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On Auger neutralization of He⁺ ions on a Ag(111) surface

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Abstract

Neutralization of He⁺ ions in grazing incidence scattering on Ag(111) is studied. A small scattered ion fraction is observed. The experimental results are discussed in terms of survival from Auger neutralization, whose rates are derived theoretically. Molecular dynamics simulations of scattered ion trajectories are performed and the surviving ion fractions are then calculated using the theoretically estimated Auger neutralization rates. The calculations agree quite well with the experimental data and empirical estimates of the neutralization rates.

(Some figures in this article are in colour only in the electronic version)

Auger neutralization of positive ions in front of metal surfaces has attracted much attention starting from the seminal works of Hagstrum [1] and has received much attention recently, when a number of theoretical treatments were developed for free-electron-like metals [2–4] including electronic excitations—plasmon-assisted neutralization [5] and ion-induced effects [6]. The recent theoretical treatments have been applied to the description of plasmon features observed in electron emission following Auger neutralization [4, 5] and to the calculation of ion fractions in low-energy scattering (LEIS) of He⁺ on Al [7]. Although it was believed that the theoretical Auger rates were too small to explain some experimental findings [8], more recently it has been shown that there is no discrepancy between theory and experiment if an appropriate energy level variation of He⁺ in front of the metal surface is used in the interpretation of the experiments [9, 10]. Van Someren *et al* [9] were also able to reproduce their experimental electron emission spectra for grazing incidence of He⁺ on Al by using the calculated Auger rates.

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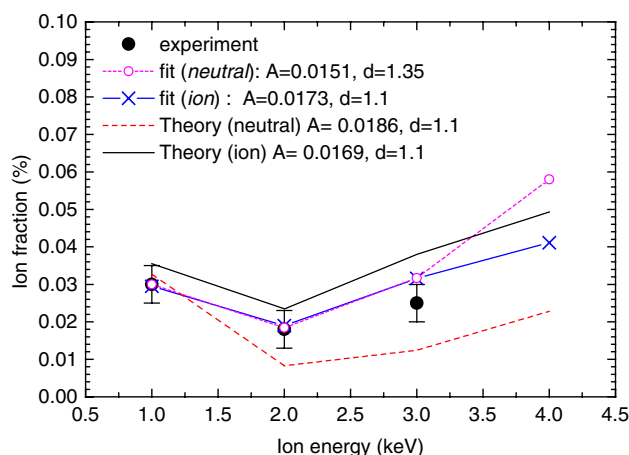


Figure 1. Experimental and calculated ion fractions. The calculations relate to the ‘neutral’ and ‘ion’ trajectories as explained in the text and are shown for the theoretically estimated and the experimentally fitted parameter. The parameters A and d are in atomic units.

In a recent experimental study we reported results of a study of He^+ neutralization of He^+ and other rare-gas ions on a chlorine-covered $\text{Ag}(111)$ surface [11, 12]. Here we present additional experimental results for He^+ neutralization on a clean $\text{Ag}(111)$ surface and discuss this in terms of theoretical estimates of Auger neutralization rates along with classical molecular dynamics trajectory simulations of ion scattering (IS). Ag is not a free-electron-like metal and a full calculation of the distance-dependent Auger rates is much more demanding because it should include the full band structure at the surface. Here we will give only a simple estimate that accounts for the experimental results.

The experiments were performed using a set-up described in detail elsewhere [13]. The set-up allows IS and time-of-flight (TOF) spectroscopy, Auger electron spectroscopy (AES) and ion-induced secondary-electron spectroscopy. He^+ ions are produced in a discharge source, mass selected and steered into the main UHV chamber. The pressure in the chamber is typically 2×10^{-10} Torr. The commercial $\text{Ag}(111)$ sample was polished to $0.05 \mu\text{m}$ and oriented to within 0.5° . The *in situ* preparation consisted of repeated cycles of Ar^+ grazing incidence sputtering and annealing. Surface cleanliness was ascertained by AES and by performing a TOF analysis of the scattered and recoiled particles for Ar^+ incident IS. A clean metal surface condition was considered to be one in which direct recoiled peaks of impurities such as H, C and O were not visible in the TOF spectra [11–13]. The clean surface work function was found to be 4.5 eV [11, 12]).

He^+ ion fraction measurements were made for fixed scattering angles of 7° using a position-sensitive 30 mm diameter channel-plate detector, equipped with three discrete anodes and set at the end of a TOF analysis tube [13]. A deflector plate assembly set before the channel-plates allows one to separate the incoming ions and neutrals, which are detected simultaneously by each of the anodes. Measurements were performed for 1–3 keV ion energies for specular scattering. The positive (Φ^+) ion fractions are defined as the ratio of the scattered He^+ flux (N^+) to the total scattered flux (N^{total}) into a given angle ψ with respect to the surface plane, i.e.

$$\Phi^+(\psi) = \frac{N^+(\psi)}{N^{\text{total}}(\psi)}.$$

The measured ion fractions are shown in figure 1. The error bars represent typical statistical scatter in a series of ion fraction measurements. The measured ion fractions are found to be

quite small. An interesting observation is that the ion fraction at 1 keV is larger than the one at 2 keV although the velocity perpendicular to the surface is higher at 2 keV and hence one would expect the ion to spend less time in front of the surface and this could lead to less efficient neutralization.

In order to analyse these results we performed calculations of the scattered ion trajectories. Since we deal with grazing IS, we performed classical molecular dynamics calculations which are known to be more accurate in these conditions than simple binary collision codes which only include the interaction with a single surface atom and hence can only be reasonable for large-angle impact. We used the programme 'Kalypso' [14] in which ZBL potentials are used. The size of the Ag(111) target was adjusted to the scattering conditions in order to cover the ion trajectory near the surface and at the same time minimize the computational time. For the case presented here we chose a slab of three atomic layers with a width corresponding to 20 atomic chains of 40 atoms (lattice constant: 7.73 au).

The calculated trajectories are then used to calculate the He⁺ ion survival probability using a rate equation approach, where we only include Auger capture processes. Other charge exchange processes are ruled out in the present experiment. Resonant capture and loss to excited states of He have been proven to be negligible both theoretically [10] and experimentally [9] for grazing incidence of He⁺ on Al and this should also be the case for Ag, the more so because its bigger work function favours resonant loss. Note that in our case of low-energy grazing incidence scattering we would exclude collision-induced neutralization and reionization of He since these require a very small distance of approach of He to a surface atom and, consequently, a threshold perpendicular energy of at least hundreds of electron volts [15]. It should also be noted that the behaviour of the low-energy ion fractions would be inconsistent with this effect since one usually observes an increase in ionization with increasing energy and one would thus expect a higher ion fraction at 2 than at 1 keV. Finally, earlier experiments on He scattering on Al [16] have shown that kinematic ionization occurs at ion velocities above 0.3 au, i.e. above 9 keV.

As suggested by the self-consistent calculations of [3], the rate for Auger capture is assumed to decay exponentially away from the jellium edge and to saturate inside the jellium edge according to

$$\Gamma(z) = \begin{cases} Ae^{-(z-z_j)/d_A}, & \text{if } z \geq z_j, \\ A, & \text{if } z \leq z_j, \end{cases} \quad (1)$$

where z_j is the position of the jellium edge. A is the bulk value of the Auger neutralization rate and d_A is the decay length, which determines the decrease of the neutralization rate as a function of ion-surface distance. The jellium edge is set as usual above the topmost atomic layer at half the atomic interlayer spacing.

An important source of uncertainty for studies of ion survival probabilities is introduced by the effect of image charge acceleration on the trajectory. To investigate how these effects may influence the analysis of the present experimental results, two sets of simulations are performed. The first set of trajectories is run for 'neutral' conditions; that is, the incident particles are scattered by the repulsive ZBL potential. However, before the repulsive potential sets in, the incident ions are first accelerated by the attractive image potential on their way towards the surface and the surviving ions finally de-accelerated on the way out, so their trajectories near the surface will be affected by this change of kinetic energy. We take this effect into account approximately by running a second set of trajectories in which the perpendicular energy has been increased by 2 eV ('ion' conditions). Although the actual value of the ion energy near the surface could depend on the specific ion-solid combination, 2 eV has turned out to be a remarkably universal figure for low-energy He⁺ on a variety of solid surfaces [1].

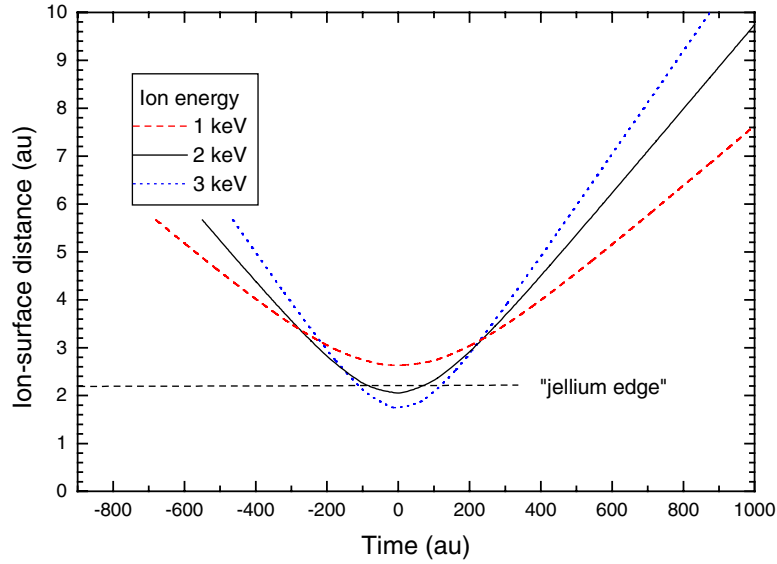


Figure 2. Trajectories calculated using the molecular dynamics code ‘Kalypso’ for ‘neutral’ conditions. The ion–surface distance here refers to the first atomic layer.

Calculated trajectories for ‘neutral’ conditions are shown in figure 2. The graphs represent the ion–surface distance as a function of time. Here the zero refers to the first atomic plane. The ‘jellium edge’ position is indicated by the dashed line. As may be seen, with increasing energy the ion approaches closer to the surface. As the energy increases, one can also notice that the trajectories become less wide in timescale. The same trends are obtained for ‘ion’ conditions. Note that in our case of a 3.5° incidence angle the effect of increasing the perpendicular energy by 2 eV is not very large. Thus the perpendicular energy ranges from 3.7 to 11 eV and for the ‘ion’ trajectories we consider incident angles of 4.3° at 1 keV and 3.8° at 3 keV. This leads to somewhat closer distances of approach: from 2.78 to 2.43 au at 1 keV and from 1.81 to 1.68 au at 3 keV.

In figure 1 we present results for the ion survival probability for ‘neutral’ and ‘ion’ conditions. The ion survival probability is obtained as

$$P_+ = \exp\left\{-\int_{-\infty}^{+\infty} dt \Gamma(z(t))\right\}, \quad (2)$$

where $z(t)$ is the trajectory of the ion obtained from the molecular dynamics simulation. We use the Auger rate of equation (1) with A and d_A first determined as fitting parameters to be compared with our theoretical estimates later on. For the ‘neutral’ trajectories $A = 0.0151$ and $d_A = 1.35$ au and for ‘ion’ trajectories $A = 0.0173$ and $d_A = 1.1$ au. The results of this fitting procedure are shown in figure 1. We point out that the minimum in ion survival probability at 2 keV is obtained in both simulations and it is the result of the competition between penetration and available time for neutralization. This can be very easily understood if we assume that the Auger neutralization rate decreases exponentially with distance for all distances of interest and that the velocity is constant. Then, the ion survival probability P_+ can be obtained analytically as

$$P_+ = \exp\left\{-2\frac{d_A\Gamma(z_{tp})}{v_z}\right\}, \quad (3)$$

where z_{tp} is the turning point of the trajectory and v_z is the velocity perpendicular to the surface. The available time for Auger neutralization is d_A/v_z . $\Gamma(z_{tp})$ increases with penetration and therefore with perpendicular velocity but the available time for neutralization decreases as $1/v_z$ and, consequently, the exponent of equation (2) may have a maximum at some velocity depending on the values of A and d_A . Notice also that the value of P_+ is very sensitive to those values due to the exponential dependence.

Realistic calculations of the Auger neutralization rate of He⁺ on free-electron metal surfaces have been performed in [3, 4, 6]. The case of noble metals is much more complicated because it is necessary to account for the d-band structure at the surface. Here we will only attempt an estimate of A and d_A based on very simple assumptions. First, A will be taken as the bulk value of the Auger neutralization rate given by [17]

$$A = 2 \sum_{\vec{k} < k_F} \int_0^\infty d\omega \int \frac{d^3\vec{q}}{(2\pi)^3} \text{Im} \frac{-1}{\varepsilon(q, \omega)} \left| \int d^3\vec{r} \psi_a^* \psi_{\vec{k}} e^{-i\vec{q}\cdot\vec{r}} \right|^2 \delta(E_k - E_a - \omega). \quad (4)$$

In equation (4), $\psi_{\vec{k}}$ is a metal wavefunction of energy $E_{\vec{k}}$ orthogonalized to the Hartree–Fock wavefunction ψ_a of He [6] of energy E_a , k_F is the Fermi wavevector and $\varepsilon(q, \omega)$ is the dielectric function of Ag. In our approximation, we consider that only the s electrons of Ag neutralize the ion and are described as a free-electron gas of $r_s = 3.02$ au, corresponding to one electron per Ag atom. This is because d electrons are very much localized around Ag atoms, with typical decay lengths of 0.25 au, and in our calculated trajectories He never gets that close to the surface. On the other hand, the possibility that either a s or a d electron is ejected in the Auger process is taken into account via the dielectric function. Here, we will consider this possibility by defining the number of effective electrons that can be excited with a given amount of energy ω . Optical properties of noble metals have been investigated for a long time [18–20]. In [18] it is shown that the effective number of electrons per atom contributing to the optical properties of Ag depends strongly on the range of incident energies; it is 1 only for energies below 4 eV (i.e. below the threshold for interband transitions from the d band to the conduction band) and can be as large as 5 for 25 eV incident energy. In our approximation, we take an effective number of electrons as a function of ω from [18] and define an energy-dependent effective r_s . Then $\varepsilon(q, \omega)$ is the Lindhard dielectric function for the effective r_s . Moreover, the value of E_a should be taken consistently with ‘ion’ or ‘neutral’ conditions. For ‘ion’ conditions, an increase in the perpendicular kinetic energy of 2 eV should be accompanied by a decrease in the potential energy by the same amount; then we take $E_a = -22.6$ eV with respect to the vacuum level. In the opposite case of ‘neutral’ conditions, the attractive interaction between He and metal is neglected and $E_a = -24.6$ eV—that is, the ionization potential of He in vacuum. The values of A that we obtain in this way are $A = 0.0186$ au for ‘neutral conditions’ and $A = 0.0169$ au for ‘ion conditions’. As regards the decay length d_A , it should not be very different from the value $d_A = 1.1$ au found for Al [3, 6]. This is because only s electrons of Ag neutralize He⁺ and the decay length is mainly controlled by the overlap between metal wavefunctions near the Fermi level and the wavefunction of He; also the work functions of Ag and Al differ by only 0.25 eV.

As one can see, the fitted and calculated coefficients agree quite well. In figure 1 we also show the ion fractions calculated using the theoretical coefficients and the trajectories for ion and neutral conditions. We see that the magnitude and the general trend are correctly reproduced by the theory. A more realistic calculation of the Auger rate, taking into account the energy level variation as a function of ion–surface distance and the actual dependence of the Auger rate on distance to the surface (which is exponential only approximately), should be performed for a still better comparison between theory and experiment.

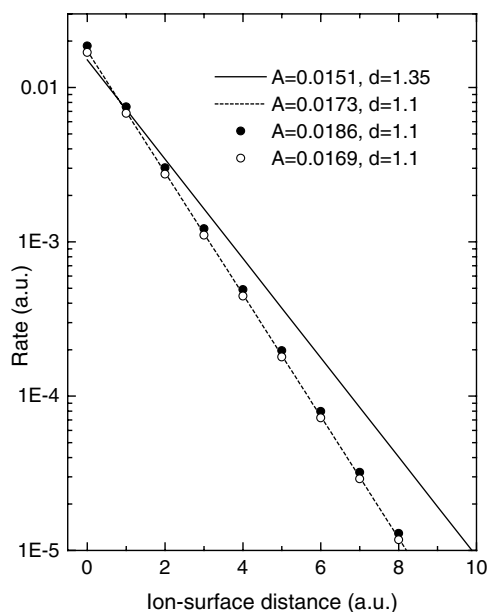


Figure 3. Experimentally derived Auger neutralization rates as a function of distance from the surface (here the jellium edge). Experimental fit—lines; theoretical estimate—points. The parameters A and d are in atomic units.

In conclusion, we report ion fractions in He^+ scattering on a $\text{Ag}(111)$ surface in the 1–3 keV energy range. In grazing incidence very small ion fractions are found and we observe that these increase below 2 keV. We discuss this in terms of theoretical estimates of Auger neutralization rates along with classical molecular dynamics trajectory simulations of IS. The Auger capture rates are assumed to decay exponentially away from the jellium edge and saturate inside it. Good agreement between the theoretical estimates and the experimental data is found. One can thus conclude that today's theoretical descriptions of the Auger process can account quite well for experimental findings, unlike the earlier interpretations of experiments.

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