

# Adsorbate-Induced Surface Stress of Chloride Monolayer on Au(111) Electrode

Rong Xie, Dongming Chen, Xueqin Wang, Tianjing He, and Fan-Chen Liu\*

Department of Chemical Physics, University of Science and Technology of China,  
Hefei, Anhui 230026, People's Republic of China

Received: May 1, 2002; In Final Form: October 9, 2002

The statistical thermodynamic theory of adsorbate-induced surface stress of anion adsorption monolayer on Au(111) has been established by using the lattice gas model and considering various components of the adsorbate–adsorbate interaction energies in the adlayer, such as the substrate-mediated interaction, the electrostatic energies, Lennard-Jones potential, and so on. The adsorbate-induced surface stress, its components due to various intermolecule forces, and the area elasticity modulus in chloride adions at the Au(111) electrode surface have been calculated. The calculated surface stress of chloride adions on Au(111) approximates the experiment results and the difference between the surface stress and the surface tension is the same order of magnitude as that of the surface stress. Among various components of the adsorbate–adsorbate interaction energies in the adlayer, the substrate-mediated interaction is significant for the adsorbate-induced surface stress, which shows that the indirect contribution of the adsorption energy of chloride adions on Au(111), through the substrate–mediated interaction energy, is very important. In the lower  $\text{Cl}^-$  coverage cases, including the contribution of  $\text{ClO}_4^-$  adions in the chloride adlayer on Au(111), the calculated surface stress is approximately linearly correlated with charge density, which indicates the essential role of the specific adsorption of the anions for the shape of the surface stress versus charge density curve. Thus the relative experiment results of the adsorbate-induced surface stress of the chloride adlayer on Au(111) electrode have been reasonably explained by the theory.

## 1. Introduction

In recent years, the influence of adsorption behavior on the surface stress of the substrate is actively investigated in many fields.<sup>1–9</sup> In surface physics, the adsorbate induced modification in the surface stress is thought to play an important role in reconstruction process.<sup>1</sup> In thin films, the influence of the adlayer on surface stress is significant in epitaxial growth, nucleation, dislocation, etc.<sup>2</sup> In biochemistry, the self-assembled molecular and biomolecular monolayers and biomolecular recognition have been investigated by means of the modulation of surface stress.<sup>3–5</sup>

In electrochemistry a major progress was recently achieved by the precise measurement of adsorbate-induced changes in the surface stress of solid electrodes,<sup>6,7</sup> which indicate a large difference between the thermodynamic properties of solid and liquid metal electrode in contact with an electrolyte. However, the interpretation of the experiment results gave rise to some controversies which were pertinently reviewed in refs 8 and 9, such as those involving solid electrodes, whether the surface stress and interfacial tension differ or not. Although there are some excellent theoretical works concerning the influence of adsorbate adlayer on the surface stress,<sup>1,9–12</sup> none of them can explain the main experiment results intuitively and self-consistently, nor there is any precise systematics explaining surface stress.<sup>10</sup>

Recently, Haiss et al.<sup>7</sup> have measured surface stress changes due to anion adsorption on Au(111) electrode and found its novel linear correlation with the charge density, and noted that, in general, surface tension and surface stress of solid electrodes may not be equated. Schmickler et al.<sup>9,11</sup> have developed a

theory to analyze influences of metal electrode, the solution represented as a Gouy–Chapman capacitor and the anion specific adsorption on the surface stress. The theoretical frame is successful. But as Schmickler et al.<sup>9,11</sup> only considered the electrostatic energy of  $\text{Cl}^-$  anions, the calculated contribution of anion adsorption to surface stress is small<sup>9</sup> and is neglected,<sup>11</sup> which differs from Haiss et al.'s experiment result.<sup>7</sup> At the same time, the theoretically calculated surface stress versus charge density curve is hyperbolic, which is conflicting with Haiss et al.'s experiment result of linear correlation.<sup>7</sup>

For the electrocompression behavior of halide adlayers on Au(111), we have established a statistical thermodynamic theory and reasonably explained the relative experiment results.<sup>13</sup> In this paper, by using the similar method and taking  $\text{Cl}^-$  anion as an example, we attempt to establish the statistical thermodynamic theory of surface stress of anion adsorption monolayer on Au(111) and to understand theoretically Haiss et al.'s experiment results. First, the statistical thermodynamic formulas of the surface stress and area elasticity modulus of anion adlayer on Au(111) are given in sections 2.1 and 2.2 on the basis of the lattice gas model. Second, the adsorbate–adsorbate (lateral) interaction energies in the anion adlayer on Au(111) are analyzed and described in section 2.3. Third, the adsorbate-induced surface stress and the difference between the surface stress and the surface intension of chloride anions on Au(111) have been calculated in sections 3.1 and 3.2. In section 3.3, the different contributions to the surface stress from various components of the lateral interaction energies of chloride anions on Au(111) have been calculated and compared. Finally, in section 4, in the low coverage of chloride adions the contribution of  $\text{ClO}_4^-$  adions on Au(111) has been introduced into the surface stress of the chloride adlayer, which changes the surface stress versus

\* Corresponding author. Email: fcliu@ustc.edu.cn.

**TABLE 1: Lattice Sums of the Hexagonal Structure**

$n$	3	4	5	6	7	8	9	10	11	12
$A_n$	10.975	7.711	6.762	6.376	6.195	6.105	6.057	6.031	6.018	6.010

charge density curve from hyperbolic to linear shape. Thus, Haiss et al.'s experiment results<sup>7</sup> have been reasonably explained by the theory. In principle, for the other chemisorption systems of anions on metal electrode, the adsorbate-induced surface stress may be similarly treated by the theory, but a new theory is needed for multicomponent coadsorption systems.

## 2. Theory

In this paper, we adopt the physical model, statistical thermodynamic method, and fundamental formulas similar to those in ref 13. Some changes have been made in this paper. To be in line with the definition of surface stress in the theory of elasticity, a normal stress component acting upon the interacting plane is considered positive when pointing away from the material side of the plane, as Ibach defined.<sup>1</sup> The area elasticity modulus has been further analyzed and applied to calculate the difference between the surface stress and surface tension in sections 2.2 and 3.2. The substrate-mediated interaction between two adatoms has been further analyzed and discussed in sections 2.3 and 3.3. Also the print errors of eqs 44 and 23 in ref 13 have been corrected. (After being corrected, the calculated results in ref 13 remain unchanged.) Here we give the main formulas, and their derivations are similar to ref 13.

**2.1. Physical Model and Partition Function.** Our physical model for chloride, bromide, and iodide adsorbate monolayers on Au(111) electrode assumes that the adsorbate monolayer consists of a regular two-dimensional lattice of halide adatoms and constitutes a canonical ensemble. By using the Bragg–Williams approximation, which is generally accepted and widely used in a system of adsorbates at a metal electrode,<sup>14</sup> the partition function (PF) to describe the halide adsorbate monolayer can be written as

$$(\text{PF}) = \frac{N_S!}{N_A!(N_S - N_A)!} j^{(S)}(T)^{N_A} \exp\left[-\frac{N_A(U + V)}{kT}\right] \quad (1)$$

where  $N_S$  and  $N_A$  are the number of substrate sites and adsorbates, respectively.  $U$  is the potential energy at the minimum in an adatom–substrate interaction energy  $U(xyz)$ .  $V$  is an average adatom–adatom interaction energy (the lateral interaction energy) per adatom

$$V = 1/2Z\theta W \quad (2)$$

where  $Z$  is the nearest-neighbor coordinate number of an adsorbate.  $\theta = N_A/N_S$  is the coverage of adsorbate relative to the substrate.  $W$  is an effective pair interaction energy between adsorbates

$$W = \frac{\sum_j V_{ij}}{Z} \quad (3)$$

where  $V_{ij}$  is a pair interaction energy between the adsorbates  $i$  and  $j$  in the adlayer. The sum in eq 3 is over all sites in the adlayer except the adsorbate  $i$ .  $j^{(S)}(T)$  is partition function of a three-dimensional harmonic oscillator with the vibrational frequencies  $\nu_x$ ,  $\nu_y$ , and  $\nu_z$ ,

$$j^{(S)}(T) = \prod_{i=x,y,z} \frac{e^{h\nu_i/kT}}{e^{h\nu_i} - 1} \quad (4)$$

Then the free energy thermodynamic function of halide adlayer on metal electrode surface is obtained as

$$\begin{aligned} F &= -kT \ln(\text{PF}) \\ &= -kTN_S \ln N_S + kTN_A \ln N_A + \\ &\quad kT(N_S - N_A) \ln(N_S - N_A) - kTN_A \ln j^{(S)}(T) + \\ &\quad N_A U + \frac{ZN_A \theta W}{2} \end{aligned} \quad (5)$$

from which thermodynamic properties of the adlayer can be deduced.

**2.2. Statistical Thermodynamic Formulas of Surface Stress and Area Elasticity.** From the definition of the surface stress  $g$  and eq 5, the statistical thermodynamic expression of surface stress can be written as<sup>9,13</sup>

$$\begin{aligned} g &= \left(\frac{\partial F}{\partial A}\right)_{N_A, T} = -\frac{kT}{a_S} \left(\frac{\partial \ln(\text{PF})}{\partial N_S}\right)_{N_A, T} \\ &= -\frac{ZW\theta^2}{2a_S} + \frac{kT}{a_S} \ln(1 - \theta) - kTN_A \frac{d}{dA} \ln j^{(S)}(T) + N_A \frac{dU}{dA} + \\ &\quad \frac{ZN_A \theta}{2} \frac{dW}{dA} \end{aligned} \quad (6)$$

where  $A$  is the area,  $a_S = A/N_S$ , and  $A = aN_A$ . On the basis of the relative discussions and deductions in ref 13, for  $X^-/\text{Au}(111)$  system,  $dU/da = 0$ ,<sup>9</sup>  $(d/da) \ln j^{(S)}(T) \approx 0$ , and eq 6 becomes

$$g = -\frac{ZW\theta^2}{2a_S} + \frac{kT}{a_S} \ln(1 - \theta) - \frac{Z\theta^3}{2a_S} \frac{dW}{d\theta} \quad (7)$$

which is the statistical thermodynamic formula for calculating the surface stress of halide adsorbate monolayers on metal electrode. It is evident that the surface stress is determined by two factors: adsorbate density and the adatom–adatom interaction energy with its derivative.

Usually a pair interaction energy between the adsorbates can be written as a sum of the inverse power of their distance (see section 2.3), the effective pair interaction energy  $W$  becomes<sup>13</sup>

$$W = \sum_n W_n \quad (8)$$

$$W_n = \frac{A_n C_n}{Z r^n} = \frac{A_n C_n}{Z r_s^n} \theta^{n/2} \quad (9)$$

where  $C_n$  is the coefficient of interaction energy.  $A_n$  is the lattice sum, whose value for hexagonal structure is calculated and shown in Table 1.  $r$  and  $r_s$  are the nearest-neighbor distance between the adsorbates in the adlayer and between the substrate sites, respectively. Setting eq 9 into eq 7, we obtain a fundamental formula for calculating the surface stress in the hexagonal-structure halide adlayer,

$$g = -\frac{1}{4a_S} \sum_n (n+2) A_n C_n \frac{1}{r_s^n} \theta^{(n+4)/2} + \frac{kT}{a_S} \ln(1 - \theta) \quad (10)$$

Similar to bulk matter, the area elasticity  $\kappa_{2D}^{-1}$  is defined as<sup>15</sup>

$$\kappa_{2D}^{-1} = a \frac{dg}{da} = -\theta \frac{d\theta}{d\theta} \quad (11)$$

Setting eq 10 into eq 11, we have

$$\kappa_{2D}^{-1} = \sum_n \frac{\sqrt{3}}{12} (n^2 + 6n + 8) \frac{A_n C_n}{r_s^{n+2}} \theta^{(n+4)/2} + \frac{2kT}{\sqrt{3}r_s^2} \frac{\theta}{1 - \theta} \quad (12)$$

which is the fundamental formula for calculating the area elasticity in the hexagonal-structure halide adlayer.

The area elasticity is an important mechanical property of adsorption adlayer. Its magnitude represents the difference between surface stress and surface tension, which is demonstrated as follows. Linford proved thermodynamically the following relations in his review paper<sup>16</sup>

$$g = \gamma_t + E^\pi \quad (13)$$

and

$$E^\pi = \frac{\partial \gamma_t}{\partial \xi} = a \frac{d\gamma_t}{da} \quad (14)$$

where  $E^\pi$  is the surface elasticity modulus,  $\gamma_t$  is the surface tension, and  $\xi = dA/A = da/a$ . Comparing eq 11 with eq 14,  $\kappa_{2D}^{-1}$  and  $E^\pi$  are both the elasticity modulus of the system and have different definitions. It can be proved that they are equal. It is shown<sup>8,9</sup> that the Shuttleworth equation is

$$g = \gamma_t + \frac{\partial \gamma_t}{\partial \xi} = \gamma_t + E^\pi \quad (15)$$

Therefore, the differential over  $\xi$  for both sides of eq 15 is

$$\kappa_{2D}^{-1} = E^\pi + \frac{dE^\pi}{d\xi} \quad (16)$$

where eqs 11 and 14 have been used. Since in the experiment measurement process of the surface stress, the sample are not much destroyed or changed and the elasticity properties  $E^\pi$  are constant during the measurement process, hence  $(dE^\pi/d\xi) \approx 0$  and  $\kappa_{2D}^{-1} = E^\pi$ . The same approximation  $(dg/d\xi) \approx (d\gamma/d\xi)$  also used in Couchman et al.'s paper.<sup>17</sup> From eq 13 we have

$$g - \gamma_t = E^\pi = \kappa_{2D}^{-1} \quad (17)$$

therefore, eq 17 indicates that the difference between surface stress and surface tension is equal to the area elasticity.

### 2.3. Adsorbate-Adsorbate (Lateral) Interaction Energy.

According to the theory of chemisorption,<sup>18–20</sup> the components of the lateral interaction energies in the halide adlayer on metal electrodes, such as Au, Ag, Pt, include: (i) the electrostatic energy among the adions; (ii) induction energy, i.e., induced dipole–induced dipole interaction energy due to the electrode potential; (iii) Lennard-Jones potential including the van der Waals attraction and Pauli repulsion; (iv) many-body interaction within the adlayer, such as the triple-dipole energy, and so on; (v) the substrate-mediated interaction energy. We consider and evaluate each as follows.

(1) *Substrate-Mediated Interaction.* Atoms adsorbed on the surface of a solid interact with each other directly as well as indirectly through the substrate. The interaction between

adsorbates on solid surfaces due to direct mechanisms is usually short-ranged (the repulsive due to the overlap of electronic orbitals) or weak (electric dipole–dipole interaction),<sup>12</sup> and therefore, the indirect or through-the-substrate mechanisms (substrate-mediated interaction) are of considerable interest. For most chemisorption systems, it is well-known<sup>18,21–23</sup> that the substrate-mediated interaction is dominant among the components in the lateral interaction energy, especially for most atoms and small molecules even at monolayer coverage.<sup>24,25</sup> The substrate-mediated interactions originate in various physical mechanisms as follows. (i) In the chemisorption adlayer, the indirect substrate-mediated interaction originates from a mutual coupling of the adatom valence shells via the conduction electrons in a metal, the so-called indirect electronic interaction.<sup>18,21,22,26,27</sup> (ii) When an atom adsorbs on the substrate, the substrate deforms and causes the classical long-range interaction between two adatoms mediated by the elastic distortion of the substrate, also called the phonon-mediated interaction.<sup>12,28</sup> (iii) In the physisorption layer, the indirect lateral interaction is the substrate-mediated dispersion energy proposed by Sinanoglu, Pitzer, and McLachlan et al.,<sup>29,30</sup> where the substrate, as a third body, acts on two adatoms. (iv) When the diameter of adatom is bigger than the nearest-neighbor distance of the substrate lattice and two adatoms adsorb on nearest-neighbor sites on the substrate lattice, they will depart from the sites with potential energy at minimum. The adsorption energy will reduce and cause apparent repulsion interaction between the two adatoms through substrate.<sup>31</sup>

The foregoing four substrate-mediated interactions have some common characteristics: (i) They are repulsive except the indirect electronic interaction in some cases. (ii) Their magnitudes are approximately directly proportional to or positively correlated with the absolute value of the adsorption energy for a single adatom. (iii) They are all long-range forces and are inversely proportional to  $r^3$ , where  $r$  is the distance between two adsorbates. The indirect electronic interaction is expected to oscillate both as a function of the position of the Fermi level and the distance, but a asymptotic behavior falling off as  $r^{-3}$  is obtained.<sup>32,33</sup> (iv) The calculation formulas for each substrate-mediated interaction are usually complicated and some simple analytical formulas are needed. For example, it can be written as a expression proportional to  $|U|/r^3$ , as the following eqs 18 and 19 show, where  $|U|$  is the absolute value of adsorption energy for a single adatom.

In physisorption adlayer, Sinanoglu, Pitzer,<sup>29</sup> and McLachlan<sup>30</sup> put forward and developed the substrate-mediated dispersion energy. The simplest expression of Sinanoglu–Pitzer–McLachlan energy is<sup>19,34</sup>

$$S(r) = \frac{9}{16} \alpha \frac{1}{r^3} \left( \frac{S_3}{L^3} \right) \quad (18)$$

where  $\alpha$  is the adatom polarizability,  $S_3/L^3$  is the negative one-adatom holding potential,  $S_3$  is the strength coefficient of adatom–substrate interactions,  $L$  is the perpendicular distance of the adatom from the substrate, and  $9/16$  is an empirical parameter. The chemisorption energy of chloride anions on Au(111) electrode surface is about 1.2 eV/mol. This indicates that the chloride anion is weakly chemisorbed on Au(111), which is approximately equivalent to a strong physisorption system. Hence for simplicity, we attempt to use a simplification form of the Sinanoglu–Pitzer–McLachlan energy, such as eq 18, to express the indirect interaction energy of halide adsorbates

**TABLE 2: Parameters Used in the Calculation of the Chloride Adlayer on Au(111) Surface<sup>a</sup>**

parameter	$S_3$ (eV Å <sup>3</sup> )	$\alpha$ (Å <sup>3</sup> )	$2L$ (Å)	$\epsilon$	$\gamma$
chloride	1.847	2.21	2.40	2.10 (−50 °C)	−0.7

parameter	$E'_{\text{Ag/AgCl}}$ (V)	$\mu_0^0$ (debye)	$r_0$ (Å)	$\epsilon$ (K)	$v$ (eV Å <sup>9</sup> )
chloride	0.73	0.2	3.80	142.1	479 ± 11

<sup>a</sup> From ref 13.

on Au(111). After considering the lattice sum of halide adlayer,<sup>13</sup> we have

$$W_{\text{sub}} = \frac{A_3}{Z} \alpha \frac{1}{r^3} \left( \frac{S_3}{L^3} \right) \quad (19)$$

where the units are  $W_{\text{sub}}$  in eV,  $r$  and  $L$  in angstroms, and  $\alpha$  in Å<sup>3</sup>. It is noteworthy that eq 19 is an empirical expression of the substrate-mediated interaction.

(2) *Electrostatic Interaction.* Many experimental results indicate that the halide ions (aq) undergo spontaneous oxidation and transfer charge to Au electrode upon chemisorption and form almost a zerovalent halide adlayer; the halide adsorbate on Au(111) can carry a rather small charge,  $(-1 - \gamma)e$ , where  $\gamma$  is the electrosorption valency. Similar to Langmuir's treatment of Cs on  $W$ ,<sup>35</sup> after derivation, the electrostatic interaction energy between adions is<sup>13</sup>

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

where  $\epsilon$  is the dielectric constant and the units are  $W_{\text{el}}$  in eV,  $r$  and  $L$  in angstroms (Figure 1).

(3) *Induction Interaction Energy.* The induced dipole–induced dipole interaction energy is<sup>13</sup>

$$W_{\text{ind}} = 0.624 \frac{A_3 \mu_0^2}{Z r^3} = 0.624 \frac{A_3}{Z} \frac{1}{r^3} \left( \mu_0^0 + \frac{1}{3} \frac{\alpha E'}{L} \right)^2 \quad (21)$$

where  $\mu_0^0$  is the dipole moment when the electrode potential  $E'$  is 0.  $\alpha$  is the polarizability of an adatom. The units are  $W_{\text{ind}}$  in eV,  $\mu_0$  and  $\mu_0^0$  in debye,  $E'$  in V,  $L$  and  $r$  in angstroms, and  $\alpha$  in Å<sup>3</sup>.

(4) *Lennard-Jones Potential.* We combine Pauli repulsion between adatoms from the wave function overlap of the closed shell and van der Waals attraction between adatoms into the Lennard-Jones potential,<sup>13</sup>

$$W_{\text{L-J}} = 8.625 \times 10^{-5} \epsilon \left[ A_{12} \left( \frac{r_0}{r} \right)^{12} - 2A_6 \left( \frac{r_0}{r} \right)^6 \right] \quad (22)$$

where  $\epsilon$  is the depth of the potential energy minimum and  $r_0$  is the van der Waals diameter of the adsorbate atoms. The units are  $W_{\text{L-J}}$  in eV,  $r_0$  in angstroms, and  $\epsilon$  in K.

(5) *Nonadditive Three-Body Potential.* The contribution of the nonadditive three body potential is present in the adlayer,<sup>13</sup>

$$W_{\text{thr}} = \frac{A_9}{Z} \frac{v}{3r^9} \quad (23)$$

where  $v$  is strength of the three body interaction. The units are  $W_{\text{thr}}$  in eV,  $v$  in eV Å<sup>9</sup>.

Summing the foregoing components of the lateral interaction in the adlayer, we get the coefficient  $C_n$ , where  $n = 3, 5, 6, 7, 9$ , and 12, in the effective pair interaction  $W$  between the adsorbates in eq 8,

$$\begin{aligned} C_3 &= \frac{28.8(1 + \gamma)^2 L^2}{\epsilon} + 0.624 \mu_0^2 + \frac{\alpha S_3}{L^3} \\ C_5 &= -\frac{86.4(1 + \gamma)^2 L^4}{\epsilon} \\ C_6 &= -1.725 \times 10^{-4} \epsilon r_0^6 \\ C_7 &= \frac{288(1 + \gamma)^2 L^6}{\epsilon} \\ C_9 &= -\frac{1008(1 + \gamma)^2 L^8}{\epsilon} + \frac{1}{3} v \\ C_{12} &= 8.625 \times 10^{-5} \epsilon r_0^{12} \end{aligned} \quad (24)$$

For the chloride adlayer the parameters in the foregoing formulas have been listed in Table 2. Their explanation and the parameters for the other halide anions refer to ref 13.

### 3. Results

Haiss et al.<sup>7</sup> measured surface stress changes due to anion adsorption on Au(111), such as  $\text{Cl}^-$  and  $\text{ClO}_4^-$ , and found a novel linear correlation between surface stress and the charge density. With reference to surface physics studies they note that, in general, the surface energy (interfacial tension) and surface stress of solid electrode may not be equal. To comprehend these experiment results and some relative controversies in electrochemistry field of solid electrodes,<sup>8,9</sup> we have calculated the adsorbate-induced surface stress of the chloride adions on Au(111) electrode and the area elasticity in the adlayer by using eqs 8, 10, 12, and 24 and the parameters in Table 2. The following problems have been studied and discussed one by one: (i) The contribution of chloride adions on Au(111) electrode to the surface stress (section 3.1). (ii) The calculations of the area elasticity in the adlayer and the difference between the surface stress and surface tension (section 3.2). (iii) Comparison between the contributions to the surface stress from various components of the adsorbate–adsorbate interaction energies (section 3.3). Before presenting these results, it is noted that Haiss et al.<sup>7</sup> established the relation between surface stress and charge density  $\sigma_M$  and electrode potential  $E_{\text{SCE}}$ , while our theoretical formulas in section 2 give the relationship between surface stress and the coverage  $\theta$ . For the convenience of comparing our theory with Haiss et al.'s<sup>7</sup> experiment, it is necessary to establish the corresponding relation among  $\theta$ ,  $\sigma_M$ , and  $E_{\text{SCE}}$ . By using abundant experimental results of Shi and Lipkowski,<sup>36</sup> the corresponding values of them have been listed in Table A in the appendix.

**3.1. The Contribution of Chloride Adions on Au(111) Electrode to the Surface Stress.** Using eq 10, we have calculated the contribution of chloride adions on Au(111) electrode to the surface stress  $g_{\text{Cl}^-}$ . The calculated result is shown in Table 3 and Figure 2.

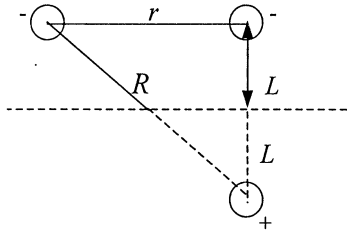
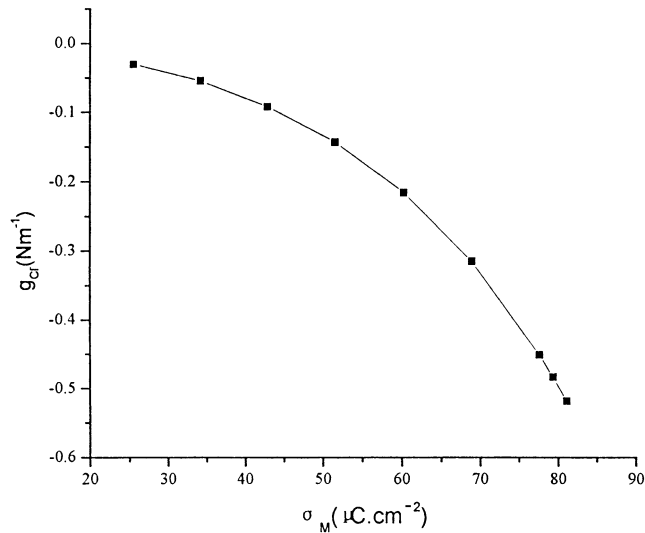
Table 3 and Figure 2 reveal two important results: (1) The contribution of chloride adions on Au(111) approximately equal to Haiss et al.'s measurement, which indicates that the contribution of  $\text{Cl}^-$  adions is significant. This differs apparently from



**TABLE 3: Contribution  $g_{\text{Cl}^-}$  of Chloride Adions on Au(111) to the Surface Stress**

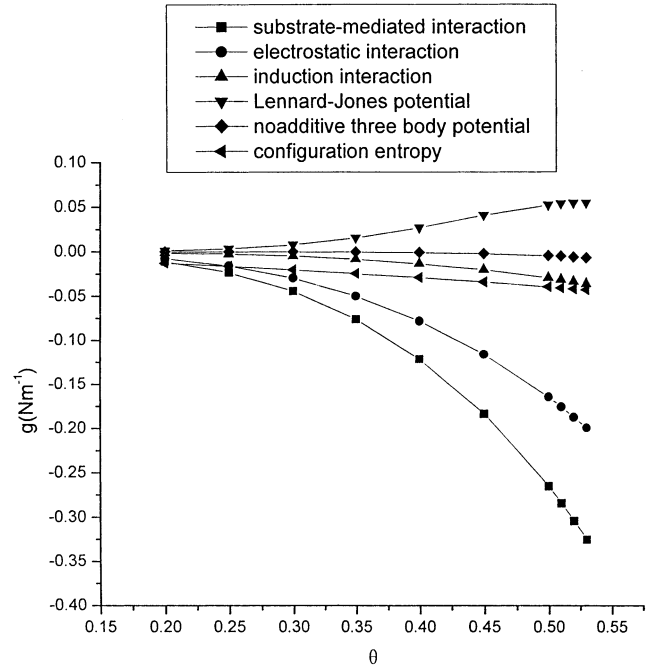
$\theta$	0.20	0.25	0.30	0.35	0.40
$\sigma_{\text{M}} (\mu\text{C cm}^{-2})$	25.55	34.24	42.93	51.61	60.30
$g_{\text{Cl}^-} (\text{N m}^{-1})$	-0.0310	-0.0551	-0.0916	-0.1439	-0.2164
$\Delta g_{\text{exp}} (\text{N m}^{-1})^a$	-0.1891	-0.2459	-0.3028	-0.3596	-0.4165
$\theta$	0.45	0.50	0.51	0.52	0.53
$\sigma_{\text{M}} (\mu\text{C cm}^{-2})$	68.99	77.68	79.41	81.15	82.89
$g_{\text{Cl}^-} (\text{N m}^{-1})$	-0.3154	-0.4510	-0.4838	-0.5188	-0.5562
$\Delta g_{\text{exp}} (\text{N m}^{-1})^a$	-0.4734	-0.5303	-0.5415	-0.5530 <sup>b</sup>	-0.5644 <sup>b</sup>

<sup>a</sup> The experimental values  $\Delta g_{\text{exp}}$  come from Haiss et al.'s Figure 2c in ref 7. <sup>b</sup> Extrapolated values  $\Delta g_{\text{exp}}$  from Haiss et al.'s Figure 2c in ref 7.

**Figure 1.** The coordinates for the electrostatic interaction between two adions.**Figure 2.** The relationship between  $g_{\text{Cl}^-}$  and  $\sigma_{\text{M}}$  of chloride adions on Au(111) electrode. The contribution of chloride adions on Au(111) to the surface stress  $g_{\text{Cl}^-}$  is obtained from the calculated values in Table 3.  $\sigma_{\text{M}}$  is the surface charge density.

theoretical hypothesize of some existing literature.<sup>11</sup> (2) The contribution of chloride adions  $g_{\text{Cl}^-}$  to surface stress is hyperbolically correlated with charge density  $\sigma_{\text{M}}$ , which is similar to the  $g-\mu/kT$  curve of Schmickler and Leiva,<sup>9</sup> yet not accordant with the experiment results of Haiss et al.,<sup>7</sup> which show a novel linear correlation between the surface stress and charge density. In the section 4, we will improve the results by including the contribution of specific adsorption of  $\text{ClO}_4^-$  anions on Au(111), and then we will discuss the improved results. In addition, in a similar way, we have calculated the contribution of  $\text{Br}^-$ ,  $\text{I}^-$  monolayers on Au(111) to surface stress, which is shown in Table 4 as a theoretical prediction.

**3.2. The Area Elasticity and the Difference between Surface Stress and Surface Tension.** By using eq 12, we have calculated the 2D isothermal compressibility  $\kappa_{2\text{D}}$  and the area elasticity  $\kappa_{2\text{D}}^{-1}$  in the hexagonal-structure halide adlayer on the Au(111) electrode, which is shown in Table 5. The experimental values in the table are preliminary estimate by

**Figure 3.** The contribution of each term of the interaction energies and configuration entropy to the surface stress from chloride adions on Au(111) electrode: (solid square) substrate-mediated interaction, (solid circle) electrostatic interaction, (solid triangle, up) induction interaction, (solid triangle, down) Lennard-Jones potential, (solid diamond) noadditive three body potential, (solid triangle, left pointing) configuration entropy contribution. The calculated values for each terms are listed in Table 6.**TABLE 4: Surface Stress in the Iodide and Bromide Adlayers on Au(111)**

	(a) In the Bromide Adlayer					
$\theta$	0.45	0.46	0.48	0.50	0.51	0.52
$g (\text{N m}^{-1})$	-0.4550	-0.4934	-0.5784	-0.6793	-0.7354	-0.7978
	(b) In the Iodide Adlayer					
$\theta$	0.36	0.40	0.409	0.415	0.43	0.45
$g (\text{N m}^{-1})$	-0.4758	-0.7081	-0.7722	-0.6473	-0.7386	-0.8828

using the method of Toney et al.<sup>37,38</sup> and the data of Shi et al.<sup>36</sup> We have proved that the difference between the surface stress and surface tension is equal to the area elasticity  $\kappa_{2\text{D}}^{-1}$  (see eq 17). With a comparison between the values in Table 3 and Table 5, it was found that the difference between surface stress and surface tension is the same order of magnitude as that of surface stress. Hence, for solid electrode, the difference between them cannot be neglected, as Haiss et al.<sup>7</sup> and Schimickler<sup>9b</sup> pointed out: in general, surface energy and surface stress of solid electrodes may not be equated and these two quantities can differ considerably.

**3.3. The Different Contributions to the Surface Stress from Various Components of the Lateral Interaction Energies.** From the formulas for calculating the surface stress eqs 7 and 10, the surface stress is mainly constituted by two parts: the contribution of the interaction energies in the adlayer with their derivatives and the configuration entropy. From the analysis in section 2.3, the interaction energies consists of five terms: (1) the substrate-mediated interaction energy; (2) the electrostatic energy among the adions; (3) the induction energy, i.e., induced dipole-induced dipole interaction energy due to the electrode potential; (4) the Lennard-Jones potential including the van der Waals attraction and Pauli repulsion between two adatoms; (5) the many-body interaction in the adlayer. To further discuss the physical origin of the surface stress, we have calculated the

**TABLE 5: Two-Dimensional (2D) Isothermal Compressibility  $\kappa_{2D}$  and Area Elasticity  $\kappa_{2D}^{-1}$  in the Chloride Adlayers on Au(111)**

$\theta$	0.20	0.25	0.30	0.35	0.40	0.45	0.50
$\kappa_{2D}^{-1}(\text{N m}^{-1})$	0.0760	0.1490	0.2626	0.4307	0.6757	1.037	1.585
$\kappa_{2D}(\text{m N}^{-1})$	13.15	6.711	3.809	2.322	1.480	0.9642	0.6309
$\kappa_{2D}^{\text{exp}}(\text{m N}^{-1})^a$	5.674	3.671	2.549	1.873	1.434	1.133	0.9178
$\sigma_M(\mu\text{C cm}^{-2})$	25.55	34.24	42.93	51.61	60.30	68.99	77.68
$E_{\text{SCE}}(\text{mV})$	205.93	263.70	323.92	370.11	423.70	485.93	549.63

<sup>a</sup> Based on refs 36 and 37.**TABLE 6: The Contribution to the Surface Stress  $g_{\text{Cl}^-}$  from Each Term of the Interaction Energies and Configuration Entropy (unit:  $\text{N m}^{-1}$ )**

$\theta$	$g_{\text{sub}}$	$g_{\text{el}}$	$g_{\text{ind}}$	$g_{L-J}$	$g_{\text{thr}}$	$g_{\text{con}}$	$g_{\text{tal}}$
0.20	-0.0107	-0.0074	-0.0012	0.0011	-0.0000	-0.0127	-0.0309
0.25	-0.0234	-0.0159	-0.0026	0.0033	-0.0001	-0.0164	-0.0551
0.30	-0.0444	-0.0296	-0.0049	0.0078	-0.0002	-0.0204	-0.0917
0.35	-0.0761	-0.0499	-0.0084	0.0155	-0.0005	-0.0246	-0.1440
0.40	-0.1214	-0.0782	-0.0135	0.0269	-0.0011	-0.0292	-0.2165
0.45	-0.1836	-0.1159	-0.0203	0.0407	-0.0024	-0.0341	-0.3156
0.50	-0.2651	-0.1645	-0.0294	0.0523	-0.0047	-0.0396	-0.4510
0.51	-0.2842	-0.1757	-0.0315	0.0537	-0.0054	-0.0407	-0.4838
0.52	-0.3041	-0.1873	-0.0338	0.0544	-0.0061	-0.0419	-0.5188
0.53	-0.3251	-0.1995	-0.0361	0.0544	-0.0069	-0.0431	-0.5563

contribution of each term to the interaction energies and configuration entropy, which is shown in Table 6 and Figure 3.

Table 6 and Figure 3 reveal that, among various terms in the surface stress, except the positive contribution of Lennard-Jones potential, all the other terms are negative, which indicate that the surface stress is compressive. Among them, the contribution of substrate-mediated interaction energy and the electrostatic energy are determinant, and the former is much larger than the latter. At lower coverage ( $\theta \leq 0.35$ ), the contribution of the configuration entropy is also significant.

Finally we discuss the contribution of the adsorption energy  $U$  to the surface stress  $g_{\text{Cl}^-}$  which is due to the change of the adsorption energy of the anion adlayer with an elastic deformation of the substrate surface. It consists of direct contribution ( $dU/da$ ) through charge-transfer mechanism<sup>1</sup> or other chemisorption process and indirect contribution through the substrate-mediated interaction  $W_{\text{sub}}$ . Schmickler and Leiva pointed out<sup>9</sup> that in the case of the adsorption of anions from the solution the adsorption energy is constant, thus  $(dU/da) = 0$ . In this report and ref 13 the assumption  $(dU/da) = 0$  also is used, i.e., the direct contribution of the adsorption energy is zero. In fact, the assumption  $(dU/da) = 0$  is often used in statistical thermodynamics calculations of the adlayer on the various surfaces,<sup>41–44</sup> which is also the essential results of the lattice gas model.<sup>45</sup> Some experiment evidences supporting the assumption  $(dU/da) = 0$  were given in ref 13.

On the other hand, in section 2.3 we have pointed out that the magnitude of the substrate-mediated interaction energy is approximately direct proportional to the adsorption energy. And in this section we have seen that the substrate-mediated interaction makes dominant contribution to the adsorption-induced surface stress  $g_{\text{Cl}^-}$ . Thus, the indirect contribution of the adsorption energy is significant and on the whole, the adsorption energy of anion on Au(111) is very important for the surface stress  $g_{\text{Cl}^-}$ . These results are essentially associated with the theory in ref 1 and 10, but through the different ways.

#### 4. Discussion: Empirical Inclusion of the Contribution of $\text{ClO}_4^-$ Adions to the Surface Stress and the Linear Relation between the Surface Stress and Charge Density

**4.1. Empirical Inclusion of the Contribution of  $\text{ClO}_4^-$  Adions.** When making a comparison between the above

theoretical result of the surface stress  $g_{\text{Cl}^-}$  and the experimental result of Haiss et al.,<sup>7</sup> two corrections are needed: at lower coverage, the contribution of  $\text{ClO}_4^-$  anions on Au(111) to the surface stress should be taken into account, and the zero point of the surface stress should be corrected when making the comparison.

(1) *The Contribution of  $\text{ClO}_4^-$ .* In section 3.1, we have calculated the contribution  $g_{\text{Cl}^-}$  of chloride adions on Au(111) to the surface stress without considering the influence of the other ions. In fact they may play important roles in the surface stress. Under actual experimental condition, Shi and Lipkowski<sup>36</sup> gave the following analysis about the constitution of the  $\text{Cl}^-$ ,  $\text{ClO}_4^-$  adlayer on the Au(111) electrode. Adsorption of perchlorate at a gold is certainly much weaker than adsorption of  $\text{Cl}^-$  ion. However, under the experimental condition, the bulk perchlorate concentration is always a few orders of magnitude higher than the concentration of  $\text{Cl}^-$  ion and hence coadsorption of  $\text{ClO}_4^-$ , particularly at lower values of the Gibbs excess of  $\text{Cl}^-$  ions  $\Gamma_{\text{Cl}^-}$ , cannot be entirely ruled out. But in higher  $\text{Cl}^-$  coverages, the coadsorption of  $\text{ClO}_4^-$  is negligible. At the same time, Magnussen et al.'s<sup>39</sup> X-ray scattering results indicate that when  $\theta \geq 0.50$ ,  $\text{Cl}^-$  adions are closed-packed on Au(111), and the contribution of  $\text{ClO}_4^-$  can be neglected. In other words, at higher coverages, the adlayer is mainly constituted by  $\text{Cl}^-$  adions, which are single-closed-packed on the substrate. At lower coverages, the adlayer is constituted by the coadsorption of  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ , etc.

For the comparison between our theoretical calculational results and the Haiss et al.'s experimental curve (Figure 2c in ref 7), when  $\theta < 0.5$ , the contribution to surface stress from  $\text{ClO}_4^-$  and  $\text{H}_2\text{O}$  adsorption in the adlayer should be taken into account, i.e., by using the additive approximation of coadsorption ions and disregarding the interactions between  $\text{Cl}^-$  and  $\text{ClO}_4^-$  adions the theoretical calculational values  $\Delta g_{\text{cal}}$  should be

$$\Delta g_{\text{cal}} \approx g_{\text{Cl}^-} + g_{\text{ClO}_4^-} \quad (25)$$

where  $g_{\text{Cl}^-}$  have been shown in Table 3 and  $g_{\text{ClO}_4^-}$  is the contribution of  $\text{ClO}_4^-$ ,  $\text{H}_2\text{O}$  coadsorption. It is evident that eq 25 is not a calculation for interpenetrating distributions of  $\text{Cl}^-$  and  $\text{ClO}_4^-$  ions. The coadsorption adlayer of  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ , and  $\text{H}_2\text{O}$ , and so on, is so complicated that we are unable to exactly calculate  $g_{\text{ClO}_4^-}$  at present and here only use the relative experimental results in the literature (e.g., refs 7 and 6) to improve the theoretical values  $g_{\text{Cl}^-}$ . Haiss et al.'s<sup>7</sup> Figure 2a presents dependence of the surface stress on charge density  $\sigma_M$  for the 0.1 M  $\text{HClO}_4$ -Au(111) system. We take his experiment values with zero-point correction (addressed in the following section) as  $g_{\text{ClO}_4^-}$ . For example, for the 0.1 M  $\text{HClO}_4$ - $5 \times 10^{-3}$  M  $\text{CsCl}$ -Au(111) system, when the coverage of  $\text{Cl}^-$  is  $\theta = 0.2$ , the electrode potential at this point  $E_{\text{SCE}} = 205.93$  mV (see Table A). By using charge density versus electrode potential curves for the Au(111) electrode in a pure 0.1 M  $\text{KClO}_4$  solution (Figure 2 in ref 36), the charge density of  $\text{ClO}_4^-$  reads  $\sigma_{\text{ClO}_4^-} = -4.54 \mu\text{C cm}^{-2}$  at  $E_{\text{SCE}} = 205.93$  mV. Then from Haiss et

**TABLE 7: Surface Stress  $\Delta g_{\text{cal}}$  of Chloride Adlayer on Au(111) (after the Correction)<sup>a</sup>**

$\sigma_M (\mu\text{C cm}^{-2})$	25.55	34.24	42.93	51.61	60.30
$\Delta g_{\text{cal}} (\text{N m}^{-1})$	-0.0602	-0.1181	-0.1769	-0.2796	-0.4185
$\Delta g_{\text{exp}} (\text{N m}^{-1})$	-0.1891	-0.2459	-0.3028	-0.3596	-0.4165
$\sigma_M (\mu\text{C cm}^{-2})$	68.99	77.68	79.41	81.15	82.89
$\Delta g_{\text{cal}} (\text{N m}^{-1})$	-0.5496	-0.4510	-0.4838	-0.5188	-0.5562
$\Delta g_{\text{exp}} (\text{N m}^{-1})$	-0.4734	-0.5303	-0.5415	-0.5530 <sup>b</sup>	-0.5644 <sup>b</sup>

<sup>a</sup> At higher coverage  $\theta \geq 0.5$  ( $\sigma_M \geq 77.68$ ), the correction is neglected (see the text). <sup>b</sup> Extrapolated values from Haiss et al.'s Figure 2c in ref 7.

al.'s Figure 2a,<sup>7</sup> we obtain the contribution of  $\text{ClO}_4^-$ ,  $g_{\text{ClO}_4^-} = 0.0407 \text{ N m}^{-1}$ . Thus, as long as we add it to  $g_{\text{Cl}^-}$  with the following zero-point correction, we will obtain the contribution of the coadsorption of  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ , etc., to the surface stress  $\Delta g_{\text{cal}}$ .

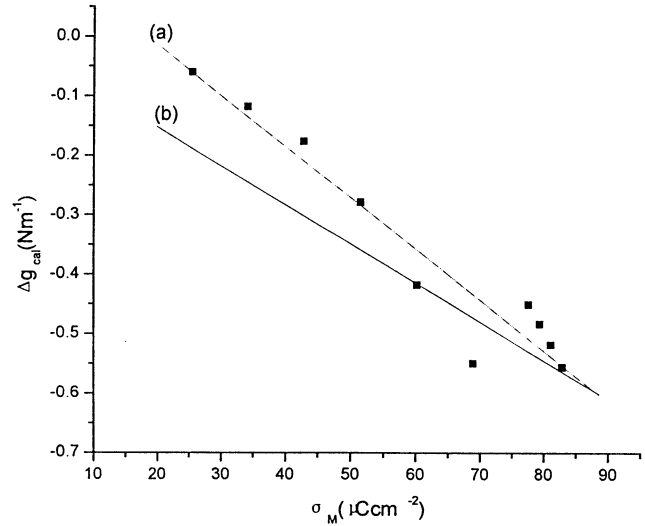
(2) *Zero-Point Correction.* Since we attempt to explain theoretically Haiss et al.'s Figure 2c in ref 7 and to take the data in their Figure 2a as  $g_{\text{ClO}_4^-}$  in eq 25, it is worthwhile to carefully compare their zero points of the surface stress.

Although Haiss et al.'s<sup>7</sup> Figure 2a and Figure 2c both choose the surface stress at the charge density  $\sigma_M = 0$  as the reference point (the zero-point), the corresponding physical status at each zero point is actually different between them. Consider a special point at the coverage of  $\text{Cl}^-$  ion  $\theta = 0$  for 0.1 M  $\text{HClO}_4$ - $5 \times 10^{-3}$  M  $\text{CsCl}$ -Au(111) system in Haiss et al.'s Figure 2c, thus  $\sigma_{\text{Cl}^-} = 0$  because of no adsorption of  $\text{Cl}^-$  ion, but the total charge density  $\sigma = -\sum_j Z_j e_0 \Gamma_j$  is not zero.<sup>40</sup> Shi and Lipkowski<sup>36</sup> give the Gibbs excess versus charge density plots for the Au(111) electrode in 0.1 M  $\text{KClO}_4 + 5 \times 10^{-3}$  M  $\text{KCl}$  (Figure 5 in ref 36). On this basis, the total charge density at the coverage of  $\text{Cl}^-$  ions  $\theta = 0$  is  $\sigma = \sigma_{\text{Cl}^-} + \sigma_{\text{ClO}_4^-} = \sigma_{\text{ClO}_4^-} = -20 \mu\text{C cm}^{-2}$ . The corresponding electrode potential at  $\sigma = -20 \mu\text{C cm}^{-2}$  is  $E_{\text{SCE}} = -243 \text{ mV}$  based on Shi et al.'s Figure 2 in ref 36. Then from Haiss et al.'s Figure 2c, the contribution of  $\text{ClO}_4^-$  to the surface stress is  $\Delta g = g_{\text{ClO}_4^-} = 0.11 \text{ N m}^{-1}$ . On the other hand, Haiss et al.'s Figure 2a for the  $\text{ClO}_4^-$ -Au(111) system gives  $g_{\text{ClO}_4^-} = 0.18 \text{ N m}^{-1}$  at the same point of  $\sigma = -20 \mu\text{C cm}^{-2}$  and  $E_{\text{SCE}} = -243 \text{ mV}$ . Thus the same physical quantity  $g_{\text{ClO}_4^-}$  at the same point ( $\sigma = -20 \mu\text{C cm}^{-2}$ ;  $E_{\text{SCE}} = -243 \text{ mV}$ ) differs by  $0.07 \text{ N m}^{-1}$  between Haiss et al.'s Figure 2a and Figure 2c. Thus, from eq 25 we obtain

$$\Delta g_{\text{cal}} \approx \begin{cases} g_{\text{Cl}^-} + g_{\text{ClO}_4^-} - 0.07 \text{ N m}^{-1} & \text{for lower coverage of } \text{Cl}^- \quad \theta < 0.5 \\ g_{\text{Cl}^-} & \text{for higher coverage of } \text{Cl}^- \quad \theta \geq 0.5 \end{cases} \quad (26)$$

where  $g_{\text{Cl}^-}$  is the calculated values in Table 3 and  $g_{\text{ClO}_4^-}$  comes from the experimental values in Haiss et al.'s Figure 2a. By using eq 26 and Haiss et al.'s experimental results (Figure 2a in ref 7), the theoretical value  $\Delta g_{\text{cal}}$  of the surface stress is calculated and shown in Table 7 and Figure 4.

In addition, since the existing experiment measures of surface stresses only give their relative values instead of the absolute value, when making a comparison between different experimental results, we should pay attention to whether their choice of zero point is accordant or not. For example, the values of the contribution to surface stress from  $\text{ClO}_4^-$  adlayer measured by Ibach et al.<sup>6</sup> apparently greatly differ from those measured by Haiss et al. (Figure 2a in ref 7), as is indicated in the third and fourth rows in Table 8. However, after zero-point correction, the values shown in the fourth and fifth row indicate that their results are closely coincident.

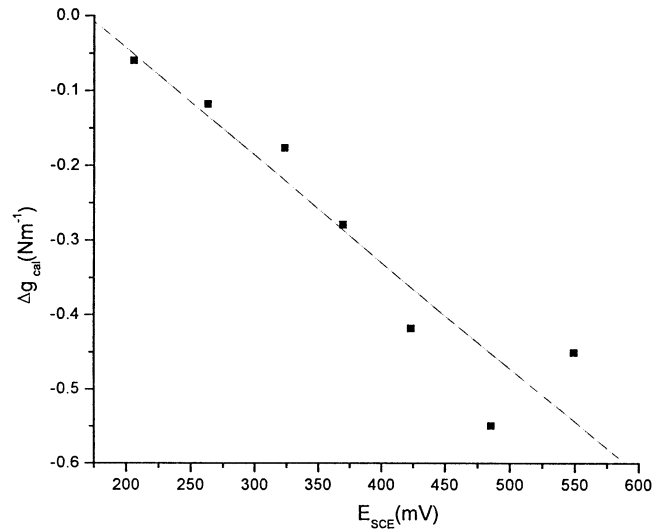


**Figure 4.** Dependence of the surface stress  $\Delta g_{\text{cal}}$  on charge density  $\sigma_M$ . (a) represents theoretical curve, (b) experimental curve. The theoretical points were obtained from Table 7, which include the contribution of all  $\text{Cl}^-$ ,  $\text{ClO}_4^-$  adions on Au(111) electrode. The experimental points were obtained from Figure 2c in ref 7.

**TABLE 8: Comparison between the Experimental Results in References 6 and 7**

$E_{\text{SCE}} (\text{mV})$	960	498.52	400.00	296.30	205.93
$\sigma_M (\mu\text{C cm}^{-2})$		19.46	11.03	0.81	-4.86
$\Delta g (\text{N m}^{-1})^a$	0 (zero point)	0.60	0.74	0.82	0.90
$\Delta g_{\text{ClO}_4^-} (\text{N m}^{-1})^b$		-0.18	-0.10	-0.01	0.05
$\Delta g' = \Delta g - 0.83$	-0.83	-0.23	-0.11	-0.01	0.07

<sup>a</sup> From ref 6. <sup>b</sup> From ref 7.



**Figure 5.** Dependence of the surface stress  $\Delta g_{\text{cal}}$  on electrode potential  $E_{\text{SCE}}$ .

(3) *Relation between  $\Delta g_{\text{cal}}$  and  $\sigma_M$ .* Figure 4 and Table 7 show clearly that the calculated surface stress  $\Delta g_{\text{cal}}$  of chloride adlayer is approximately linear-correlated with the charge density, which is accordant with Haiss et al.'s results.<sup>7</sup> In addition, the relationship between the calculated surface stress  $\Delta g_{\text{cal}}$  and the electrode potential  $E_{\text{SCE}}$  is drawn in Figure 5 and is also shown as being linearly correlated in the investigated range.

Comparing Figure 2 with Figure 4, we can see that introducing the contribution of chemisorption  $\text{ClO}_4^-$  anions on Au(111) to the surface stress in low coverage  $\theta < 0.5$  cases can change the shape of  $\Delta g_{\text{cal}} - \sigma_M$  curve from an approximate hyperbolic type to a linear type. This gives a broad hint that the large



enough contribution from the specific adsorption of anions linearizes the  $\Delta g_{\text{cal}} - \sigma_{\text{M}}$  curve. In section 3.1 and Figure 2, without including the contribution of  $\text{ClO}_4^-$  anions, only the contribution of the specific adsorption of  $\text{Cl}^-$  anions is not large enough to change the shape of  $\Delta g_{\text{cal}} - \sigma_{\text{M}}$ , and in section 4 and Figure 4, the inclusion of the contribution of all  $\text{Cl}^-$ ,  $\text{ClO}_4^-$  anions makes the adsorbate-induced surface stress to be large enough to linearize the shape of  $\Delta g_{\text{cal}} - \sigma_{\text{M}}$ . Our results indicate that the surface stress is mainly caused by the response of the metal,<sup>9</sup> which varies smoothly with surface charge density or potential, but the contributions from specific adsorption anions are also very important, especially for the shape of the surface stress versus charge density curve. As Schmickler and Leiva pointed out,<sup>9</sup> the main variation is governed by the metal, while the fine structure is caused by specific adsorption.

In this section, we empirically introduce the contribution of  $\text{ClO}_4^-$  anion based on the relative experimental data. This is not a real theoretical calculation. In addition, the additive approximation of the coadsorption ions assumed in eqs 25 and 26 seems to be oversimplifying the problems. The difference between the theoretical and experimental results at lower coverage in Figure 4 might reflect the restriction on the use of the additive approximation. Even though the additive approximation might be used as a starting point in studies of this type of problems, in some cases coadsorption can produce enhanced adsorption where the presence of adsorbate B enhances the coverage with A, and poisoning where the presence of B inhibits the adsorption of A.<sup>9b,46</sup> Therefore, from the theoretical viewpoint, because the empirical introducing of the contribution of  $\text{ClO}_4^-$  to surface stress is not ideal, a new theory is needed for a multicomponent coadsorption systems.

**4.2. Some Methodological Aspects.** Finally, we discuss some methodological aspects of the theoretical study on the adsorbate-induced surface stress in which Schmickler's some analysis results in his review paper<sup>9b</sup> have been quoted. For adsorption problems in electrochemistry systems which include the adsorbate-induced surface stress, there are two possible strategies to deal with such complex systems: the first-principle and the phenomenological approaches. In the first methods one focuses on a particular aspect of the problem and treats this by first-principles or similar methods, such as Hartree-Fock and density function theory in computational quantum chemistry. For the second method one sets up a phenomenological model Hamiltonian accounting for all important features, explores its consequences, and fits the interaction parameters to experimental data. Both approaches are useful and, to a certain extent, complementary. First-principles methods usually focus on the interaction of the adsorption with the metal electrode and ignoring the other interactions in electrochemistry system, such as adsorbate-adsorbate interactions, which were considered as the most important causes for the adsorbate-induced surface stress.<sup>1,9a</sup> On the other hand, the cluster calculations in quantum chemistry methods for modeling surfaces are useful for studying the adsorption of a single particle on an uncharged surface. They do not work well for charged surfaces.<sup>9b,46a</sup>

New experiment results for the adsorbate-induced surface stress have spawned model calculations<sup>1,9a</sup> and quantum-chemical methods.<sup>1,10,11</sup> Quantum-chemical methods<sup>10,11,47</sup> can calculate the surface tension and stress of adsorbate-solid metals and confirm that these two quantities can differ considerably. The present quantum-chemical calculations of adsorbate-induced surface stress have been performed for uncharged surface, so any variation in the surface stress caused by a change in the surface-charge density is disregarded. However, since the

absolute values of the surface stress cannot be measured, electrochemists are more interested in their variation with the electrode potential or, equivalently, with the surface-charge density. By using the phenomenological approach, Schmickler and Leiva<sup>9a</sup> have investigated the contribution of an adsorbate to the interfacial stress and considered that the most likely cause for the adsorbate-induced surface stress would be adsorbate-adsorbate interactions. The phenomenological approach has been most fruitful for the study of adsorbate-adsorbate interactions. The lattice-gas model is natural starting point for setting up a model Hamiltonian, and has indeed been used by the majority of workers in this field.<sup>9,14</sup> Following refs 9 and 13, we also used the phenomenological approach and lattice-gas model in this paper. Since we consider the contribution of the substrate-mediated interaction and replace the full Hamiltonian with a lattice-gas Hamiltonian with the addition interaction cubic terms attributed to the indirect coupling between the adsorbates via the substrate, we have gone beyond lattice gas model to a certain extent on the basis of the analysis of effective lattice gas models in sections 2.5.2 and 2.5.4 in ref 45. The Bragg-Williams approximation in the lattice gas model may be worrisome for higher adsorbate coverages, and in this paper the coverage goes up to half a monolayer, which reaches nearly to saturated monolayer of the adsorbates. However, Price and Venables<sup>34</sup> pointed out that as the coverage reaches nearly to saturated monolayer, the Bragg-Williams approximation becomes equivalent to assuming a random distribution of a small number of noninteracting vacancies. This approximation is good and much better than the normal application to regions of low coverage. But still more investigations for various systems and different methods, for example quasi-chemical approximation, are needed, also in the future the various parameters in these models can be obtained from quantum-chemical calculations.

Among the various components of intermolecular forces the substrate-mediated interaction energy makes most important contribution to the adsorbate-induced surface stress. We emphasize that like the other intermolecular forces, such as the Lennard-Jones (n-6) potential, eq 19 for the substrate-mediated interaction is an empirical expression since the difficulties of the theoretical evaluation of the through-substrate interactions including four mechanisms (see section 2.1) lead to a heuristic approach to their determination. The inverse cube interaction in eq 19 can be adequate for the substrate-mediated dispersion energy<sup>19,34</sup> and phonon-mediated interaction.<sup>28,31</sup> But for the indirect electronic interaction the situation is complex, the indirect electronic interaction is expected to oscillate both as a function of the position of the Fermi level and the distance, but a asymptotic behavior falling off as  $r^{-3}$  or  $r^{-5}$  is obtained.<sup>32,33</sup> Many experimental results<sup>48,49</sup> indicate that the adatom-adatom interaction in halide adlayer on Au(111) is strongly repulsive in a wide range of the coverage  $\theta$  and is not oscillatory in sign with the adatom-adatom distance. This is indicated not only by the formation of two-dimensional adlayer structure, patterns of which show that it is repulsive,<sup>45,50,51</sup> but also by the core level binding energy shifts with increasing coverage.<sup>49</sup> Ocko et al.'s<sup>50</sup> and Weaver et al.'s<sup>51</sup> experiment and theoretical results on the structure and phase behavior of halide on single-crystal metal surfaces demonstrated this lateral repulsive interaction. However, on the whole, a satisfactory analytical formulas for the description of the substrate-mediated interactions including all the four mechanisms are need to be further established for the theory of adsorbate-induced surface stress, based on analytical theories and quantum-chemical calculations.



## 5. Conclusion

The statistical thermodynamic theory of the adsorbate-induced surface stress of adion monolayer on Au(111) has been established by using the lattice gas model. The effective pair interaction energy, the surface stress, and its components due to various intermolecule forces, and the area elasticity modulus  $\kappa_{2D}^{-1}$  in the chloride adlayer at the Au(111) electrode surface, have been calculated. The calculational result of surface stress of chloride adlayer is associated with the experiment. At lower  $\text{Cl}^-$  coverage, considering the contribution of  $\text{ClO}_4^-$  in addition to  $\text{Cl}^-$  adions, the change of surface stress is approximately linearly correlated with charge density. For  $\text{Cl}^-/\text{Au}(111)$  system, the difference between surface stress and surface tension is the same order of magnitude as that of surface stress, which cannot be neglected. Therefore, Haiss et al.'s experiment results<sup>7</sup> have been reasonably explained by the theory. About the physical origin of the adsorbate-induced surface stress in chloride adlayer on Au(111) electrode, the analysis for various components of intermolecular forces indicates that the substrate-mediated interaction energies dominantly contribute to the adsorbate-induced surface stress, through them the adsorption energy of adions on Au(111) plays a very important indirect role.

**Acknowledgment.** This work was supported by the National Natural Science Foundation of China (Grant No. 20173051) and The Science Foundation of Anhui Province in China. We are most grateful to the referees for their helpful and instructive comments.

## Appendix A: Relation among $\theta$ , $\sigma_M$ , and $E_{\text{SCE}}$ Describing the Chloride Adsorption at Au(111) Electrode Surface.

Shi and Lipkowski gave the detailed electrochemical data of the  $\text{Cl}^-/\text{Au}(111)$  system.<sup>36</sup> Figures 2 and 4 in ref 36 show the curves of  $\sigma_M-E$ ,  $\Gamma_{\text{Cl}^-}-E$ , and  $\Gamma_{\text{Cl}^-}-\sigma_M$  ( $\Gamma_{\text{Cl}^-}$  is the Gibbs excess of  $\text{Cl}^-$ ). On the bases of these curves, in the conditions of Haiss et al.'s experiment,<sup>7</sup> the corresponding values of  $\theta$ ,  $\sigma_M$ , and  $E_{\text{SCE}}$  describing the chloride adsorption at Au(111) electrode are presented in Table A.

**TABLE A: Relation among  $\theta$ ,  $\sigma_M$ , and  $E_{\text{SCE}}$  Describing the Chloride Adsorption at Au(111) Electrode**

$\theta$	0.20	0.25	0.30	0.35	0.40
$\sigma_M (\mu\text{C cm}^{-2})$	25.55	34.24	42.93	51.61	60.30
$E_{\text{SCE}} (\text{mV})$	205.93	263.70	323.92	370.11	423.70
$\theta$	0.45	0.50	0.51	0.52	0.53
$\sigma_M (\mu\text{C cm}^{-2})$	68.99	77.68	79.41	81.15	82.89
$E_{\text{SCE}} (\text{mV})$	485.93	549.63	567.41	585.19	594.07

## References and Notes

- (1) (a) Ibach, H. *J. Vac. Sci. Technol. A* **1994**, *12*, 2240. (b) Ibach, H. *Surf. Sci. Rep.* **1997**, *29*, 193.
- (2) (a) Spaepen, F. *Acta Mater.* **2000**, *48*, 31. (b) Cammará, R. C. *Prog. Surf. Sci.* **1994**, *46*, 2.
- (3) Berger, R.; Delamarche, E. et al. *Science* **1997**, *276*, 2021.
- (4) Fritz, J.; Gerber, C.H.; et al. *Science* **2000**, *288*, 316.
- (5) Lavrik, N. V.; Tipple, C. A.; Sepaniak, M. J.; Datskos, P. G. *Chem. Phys. Lett.* **2001**, *336*, 371.
- (6) Ibach, H.; Bach, C. E.; Giesen M.; Grossmann, A. *Surf. Sci.* **1997**, *375*, 107.
- (7) Haiss, W.; Nichols, R. J.; Sass, J. K.; Charle, K. P. *J. Electroanal. Chem.* **1998**, *452*, 199.
- (8) (a) Lipkowski, J.; Schmickler, W.; Kolb, D. M.; Parsons, R. *J. Electroanal. Chem.* **1998**, *452*, 193. (b) Guidelli, R. *J. Electroanal. Chem.* **1998**, *453*, 69. (c) Efimov, I. O.; Heusler, K. E. *J. Electroanal. Chem.* **2000**, *490*, 1.
- (9) (a) Schmickler, W.; Leiva, E. *J. Electroanal. Chem.* **1998**, *453*, 61. (b) Schmickler, W. *Annu. Rep. Prog. Chem., Sect. C* **1999**, *95*, 117.
- (10) Feibelman, P. J. *Phys. Rev. B* **1997**, *56*, 2175.
- (11) Leiva, E. P.; Del Pópolo M. G.; Schmickler, W. *Chem. Phys. Lett.* **2000**, *320*, 393.
- (12) Brako, R.; Sokceyic, D. *Surf. Sci.* **2000**, *454–456*, 623.
- (13) Wang, X. Q.; Chen, R.; Wang, Y.; He, T. J.; Liu, F. C. *J. Phys. Chem. B*, **1998**, *102*, 7568.
- (14) Guidelli, R. In *Adsorption of Molecules at Metal Electrodes*; Lipkowski, J., Ross, P. N., Eds.; VCH: New York, 1992; Chapter 1.
- (15) Dash, J. G. *Films on Solid Surfaces*; Academic Press: New York, 1975; p 169.
- (16) Linford, R. G. *Chem. Rev.* **1978**, *78*, 81.
- (17) Couchmen, P. R.; Jessor, W. A. *Surf. Sci.* **1972**, *33*, 429.
- (18) Muscat, J.-P. *Prog. Surf. Sci.* **1987**, *25*, 211.
- (19) Bruch, L. W. *Surf. Sci.* **1983**, *125*, 194.
- (20) Lombardo, S. J.; Bell, A. T. *Surf. Sci. Rep.* **1991**, *13*, 1.
- (21) Muscat, J.-P.; Newns, D. W. *Prog. Surf. Sci.* **1978**, *9*, 1.
- (22) Einstein, T. L. In *Chemistry and Physics of Solid Surfaces*; Vanselow, R., Ed.; CRC Press: Boca Raton, 1979; Vol. 2, p 181.
- (23) Schweizer, E.; Person, B. N. J.; Tushaus, M.; Hoge, D.; Bradshaw, A. M. *Surf. Sci.* **1989**, *213*, 249.
- (24) Zhdanov, V. P. *Elementary Physicochemical Process on Solid Surfaces*; Plenum: New York, 1991; p 105.
- (25) Nørskov, J. K. In *Chemistry Physics of Solid Surface*; King, D. A., Ed.; Elsevier: Amsterdam, 1993; Vol. 6, Chapter 1.
- (26) Gomer, R. *Acc. Chem. Res.* **1975**, *8*, 420.
- (27) Steele, W. *Chem. Rev.* **1993**, *93*, 2355.
- (28) Lau, K. H.; Kohn, W. *Surf. Sci.* **1977**, *65*, 607.
- (29) Sinanoglu, O.; Pitzer, K. S. *J. Chem. Phys.* **1960**, *32*, 1279.
- (30) MacLachlan, A. D. *Mol. Phys.* **1964**, *7*, 381.
- (31) Koper, M. T. M. *J. Electroanal. Chem.* **1998**, *450*, 189.
- (32) Grimley, T. B. *Proc. Phys. Soc. London* **1967**, *90*, 751.
- (33) Desjonqueres, M. C.; Spanjard, D. *Concepts in Surface Physics*; Springer: Berlin, 1993; (a) Section 6.5, (b) pp 490–492.
- (34) Price, G. L.; Venables, J. A. *Surf. Sci.* **1976**, *59*, 509.
- (35) Langmuir, I. *J. Am. Chem. Soc.* **1932**, *54*, 2798.
- (36) Shi, Z.; Lipkowski, J. *J. Electroanal. Chem.* **1996**, *403*, 225.
- (37) Toney, M. F.; Gordon, J. G.; Samant, M. G.; Borge, G. L.; Melroy, O. R. *Phys. Rev. B*, **1992**, *45*, 9362.
- (38) Toney, M. F.; Samant, M. G.; Borge, G. L.; Wiesler, D. G.; Yee, D.; Soresen, L. B. *Langmuir* **1991**, *7*, 796.
- (39) Magnussen, O. M.; Ocko, B. M.; Wang, J. X.; Adzic, R. R. *J. Phys. Chem.* **1996**, *100*, 5500.
- (40) Schmickler, W. *Interfacial Electrochemistry*; Oxford University Press: New York, 1996; p 220.
- (41) Bruch, L. W.; Cohen, P. I.; Webb, M. B. *Surf. Sci.* **1976**, *59*, 1.
- (42) Bruch, L. W.; Philips, J. M. *Surf. Sci.* **1980**, *91*, 1.
- (43) Shaw, C. G.; Fain, S. C., Jr. *Surf. Sci.* **1979**, *83*, 1.
- (44) Unguris, J.; Bruch, L. W.; Moog, E. R.; Webb, M. B. *Surf. Sci.* **1981**, *109*, 522.
- (45) Person, B. N. *J. Surf. Sci. Rep.* **1992**, *15*, 1.
- (46) (a) Gomes, J. A. N. F.; Ignaczak, A. *J. Mol. Structure (THEOCHEM)*, **1999**, *463*, 113. (b) Rikvold, P. A.; Collins, J. B.; Hasen, G. D.; Gunton, J. D. *Surf. Sci.* **1988**, *203*, 500.
- (47) Needs, R. J. *Phys. Rev. Lett.* **1986**, *58*, 53.
- (48) Dowben, P. A. *CRC Crit. Rev. Solid State Mater. Sci.* **1987**, *13*, 191.
- (49) Somerton, C.; McConville, C. F.; Woodruff, D. P.; Jones, R. G. *Surf. Sci.* **1984**, *136*, 23.
- (50) (a) Ocko, B. M.; Wandlowski, Th. In *Proceedings of the Materials Research Society: Electrochemical Synthesis and Modification of Materials*; Delplancke, J., Corcoran, S., Moffat, T., Eds.; November, 1996; pp 1–13, BNL-64333. (b) Wang, J. X.; Wandlowski, Th.; Ocko, B. M. In *Proceeding of the Symposium on The Electrochemical Doublelayer, Physical Electrochemistry Proceedings*; Korzeniewski, C., Conway, B. E., Eds.; The Electrochemical Society, Inc.: Volume 97-17; pp 293–301. (c) Magnussen, O. M. *Chem. Rev.* **2002**, *102*, 679–725.
- (51) (a) Weaver, M. J.; Gao, X. *Annu. Rev. Phys. Chem.* **1993**, *44*, 459. (b) Gao, X.; Edens, G. J.; Liu, F.-C.; Hamelin, A.; Weaver, M. J. *J. Phys. Chem.* **1994**, *98*, 8086.