

Electron Transfer in the Interaction of Fluorine and Hydrogen with Pd(100): The Case of a Transition Metal versus Jellium

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(Received 17 November 1998)

Results of a study of electron transfer processes in the interaction of fluorine and hydrogen with Pd(100), resulting in anion formation, are reported for a wide range of particle scattering conditions. We observe that the negative ion yield is much larger than what would be expected for a jelliumlike metal surface with a similar work function. These results indicate that capture occurs efficiently in the case of this very high work function surface and that the electron loss rates are much *smaller* than for the jelliumlike simple metal (e.g., aluminum) case.

PACS numbers: 79.20.Rf, 34.50.Dy, 82.65.My

In gas-surface interactions, electron transfer processes between an atom or a molecule and the surface play an important role. Thus, e.g., CO adsorption on Pd involves electron exchange with the surface [1]. An important question in this context is the manner in which the electronic states of a gas phase particle approaching the surface are affected by it and the dynamics of the electron transfer process. For some model systems the answers can be obtained from the study of negative ion formation which involves resonant electron transfer (RET) of electrons near the Fermi level, also important in many reactions at surfaces. The understanding of negative ion formation is also of fundamental interest in chemisorption and reactions at surfaces, where negative ions play a role as intermediates [2], in electron or photon stimulated desorption processes [3], as well as in studies of surface composition in secondary negative ion mass spectroscopy [4].

A number of theoretical descriptions of RET and negative ion formation [5–7] have been developed based on a *jellium* model for the surface. The theoretical predictions concerning the energy positions and widths of the atomic negative ion states near the surface and the dynamics of electron transfer could be tested by comparing with quantitative data on the probabilities of negative ion formation determined in atom scattering experiments. Most detailed experiments of this type have focused on simple metals [8–15] such as Mg, Al, and Ag. In the case of H⁻ and F⁻ formation, remarkably good agreement with existing theories has been found. Even in the case of Ag [polycrystals and Ag(110)], where *d* electrons are important, good agreement is reached [14,15]. This may not be so surprising since the *d* band lies well below (3 eV) the Fermi level and the resemblance of the *s* band with a free electron band is strong.

The very important case of transition metals has not yet been treated. Attempts at describing RET and O⁻ formation, observed in sputtering experiments involving V, Nb, and Ni surfaces [16] have been made using

a jellium description [16–18]. The situation, however, appears different in this case. An intense *d* band extends through the Fermi energy, and the density of levels is much higher in the *d* band (~ 3.5 states/eV) than the free electron density (~ 0.2 states/eV). From a simple Friedel-type model of transition metals [19,20], one would conclude that the density of states of the free electrons is several times *smaller* than for simple metals at binding energies in the vicinity of the Fermi level of interest for negative ion formation and other reactions (e.g., ~ 0.4 states/eV for Al and ~ 0.2 states/eV for Pd [20]). Strong *sp-d* hybridization effects induce the appearance of gaps and surface states [19–21]. In the region of the *d* band and near the Fermi level rather strong deviations from a free-electron-like *sp* band occur.

In view of these interesting characteristics of transition metals, we decided to perform a study of RET for these systems. We chose Pd which is of more interest in catalysis. As a free atom, Pd has a $4d^{10}5s^0$ electronic configuration. In the metal, an *sp* character is acquired and, as for other transition metals, the number of “free electrons” would be about 0.5 [19,20]. The Pd(100) band is schematized in Fig. 1 on the basis of recent calculations of Dong *et al.* [21]. Similar results have been obtained by Barreteau *et al.* [22]. In Fig. 1 we have sketched the total density of states (DOS) of a surface Pd atoms and the 5*s* contribution. At the bottom of Fig. 1 we show the band structure of the bulk projected to the surface Brillouin zone [21]. The dots mark the dispersion relation of surface states. This figure shows the characteristic, for the (100) face, band gaps in the *XM* region near and just above the Fermi level and higher-lying band gaps at X and Γ .

In this paper we present results of a study of H⁻ and F⁻ formation. The positions of the affinity levels with respect to the parent atoms (0.75 and 3.4 eV) are shown in Fig. 1 along with a qualitative sketch of the level shifts due to image potential effects. As usual, we relate surface and atomic binding energies, and hence the vacuum level and parent atomic state position are taken as the energy zero.

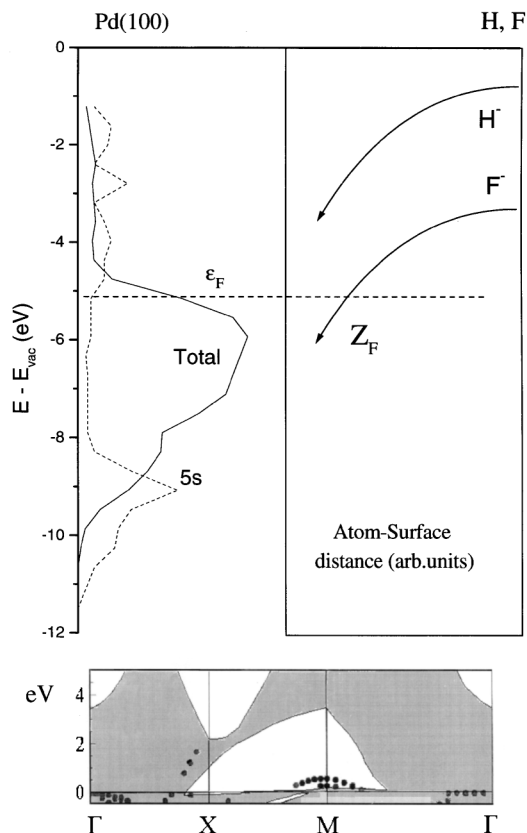


FIG. 1. Schematic diagram of the density of states of Pd(100) following Dong *et al.* [21], and a schematic diagram of the position of the H^- and F^- levels. The DOS is in arbitrary units [21] and the $5s$ intensity is arbitrarily amplified. The band structure of the bulk projected to the surface Brillouin zone is shown at the bottom of the figure. The dots mark the dispersion of surface states. The zero of the energy scale (in eV) is set at the Fermi level.

The remarkable and important feature of our experimental results, which we wish to underline here, is that we find a much *higher* probability of forming negative ions than what one would expect on the basis of earlier experimental and theoretical results for simple “jellium-like” metals. We relate this to the specific features of the electronic structure of transition metals and specifically Pd(100) described above and illustrated in Fig. 1. They clearly demonstrate that, although in the past electron transfer on transition metals was tentatively described within a jelliumlike description, this does not appear appropriate. It is hoped that these results will stimulate theoretical studies of atom/molecule interactions with these systems that are of major practical interest.

Our experiments were performed on a previously described setup [23]. Ions were produced in a discharge source, mass selected, and steered into the main ultra-high vacuum (UHV) chamber. The pressure in the chamber was 2×10^{-10} Torr. The sample was polished to $0.05 \mu\text{m}$ and oriented to within 0.5° by the supplier. The incidence beam direction was 10° from the [110]

azimuth. *In situ* preparation consisted of Ar^+ grazing sputtering and annealing to about 700°C . A clear low-energy electron diffraction (LEED) pattern was obtained at this stage. Surface cleanliness was ascertained by Auger electron spectroscopy (AES), and a time-of-flight (TOF) analysis of scattered and recoiled particles under Ar^+ bombardment was performed. A clean surface condition was considered to be one in which direct recoiled peaks of H, C, and O were no longer visible in the TOF spectra [23]. The Pd work function (ϕ) was measured by performing low-energy secondary electron spectroscopy under He^+ bombardment and monitoring the zero energy cutoff in the electron spectra. The cutoff for Pd was compared to that for Ag(110), for which $\phi = 4.3$ eV [24]. We found $\phi_{\text{Pd}} = 5.15$ eV, in agreement with published data [21].

We report anion formation probabilities or ion fraction measurements made for fixed scattering angles (7° and 38°) using position sensitive channel plate detectors with three discrete anodes [23]. Deflectors allow separation of ions and neutrals, which are detected simultaneously by the anodes. Measurements were performed for ion energies (E_0) in the 0.5 to 4 keV range. The incidence (α) and exit (ψ) angles (Fig. 2) with respect to the surface plane were varied by rotating the sample. In case of the 38° TOF detector, this allows one to scan an exit angle (ψ) range up to 38° ($\alpha + \psi = 38^\circ$). The angular acceptance of the detectors are 0.08° for the 7° and 0.12° for the 38° one. The negative (Φ^-) ion fractions are defined as the ratio of the scattered flux in a given charge state to the total scattered flux into a given ψ . Here we concentrate on the low-energy scattering data, where inelastic (excitation/ionization) effects are not important. Indeed, in the case of F^- for $E_0 > 1$ keV, some F^+ are observed (about 10% at 4 keV for $\psi = 30^\circ$) for incident F^- .

Results are shown in Fig. 2 for H^+ and F^- incident ions. In previous RET studies for Al, Ag, and Mg the initial charge state of the ion was not found to play a role. In the case of F^- for $E_0 = 500$ eV, a 40% fraction is obtained at large ψ . At small angles a rapid increase is observed. Results for the 7° and 38° TOF detectors are of similar magnitude (for small exit angles), showing that the incident ion beam trajectory (e.g., for 3.5° and 34.5° incidence angles) is not important. Measurements using F^- neutral beams did not reveal any differences with respect to a F^- incident beam at 1 keV. The F^+ fraction was very small (0.6% at 20°).

For H^+ scattering, the Φ^- display the same behavior as for F^- but are smaller, attaining 3% at large angles. The H^+ fraction was smaller (0.8% at 20°).

The general trend as a function of ψ qualitatively resembles that for Al and Ag [12–15]. However, smaller F^- fractions are found for Pd. For comparison, the results for Ag(110) [15] are also shown in Fig. 2(a). On the other hand, the Φ^- for H^- is of similar magnitude to these for Al and Ag [12]. The Φ^- for Al and Mg targets [12] are shown as lines in Fig. 2(b) for comparison.

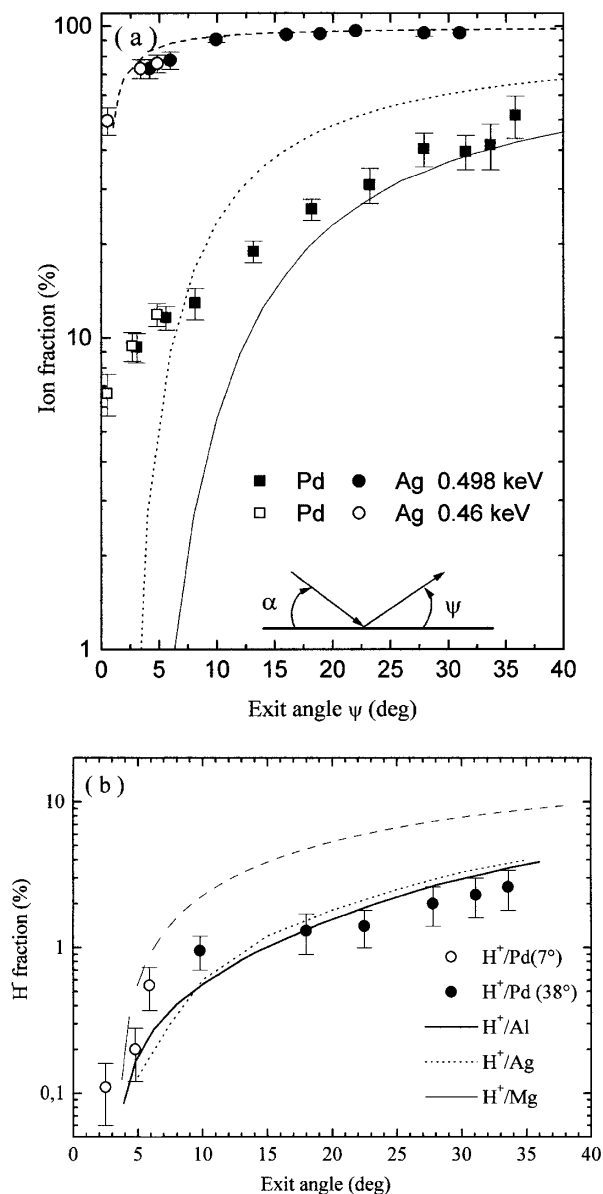


FIG. 2. (a) F^- ion fractions for 0.5 keV incident ions, as a function of the exit angle to the surface. The solid and open squares are our data for Pd(100) for the 7° and 38° detectors, respectively. The circles are data for Ag(110) [15] shown for comparison. The solid (dashed) line is the rate equation calculation for Pd(100) [and Ag(110)] using the widths for jellium with appropriate work function values. The dotted line indicates the result of the calculation with a width decreased by a factor of 2. (b) H^- ion fractions for 1 keV incident ions. The open and solid circles are the H^- data measured using the 7° and 38° detectors, respectively. The solid and dashed lines show the trend of the data for Ag, Al, and Mg [12].

Given the *higher work function* for Pd(100) ($\phi = 5.15$ eV) than for Al or Ag ($\phi = 4.3$ eV), one could expect that the Φ^- would be *smaller*. As schematized in Fig. 1 the downward shifted affinity level of the atom can be populated by RET from the occupied states of the valence band of a metal, when the affinity level lies beneath the Fermi level (E_F , Fig. 1), for distances smaller

than a critical distance Z_F ($Z_F \sim 3.9$ a.u. from the image plane). The population of the affinity level will depend on its width and the time spent in the regions, where capture ($Z < Z_F$) and loss ($Z > Z_F$) can occur. For a higher ϕ , Z_F becomes smaller (see Fig. 1). Hence the range of distances at which capture can occur becomes smaller, while that corresponding to losses increases. Therefore Φ^- should be smaller for a higher work function surface. Thus for Al and Ag ($\phi \approx 4.3$ eV) we obtained smaller H^- fractions than for Mg ($\phi \approx 3.64$ eV) [12].

In order to verify if the observed lower F^- fraction is indeed simply consistent with the larger work function ($\phi = 5.15$ eV), we estimated the value of Φ^- that would be obtained for a free-electron-like metal using calculated [25] widths of F^- for the jellium case. We assumed that capture occurs with unit probability (this is reasonable for small velocities corresponding to small ψ) and calculated losses in a rate equation approach. This procedure, which gives an *upper limit* for Φ^- , yields results in good agreement with Al and Ag [14,15,25]. This is illustrated in Fig. 2(a) for Ag. The increase in the value of Φ^- for larger ψ is due to larger survival at larger velocities perpendicular to the surface. The Φ^- calculated for the Pd(100) case are shown by the solid line in Fig. 2(a). A notable feature is that the experimental Φ^- are *considerably larger than the calculated ones*, especially at small ψ .

We did not calculate Φ^- in the case of H^- since, even for the lowest 1 keV energy, this would require taking properly into account the so-called parallel velocity effect [8], which plays an important role in negative ion formation [12]. However, on qualitative grounds, one can expect that the ion fractions would be considerably smaller than those for Mg and Al because of the higher value of the Pd work function. This effect was illustrated in Fig. 2(b) on the example of Mg and Al. However, as noted above, the ion fractions for Pd are *not* smaller than for Al.

Thus a most interesting feature of these results is that both H^- and F^- are formed with a considerably *higher* probability on Pd than one would expect for the case of a jelliumlike metal with the same work function. A rough estimate of the F affinity level width for Pd was made by arbitrarily reducing the width [25] in order to fit Φ^- in the vicinity of $\psi = 5^\circ$. The atom-surface distance dependence of the width was left the same. A width about 2 times smaller was required, but the overall shape could not be fitted, as shown in Fig. 2(a) by a dotted line. It should be noted that at the larger angles the velocity perpendicular to the surface becomes large, and one could conjecture that interaction time becomes insufficient for population of the affinity level with a unit probability. Thus better fits could be obtained only by modifying the capture rate or assuming larger minimum atom/surface distances of approach.

We thus find that electron *capture* occurs efficiently and the electron loss rates appear to be *smaller* than what

would be expected in terms of a jelliumlike simple metal model. We tentatively attribute this discrepancy to the notable deviations of the electronic structure of Pd(100) from the free-electron-like model, neglecting the role of d electrons. As mentioned in the introduction and as may be seen in Fig. 1, the free-electron-like DOS is very strongly perturbed in the d band region and is smaller (~ 0.4 states/eV for Al and ~ 0.2 states/eV for Pd) and generally different from a jelliumlike model at the binding energies of interest here. The loss widths could therefore be smaller than in the jelliumlike Al case, as follows from our estimate. As noted above, capture rates also had to be reduced. This could, in particular, be related to the fact that the capture process may involve d electrons. The atom-surface distance dependence of transfer rates could be quite different. For a correct description of the process, one should consider the specific characteristics of these levels.

Another aspect of this problem is related to the existence of gaps characteristic for the (100) surface (Fig. 1). This signifies that loss processes will not always be possible, leading to higher ion fractions. Thus for F^- the loss could be hindered by the gap in the XM region. For H^- we would also have to take into account the other gap regions lying higher above the Fermi level (at X and Γ). Recently the role of the gap at Γ for the Cu(111) surface was investigated theoretically [26] and it was indeed found that the loss rates of atomic states would be smaller because decay cannot occur along the surface normal. These authors found, however, that the overall characteristics of RET were strongly dependent on the collision dynamics. We note in this context that, in our recent preliminary investigation of F^- formation on the [similar to Cu(111)] Ag(111) case [27] and in scattering conditions similar to the ones discussed for Pd(100), we did not observe any significant modifications in anion formation rates attributable to this gap that would differentiate capture and loss on this surface from the Ag(110) and polycrystalline Ag case [14,15]. A study of electron transfer on Pd(111) may be of interest in this context. Also, a study of the crystal azimuthal dependence would be of interest.

In summary, we find higher ion fractions than expected for a jelliumlike metal, an effect which could be due to a reduced s -electron DOS and the existence for gaps characteristic for Pd(100). Much effort has been invested into the theoretical description of electron transfer processes and the properties of atomic and molecular states near simple metal surfaces, and remarkable agreement with experiment has been achieved. We hope that this work,

which shows that results for transition metals do not fall into the simple picture, will stimulate theoretical work on electron transfer involving these more complex systems, which are of immense practical interest.

The authors are grateful to A. Borisov, D. Spanjaard, and M. C. Desjonqueres for useful comments about their work. E.S. acknowledges FOMEC, Fundación Antorchas (A-13561/1-21) and SECyT (PICT97 No. 03-00004-00110) for partial financial support.

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