



Adsorbate-Induced Surface Stress of Methanol Monolayer on Au(III) Surface†

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By using established statistical thermodynamic theory of adsorbate-induced surface stress of adsorption monolayer on metal surface, the surface stress Δg of methanol on Au(III) surface has been calculated. The calculated results indicate that the adsorbed methanol caused compressive surface stress, which is approximately linearly correlated with coverage. Among various terms of intermolecular forces, both the substrate-mediated interaction energy and the induction energy are important to the surface stress.

Keywords: Surface stress, Methanol monolayer, Au(III) surface.

INTRODUCTION

Surface stress plays a central role in the thermodynamics of solid surfaces¹. During the last decade increasing interest has been paid to processes which are strongly influenced by surface stress effects. Recently, it has been recognized that surface stress is a quantity which is important for a qualitative and sometimes even quantitative understanding of microscopic and mesoscopic surface processes. Increased knowledge about the surface stress of clean and adsorbate-covered metals has also been established by the development of new theoretical methods. The importance of surface stress for technological applications is demonstrated by the development of micro-cantilever sensors, which allow the detection of extremely small amounts of substances in gases or liquids².

Recently there has been considerable interest in the chemical behaviour of methanol on transition metal surfaces, inspired in part by the use of copper as a catalyst in methanol synthesis. The adsorption and decomposition of methanol have been investigated over various metal surfaces³. The most studied surface is Au(III) as the study of gold single crystal surfaces using the surface science approach provides useful fundamental information relevant to reaction mechanisms and the nature of active centers of supported gold catalysts⁴. By using the lattice gas model with the Bragg-Williams approximation, we have established a statistical thermodynamic theory of adsorbate-induced surface stress⁵⁻⁷. For the Cl⁻/Au(III) system

and alkanethiols SAMs/Au(III) system, the adsorbate-induced surface stress and its components due to various intermolecular forces have been calculated. The calculated results were in accordance with the related experimental results^{2,8}. Now we apply the theory to the methanol/Au(III) system to calculate the adsorbate-induced surface stress and its components due to various intermolecular forces as a theoretic predict.

THEORY

In order to apply our established statistical thermodynamic theory to methanol monolayer on Au(III), here we quote the main formulae and necessary explanations from reference 5 and 6.

From the definition of the surface stress, we have deduced the statistical thermodynamic formula for calculating the surface stress in adsorbate monolayers on metal surface

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

where Z is the nearest-neighbor coordinate number of an adsorbate. θ is the coverage of adsorbate relative to the substrate. a_s is the area of a single Au atom. For Au(III), the nearest-neighbor distance between the substrate sites $r_s = 2.885 \text{ \AA}$,

$a_s = \sqrt{\frac{3r_s^2}{2}}$. W is an effective pair interaction energy between adsorbates. It is evident that the surface stress is determined

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by two factors: adsorbate density and the adatom-adatom interaction energy with its derivative. The third term represents the contribution of configurational entropy.

Usually a pair interaction energy between the adsorbates W can be written as a sum of the inverse power of their distance⁶

$$W = \sum_n W_n \quad (2)$$

$$W_n = \frac{A_n C_n}{Z r^n} = \frac{A_n C_n}{Z r_s^n} \theta^{n/2} \quad (3)$$

where C_n is the coefficient of interaction energy. A_n is the lattice sum, whose value for hexagonal structure has been calculated and shown in reference 5. r is the nearest-neighbor distance between the adsorbates in the adlayer. Setting eqn. 3 into eqn. 1, we obtain a fundamental formula for calculating the surface stress in the hexagonal-structure methanol adlayer

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

According to the theory of chemisorption⁹⁻¹¹, the components of the lateral interaction energies in the adlayer on metal electrode like Au, Ag, Pt mainly include the substrate-mediated interaction energy, induced dipole-induced dipole interaction energy and Lennard-Jones potential including the van der Waals attraction and Pauli repulsion. We consider and evaluate each as follows.

For most chemisorption systems, the substrate-mediated interaction is dominant among the components in the lateral interaction energy. Based on the expression of substrate-mediated dispersion energy, we have introduced an exponential expression of substrate-mediated interaction as follows^{5,6}

$$W_{\text{sub}} = \frac{A_3}{Z} \alpha \frac{1}{r^3} E \quad (5)$$

where E is the adsorption energy of a single adsorbate. α is the molecular polarizability. The units are E in eV, r in Å and α in Å³. For methanol, $E = 0.389$ eV¹², $\alpha = 3.29$ Å³¹³. Using eqns. 4 and 5, the contribution of substrate-mediated interaction to the surface stress Δg_{sub} is

$$\Delta g_{\text{sub}} = -\frac{1}{4a_s} \sum_n (n+2) A_n C_n \frac{1}{r_s^n} \theta^{\frac{n+4}{2}} = -\frac{5A_3 C_3}{4a_s r_s^3} \theta^{7/2} \quad (6)$$

where the following parameters have been used: $n = 3$, $A_3 = 10.975$, $C_3 = \alpha E$ and r_s is in eV/Å².

The induced dipole-induced dipole interaction energy is⁶

$$W_{\text{ind}} = 0.624 \frac{A_3 \mu_0^2}{Z r^3} \quad (7)$$

where μ_0 is the dipole moment. The units are W_{ind} in eV, μ_0 in Debye, r in Å and α in Å³. For methanol, $\mu_0 = 1.70$ Debye. Using eqns. 4 and 7, the contribution of induction interaction to the surface stress Δg_{ind} is

$$\begin{aligned} \Delta g_{\text{ind}} &= -\frac{1}{4a_s} \sum_n (n+2) A_n C_n \frac{1}{r_s^n} \theta^{\frac{n+4}{2}} = -\frac{5A_3 C_3}{4a_s r_s^3} \theta^{7/2} \\ &= -\frac{0.78A_3 \mu_0^2}{a_s r_s^3} \theta^{7/2} \end{aligned} \quad (8)$$

where the unit is Δg_{ind} in eV/Å².

We combine Pauli repulsion from the wave function overlap of the closed shell and van der Waals attraction into the Lennard-Jones potential

$$W_{\text{L-J}} = 8.625 \times 10^{-5} \frac{\epsilon}{Z} \left[A_{12} \left(\frac{r_0}{r} \right)^{12} - 2A_6 \left(\frac{r_0}{r} \right)^6 \right] \quad (9)$$

where ϵ is the depth of the potential energy minimum, r_0 is the van der Waals diameter of the adsorbates. The units are $W_{\text{L-J}}$ in eV, r_0 in Å, ϵ in K. For methanol, $r_0 = 3.626$ Å, $\epsilon = 481.8$ K¹⁴. Using eqns. 4 and 9, the contribution of Lennard-Jones potential to the surface stress $\Delta g_{\text{L-J}}$ is

$$\begin{aligned} \Delta g_{\text{L-J}} &= -\frac{1}{4a_s} \sum_{n=6,12} (n+2) A_n C_n \frac{1}{r_s^n} \theta^{\frac{n+4}{2}} \\ &= -\frac{8.625 \times 10^{-5} \epsilon}{2a_s} \left[7A_{12} \left(\frac{r_0}{r_s} \right)^{12} \theta^8 - 8A_6 \left(\frac{r_0}{r_s} \right)^6 \theta^5 \right] \end{aligned} \quad (10)$$

where the unit is $\Delta g_{\text{L-J}}$ in eV/Å².

Summing the contributions of Δg_{sub} , Δg_{ind} , $\Delta g_{\text{L-J}}$ and configurational entropy, we get the adsorbate induced surface stress due to the adsorbed methanol on Au(III)

$$\Delta g = \Delta g_{\text{sub}} + \Delta g_{\text{ind}} + \Delta g_{\text{L-J}} + \frac{kT}{a_s} \ln(1-\theta) \quad (11)$$

RESULTS AND DISCUSSION

Using eqn. 11, we have calculated the contribution of methanol monolayer on Au(III) to the surface stress. The calculated result is shown in Table-1 and Fig. 1.

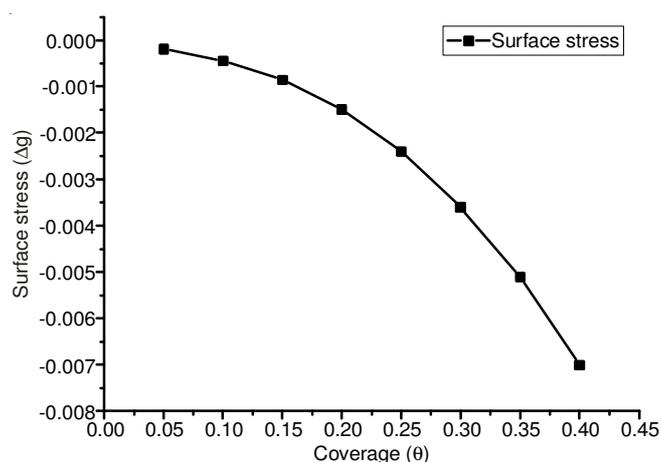


Fig. 1. Relationship between surface stress and coverage of methanol adlayers on Au(III)

TABLE-1
CALCULATED SURFACE STRESS (IN eV/Å²) IN THE METHANOL ADLAYERS ON Au(III)

θ	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
Δg	-0.00019	-0.00045	-0.00085	-0.00149	-0.00240	-0.00360	-0.00511	-0.00701

In Table-1, we have listed the calculated surface stress of methanol monolayer on Au(III). Apparently, the adsorbed methanol caused compressive surface stress. At high coverage, the change of surface stress is approximately linearly correlated with coverage. In this model, the Bragg-Williams approximation is used, which is generally accepted and widely used in a system of adsorbates at a metal electrode. Price and Venables¹⁵ pointed out at high coverage, 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.

In order to further discuss the physical origin of the surface stress, we have calculated the contribution of each term of the interaction energies and configuration entropy, which is shown in Table-2 and Fig. 2.

θ	Δg_{sub}	Δg_{ind}	$\Delta g_{\text{L-J}}$	Δg_{com}	Δg
0.05	0.00000	0.00000	0.00000	-0.00018	-0.00019
0.10	-0.00003	-0.00005	0.00001	-0.00038	-0.00045
0.15	-0.00013	-0.00019	0.00004	-0.00058	-0.00085
0.20	-0.00036	-0.00051	0.00018	-0.00079	-0.00149
0.25	-0.00079	-0.00112	0.00054	-0.00102	-0.00240
0.30	-0.00150	-0.00211	0.00128	-0.00127	-0.00360
0.35	-0.00257	-0.00363	0.00262	-0.00153	-0.00511
0.40	-0.00411	-0.00579	0.00470	-0.00182	-0.00701

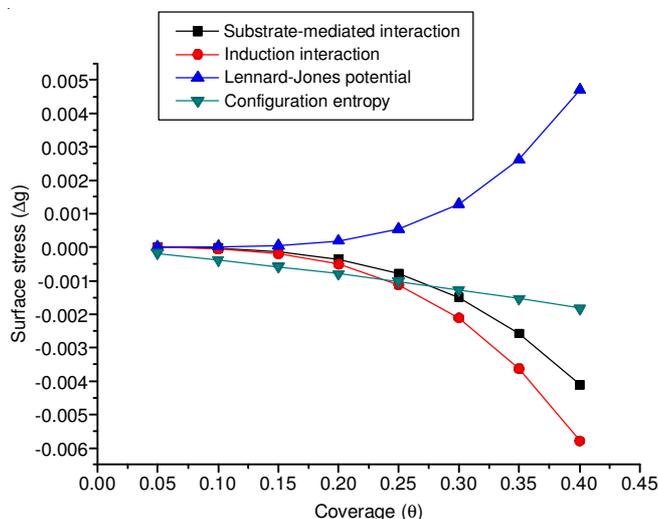


Fig. 2. Contribution of each term of the interaction energies and configuration entropy to the surface stress from methanol adlayers on Au(III)

Table-2 and Fig. 2 reveal that, among various terms in the surface stress, except the positive contribution of Lennard-Jones potential, all the other terms are negative, which give that the surface stress is compressive. Among them, the contribution of substrate-mediated interaction energy and the induction energy are determinant, which shows that for the system of methanol adsorbing on Au(III), not only the indirect contribution of the adsorption energy of methanol through the substrate-mediated interaction, but also the contribution of the dipolar repulsive forces is very important.

Conclusion

By using established statistical thermodynamic theory of adsorbate-induced surface stress of adsorption monolayer on metal surface, the surface stress of methanol on the Au(III) surface and its components due to various intermolecule forces of methanol adlayer have been calculated. At high coverage, the change of surface stress is approximately linearly correlated with coverage. About the physical origin of the adsorbate-induced surface stress in methanol adlayer on Au(III) surface, the analysis for various components of intermolecular forces indicates that both the substrate-mediated interaction energy and the induction energy are important to the surface stress.

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REFERENCES

1. W. Haiss, *Rep. Prog. Phys.*, **64**, 591 (2001).
2. R. Berger, E. Delamarche, H.P. Lang, C. Gerber, J.K. Gimzewski, E. Meyer and H.-J. Güntherodt, *Science*, **276**, 2021 (1997).
3. W.-K. Chen, S.-H. Liu, M.-J. Cao, Q.-G. Yan and C.-H. Lu, *J. Mol. Struct. Theochem*, **770**, 87 (2006).
4. S.A.C. Carabineiro and B.E. Nieuwenhuys, *Gold Bull.*, **42**, 288 (2009).
5. R. Xie, Chen, Wang, He and F.-C. Chen, *J. Phys. Chem. B*, **106**, 12948 (2002).
6. X. Wang, R. Chen, Y. Wang, T. He and F.-C. Liu, *J. Phys. Chem. B*, **102**, 7568 (1998).
7. R. Xie, *Surf. Rev. Lett.*, **16**, 807 (2009).
8. W. Haiss, R.J. Nichols, J.K. Sass and K.P. Charle, *J. Electroanal. Chem.*, **452**, 199 (1998).
9. J.-P. Muscat, *Prog. Surf. Sci.*, **25**, 211 (1987).
10. L.W. Bruch, *Surf. Sci.*, **125**, 194 (1983).
11. S.J. Lombardo and A.T. Bell, *Surf. Sci. Rep.*, **13**, 3 (1991).
12. T.J. Lawton, J. Carrasco, A.E. Baber, A. Michaelides and E.C.H. Sykes, *Phys. Rev. Lett.*, **107**, 256101 (2011).
13. R.C. Weast, *CRC Handbook of Chemistry and Physics*, CRC Press: Boca Raton (2000).
14. R.A. Svehla, *Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures*, NASA Technical Report R-132 (1962).
15. G.L. Price and J.A. Venables, *Surf. Sci.*, **59**, 509 (1976).