Overview

As a prototypical dispersion-dominated physiosorption problem, we analyze here the performance of dispersionless and dispersion-accounting methodologies on the helium interaction with the TiO$_2$(110) surface [1]. A special focus has been given to the dispersionless density functional (ddF) and the ddF+D$_{\text{dlDF}}$ construction for the total interaction energy [2], where D$_{\text{dlDF}}$ is an effective interatomic 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.

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 highlights 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 ddF+D$_{\text{dlDF}}$ 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 ddF+D$_{\text{dlDF}}$ approach including periodic boundary conditions as a cost-efficient and accurate method to treat van der Waals adsorbate-surface interactions.