Energy Gain of Highly Charged Ions in Front of LiF

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We present estimates of the energy gain of highly charged ions approaching a LiF surface, based on a modified classical-over-barrier model for insulators. The analysis includes the energy gain by image acceleration as well as the deceleration due to charge-up of the surface in a staircase sequence. The role of the frequency-dependent dielectric response of LiF is emphasized. The resulting velocity dependent total energy gain is studied in detail and the results are compared with experimental data.

1 Introduction

The interaction of slow highly charged ions (HCIs) with insulator surfaces, in particular LiF, has recently received much attention [1–8]. Earlier, the interaction of HCIs with metal surfaces has been studied in detail [9–12] and a scenario for the neutralization of the HCI in front of a metal has emerged. As the HCI approaches the surface, it induces a rearrangement of the electron density in the solid (i.e. an "image") which, in turn, accelerates the ion towards the surface. This is known as image acceleration and the resulting energy change as image energy gain. As soon as the potential barrier separating the electronic motion in the surface and in the ion becomes lower than the Fermi edge, electrons are transferred in classical-over-barrier (COB) transitions between the metal and the ion. The interaction time (typically around $\sim 10^{-14}$s) is determined by the inverse perpendicular velocity of the HCI, which has a lower bound given by the image energy gain. The neutralization

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24 September 1996

of the HCI occurs by electron transfer into highly excited levels of the ion leading to the formation of so-called "hollow atoms". A COB-model developed by Burgdörfer et al. [10–12] could, in spite of its inherent simplifications, explain the transient above-surface neutralization of an HCI near a metal, in particular the above-surface component of the K-Auger emission [13] and the image energy gain. It was also indicated by the model that the atom remains hollow above the surface, i.e. the relaxation to the neutral ground state takes place only in close collisions with surface- and below-surface layers of the solid.

First experimental results for HCIs incident on LiF have shown both similarities and differences to metals which are not yet well understood: the image energy gain in grazing incidence scattering was found to be similar to that of metals [1,2]. On the other hand, the KLL Auger peak with the minimal L population, signifying the hollow atom formation by above-surface neutralization for metals, was found to be missing [3] suggesting that hollow-atom formation is suppressed. We here present an analysis of the energy gain for grazing incidence ions on a LiF surface based on a modified COB-model for insulators [8]. In the calculation we account for energy gain by image acceleration as well as for the deceleration caused by the charge-up of the surface from sequential removal of electrons. Charge and velocity dependencies are analyzed and comparisons to experimental data are made. In the following atomic units are used unless otherwise stated.

2 The Electronic Surface Potential

Consider an HCI with charge Q and velocity v approaching an ionic crystal. A realistic surface potential for an electron crossing the barrier between an ion and an ionic crystal can be written as

$$V(r,R) = V_e(r) + V_{pe}^I(r,R) + V_{pe}(r,R), \tag{1}$$

where $r = (x,y,z)$ is the position of the electron, with x and y parallel to the surface and z perpendicular to the surface, and $R = (R_x, R_y, R_z)$ is the position of the projectile. The origin of the coordinate system is chosen at an F^- ion in the surface. The interaction between the electron and the image of the projectile is given by $V_{pe}^I(r,R)$ while $V_{pe}(r,R)$ is the Coulomb interaction between the electron and the projectile itself, and $V_e(r)$ is the electronic surface potential in absence of the projectile. The latter contains four terms:

$$V_e(r) = V_{pol}(r) + V_M(r) + V_{sc}(r) + V_e^{SI}(z), \tag{2}$$

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representing the polarization potential, $V_{pol}(r)$, which describes the interaction between the electron and the halide atom, the Madelung potential $V_M(r)$, which is the interaction between the electron and the ionic lattice of the crystal, $V_{sc}(r)$, which accounts for the screening of the localized positive charge left in the surface, and $V_e^{SI}(z)$, the interaction between the electron and its own image. Here we only emphasize the differences between image potentials for metals and for LiF, while details on the calculation of the potentials can be found in [8].

In the analysis of the image potentials it is necessary to treat the dielectric response of the target. For a material with a frequency independent dielectric function, ϵ, the strength of the image of the HCI is given by $Q_I = Q(\epsilon - 1)/(\epsilon + 1)$. For LiF it is necessary to treat the dynamic response of the crystal through the inclusion of a frequency-dependent dielectric function $\epsilon(\omega)$ [8]. Experimental values of $\epsilon(\omega)$ for LiF are given by Palik and Hunter [14]. A major difference between a metal and an insulator is the behavior of the dielectric function $\epsilon(\omega)$ in the limit $\omega \to 0$. For a metal $|\epsilon(0)| \to \infty$ while for an insulator $\epsilon(0)$ is finite. The static value of the dielectric function of LiF, reached at frequencies $\omega < 10^{-4}$ a.u., is $\epsilon(0) \sim 9.1$ while the "optical value" ($\omega \sim 10^{-2} - 10^{-1}$ a.u.) is $\epsilon(\infty) \sim 1.96$ [14]. In between these two limits, $\epsilon(\omega)$ varies strongly with ω which gives rise to velocity dependent image potentials.

For LiF we define a dielectric response function $\chi(z, R_z)$, representing a "weighted" value of the ratio $(\epsilon(\omega) - 1)/(\epsilon(\omega) + 1)$ such that $Q_I = Q\chi$. This effective response function is obtained from the image potential, V_{pe}^I, at $x = R_x, y = R_y$. Neglecting dispersion and assuming grazing incidence ($v = (v_{||}, -v_z)$ where $|v_{||}| \gg |v_z|$) the dielectric response function along the saddle is [8]:

$$\chi(z, R_z) = \frac{2|z + R_z|}{\pi} \int_0^\infty dK_x \left\{ \frac{\epsilon(K_x v_{||}) - 1}{\epsilon(K_x v_{||}) + 1} \right\} K_0(K_x(R_z + z)) \quad . \qquad (3)$$

where K_0 is a modified Bessel function. The limits of the response function are given by $0 \leq \chi \leq 1$ where the upper limit is reached for a metal. As expected, the response function for LiF reaches the optical limit at high velocities and the static limit at low velocities.

3 Energy Gain

As the HCI approaches the surface it experiences the acceleration due to the self image potential

$$V_p^{SI}(R_z) = \chi(z = R_z, R_z)\left(-\frac{Q^2}{4R_z}\right) . \tag{4}$$

The resulting energy gain has been measured for insulators as well as metals [1,2,15,16] which gives direct information on the distances at which the neutralization process of the HCI sets in. In the COB-model the neutralization sequence begins at a critical distance $R_z = R_c$ (obtained using Eq. (1)) where the barrier between the ion and the surface falls below the highest lying occupied target levels and the electron transfer becomes classically allowed. The image energy gain at the point of first capture is given by

$$\Delta E_1^I = V_p^{SI}(\infty) - V_p^{SI}(R_c) = \frac{Q^2}{4R_c}\chi(R_c, R_c) \tag{5}$$

For metals ΔE_1^I was shown to be the dominant contribution to the total energy gain ΔE which was calculated in a full COB simulation as well as from the so called staircase model [11,12]. Within the staircase model, the charge is assumed to change instantaneously from Q to $Q-1$ at $R_c(Q)$, from $Q-1$ to $Q-2$ at $R_c(Q-1)$ etc. until complete neutralization is reached.

For an insulator surface we have a different scenario due to the more localized character of the electrons initially bound to the crystal. The charge transfer from the crystal to the projectile causes a local positive charge-up of the surface which decelerates the HCI and, to some extent, counteracts the effect of the subsequent image acceleration. The total energy change of the HCI approaching the insulator surface is hence

$$\Delta E = \Delta E^I + \Delta E^D , \tag{6}$$

where ΔE^I is the energy gain due to image acceleration and ΔE^D is the energy loss due to the charge-up deceleration.

Assuming the staircase model is valid also for LiF the total image energy gain is

$$\Delta E^I = \Delta E_1^I + \sum_{i=1}^{Q-1} \frac{(Q-i)^2}{4} \left[\frac{\chi(R_c(Q-i), R_c(Q-i))}{R_c(Q-i)}\right.$$

$$-\frac{\chi(R_c(Q-(i+1)),R_c(Q-(i+1)))}{R_c(Q-(i+1))}\Bigg] \quad . \tag{7}$$

The energy loss caused by the deceleration, ΔE^D, is obtained by a similar staircase approximation where we calculate the sequence of impulsive momentum transfers due to the repulsive force between the instantaneous ionic charge $Q-\Delta Q_i$ and the charged-up surface with charge ΔQ_i. Consequently,

$$\Delta E^D = \sum_{i=1}^{Q-1}\left[-\left(\frac{v_z(i)}{|v_{||}|}\right)T(i)+\left(\frac{1}{2M|v_{||}|^2}\right)T^2(i)\right] \tag{8}$$

where M is the mass of the ion, $v_z(i)$ is the perpendicular velocity which changes with each capture, and

$$T(i)=\frac{(Q-i)\{1-\chi(R_c(Q-i),0)\}S(i)}{R_c(Q-i)} \tag{9}$$

In Eq. (9) the factor $S(i)$ is given by

$$S(i)=\sum_{j=1}^{i}\frac{D(j,i)}{(R_c^2(Q-i)+D^2(j,i))^{1/2}}-\sum_{j=1}^{i-1}\frac{D(j,i-1)}{(R_c^2(Q-i)+D^2(j,i-1))^{1/2}} \tag{10}$$

with

$$D(j,i)=\sum_{k=j}^{i}\Delta R_{||}(Q-k) \quad . \tag{11}$$

As the ion travels the distance $\Delta R_{||}(Q-k) = R_{||}(Q-k) - R_{||}(Q-(k+1))$ along the surface, it comes $\Delta R_c(Q-k) = R_c(Q-k) - R_c(Q-(k+1))$, i.e. the difference between the critical distances of two adjacent charge states, closer to the surface. A schematic picture of the trajectory of the incident ion is given in Figure 1. Accordingly, we have $\Delta R_{||}(Q-k) = \Delta R_c(Q-k)|v_{||}|/v_z(k)$, where the initial ratio $v_z(0)/|v_{||}|$ is typically of the order 2×10^{-2} a.u. in grazing incidence experiments. Because of the large mass of the ion ($M\sim10^4$a.u.) the first term in the sum in Eq.(8) will dominate the deceleration. The major contribution to the total energy change ΔE is, as for metals, the image energy gain at the point of first capture, ΔE_1^I. However, the effect of the subsequent image acceleration is, to some extent, off-set by the deceleration for LiF.

A classical trajectory Monte Carlo (CTMC) simulation for a slow HCI approaching a LiF-surface was performed [8] and a significant time delay in the over-barrier capture was found. Although transfer of electrons is energetically allowed already at the critical distance R_c, there is a delay of about 3 a.u. before the first electron is captured. This is explained by the fact that the electron does not only need sufficient energy but also enough linear momentum in the required direction to escape through the saddle. Here we use R_c values [8] which are corrected for a shift of ~3 a.u. to evaluate Eq. (6). In other words, we account for a delayed formation of hollow atoms.

In Figure 2 the energy gain for a grazing incidence HCI with velocity $|v_{||}|$ =0.1a.u. is shown as a function of the charge Q of the projectile. The image energy gain at the point of first capture, ΔE_1^I, as well as the total energy gain, ΔE, are compared with experimental and theoretical data from Auth et al. [1]. Remarkably, when our values are compensated for delayed capture they come close to the estimates of Auth et al. [1] which do not take this mechanism into account. Also, for this velocity the two counteracting effects of acceleration and deceleration largely cancel out and the total energy change ΔE is close to ΔE_1^I.

Figure 3 illustrates the parallel velocity dependence for a grazing incidence collision of a $Q = 6$ ion with a LiF surface. Results for both ΔE_1^I and ΔE are shown together with experimental data of Auth et al. [1] and Yan and Meyer [2]. Our calculations suggest that the study of the velocity dependence of the energy gain for a fixed charge state might prove a measure for the differences in the neutralization dynamics of metals and insulators. While for a metal the energy gain is expected to be energy independent (as long as $v_{||} << v_F$), the energy gain for LiF decreases with increasing velocity because of the frequency dependent polarizability of the LiF surface.

Our calculations are in good agreement with the data of Ref. [2] within the experimental uncertainty. The significance of this agreement should be viewed with caution at the present. Recent experimental data for the velocity dependence of the exit charge state of several neutral atoms and negative ions can be explained by the hypothesis of a partially occupied band of surface states with an approximately quadratic dispersion [2]. Surprisingly, using the same hypothesis in the COB model for metals yields an energy gain which also agrees with the data at a comparable level of accuracy. Further experimental and theoretical studies are therefore necessary to disentangle these different charge transfer mechanisms.

This work was funded by the NSF and by the US DOE, OBES, Div. of Chemical Sciences under Contract No. DE-AC05-96OR 22464 with ORNL and managed by LMERC. L.H. also gratefully acknowledges support from the Swedish Foundation for International Cooperation in Research and Higher Education (STINT) and from the Swedish Natural Science Research Council (NFR).

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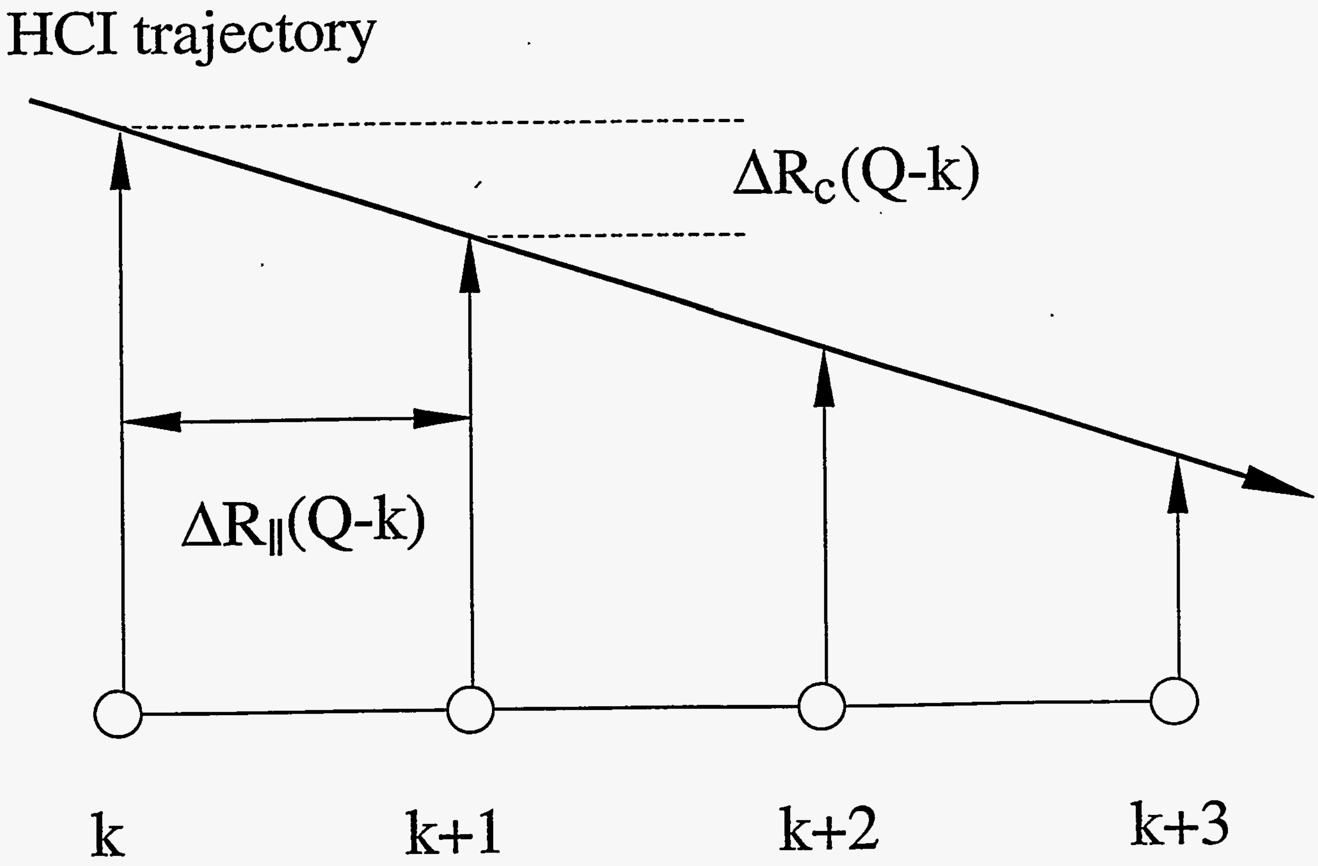
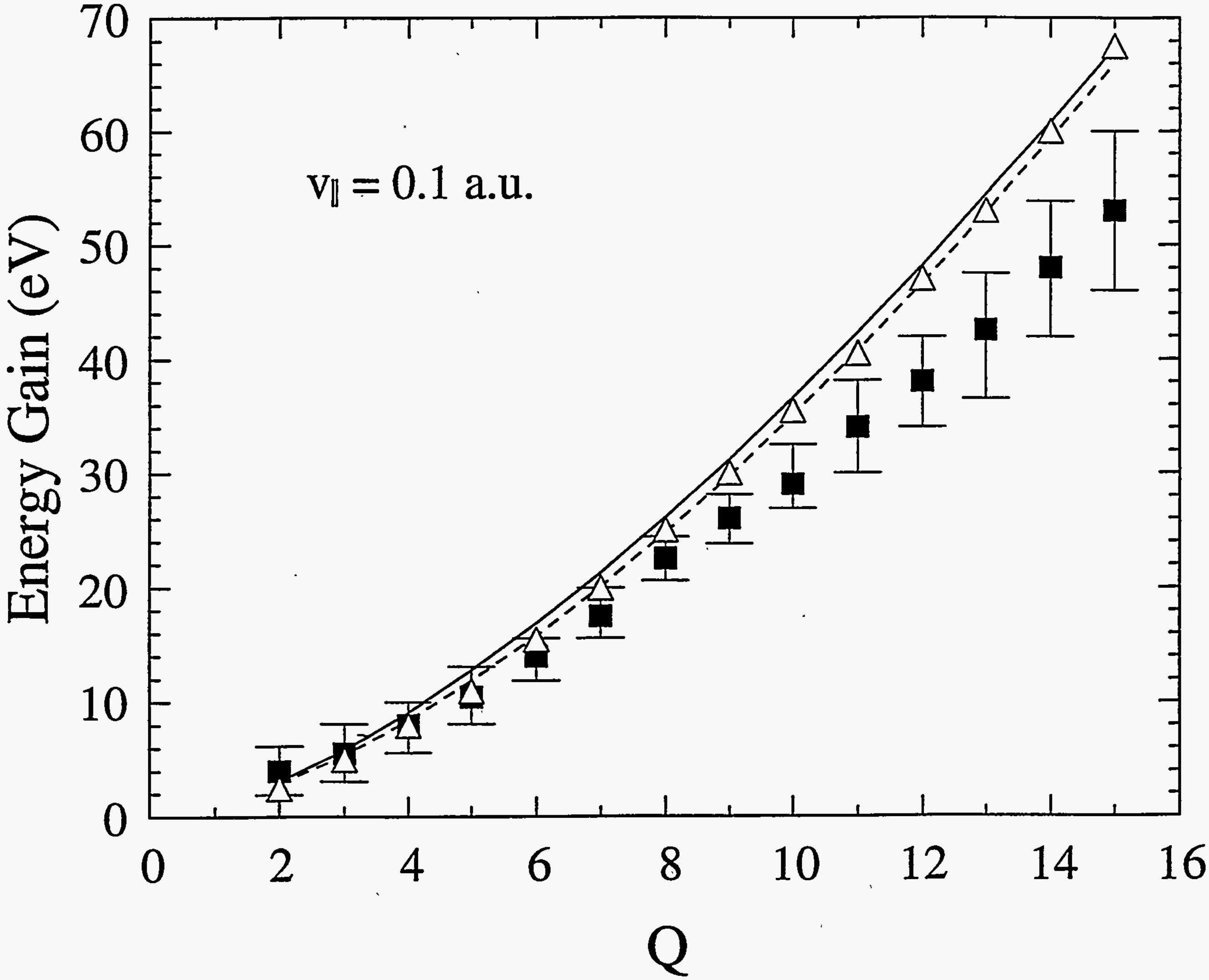
Fig. 1. A schematic picture of the trajectory of the HCI in grazing incidence. The initial charge is Q. The ion travels $\Delta R_c(Q-k)$ closer to the surface between two consecutive captures, k and $k+1$, while it moves $\Delta R_{||}(Q-k)$ along the surface.

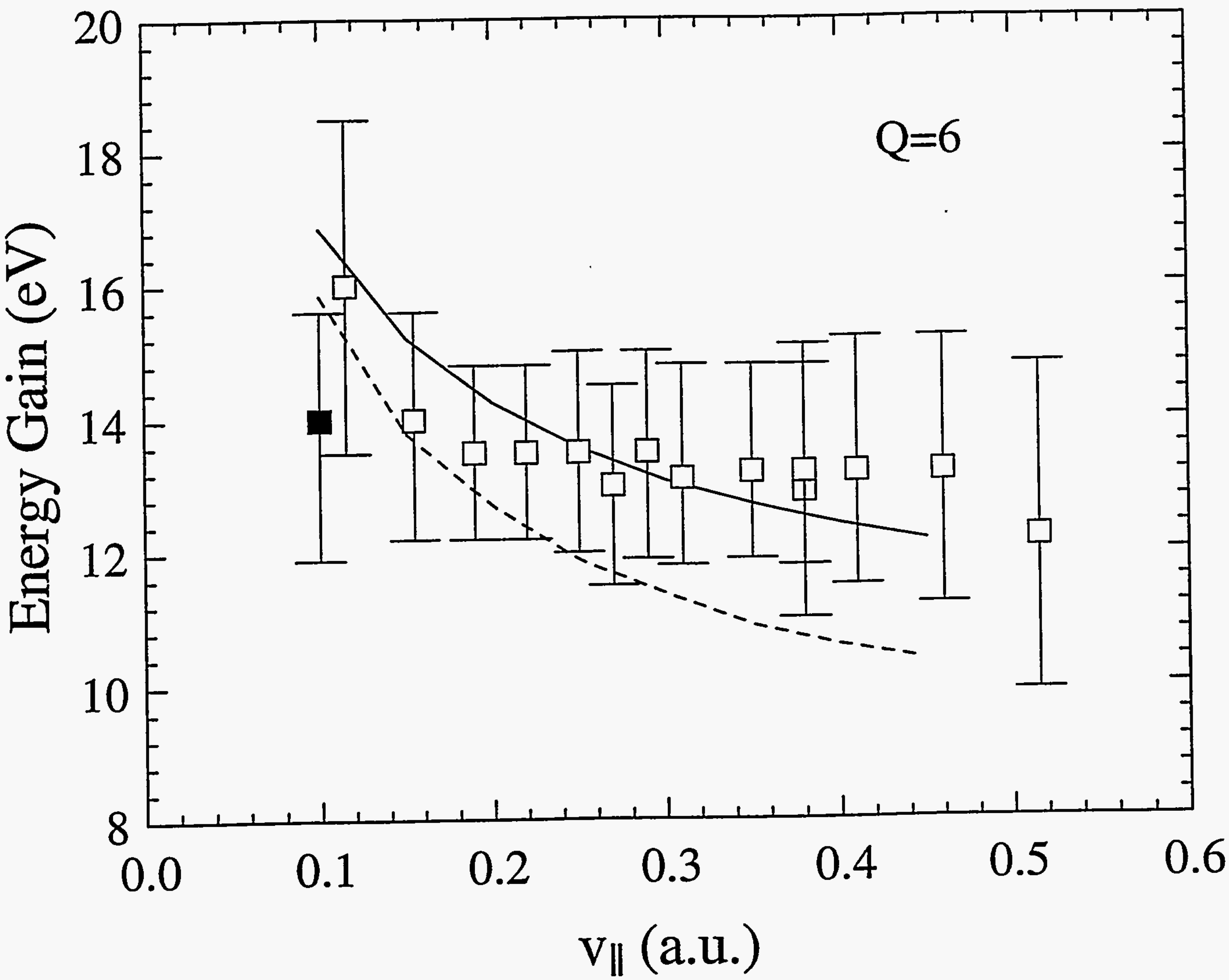
Fig. 2. The energy gain as a function of the charge state Q of the projectile. The image energy gain at the point of first capture, ΔE_1^I, is displayed as a dashed line and the total energy gain, ΔE, as a solid line. Experimental values from Auth et al. [1] are shown as filled squares and their calculated values as triangles.

Fig. 3. The energy gain for charge-state $Q=6$ as a function of the velocity $v_{||} = |v_{||}|$. The dashed line is the image energy gain at the point of first capture, ΔE_1^I, and the solid line is the total energy gain, ΔE. Experimental values from Yan and Meyer [2] are shown as empty squares and the experimental value from Auth et al. [1] as a filled square.


HCI trajectory
ΔRc(Q-k)
ΔR||(Q-k)
k
k+1
k+2
k+3



70
60
50
40
30
20
10
0
Energy Gain (eV)
v‖ = 0.1 a.u.
0
2
4
6
8
10
12
14
16
Q



Q=6
Energy Gain (eV)
20
18
16
14
12
10
8
0.0
0.1
0.2
0.3
0.4
0.5
0.6
v∥ (a.u.)