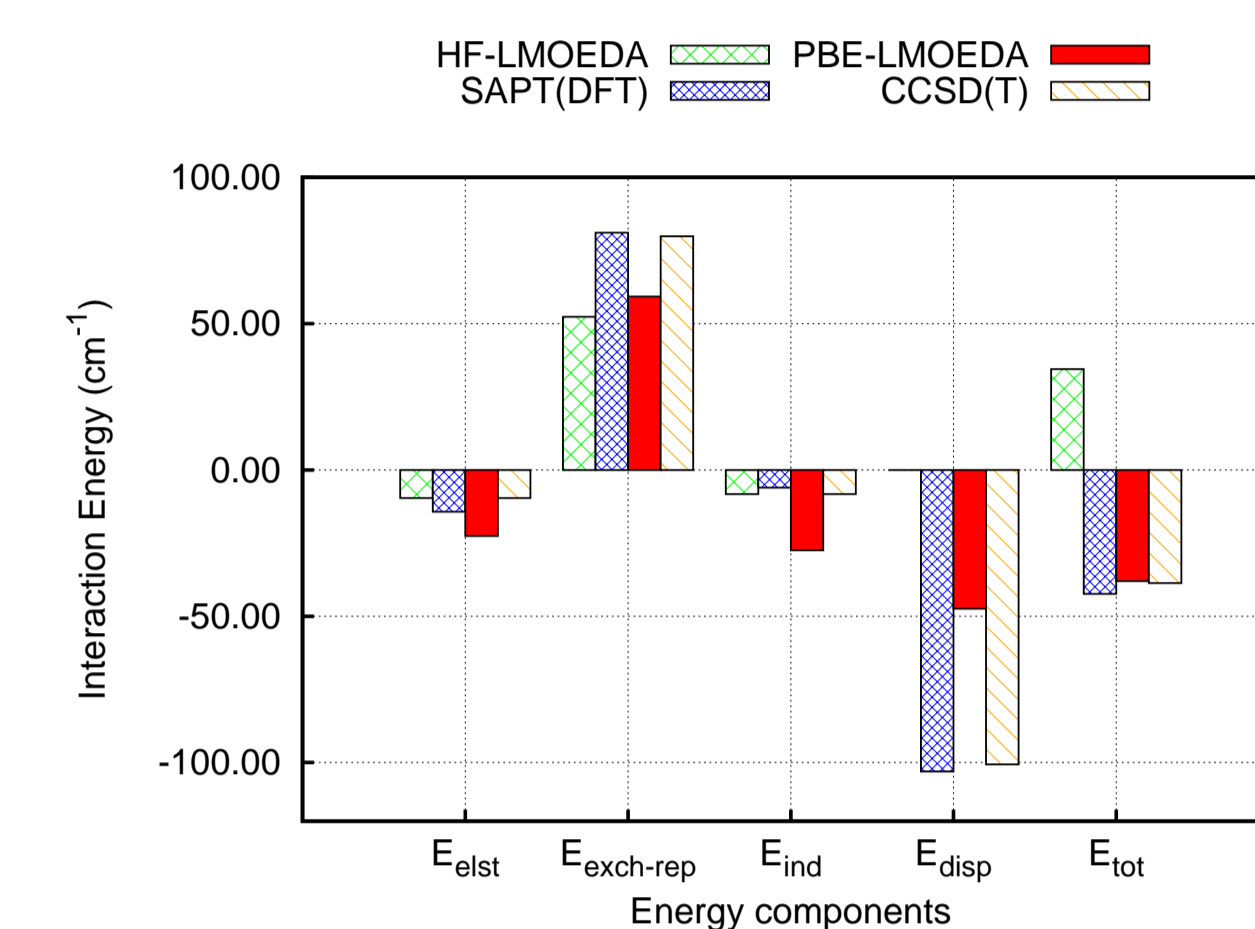
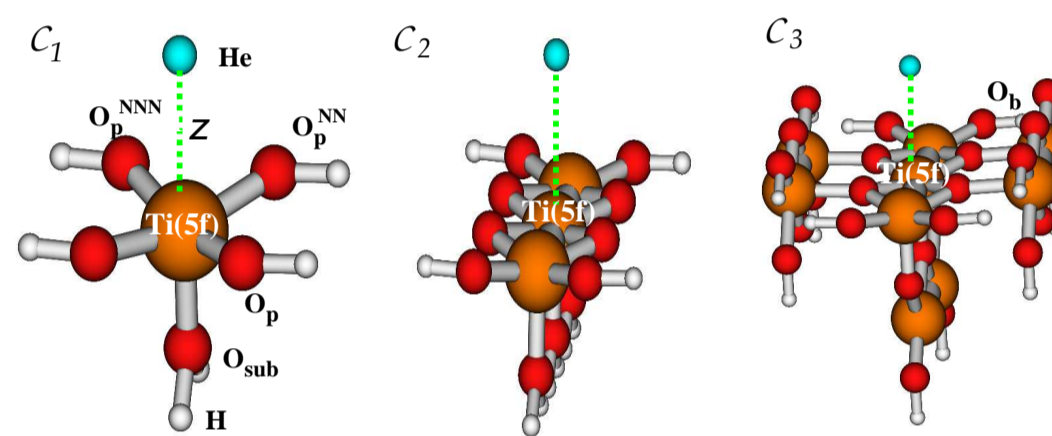


FIGURE 2: Electrostatic, exchange-repulsion, induction, and dispersion contribution to the total interaction energies of the He-(TiO₂)(H₂O)₃ complex at the He-Ti distance of $R = 3.5$ Å. The PBE0 functional has been used within the SAPT(DFT) framework. The partitioning of the PBE and HF interaction energies is based on the LMO-EDA approach. The CCSD(T) energy components have been obtained by adding the exchange-repulsion and dispersion-like contributions extracted with the method of increments to the HF counterparts.

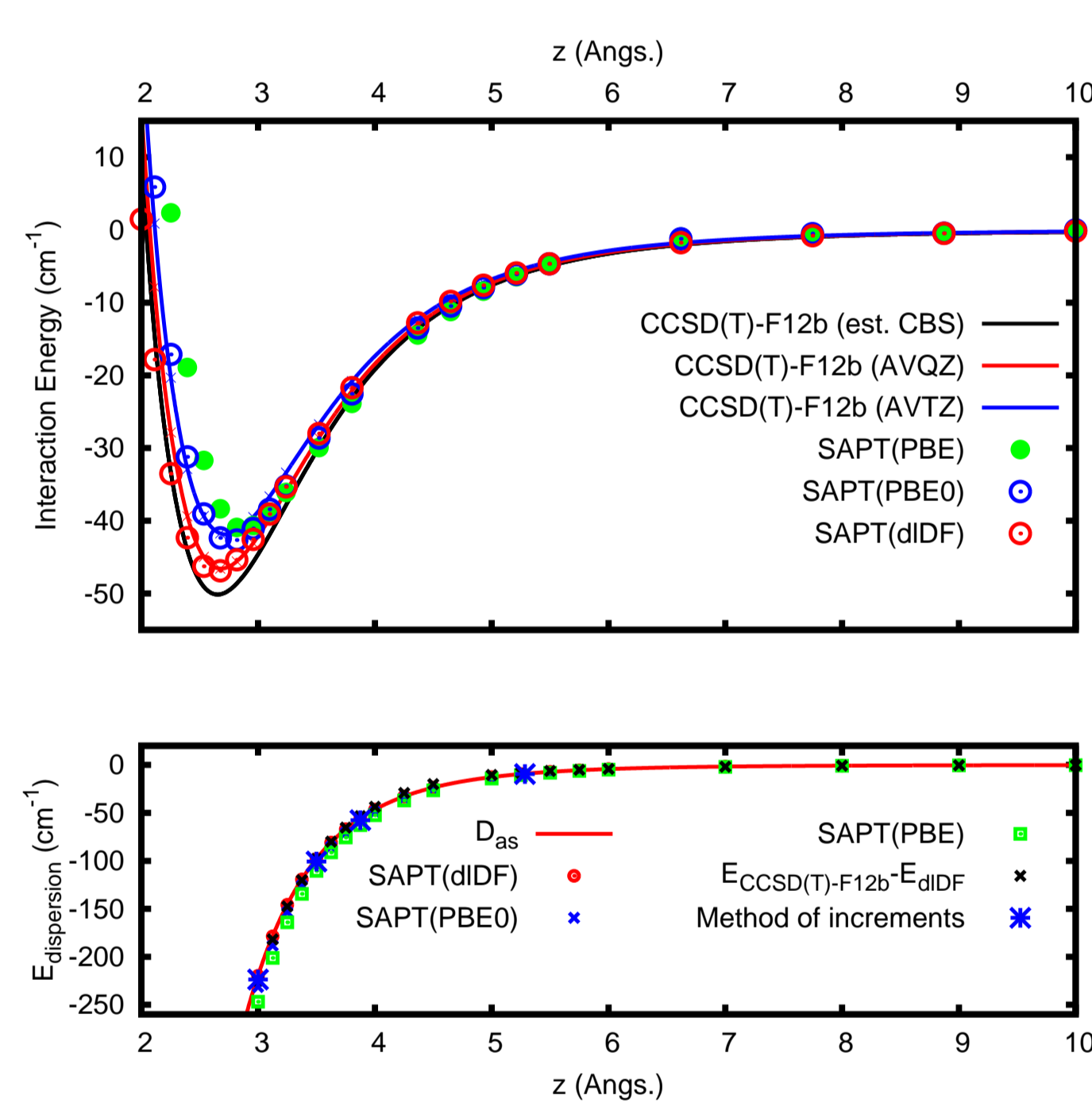


FIGURE 3: Upper panel: Potential energy curves for the He-C₁ complex as obtained with the CCSD(T)-F12b and SAPT(DFT) methods. Bottom panel: Dispersion energies corresponding to the He-C₁ interaction. The dispersion energies obtained with the method of increments include three-body contributions.

$$E_{\text{int}}^{\text{tot}} = E_{\text{int}}^{\text{dIDF}} - \sum_{x \in C_1} \sum_{n=6,8} -\frac{\sqrt{C_n^{\text{He}} C_n^x}}{R_{\text{He}-x}^n} f_n(\sqrt{\beta_{\text{He}} \beta_x} R_{\text{He}-x})$$

$$E_{\text{int}}^{\text{inter-corr}} = \sum_i \eta_{Ai} + \sum_{i < j} \eta_{Aij} + \sum_{i < j < k} \eta_{Aijk} + \dots$$

$$\eta_{Ai} = \epsilon_{Ai} - \epsilon_A - \epsilon_i$$

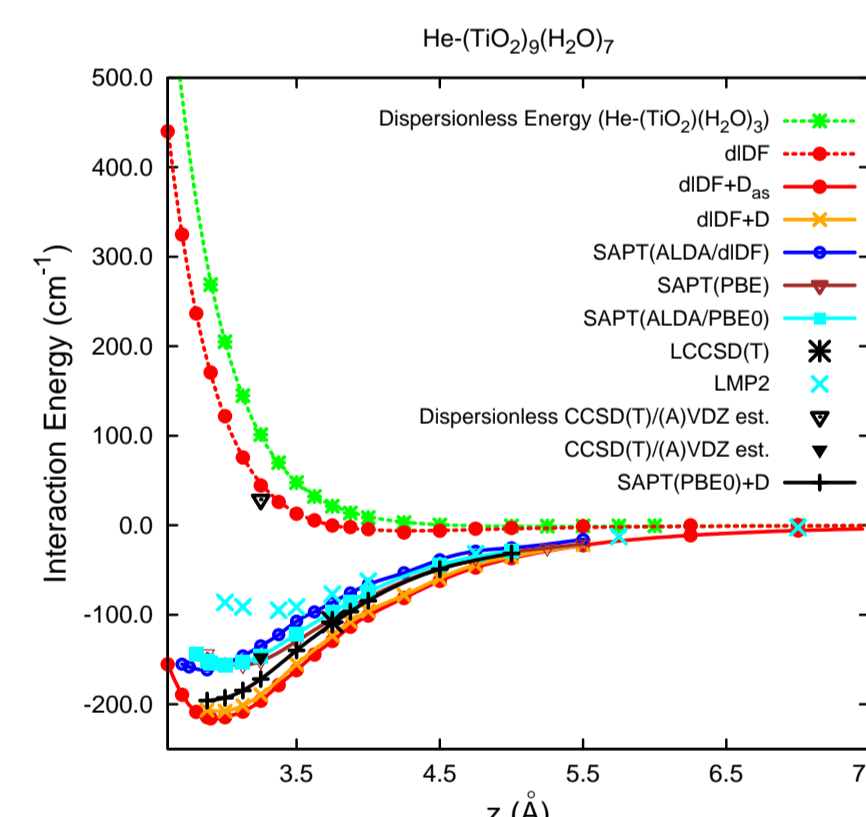


FIGURE 7: Interaction energies of the He-C₃ complex as a function of the He-Ti(5f) distance using different methods. The LMP2 interaction energies are taken from Ref. 4. The dispersionless energy of the He-(TiO₂)(H₂O)₃ complex has been calculated as the difference between CCSD(T)-F12b/CBS interaction energies and the dispersion energy components extracted with the method of increments. The SAPT(PBE0)+ D notation refers to the sum of dispersionless SAPT(PBE0) interaction energies and dispersion energies calculated with the SAPT(PBE) approach. The CCSD(T) estimations correspond to the sum of the HF interaction energy and the main correlation contributions, as calculated with the method of increments at CCSD(T)-(A)VDZ level of theory.

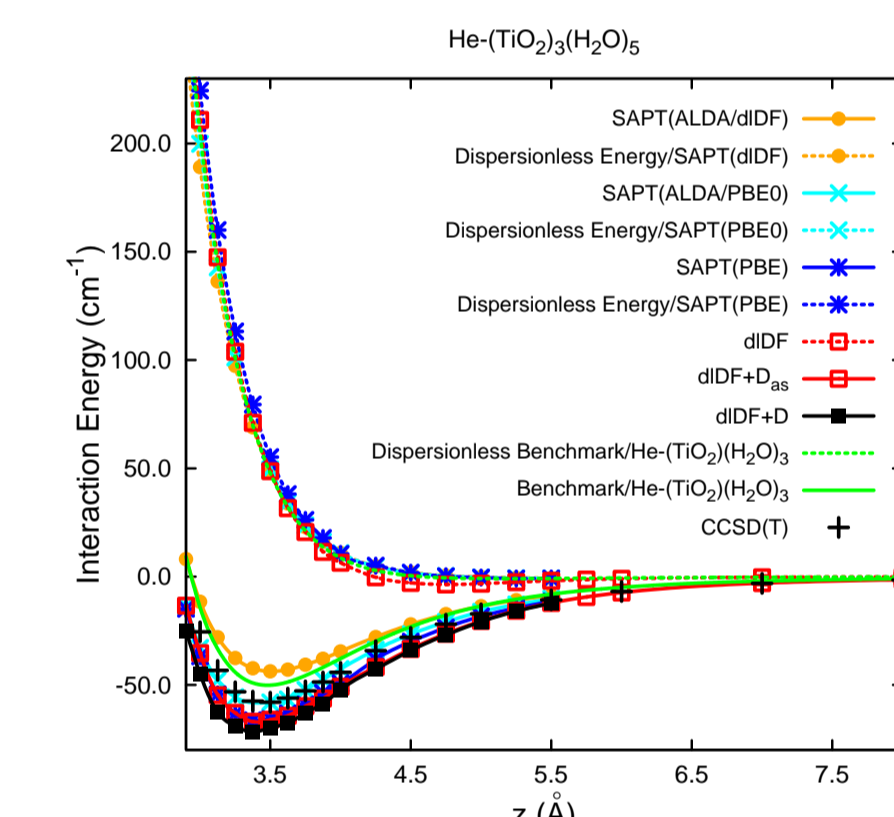


FIGURE 4: Interaction energies of the He-C₂ complex as a function of the He-Ti(5f) distance using different methods. The benchmark for the He-(TiO₂)(H₂O)₃ complex corresponds to the CCSD(T)-F12b/CBS total interaction energies. The dispersionless benchmark refers to the difference between CCSD(T)-F12b/CBS total interaction energies and the dispersion energies calculated with the method of increments. The notation SAPT(ALDA/PBE0) and SAPT(ALDA/dIDF) indicates the use of a pure ALDA kernel in calculating dispersion energies with the hybrid PBE0 and dIDF functionals.

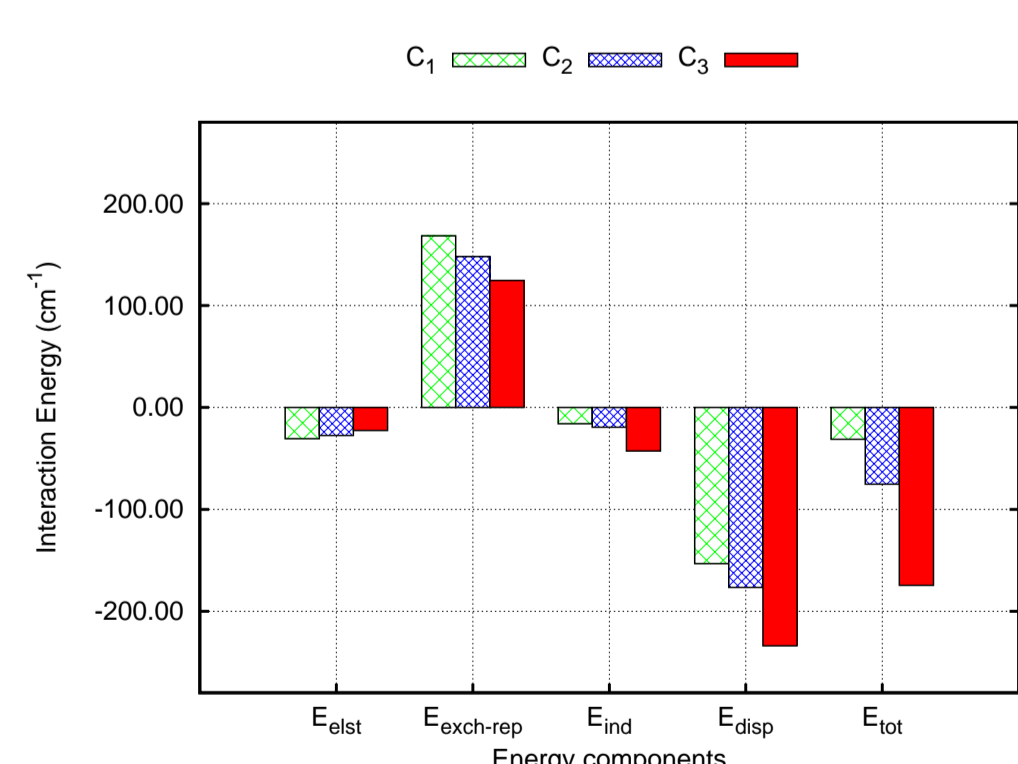


FIGURE 5: Electrostatic, exchange-repulsion, induction, and dispersion contribution to the total interaction energies of the He-C₁, He-C₂, and He-C₃ complexes at the He-Ti(5f) distance of $R = 3.25$ Å. The interaction energy components have been calculated with the SAPT(PBE0) method with the exception of the E_{disp} term in C₂ and C₃, which has been calculated using the PBE functional.

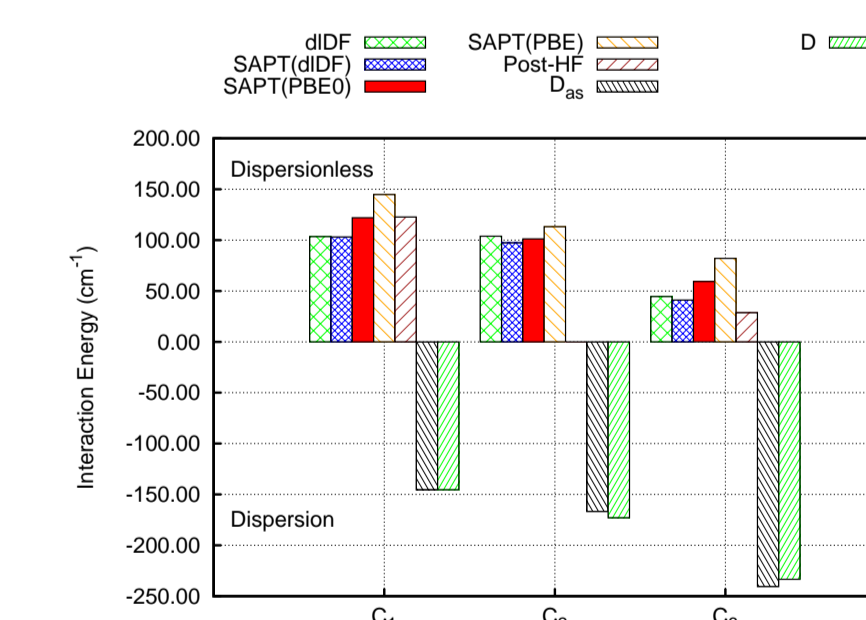


FIGURE 6: Dispersionless contribution to the total interaction energies of the He-C₁, He-C₂, and He-C₃ complexes at the He-Ti(5f) distance of $R = 3.25$ Å, as calculated with the dIDF and SAPT(DFT) approaches. The post-HF values correspond to the sum of the HF interaction energy and the intra-monomer correlation contribution, as extracted with the method of increments at CCSD(T) level of theory using the (A)VTZ and (A)VDZ basis sets for the He-C₁ and He-C₃ complexes, respectively. In the He-C₃ case, only the main incremental contributions to the intra-monomer correlation have been accounted for. For comparison purposes, the dispersion energies fitted from the calculations on the He-C₁ complex (referred to as D_{as}), and directly calculated for the He-C₂ and He-C₃ complexes (denoted as D) are also represented.

References

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Conclusions

The cluster size evolution of dispersionless and dispersion-accounting energy components reveals the reduced role of the dispersionless interaction and intra-monomer correlation when the extended nature of the surface is better accounted for. On the contrary, both post-Hartree-Fock and SAPT(DFT) results clearly demonstrate the high transferability character of the effective pairwise dispersion interaction whatever the cluster model is. Our contribution also illustrates how the method of increments can be used as a valuable tool not only to achieve the accuracy of CCSD(T) calculations using large cluster models, but also to evaluate the performance of SAPT(DFT) methods for the physically well-defined contributions to the total interaction energy. Overall, our work indicates the excellent performance of a dIDF+ D_{as} approach in which the parameters of the dispersion function are optimized using the smallest cluster model of the target surface. It also paves the way for further assessments of the dIDF+ D_{as} approach including periodic boundary conditions as a cost-efficient and accurate method to treat van der Waals adsorbate-surface interactions.