Communication: A combined periodic density functional and incremental wave-function-based approach for the dispersion-accounting time-resolved dynamics of 4He nanodroplets on surfaces: 4He/graphene

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A Combined Periodic Density Functional and Incremental Wave-Function-based Approach for the Dispersion-Accounting Time-Resolved Dynamics of ^{4}He Nanodroplets on Surfaces: ^{4}He/Graphene

Supplementary Material: Selective Adsorption States of ^{4}He on Graphene and Graphite

As discussed in the main text, we have proved the performance of the composite approach by determining the nuclear bound-state energies corresponding to the low-lying selective adsorption states and comparing them with the best available theoretical data (see Table I). To obtain the laterally averaged potential, dispersionless interaction energies were first calculated for the helium atom at the "hollow", "bridge", and "on top" positions adsorption sites shown in Fig. 1 of the main text. Next, the dispersion energies obtained with the new D^*_{as} parametrization were added to each potential energy curve. Finally, the average potential was obtained from these curves using geometrical (i.e. positions density counting) weighting. The reference values were obtained by Bartolomei et al. [1] by fine-tuning atom-bond potential model parameters with SAPT(DFT) and MP2C [2] benchmark interaction energies. Using the same computational setup [1], we calculated SAPT(DFT) dispersion energies for the D_{as} parametrization and compared it with the new D^*_{as} parametrization using the method of increments. Estimated values for ^{4}He/graphite were also calculated with the substrate modeled as an assembly of graphene layers (as many as needed to reach convergence), assuming the $D^*_{as}(D_{as})$ parametrization obtained on graphene cluster models and the same dispersionless interaction. We can clearly notice from Table I the systematic improvement of the incremental D^*_{as} and D_{as} schemes upon increasing the cluster model so that for coronene both dlDF+incremental D^*_{as} and dlDF+D_{as} bound-state energies are very close to each other and to the theoretical values reported in Ref. 1. For graphene (graphite), the maximum absolute deviation is 0.3 meV (0.2 meV) whereas, apart from the highest state, the largest deviation percentage is 9% (4%). As compared with the original D_{as} formulation [3], one advantage of the new incremental D^*_{as} scheme is that the negligible role of the dangling bonds (to within 0.01 meV) allows to assess the convergence with respect to the cluster size. Remarkably, the D_{as} parametrization with the adsorbate at the hollow site provides dispersion energies at the other two adsorption positions shown in Fig. 1 of the main text with relative root-mean-square errors below 2%. The theoretical reference [1], and the dlDF+ incremental D^*_{as} (D_{as}) energies using the coronene cluster model differs by about 15%-17% (0.5−0.7 meV) on average from the experimental measurements on graphite, which have a resolution of ± 0.1 meV [4]. The mean deviation from the experimental values become 6% lower when going from single-layer to bilayer naphthalene cluster models. Graphite internal layers must then be explicitly accounted for to achieve theoretical estimations with an accuracy better than 15%.

TABLE I: Energies of the low-lying nuclear bound states ϵ_n (in meV) supported by the laterally averaged He-surface potential using the periodic dlDF+incremental D^*_{as} and the periodic dlDF + D_{as} approaches. The cluster model used for the D^*_{as} and D_{as} parameterizations is given in parenthesis. (a)Dangling bonds are accounted for. (b)Best available theoretical values from Ref. 1. (c)Using a bilayer naphthalene ($C_{20}H_{16}$) cluster model.

	^{4}He/graphene					
	ϵ_0	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5
$D^*_{as}(C_6H_6)$	−14.00	−7.85	−3.77	−1.45	−0.39	−0.05
$D_{as}(C_{10}H_8)$	−13.57	−7.40	−3.41	−1.23	−0.30	−0.03
$D_{as}(C_{24}H_{12})$	−12.57	−6.71	−3.00	−1.03	−0.23	−0.02
$D^*_{as}(C_{24}H_{12})$	−12.88	−6.95	−3.16	−1.12	−0.27	−0.03
$D^*_{as}(C_{24}H_{12})^{(a)}$	−12.92	−6.96	−3.16	−1.11	−0.26	−0.03
theory(b)	−12.63	−6.68	−2.93	−1.03	−0.24	−0.04
	^{4}He/graphite					
$D_{as}(C_{10}H_8)$	−14.74	−8.37	−4.15	−1.73	−0.58	−0.14
$D_{as}(C_{10}H_8)^{(c)}$	−14.00	−7.79	−3.74	−1.48	−0.45	−0.10
$D_{as}(C_{24}H_{12})$	−13.69	−7.64	−3.70	−1.49	−0.48	−0.11
$D^*_{as}(C_{24}H_{12})$	−14.04	−7.91	−3.89	−1.61	−0.53	−0.13
theory(b)	−13.92	−7.73	−3.76	−1.56	−0.52	−0.13
exp. [4]	−12.27	−6.56	−3.08	−1.20	−0.49	−0.13

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