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FIELD ADSORPTION AND EVAPORATION

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Abstract - A microscopic tight-binding cluster model is used to calculate the field-induced adsorption of He on tungsten. Likewise field evaporation of tungsten ions is computed as a function of electric field strength. The importance of local field effects - here taken from self-consistent jellium calculations - is emphasized.

I. INTRODUCTION

Adsorption of gases on metals is strongly enhanced in large electric fields of the order of several volts per Angstrom. Theoretical understanding of field-induced adsorption has been sought within the framework of phenomenological models of which the very first one by Tsong and Müller /1/ still seems the most popular. It assumes:

(i) the metal-gas system can be modeled by a gas atom-metal atom dimer, i.e. the metal bulk properties are of lesser importance;

(ii) the electric field is constant over the dimer, in contrast to standard electrostatics according to which the electric field drops to zero at the image plane just outside the metal;

(iii) the binding comes about through the interaction of the induced dipoles on the two atoms of the dimer. The field-induced binding energy is then given by

\[ Q = \frac{1}{2} \alpha_A \left( \frac{1+2 \alpha_W/d^3}{1-4\alpha_A\alpha_W/d^6} \right)^2 - 1 \] \[ F^2 \text{ext} \] (1)

Here \( \alpha_A \) and \( \alpha_W \) are the polarizabilities of the surface metal atom and the adsorbed atom, respectively, and \( d \) is their separation. Recent calculations within the jellium model of a metal give evidence how the electric field decays into the metal and how this decay depends on the field strength far from the metal, and on the electron density in the conduction band (see Fig. 1 for examples). In the first accounts /1/ of the model \( \alpha_W \) was given as 3.44 \( \text{Å}^3 \) and 4.6 \( \text{Å}^3 \) for tungsten, a recent measurement /2/ gives \( \alpha_W = 14.4 \text{Å}^3 \). This changes the value of \( Q \) for He on W from 0.14 eV to 0.2 eV to 0.95 eV in a field \( F = 4.5 \text{ V/Å} \) if one takes \( d = 2.59 \text{ Å} \) as the sum of atomic radii of a W and a He atom.

We note that in zero field, the minimum of the physisorption potential of He on most metals is more than 3.5 \( \text{Å} \) from the topmost lattice plane. Moreover, there is no reason to believe that \( d \) stays constant as the electric field pushes the surface electrons into the metal decreasing \( d \) appreciably to the point, where dipole interactions are insufficient and electronic effects come into play, eventually leading to chemisorption. We have developed a microscopic theory of field adsorption and evaporation that follows up on these ideas /3/.

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The theory is based on the ASED-MO (atom superposition and electron delocalization molecular orbital) cluster model. One assumes that the single electron properties (energy levels and wavefunctions) of the isolated atoms are known. Bringing N metal atoms together to form a metal cluster one calculates its potential energy as the sum of Coulomb energies between the unperturbed atoms plus a contribution from mutual electron overlap (tight binding Hückel type). The applied electric field, as taken from selfconsistent jellium calculations /4/, is taken fully into account in the Hamiltonian of the metal cluster plus-gas-atom. It leads to position dependent shifts in the electron levels of the various atoms of the cluster and additional off-diagonal matrix elements that can be analyzed as contributing to polarization, hyperpolarization, gradient corrections, etc. /5/.

2. FIELD ADSORPTION

In Fig. 1 we show the potential energy curves for He in front of a cluster of 4 to 14 atoms representing W(111) surfaces in an asymptotic field \( F = 3 \text{ V/Å} \). Also shown is the field potential \( V_F(z) \) and the field \( F(z) = -\frac{dV_F(z)}{dz} \) for a metal with Wigner-Seitz radius \( r_s = 3 \). Curves (a) to (c) are approximations in which only local energy shifts (a) plus linear polarization of He (b) plus linear polarization of W (c) are successively added. Curve (d) takes all field effects into consideration. To summarize the results as a function of asymptotic field strength we give in Fig. 2 the position of the binding minimum \( z_{\text{min}} \), the activation energy \( Q \) (difference between minimum and top of the activation barrier) and the charge transfer \( \Delta q \) at the binding minimum. To demonstrate how important the local electric field is for field adsorption we give the same data in Fig. 3 for a metal with \( r_s = 1.5 \), a value more acceptable for tungsten (one has to be aware of some difficulties to associate a jellium model of s-electrons with a transition metal). We note:

(i) a drastic inward motion of the adsorption site for fields larger than about 3 V/Å;

(ii) a concurrent increase in binding energy from about 10 meV in \( F = 0 \) to a few hundred meV;

(iii) an appreciable charge transfer to the metal. These trends can be characterized as a transition from physisorption in zero field (with van der Waals attraction) to chemisorption in strong fields due to electronic bond formation.

Fig. 1 - Potential energy curves for the He/W(111) system. The electric field \( F \) and electric potential \( V_F \) are taken from jellium calculations /4/. The tungsten cluster has 14 atoms. Curves (a) includes only local single electron energy shifts; (b) includes polarization of He; (c) also of W and (d) includes all field effects.
3. FIELD EVAPORATION

Field evaporation can only take place if the electric field penetrates into the metal. Taking the local field variations again from the selfconsistent jellium calculations /4/, we show in Fig. 4 that the activation barrier disappears for \( r_s = 3 \) in a field of \( 4 \, \text{V/Å} \) and for \( r_s = 1.5 \) at \( 8 \, \text{V/Å} \). The fact that the zero field binding energy is only 6.8 eV per atom rather than 8.2 eV as suggested by the cohesive energy of tungsten is not surprising as Hückel-type calculations typically are not better than 20 - 50 %, anyway. However, the trend of activation energy as a function of field strength as depicted in Fig. 4 is trustworthy. Higher electron densities (lower \( r_s \)) reduce field penetration and thus require larger evaporation field strengths.

To allow a comparison of our He-tungsten results with experimental data, we suggest to (i) characterize tungsten with \( r_s = 1.5 \) and (ii) to scale the electric field such that our evaporation field of \( 8 \, \text{V/Å} \) is set equal to the experimental value of 5.6 V/Å. The activation energy (curve (d) from Fig. 3) can then be compared with data by Ernst et al. (Fig. 1 and 2 in the following contribution of this volume by Ernst et al).

4. CONCLUSIONS

We have discussed a microscopic theory of field adsorption and evaporation. First results are very encouraging. They show, in particular, that field adsorption must be understood as a transition from physisorption to chemisorption. There is much
Fig. 4 - The activation energy for field evaporation for W from a W cluster.

left to improve the cluster model, in particular, to make it self-consistent with the field calculated for a specific adsorption site rather than a flat jellium surface.

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