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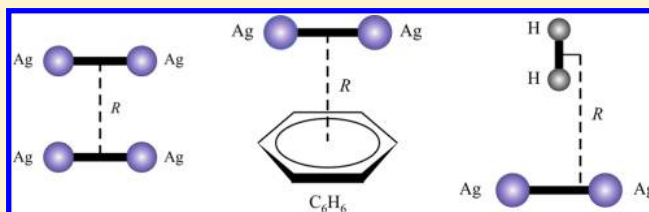
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An ab Initio Study of van der Waals Potential Energy Parameters for Silver Clusters

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ABSTRACT: We employ ab initio calculations of van der Waals complexes to study the potential energy parameters (C_6 coefficients) of van der Waals interactions for modeling of the adsorption of silver clusters on the graphite surface. Electronic structure calculations of the $(\text{Ag}_2)_2$, $\text{Ag}_2\text{--H}_2$, and $\text{Ag}_2\text{--C}_6\text{H}_6$ complexes are performed using a coupled-cluster approach that includes single, double, and perturbative triple excitations (CCSD(T)), Møller–Plesset second-order perturbation theory (MP2), and spin-component-scaled MP2 (SCS-MP2) methods. Using the atom pair approximation, the C_6 coefficients for silver–silver, silver–hydrogen, and silver–carbon atom systems are obtained after subtracting the energies of quadrupole–quadrupole interactions from the total electronic energy.



INTRODUCTION

The role of van der Waals (vdW) interactions (long-range dispersion forces) is often ignored in computational studies of the energies of metal clusters adsorbed on different sites of solid surfaces. Calculations of the cluster-surface binding energy are often done using density functional theory (DFT) with boundary conditions. The functionals typically employed in common DFT electronic structure codes usually lack the effects of electronic correlation at long distances. This makes the codes (and calculations done using them) less useful in systems where dispersion forces are important. One possibility to get around the problem is to develop new functionals^{1–4} or relatively complex schemes^{5,6} for a quantitative description of nonbonded interactions within DFT. Recently, such a scheme was applied to DFT calculations of the structure and energetics of azobenzene adsorption on Ag(111).⁷ Another approach, with successful applications in physics, chemistry, and biology,^{8–10} adopts an empirical formula consisting of an inverse-sixth-power (R^{-6}) term for atomic pairs. In this model, the vdW energy provides an empirical contribution to the total energy.

From the microscopic point of view, the dispersion interaction energy and thus the C_6 dispersion coefficients of the R^{-6} term of atomic pairs are related to the dynamic electric dipole polarizability of atoms (or molecules).^{11–13} Hølgren has reviewed the treatment of vdW interactions in the framework of empirical potentials with schemes to calculate R^{-6} coefficients from the atomic polarizabilities.¹⁴ The use of only polarizabilities underestimates the C_6 dispersion coefficients. Other closely related empirical models also exist to provide these coefficients more accurately, but unfortunately, these produce rather different values for the silver dimer.¹⁵ Symmetry-adapted perturbation theory (SAPT) can also be used to calculate C_6 dispersion coefficients.¹⁶ To the best of our knowledge, no C_6 coefficients that describe the interaction of Ag_2 with other species have been obtained using

any wave function-based first-principles method. Here, we estimate these C_6 coefficients on the basis of ab initio calculations of appropriate vdW species involving Ag_2 .

Supermolecular ab initio calculations of pairs of closed-shell molecules have been an important source of information on pair interactions (excluding three- and many-body interactions) and thus on the intermolecular potential energy surfaces (PES). The first-principles calculations have been used to evaluate PESs in an increasingly routine manner because of the rapid progress in computational algorithms and computer hardware. Many ab initio data of the structures and PESs on vdW clusters have been published.^{17–20} This kind of work often concentrates on the PESs near the global minimum where the energy arises from four basic components: electrostatic, exchange, induction, and dispersion contributions. Fortunately, intermolecular exchange interactions decrease exponentially as the separation between two monomers increases, and so at long range the dominant terms are the vdW dispersion, electrostatic, and induction contributions. The electrostatic and induction contributions can be readily evaluated if the electrical properties of the monomers are known. This permits the extraction of long-range vdW dispersion contributions from supermolecular ab initio calculations at large intermolecular distances.

In this work, we study the vdW species $(\text{Ag}_2)_2$, $\text{Ag}_2\text{--H}_2$, and $\text{Ag}_2\text{--C}_6\text{H}_6$ using a coupled-cluster approach that includes single, double, and perturbative triple excitations (CCSD(T)); second-order Møller–Plesset perturbation theory (MP2); or spin-component-scaled MP2 (SCS-MP2)²¹ methods to determine accurate interaction potentials. The counterpoise (CP) method has been adopted to correct for basis set superposition error (BSSE)

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in the computations of the potential energy surface points.^{22–24} The quadrupole–quadrupole interaction energies are calculated and subtracted from the total electronic energies in order to extract the van der Waals contribution to the potential energy surface. The C_6 coefficients are obtained from an analytical representation of the computed potential energy points using an appropriate function least-squares fitting. We demonstrate how to obtain the C_6 coefficients for Ag–Ag, Ag–H, and Ag–C in order to compute van der Waals energies for silver clusters adsorbed on the graphite surface.¹⁵ The next section describes the ab initio methods and the vdW model used. The third section gives the results and the discussions. Conclusions are given in the final section.

■ AB INITIO METHODS AND THE LONG-RANGE INTERACTION MODELS

Quadrupole–Quadrupole Interaction. At long range, the dominant electrostatic contribution to the PES that describes interactions between the silver dimer Ag_2 and the species Ag_2 , H_2 , and C_6H_6 is the quadrupole–quadrupole interaction. We can evaluate the magnitude of this interaction in two ways: By extracting effective quadrupole moments of the two monomers from an analysis of the interaction of the monomers at large distances or by computing the quadrupole moments of the two monomers using ab initio techniques.

Diep and Johnson extracted the quadrupole moment of H_2 from an analysis of the long-range interaction between two H_2 molecules.^{25,26} We follow their approach to estimate the quadrupole moment of Ag_2 from an analysis of the long-range Ag_2 – H_2 interaction. The interaction between two homonuclear diatomic molecules can be written in the form

$$V(R, \theta_1, \theta_2, \phi_{12}) = \sum_{l_1, l_2, l} V_{l_1, l_2, l}(R) G_{l_1, l_2, l}(\theta_1, \theta_2, \phi_{12}) \quad (1)$$

where R is the separation between the centers of mass of the monomer units, θ_1 and θ_2 are angles which give the orientations of the monomer units with respect to the line joining the centers of the mass of the monomer units, and ϕ_{12} is the torsional angle describing the deviation from the planar structure (see Figure 1). The $V_{l_1, l_2, l}(R)$ terms are functions of the center of the mass distance and the $G_{l_1, l_2, l}(\theta_1, \theta_2, \phi_{12})$ terms are coupled spherical harmonics describing the angular dependencies. The most important $G_{l_1, l_2, l}(\theta_1, \theta_2, \phi_{12})$ functions in the present application are

$$G_{0,0,0}(\theta_1, \theta_2, \phi_{12}) = 1 \quad (2)$$

$$G_{2,0,2}(\theta_1, \theta_2, \phi_{12}) = \frac{5}{2}(3 \cos^2 \theta_1 - 1) \quad (3)$$

$$G_{0,2,2}(\theta_1, \theta_2, \phi_{12}) = \frac{5}{2}(3 \cos^2 \theta_2 - 1) \quad (4)$$

$$G_{2,2,4}(\theta_1, \theta_2, \phi_{12}) = \frac{45}{4\sqrt{70}}[2(3 \cos^2 \theta_1 - 1)(3 \cos^2 \theta_2 - 1) - 16 \sin \theta_1 \cos \theta_1 \sin \theta_2 \cos \theta_2 \cos \phi_{12} + \sin^2 \theta_1 \sin^2 \theta_2 \cos(2\phi_{12})] \quad (5)$$

We have computed the ab initio PES of the Ag_2 – H_2 complex using the CCSD(T) level of theory. The BSSE error has been corrected with the CP method. It arises because of a spurious attractive contribution: the monomers are stabilized in the

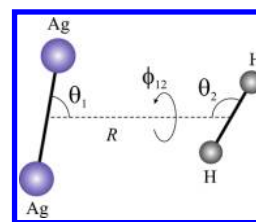


Figure 1. Coordinates of Ag_2 – H_2 .

complex because the basis functions on one monomer add flexibility to the basis on the other.²³ Therefore, all energies are evaluated using the basis set of the whole dimer. The interaction potential of two species $A = \text{Ag}_2$ and $B = \text{H}_2$ at the point $(R, \theta_1, \theta_2, \phi_{12})$ has been computed as follows:

$$V_{AB} = E_{AB} - E_A^{(\text{CP})} - E_B^{(\text{CP})} \quad (6)$$

where the total electronic energy of the interacting system E_{AB} and the energies of the two isolated monomers A and B , $E_A^{(\text{CP})}$ and $E_B^{(\text{CP})}$, respectively, have been computed with the AB dimer basis at different $(R, \theta_1, \theta_2, \phi_{12})$ points.

In our calculations, we have kept the H_2 bond length fixed at 0.7668 Å (the vibrationally averaged bond length²⁵ for the $v = 0$ state of H_2 , 1 Å = 10^{-10} m) and the Ag_2 bond length fixed at 2.53 Å, which is the experimentally determined value.^{27,28} The correlation-consistent polarized valence triple- ζ basis with the use of small-core relativistic pseudopotential (cc-pVTZ-PP)²⁹ has been used for the silver atom. The Dunning basis set aug-cc-pVQZ (augmented correlation-consistent polarized valence quadruple- ζ)³⁰ has been adopted for the hydrogen atom. It was unfeasible to employ larger augmented basis functions because of computational resources available. Ab initio calculations are carried out on a grid in $(R, \theta_1, \theta_2, \phi_{12})$. Nineteen R values ranging from 3 Å to 13 Å have been used, while the angles $(\theta_1, \theta_2, \phi_{12})$ are all taken to be multiples of 30°. Calculations have been performed with the MOLPRO computer program.³¹ The PES has been fitted with the least-squares method by including the most significant terms using the function²⁵

$$V(R, \theta_1, \theta_2, \phi_{12}) = V_{0,0,0}(R)G_{0,0,0}(\theta_1, \theta_2, \phi_{12}) + V_{0,2,2}(R)G_{0,2,2}(\theta_1, \theta_2, \phi_{12}) + V_{2,0,2}(R)G_{2,0,2}(\theta_1, \theta_2, \phi_{12}) + V_{2,2,4}(R)G_{2,2,4}(\theta_1, \theta_2, \phi_{12}) \quad (7)$$

Including the angular functions $G_{2,2,0}$ and $G_{2,2,2}$ in the fit does not lead to substantial changes in the $V_{0,0,0}$, $V_{0,2,2}$, $V_{2,0,2}$, and $V_{2,2,4}$ coefficients. The radial coefficients $V_{0,0,0}$, $V_{0,2,2}$, $V_{2,0,2}$, and $V_{2,2,4}$ at each value of R are given in Table 1 and have been plotted as a function of R in Figure 2.

The $G_{2,2,4}(\theta_1, \theta_2, \phi_{12})$ term as given in eq 5 possesses the same angular dependence as the electrostatic quadrupole–quadrupole interaction for which the energy is²⁵

$$E^{(\text{Q-Q})} = \frac{3Q_1Q_2}{4R^5}[2(3 \cos^2 \theta_1 - 1)(3 \cos^2 \theta_2 - 1) - 16 \sin \theta_1 \cos \theta_1 \sin \theta_2 \cos \theta_2 \cos \phi_{12} + \sin^2 \theta_1 \sin^2 \theta_2 \cos(2\phi_{12})] \quad (8)$$

Comparing eqs 5 and 8, we obtain

$$\frac{45V_{2,2,4}}{4\sqrt{70}} = \frac{3Q_1Q_2}{4R^5} \quad (9)$$

Table 1. Radial Coefficients of the $\text{Ag}_2\text{--H}_2$ Complex^a

R	$V_{0,0,0}$	$V_{0,2,2}$	$V_{2,0,2}$	$V_{2,2,4}$
3.0	0.156693	0.0183878	0.044432	0.0302595
3.3	0.0510573	0.00333728	0.00721094	0.00883353
3.4	0.0354891	0.00133534	0.00359628	0.00624216
3.6	0.0142329	−0.000273549	0.000241686	0.00339459
3.8	0.00298516	−0.000708938	−0.000747846	0.0021528
4.0	−0.00278645	−0.000726849	−0.000981893	0.00155065
4.2	−0.00545407	−0.000605459	−0.000972875	0.00120795
4.4	−0.00641632	−0.000500916	−0.000927695	0.000974845
4.7	−0.00619726	−0.000349242	−0.000788792	0.000732855
5.0	−0.00520378	−0.000241203	−0.000643362	0.000548774
5.5	−0.00340795	−0.000129263	−0.000409073	0.000354134
6.0	−0.00209481	−0.0000708426	−0.000244822	0.000230179
7.0	−0.000796964	−0.0000212011	−0.0000804702	0.00010807
8.0	−0.000330661	-7.59911×10^{-6}	−0.0000286521	0.0000560129
9.0	−0.000162547	-3.26847×10^{-6}	−0.0000115431	0.0000312868
10.0	−0.000086856	-1.53383×10^{-6}	-5.26951×10^{-6}	0.0000186544
11.0	−0.000050916	-8.71005×10^{-7}	-2.60594×10^{-6}	0.0000115051
12.0	−0.000032574	-5.02917×10^{-7}	-1.39628×10^{-6}	7.45195×10^{-6}
13.0	−0.000022601	-3.05714×10^{-7}	-7.94644×10^{-7}	4.99668×10^{-6}

^a The intermolecular distance R is given in units of Å, and the coefficients are in units of eV = 0.160 217 7 aJ.

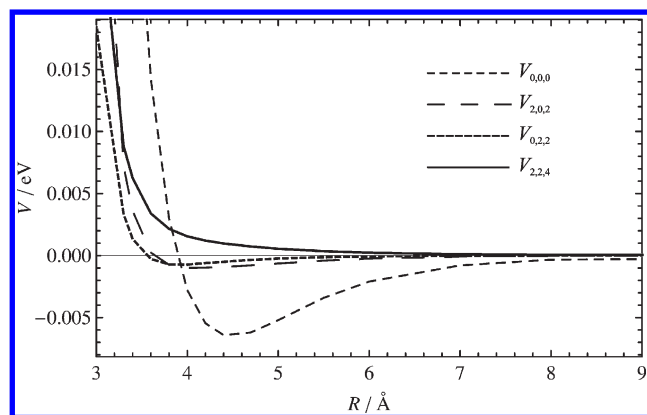


Figure 2. The radial coefficients $V_{0,0,0}$, $V_{0,2,2}$, $V_{2,0,2}$, and $V_{2,2,4}$ of the $\text{Ag}_2\text{--H}_2$ complex plotted as a function of R .

where Q_1 and Q_2 are the quadrupole moments of the silver dimer and the hydrogen molecule, respectively. Thus, we obtain the value 8.13251 D Å for the quadrupole moment of the silver dimer using the quadrupole moment 0.650 D Å of H_2 ($1 \text{ D} = 3.33564 \times 10^{-30} \text{ C} \cdot \text{m}$).²⁶ For comparison, the quadrupole moment of the silver dimer calculated using the Gaussian09 program³³ is 6.7469 D Å at the HF/cc-pVTZ level and 5.9712 D Å at the CCD/aug-cc-pVTZ level. Our calculated value of 8.13251 D Å has been used in subsequent calculations unless stated otherwise. The accurate method used for two homonuclear diatomic molecules H_2 and Ag_2 cannot be applied to the $\text{Ag}_2\text{--benzene}$ complex. Fortunately, it has been observed that the HF method produces accurate quadrupole moments for benzene.³³ Therefore, only the Gaussian09 program was used to compute the benzene quadrupole moment $-5.8859 \text{ D} \cdot \text{Å}$, which compares well with the experimental values -5.65 and $-6.07 \text{ D} \cdot \text{Å}$ (the experimental values are multiplied by the factor 1.5 because of different definitions of the quadrupole moment).^{34,35} These computed moments were used to subtract the quadrupole–quadrupole interaction energies from the total electronic interaction energies of the $(\text{Ag}_2)_2$, $\text{Ag}_2\text{--H}_2$, and $\text{Ag}_2\text{--C}_6\text{H}_6$ complexes in order to obtain the C_6 van der Waals coefficients for the Ag--Ag , Ag--H , and Ag--C atom pairs.

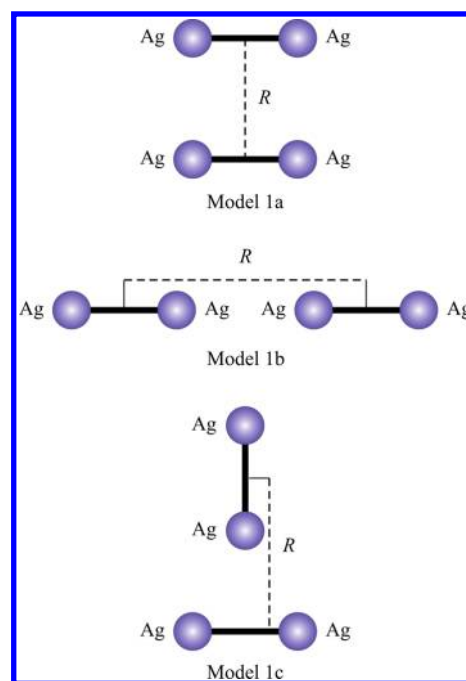


Figure 3. The vdW models 1a–1c.

At large R values, the $\text{Ag}_2\text{--X}$ interaction energies obtained from our ab initio calculations include small contributions from induction effects and from three-body dispersion effects. These two contributions both have magnitudes that are only a few percent of the total interaction energy, which is comparable to the fitting error in the least-squares fits we describe below. They are also typically opposite in sign. Consequently, for the sake of simplicity, we have neglected these minor contributions to the $\text{Ag}_2\text{--X}$ PES.

van der Waals Models. The vdW interactions come from correlations of electron density fluctuations in the regions separated in space. We wish to estimate the vdW dispersion energies for large distances with the aim to study the silver clusters adsorbed on the graphite (graphene) surface.¹⁵ We design vdW dimer models shown in Figures 3–5 to perform the ab initio calculations of the potential energy points as a function of the intermolecular distance R . In model 1a (see Figure 3), one Ag_2 silver cluster is parallel to another Ag_2 cluster. In model 1b, two Ag_2 clusters are on the same line. In model 1c, two Ag_2 clusters are perpendicular to each other forming a T shape. The nuclear distance in each monomer unit is kept fixed at $R_{\text{AgAg}} = 2.530 \text{ Å}$.^{27,28} Similarly, in model 2a, one Ag_2 silver cluster is parallel to one hydrogen molecule; in model 2b, one Ag_2 silver cluster and one hydrogen molecule are located on the same line; and in model 2c, one silver cluster and one hydrogen molecule are in a T shape (see Figure 4). The nuclear distance in the Ag_2 silver cluster is kept fixed at 2.530 Å , and the nuclear distance in the H_2 molecule is fixed at $R_{\text{HH}} = 0.7668 \text{ Å}$ in models 2a, 2b, and 2c. Models 3a and 3b illustrate two different structures of vdW clusters where one Ag_2 silver cluster is attached to C_6H_6 (see Figure 5). In model 3a, the silver cluster is parallel to the line of two carbon atoms crossing the benzene center above the benzene molecule. In model 3b, the silver cluster is perpendicular to the benzene plane on the top of its center of mass. The Ag--Ag distance of the Ag_2 silver cluster and the C=C and C--H bond lengths of benzene are kept fixed at the values of the corresponding isolated

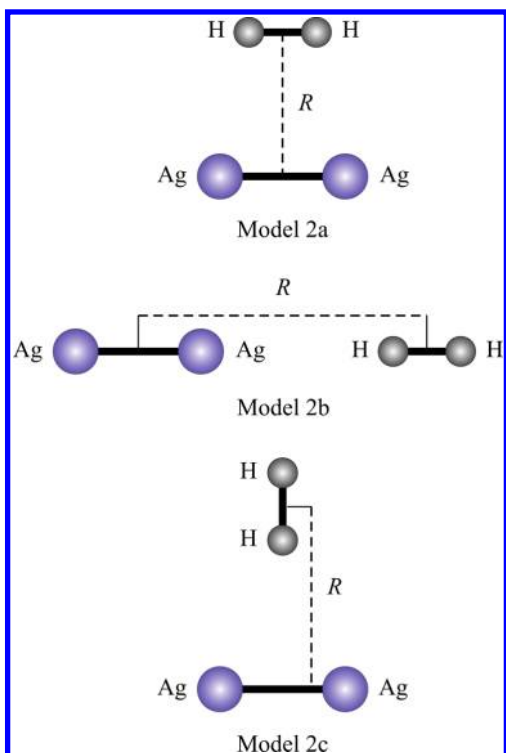


Figure 4. The vdW models 2a–2c.

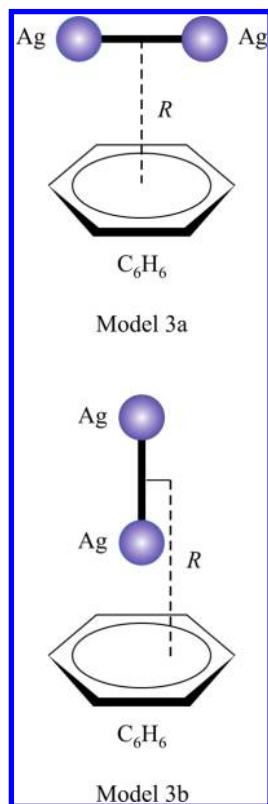


Figure 5. The vdW models 3a and 3b.

molecules, that is, $R_{\text{AgAg}} = 2.530 \text{ \AA}$ for Ag–Ag, $R_{\text{CC}} = 1.391 \text{ \AA}$ for C=C, and $R_{\text{CH}} = 1.095 \text{ \AA}$ for C–H distances.³⁶

We use the CCSD(T) method to obtain BSSE-corrected interaction potentials for models 1a, 1b, 1c, 2a, 2b, and 2c. We

have been limited to the SCS-MP2 and ordinary MP2 methods to calculate potential energies for models 3a and 3b because of computational costs. Potentials are obtained by varying the distance R as defined in Figures 3–5. We have been able to use augmented (diffuse) basis functions for these computations. Therefore, the aug-cc-pVTZ-PP basis sets have been used for the silver atom, and the aug-cc-pVQZ and aug-cc-pVTZ basis sets have been used for the hydrogen and carbon atoms, respectively. The frozen core approximation has been used for the 1s electrons of the carbon atoms in all calculations.

We have removed the quadrupole–quadrupole interaction energy from the total electronic interaction energy using eq 8. The magnitude and sign of the quadrupole–quadrupole interaction depends on the relative orientations of the molecules. In models 1a, 1b, 2a, 2b, and 3a, the quadrupole–quadrupole interaction is repulsive, and in 1c, 2c, and 3b, it is attractive. The quadrupole–quadrupole interaction and the dispersion interaction have roughly the same order of magnitude in these systems.

After removing the quadrupole–quadrupole interaction contribution, we assume that the potential energies at large distance result from the contribution of the London type dispersion interaction energies¹¹ as

$$V = - \sum_i C_6^{(i)} R_i^{-6} \quad (10)$$

where the summation is over atomic pairs and C_6 is a vdW coefficient for each atom pair. The potential energies of our specific systems can then be written as

$$-V = C_6^{(\text{AgAg})} [2R^{-6} + 2(R^2 + R_{\text{AgAg}}^2)^{-3}] \quad (11)$$

$$-V = C_6^{(\text{AgAg})} [(R - R_{\text{AgAg}})^{-6} + 2R^{-6} + (R + R_{\text{AgAg}})^{-6}] \quad (12)$$

$$-V = 2C_6^{(\text{AgAg})} \left\{ \left[\left(R - \frac{1}{2}R_{\text{AgAg}} \right)^2 + \frac{1}{4}R_{\text{AgAg}}^2 \right]^{-3} + \left[\left(R + \frac{1}{2}R_{\text{AgAg}} \right)^2 + \frac{1}{4}R_{\text{AgAg}}^2 \right]^{-3} \right\} \quad (13)$$

$$-V = C_6^{(\text{AgH})} \left\{ 2 \left[R^2 + \frac{1}{4}(R_{\text{AgAg}} + R_{\text{HH}})^2 \right]^{-3} + 2 \left[R^2 + \frac{1}{4}(R_{\text{AgAg}} - R_{\text{HH}})^2 \right]^{-3} \right\} \quad (14)$$

$$-V = C_6^{(\text{AgH})} \left[\left(R - \frac{1}{2}R_{\text{AgAg}} - \frac{1}{2}R_{\text{HH}} \right)^{-6} + \left(R + \frac{1}{2}R_{\text{AgAg}} - \frac{1}{2}R_{\text{HH}} \right)^{-6} + \left(R - \frac{1}{2}R_{\text{AgAg}} + \frac{1}{2}R_{\text{HH}} \right)^{-6} + \left(R + \frac{1}{2}R_{\text{AgAg}} + \frac{1}{2}R_{\text{HH}} \right)^{-6} \right] \quad (15)$$

$$-V = 2C_6^{(\text{AgH})} \left\{ \left[\left(R - \frac{1}{2}R_{\text{HH}} \right)^2 + \frac{1}{4}R_{\text{AgAg}}^2 \right]^{-3} + \left[\left(R + \frac{1}{2}R_{\text{HH}} \right)^2 + \frac{1}{4}R_{\text{AgAg}}^2 \right]^{-3} \right\} \quad (16)$$

$$\begin{aligned} -V - C_6^{(\text{AgH})} & \left\{ 2 \left[R^2 + \left(R_{\text{CC}} + R_{\text{CH}} - \frac{1}{2}R_{\text{AgAg}} \right)^2 \right]^{-3} + 2 \left[R^2 + \left(R_{\text{CC}} + R_{\text{CH}} + \frac{1}{2}R_{\text{AgAg}} \right)^2 \right]^{-3} \right. \\ & + 4 \left[R^2 + \frac{1}{4}(R_{\text{AgAg}} - R_{\text{CC}} - R_{\text{CH}})^2 + \frac{3}{4}(R_{\text{CC}} + R_{\text{CH}})^2 \right]^{-3} \\ & \left. + 4 \left[R^2 + \frac{1}{4}(R_{\text{AgAg}} + R_{\text{CC}} + R_{\text{CH}})^2 + \frac{3}{4}(R_{\text{CC}} + R_{\text{CH}})^2 \right]^{-3} \right\} \\ & = C_6^{(\text{AgC})} \left\{ 2 \left[R^2 + \left(R_{\text{CC}} - \frac{1}{2}R_{\text{AgAg}} \right)^2 \right]^{-3} + 2 \left[R^2 + \left(R_{\text{CC}} + \frac{1}{2}R_{\text{AgAg}} \right)^2 \right]^{-3} \right. \\ & + 4 \left[R^2 + \frac{1}{4}(R_{\text{AgAg}} - R_{\text{CC}})^2 + \frac{3}{4}(R_{\text{CC}})^2 \right]^{-3} \\ & \left. + 4 \left[R^2 + \frac{1}{4}(R_{\text{AgAg}} + R_{\text{CC}})^2 + \frac{3}{4}(R_{\text{CC}})^2 \right]^{-3} \right\} \quad (17) \end{aligned}$$

and

$$\begin{aligned} -V - C_6^{(\text{AgH})} & \left\{ 6 \left[\left(R - \frac{1}{2}R_{\text{AgAg}} \right)^2 + (R_{\text{CC}} + R_{\text{CH}})^2 \right]^{-3} + 6 \left[\left(R + \frac{1}{2}R_{\text{AgAg}} \right)^2 + (R_{\text{CC}} + R_{\text{CH}})^2 \right]^{-3} \right\} \\ & = C_6^{(\text{AgC})} \left\{ 6 \left[\left(R - \frac{1}{2}R_{\text{AgAg}} \right)^2 + R_{\text{CC}}^2 \right]^{-3} + 6 \left[\left(R + \frac{1}{2}R_{\text{AgAg}} \right)^2 + R_{\text{CC}}^2 \right]^{-3} \right\} \quad (18) \end{aligned}$$

where eqs 11–18 refer to models 1a–3b, respectively. If we use the linear equation $Y = CX + \dots$ to least-squares fit the points of Y versus X , when Y and X are equal to the corresponding values eqs 11–18, the slopes of the lines are the corresponding C_6 coefficients.

RESULTS AND DISCUSSION

The ab initio computed potential energies of molecular models 1a–3b are obtained using the method introduced in the previous section. The numerical values for the potential energy minima

Table 2. Potential Energy Minimum Values and the Equilibrium Separations for the Molecular Systems in Models 1b–3b

model	V_{min}/eV	$R_e/\text{\AA}$
1a	−0.1276305	3.11
1b	−0.3072458	5.27
1c	−0.8390004	3.73
2a	−0.0022253	4.67
2b	−0.0079236	4.34
2c	−0.0137295	4.03
3a	−0.1697626	3.32
3b	−0.3579442	3.86

and equilibrium distances are given in Table 2. The C_6 coefficients of the potential energy functions in eqs 11–18 were optimized with the least-squares method using the computed ab initio points as data. Figure 6 shows the potential energy curves as the function of the distance R for models 1a–3b. The smallest R value used in the least-squares fit for various models was 5.5, 6, 7.5, 5.5, 7, 5.5, 8, and 6.5 Å for models 1a–3b, respectively. The largest R value used in the least-squares fit was 15 Å for all eight models. The vdW C_6 coefficients for silver–silver, silver–hydrogen, and silver–carbon atoms from these different molecular models are given in Table 3. All calculated coefficients are well-defined as the associated standard deviations are small. The average values of $C_6^{(\text{AgAg})}$, $C_6^{(\text{AgH})}$, and $C_6^{(\text{AgC})}$ for different models are also given in Table 3.

We see that our calculations yield slightly different values for the C_6 coefficients depending on the mutual orientations of the two species. As we mentioned above, we have neglected some higher-order contributions that are small in magnitude to simplify our treatment. It is possible that the orientational dependence of the computed C_6 coefficients originates in the neglect of these small higher-order contributions. To probe more deeply into this question, we first need to investigate the basis set dependence of these higher-order contributions to ensure that they are converged at the levels of theory employed here. However, this is beyond the scope of the present work and will be revisited in a future investigation.

The CP corrected potential energy minima and equilibrium distances were computed with CCSD(T) method for models 1a–2c and with SCS-MP2 for models 3a and 3b. As shown in Table 2, for the $\text{Ag}_2\text{--Ag}_2$ complex, the configuration in model 1c is the most stable one which is expected because of the attractive quadrupole–quadrupole interaction. The configurations in models 1a and 1b are significantly less stable than the one in 1c (i.e., −0.128 and −0.307 eV compared to −0.839 eV, respectively) because of the repulsive quadrupole–quadrupole interaction. The interaction energies of models 2a–2c show a pattern analogous to that for models 1a–1c, although their magnitudes are much smaller with the potential energy minimum values being −0.00223, −0.00792, and −0.01373 eV for models 2a, 2b, and 2c, respectively. In a similar way, the $\text{Ag}_2\text{--C}_6\text{H}_6$ complex possesses a more stable structure when the quadrupole–quadrupole interaction is attractive yielding potential energy minimum values of −0.358 eV for model 3b and −0.170 eV for model 3a.

For models 1a–1c, the C_6 coefficients were calculated at different levels of theory (MP2, SCS-MP2, and CCSD(T)) in order to study the effect of different ab initio methods on dispersion energy. Moreover, we calculated the C_6 coefficients using the two

different quadrupole moment values for the silver dimer obtained in the previous section. The MP2 theory is known to overestimate the interaction energies of complex systems.^{37–39} There are also convergence problems in the MP n series ($n = 2, 3$, and 4).⁴⁰

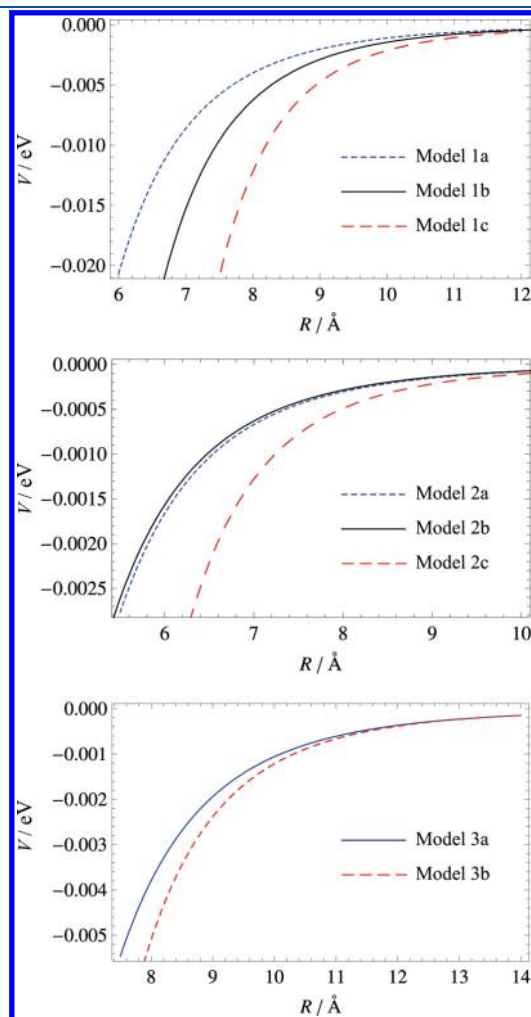


Figure 6. The potential energy curves with the quadrupole–quadrupole contribution subtracted as the function of the distance R for models 1a–3b.

However, the SCS-MP2 method largely corrects these problems.^{21,41} Our C_6 calculations support the previous conclusions on the MP2 methods. As shown in Table 3, the MP2 method gives much larger values than the CCSD(T) method when augmented basis sets are employed. We also did MP2 calculations using a nonaugmented basis which yielded C_6 values close to the CCSD(T) results tabulated in Table 3. This good agreement is likely due to two canceling errors, the shortcomings of the approximations in the MP2 method, and the neglect of the diffuse functions in the basis set.

The SCS-MP2 C_6 coefficients are systematically closer to the CCSD(T) coefficients than to the MP2 coefficients for all models. Interestingly, looking at the average values, the ratio between the MP2 and the SCS-MP2 values is 1.36 for $C_6^{(\text{AgAg})}$ and 1.27 for $C_6^{(\text{AgC})}$, which are similar numbers. We can extrapolate the average CCSD(T) value for the Ag–C coefficient using MP2 results if we assume that the ratio between the average SCS-MP2 and CCSD(T) values is also similar for $C_6^{(\text{AgAg})}$ and $C_6^{(\text{AgC})}$. This assumption allows us to roughly estimate the CCSD(T) $C_6^{(\text{AgC})}$ coefficient as shown in Table 3. Model 1a–1c calculations show that using the quadrupole moment calculated with lower level of theory hardly influences the average $C_6^{(\text{AgAg})}$ values (see the comparison in Table 3). We believe that these conclusions also apply to our values of the $C_6^{(\text{AgC})}$ coefficients. Thus, we estimate that the error caused by the SCS-MP2 method to the average C_6 coefficients is around 10%.

The three small values of $C_6^{(\text{AgH})}$ coefficients shown in Table 3 indicate weak van der Waals interaction between H and Ag. It is interesting that models 2a, 2b, and 2c show similar behavior as 1a, 1b, and 1c. The a models produce the highest values and the b models the lowest values. For models 1a–1c, the CCSD(T) coefficients shown in the last column of Table 3 give values which are close. This is encouraging because these results are produced with the highest level of theory of our calculations and should be closest to the true values.

The van der Waals potential energy coefficients we have obtained can be compared with the four sets (numbered 1–4) of empirical model results for the $C_6^{(\text{AgAg})}$ coefficient.¹⁵ These empirical model results were obtained as follows. The set 1 expression is based on Elstner et al.'s model⁸ and is written as

$$C_6^{(\alpha\alpha)} = \frac{3}{4} \sqrt{N_\alpha P_\alpha^3} \quad (19)$$

Table 3. van der Waals C_6 Coefficients for the Silver–Silver, Silver–Hydrogen, and Silver–Carbon Atoms Obtained from Models 1a–3b^a

model	MP2	MP2 ^b	SCS-MP2	SCS-MP2 ^b	CCSD(T)
1a	482.80(255)	426.54(357)	378.09(186)	321.82(283)	298.94(145)
1b	329.26(164)	310.72(205)	265.82(142)	247.28(255)	266.23(202)
1c	367.76(262)	425.22(78)	286.11(216)	343.57(71)	279.84(200)
average $C_6^{(\text{AgAg})}$	393.27	387.49	310.00	304.22	281.67
2a					20.66(9)
2b					18.73(3)
2c					19.29(5)
average $C_6^{(\text{AgH})}$					19.56
3a	105.95(200)		79.98(183)		
3b	86.94(241)		62.23(40)		
average $C_6^{(\text{AgC})}$	96.45		71.10		64.60 ^c

^a The uncertainties given in parentheses are one-standard errors in the least significant digit. The coefficients are in units of $\text{eV}\text{\AA}^6$. ^b Silver quadrupole moment 6.7469 DÅ computed at the HF/cc-pVTZ level was used in these calculations. ^c Extrapolated value from MP2 results.

The quantity P_α is the polarizability of the silver atom. The Slater–Kirkwood effective number of valence electrons N_α for the silver atom is estimated using the data for the Sn–Xe atoms. The set 2 value has been calculated using Amar’s method⁴² where C_6 has been obtained from a system where a silver atom interacts with a Ag(100) surface. It has been noticed that the calculated coefficients are smaller than those employed in the previous simulations of the same system.⁴² The set 3 value is taken from work where the coefficients are obtained from the molecular system Ag₂Te.⁴³ The set 4 result is computed with Grimme’s method⁴⁴ where the van der Waals parameter in units of J nm⁶ mol^{−1} is

$$C_6^{(\alpha\alpha)} = 0.05N_I^{(\alpha)}P_\alpha \quad (20)$$

The quantity I_P is the atomic ionization potential and P is the static dipole polarizability, both expressed in atomic units. The value of N is 2, 10, 18, 36, and 54 for the atoms in rows 1–5 of the periodic table.

The mixed empirical van der Waals interaction coefficients $C_6^{(\alpha\beta)}$ have been obtained from two different formulas. The first is written as follows⁸

$$C_6^{(\alpha\beta)} = \frac{2C_6^{(\alpha\alpha)}C_6^{(\beta\beta)}P_\alpha P_\beta}{P_\alpha^2 C_6^{(\beta\beta)} + P_\beta^2 C_6^{(\alpha\alpha)}} \quad (21)$$

and the second one, which puts less emphasis on the contribution from a lighter atom, is⁴⁴

$$C_6^{(\alpha\beta)} = \sqrt{C_6^{(\alpha\alpha)}C_6^{(\beta\beta)}} \quad (22)$$

Four values, 486.14, 60.60, 389.22, and 285.25 eVÅ⁶ of $C_6^{(\text{AgAg})}$, which belong to sets 1–4, respectively, are given by Jalkanen et al.¹⁵ Clearly, the set 4 value 285.25 eVÅ⁶ agrees best with our 281.67 eVÅ⁶ ab initio number.

As shown in Table 3, the calculated values (105.95 and 86.94 eVÅ⁶ for the MP2 and 79.98 and 62.23 eVÅ⁶ for the SCS-MP2) of the $C_6^{(\text{AgC})}$ coefficients show trends similar to those of the $C_6^{(\text{AgAg})}$ coefficients. The MP2 method overestimates the coefficients, and models 1a and 3a give higher values than models 1b and 3b, respectively. The empirical results for the $C_6^{(\text{AgC})}$ coefficients¹⁵ were obtained using eq 21 for sets 1–3 and eq 22 for set 4. The empirical numbers are 125.24, 26.60, 110.68, and 75.97 eVÅ⁶ for sets 1–4, respectively. The set 4 value is clearly closest to our average ab initio value of 71.10 eVÅ⁶.

The empirical models used to compute the C_6 dispersion coefficients produce different values depending on the theoretical approach and on the parameters required. However, our new ab initio method provides a possibility to yield accurate C_6 dispersion coefficients without using any experimental parameters, such as atomic polarizabilities, the Slater–Kirkwood effective number, and so forth. They are obtained directly from the potential energy surface at large nuclear distances for an appropriate vdW complex.

CONCLUSION

Weak interactions at long nuclear separations are often not well characterized, although they are important in many different types of systems such as molecular complexes, biological molecules, metal clusters, and molecules adsorbed on surfaces. Modern density functional theory has become a practical computational tool to study these systems, but unfortunately, many current functionals do not model weak van der Waals type interactions very well. More sophisticated electronic structure

calculation methods would be better in this respect, but unfortunately, their usefulness is often limited to smaller systems than in the case of the DFT methods. Consequently, when larger systems are studied, one possibility is to correct DFT energies with London type empirical formulas. In this contribution, we have investigated how to obtain these empirical corrections accurately in the case of metal clusters. A new method to obtain C_6 dispersion coefficients using ab initio calculations of appropriate vdW dimers is introduced. Eight different vdW dimer systems are designed to obtain intermonomer potential energy surfaces using CCSD(T), MP2, and SCS-MP2 methods. The C_6 coefficients for silver–silver, silver–hydrogen, and silver–carbon atom systems are obtained accurately from the analytical representations of the computed ab initio potential energy points. The new method can be extended to other atom pairs. No experimental parameters are needed.

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REFERENCES

- (1) Rydberg, H.; Lundqvist, B. I.; Langreth, D. C.; Dion, M. *Phys. Rev. B* **2000**, *62*, 6997.
- (2) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2004**, *92*, 246401.
- (3) Ziambaras, E.; Kleis, J.; Schröder, E.; Hyldgaard, P. *Phys. Rev. B* **2007**, *76*, 155425.
- (4) Swart, M.; Sola, M.; Bickelhaupt, F. M. *J. Chem. Phys.* **2009**, *131*, 094103.
- (5) Silvestrelli, P. L. *Phys. Rev. Lett.* **2008**, *100*, 053002.
- (6) Tkatchenko, A.; Scheffler, M. *Phys. Rev. Lett.* **2009**, *102*, 073005.
- (7) Mercurio, G.; McNellis, E. R.; Martin, I.; Hagen, S.; Leyssner, F.; Soubatch, S.; Meyer, J.; Wolf, M.; Tegeder, P.; Tautz, F. S.; Reuter, K. *Phys. Rev. Lett.* **2010**, *104*, 036102.
- (8) Elstner, M.; Hobza, P.; Frauenheim, T.; Suhai, S.; Kaxiras, E. *J. Chem. Phys.* **2001**, *114*, 5149.
- (9) Du, A. J.; Smith, S. C. *Nanotechnology* **2005**, *16*, 2118.
- (10) Williams, R. W.; Malhotra, D. *Chem. Phys.* **2006**, *327*, 54.
- (11) London, F. Z. *Phys.* **1930**, *63*, 245.
- (12) Slater, J. C.; Kirkwood, J. G. *Phys. Rev.* **1931**, *37*, 682.
- (13) Casimir, H. B. G.; Polder, D. *Phys. Rev.* **1948**, *73*, 360.
- (14) Halgren, T. A. *J. Am. Chem. Soc.* **1992**, *114*, 7827.
- (15) Jalkanen, J.; Halonen, M.; Fernandez-Torre, D.; Laasonen, K.; Halonen, L. *J. Phys. Chem. A* **2007**, *111*, 12317.
- (16) Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, 1887.
- (17) Hobza, P.; Zahradnik, R. *Chem. Rev.* **1988**, *88*, 871.
- (18) Chalasinski, G.; Gutowski, M. *Chem. Rev.* **1988**, *88*, 943.

- (19) Buckingham, A. D.; Fowler, P. W.; Hutson, J. M. *Chem. Rev.* **1988**, *88*, 963.
- (20) Chalasinski, G.; Szczesniak, M. M. *Chem. Rev.* **1994**, *94*, 1723.
- (21) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095.
- (22) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- (23) Johansson, A.; Kollman, P.; Rothenberg, S. *Theor. Chim. Acta* **1973**, *29*, 49.
- (24) Tsuchiya, T.; Abe, M.; Nakajima, T.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 4463.
- (25) Diep, P.; Johnson, J. K. *J. Chem. Phys.* **2000**, *112*, 4465.
- (26) Diep, P.; Johnson, J. K. *J. Chem. Phys.* **2000**, *113*, 3480.
- (27) Ran, Q.; Schmude, R.; Gingerich, K.; Wilhite, D.; Kingcade, J. *J. Phys. Chem.* **1993**, *97*, 8535.
- (28) Krämer, H.; Beutel, V.; Weyers, K.; Demtröder, W. *Chem. Phys. Lett.* **1992**, *193*, 331.
- (29) Peterson, K. A.; Puzzarini, C. *Theor. Chem. Acc.* **2005**, *114*, 283.
- (30) Dunning, T. H., Jr. *Chem. Phys.* **1989**, *90*, 1007.
- (31) Werner, H.-J. et al. *MOLPRO*, version 2009.1, a package of ab initio programs; 2009; see <http://www.molpro.net>.
- (32) Frisch, M. J. et al. *Gaussian 09*, revision A.1.; Gaussian Inc.: Wallingford, CT, 2009.
- (33) Hernández-Trujillo, J.; Vela, A. *J. Phys. Chem.* **1996**, *100*, 6524.
- (34) Battaglia, M. R.; Buckingham, A. D.; Williams, J. H. *Chem. Phys. Lett.* **1981**, *78*, 421.
- (35) Ritchie, G. L. D.; Watson, J. N. *Chem. Phys. Lett.* **2000**, *322*, 143.
- (36) Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier: New York, 1987.
- (37) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem.* **1996**, *100*, 18790.
- (38) Sinnokrot, M. O.; Valeev, E. F.; Sherrill, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 10887.
- (39) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M. *J. Chem. Phys.* **2004**, *120*, 647.
- (40) Olsen, J.; Christiansen, O.; Koch, H.; Jørgensen, P. *J. Chem. Phys.* **1996**, *105*, 5082.
- (41) Piacenza, M.; Grimme, S. *ChemPhysChem* **2005**, *6*, 1554.
- (42) Amar, J. *Phys. Rev. B* **2003**, *67*, 165425.
- (43) Surong, Q.; Zhao, Y.; Jing, X.; Li, X.; Su, W. *Int. J. Quantum Chem.* **2004**, *100*, 293.
- (44) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.