Field Adsorption of Helium on Tungsten

N. Ernst, W. Drachsel, Y. Li,[a] and J. H. Block

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, Federal Republic of Germany

and

H. J. Kreuzer

Department of Physics, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada

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Using atom-probe spectroscopy we measured the activation energy for desorption and the position of He on W for fields between 3 and 5 V/Å. A tight-binding cluster model with local fields from jellium calculations reproduces the data and gives the image plane as 0.8 Å above the topmost lattice plane. The desorption energy increases by a factor of 20 and the equilibrium position reduces from 3.3 Å in $F=0$ to ~ 2 Å in $F>3$ V/Å. This is interpreted as a transition from physisorption to weak field-induced chemisorption.

Rare gases, and most surprisingly helium, are long known to adsorb in electric fields of the order of volts per angstrom on field-emitter tips at temperatures as high as 200 K.[1] For helium the activation energy for desorption in a field $F/F_{ev}=0.66$ is found to be $Q=128$ meV and in $F/F_{ev}=0.93$ to be $Q=246$ meV (see Fig. 2). Here $F_{ev}\approx 5.6$ V/Å is the field strength at which tungsten starts to evaporate. In this Letter we report a measurement and a calculation of the field dependence of Q and

also of the equilibrium position of the field-adsorbed He atom.

In the experiments we have employed two methods including atom-probe field-ion microscopy, (i) electron-stimulated field desorption (ESFD),[2,3] and (ii) laser-stimulated field desorption (LSFD).[4,5] In ESFD adatoms are ionized by electron impact and are subsequently field desorbed as singly or doubly charged ions, as outlined in Fig. 1. The electrons are generated by space-
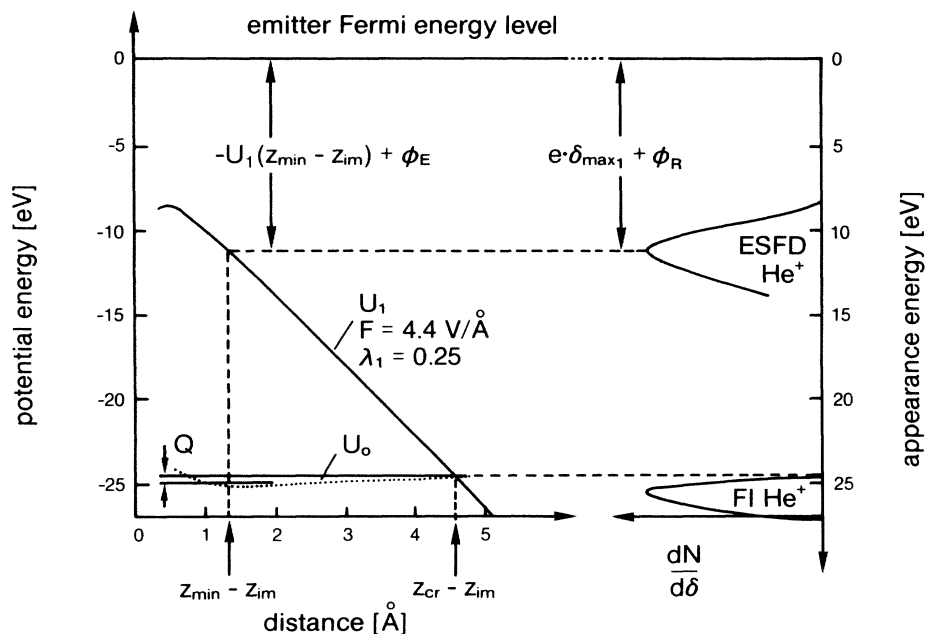

FIG. 1. One-dimensional potential-energy scheme drawn on scale (left-hand side) for explaining the occurrence of distinct appearance energies derived from retarding-potential analysis of electron-stimulated field-desorbed He^{n+} (ESFD, $n=1$) and field-ionized He^+ (FI) (Ref. 2). A field-adsorbed He, initially vibrating around the equilibrium position $z_{min}-z_{im}$, is ionized by electron impact and immediately desorbed as He^+ (or He^{2+}) because of the applied electric field F. ESFD He^+ displays a peak in the appearance kinetic energy distribution allowing the determination of the equilibrium distance (with respect to the image plane) $z_{min}-z_{im}$ as indicated by the dashed line. U_1 represents the potential energy for He^+, and U_0 indicates the potential energy for adsorbed He.

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field ionization of H_2 added to the rare gas. LSFD of He (and also of Ne) is initiated by a nanosecond laser pulse that heats the emitter tip leading to thermal desorption of adatoms that are field ionized as they leave the tip. The temperature dependence of the ion rates can be fitted on the assumption of a Volmer isobar for a mobile He adsorbate; it yields the desorption-energy data shown in Fig. 2(a). We note that in the accessible temperature range from 80 to 200 K the coverage drops by about a factor of 100.

To determine the equilibrium position of field-adsorbed atoms from ESFD data we treat the ionization process by electron impact in the Born-Oppenheimer approximation. The kinetic-energy distribution of the ions is then directly related to the deficit in potential energy for He^{n+} at the point of ionization (equilibrium position) as shown in Fig. 1. To deduce a value for the equilibrium

position one must know the shape of the local ionic potential energy. It is approximately given for n-fold charged ions by addition of a linear field term $-neF(z-z_0)$ to the classical image potential $-3.6n^2\lambda_n/(z-z_0)$, where z and z_0 are measured from the position of the topmost lattice plane. From the analysis of appearance (retarding potential) energy data one finds that the image potential is screened by a factor $0 < \lambda_n < 1$ that depends on the charge state of the ion. It arises from the fact that the ions are formed within 1-2 Å from the image plane so that electron overlap with the metal leads to repulsion, weakening the (attractive) image potential. One adjusts λ_n so that the hump of the ionic-potential curve aligns with the high-energy cutoff of the appearance-energy distribution, yielding $\lambda_1 = 0.25$ for He^+ and $\lambda_2 = 1.0$ for He^{2+}. Emitter and retarder work functions, ϕ_e and ϕ_r, must be taken into account as indicated in Fig. 1. The
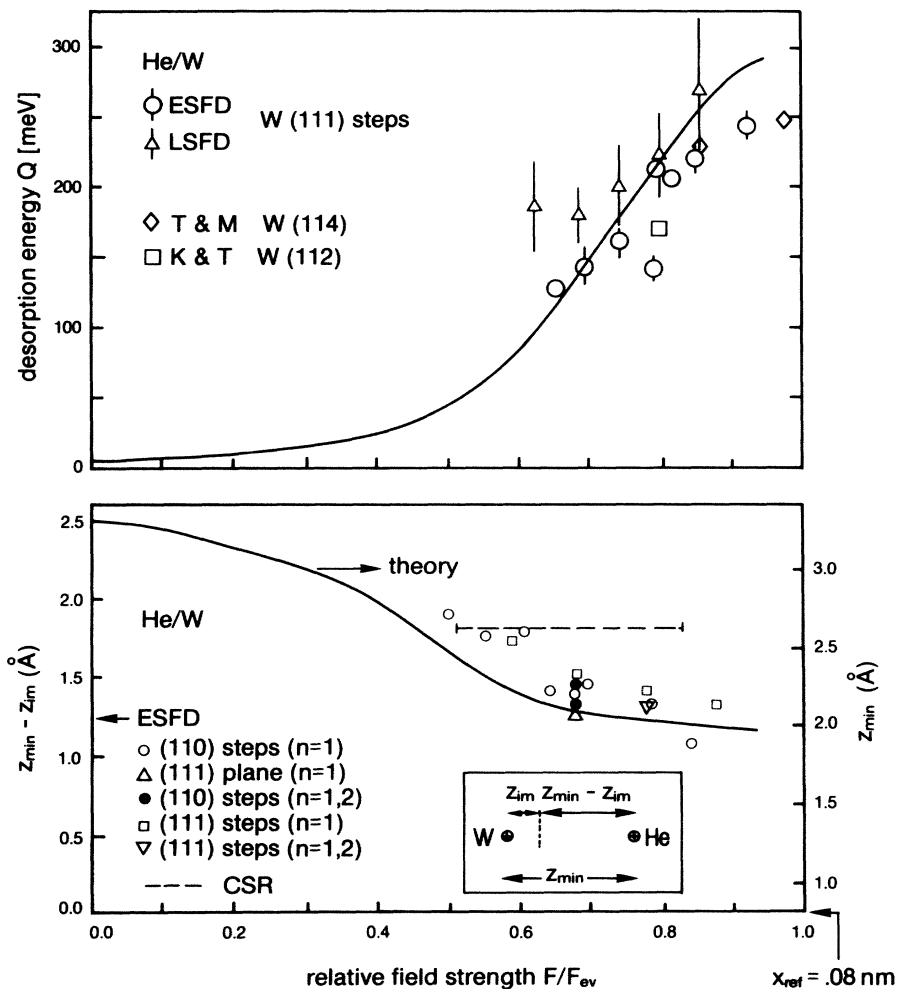

FIG. 2. (a) Comparison of experimental and theoretical data of desorption energies of field-adsorbed He as a function of relative field strength $(F_{ev} = 5.6$ V/Å). Data labeled T&M from Tsong and Muller (Ref. 6), and the K&T data from Kinkus and Tsong (Ref. 7). (b) Equilibrium position of field-adsorbed He as a function of field strength. Experimental points refer to left-hand scale; theoretical curve refers to the right-hand scale, which has been shifted to fit the datum point (triangle) on the (111) plane. Dashed curve refers to data from Culbertson, Sakurai, and Robertson (Ref. 8) obtained without a retarding-potential energy analysis and by averaging over the indicated field range.

equilibrium position z_{min} of field-adsorbed atoms can then be determined from

$$z_{min} - z_{im} = [(e\delta_{max_n} + \phi_r - \phi_e)/2F] + \{[(e\delta_{max_n} + \phi_r - \phi_e)/2F]^2 - (0.36n\lambda_n)/F\}^{1/2}, \qquad (1)$$

where $z_0 = z_{im}$ is the image plane position, measured from the topmost lattice plane, and δ_{max_n} is the maximum value of the (differential) appearance energy distribution of n-fold charged ESFD ions. For the analysis of the data we neglect a small field dependence of z_{im} in the range $F \approx 3-5$ V/Å. The work function for the retarder electrode is given by $\phi_r = I_1 - e\delta_0$, where I_1 is the first ionization energy of the He atom and δ_0 is the onset voltage of the retardation curves of singly charged field-ionized atoms, measured at low temperature.[2] The local work function ϕ_e of the emitter tip is less well known; we take values tabulated in the literature. The field strengths F are calibrated with the metal-evaporation field strength at low temperature, $F_{ev} = 5.6$ V/Å.

The resulting distances of field-adsorbed He are given in Fig. 2(b). The quality of this procedure can be checked independently by our noting that for a combined measurement of singly and doubly charged ESFD ions, the equilibrium position of the field-adsorbed atom can be determined according to

$$z_{min} - z_{im} = [0.36(2\lambda_2 - \lambda_1)]/(\delta_{max_2} - \delta_{max_1}), \qquad (2)$$

eliminating any uncertainties in the work functions and the field strength. Because of very low He^{++} yields, this check could only be made at two field strengths, yielding agreement with results derived from (1).

To understand the data collected in Figs. 2(a) and 2(b) and, in particular, to determine the position of the image plane, z_{im}, we now present the results of a microscopic theory of field adsorption of rare gases that uses the atom-superposition and electron-delocalization method[9] to calculate binding or activation energies, bond lengths, and charge transfers of rare gases adsorbed on metal surfaces in strong electric fields. On the basis of a charge-partitioning model one writes the total energy E as a sum of a repulsive term E_r that accounts for the Coulomb interaction of isolated atoms with each other and a remainder E_{npf} that entails the rearrangement within the atoms in the presence of each other. The latter is calculated from a Hamiltonian

$$H = \sum_{i\alpha} H_{ii}^{\alpha\alpha} |\phi_i^\alpha\rangle\langle\phi_i^\alpha| + \sum_{ijab} H_{ij}^{\alpha\beta} |\phi_i^\alpha\rangle\langle\phi_j^\beta|, \qquad (3)$$

where in the spirit of an extended Hückel scheme one puts the diagonal elements $H_{ij}^{\alpha\beta} = -E_i^\alpha \delta_{ij}\delta_{\alpha\beta}$ equal to the negative of the ionization energy of level i on atom α, taken from experiment. The remaining off-diagonal elements are from a modification of the extended Hückel formula $H_{ij}^{\alpha\beta} = \kappa(H_{ii}^{\alpha\alpha} + H_{jj}^{\beta\beta})S_{ij}^{\alpha\beta}\exp(-aR_{\alpha\beta})$, with $S_{ij}^{\alpha\beta} = \langle\phi_i^\alpha | \phi_j^\beta\rangle$ the overlap integral between the ith atomic orbital on atom α and the jth orbital on atom β, the latter being a distance $R_{\alpha\beta}$ away. Fitting bond strengths and lengths to first-row diatomics, we determined the parameters to be $\kappa = 1.125$ and $a = 0.13$ Å^{-1}.

To incorporate field-penetration effects in our cluster calculations we assume that the electric field has only a z component that, in addition, only depends on z. According to recent self-consistent calculations[10] of the electric field at a (flat) jellium surface, the field has Friedel oscillations, decaying into the metal, and an exponential rise to the asymptotic constant value in vacuo. This z-dependent electric field adds diagonal terms in the Hamiltonian (3) that lead to the raising of the energy levels E_i^α in $H_{ij}^{\alpha\beta}$ by the local field energy $e\int_{-\infty}^{z_\alpha} F(z)dz$, where z_α are the positions of the nuclei, as done previously.[11] Some off-diagonal elements are proportional to the overlap integrals between atomic orbitals on different atoms. They have been accounted for by modification of the Hückel-type hopping matrix elements by again raising the energy levels by the field energy.[11] The off-diagonal elements on the same atom lead to polarization effects.

We have calculated the adsorption energy of helium adsorbed on a cluster of 14 W atoms, simulating the (111) surface, as a function of the He distance from the W cluster. We note that neglecting polarization effects, i.e., only shifting the atomic energy levels according to the local field energy as done previously, overestimates the activation energy by a factor of 2 to 3 for most field strengths. We have taken the local field variation from the jellium calculations by Gies and Gerhardts for a Wigner-Seitz radius $r_s = 1.5$. We find that up to an asymptotic field of 3–4 V/Å the activation energy Q of He stays below 10 meV and the equilibrium position is about 3.3 Å above the topmost W layer. For fields larger than 4 V/Å, Q increases dramatically to a few hundred millielectronvolts at 7 V/Å with q_{min} decreasing to about 2 Å signaling the changeover from physisorption to field-induced chemisorption. Obviously, this change occurs at too-high field strengths. However, we would argue that the absolute value of the field strength is rather uncertain in the comparison of theory and experiment. After all, we have transferred the field variation at a flat jellium edge to a transition-metal cluster and are comparing the results with desorption data from (most likely) kink sites. To make a meaningful comparison we have therefore also calculated the binding energy of a tungsten atom on a cluster surface as a function of field. We find that it drops from 6.8 eV in $F = 0$ (somewhat less than the cohesive energy 8.66 eV) to zero, i.e., leading to field evaporation, around $F = 8$ V/Å. Setting this field strength equal to $F_{ev} = 5.6$ V/Å we can then compare theory and experiment as done in Fig. 2. As for the activation energies the agreement is embarrassingly good and should be taken as somewhat accidental because the theory is not accurate to this extent.

A direct comparison of the equilibrium positions is not

possible because experiment only determines $z_{min} - z_{im}$. However, we can shift the theoretical curve to fit the data. This obviously allows us to find the position z_{im} of the image plane relative to the topmost lattice plane; we get $z_{im} \approx 0.8$ Å. The theoretical z_{min} data have been fitted to experimental $(z_{min} - z_{im})$ data measured on the flat W(111) plane [triangle in Fig. 2(a)]. The separation between adjacent layers of W(111) is $a/2\sqrt{3} = 0.91$ Å, so that the jellium edge is 0.46 Å above the topmost W(111) layer. This is in good agreement with simple estimates that put z_{im} at half the interplanar distances and also with jellium calculations of Gies and Gerhardts.[10]

In summary, new data on the field dependence of the activation energy and equilibrium position of field-adsorbed He can be understood within a microscopic theory as a transition from zero-field physisorption to weak field-induced chemisorption. The comparison of theory and experiment produces a first determination of the image plane position for He^{n+} ions above the metal surface.

(a)On leave from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, People's Republic of China.

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