# Interaction Time Dependence of Electron Tunneling Processes between an Atom and a Surface

L. Guillemot and V. A. Esaulov*

*Laboratoire des Collisions Atomiques et Moléculaires (Unité associée au CNRS), Université Paris Sud, bât 351, 91405 Orsay, France*

Results of a study of electron transfer processes in the interaction of fluorine and hydrogen with Ag(111) are reported for a wide range of interaction times. For long interaction times the yield of $H^-$, resulting from resonant electron exchange, is larger than expected for a jelliumlike metal surface with a similar work function. For short interaction times, the yields follow the trend for jelliumlike surfaces. These results confirm the predictions of the theoretical work [Borisov *et al.* Phys. Rev. Lett. **80**, 1996 (1998)] on electron transfer on surfaces with an $L$ band gap. In the case of $F^-$, significant effects were, however, not observed.    [S0031-9007(99)09233-9]

Electron tunneling between an atom or molecule and a surface has been the object of numerous experimental and theoretical studies because of its importance as an intermediate step in many reactions at surfaces and in processes of ion desorption or neutralization [1–3]. Resonant electron transfer, involving one electron transition between an atomic level and metal states of the same energy, has been quite extensively studied using the example of negative ion formation [4,5]. A number of nonperturbative theoretical methods describing these processes [6–9] have been recently developed and applied to their description on simple metallic surfaces using a jellium model for the surface. Excellent agreement between the experimental and theoretical predictions has been found for $H^-$ [10–12] and $F^-$ [13–15] formation on polycrystalline Mg, Al, Ag, Al(111), and Ag(110).

An exciting new development in this field is a recent work of Borisov *et al.* [16] who points out that resonant charge transfer could be strongly affected by the peculiarities of the 3D band structure of a monocrystalline target. This theoretical work discussed the modifications which would be induced by the existence of the $L$ band gap along the distance normal to the surface for the Cu(111), Ag(111), and Au(111) surfaces [17,18], which would partially inhibit electron tunneling between the atom and the surface. The formation of $H^-$ ions on a Cu(111) surface was studied using a wave packet propagation treatment developed by Ermoshin and Kazansky [19] and it was shown that the widths of the $H^-$ state are smaller than the ones predicted for a jelliumlike surface. A remarkable feature of these results was that these differences were found to be *dependent on the interaction time* of the atom with the surface. Much smaller electron transfer probabilities (losses) from the atom were found for *long interaction times,* while for high velocities or short interaction times the results were similar to the ones obtained for jellium. Thus, for instance, in the case of a $6a_0$ atom–Cu(111) surface distance the electron loss probability from $H^-$ was found to be an order of magnitude smaller than for jellium for a 0.02 a.u. velocity, while for a 0.2 a.u. velocity the result is

similar to the jellium case. These differences were found to augment with atom-surface distance. The wave packet propagation treatment shows that this is related to the fact that for long interaction times an electron from the ion has enough time to be reflected by the potential in the metal and travel back to the ion several times—conditions under which the "reflectivity" of the metal is fully "sensed" by the electron. This results in a smaller probability of electron loss from the anion. At short interaction times the system behaves as if there was no reflectivity, and the losses are the same as in the jellium model. For such a time dependent electron tunneling process *a rate equation approach is inadequate* [16].

The implications of these findings are profound for, e.g., surface chemistry, which involves low-energy atom/molecule interactions with surfaces and where changes in electron transfer rates would affect the probability of various reactions where this process occurs. An experimental study of electron transfer for these surface was obviously urgently required in order to investigate this most intriguing and hitherto unknown effect. We therefore studied $H^-$ and $F^-$ formation on Ag(111). Silver was chosen since we had previously studied electron transfer on polycrystalline Ag ($p$-Ag) and Ag(110) for which the results are in agreement with a jelliumlike treatment [11–15] and hence provided a basis for comparison. The two anions chosen present examples of extreme situations with a low (0.75 eV, $H^-$) and high (3.4 eV, $F^-$) binding energies. The positions of the affinity levels with respect to the parent atoms are shown in Fig. 1. The electronic structure of Ag(111) [18] is depicted in the left panel of Fig. 1. As usual, we relate metal and atomic electron binding energies, and hence the vacuum level and parent atomic state position are taken as the energy zero in Fig. 1. As may be seen at large distances the ion level is located in the band gap for one-dimensional electron motion normal to the surface. For three-dimensional motion, decay can occur in the two-dimensional continuum of the surface state corresponding to movement parallel to the surface and the three-dimensional valence band continuum.
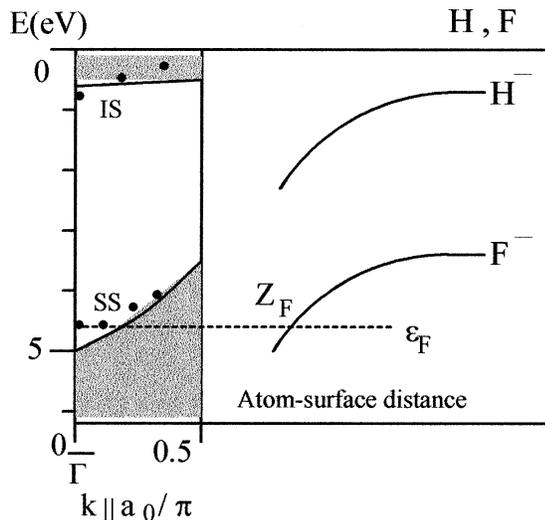
FIG. 1. Schematic diagram of the density of states of Ag(111) and a schematic diagram of the position of the anion levels. The shift of the anion levels represents an image potential shift. The left area of the figure shows various states of Ag(111) as a function of $k_{\parallel}$: the surface (SS) and image (IS) ($n = 1$ states). The gray area represents the valence band continuum.

In this Letter we present the main experimental data, which for $H^-$ formation *fully confirm* the results of the theoretical study. Indeed we found that in grazing scattering conditions, when the velocity component normal to the surface ($v_\perp$) is small and hence the interaction time with the surface is large, the ion fractions are substantially higher than for jelliumlike surfaces, while for large normal velocities the anion yields tend to follow the trends for the jelliumlike $p$-Ag and Ag(110). These results thus vividly illustrate the time dependent characteristics of the electron tunneling process in this case.

Our experiments were performed on an apparatus described elsewhere [20]. Ions were produced in a discharge source, mass selected, and steered into the main UHV chamber (base pressure $\approx 2 \times 10^{-10}$ Torr). The commercial sample Ag(111) was polished to 0.05 $\mu$m and oriented to within 0.5°. *In situ* preparation consisted of $Ar^+$ grazing, sputtering, and annealing to 500 °C. Surface cleanliness was initially ascertained by Auger-electron spectroscopy, when impurities such as sulfur were first eliminated. A clear low-energy electron diffraction pattern was obtained at this stage. Thereafter a time-of-flight (TOF) analysis of scattered and recoiled particles for $Ar^+$ incident ion bombardment was used to check for the absence of impurities such as H, C, and O [20]. The surface work function ($\phi$) was measured by performing low-energy secondary electron spectroscopy under $He^+$ bombardment and monitoring the zero-energy cutoffs in the electron spectra. The cutoff for Ag(111) was compared to that for Ag(110), whose $\phi$ has been given as 4.3 eV [21]. We found that $\phi = 4.5$ eV for Ag(111), in good agreement with published data [22].

We report anion formation probabilities or ion fraction measurements made mainly for specular scattering

using a position sensitive channel plate detector, equipped with three discrete anodes [20]. Deflectors allow separation of incoming ions and neutrals, which are then detected simultaneously by the anodes. The detector rotates around the sample vertical axis, and here the measurements spanned a 0° to 70° range. These were made in a continuous beam mode. Some measurements were performed with similar detectors set at the end of TOF tubes at fixed 7° and 38° scattering angles. Both continuous beam mode ion fraction measurements and TOF analysis of the energy losses of the scattered particles were performed, in order to correct the ion fractions determined in the continuous beam mode. This correction was found to be unnecessary. Measurements spanned ion energies in the 0.5 to 6 keV range.

We shall first briefly discuss the $F^-$ case. The anion ($\Phi^-$) fractions are defined as the ratio of the scattered anion flux to the total flux in a given angle $\psi$ with respect to the surface plane. Results are shown in Fig. 2(a) for a 500 eV incident energy and specular scattering. Results for Ag(110) are also shown in Fig. 2(a). The general behavior of $\Phi^-$ is similar to that observed earlier on $p$-Ag and Ag(110) [12–15], although its magnitude was larger in the latter cases. Given the higher work function for Ag(111) (4.5 eV) than for Al or Ag (4.3 eV), one would expect this. Indeed the affinity level of the atom, which is downward shifted due to the effect of the image potential (Fig. 1), can be populated by a transition of an electron from the occupied states of the valence band of a jelliumlike metal, when it lies beneath the Fermi level ($E_F$, Fig. 1), for distances smaller than a critical distance $Z_F$. The population of the affinity level will depend on its width ($\Gamma$, which is interaction time *independent* in the jellium case) and the time spent in the regions, where capture ($Z < Z_F$) and loss ($Z > Z_F$) can occur (the capture or loss rate is given by $\Gamma dt$). For a higher work function the distance at which the affinity level crosses below the Fermi level $Z_F$ becomes smaller (see Fig. 1). Hence the range of distances at which capture can occur becomes smaller, while that corresponding to losses increases. Therefore $\Phi^-$ should be smaller, as we observe.

We estimated the value of $\Phi^-$ that would be obtained for a jelliumlike metal using calculated [15] widths of the $F^-$ affinity level in a rate equation approach [4,13]. We assumed that capture occurs with unit probability (an approximation that is reasonable for small velocities). This procedure, which gives an upper limit for the ion fraction (unit capture probability), results in good agreement for $p$-Ag [13] and Ag(110) [Fig. 2(a)]. The increase in $\Phi^-$ for larger $\psi$ is due to larger survival at larger $v_\perp$ to the surface. The ion fractions calculated for the Ag(111) case using a value of 4.5 eV for the clean surface work function are shown by the solid line in Fig. 2(a). The calculated $\Phi^-$ are slightly larger than the experimental ones [$\approx 10\%$ at 30° for Ag(111)]. This is due to the neglect of the so-called parallel velocity effect (see Refs. [11,12,15] for details). Excellent agreement is in fact reached when this effect is included, as shown by some preliminary
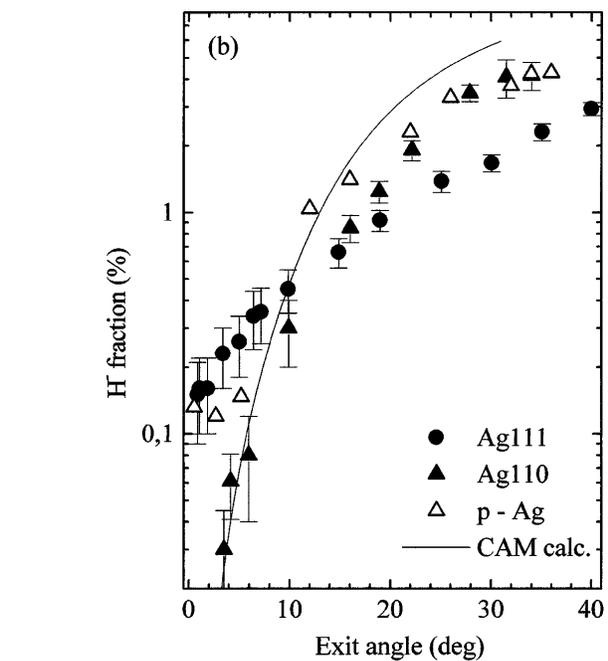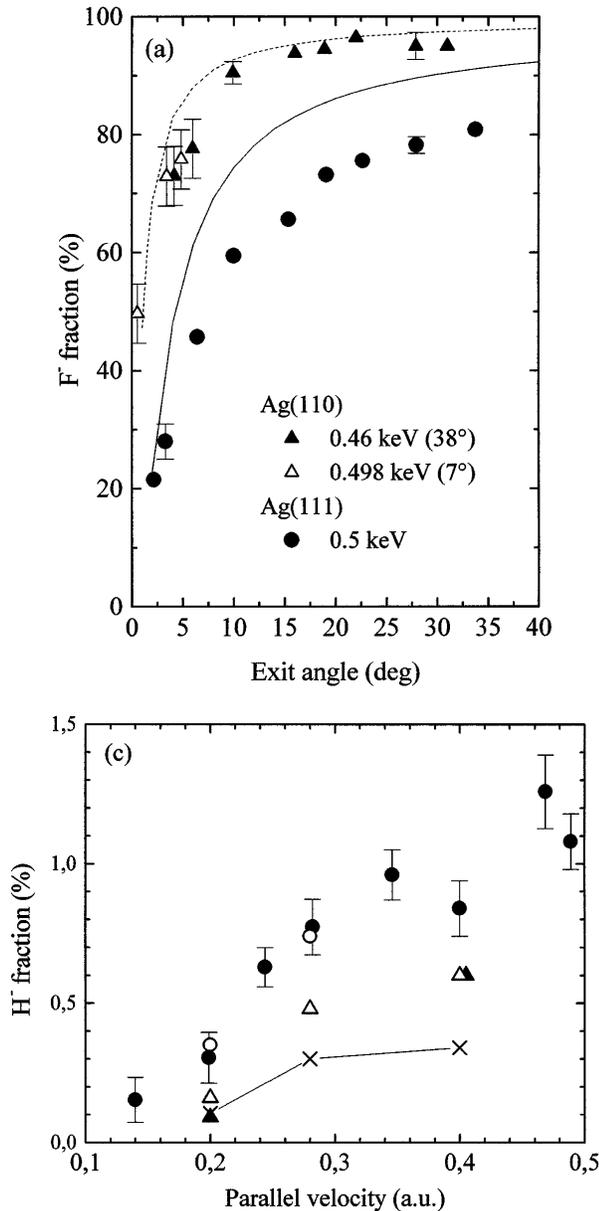
FIG. 2. (a) $F^-$ ion fractions as a function of the exit angle to the surface for 500 eV incident ions. The final energy varies from 0.5 to 0.46 keV at larger angles. The data for Ag(110) [15] are shown for comparison. The solid (dashed) line is the rate equation calculation for Ag(111) [Ag(110)] using the widths for jellium [15] with appropriate work function values. (b) $H^-$ ion fractions for 1 keV incident ions. The solid circles are data for Ag(111) for $H^+$ incidence. Open and solid triangles are data for $p$-Ag [12] and Ag(110) [24]. The solid line is a jellium model calculation of the $H^-$ ion fraction [12] for Ag ($\phi = 4.3$ eV). (c) The $v_{\parallel}$ dependence of the $H^-$ ion fraction for a 0.02 a.u. perpendicular velocity. The ion energies range from 0.5 to 6 keV. The open and solid circles are Ag(111) data for $H^-$ and $H^+$ incidence. The open and solid triangles are $p$-Ag [12] and Ag(110) [24] data. The line and crosses are jellium model calculation for Ag [12].

calculations [23]. Thus in the case of fluorine the data can be described using the anion widths for jellium and we do not observe any special effects related to the existence of the gap for these scattering conditions.

The ion fractions measured for the $H^-$ case for 1 keV are shown in Fig. 2(b), where they are compared with our previous results for $p$-Ag [12] and Ag(110) [24]. The line in the figure represent theoretical ion fractions for a jelliumlike surface [12]. Again, the ion fractions display the same general trend as a function of the exit angle to the surface. However, we *observe a larger ion fraction at small angles in the case of Ag(111)*. On the other hand, *at large angles, the ion fraction becomes smaller than for p-Ag and Ag(110)*. Similar results were obtained at the other energies.

As illustrated in the $F^-$ case, the larger work function of the Ag(111) surface would lead us to expect a smaller

$\Phi^-$ for Ag(111), in agreement with our observation at large angles. The larger $\Phi^-$ at small angles (corresponding to small $v_\perp$ and hence long interaction times) is in clear contradiction with this expectation and we attribute it to a smaller electron loss probability as predicted by Borisov *et al.* [16] for surfaces with an $L$ gap.

At this point it is necessary to mention that surface roughness can result in larger values of $\Phi^-$ since, as may be seen from the theoretical result in Fig. 2(b), $\Phi^-$ increases very rapidly at small angles. We would indeed attribute the larger value of $\Phi^-$ for $p$-Ag to a rougher surface than for the monocrystalline Ag(110). This leads to the flat region in the $p$-Ag data at small angles as opposed to the drop for Ag(110). In order to check the degree of surface roughness we measured the angular scattering profile of $H$ atoms and compared it to our earlier results for $p$-Ag. We found a FWHM of 3.5° for

Ag(111) while this was 6° for *p*-Ag [12], indicating that the Ag(111) surface roughness is *inferior* to that of *p*-Ag. The larger value of $\Phi^-$ is therefore not due to roughness. This confirms our attribution of the larger value of $\Phi^-$ on Ag(111) to the existence of the *L* gap.

The other important feature is the above-mentioned fact that $\Phi^-$ is smaller at large angles, i.e., for larger normal velocities and shorter interaction times, that for *p*-Ag and Ag(110). In the jellium case this is consistent with the larger work function. For short interaction times the losses thus tend to follow the trend for the jellium case. *The overall behavior of the ion fraction thus illustrates the time dependent characteristics of the electron transfer probabilities and gives a vivid illustration of the predictions of the theory of Borisov et al. [16].*

As shown in previous experiments [11,12], $H^-$ formation on metal surfaces is strongly aided by fast movement parallel to the surface. For this low binding energy system, the addition of velocities ($v_{ion} + v_{Fermi}$, see Refs. [11,12] for details) helps in matching, or bringing into resonance, the energies of the electrons in the solid with the affinity level. Borisov *et al.* [16] pointed out that, in the *L*-gap case, one could expect a different $v_\parallel$ dependence because of the 2D nature of the electron loss continuum. In Fig. 2(c), we therefore plotted the $H^-$ ion fractions for the three Ag surfaces for a $v_\perp = 0.02$ a.u. (6° exit angle for 1 keV) as a function of $v_\parallel$ in an energy range from 0.5 to 6 keV. We see that the $v_\parallel$ dependence is similar in this velocity range, but the Ag(111) data lie higher than those for the other surfaces, as already noted for 1 keV. Thus for this system and in this $v_\parallel$ range no qualitative difference appear to exist. Note that for other $v_\perp$ the dependence on $v_\parallel$ is similar.

A final question that comes to mind regards *memory effects* or the influence of the initial charge state of the ion. We therefore also made some measurements with an incident $H^-$ beam. Results for $H^+$ and $H^-$ incidence were similar [see Fig. 2(c)], indicating that memory of the initial charge state is lost, as in the jellium case [12], although the electron loss probabilities at small $v_\perp$ are smaller than for jellium.

In summary, we thus see that our $H^-$ data confirms the time dependent characteristics of electron transfer between an ion and a surface with an *L* gap predicted by Borisov *et al.* [16]. The electron loss process is strongly reduced for small normal velocities, as compared to the jellium case, and the observed differences decrease with increasing normal velocity. In a more general context, we could thus indeed expect that some reactions involving electron exchange with such surfaces and processes of anion desorption would be strongly affected. Note, however, that our data on $F^-$, where we do not observe notable differences, show that some important questions remain open. A possible reason that this effect is not observed for $F^-$ could be that the affinity level lies quite close to the Fermi level and is located towards the bottom of the band gap and close to the surface state. Thus, even though the normal velocity is quite small for 500 eV $F^-$ ions, the interaction time during which the level lies above the Fermi level would be too short. In this context, work on higher work function Cu(111) or Au(111) surfaces might be useful. It should, however, also be borne in mind that the 2*p*-electron nature of the $F^-$ problem and, in particular, the existence of $m = 0$ and $m = \pm 1$ states (pointing towards and along the surface) render the situation more complex. For the jellium case the widths of these states [15,25] are different and it is not clear *a priori* if they would be affected in a similar manner by the existence of the gap. Further theoretical work on such, very common, *p*-electron anions should be undertaken, and we hope this paper will stimulate such investigations.

The authors are grateful to A. G. Borisov, A. K. Kazanskii, and J-P. Gauyacq for comments.

*Corresponding author.
[1] R. Hoffman, Rev. Mod. Phys. **60**, 601 (1988).
[2] T. Greber, Surf. Sci. Rep. **28**, 1 (1997).
[3] N. J. Sack, M. Akbulut, and T. E. Madey, Phys. Rev. Lett. **73**, 794 (1994).
[4] J. Los and J. J. C. Geerlings, Phys. Rep. **190**, 133 (1990).
[5] A. Kleyn, in "Negative Ions", edited by V. Esaulov, (Cambridge University Press, Cambridge, England, to be published).
[6] P. Nordlander and J. C. Tully, Phys. Rev. Lett. **61**, 990 (1988).
[7] D. Teillet-Billy and J. P. Gauyacq, Surf. Sci. **239**, 343 (1990).
[8] H. Shao, D. C. Langreth, and P. Nordlander, Phys. Rev. B **49**, 13 929 (1994).
[9] A. G. Borisov *et al.,* Phys. Rev. Lett. **68**, 2842 (1992).
[10] U. Van Slooten *et al.,* Chem. Phys. **179**, 227 (1994).
[11] F. Wyputta, R. Zimny, and H. Winter, Nucl. Instrum. Methods Phys. Res., Sect. B **58**, 379 (1991).
[12] M. Maazouz *et al.,* Phys. Rev. B **55**, 13 869 (1997).
[13] M. Maazouz *et al.,* Surf. Sci. **409**, 189 (1998).
[14] S. Ustaze *et al.,* Surf. Sci. **415**, L1027 (1998).
[15] N. Lorente, A. G. Borisov, D. Teillet-Billy, and J. P. Gauyacq (to be published).
[16] A. G. Borisov, A. K. Kazanskii, and J. P. Gauyacq, Phys. Rev. Lett. **80**, 1996 (1998).
[17] S. L. Hulbert *et al.,* Phys. Rev. B **31**, 6815 (1985).
[18] S. L. Hulbert *et al.,* Phys. Rev. B **32**, 3451 (1985).
[19] V. A. Ermoshin and A. K. Kazanskii, Phys. Lett. A **218**, 99 (1996).
[20] V. Esaulov *et al.,* Rev. Sci. Instrum. **67**, 1 (1996).
[21] M. Canepa *et al.,* Phys. Scr. **41**, 226 (1992).
[22] R. Paniago *et al.,* Surf. Sci. **36**, 113 (1995).
[23] A. G. Borisov (private communication).
[24] S. Ustaze, S. Lacombe, L. Guillemot, and V. A. Esaulov (to be published).
[25] P. Nordlander, Phys. Rev. B **46**, 2584 (1992).