# Femtosecond Neutralization Dynamics in Cluster-Solid Surface Collisions

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Experimental results for the relative electron emission yields $\gamma(N)$ of charged clusters colliding at low energies with different surfaces are presented. For fixed collision energy a remarkable cluster size dependence of $\gamma(N)$ is obtained using highly oriented pyrolytic graphite as target. By studying theoretically the collision process within a microscopic model we find that the nonadiabatic survival probability of the charged clusters shows the same behavior as $\gamma(N)$. Thus, $\gamma(N)$ reflects the femtosecond neutralization dynamics during the collision, which may result in damped Stückelberg oscillations for targets with narrow densities of states. [S0031-9007(97)04139-2]

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Quantum effects observed when two macroscopic objects interact via a tunneling gap are always exciting as they might be important for future nanoelectronic devices. In addition they sometimes allow intriguing insight into the physics of quantum states induced by the charge confinement in a system of reduced dimensionality. As a matter of fact, however, the dynamics of the electron motion usually remains hidden due to the extremely short time scales involved. Only recently the pump-probe techniques with femtosecond laser light pulses have started to give some progress in the understanding of such processes.

Here we will raise the question of whether the transient character of a collision process of a charged metal atom cluster with a solid surface might elucidate the dynamics of the electron motion between the two partners. Will there be a single electron jump as in a classical picture, or might there be a resonant tunneling process where the charge density—once the collision partners overcome a minimum threshold distance—fluctuates between cluster and surface?

So far, this question has not been tackled. A variety of collision experiments between clusters and solid surfaces were performed during the last decades. These can be grouped into investigations involving (i) surface modification by cluster bombardment or deposition [1,2], (ii) scattering of intact species and their fragments [3,4], and (iii) electron emission [5–7]. Such studies gave, for instance, insight into the stability of small particles and, to a certain extent, their geometry; energetic cluster impact can modify the formation of thin films. During energetic impact there exist nonequilibrium conditions similar to those in shock tubes, but on a very different time scale, a femtosecond scale. New types of chemical reactions, characterized by extremely high density, pressure, and kinetic temperature, are expected to occur. All these experiments give no hints of possible quantum effects, which are the topic of this Letter.

The setup of the experiment for collision induced electron emission measurements will be described in detail elsewhere [8]. In short, the clusters are produced in a source of the PACIS type [9]. After acceleration to their final collision energy $E_{\mathrm{coll}}$, they are mass separated in a Wien velocity filter (Colutron 600 B) which is followed by a distance of free drift [10]. The selected clusters enter the target region, which is magnetically shielded. Collisions are performed at normal incidence. The emitted electrons are guided from the target to a channeltron. A second detector (channeltron or Daly type) determining the ion intensity is mounted directly behind the movable target. We perform sample preparation either by cleaving highly oriented pyrolytic graphite (HOPG) parallel to the (0001) plane prior to mounting it into vacuum, or in the case of slightly oxidized aluminum by chemical cleaning. The base pressure in the collision region ranges below $10^{-9}$ mbar.

For the measurement of the relative electron yield a Wien filter mass spectrum has to be recorded in order to assign a given filter setting to the corresponding cluster mass. The mass spectra of $\mathrm{Pt}_N^-$ are resolved up to $N = 20$. With reduced resolution, particles with up to $N = 1000$ can be detected using the present setup. For each selected mass peak, we count cluster ions and emitted electrons under the same conditions. Furthermore, the background noise has to be recorded and subtracted separately. The relative electron yield $\gamma(N)$ is given by the number of electrons divided by the number of cluster ions. $\gamma(N)$ may be wrong by a factor which takes into account the ion and electron detection efficiency and which is constant for a defined collision system, i.e., fixed cluster and target type. The collision energy can be varied between 200 and 1.1 keV.

Figure 1(a) shows the measured $\gamma(N)$ of Pt cluster anions colliding with an HOPG surface, at a collision energy of 500 eV in addition to the energy from the supersonic expansion. $\gamma_{\mathrm{HOPG}}(N)$ decreases with $N$, and is alternating

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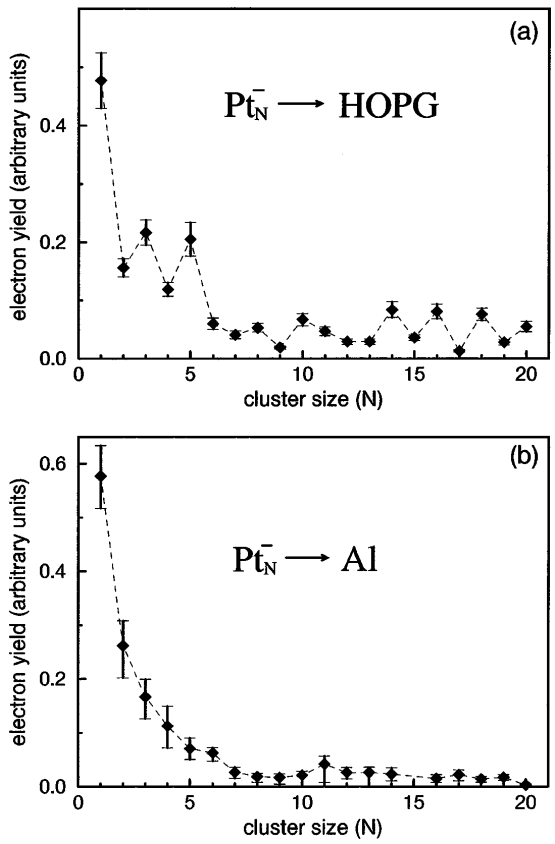


FIG. 1. Experimentally determined relative electron yield $\gamma$ as a function of size $N$ for $Pt_N^-$ clusters colliding with (a) a graphite (HOPG) target, and (b) an aluminum surface. The collision energy is $E_{\mathrm{coll}} = 500$ eV.

for $N = 1, \ldots, 4$ (maxima for $N$ odd) and $N = 13, \ldots, 20$ (maxima for $N$ even). An additional and interesting observation is that if $E_{\mathrm{coll}}$ is changed, the dependence of $\gamma_{\mathrm{HOPG}}$ on the cluster size changes, and in particular the odd-even alternations are modified. For $E_{\mathrm{coll}} < 300$ eV the size oscillations cannot be distinguished any more within experimental resolution. In contrast to the results of Fig. 1(a), experiments performed under the same conditions but using Al as a target give a smoothly decreasing $\gamma(N)$ ($\gamma \approx 0.03$ already for $N \geq 8$) and further significant size-dependent features are absent.

In a first attempt to understand the remarkable experimental features shown in Fig. 1(a), one could associate the alternation in $\gamma_{\mathrm{HOPG}}(N)$ with the well-known "odd-even effect" observed in the ionization potentials (IP) of some metal clusters. However, the affinity energies of $Pt_N$ clusters $E_A(N)$ (which are also the IP of $Pt_N^-$ clusters) do not exhibit any kind of odd-even alternation [11]. Furthermore, the fact that no oscillations are present in $\gamma_{\mathrm{Al}}(N)$ (Al as target) indicates that the cluster-surface interaction is more important for this effect than the electronic structure of the cluster itself. A rough analysis of the known mechanisms for ejection of electrons upon particle-surface collisions does not help much to understand our experimental results. Potential emission is, in this case, energetically not allowed. Thermionic emission (TE) from the negatively charged cluster after the collision is, in principle, possible. However, the corresponding electron yield $\gamma_{\mathrm{TE}}(N)$ would reflect the size dependence of the affinity energies $E_A(N)$ of the $Pt_N$ clusters which, as mentioned above, are a smooth function of $N$ (at least for $N > 3$) and show no similarities with the electron yields of Fig. 1. The other possible mechanism is kinetic emission (KE). In the last years, KE threshold velocities below 10 km/s have been measured [12], i.e., of the same order of magnitude as the collision energies considered in this work. However, the resulting electron yield $\gamma_{\mathrm{KE}}(N)$ should be, in principle, a monotonic function of the cluster size. Thus, none of the known mechanisms for electron emission, in their simplest form, yield a consistent description of our observed $\gamma(N)$. A further analysis of the collision process is therefore necessary.

The nontrivial dependence of $\gamma$ on $N$ and the strong sensitivity of $\gamma(N)$ to $E_{\mathrm{coll}}$ suggests that $\gamma$ depends on the velocity of the colliding clusters. Now, the velocity of an atomic ion colliding with a surface is the parameter which governs the neutralization dynamics of the projectile [13,14]. Analogously, during the collision of a cluster the electronic charge may jump from the cluster to the surface and backwards. Thus, independently of the ultimate mechanism for the ejection of the electrons, we expect the electron yield to be sensitive to the whole neutralization dynamics, and, in particular, to the charge state of the cluster when it reaches the surface. Therefore, we propose a new model based on the following fundamental assumption: the electron yield $\gamma(N)$ for fixed $E_{\mathrm{coll}}$ is a monotonic function of the nonadiabatic survival probability $P_s(N)$ of the charged projectiles. This means that only if a cluster reaches the surface unneutralized, an electron can be emitted. For simplicity, we shall assume in what follows, that $\gamma(N) \propto P_s(N)$.

$P_s(N)$ is now determined by using a microscopic theory. We describe the dynamics of the extra electron of the $Pt_N^-$ clusters by considering a single state (affinity level) which interacts during the collision process with a band of states at the surface. This leads, as in the case of atom-surface interactions [13–16], to a time-dependent Anderson type Hamiltonian of the form

$$H(t) = \varepsilon_0(t) c_0^+ c_0 + \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} c_{\mathbf{k}}^+ c_{\mathbf{k}} + \sum_{\mathbf{k}} [V_{\mathbf{k}0}(t) c_{\mathbf{k}}^+ c_0 + V_{\mathbf{k}0}^*(t) c_0^+ c_{\mathbf{k}}], \qquad (1)$$

where the subscripts $\mathbf{k}$ and 0 refer to states at the surface and in the cluster, respectively. The time dependence of $H$ arises from the classical trajectory approximation that the cluster moves with constant velocity $v$ towards the surface. $\varepsilon_0(t)$ is the affinity level of the cluster. $V_{\mathbf{k}0}(t)$ is the matrix element that describes the electron hopping between the projectile and the state $\mathbf{k}$ of the target.

The Heisenberg equation of motion leads to the following coupled differential equations:

$$i\hbar \frac{\partial c_0}{\partial t} = \varepsilon_0(t)c_0(t) + \sum_{\mathbf{k}} V^*_{\mathbf{k}0}(t)c_{\mathbf{k}}(t), \qquad (2)$$

$$i\hbar \frac{\partial c_{\mathbf{k}}}{\partial t} = \varepsilon_{\mathbf{k}} c_{\mathbf{k}}(t) + V_{\mathbf{k}0}(t)c_0(t), \qquad (3)$$

which have to be integrated to calculate the nonadiabatic cluster-level occupation $n_0(t_0) = \langle c_0^+(t_0)c_0(t_0)\rangle$, $t_0$ being the time at which the cluster reaches the surface.

For the particular case of negatively charged colliding clusters, $P_s$ is identical to $n_0(t_0)$, and the subscripts $\mathbf{k}$ refer to the unoccupied surface states. The interaction of the cluster affinity level with surface states below the Fermi level is not taken into account. The neglect of filled bands is justified if the energy difference between the occupied states and the cluster level is sufficiently large. The relevant matrix elements $V_{\mathbf{k}0}$ for $\mathbf{k} \in$ HOPG are those involving the $2p_z$ orbitals of graphite (with the $z$ quantization axis perpendicular to the planes, i.e., parallel to the collision coordinate). These $2p_z$ orbitals are mainly responsible for the two peaks (one above and one below the Fermi level) in the density of states (DOS) of graphite [17,18].

We have solved numerically Eqs. (2) and (3) by taking into account 20 surface states for HOPG and 200 for Al, distributed in such a way as to reproduce the major features of the DOS of the targets. For simplicity, we use rectangular DOS of different width $W$, depending on the target material, but more states and more complicated DOS can be taken into account.

Thus, we represent the density of unoccupied states of HOPG which interact with the cluster by a narrow band of width $W_{\mathrm{HOPG}}$. In contrast, the width of the DOS of Al ($W_{\mathrm{Al}}$) is taken to be large. The time dependence of the hopping matrix elements is given by $V_{\mathbf{k}0} = V_s \exp(vt/d)$, since $V_{\mathbf{k}0}$ decreases exponentially for increasing distance between cluster and surface [19]. Note that $\varepsilon_0(t)$ is a function of $N$. Its time dependence is determined by the velocity $v$ and the distance dependence of the cluster-surface interactions (image forces, etc.) [19]. For fixed $N$ we require $\varepsilon_0(t \to -\infty) = E_A$. The affinity energies $E_A(N)$ are taken from photodetachment experiments [11]. We model the distance dependence of the affinity level when approaching the surface by a constant $E_A(N)$ until the cluster reaches the point $z_c$ and then a decrease with a constant rate $\partial\varepsilon_0/\partial z = a$.

In Figs. 2(a) and 2(b) we present theoretical results for the survival probability $P_s(N)$ of $\mathrm{Pt}_N^-$ clusters impinging on HOPG and Al surfaces with $E_{\mathrm{coll}} = 500$ eV.

For HOPG as target we use the following parameters: $W_{\mathrm{HOPG}} = 0.72$ eV [20], $V_s = 2.2$ eV, $d = 0.48$ Å, $z_c = 1.9$ Å, and $a = 1.5$ eV/Å.

The position of the narrow $2p_z$ band of graphite is obtained from photoyield experiments [18]. The value for

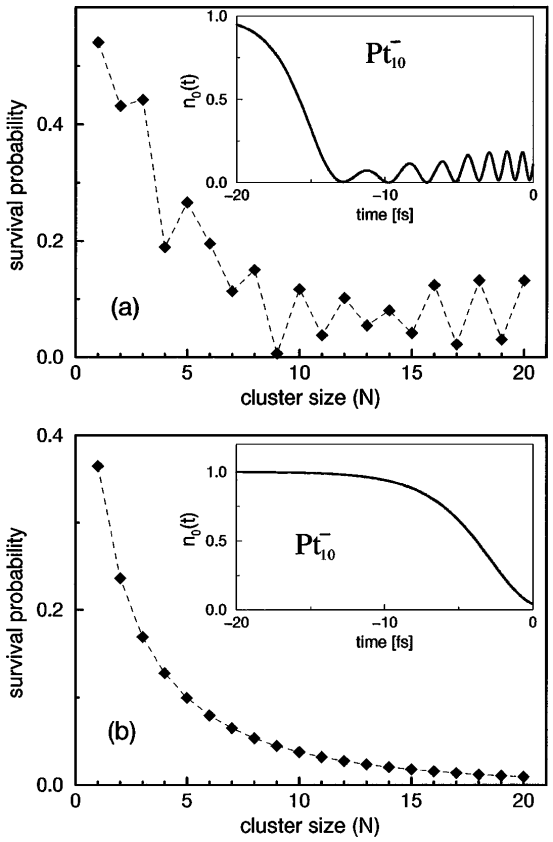


FIG. 2. Theoretical results for the survival probability $P_s(N)$ of $\mathrm{Pt}_N^-$ clusters impinging on (a) a HOPG surface, and (b) an Al surface. The collision energy is $E_{\mathrm{coll}} = 500$ eV. In the inset figures, the time-dependent level occupation $n_0(t)$ of $\mathrm{Pt}_{10}^-$ colliding with both targets is shown.

$W_{\mathrm{HOPG}}$ is also in agreement with calculated DOS [17]. $P_s(N)$ shows oscillations as a function of the cluster size, which reflect the time oscillations of the neutralization process, as shown in the inset of Fig. 2(a). This effect resembles the well-known Stückelberg oscillations, which arise from resonant or quasiresonant hopping between two well-defined levels corresponding to systems which approach each other with a given velocity. Such oscillations have been observed in atom-ion collisions [21], and also in collisions between $\mathrm{He}^+$ ions and Pb surfaces [22], where the completely localized $d$ orbitals of Pb play the role of the well-defined level [13]. In the particular case of HOPG, the $2p_z$ band is narrow enough to produce such oscillations.

$P_s(N)$ for HOPG exhibits maxima and minima at the same cluster sizes as $\gamma_{\mathrm{HOPG}}(N)$. From Fig. 2(a) it is clear that the odd-even alternation of $P_s(N)$ [and consequently of $\gamma_{\mathrm{HOPG}}(N)$ if our assumption is valid] is just a consequence of the oscillating neutralization dynamics for a particular choice of the collision energy. We also find that for low $E_{\mathrm{coll}}$ ($\sim$100 eV) the size oscillations of $P_s(N)$ disappear [23]. One can understand the results of Fig. 2(a) qualitatively as follows. For all cluster sizes, $n_0(t)$

exhibits a time dependence like the one shown in the inset of Fig. 2(a). The phase and frequency of these time oscillations change with the cluster size. In particular, these dynamics result roughly in a periodic dependence of $P_s$ [$= n_0(t_0)$] on the reciprocal velocity of the cluster $1/v$. Since $E_{\mathrm{coll}}$ is the same for all sizes, $P_s(N)$ also oscillates as a function of the size (more precisely of $\sqrt{N}$). Note, however, that there is an additional contribution to $P_s$ due to the affinity energies. Upon a change of $E_{\mathrm{coll}}$, this particular odd-even scenario may change, as we have experimentally observed. Moreover, the size oscillations of $P_s(N)$ are damped, suggesting an even more complex size dependence. There are two sources of damping. One of them is Landau-Zener-like [$\sim \exp(-\mathrm{const}/v)$] involving the crossing of the affinity level of the cluster with the $2p_z$ levels of HOPG. But the most important effect causing damping is the nonzero width of the $2p_z$ band. The larger the width $W$ of the target DOS, the stronger the damping. On the basis of the previous discussion it is now easy to understand the behavior of $P_s(N)$ for an Al target. The DOS of Al is characterized by a broad band, which causes a complete damping of the oscillations. As shown in the inset of Fig. 2(b), $n_0(t)$ exhibits no oscillations. Once the extra electron of $Pt_{10}^-$ jumps to the surface, it quickly delocalizes within the target and does not jump back to the cluster. The same dynamics are observed for all cluster sizes considered. For the characterization of the $Pt_N^- \rightarrow$ Al collision we used $W_{\mathrm{Al}} = 5$ eV, $V_s = 0.8$ eV, and $d = 0.36$ Å. Because of the broad band the results turned out to be almost independent of the parameters $z_c$ and $a$. Figure 2(b) shows that a bandwidth $W$ of 5 eV yields an exponential decrease. For even broader bands we obtain the asymptotic behavior $P_s \sim \exp(-\Delta d/\hbar v)$ [15], with $\Delta = \pi \rho V_s^2$ (and $\rho =$ DOS of the target).

Summarizing, our results suggest that electron emission due to collisions between charged clusters and surfaces reflects the neutralization dynamics of the clusters. The purpose of our model calculations is to describe the physical picture underlying the experimental results of Fig. 1. The parameters $V_s$, $d$, $z_c$, and $a$ have been chosen to give a qualitative demonstration of the effect. Preliminary experimental results obtained for fixed $N$ and different values of $v$ show strong evidence for the presence of Stückelberg oscillations.

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