ARTICLE

DFT Study on the Intermolecular Substrate-mediated Interaction Energy in the Self-assembly of Alkanethiols on Silver

Rong Xie[a,b], Tian-jing He[a*], Li He[c], Dong-ming Chen[a], Fan-chen Liu[a]

a. Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China; b. Department of Material Science and Engineering, Anhui Institute of Architecture and Industry, Hefei 230022, China; c. Department of Electronic Science and Technology, University of Science and Technology of China, Hefei 230027, China

The B3LYP/LanL$_1$MB and B3LYP/LanL$_2$DZ methods for Ag atom in conjunction with the 6-31G(d) basis set for S, C and H atoms were used to optimize the geometries and calculate the energies for $(SCH_3)_m Ag_{20}$ (m=1-4), respectively. A single molecular adsorption energy of $(SCH_3)_m$ (m=1-4) on Ag_{20} and the intermolecular substrate-mediated interaction energy were evaluated. The results revealed that there is a proportional relation between the single molecular adsorption energy and the substrate-mediated intermolecular interaction energy. The results qualitatively demonstrated the semi-empirical expression for the substrate-mediated interaction energy proposed previously by us is consistent with the results of the density functional theory.

Key words: Self-assembled monolayer, Substrate-mediated interaction, Density functional theory, Alkanethiol

I. INTRODUCTION

It is well known that the interaction between adsorbates is one of the most important factors to determine the surface adsorption behavior on solid surface [1-8]. It decides the formation of two-dimensional structure, phase transformation, the dependence of adsorption heat on degree of coverage, adsorptive dynamics, surface diffusion and catalytic activity, etc. [2,3,8,9]. In recent years, the influence of adsorption behavior on the surface stress of the substrate is actively investigated in many fields [10-16]. The interaction energy between adsorbates takes determinant effect in adsorbate-induced surface stress, especially the substrate-mediated interaction energy is dominant among the components in the lateral interaction energy [17-20].

The interaction energy W between adsorbates consists of direct and indirect parts. The interaction between adsorbates on solid surfaces due to direct mechanisms is usually short-ranged and weak, and therefore the indirect or through-the-substrate mechanism is of considerable interest [1-4]. From the common characteristics of substrate-mediated interaction energy W_{sub}, we had ever brought forward [17,19,20] that for weakly adsorbed molecules (such as halide ion, alkanethiol molecule), similar to Sinanoglu-Pitzer-McLachlan's expression of substrate-effected dispersion energy, the substrate-mediated interaction energy can be written
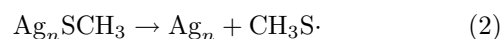
as [17]:

$$W_{sub} = \frac{A_3}{Z} \alpha \frac{|U|}{r^3} \qquad (1)$$

where A_3 is the lattice sum, Z is the nearest-neighbor coordinate number of an adsorbate, α is the molecular polarizability. U is the monatomic or single head-group adsorption energy of adsorbates. r is the adsorbate-adsorbate distance.

Using Eq.(1), we have successfully calculated the electrocompression and the adsorption-induced surface stress of halide adlayer on Au, and studied the sign, magnitude and variational rule of adsorption-induced surface stress of alkanethiols on Au. The results indicate that Eq.(1) reflects the essence of the indirect interaction between adsorbates. However, compared with other formulas of molecular interaction, such as Lennard-Jones potential, Eq.(1) is just a semi-empirical expression. To disclose the essential characters of the substrate-medicated interaction, its quantum chemistry calculation is necessary. However, this kind of calculations has not been reported yet. In this work, we choose $(SCH_3)_m$ (m=1-4) on Ag(111) as the typical mimic molecules of alkanethiols on Ag(111) [24] to make some elementary exploration for the substrate-mediated interaction energy. The idea for the calculation is as follows.

Eq.(1) indicates that the indirect interaction energy W_{sub} directly correlates with the absolute value of unimolecular adsorption energy $|U|$. By calculating the influence of near-neighbor molecule on the unimolecular adsorption energy, we can study the indirect interaction energy. If there is only one CH_3S adsorbate on Ag(111),

$$Ag_n SCH_3 \rightarrow Ag_n + CH_3S \cdot \qquad (2)$$

*Author to whom correspondence should be addressed. E-mail: tj16@ustc.edu.cn

406

where the unimolecular adsorption energy is U_1. If there are $m\,CH_3S$ adsorbates on Ag(111),

$$Ag_n(SCH_3)_m \rightarrow Ag_n(SCH_3)_{m-1} + CH_3S\cdot \qquad (3)$$

the unimolecular adsorption energy U_m of a given molecule CH_3S is composed of two components:

$$U_m = U_1 + (m-1)W \qquad (4)$$

where W is the pair interaction energy between two adsorbates $CH_3S\cdot$. Thus

$$W = \frac{U_m - U_1}{m - 1} \qquad (5)$$

Based on Eqs.(2) and (3) and using density functional theory (DFT), we can directly compute U_1 and U_m, and using Eq.(5), we can calculate the intermolecular interaction energy W. After determining the direct intermolecular interaction energy, we can calculate the indirect interaction energy W_{sub}.

II. COMPUTATIONAL METHOD

An 11-electron relativistic effective core potential (11e-RECP) and 19-electron relativistic effective core potential (19e-RECP), the B3LYP/LanL$_1$MB and B3LYP/LanL$_2$DZ for heavy atom Ag, in conjunction with the 6-31G(d) basis set for C, S and H atoms were used to optimize the geometries and calculate the energies, respectively. All calculations were performed with the GAUSSIAN-98 package [22].

We used the cluster model Ag$_{20}$ to describe the surface of silver. Twenty Ag atoms in the model were set in the double layer, as shown in Fig.1, thirteen Ag atoms on the upper layer (labeled by Arabic numerals) and seven Ag atoms on the under layer (labeled as X$_n$, n=6-8,14,15,19,20). The nearest-neighbor distance of Ag-Ag in bulk of silver 2.890 Å was used in the model without optimization.
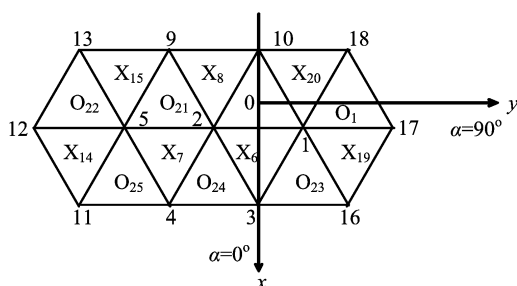

FIG. 1 Model of the Ag$_{20}$ cluster.

III. RESULTS AND DISCUSSION

The geometries of $(SCH_3)_m$ (m=1-4) on Ag$_{20}$ were optimized. The results showed that the $CH_3S\cdot$ adsor-

bate on the Ag surface has two kinds of horizontal positions: O and X positions shown in Fig.1.

The geometry of $CH_3-S-S-CH_3$ formed by two non-adsorbed $CH_3S\cdot$ was calculated and shown in Fig.2, where the two SCH_3 molecules are not in a plane and the total energy is $E=-876.207443$ Hartree.
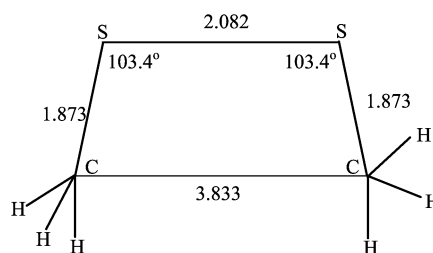

FIG. 2 $(SCH_3)_2$ structure.

The geometry parameters of SCH_3 on Ag$_{20}$ include the adsorption position, the azimuth angle α and rotation angle θ of S−C bond. The azimuth angle α describes the direction of S−C bond relative to the x-axis on the plane of x-y and θ is the angle between the S−C bond and the normal line of the surface of Ag$_{20}$. The geometries and total energies of Ag$_{20}(SCH_3)$ for two examples were optimized and calculated, as shown in Table I. The other O and X positions have similar results. Table I shows that the optimized rotation angle θ is 30° which is in agreement with the experiments [25].

TABLE I Adsorption structure and total energy E of Ag$_{20}(SCH_3)$

Adsorption site	α	θ	E/Hartree	ΔE^a/(kJ/mol)
O$_1$	0	0	−1213.9774685	
O$_1$	30[b]	30[b]	−1213.9819518[b]	−11.77[b]
X$_8$	0	0	−1213.9809311	
X$_8$	60[b]	30[b]	−1213.9841988[b]	−8.58[b]

[a] ΔE is the energy difference between two adsorption structures.
[b] The optimized results.

The adsorption structures, energies and atomic charge densities of Ag$_{20}(SCH_3)_2$ were optimized and calculated, and some of them are shown in Table II. The optimized adsorption positions (with the lowest energy) for two adsorbed SCH_3 are: one SCH_3 on O position and the other on X position to form O$_1$X$_8$ structure, which agrees with the experiments [25]. The optimized distance between two SCH_3 in O$_1$X$_8$ adsorption position is r_{S-S}=4.41 Å and much larger than that of free $(SCH_3)_2$ in Fig.1 (r_{S-S}=2.082 Å). This result demonstrates there is an effective repulsive interaction between the adsorbates SCH_3 due to the substrate Ag$_{20}$ and supports qualitatively the substrate-mediated interaction energy Eq.(1).

TABLE II The charge densities and total energy E of $Ag_{20}(SCH_3)$

Adsorption structure	S	C	H	H	H	E/Hartree
$\alpha = 60°$, $\theta = 30°$[a]	-0.6179	-0.741	0.239	0.232	0.240	-1652.091748
$\alpha = 0°$, $\theta = 0°$	-0.626	-0.753	0.238	0.233	0.232	-1652.0829638

[a] The optimized results.

TABLE III The adsorption energy U of a single SCH_3 in $(SCH_3)_m/Ag_{20}$ (in kJ/mol)[a]

System	Unimolecular adsorption energy	U/(kJ/mol)	
		X_8 position	O_1 position
$(SCH_3)_1/Ag_{20}$	$U_1 = \Delta E_{0\to1}$	-143.1	-128.3
$(SCH_3)_2/Ag_{20}$	$U_2 = \Delta E_{1\to2}$	-132.7	-118.0
$(SCH_3)_4/Ag_{20}$	$U_4 = \Delta E_{3\to4}$	-112.1	-107.2

[a] The basis set for Ag is $LanL_2DZ$. The $LanL_1MB$ basis set has similar results.

The calculated result of charge densities in Table II indicates: (i) When the SCH_3 molecule adsorbs on Ag_{20}, it exists with the ionic state of $(SCH_3)^{-0.65}$, which supports Sellers *et al.*'s result that alkanethiols's chemiadsorption on Au, Ag is in the form of the ion state (RS^-) [25], thus justifies our calculation model in this work. (ii) In the process of chemiadsorption, 0.35 electron flows from SCH_3 to Ag_{20}. This charge transfer is probably the major factor of the chemiadsorption energy of SCH_3 on Ag_{20}. The two adsorbed molecules both transfer charge to Ag_{20} simultaneously, thus they associate with each other through the electron of the substrate and lead to the indirect interaction energy, which is similar to the three-body interaction of orbit interaction theory [32]. (iii) Furthermore, the existence of $(SCH_3)^{-0.65}$-Ag_n^+ indicates there are contributions of the electrostatic interaction to the intermolecular interaction energy and surface stress, which can be investigated by the similar method to that in calculating the electrostatic interaction energy of Cl^--Au_n^+ system [17-20].

After optimizing the adsorption geometries and calculations of energy, we can calculate the unimolecular adsorption energy U_m of $CH_3S\cdot$ on Ag_{20}, as shown in Table III, where

$$U_m = E(Ag_{20}(SCH_3)_m) - [E(Ag_{20}(SCH_3)_{m-1}) + E(CH_3S\cdot)] \quad (6)$$

From Table III, we can see that for both the X_8 and O_1 positions, $|U_4| < |U_2| < |U_1|$ always holds, and for each X_8 position, the absolute value of the adsorption energy is larger than that for O_1 position.

Using Eq.(5) and the data of unimolecular adsorption energy in Table III, we can calculate the intermolecular interaction energy W. For examples, for the adsorption at X_8 position, from the values of U_1 and U_2 we get

$$W = -132.7 + 143.1 = 10.4 \quad (kJ/mol) \quad (7)$$

while from the value of U_4,

$$W = \frac{1}{4-1}(-112.1 + 143.1) = 10.3 \quad (kJ/mol) \quad (8)$$

Thus the magnitudes of intermolecular interaction energy W calculated in these two cases are the same, and are also close to the calculated value from the semi-empirical formula [17,18]. It is known [1-4,17,18] that the intermolecular interaction energy W is the summation of the direct W_d and the indirect interaction energy W_{sub}

$$W = W_d + W_{sub} \quad (9)$$

After determining the direct interaction energy W_d and from W, we can get the indirect interaction energy W_{sub}. We will calculate W_d by the semi-empirical method [17-20].

Although the intermolecular direct interaction energy consists of many components [17-20], in this system studied Lennard-Jones potential and electrostatic interaction energy are dominant, and the other ingredients can be ignored [17-19], thus

$$W_d \approx W_{L-J} + W_{el} \quad (10)$$

Salem pointed out that based upon the summation of the interaction between atoms, the total van der Waals attraction of two long saturated chains can be expressed by the single point interaction energy [26]. For two linear chains of length N (the numbers of CH_3 and CH_2 for alkanethiol molecule), the total van der Waals energy can be expressed by Lennard-Jones (5-25) potential [26],

$$W_{L-J} = \frac{\in^*}{4}\left[\left(\frac{r_0}{r}\right)^{25} - 5\left(\frac{r_0}{r}\right)^5\right] \quad (11)$$

where r_0 is the intermolecular equilibrium distance. $\in^*$ is the Lennard-Jones potential well depth which is proportional to N as

$$\in^* = (N+1) \in \quad (12)$$

Grunze et $al.$ gave $\in^*=25$ kJ/mol for the alkanethiol $C_{10}S$ ($N=10$) [26], thus $\in=25/11$ kJ/mol. By use of Eqs.(11) and (12) we can calculate the Lennard-Jones potential between SCH_3 molecules in $Ag_{20}(SCH_3)_m$ where $N=1$ and $r=r_0$,

$$W_{L-J} = -2 \in = -2 \times \frac{25}{11} = -4.56 \text{ kJ/mol} \quad (13)$$

Grunze et $al.$ pointed out that in the dynamical simulation computation, sometimes the united-atom approximation was used in the methylene and methyl groups, in this case, $-CH_3$ was treated as a united-atom [26]. From Table II, $-CH_3$ as an united-atom can be considered nearly neutral. So the electrostatic energy between SCH_3 molecules on Ag_{20} is approximately equal to that between anions $S^{-0.62}$ on Ag. Similar to the calculation of the electrostatic energy of $Cl^-/Au(111)$ [17], we can calculate the electrostatic energy of $S^{-0.62}/Ag(111)$ system.

Following Langmuir's treatment of Cs on W [27], the electrostatic interaction energy between adions on the metal was derived [18]

$$W_{el} = \frac{14.4(1+\gamma)^2}{Z\varepsilon} \left(\frac{2A_3L^2}{r^3} - \frac{6A_5L^4}{r^5} + \frac{20A_7L^6}{r^7} - \frac{70A_9L^8}{r^9} \right) \quad (14)$$

where ε is the dielectric constant in the adlayer, L is the perpendicular distance of the adatom from the substrate and $(1+\gamma)$ is the charge carried on the adions. The units are W_{el} in eV, r and L in Å. For the $S^{-0.62}/Ag(111)$ system, the used parameters are: $(1+\gamma)^2=0.62^2$, $r=r_0=4.41$ Å, $L=a=2.32$ Å (DFT result, calculation [28]). By using Eq.(14), W_{el} are calculated $W_{el}=21.2$ meV$=2.04$ kJ/mol. Therefore, the intermolecular direct interaction energy between SCH_3 molecules on Ag_{20}

$$\begin{aligned} W_d &= W_{L-J} + W_{el} \\ &= -4.56 + 2.04 = -2.52 \text{ (kJ/mol)} \end{aligned} \quad (15)$$

From Eq.(9) and the intermolecular interaction energy $W=10.4$ kJ/mol calculated by DFT, we get the substrate-mediated interaction energy

$$W_{sub} = W - W_d = 12.9 \text{ (kJ/mol)} \quad (16)$$

In order to examine the application of the semi-empirical Eq.(1), W'_{sub} was calculated by Eq.(1) and compared with the DFT result. For $Ag_{20}(SCH_3)_m$ the parameters in Eq.(1) were chosen as follows. The polarizability of alkanethiol can approximatively be written as the sum of the polarizability of its consistent groups [28]

$$\alpha = \alpha_{SH} + N\alpha_{CH_2} \quad (17)$$

where $\alpha_{CH_2}=1.84\times10^{-24}$ cm^3, $\alpha_{SH}=2.75\times10^{-24}$ cm^3, $N=1$, thus $\alpha\approx\alpha_{SH}+\alpha_{CH_2}=4.59$ Å^3. The other quantities in Eq.(1) are $r=r_0=4.41$ Å, the lattice sum $A_3=10.975$ and $Z=6$ [17]. $|U|=U_m$ is the absolute value of the unimolecular adsorption energy in Table III. $Ag_{20}(SCH_3)_4$ is probably more similar to the self-assembly monolayer of alkanethiols on Ag, and $|U_4|=112.1$ kJ/mol. Using these parameters and Eq.(1), the calculated substrate-mediated interaction energy is $W'_{sub}\cong12.6$ kJ/mol.

By comparing the substrate-mediated interaction energy calculated directly from DFT $W_{sub}=12.9$ kJ/mol with the $W'_{sub}=12.6$ kJ/mol calculated from the semi-empirical Eq.(1), we can see that they are approximately equal with each other. Thus, the DFT results demonstrate the semi-empirical Eq.(1), particularly, supports the idea that the substrate-mediated interaction energy is directly proportional to the absolute value of unimolecular adsorption energy.

It should be noted that although the calculated values of the substrate-mediated interaction energy from two different methods are very close, it does not mean that the very high calculation precision was achieved. The results should be considered as qualitative and primary, because the studied system is too complicated. However, this work provides a new approach to calculate the substrate-mediated interaction energy by DFT.

IV. CONCLUSION

In this work, by using the DFT method and the cluster model $Ag_{20}(SCH_3)_m$, we evaluated the substrate-mediated intermolecular interaction energy W_{sub} in the self-assembly of alkanethiols on Ag for the first time. The results qualitatively demonstrated the semi-empirical expression for the substrate-mediated interaction energy proposed previously by us is consistent with the results of the DFT theory. The results also revealed that there is a proportional relation between the single molecular adsorption energy and the substrate-mediated intermolecular interaction energy W_{sub}.

V. ACKNOWLEDGMENTS

[1] R. Brako and D. Sokceyic, Surf. Sci. **454/456**, 623 (2000).
[2] J. P. Muscat, Prog. Surf. Sci. **25**, 211 (1987).
[3] L. W. Bruch, Surf. Sci. **125**, 194 (1983).
[4] K. H. Lau and W. Kohn, Surf. Sci. **65**, 607 (1977).

[5] T. B. Grimley, Proc. Phys. Soc. London **90**, 751 (1967).

[6] O. Sinanoglu and K. S. Pitzer, J. Chem. Phys. **32**, 1279 (1960).

[7] A. D. Maclachlan, Mol. Phys. **7**, 381 (1964).

[8] M. T. M. Koper, J. Electroanal. Chem. **450**, 189 (1998).

[9] A. W. Adamson, *Physical Chemistry of Surfaces*, New York: Wiley, Ch. 15 (1976).

[10] (a) H. Ibach, J. Vac. Sci. Technol. A **12**, 2240 (1994). (b) H. Ibach, Surf. Sci. Rep. **29**, 193 (1997).

[11] R. C. Cammara, Prog. Surf. Sci. **46**, 2 (1994).

[12] R. Berger, E. Delamarche, H. P. Lang, C. Gerber, J. Gimzewski, E. Meyer and H. J. Guntherodt, Science **276**, 2021 (1997).

[13] J. Fritz, C. H. Gerber, *et al.*, Science **288**, 316 (2000).

[14] N. V. Lavrik, C. A. Tipple, M. J. Sepaniak and P. G. Datskos, Chem. Phys. Lett. **336**, 371 (2001).

[15] W. Schmickler and E. Leiva, J. Electroanal. Chem. **453**, 61 (1998).

[16] F. Spaepen, Acta Mater. **48**, 31 (2000).

[17] R. Xie, D. M. Chen, X. Q. Wang, T. J. He and F. C. Liu, J. Phys. Chem. B **106**, 12948 (2002).

[18] X. Q. Wang, R. Chen, Y. Wang, T. J. He and F. C. Liu, J. Phys. Chem. B **102**, 7568 (1998).

[19] R. Xie, D. M. Chen, T. J. He and F. C. Liu, Chin. J. Chem. Phys. **17**, 5 (2004).

[20] R. Xie, D. M. Chen, X. Q. Wang, T. J. He and F. C. Liu, Chin. J. Chem. Phys. **15**, 405 (2002).

[21] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[22] M. J. Frisch *et al.*, *GAUSSIAN 98*, Revision A. 9, Pittsburgh, PA, Gaussian, Inc. (1998).

[23] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985).

[24] I. N. Levine, *Quantum Chemistry*, 5th Ed., New Jersey: Printice Hall, 492 (2000).

[25] (a) H. Sellers, A. Ulman, Y. Shnidman and J. E. Eilers, J. Am. Chem. Soc. **115**, 9389 (1993). (b) O. Azzaromi and R. C. Salvarezza, J. Phys. Chem. B **106**, 12267 (2002).

[26] L. Salem, J. Chem. Phys. **37**, 2100 (1962).

[27] C. Taut, A. J. Pertsin and M. Grunze, Langmuir **12**, 3481 (1996).

[28] I. Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932).

[29] R. C. Weast, Ed.; *CRC Handbook of Chemistry and Physics*, Beca Raton: CRC Press, (2000).

[30] V. P. Zhdanov, *Elementary Physicochemical Processes on Solid Surfaces*, New York: Plenum, 105 (1991).

[31] F. Schreiber, Progress in Surface Science **65**, 151 (2000).

[32] R. Hoffmann, Acc. Chem. Res. **4**, 1 (1971).