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Combining density functional and incremental post-Hartree-Fock approaches for van der Waals dominated adsorbate-surface interactions: Ag₂/graphene

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A combined density functional (DFT) and incremental post-Hartree-Fock (post-HF) approach, proven earlier to calculate He-surface potential energy surfaces [de Lara-Castells *et al.*, J. Chem. Phys. **141**, 151102 (2014)], is applied to describe the van der Waals dominated Ag₂/graphene interaction. It extends the dispersionless density functional theory developed by Pernal *et al.* [Phys. Rev. Lett. **103**, 263201 (2009)] by including periodic boundary conditions while the dispersion is parametrized via the method of increments [H. Stoll, J. Chem. Phys. **97**, 8449 (1992)]. Starting with the elementary cluster unit of the target surface (benzene), continuing through the realistic cluster model (coronene), and ending with the periodic model of the extended system, modern *ab initio* methodologies for intermolecular interactions as well as state-of-the-art van der Waals-corrected density functional-based approaches are put together both to assess the accuracy of the composite scheme and to better characterize the Ag₂/graphene interaction. The present work illustrates how the combination of DFT and post-HF perspectives may be efficient to design simple and reliable *ab initio*-based schemes in extended systems for surface science applications. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919397>]

I. INTRODUCTION

Due to their striking optical properties (e.g., large wavelength-dependent cross-section for absorption, scattering, and photostability), noble metal nanoparticles (NPs), typically gold and silver, are being extensively used as functionalized plasmonic nanostructures^{1–3} including biosensors⁴ with properties that can be controlled by adjusting their size, shape, composition, and interaction with the support. The development of the ultra-cold ⁴He droplet-assisted synthesis and soft-landing deposition technique of metal NPs in thin and elongated nanowires^{5–13} has opened up new possibilities within this area. Most of the experimental studies so far have used amorphous carbon-based surfaces and silver NPs as the target species. As the simplest carbon-based surface and silver NP, the present work provides a theoretical study of the adsorption of the silver dimer on a single graphene sheet. Due to its unique properties such as high charge-carrier mobility, optical transparency, and thermal conductivity,¹⁴ very recent studies^{15,16} have considered graphene as a surface-enhanced Raman spectroscopy support of plasmonic NPs. Naturally, the silver/graphene interaction is important in many other technological applications such as the design of the nanocontacts of graphene-based electronic devices and efficient catalysts, to name just two. Previous theoretical studies have addressed the basic mechanism regulating the ⁴He droplet-assisted soft-

landing of the metal NPs¹⁷ as well as the impact of the van der Waals (vdW)-type He-surface interaction in the spreading of the ⁴He droplet.¹⁸ Clearly, the subsequent diffusion and aggregation of silver NPs is very sensible to the surface-metal interaction which is also van der Waals dominated.^{19–23}

Van der Waals complexes are bound mainly due to *intermonomer* (dispersion-like) electronic correlation effects which are naturally attractive and become dominant in the potential minimum region and at longer distances. The most accurate way to evaluate these interactions is to use the explicitly correlated coupled-cluster singles, doubles, and non-iterative triples [CCSD(T)-F12] method.^{24,25} *Ab initio* estimations of the interaction in vdW molecular complexes can be also obtained through Symmetry-Adapted Perturbation Theory (SAPT).^{26,27} It decomposes the total interaction into physically interpretable electrostatic, exchange-repulsion, induction, and dispersion contributions. Wave-function-based SAPT approaches start with a Hartree-Fock (HF) description of the monomers via second-order perturbation theory²⁶ [referred to as SAPT(HF)], and third- and higher-order terms are gradually included (for a recent review, see Ref. 28). Density-functional-theory (DFT)-based SAPT methods use a DFT description of the monomers as, for example, the SAPT(DFT)²⁹ and DFT-SAPT³⁰ approaches where the dispersion is computed via time-dependent DFT response theory. We will refer to these methods as SAPT(DFT), replacing DFT by the particular functional considered. The SAPT(DFT) technique has been applied to different physisorption problems.^{31–33}

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SAPT(HF) and SAPT(DFT) approaches can be also combined to correct the interaction energies obtained at second-order Möller-Plesset (MP2) perturbation theory such as the coupled MP2 (MP2C) treatment.^{34,35}

Cost-efficient periodic calculations accounting for the extended nature of the vdW-dominated adsorbate/surface system use electronic structure codes where DFT, HF, and hybrid HF/DFT approaches are implemented using either localized atom-centered Gaussian-type orbitals (e.g., CRYSTAL^{36,37}) or plane-wave-based one-electron basis sets (e.g., Vienna *Ab initio* Simulation Package (VASP)³⁸). Due to the inability of commonly used semi-local density functionals to describe long-range correlation effects, the explicit inclusion of dispersion corrections is the current standard in DFT-based calculations. During the last decade, different vdW-corrected DFT methods^{39–46} (referred to as DFT + D) have been developed and implemented into periodic codes, with numerous applications to physisorption problems (for a recent review, see, e.g., Ref. 47). For example, dispersion-corrected DFT energies can be obtained by adding damped interatomic vdW C_6/R^6 terms using the parameterization DFT-D2 of Grimme³⁹ or that of Tkatchenko and Scheffler,⁴⁰ or maximally localized Wannier functions,⁴¹ including a non-local correlation functional,⁴² or applying density-dependent dispersion corrected schemes.⁴³

In DFT + D methods, it is usually assumed that the dispersionless electronic correlation is well accounted for by the chosen density functional so that the dispersion-like corrections can be safely added. The dispersionless density functional (dIDF) of Pernal *et al.*⁴⁸ was explicitly designed for this purpose. It has been recently implemented within the modified development version³³ of the MOLPRO package⁴⁹ and also in the CRYSTAL14 periodic code.¹⁸ This is a hybrid meta-GGA functional which differs from the Minnesota M05-2X functional of Zhao, Schultz, and Truhlar⁵⁰ in the number and values of DFT parameters optimized to reproduce benchmark dispersionless interaction energies of weakly bound dimers.⁴⁸ It was developed along with an effective pairwise functional for the dispersion (denoted as D_{as}), parametrized by the fitting of dispersion energies evaluated by means of the SAPT(DFT) approach.

Within the category of fully periodic models, post-HF *ab initio* methods start with the HF wave-function on top of which both dispersionless and dispersion-accounting electronic correlation effects are added. One possibility is to apply the local MP2 (LMP2) treatment with the CRYSCOR implementation developed by Pisani *et al.*⁵¹ (see, e.g., Ref. 52 for a recent application to the He/surface interaction). Using the projector-augmented-wave method and plane-wave representations, implementations of non-local *canonical* MP2 and coupled-cluster approaches have been also introduced^{53,54} and successfully applied to solids including those layered by vdW-dominated interactions.⁵⁵ As an alternative to DFT + D and post-HF approaches, it is also possible to introduce boundary conditions using the stochastic Diffusion Monte Carlo (DMC) method.⁵⁶ Subchemical accuracy (to within 0.1 kcal/mol) has been achieved using DMC implementations on noncovalent complexes,^{57,58} with successful application to the hydrogen interaction with graphene.⁵⁹ Very recently, the full configura-

tion interaction quantum Monte Carlo technique⁶⁰ has been extended by including periodic boundary conditions and used as a benchmark to demonstrate the adequacy of the CCSD(T) method in predicting the interaction of solid-state materials.⁵⁵

Besides finite-cluster and fully periodic approaches, the third *ab initio* strategy to deal with vdW-dominated adsorbate-surface complexes consists in including the periodic boundary conditions at HF level while higher level *ab initio* methods such as CCSD(T) are applied on surface cluster models. The method of increments is the most widely applied treatment within this framework. This method was originally developed by Stoll in 1992⁶¹ and successfully applied to account for correlation effects in many extended systems such as carbon-based surfaces, diamond, and bulk rutile.^{61–63} The localized orbitals are the essential building units making the method of increments very efficient in calculating the electron correlation effects in both extended and finite systems.⁶⁴ This method has been applied to many adsorption and physisorption problems,^{65–70} using both hydrogen-saturated clusters⁷⁰ and point-charge-based cluster embedding.^{66,68} More sophisticated embedding cluster modeling uses the *cluster-in-solid* technique,⁷¹ which is implemented as an interface⁷² between the CRYSTAL and the MOLPRO packages. It has been applied to different problems of correlation in extended systems.^{73–77} Special embedding based on orbital space partitioning has been also developed to deal with metal surfaces.⁷⁸ As an alternative to these embedding methods, DFT-based embedding theory has been extensively developed (see Refs. 79 and 80 for recent overviews).

Within the method of increments, the electronic correlation is expressed as a cumulant expansion in terms of contributions from localized orbital groups. According to the local nature of the electronic correlation hole,⁸¹ the incremental expansion converges rapidly. An advantage of the incremental approach is that it allows to separate the electronic correlation into *intramonomer* and *intermonomer* contributions univocally. The recently proposed periodic dIDF + incremental D_{as}^* scheme¹⁸ is based on this separability and was successfully used for efficient and reliable determinations of He-surface interaction potentials.^{17,18,33} It applies the dIDF density functional^{48,82,83} with the periodic conditions included to estimate the *intramonomer* correlation contribution. On the other hand, the *intermonomer* correlation evaluated on surface clusters with the incremental scheme is fitted by means of the D_{as} functional of Szalewicz and collaborators,^{48,82,83} and then computed on the extended system. As shown in Refs. 17 and 18, the incremental D_{as}^* treatment behaves very similarly to the original D_{as} approach for He/surface interactions.^{48,82,83} When applied to the He-surface interaction, the periodic dIDF + D_{as} /incremental D_{as}^* approaches have been shown not only to be accurate and conceptually simple but also efficient due to the rapid convergence of the *intermonomer* correlation as a function of the surface cluster size.^{17,18,33}

The present work extends the periodic dIDF + incremental D_{as}^* scheme to vdW-dominated metal-surface interactions, with the Ag₂/graphene system as an illustrative case. Using the elementary surface cluster model (benzene), the Ag₂/surface interaction is first characterized via the method of increments. The small surface cluster size allows to apply both CCSD(T)

and CCSD(T)-F12 methods and to estimate the accuracy of the MP2 and coupled MP2 (MP2C)³⁵ approaches. Next, a more realistic cluster model (coronene) is used to compute the *intermonomer* increments for the *ab initio* D_{as}^* parametrization. The accuracy of the dIDF + incremental D_{as}^* approach is further validated using the coupled MP2 method as a reference. Finally, the periodic dIDF + incremental D_{as}^* scheme is applied to graphene periodic models together with the vdW-corrected DFT approaches.

The structure of this paper is as follows: Sec. II presents the method of increments as applied to vdW-dominated adsorption problems as well as the periodic dIDF + incremental D_{as}^* scheme. The computational approach and structural models are presented in Sec. III and the main results are discussed in Sec. IV. The work is summarized in Sec. V.

II. THEORETICAL APPROACHES

A. Method of increments for adsorbate-surface interaction energies

Applying the method of increments of Stoll⁶¹ to solids, the correlation energy $E_{\text{solid}}^{\text{corr}}$ of the extended system is expressed as a cumulant expansion in terms of contributions (increments) from occupied localized orbital groups (LOGs) centered at the solid ($i, j, k, \dots$),

$$E_{\text{solid}}^{\text{corr}} = \sum_i \epsilon_i + \sum_{i<j} \Delta\epsilon_{ij} + \sum_{i<j<k} \Delta\epsilon_{ijk} + \dots$$

The one-body term ϵ_i represents the correlation energy obtained when the electrons occupying the LOG i are correlated, via excitations into the available virtual orbitals, and freezing the rest of LOGs. Similarly, the two-body increment $\Delta\epsilon_{ij}$ is defined as the non-additive part of the correlation energy calculated when the electrons occupying the LOGs i and j are correlated, $\Delta\epsilon_{ij} = \epsilon_{ij} - \epsilon_i - \epsilon_j$. The increment values decrease rapidly with the order of the increment and the distance between the centers of the involved LOGs. Therefore, fourth- and higher-order contributions can often be safely neglected.

To calculate the electronic correlation contributions to the adsorbate-surface interaction energy, it is necessary to consider the LOGs centered at both the adsorbate (A) and the surface ($i, j, \dots$) which are close enough to interact. Within the incremental approach, the total interaction energy $E_{\text{int}}^{\text{total}}$ of the adsorbate-surface complex is expressed as

$$E_{\text{int}}^{\text{total}} = E_{\text{int}}^{\text{HF}} + E_{\text{int}}^{\text{intra-corr}} + E_{\text{int}}^{\text{inter-corr}}, \quad (1)$$

where $E_{\text{int}}^{\text{HF}}$, the HF interaction energy, is calculated using periodic models to account for long-range induction effects, while the *intramonomer* and *intermonomer* correlation contributions ($E_{\text{int}}^{\text{intra-corr}}$ and $E_{\text{int}}^{\text{inter-corr}}$) are computed on surface clusters.

The *intermonomer* correlation contribution to the interaction ($E_{\text{int}}^{\text{inter-corr}}$) is defined as the sum of the increments involving both adsorbate and surface LOGs,

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

Following the usual notations of the method of increments in adsorption problems,⁷⁰ the $\Delta\epsilon$ increments will be denoted with η below.

The *intramonomer* correlation contribution is defined in terms of the modifications of the adsorbate and surface increments due to the adsorbate-surface interaction. The one-body *intramonomer* incremental contributions from surface increment modifications are calculated as

$$\Delta\eta_i = \epsilon_i^{\text{A-surface}} - \epsilon_i^{\text{free surface}}.$$

Similarly, the one-body adsorbate increment modification is expressed as $\Delta\eta_A = \epsilon_A^{\text{A-surface}} - \epsilon_A^{\text{free A}}$. The two-body *intramonomer* correlation contributions arising from the surface i and j LOGs are evaluated as the increment modifications due to the presence of the adsorbate,

$$\Delta\eta_{ij} = \eta_{ij}^{\text{A-surface}} - \eta_{ij}^{\text{free surface}}.$$

It should be noticed that all the increments are computed using the basis set of the adsorbate-surface system and hence are counterpoise-corrected.⁸⁴ Therefore, the total *intramonomer* correlation contribution can be expressed with the following incremental expansion:

$$E_{\text{int}}^{\text{intra-corr}} = \Delta\eta_A + \sum_i \Delta\eta_i + \sum_{i<j} \Delta\eta_{ij} + \sum_{i<j<k} \Delta\eta_{ijk} + \dots$$

As shown for the He-surface interaction,^{17,18,33} three-body and higher-order *intramonomer* contributions are insignificant and can be neglected. All the increment contributions presented in the present work have been calculated at the CCSD(T) level of theory.

B. The dIDF + incremental D_{as}^* scheme

As discussed in Refs. 17 and 33, the *intramonomer* correlation term of Eq. (1) ($E_{\text{int}}^{\text{intra-corr}}$) can be identified with the dispersionless correlation contribution and approximated in surface cluster calculations as

$$E_{\text{int}}^{\text{intra-corr}} \approx -E_{\text{int}}^{\text{HF}} + E_{\text{int}}^{\text{dIDF}}, \quad (2)$$

where the term $E_{\text{int}}^{\text{dIDF}}$ is the interaction energy calculated with the dispersionless functional dIDF.^{48,82,83} This term is to be added to the periodic HF interaction energy. A more practical route implemented in Ref. 18 consists in including the periodic conditions in the dIDF calculations directly. It has been shown that both approaches provide very close results when a realistic surface cluster is used to estimate the *intramonomer* correlation contribution.¹⁷ Therefore, any periodic HF implementation could presumably be used in Eq. (2), in conjunction with methods implemented in standard quantum-chemistry molecular packages such as MOLPRO,⁴⁹ including the dIDF functional.³³

Within the incremental D_{as}^* scheme, the *intermonomer* correlation contribution is identified with the dispersion-like contribution, fitted by means of the effective pairwise D_{as} functional of Szalewicz and collaborators,^{82,83} and then computed on the extended system. For $\text{Ag}_2/\text{graphene}$, the

calculation of $E_{\text{int}}^{\text{total}}$ would be then reduced to

$$E_{\text{int}}^{\text{tot}} = E_{\text{int}}^{\text{dIDF}} - \sum_{\text{Ag}} \sum_{\text{C}} \sum_{n=6,8} \frac{\sqrt{C_n^{\text{Ag}} C_n^{\text{C}}}}{R_{\text{AgC}}^n} f_n \left(\sqrt{\beta_{\text{Ag}} \beta_{\text{C}}} R_{\text{AgC}} \right),$$

where the sum in the second term (the D_{as} function) runs over as many graphene C atoms as necessary to get convergence and f_n are the damping functions of Tang and Toennies.⁸⁵ Obviously, the efficiency and accuracy of this scheme depends on the size and transferability properties of the surface cluster used to fit the *intermonomer* correlation. For He/TiO₂(110), it has been demonstrated that the relevant *intermonomer* correlation increments are highly transferable from one surface cluster to another and that an elementary building cluster is capable of providing a good D_{as}^* parametrization.^{17,33} The same holds true when the original D_{as} approach^{48,82,83} is applied using dispersion energies calculated by means of the SAPT(DFT) treatment.^{17,33} Due to the higher degree of the electronic delocalization in graphene, a coronene-like cluster model was necessary to get an accurate D_{as}^* parametrization for the He/graphene interaction.¹⁸ The other question concerns the influence of the hydrogen saturation for the surface clusters: the negligible role of the capping of dangling bonds on the D_{as}^* parametrization can be used as a diagnostic to assess the convergence with respect to the cluster size. To demonstrate the accuracy of the method, the weakly bound states supported by the laterally averaged potential were calculated and compared¹⁸ with those determined from either fine-tuning of semiempirical potential model parameters for ⁴He/graphene⁸⁶ or scattering experiments on ⁴He/graphite.⁸⁷ The average absolute (relative) deviations were 0.3–0.7 meV (4%–17%) and 0.01 meV at most for the highest bound state. The coronene C—H bonds contribution was within 0.01 meV. This accuracy is similar to that achieved on He/Mg(001) using the periodic MP2 treatment and very precise coupled-cluster benchmarking on cluster models:⁵² a comparable average absolute deviation of 1 meV was found. This scheme has been also successfully applied to He/TiO₂(110) to provide the first theoretical evidence of the experimentally identified ⁴He droplet-mediated soft-landing deposition of metal species.¹⁷

C. Additional methods

To evaluate the performance of the dIDF + incremental D_{as}^* technique using the coronene surface cluster, we have also applied the MP2C approach of Heßelmann and Pitonák^{34,35} by replacing the uncoupled second-order dispersion contribution contained in the MP2 interaction energy with the coupled dispersion energy evaluated via the DFT-SAPT implementation.^{30,88} On the other hand, the accuracy of the MP2C approach itself has been demonstrated for the Ag₂/benzene interaction using the CCSD(T) method as a benchmark. Finally, the interaction energies calculated with the periodic dIDF + incremental D_{as}^* scheme for the Ag₂/graphene interaction were compared with those obtained using DFT + D treatments. We have applied the Perdew-Burke-Ernzerhof (PBE) functional⁸⁹ which is one of the most often used DFT approaches in extended systems, together with the DFT-D2

and DFT-D3 vdW-corrected schemes of Grimme and collaborators.^{39,90} Within the framework of methods developed by Langreth and co-workers,⁴² we have chosen the original vdW-DF treatment,⁴² that uses the revPBE exchange functional,⁹¹ and the more recent vdW-DF2 approach,⁹² based on the revised exchange PW86 functional.⁹³ The vdW-DF2 approach has been shown to perform better than its precursor for the adsorption of small molecules on surfaces (see, e.g., Ref. 94 for a recent overview).

III. STRUCTURAL MODELS AND COMPUTATIONAL DETAILS

A. Structural models

The structural models and computational details closely follow those reported in Refs. 18, 70, and 86. The cluster and periodic models are illustrated in Figure 1. Benzene and coronene-like fragments were chosen as the surface cluster models with the C—C bond lengths and C—C—C angles set to experimental values (1.42 Å and 120°, respectively). The dangling bonds were saturated with hydrogen atoms, with the C—H distances and C—C—H angles chosen to be 1.09 Å and 120°. The Ag₂ internuclear distance was fixed to the experimentally determined value⁹⁵ (2.531 Å). Cluster calculations considered two main orientations of the Ag₂ dimer: (1) perpendicular to the surface plane and (2) parallel to the surface plane and perpendicular to the C—C bonds. For both cases, the Ag₂

FIG. 1. Figure illustrating a graphene sheet and the coronene- and benzene-like fragments chosen to perform the CCSD(T) calculations with the method of increments and the dIDF + incremental D_{as}^* scheme. For coronene, the $\sigma + \pi$ groups oriented radially and tangentially with respect to the central ring are highlighted in yellow and red, respectively. Z is defined as the distance between the center of Ag₂ dimer and the carbon-ring plane. Perpendicular ($\theta = 0$) and parallel ($\theta = \pi/2$) orientations of the Ag₂ with respect to the surface plane were considered.

dimer was located on top of the central carbon hexagon (the “hollow” adsorption position). The periodic calculations were carried out using graphene supercell models considering the same adsorption site, as shown in Figure 1.

B. Computational details

All surface cluster calculations were carried out using correlation consistent basis sets with the MOLPRO package⁴⁹ including the dIDF implementation.³³ The CCSD(T), MP2, MP2C, and dIDF treatments used the augmented polarized correlation-consistent triple- ζ basis of Dunning and collaborators⁹⁶ (aug-cc-pVTZ) for C and H atoms, while the aug-cc-pVTZ-PP basis set was employed for silver,^{97,98} including a small-core (19-valence-electron) relativistic pseudopotential.⁹⁹ This basis set will be collectively denoted as avtz(-PP). To determine the errors arising from the use of the pseudopotential, second-order Douglas-Kroll-Hess CCSD(T) calculations^{100–102} were performed with aug-cc-pVTZ-DK basis sets.^{98,103} For Ag₂/benzene and both parallel and perpendicular equilibrium geometries, the errors amounted to 0.01–0.02 kcal/mol and 0.5% of the interaction energy. All interaction energies were counterpoise (CP)-corrected.⁸⁴ The complete basis set (CBS) limits of the interaction energies for the equilibrium perpendicular and parallel Ag₂/benzene structures were also estimated as follows: First, the correlation energies evaluated at CCSD level using the avtz(-PP) and avqz(-PP) basis sets were extrapolated using the n^{-3} scheme of Helgaker and co-workers¹⁰⁴ with $n = 3$ and 4,

$$E_n^{corr} = E_{CBS}^{corr} + A n^{-3}.$$

The same extrapolation scheme was adopted for the correlation contribution from perturbative triples (T) but using $n = 2$ and 3. Next, the extrapolated CBS estimations for the correlation contributions were added to the CBS counterpart at HF level (obtained using exponential extrapolation). In this way, the CCSD(T) interaction energies calculated with the employed avtz(-PP) basis were found to be converged to within 13%. Adapting this procedure to the MP2C case, a convergence to within 14% was estimated for the MP2C interaction energies with the same basis.

Explicitly correlated CCSD(T)-F12b calculations²⁵ were performed using the same orbital avtz(-PP) basis set. Density-fitting within the correlation treatment and the Fock matrix fitting used the recommended avtz(-PP)/MP2FIT¹⁰⁵ and avtz(-PP)/JKFIT¹⁰⁶ auxiliary basis sets. The complementary auxiliary basis approach¹⁰⁷ for the resolution of the identity (RI) employed the OptRI auxiliary basis sets matching to the corresponding avtz(-PP) basis sets^{108–110} as well as the AV n Z-RI auxiliary sets ($n = T, Q, 5$).¹⁰⁵ CP-corrected values were found to vary very little upon the n augmentation applying both AV n Z-RI and aV n Z/OptRI auxiliary basis sets, with interaction energies differing by 1% at worst. The value of the geminal Slater exponent γ was fixed to $1.4 a_0^{-1}$. CP-corrected interaction energies evaluated with the γ value set to 1.0 differed by less than 1.5%. In all CCSD(T) and CCSD(T)-F12b calculations presented in this work, the 4d shells of the Ag atoms were correlated.

The uncoupled HF and coupled dispersion energies necessary to apply the MP2C approach were obtained using the SAPT(HF) and SAPT(DFT) MOLPRO implementations⁸⁸ and the PBE functional⁸⁹ for the monomers. The exchange-correlation PBE potential was asymptotically corrected¹¹¹ with the ionization potential values reported in the NIST Chemistry Web Book.¹¹²

1. Application of the density-fitting technique on coronene

MP2C and dIDF calculations on coronene utilized the density-fitting technique with the avtz(-PP)/MP2FIT¹⁰⁵ and avtz(-PP)/JKFIT¹⁰⁶ auxiliary basis sets. For Ag₂/benzene, the MP2 interaction energies and the SAPT(PBE) dispersion energies with and without density-fitting differed by less than 0.1% and 2%, respectively. Since the current density-fitting SAPT implementation within MOLPRO⁸⁸ can only deal with local exchange potentials, the localized HF (LHF) method¹¹³ was applied to get uncoupled dispersion energy contributions on Ag₂/coronene. Dispersion energies calculated by means of the SAPT(LHF) and SAPT(HF) approaches were found to differ by less than 6%. As previously noticed in studies applying the SAPT(DFT) approach on coronene,^{86,31} the employment of the aug-cc-pVTZ basis set caused linear dependence problems. The exponent of the most diffuse function of each angular momentum function was multiplied by a factor of 2.3 to avoid them.^{86,114} To test the adequacy of this basis set, additional SAPT(DFT) calculations were carried out adopting the aug-cc-pVQZ basis set on Ag atoms, getting dispersion energies differing by 1% for the Ag₂/coronene interaction.

2. Application of the method of increments

For applying the method of increments, LOGs were defined using the Foster-Boys localization procedure.¹¹⁵ Correlation contributions were evaluated at the CCSD(T) level, using pseudo-canonical orbitals within the active space of the LOGs constituting a given increment. For Ag₂/benzene, the cc-pVTZ basis set was employed for C and H atoms, while the silver atom was described with the aug-cc-pVTZ-PP basis set [this basis will be referred to as vtz(-PP)]. Additional calculations were carried out by adding diffusion functions on carbon atoms through the aug-cc-pVTZ basis [denoted as (a)vtz(-PP)]. Incremental calculations on Ag₂/coronene used the aug-cc-pVTZ-PP basis set on Ag atoms, while the cc-pVTZ basis was adopted for the coronene atoms defining the LOGs of a given increment and the cc-pVDZ set otherwise.

Applying the localization procedure (see Fig. 1), the localized orbital groups of Ag₂/benzene are (1) the LOG at the Ag₂ dimer composed by the 5s-like and 4d orbitals centered on the Ag atoms, (2) the three σ C—C bond orbitals, (3) the three $\sigma + \pi$ C=C bond orbitals, and (4) the six C—H σ orbitals. On the other hand, the six LOGs characterizing the Ag₂/coronene complex are formed from (1) the LOG centered on the Ag₂ dimer, (2) the six σ C—C bond orbitals located at the central benzene-like ring, (3) the twelve σ orbitals of the outer rings, (4 and 5) the $\sigma + \pi$ C=C bond orbitals of the outer rings, 6 oriented radially and another 6 tangentially from the midpoint,

and (6) the twelve C—H σ orbitals. Since all the incremental contributions are summed, the total correlation energies were not influenced by the rings inequivalency produced by the localization procedure.

3. Periodic calculations

The periodic calculations were performed with both the CRYSTAL14 code and the VASP.^{38,116} In both cases, the 3×3 graphene supercell was employed. The CRYSTAL calculations were realized with the same computational setup as reported by Voloshina *et al.*,⁷⁰ using the aug-cc-pVDZ basis set on carbon atoms. The relativistic small-core Ag pseudopotential of Andrae *et al.*¹¹⁷ was used together with the corresponding basis set (modified for CRYSTAL by Doll and Harrison¹¹⁸). The Brillouin-zone integrations were carried out with a Monkhorst-Pack grid¹¹⁹ 12×12 . VASP calculations were performed using the projector augmented method¹²⁰ and plane wave basis sets with the kinetic energy cutoff set to 600 eV. We employed the projector-augmented-wave (PAW) PBE-based pseudopotentials supplied with the VASP code. The total energy calculations used a Γ -centered $9 \times 9 \times 1$ k -point mesh and the linear tetrahedron method to smear out the single particle wavefunctions. Structural relaxation effects of the carbon atom positions were not included after verifying their negligible effect on PBE-based calculations.

IV. RESULTS AND DISCUSSIONS

A. Ag₂/Benzene

Figure 2 shows the total interaction energies as a function of the distance from the Ag₂ bond midpoint to the carbon-ring plane for both perpendicular and parallel Ag₂/benzene geometries while the dispersion contributions are plotted in the lower panel. For the perpendicular configuration (see Table I), we have separated the total interaction energy into the HF and correlation contributions in the potential minimum region and at larger distances. The individual increments η associated to the *intermonomer* correlation energy component as well as the increment modifications $\Delta\eta$ associated to the *intramonomer* correlation contributions are also tabulated.

From Fig. 2, it can be seen that the potential minimum is much deeper when the dimer approaches benzene along the surface normal direction. The long-range electrostatic quadrupole-quadrupole interaction is attractive for the perpendicular structure and repulsive when the dimer axis is oriented parallel to the carbon-ring plane.⁴⁴ This is the reason of the very long-ranged attractive tail of the HF interaction energy for the perpendicular configuration (see Table I). At smaller Ag₂/benzene distances, the non-negligible role of the inductive interaction due to the polarization of the Ag₂ dimer in a direction perpendicular to the surface becomes reflected in the shallow minimum of the HF potential energy curve that is absent for the parallel structure (see Fig. 2). This partially explains why the HF interaction is significantly less repulsive at the equilibrium of the perpendicular structure as compared with the parallel counterpart (about 2 and 6.5 kcal/mol, respectively). It is further clarified through the SAPT(HF) decomposition: the values of the electrostatic and

FIG. 2. Ag₂/benzene intermolecular interaction (upper panel) and dispersion-like contributions (lower panel). The solid and dashed lines correspond to the perpendicular and parallel (perpendicular to the C—C bonds) orientations of the Ag₂ dimer with respect to the benzene plane, respectively. The dimer is located on top of the benzene center, with Z being the distance between the benzene plane and the Ag₂ center.

inductive terms in the equilibrium perpendicular geometry are -21 and -10 kcal/mol, respectively. These values are a factor of two and four larger than in the equilibrium parallel structure. Taking the same distance from the benzene plane to the nearest-neighbour Ag atom of the dimer in perpendicular and parallel orientations, the exchange-repulsion is also larger for the parallel configuration. This is consistent with steric considerations: two Ag atoms (rather than one) are in contact with benzene, for the parallel configuration, and the effective silver vdW radii (~ 1.72 Å for the monomer¹¹²) extend beyond the benzene ring diameter (~ 2.84 Å). These two factors lead to a shorter equilibrium distance between benzene and the closest Ag atom for the perpendicular approach. Therefore, the dispersion energy arising from the *intermonomer* correlation contribution is larger for the equilibrium perpendicular geometry (-15.61 vs. -8.23 kcal/mol).

Let us now analyze the vdW contribution to the interaction for the perpendicular structure with the method of increments. As can be seen in Table I, the attractive vdW interaction arising from the *intermonomer* correlation is clearly dominated by the attractive two-body η (Ag₂/C $\equiv$ C) increments that involve the benzene $\sigma + \pi$ localized orbitals and the LOG

TABLE I. Decomposition of the $\text{Ag}_2/\text{benzene}$ interaction energy and increment contributions at different distances (Z) between the benzene plane and the Ag_2 bond midpoint, with the dimer axis perpendicular to the benzene ring plane. All increments include the appropriate weight factors and were calculated with the vtz(-PP) basis set, while the larger (a)vtz(-PP) basis was used to get the values in parentheses (see text).

$\text{Ag}_2/\text{benzene}$	Z (Å)			
Energy(kcal/mol)	3.666	4.466	5.266	7.266
Two-body <i>intermonomer</i> increments				
$\eta(\text{Ag}_2/\text{C}-\text{C})$	-2.49 (-2.59)	-0.68 (-0.71)	-0.12 (-0.12)	-0.02 (-0.02)
$\eta(\text{Ag}_2/\text{C}=\text{C})$	-16.02 (-16.57)	-4.97 (-5.23)	-0.82 (-0.90)	-0.15 (-0.17)
$\eta(\text{Ag}_2/\text{C}-\text{H})$	-2.99 (-3.09)	-1.09 (-1.13)	-0.25 (-0.26)	-0.06 (-0.06)
Three-body <i>intermonomer</i> increments				
$\eta(\text{Ag}_2/\text{C}=\text{C}/\text{C}=\text{C})$	0.78	0.28	0.07	0.02
$\eta(\text{Ag}_2/\text{C}=\text{C}/\text{C}-\text{C})$	1.03	0.32	0.05	0.01
$\eta(\text{Ag}_2/\text{C}=\text{C}/\text{C}-\text{H})$	0.70	0.21	0.03	0.01
One-body <i>intramonomer</i> increment modifications				
$\Delta\eta(\text{Ag}_2)$	2.68	0.86	0.19	0.07
$\Delta\eta(\text{C}-\text{C})$	0.14	0.03	0.01	0.0
$\Delta\eta(\text{C}=\text{C})$	1.94	0.66	0.16	0.05
$\Delta\eta(\text{C}-\text{H})$	-0.05	-0.02	0.01	0.0
Two-body <i>intramonomer</i> increment modifications				
$\Delta\eta(\text{C}=\text{C}/\text{C}=\text{C})$	0.33	0.02	0.02	0.01
$\Delta\eta(\text{C}=\text{C}/\text{C}-\text{C})$	0.23	0.08	0.02	0.01
$E_{\text{int}}^{\text{HF}}$	6.06	-1.54	-0.95	-0.35
$E_{\text{int}}^{\text{inter-corr}}$	-18.99	-5.93	-1.03	-0.20
$E_{\text{int}}^{\text{intra-corr}}$	5.27	1.64	0.41	0.14
$E_{\text{int}}^{\text{tot}}$	-7.66	-5.83	-1.57	-0.42

centered at the Ag_2 dimer. Their values decay slowly as the Ag_2 -benzene distance increases and represent more than 75% of the total *intermonomer* contribution. Notice also that the capping C—H bonds have a significant weight (more than 15% of the total two-body *intermonomer* contribution) and are also long-ranged. The repulsive three-body terms contribute to 15% on average to the total *intermonomer* term, with a quarter of the fraction arising from increments where the C—H bonds are involved. The augmentation of the carbon atoms basis set with diffuse basis functions made the *intermonomer* increments about 4% larger. It should be stressed that the total *intermonomer* correlation contribution can be very well identified with the dispersion energy component, as also reflected in the lower panel of Fig. 2 by the rather close values obtained using the SAPT(DFT) treatment. On the other hand, the non-negligible contribution of the C—H bonds indicates that the benzene cluster is too small to provide an accurate D_{as}^* parametrization.

Focusing on the *intramonomer* correlation contribution to the $\text{Ag}_2/\text{benzene}$ interaction for the perpendicular geometry (see Table I), we notice that it is by overall repulsive and grows exponentially when the adsorbate-surface distance is decreased. For the attractive potential energy region considered in Table I, the total interaction energy is dominated by the attractive dispersion-like *intermonomer* term but the

intramonomer correlation still represents a significant fraction (e.g., about 1/3 at the minimum) competing with the HF contribution. Half of the *intramonomer* correlation contribution is due to the one-body $\Delta\eta(\text{Ag}_2)$ increment modification. This contribution turns out to be repulsive as the correlation energy obtained by correlating the LOG centered at the Ag_2 dimer is smaller in the $\text{Ag}_2/\text{benzene}$ complex than in the free Ag_2 molecule. This repulsive effect can be explained by the correlation space truncation for each monomer.^{33,61,68} In the free molecule, the electrons occupying the Ag_2 LOG are correlated through their excitations to all virtual orbitals. Part of the available virtual orbital space becomes blocked by the benzene occupied LOGs. As reflected in the large magnitude of the $\Delta\eta(\text{C}=\text{C})$ increment change upon the adsorption of the Ag_2 dimer, the same holds for the correlation of the π orbitals: the Ag_2 occupied LOG blocks virtual excitations of the electrons occupying the π orbitals. From Table I, it can be also seen that the two-body terms represent a minor fraction of the total *intramonomer* contribution (10% on average).

Figure 3 shows the components of the interaction as a function of the distance from the nearest neighbour Ag atom to the benzene plane for both parallel and perpendicular geometries. Interestingly, for the parallel configuration, the attractive dispersion-like *intermonomer* correlation contribution is largely cancelled by the repulsive HF energy term mainly arising from the Pauli repulsion. As a result, the potential energy curve corresponding to the *intramonomer* correlation term closely follows that of the total interaction energy despite of being a minor correlation contribution. The appearance of attractive *intramonomer* correlation terms when an adsorbate locates on top of surface atoms has been found by Voloshina⁶⁹ in metal surfaces and explained by the redistribution of the surface electronic density to screen the perturbation of the adsorbing species. As occurs for the $\text{Ag}_2/\text{benzene}$ complex, the *intramonomer* correlation contribution was instead found to be repulsive for the adsorbate on top of the surface “hollow” site. We also found that the total interaction energies are almost identical for different parallel orientations of the silver dimer.

Our analysis thus shows that the dispersion-like *intermonomer* correlation is mostly responsible for the binding of Ag_2 on benzene, in agreement with the detailed study by Granatier *et al.*²² This could partially explain the insensitivity of the interaction energies to the better description of the

FIG. 3. HF and correlation contributions to the total energy for $\text{Ag}_2/\text{benzene}$ as a function of the distance between the benzene plane and the Ag_2 midpoint for parallel (dashed lines) and perpendicular (solid line) orientations.

inter-electronic cusp by the explicitly correlated CCSD(T)-F12b method, as clearly apparent from Fig. 2. It is even more evident by comparing the MP2 and MP2C potential energy curves (PECs) (see Fig. 2): when replacing the uncoupled dispersion energy obtained with the MP2 approach by the more accurate coupled counterpart using the SAPT(PBE) method, the interaction potentials become very close to the CCSD(T) benchmarks. For the perpendicular geometry, the corresponding PECs are almost indistinguishable. For the parallel approach, the slight underestimation of the attractive contribution can be corrected by rescaling the dispersion energy by an enhancement factor of 1.1, corresponding to the ratio between the SAPT(PBE) dispersion energy and the *intermonomer* correlation evaluated with the method of increments (see above).

At this point, we would like to stress that, within the incremental D_{as}^* scheme, it is implicitly assumed that all the vdW contributions are included as *intermonomer* correlation, while electrostatic and induction terms are well accounted for at the HF level. A different approach has been developed by Halonen and collaborators⁴⁴ to extract the long-range vdW contribution by subtracting the electrostatic portion from the total CCSD(T) interaction energy. In this way, an effective C_6 coefficient of $64.60 \text{ eV/\AA}^6$ was obtained for the Ag-C atomic pair.⁴⁴ This value is in an impressive agreement (within 2%) with that obtained here with the incremental D_{as}^* approach ($63.46 \text{ eV/\AA}^6$).

B. Ag₂/Coronene

1. Perpendicular Ag₂/coronene structure: Application of the method of increments and D_{as}^* parametrization

As discussed for the He/graphene complex,¹⁸ the coronene-like cluster shown in Fig. 1 is a good surface model to extract an accurate D_{as}^* parametrization via the method of increments. Table II collects the relevant *intermonomer* correlation incremental contributions to the vdW interaction energy. About one half of the vdW contribution arises from the attractive two-body $\eta(\text{Ag}_2/\text{C}=\text{C})$ increment which involves the π localized orbitals closest to the Ag₂ dimer. Notice also that the values of the increments comprising π groups decrease only moderately as the perpendicular distance from the coronene plane increases. In contrast, the increments including the nearest neighbor σ orbital groups contribute with about 40% at the shortest distance but with less than 20% in the potential minimum region and 10% at larger distances. The repulsive three-body terms are dominated by the interaction of the Ag₂ LOG with the nearest neighbors π and σ orbital groups and the total three-body contribution represents a fraction of about 10%. Besides the large differences between the magnitudes of the vdW interaction energies for He/coronene¹⁸ and Ag₂/coronene (about a factor of 75 in the potential minimum region), the σ C—C bonds play a much more relevant role for the silver dimer than for atomic helium. These findings are in line with the largely increased polarizability of Ag (by a factor

TABLE II. Partition of the interaction energy and individual *intermonomer* increments (in kcal/mol) as a function of the distance (Z) between the coronene plane and the center of the Ag₂ dimer for the perpendicular structure. All increments include the appropriate weight factors and were obtained by correlating the 5s shell of the Ag₂ dimer and the 4d shell of the Ag atom closest to coronene. The correlation of the 4d shell of the farthest Ag atom was included to obtain the underlined values, while those highlighted with braces correspond to the correlation of the 5s-like shell only. The $E_{\text{int}}^{\text{intra-corr}}$ term was estimated with the dIDF approach (see text).

Ag ₂ /coronene	Z (Å)			
Energy (kcal/mol)	2.4	3.2	4.0	6.0
Two-body <i>intermonomer</i> increments				
$\eta(\text{Ag}_2/\text{C}=\text{C}$ inner ring)	−54.70 −54.60 − 2.93	−13.07 −12.87 − 1.58	−3.09 −2.91 − 0.91	−0.20 −0.17 − 0.10
$\eta(\text{Ag}_2/\text{C}=\text{C}$ outer rings)	−5.95	−2.63	−1.07	−0.17
$\eta(\text{Ag}_2/\text{C}=\text{C}$ radial)	−62.63 −63.06 − 9.24	−27.33 −27.27 − 5.67	−9.89 −9.66 − 3.57	−0.87 −0.82 − 0.55
$\eta(\text{Ag}_2/\text{C}=\text{C}$ tangential)	−10.42	−5.76	−2.70	−0.52
$\eta(\text{Ag}_2/\text{C}=\text{H})$	−2.05	−1.08	−0.55	−0.15
Three-body <i>intermonomer</i> increments				
$\eta(\text{Ag}_2/\text{C}=\text{C}/\text{C}=\text{C}$ inner ring/radial)		2.73		
$\eta(\text{Ag}_2/\text{C}=\text{C}/\text{C}=\text{C}$ radial/radial)		1.84		
$\eta(\text{Ag}_2/\text{C}=\text{C}/\text{C}=\text{C}$ inner ring)		0.53		
$E_{\text{int}}^{\text{HF}}$	341.60	39.83	5.09	−0.46
$E_{\text{int}}^{\text{inter-corr}}$	−135.76	−49.87	−17.13	−1.91
$E_{\text{int}}^{\text{intra-corr}}$	34.39	21.81	5.22	0.16
$E_{\text{int}}^{\text{tot}}$	240.24	11.77	−6.42	−2.21

of ~ 40), with respect to He, the angular anisotropy of the $4d$ shells, and the fact that the effective distance (of the nearest-neighbor Ag atom from the coronene plane) is much smaller than Z .

From the increments collected in Table II, it is very important to realize that most of the vdW contribution arises from the correlation of the polarizable $4d$ shell of the Ag atom closest to the surface cluster, while the $5s$ -like orbital group plays a minor role, especially when correlated along with the coronene σ orbital groups. Notice also that the $4d$ shell centered on the Ag atom farthest from the surface leads to an effective reduction of the vdW two-body terms by $\sim 1\%$. From the inter-atomic pairwise model for the dispersion, one would expect that the outermost Ag atom contributes to increase the attractive vdW interaction by $\sim 3\%$. This can be interpreted on the basis of both the interatomic metal screening exerted by the closest Ag atom and the polarization of the $4d$ electronic cloud. In any case, the deviation from screening/polarization effects is relatively small and our results mostly reflect an effective atomic-like behaviour of the silver unit with respect to its dispersion contribution.

The C_n coefficients and the damping β parameters of the D_{as}^* parametrization for the silver atoms were obtained through the global fitting of the total *intermonomer* correlation contribution including all the two-body increments and their effective reduction when the most relevant three-body counterparts are accounted for. Other parameters were kept fixed to the values reported by Szalewicz and collaborators in Ref. 83. It should be stressed that the negligible contribution of the C—H bonds in the D_{as}^* parametrization indicates the adequacy of the coronene cluster model to extract the dispersion contribution for the extended system. We have tested that $\text{Ag}_2/\text{graphene}$ interaction energies deviate by less than 1% when the $\eta(\text{Ag}/\text{C—H})$ increments are included in the D_{as} parametrization. The dispersion energies obtained with the incremental scheme differed from those calculated with the SAPT(PBE) approach by 7.8% and 4.9% (on average) for the

perpendicular and parallel $\text{Ag}_2/\text{coronene}$ structures, respectively. As found for helium as the adsorbate,¹⁸ the dispersion coefficients for the Ag atoms decreased from the values obtained using the benzene cluster model, leading to an effective reduction of the *intermonomer* correlation contribution of about 20%. This can be interpreted as the result of the screening from the coronene carbon atoms.

Focusing now on the HF interaction energy component (see Table II and Fig. 4), the polarization of the silver dimer is not reflected in a minimum for the HF potential energy curve, as could have been expected from the role played by induction effects. Still, a slightly attractive long-range tail is present and, as for benzene, it can be attributed to the electrostatic quadrupole-quadrupole interaction (see Table II). What is relevant to note here is that the HF interaction becomes significantly more repulsive for $\text{Ag}_2/\text{coronene}$ than for $\text{Ag}_2/\text{benzene}$ as the Ag_2 -cluster distance increases. For instance, at the corresponding minima, the repulsive HF contributions are equal to ~ 2 and 6 kcal/mol for benzene and coronene, respectively. For comparison, the well-depth values are around 8 kcal/mol. This is an indication of an enhanced exchange-repulsion on coronene which is not counterbalanced by a more attractive induction and electrostatic contributions due to the polarization of the silver dimer, as is quantitatively confirmed by using the SAPT(LHF) decomposition.

Similarly to benzene, the *intramonomer* correlation contribution is repulsive for the perpendicular $\text{Ag}_2/\text{coronene}$ geometry. The repulsive nature of the *intramonomer* correlation term is well characterized with the dIDF approach so that the corresponding interaction potential lies above the HF potential (see Fig. 4). The weight of this contribution is small relative to that of the HF term (see Table II), and minor differences arise between the benzene and coronene cluster models. Altogether, as compared to benzene, the more attractive dispersion interaction with the additional carbon atoms of coronene is compensated by the larger exchange-repulsion. As a result, the well-depth and the equilibrium distance are very close

FIG. 4. $\text{Ag}_2/\text{coronene}$ intermolecular interaction for perpendicular (left panel) and parallel (right panel) orientations of the dimer axis with respect to the coronene plane. The Ag_2 dimer is located on top of the coronene central ring, with Z as the distance between the coronene plane and the Ag_2 bond midpoint, as shown in Fig. 1.

TABLE III. Well-depth (D_e , in kcal/mol) and equilibrium distance (Z_e , in Å) for Ag_2 adsorbed on the hollow site of benzene, coronene, and graphene. The dimer axis was oriented both perpendicular and parallel to the carbon surface. The equilibrium distance is defined with respect to the Ag_2 center, as shown in Fig. 1. Underlined values were obtained without including three-body terms.

Method	Perpendicular		Parallel	
	D_e	Z_e	D_e	Z_e
$\text{Ag}_2/\text{benzene}$				
MP2	13.15	3.69	7.52	3.05
MP2C	8.15	3.91	2.61	3.49
MP2C/estimated CBS	9.06		3.04	
CCSD(T)	8.53	3.87	3.45	3.32
CCSD(T)/estimated CBS	9.51		3.96	
$\text{Ag}_2/\text{coronene}$				
MP2C	8.01	3.90	3.82	3.67
dIDF + incremental D_{as}^*	6.29	4.19	4.51	3.68
			<u>5.55</u>	<u>3.58</u>
$\text{Ag}_2/\text{graphene}$				
PBE-D3	6.60	4.20	7.90	3.39
vdW-DF2	5.92	4.31	6.97	3.52
vdW-DF	6.28	4.47	6.27	3.61
Periodic dIDF + incremental D_{as}^*	6.15	4.25	7.14	3.63
Periodic HF/dIDF + incremental D_{as}^*	6.64	4.23		
EE-vdW Ref. 22			5.7	3.55

to the benzene case (see Table III). Once again, the role of dispersion effects at the minimum and at longer distances is clearly evident when the MP2 and MP2C potential energy curves are compared, which differ only in the dispersion component. As for $\text{Ag}_2/\text{benzene}$, the overestimation of the attractive interaction with the MP2 approach is largely rectified by correcting the dispersion energy contribution. Also, the spin-component-scaled (SCS)-MP2 treatment significantly improves the interaction energies (see Fig. 4).

2. Parallel $\text{Ag}_2/\text{coronene}$ structure

As opposed to the perpendicular configuration, the potential minima for the parallel $\text{Ag}_2/\text{coronene}$ geometry are at least a factor of 1.5 more attractive than on benzene (see Table III). However, as seen from Fig. 4, the potential energy curve is still significantly more shallow for the parallel orientation than for the perpendicular approach of the Ag_2 dimer. Similarly to the $\text{Ag}_2/\text{benzene}$ case (see Fig. 3), the *intramonomer* correlation for the parallel orientation becomes attractive at distances larger than the equilibrium distance, where the dIDF potential lies below the HF counterpart (see Fig. 4). At the potential minimum, it is about an order of magnitude smaller than the dispersion contribution. The increase of the exchange-repulsion for the $\text{Ag}_2/\text{coronene}$ interaction results in larger equilibrium distances compared to those in $\text{Ag}_2/\text{benzene}$ (see Table III). As opposed to the perpendicular geometry, the larger exchange-repulsion is rather compensated by that of attractive electrostatic and induction terms, as calculated through the SAPT(LHF) approach. Therefore, we attribute the larger well-depth on coronene to the increase of dispersion.

3. Comparing the MP2C and the dIDF + incremental D_{as}^* treatments

As can be seen in Fig. 4, the interaction potentials evaluated with the dIDF + incremental D_{as}^* approach closely follow those obtained with the MP2C method. Still, we can notice three main differences: (1) the long-range tails are slightly more attractive within the incremental D_{as}^* approach, (2) the minimum of the MP2C potential for the perpendicular orientation is deeper and shifted to a shorter distance, and (3) the MP2C potential for the parallel configuration is slightly less attractive. The first feature can be explained by considering that the dispersion-like component is a little bit more attractive when extracted with the method of increments (see above), becoming more evident at long range. The second deviation points to an overestimation of the repulsive *intramonomer* correlation contribution with the dIDF approach for the perpendicular orientation since, according to the CCSD(T) benchmark for benzene, the MP2C approach provides a very accurate estimate. To evaluate these deviations in coronene, we performed additional calculations of the *intramonomer* increments at the repulsive potential wall, where their influence is more pronounced. It was found that the dIDF approach indeed overestimates the repulsive dispersionless interaction up to 15%. By rescaling the dIDF interaction energy with this factor, values of 7.6 kcal/mol and 4.0 Å were estimated for the well-depth and the equilibrium distance. Since *intramonomer* correlation contribution is less important in the potential minimum region, this value can be considered as an upper limit with the employed basis set. Hence, our analysis indicates that the dIDF + incremental D_{as}^* approach may underestimate the well-depth for the perpendicular orientation by up to 15%, while the equilibrium distance may be up to 5% too large. For the parallel configuration, the MP2C approach was found to slightly underestimate the attractive $\text{Ag}_2/\text{benzene}$ interaction (see Fig. 2 and Table III), which is in line with the small differences between the MP2C and dIDF + incremental D_{as}^* in the potential minimum regions observed for coronene. It should be also taken into account that the three-body *intermonomer* contributions were assumed to have the same weight as for the perpendicular structure. An upper limit for errors introduced by this approximation can be estimated by completely neglecting three-body terms for the parallel structure. As can be seen in Table III, this leads to differences of 1 kcal/mol and 0.1 Å. Apart from these small deviations, the overall good agreement between the MP2C and dIDF + incremental D_{as}^* PECs is very satisfactory, taking also into account the totally different backgrounds of the two treatments.

C. $\text{Ag}_2/\text{Graphene}$

1. dIDF + incremental D_{as}^* approach

To apply the dIDF + incremental D_{as}^* approach to the extended system, we considered basis set incompleteness effects on both the dIDF interaction energies and the D_{as}^* parametrization. As mentioned above (see Table I), the addition of diffuse functions on carbon atoms results in an increase of the magnitude of the two-body *intermonomer* increments by 4% (on average). The increase of the Ag atom basis from the

aug-cc-pVTZ-PP to the aug-cc-pVQZ-PP set modified the two-body increments very little (to within 2%-3%). To consider these modifications for the perpendicular structure, the two-body increments were upscaled by a factor of 7% and the effective reduction due to the repulsive contribution of the three-body increments (about 10%) was included. Actually, the exclusion of three-body terms largely compensates basis set incompleteness effects and it is recommended when no precise information on the weight of the three-body terms is available. We used this option for all other (non-perpendicular) configurations.

The effect of the basis-set incompleteness on the CP-corrected dIDF interaction energies obtained with the periodic CRYSTAL dIDF implementation¹⁸ was found to be very modest. To quantify it, additional HF calculations were carried out using a plane-wave representation by means of the VASP code. Next, the *intramonomer* correlation contribution evaluated via dIDF and HF cluster calculations on coronene (see Eq. (2)) was added. This treatment is denoted as periodic HF/dIDF + incremental D_{as}^* . As can be seen from Fig. 5, the calculated interaction energies (shown with open circles) closely follow the potential energy curve obtained via the periodic dIDF calculations. In addition to validating the CRYSTAL results, this proves that the coronene cluster model is large enough to quantify the repulsive *intramonomer* correlation contribution. In contrast, the periodic conditions have to be included in the HF treatment to account for the long-range induction.

As for the Ag_2 /coronene interaction, we estimated an upper limit to the well-depth and the equilibrium distance by rescaling the dIDF interaction energies by a factor of 0.85. This is considered to be an upper limit because the deviation percentage has been calculated in the region where it is larger (the repulsive potential wall). Moreover, the more repulsive HF interaction on graphene (see below) is expected to smooth out deviations in the dispersionless correlation term. The well-depth calculated using this procedure was ~ 1 kcal/mol larger than that evaluated with the periodic dIDF + incremental D_{as}^*

FIG. 5. Intermolecular interaction potential for the perpendicular Ag_2 /graphene structure. The Ag_2 dimer is located on top of the arene central ring, with Z as the distance between the graphene plane and the Ag_2 bond midpoint, as shown in Fig. 1.

approach, with the equilibrium distance being 0.1 Å shorter. If, as an alternative, the difference of the dIDF and HF interaction energies is rescaled using the benzene *intramonomer* increments of Table I, the differences become even smaller (0.5 kcal/mol and 0.04 Å).

Let us now consider the differences of the Ag_2 /graphene interaction when using coronene cluster and periodic models. Starting with the perpendicular configuration, marginal differences are found in both the interaction strengths and the equilibrium distances (to within 2%). On the one hand, the *intramonomer* correlation contribution remains almost unmodified by the inclusion of periodic conditions, as shown above. On the other hand, the portion of dispersion energy gained on the extended system is almost cancelled by the more repulsive HF interaction due to the enhanced exchange-repulsion. In contrast, for the parallel configuration, the potential energy minimum becomes deeper by about 2 kcal/mol. The increased attraction arises from the dispersion contribution, while the dispersionless component (at the potential minimum region) becomes 5% more repulsive only. Since *intramonomer* correlation effects leave the interaction energies nearly unperturbed in this region (see Fig. 4), our results indicate that the exchange-repulsion component of the Ag_2 /surface interaction is well represented within the dimer/coronene complex, with the long-range induction effects playing a minor role. In contrast, the polarization experienced by the Ag_2 dimer in the perpendicular approach affects both the long-range induction and the exchange-repulsion energy components. On the whole, the inclusion of delocalization effects makes the vdW Ag_2 /graphene interaction strength much less sensitive to the particular orientation of the silver molecule. The small differences of the well-depths for the perpendicular and parallel Ag_2 /graphene geometries (see Table III) are not necessarily indicative since they are of the same order of magnitude as the estimated uncertainty for the well-depth (0.5–1 kcal/mol, see above).

2. Comparing the periodic dIDF + incremental D_{as}^* approach with vdW-corrected DFT-based methods

For the sake of clearness, we will use the terms *intramonomer* and *intermonomer* correlation contributions as defined within the method of increments in comparing our approach with DFT-based treatments. As discussed above, the *intermonomer* correlation is identified with the dispersion, while the *intramonomer* term mainly corresponds to the dispersionless correlation contribution to the exchange-repulsion.

a. Comparing the periodic dIDF approach with pure density functional treatments. Let us first compare the pure DF approaches (the PBE and revPBE density functionals, see Fig. 6) with the dIDF and HF treatments. The dIDF functional adds the *intramonomer* correlation to the uncorrelated HF interaction energies. Calculated with the method of increments, this correlation contribution is repulsive and, accordingly, the dIDF potential lies above the HF counterpart. Although there exists no unique way of separating *intramonomer* and *intermonomer* contributions in DFT, it is instructive to consider for this purpose the localized molecular orbital energy decomposition analysis (LMO-EDA) scheme.¹²¹ It

FIG. 6. Interaction energies for the perpendicular Ag_2 /graphene structure (see Fig. 1) using the HF method and the dIDF, PBE, and revPBE density functionals.

expresses the short-range dispersion-like (*intermonomer*) correlation contribution as

$$E_{\text{int}}^{\text{inter-corr}} \approx E_c^{sl}[n_{A/\text{surface}}] - \{E_c^{sl}[n_A] + E_c^{sl}[n_{\text{surface}}]\},$$

where $E_c^{sl}[n]$ is the semilocal correlation functional of the electronic density n , with n_A and n_{surface} as Kohn-Sham (KS) densities of the free adsorbate and surface, respectively. On the other hand, the term $n_{A/\text{surface}}$ denotes the electron density minimizing the KS energy of the full system. It seems clear that the short-range *intermonomer* correlation can be described through $E_c^{sl}[n]$ in the region where the densities of the adsorbate and the surface overlap. It is tempting to attribute the global attractive correlation contribution obtained with the revPBE approach to this term (see Fig. 6). The *intramonomer* counterpart is better identified with the correlation contribution to the exchange-repulsion which, within the LMO-EDA scheme, is characterized by means of the exchange functional $E_{\text{exch}}[n]$. Since PBE and revPBE approaches differ only in one parameter characterizing this functional and the PBE interaction potential has a minimum which is absent in the revPBE case (see Fig. 6), it follows that the minimum is an exchange-

alone contribution. Within this context, the PBE *intramonomer* correlation contribution turns to be attractive. As found also for the averaged $\text{He}/\text{TiO}_2(110)$ interaction potential,¹⁷ the PBE approach describes very well the repulsive potential wall of the Ag_2 /graphene interaction (see Fig. 5), indicating the good behaviour of the functional “on a whole” in the short-range region.

b. Comparing the periodic dIDF + incremental D_{as}^ scheme with vdW-corrected DFT-based approaches.* For the perpendicular structure, Figure 5 presents the Ag_2 /graphene interaction potential obtained with the periodic dIDF + incremental D_{as}^* approach along with the different DFT + D treatments. To evaluate the performance of these methods for molecular dynamics simulations of the metallic nanoparticle motion, accurate interaction forces are necessary. For this purpose, first derivatives of the PECs have been plotted in Figure 7, for both perpendicular and parallel structures. The most striking feature is the nearly perfect agreement of the interaction forces as a function of the Ag_2 /graphene distance calculated with the vdW-DF2 method and the periodic dIDF + incremental D_{as}^* approach. The vdW-DF approach is found to describe less accurately both the long-range tail and the curvature of the potential in the minimum region whatever the Ag_2 /graphene structure be. In the repulsive potential region, however, it behaves similarly to the periodic dIDF + incremental D_{as}^* approach and to the vdW-DF2 treatment.

To clarify our comparative analysis, we first recall briefly the grounds of the applied vdW-corrected DFT-based approaches. The key feature of the vdW-DF-based treatments developed by Langreth and co-workers^{42,92} is the inclusion of a non-local correlation functional of the electronic density n (referred to as $E_c^{nl}[n]$) to account for the long-range *intermonomer* correlation contributions missed in local and semilocal DFT-based formulations. To avoid their overcounting at short range, it replaces the semilocal correlation functional $E_c^{sl}[n]$ by the purely local counterpart. Moreover, the original vdW-DF approach⁴² substitutes the PBE by the revPBE

FIG. 7. Interaction forces for the perpendicular (left panel) and parallel (right panel) Ag_2 /graphene structures. The Ag_2 dimer is located on top of the arene central ring, with Z as the distance between the graphene plane and the Ag_2 bond midpoint (see Fig. 1).

exchange functional to avoid exchange-only binding effects (see Fig. 6). As compared to vdW-DF,⁴² the gradient correction factor within the functional $E_c^{nl}[n]$ of the vdW-DF2 approach is more than twice larger. This enlargement factor was evaluated on the basis of scaling laws for atoms. For the vdW-DF treatment, the gradient correction for the $E_c^{nl}[n]$ functional is built following the gradient expansion of the electron gas with a slowly varying n . This difference qualitatively explains why the long-range tails evaluated with the vdW-DF2 approach decay more rapidly and the interaction forces are peaked at higher values as compared with the vdW-DF treatment (see Fig. 7).

Comparing the PBE and vdW-corrected PBE treatments with the periodic dIDF + incremental D_{as} scheme, the improvement in going from the DFT-D2 treatment to the DFT-D3 approach is evident at the whole range of Ag_2 /graphene distances, being specially impressive for the parallel structure (see right panel of Fig. 7). The dispersion correction in the DFT-D3 approach of Grimme and collaborators⁹⁰ is written as a sum of the dispersive interaction of the atomic pairs $Ag-C$ in Ag_2 /graphene similar to that contained in the D_{as}^* parametrization, including a damping function (see Sec. II B). The dispersion coefficients C_6 are evaluated according with the Casimir-Polder formula and adjusted to the local chemical environment of silver and carbon atoms. Within the DFT-D2(D3) schemes, the damping function avoids the overcounting of correlation effects at short-range by pure DF functionals which are assumed to already include them. Besides the local chemical correction, the other important difference between DFT-D2 and -D3 treatments is the inclusion of the three-body *intermonomer* correlation corrections.

As can be seen in Figs. 5 and 7, the PBE-D3 approach largely corrects the underestimation by the PBE-D2 method of the attractive *intermonomer* correlation in the medium- and long-range potential regions, the too attractive potential well, and the less repulsive potential wall. In fact, the very good description of the repulsive potential wall by the PBE method can only be worsened by the inclusion of any attractive energy contribution. The damping function of the D2 functional partly circumvent this problem but, then, an underestimation of the long-range *intermonomer* correlation contribution gets in (see right panel of Fig. 7). It is remarkable that the DFT-D3 treatment fixes two shortcomings going in opposite directions. This could be qualitatively explained by considering that the (long-range) two-body *intermonomer* correlation contributions are more attractive than those contained in the general-purpose D2 parametrization, while the repulsive three-body corrections introduced by the DFT-D3 approach affect mostly the short-range potential region, particularly for the parallel structure. Somewhat poorer agreement was found using the PBE-D3 approach for the $He/TiO_2(110)$ interaction,¹⁷ with the well-depth being overestimated by about 20%.

Using vdW-DF-based methods, different parallel Ag_2 /graphene structures have been discussed in great detail by Hobza and collaborators.²² As can be seen in Table III, the reported well-depth by means of the exact exchange (EE)-vdW method²¹ differ only slightly (1.4 kcal/mol at most) from the values obtained in the present work with vdW-DF-based treatments and the incremental D_{as}^* approach, with the esti-

mated equilibrium distances within 2% or 0.1 Å. The EE-vdW approach²¹ replaces one quarter of the DFT-based exchange contained in the vdW-DF treatment by the single determinant HF-like counterpart. A study of the interaction between silver-coated atomic force microscopy tips and graphene by Lazar *et al.*²³ indicated that the HF-like portion is very important to get quantitative agreement with the experimental measurements of the interaction forces.

V. SUMMARY AND FUTURE PROSPECTS

Applying the method of increments,⁶¹ this work is mainly aimed to evaluate the performance of the periodic dIDF + incremental D_{as}^* scheme¹⁸ for the description of the interaction between noble metals and the graphene surface, choosing the Ag_2 dimer as the metal species. For the sake of comparison, modern *ab initio* methods for intermolecular interactions and vdW-corrected DFT-based approaches are applied. The periodic dIDF + incremental D_{as}^* scheme combines the dispersionless density functional, dIDF, of Szalewicz and collaborators⁴⁸ with a parametrization of two- and three-body dispersion contributions, calculated at CCSD(T) level via the method of increments.¹⁸ It has been already very successful in the calculation of precise He/surface interaction potentials.^{18,17} The present study demonstrates that it also provides the accurate interaction forces which are necessary for realistic dynamical simulations of the motion of the metallic nanoparticle on surfaces.

Starting with benzene as the smallest surface fragment, it is shown that the interaction with Ag_2 is dominated by HF and dispersion energy contributions, with the former being rather sensitive to the Ag_2 dimer orientation relative to the benzene plane. *Intramonomer* correlation effects are repulsive at short-range for both orientations and are attractive at medium-range when the dimer axis is oriented parallel to the carbon-ring plane. The difference in the interaction strength for both configurations is reduced when the extended nature of graphene is better accounted for using coronene and periodic models. The inclusion of more carbon atoms naturally increases the attractive dispersion contribution but also makes the exchange-repulsion larger, specially for the perpendicular geometry where polarization effects are important.

For the Ag_2 /benzene interaction, the MP2C approach of Pitonák and Heßelmann³⁵ is shown to yield reliable results, successfully correcting the overbinding effect of the MP2 treatment. Since both approaches differ in the dispersion energy component only, this confirms that the Ag_2 dimer binds to the surface mostly due to vdW-type contributions, as also found in previous studies.^{19–23} The dispersion energies calculated with the SAPT(PBE) treatment agree well with those extracted with the method of increments using both benzene and coronene cluster models.

Next, using the coronene surface cluster model, the parameters of the D_{as}^* functional are fitted to the sum of two-body dispersion contributions including the effective reduction due to three-body terms. The negligible role of the coronene C—H capping bonds confirms the adequacy of the obtained D_{as}^* parametrization for the extended system. The potential energy curves calculated with the MP2C and dIDF + incremental D_{as}^*

treatments are very close. The periodic dIDF + incremental D_{as}^* scheme is further applied to the graphene layer model with the CRYSTAL periodic code. The interaction energies are very similar to those obtained with the periodic HF/dIDF + incremental D_{as}^* approach, using a plane-wave representation of the HF wave-function with the VASP code.

VdW-corrected DFT-based methods are also applied to calculate interaction energies and forces as a function of the distance between the silver dimer and the graphene plane. The interaction forces evaluated with the vdW-DF2 method of Langreth and co-workers⁹² match very well with those obtained by means of the periodic dIDF + incremental D_{as}^* approach. We also found a good agreement with the DFT-D3 treatment of Grimme and collaborators.⁹⁰

The partition of the interaction energy with the post-HF/DFT approach allows to estimate possible uncertainties introduced by the dIDF approach for the dispersionless correlation contribution. This can be very useful when there are no reference interaction energies available. In this way, we estimate the uncertainty of the interaction energies of the dIDF + incremental D_{as}^* scheme to be 0.5–1 kcal/mol (~15% of the well-depth). This can be compared with the accuracy reached for the ⁴He/graphene(graphite) interaction¹⁸ (better than 1.0 meV and 3% of the well-depth). Since the underlying ideas of the dIDF + incremental D_{as}^* scheme are very different from those of state-of-the-art vdW-corrected DFT-based techniques, it can serve as an independent test of DFT-based approaches.

Work is in progress to apply the periodic dIDF + incremental D_{as}^* technique to dynamical simulations of the helium droplet-mediated deposition of silver clusters on carbon-based surfaces. One important question concerns the transferability properties of the D_{as}^* parametrization. The results of the present work indicate that the particular position of the Ag₂ dimer affects very little the differences between the dispersion energies estimated via the D_{as}^* functional and directly calculated by means of the SAPT(DFT) approach. The second relevant issue is the adequacy of the atomic two-body potential representation typically used in classical molecular dynamics simulations. This study indicates that dimers may be conveniently used as building blocks to model the interaction.

Finally, we wish to stress that periodic calculations with the dispersionless dIDF functional are not more costly than those performed with the HF treatment and that modest surface cluster sizes are sufficient to parametrize the dispersion interaction at the CCSD(T) level via the method of increments. Thus, the periodic dIDF + incremental D_{as}^* approach not necessarily implies much higher computational cost than standard vdW-corrected DFT methods. The interpretative chemical and physical aspect brought by the composite post-HF/dIDF approach is also worth recalling when applied together with the HF treatment on finite cluster and periodic models. Therefore, we hope that this study, together with previous works,^{33,18,17} can be useful to illustrate that *ab initio*-based schemes combining post-HF and DFT perspectives are practical and realistic in dealing with vdW-type extended systems. Still, further work is necessary to establish more generally the range of applicability of the composite post-HF/DFT approach.

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