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Effects of the atomic level shift in the Auger neutralization rates of noble metal surfaces

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ABSTRACT

In this work we compare characteristics of Auger neutralization of He^+ ions at noble metal and free-electron metal surfaces. For noble metals, we find that the position of the energy level of He with respect to the Fermi level has a non-negligible influence on the values of the calculated Auger rates through the evaluation of the surface dielectric susceptibility. We conclude that even though our calculated rates are accurate, further theoretical effort is needed to obtain realistic values of the energy level of He in front of these surfaces.

1. Introduction

Electron and energy transfer processes between an atom or molecule and a surface are extremely important for their many applications in physics and chemistry such as, e.g., surface analytical tools, particle detection, plasma wall interactions, or catalysis. Therefore, a substantial body of work is devoted to the understanding of the relevant microscopic mechanisms [1–5]. In this respect, it is desirable to design model systems where single processes can be studied under well-defined conditions. The two basic charge transfer mechanisms are known as resonant and Auger. Resonant processes are single electron mechanisms in which an electron tunnels from/to the atom to/from the solid when the energy level of the atom is in resonance with the continuum of states of the solid. Resonant processes, being one-electron ones have been described abundantly in the literature using different techniques [1,3–6].

Besides resonant tunneling, Auger processes are the second fundamental electron transfer processes for ion–surface interactions. Auger neutralization (AN) and Auger ionization (AI) are two-electron processes. In AN, one electron from the surface is transferred to a bound state (often the ground state) of the atom while, by virtue of electron–electron interaction, energy and momentum are transferred to the solid creating surface excitations (electron–hole pairs and plasmons). In AI an electron bound to the atom is transferred to a state above the Fermi energy with the creation of surface excitations. Energy conservation requires kinetic energy from the atom and therefore AI is only possible above a threshold kinetic energy. Being two-electron processes, Auger processes are generally less efficient than resonant charge transfer and can be best studied in situations where the latter are energetically forbidden. In this work we will be concerned with systems in which slow noble gas ions are incident on high work function metal surfaces. For these systems the atomic ground state is non-degenerate with the occupied electronic states of the surface and the atomic excited states are resonant with the empty states of the metal. Fig. 1 illustrates schematically the relative positions of the different energy levels for the case of He^+. Moreover, since the ion velocity is typically much smaller that the Fermi velocity of the metal electrons, AI processes are not possible. Therefore, these are ideal systems to isolate and study Auger neutralization since it is the only possible mechanism of charge transfer.

Since the pioneering work of Hagstrum [7], a fair number of experimental and theoretical studies have been devoted to the neutralization of He^+ ions in front of metal surfaces. However, the difficulty of dealing with electron–electron interactions in many-electron systems has been the main cause why Auger processes have not been described with a good accuracy until recently. Most of the calculations of the Auger neutralization rate of an ion in front of a metal surface have been performed within the jellium model, focusing on plasmon excitation [8–14] and/or effects of the surface barrier [15]. However, experiments of He^+ interacting with Ag [16–18] and Al [19,20] surfaces at grazing incidence and also with Cu and Au surfaces at normal incidence [21,22] revealed a pronounced dependence of ion fractions on the crystallographic

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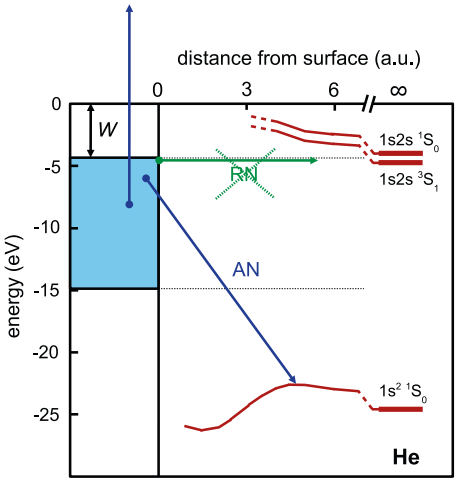

Fig. 1. Schematic energy diagram for interaction of He with a high work function metal surface. *W*: work function; blue shaded area: occupied states of conduction band; brown curves: energy levels of He as function of distance from the surface for states indicated. Green arrow: resonant neutralization (RN), blue arrows: Auger neutralization (AN). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

face of the target surface. Differences in the ion fractions measured along different directions of the same face have also been found. The jellium model, being translationally invariant with respect to the surface, can only model the face dependence by placing the "jellium edge" at a distance of $\frac{1}{2}d$ in front of the first atomic layer, d being the interplanar distance [23], and it was applied in this way to explain the observed differences between ion fractions of Ag (1 1 0) and Ag (1 1 1) surfaces in [16,17]. It is, however, completely unable to distinguish between different atomic directions within the surface. Then, a theory of Auger neutralization beyond the jellium model becomes essential to be able to account for all these crystalline effects and for a better understanding of the microscopic Auger mechanism. With this aim, the theory was reformulated to include corrugation effects in the way we describe in Section 2.

The question of how well any theory of AN is able to quantitatively reproduce the experiments is deeply connected to the problem of how the energy levels of atoms change in the proximity of a solid surface. This was at the origin of a historical controversy only solved recently. Measurements of the high-energy tails of the electron distributions [7] and measurements of energy gains of ions prior to neutralization [24] showed changes in the energy level of the incident ions of about 2 eV. From this value and making use of concepts of the classical image potential, He^+ was assumed to be neutralized at distances of ca. 7 a.u. from the surface which required AN rates orders of magnitude larger than theoretically predicted [7,24]. However, Merino et al. [25], More et al. [26], and van Someren et al. [27] pointed out that the He-1s level shift might be substantially reduced compared to the classical behavior for distances of some atomic units in front of the surface, as a consequence of the breaking of the classical image–potential concept at close distances. Actually, theoretical calculations of the He-1s level energy shift showed reduced values or even negative shifts close to the surface as a result of chemical interactions with the surface [26,25,28]. Similar deviations from the classical behavior were also calculated for the 1s state of H [29] and for excited states of He in front of an Al surface [30], and are also predicted for other systems [31]. Finally, agreement between theory and experiment was established based on measurements of shifts of the high-energy tails of Auger electron distributions [32] and shifts of angular distributions for incident neutrals and ions for different energies (different distances of neutralization) [19]. The latter was an experiment proposed by More et al. [26], that directly measured reduced (and even negative) energy shifts of the ground state energy of He close to the surface. A similar downward shift was also found for the ground state of Ar in front of a KCl (0 0 1) surface [33]. The problem of energy level variation of atoms in front of noble metal surfaces is addressed in section III. In Section 4 we present the results of our investigation on the influence of the atomic level position on the calculated Auger neutralization rates and the conclusions are expounded in Section 5.

Atomic units ($e = \hbar = m_e = 1$) are used throughout this article unless otherwise stated.

2. Theory of the corrugated Auger neutralization rate

In this section we briefly resume the basic steps in the formulation of a theory for including corrugation in the calculation of the Auger neutralization rate. We refer the interested reader to Refs. [11,13,34] for more details.

Following Fermi's golden-rule of first-order perturbation theory, it is possible to write down the formula for the probability per unit time that an electron of the solid, in the n-band with wave vector $\vec{k}$ and energy $\epsilon_{\vec{k},n}$, described by the Bloch wave function $\varphi_{\vec{k},n}(\vec{r})$, experiences a transition to the atomic state of the projectile $\varphi_a(\vec{r}-\vec{R}_a)$ (which we assume to be at rest at a position $\vec{R}_a$) while transferring energy ω and momentum parallel to the surface $q_\parallel$ as [11–13]

$$\frac{1}{\tau}(\vec{R}_a) = 2\sum_{\vec{k},n}\int_0^\infty d\omega \int \frac{d^2\vec{q}_\parallel}{(2\pi)^2}\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \\ -\mathrm{Im}\chi(\vec{q}_\parallel,\omega;z,z')V_{\vec{k},n}(\vec{q}_\parallel,z)\; V^*_{\vec{k},n}(\vec{q}_\parallel,z')\;\delta(\omega+E_a \\ -\epsilon_{\vec{k},n}), \qquad (1)$$

with,

$$V_{\vec{k},n}(\vec{q}_\parallel,z) = \frac{2\pi}{q_\parallel} < \varphi_{\vec{k},n}(\vec{r}_2)|e^{i\vec{q}_\parallel\cdot\vec{\rho}_2}e^{-q_\parallel|z-z_2|}|\varphi_a(\vec{r}_2-\vec{R}_a) > . \qquad (2)$$

In Eqs. (1) and (2), $V_{\vec{k},n}(\vec{q}_\parallel,z)$ represents an "external" potential acting on the metal as a consequence of the neutralization event and $\chi(\vec{q}_\parallel,\omega;z,z')$ is the dielectric response of the surface which

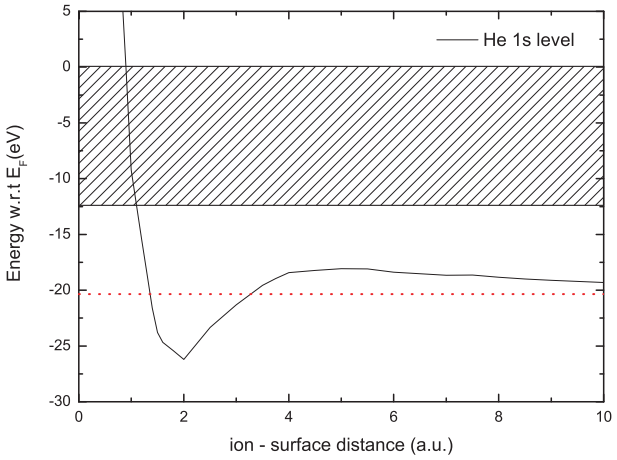

Fig. 2. Calculated dependence of the He-1s level with the distance to the Al surface (continuous black line) [28]. The conduction band of the Al surface is indicated with the dashed area. The red dotted line represents the position of the unperturbed He-1s level. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)