Dynamical Resonant Electron Capture in Atom-Surface Collisions: H⁻ Formation in H-Al(111) Collisions

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(Received 9 December 1991)

The formation of H⁻ ion by grazing-angle collisions of hydrogen on an Al(111) surface is investigated with the newly developed coupled angular mode method. The capture process involves a dynamical resonant process induced by the collision velocity. All the resonance properties of the H⁻ level in front of an Al(111) surface are determined: position, width, and angular distribution of ejected electrons. The results are shown to account for the recent observations on H⁻ formation by Wyputta, Zimny, and Winter.

Charge transfer between a moving atom and a surface is one of the fundamental aspects of the atom-surface interaction processes. Among these processes, the formation of an atomic or molecular negative ion during an interaction with a surface recently received a lot of experimental and theoretical attention [1]. Indeed negative ions have been invoked in quite a few different situations: charge transfer in atom-surface collisions [1], in particular in connection with the production of intense ion beams, resonant electron scattering by adsorbed molecules [2], desorption [3], and reactive scattering [4]; for all these processes the ion formation and destruction processes are of the greatest importance. Although the charge-transfer process has been the subject of numerous theoretical investigations, very few studies have been addressing this problem by quantitatively accurate methods.

In the present paper, we report on the first nonperturbative parameter-free study of negative ion formation by dynamical resonant capture applied to the H-Al(111) collisional system. The H electron affinity is much smaller than the surface work function and H⁻ formation by resonant capture should be inefficient. However, the experimental results of Wyputta, Zimny, and Winter showed that H⁻ was formed in grazing-angle collisions [5], and this was interpreted as due to a dynamical resonant capture. Indeed, when the collision velocity parallel to the surface is important, one must take into account the effect of the frame transformation between the atom and the surface; this changes the energetical resonance condition and leads to a dynamical capture process.

Until now, the dynamical resonant capture was only studied by perturbative methods [6–8] containing parameters that can be used in an adjustment procedure; in the H⁻-Al case, these were found [8] to fail to reproduce the experimental results [5]. Recently, two methods [9,10] going beyond the perturbation level were developed to study the position and lifetime of atomic levels in front of metal surfaces. Since they did not take the dynamical resonance effect into account, their use was limited to studies of the charge-transfer process at low collision velocities. In the present work, we show that one of them, the coupled angular mode (CAM) method [10], can han-

dle this dynamical effect which is very important for light negative ions as well as for systems with an electron affinity much smaller than the surface work function.

The H⁻ negative ion has an open shell structure of the type $1s1s'$, with a $1s$ inner orbital very close to the $1s$ atomic orbital of the neutral atom and a very diffuse $1s'$ orbital corresponding to the outer loosely bound electron. The CAM method [10] studies how this electron can jump between the atom and the metal. The CAM method is basically a scattering method: It considers the scattering of the active electron by the compound system consisting of the neutral atom and the metal surface. In other words, one studies an electron-atom scattering problem with the atom imbedded in the anisotropic environment provided by the metal surface. At finite distance from the surface, the H⁻ level is embedded in the quasicontinuum of metal states and thus appears as a resonant feature in the e^- scattering problem.

The e^--atom interaction is modeled by the effective range approximation (ERT) [11], while the e^--Al(111) surface interaction is represented by a local potential $V(z)$, only a function of z, the e^--surface distance, taken from the work of Jennings, Jones, and Weiner [12]. These two potentials have different symmetry properties. The electron scattering problem is described by an expansion over spherical harmonics, centered around the atom, and then well adapted to treat the e^--atom interaction. The e^--surface interaction introduces coupling terms between these atomic angular modes. The collision problem is solved yielding the scattering S matrix. From it, the time delay matrix Q is defined [13]. The largest eigenvalue of Q, q_{max}, presents a resonance structure at a negative energy which corresponds to the H⁻ level. The energy position of the maximum q_{max} gives the H⁻ level position and the resonance width is given by $\Gamma = 2/q_{max}$. In a preliminary version of this study [14], the width and position were determined for the H⁻-Al system. The width was found to be considerably larger than the one found by a perturbative approach [8]. The eigenfunction associated with the resonant eigenvalue of Q gives the angular distribution associated with the resonance state, i.e., the angular distribution of the electron ejected by the H⁻ ion de-

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cay. Since the resonance is located at a negative energy with respect to vacuum, the electron is ejected into the metal and this distribution cannot be observed. It will be shown below how this distribution leads to a treatment of the dynamical resonance. Figure 1 presents this angular distribution $|\varphi_{res}(Z,\theta)|^2$ as a function of the scattering angle θ (θ is measured from the surface normal), for different atom-surface distances Z (Z is measured from the image reference plane). The angular distributions are strongly peaked toward the metal. The width of the distribution increases when the atom approaches the surface. This point can be understood by looking at the contour plots of the potential felt by the electron (superposition of e^--atom and e^--metal interactions). In Figs. 2(a) and 2(b), the dotted line represents the equipotential associated with the resonance energy. At $Z=10a_0$, this equipotential has a closed part around the atom and the electron is ejected toward the continuum by tunneling through a potential barrier. However, at smaller distances like $7a_0$, the dotted line is open, which means that the resonance does not decay by tunneling, and the electron can escape over the barrier and go into the metal. The electron is held in this resonance state, because this open hole toward the metal only concerns a limited fraction of the 4π solid angle around the atom. However, the resonance width is then a significant fraction of the level energy. When the atom approaches the surface, the hole widens and consequently the angular distribution of ejected electrons broadens.

The angular distribution can be used to compute the dynamical resonance process. The effect of $v_{\parallel}$, the collision velocity parallel to the surface, leading to a dynamical resonance was first discussed by Van Wunnick et al. [15]. For a sizable $v_{\parallel}$, one must take into account the frame transformation between the ion and metal frames: This leads to a shift of the metal state wave vector $\mathbf{k}$ by
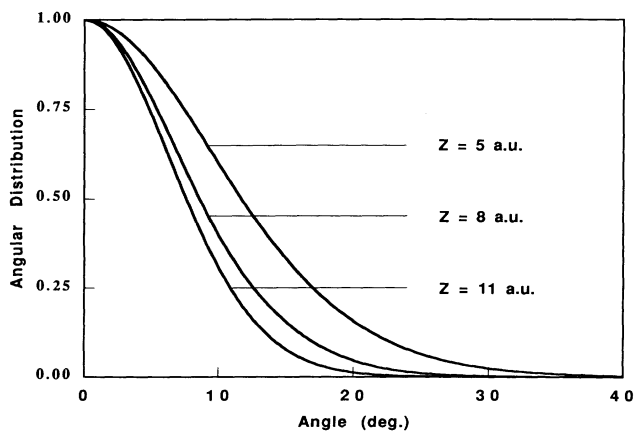
$v_{\parallel}$. This allows the definition of the capture and detachment widths Γ_{cap} and Γ_{det}:

$$\Gamma_{cap} = \frac{\Gamma}{2} \int_{\Omega_1} |\varphi_{res}(\theta)|^2 d\Omega \,,$$

$$\Gamma_{det} = \Gamma \int_{\Omega_2} |\varphi_{res}(\theta)|^2 d\Omega \,.$$

(1)

If $\mathbf{k}$ is the ejected electron momentum in the atomic frame, Ω_1 (respectively Ω_2) is defined as the region of solid angles in the atomic frame where $|\mathbf{k}+\mathbf{v}_{\parallel}| \le k_F$ (respectively $\ge k_F$). Ω_1 (Ω_2) corresponds to the metal states that are occupied (empty) at 0 K. k_F is the Fermi momentum and the factor ($\frac{1}{2}$) in (1) is a statistical factor. Until now, the $\Gamma_{cap}, \Gamma_{det}$ sharing has only been evaluated by perturbative methods, using the Fermi "golden rule." In this case, the width is obtained as an integral over the continuum states of coupling matrix elements between the discrete state and the continuum states, and the $\Gamma_{cap}, \Gamma_{det}$ sharing is directly deduced from the definition of occupied and empty states. In the CAM method, the an-
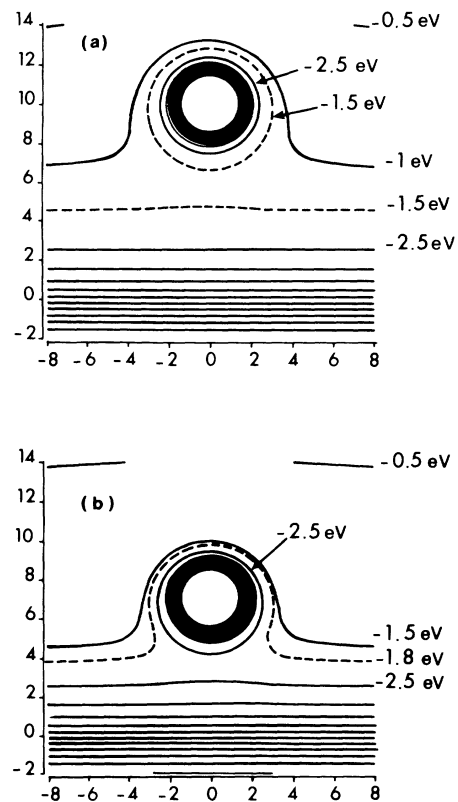

FIG. 2. Potential energy for the electron motion represented as contour plots. The solid line equipotentials have an energy spacing of 1 eV and are drawn from -14.5 to -0.5 eV. The dashed line equipotential corresponds to the resonance energy. The vertical and horizontal lines scale the electron distance from the metal surface and from the atomic axis normal to the surface, respectively. The atom is located at (a) $Z=10$ a.u. and at (b) $Z=7$ a.u. from the surface.

FIG. 1. Angular distributions of the ejected electron $|\varphi_{res}(Z,\theta)|^2$ vs the electron scattering angle θ, normalized to 1 at $\theta=0°$, for three different H^--surface distances $Z=5,8,11$ a.u.

gular distribution directly yields this sharing. This angular distribution cannot be observed directly in the present case which corresponds to negative energies. However, it can be observed experimentally in the case of resonant scattering by molecules adsorbed on metal surfaces [16].

The time evolution of the negative ion population P^- can be determined by a rate equation, corresponding to the competition between Γ_{cap} and Γ_{det}:

$$\frac{dP^-}{dt} = -\Gamma_{det}P^- + \Gamma_{cap}(1 - P^-) . \qquad (2)$$

The validity of a rate equation approach was shown in the case of a high temperature as well as under semiclassical conditions [17,18]. In grazing-angle collisions, the parallel velocity introduces a broadening of the electron distribution similar to a very high temperature, justifying the use of a rate equation.

In this equation, the H nucleus is supposed to follow a classical trajectory $Z(t)$ unperturbed by the charge-transfer process. Two trajectories are considered: a straight line and the motion corresponding to the image charge potential. These two trajectories can be thought to be well adapted to the treatment of neutral or ionic hydrogen motions. Equation (2) is solved for the outgoing part of the trajectory. Because of the importance of the width Γ, the final charge fraction is not influenced by the initial conditions, i.e., by the small H-Al distances, nor by the first half of the collision when the atom approaches the surface. This justifies the use of the CAM method that is only valid for large H-Al distances.

The final negative ion formation probability is presented in Fig. 3 for different normal velocities ($v_\perp$), as function of the velocity parallel to the surface, together with the experimental results of Wyputta, Zimny, and Winter [5]. The capture process is rather weak (probabilities around 10^{-3}) and it displays a typical resonance feature. It is noteworthy that the experiment actually concerned H^+ collisions on an Al(111) surface. However, it was shown by Zimny, Nienhaus, and Winter [8] that the neutralization and negative ion formation steps could be studied separately: Indeed, due to the large values of Γ for H^- formation, the system forgets its initial conditions and the Z region where the final H^- population is determined corresponds to rather large distances (typically $8a_0$), far out from the region where the H^+ neutralization occurs.

A quite satisfactory agreement is obtained with experiment for a rather large range of parallel and perpendicular velocities, the theory reproducing all the trends observed experimentally. It is worth noting that the present theoretical approach is free of adjustable parameters. It yields the level width, the level position, and the resonance angular distribution in a consistent way. Figure 3 presents the results obtained with the two different trajectories (ionic or neutral). For the largest perpendicular velocity (measured at infinity), the trajectory effect is
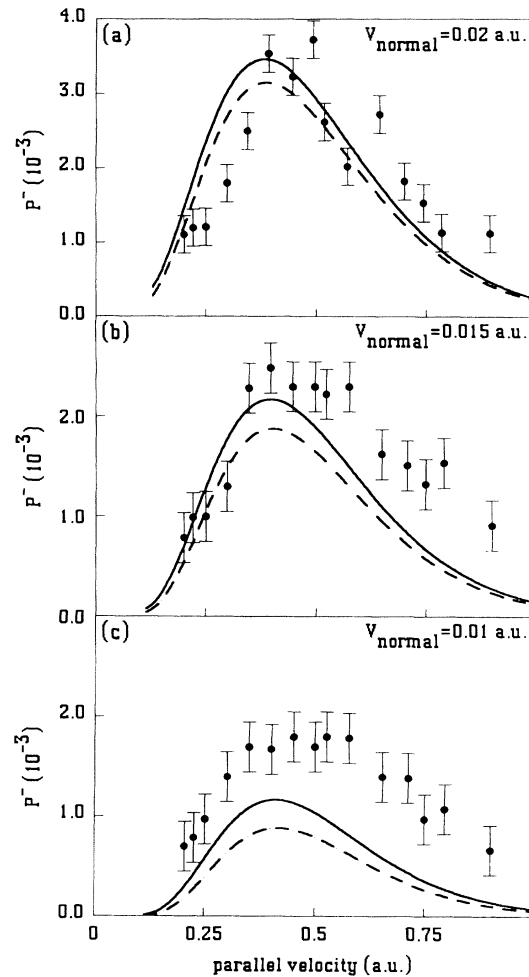

FIG. 3. Capture probability P^- for the formation of H^- as a function of hydrogen parallel velocity for three different normal velocities ($v_\perp = 0.02$, 0.015, 0.01 a.u.) assuming a straight line trajectory (dashed line) or an ionic trajectory (solid line). The points with the error bars are the experimental results of Wyputta, Zimny, and Winter [5].

rather limited (around 10%) and it increases at lower perpendicular velocity. This difference can be considered as a measure of the defect of the approximation of a unique classical trajectory for the hydrogen. At very low velocity, the semiclassical approach leading to (2) is not valid anymore. This trajectory effect also affects the experimental side: Indeed ions and neutrals are observed at different angles [19] and this could be a reason for the discrepancy between theory and experiment at low $v_\perp$.

This dynamical resonant electron capture has been previously studied with a perturbative approach [8], which yielded too small a width for the ionic level and consequently too large capture probabilities [5]. This is due to the choice of the metal electron wave functions in the perturbation treatment: They were defined with a step potential, neglecting the long-range image potential. The

difference is very important in the present system which considers rather weakly bound electrons: The metal electron wave function extends much further out into the vacuum due to this long-range potential and this increases the charge-transfer rate [14]. Recently, new perturbation calculations using Jenning's potential were performed (Borisov, Teillet-Billy, and Gauyacq [20]); the final results on the capture probability are still different from the present ones, although a significant improvement is achieved (see discussion in [20]).

In conclusion, the new coupled angular mode method has been shown to be able to treat dynamical resonant electron capture which is very important for collisional systems with a very large collision velocity. The method is of rather broad applicability: It can be used for any one-electron charge-transfer process (electron capture or loss processes for neutral or positive ions). Using an electron scattering approach, all the properties of the resonance state of H^- in front of an Al surface are determined, allowing a quantitative study of the charge-transfer problem. Agreement with the experimental results of Wyputta, Zimny, and Winter confirms the interpretation of H^- formation as due to dynamically induced resonant charge transfer.

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