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Ne^{**} autoionizing states and Ne^+ charge fractions scattered from a magnesium surface

O. Grizzi,* M. Shi, H. Bu, and J. W. Rabalais
Department of Chemistry, University of Houston, Houston, Texas 77204-5641

R. A. Baragiola
Department of Physics and Astronomy and Laboratory for Surface Modification, Rutgers University, Piscataway, New Jersey 08855

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The first correlation of autoionization, inelastic energy loss, and charge fractions for ions scattered from surfaces is reported. A mechanism for efficient ionization of atoms receding from surfaces has been identified and confirmed. It involves the formation of an autoionizing atom which, due to its long lifetime, ionizes far from the surface where reneutralization is unlikely. This is exemplified by keV Ne^+ on a Mg surface, where a fraction of the Ne^+ can be doubly excited to $Ne^{**}(2p^4 3s^2)$ states when the interatomic distance is ≤ 0.6 Å. The behavior is described by electron promotion and by fast electron transfer with the solid.

One of the basic unsolved problems in the interaction of low-energy ions with surfaces is the mechanism of charge transfer and prediction of the charge composition of the flux of scattered and sputtered atoms. Besides its basic interest, the pursuit of the solution of this problem has practical significance, since the knowledge of the ion yield is a requisite for the quantification of widely used techniques for surface analysis, e.g., ion scattering spectrometry (ISS) and secondary ion-mass spectrometry (SIMS).

A simple picture[1] based on resonant electron transfer processes between the ion and surface predicts that ion yields are determined by the ratio of the energy difference of the surface-shifted atomic ionization potential (I) and the surface work function ϕ, i.e., $I-\phi$, and the energy uncertainty $\hbar v/a$ associated with the time of passage of the ion through the surface layer. Here v is the component of the ion velocity normal to the surface and a is the width of the tail of the electron penetration through the surface barrier. This model has been able to explain the majority of experimental observations in ISS and SIMS. It fails for the interaction of Ne^+ ions with the surfaces of the light elements Mg, Al, and Si. Anomalous behavior at keV energies has been observed in the total electron yield from Al,[2] in the selective production of autoionizing electrons in collisions with Mg, Al, and Si,[3,4] and in the high ion fraction [up to ~70% (Refs. 5 and 6)] of Ne scattered from Mg. These findings suggest a process in which a high cross section for production of doubly excited Ne^{**} leads, upon decay in vacuum, to high yields of autoionization electrons and residual ions. Although autoionization has been proposed[5] to account for the ISS results, there have been no experimental studies of the correlation of autoionization and ion yields.

In order to understand this anomalous scattering of Ne^+ ions, we have studied the emission of *autoionization electrons* and the electronic *energy loss* and *charge state* of scattered ions for 1–4-keV Ne^+ bombardment of clean and oxidized magnesium surfaces. This is the first correlation of these three observables from electronic processes in ion-surface collisions.

The current understanding of inelastic collisions at low velocities is based on the evolution of the molecular orbitals (MO's) of the transient quasimolecule formed during the collision. As the interatomic distance decreases, MO's evolve from the atomic orbitals (AO's) of the separate atoms of atomic number Z_1 and Z_2 to the AO of the "united" atom of atomic number (Z_1+Z_2). This evolution of the MO's is governed by (i) an increased binding energy at long distances due to the larger nuclear charge attracting the electrons, (ii) a reduced binding energy at short distances due to repulsion between electrons, and (iii) the availability of electronic states as constrained by the Pauli principle and symmetry rules. MO promotion has been invoked to interpret most of the inelastic collision phenomena for multielectron atoms,[7] and will be the basis for the interpretation of our results. In particular, for the Ne-Mg system, Ne $2p$ electrons are promoted into the $4f\sigma$ MO at internuclear distances $R\sim 0.6$ Å.

The experiments used a collimated, mass-analyzed beam of Ne^+ ions incident on a polycrystalline Mg surface in a UHV system that is described elsewhere.[5,8,9] Electrons ejected from the sample were energy analyzed with a hemispherical electrostatic analyzer (ESA) with the angle between the ion beam and ESA fixed at 75°. The ion-beam incident angle α was 15° with respect to the surface plane. Scattered neutrals and ions were velocity analyzed by pulsing the Ne^+ beam and measuring their time of flight (TOF). TOF measurements were made with continuous variation of the scattering angle θ and rotation of the sample about an axis perpendicular to the plane determined by the incident beam and the detector in order to vary the beam incident α and exit β angles. Ion fractions were determined by measuring the TOF spectra with and without a voltage applied to a deflecting plate in front of the electron multiplier. The Mg sample was cleaned by low-energy Ar^+ ion sputtering and annealing. Oxidized surfaces were prepared *in situ* by exposure to a dose of 10 L (where 1 L $=10^{-6}$ Torr sec) of O_2.

Representative TOF spectra of neutrals plus ions $(N+I)$, neutrals (N) only, and ions (I) only are shown in

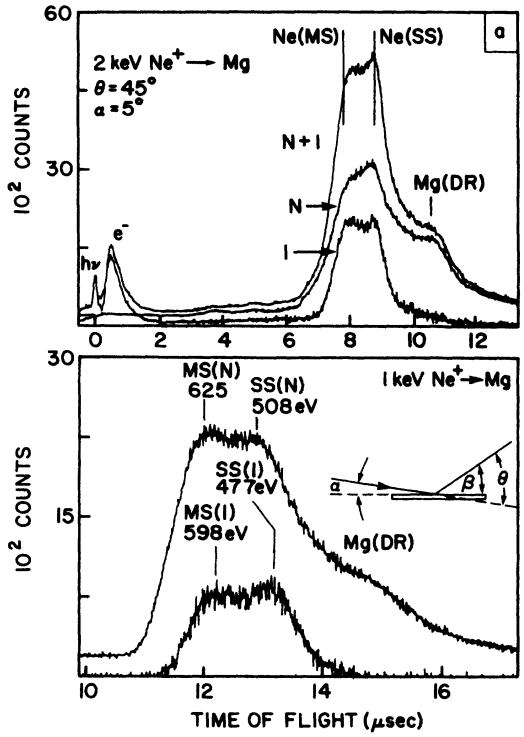

FIG. 1. TOF spectra of neutrals+ions ($N+I$), neutrals (N), and ions (I) for Ne^+ scattering from a clean magnesium surface at 1- and 2-keV incident energies. Ion-induced photons ($h\nu$) and electrons (e^-) and quasi-single-scattering (SS), quasi-multiple-scattering (MS), and direct recoil (DR) Mg atoms are indicated. The vertical lines and energies on the spectra represent, respectively, the centroids of the overlapping peaks and the Ne energies corresponding to the measured velocities. The incident energies are nominal values.

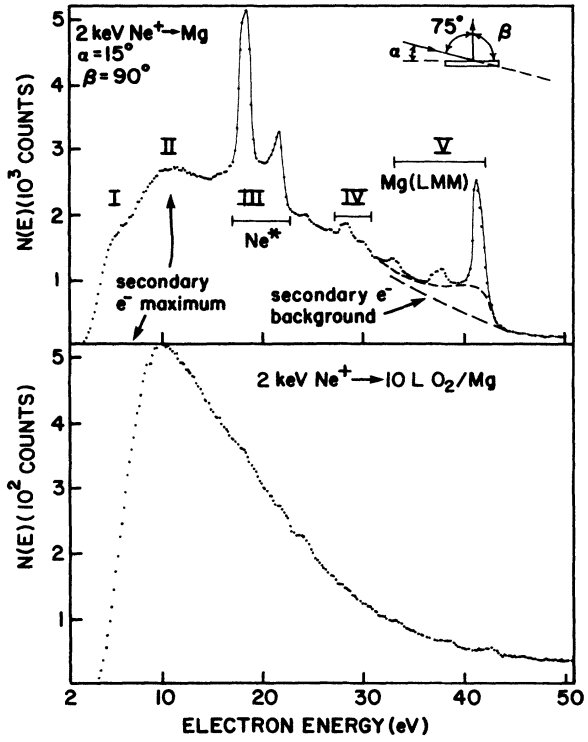

FIG. 2. Electron energy distributions from a clean and oxidized magnesium surface stimulated by 2-keV Ne^+ ions.

Fig. 1. They consist of peaks due to scattered and recoiled particles as well as emitted photons and electrons. The photon peak determines the origin of the time scale. Identification of the scattered and recoiled particles is obtained through kinematic relations,[5] considering quasi-single-scattering (SS) and quasi-multiple-scattering (MS). It is observed[10] that larger ion fractions result from the SS collisions at high E and high θ where the average individual collisions are most violent.

Representative electron energy spectra from clean and oxygen covered Mg are shown in Fig. 2. The spectrum from the clean surface shows two groups of lines on top of a smooth background. The low-energy lines near 20 eV correspond[11] to autoionization of $Ne^{**}(2p^4 3s^2)$ in vacuum to $Ne^+(2p^5)$ and those near 40 eV correspond to the Auger decay of inner-shell excited Mg recoils.[12] These peaks are shifted and broadened by the Doppler effect due to the velocity distribution of the emitting atoms. Such effects have been observed[3,4] in gas-phase collisions and appear to be similar on surfaces. A new finding is the nearly complete disappearance of the autoionizing features upon oxygen chemisorption.

The fraction (f^+) of Ne particles that are scattered as Ne^+ ions were derived from the area of the SS TOF spectral peaks obtained for ($N+I$) and N. This SS peak was deconvoluted from the MS peak, with an uncertainty of $< 20\%$ of the SS intensity. The f^+ values were measured as a function of continuously varying scattering angle for several fixed projectile energies. Figure 3 shows f^+ plotted as a function of the distance of closest approach (R_c) for different projectile energies. The values of R_c were calculated from classical two-body collisions using the Moliére interatomic potential. A dramatic increase in f^+ is observed to occur as R_c decreases, with a sharp rise near $R_c \approx 0.55$ Å. These results are in agreement with previous measurements in which the ion fractions were determined as a function of ion energy for fixed scattering angles.[6]

At small scattering angles, the R_c in a Ne-Mg collision is too large to promote the $4f\sigma$ MO and, as a result, no Ne $2p$ excitation results. It is expected that Ne^+ will be neutralized very efficiently by resonant and Auger transfer of a Mg valence electron,[1] resulting in a very low f^+. The results[10] for small θ show that neutralization is accompanied by an energy loss of ≈ 12 eV. The requirement of a small R_c for a large f^+ explains the increase in f^+ with increasing energy. When the distance of approach is reduced to $\approx R_c$ as a result of increased energy or scattering angle, up to two Ne $2p$ electrons can be promoted into the $4f\sigma$ MO. The critical distance R_c that is obtained from the increase in f^+ in Fig. 3 is in agreement with that derived from the energy threshold[3] for the emission of autoionization electrons from doubly excited Ne. For these violent collisions, we observe (Fig. 1) that scattered *ions* are accompanied by an additional energy loss of ≈ 30 eV.

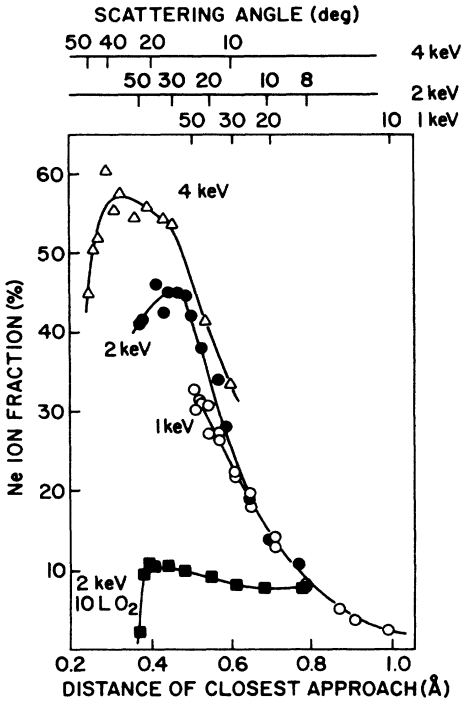

FIG. 3. Scattered Ne^+ ion fraction f^+ as a function of the distance of closest approach R_c of the projectile and target atoms for 1-, 2-, and 4-keV energies on clean Mg and for 2 keV on oxidized Mg. The data was collected at fixed projectile energy by varying the scattering angle continuously. The vertical displacement of the curves for different primary energies is due to the different resonant and Auger neutralization probabilities as a function of ion velocity. The steep slope in the region -0.4 Å $< R_c < -0.7$ Å is due to autoionization after two-electron promotion in the close encounter. The dropoffs for $R_c < -0.4$ Å are due to neutralization by vacancy exchange.

Taking into account the partition of elastic and inelastic energy in a binary Ne-Mg collision, we obtain that the inelasticity[13] of these violent collisions amounts to ≈ 45 eV, in agreement with the electronic energy required to form doubly excited Ne^{**}.

The question arises as to why the excitation of a single Ne $2p$ electron with an inelasticity of ≈ 20 eV is not observed in the ion TOF spectra. Due to fast ($\approx 10^{-15}$ sec^{-1}) transition rates, singly ionized Ne^+ is very likely to undergo resonant neutralization from a Mg $3s$ electron in the metal valence band to form $Ne^*(2p^5 3s^1)$. This neutralization transition is the origin of the resonant photons emitted[14] and the scattered metastable Ne^* atoms.[15] In contrast, neutralization of Ne^+ resulting from autoionization should occur much less readily, since the long lifetime[16] of Ne^{**} ($\approx 1.5\times 10^{-14}$ sec) will result in decay to Ne^+ when the particle is away from the surface where there is a much lower overlap with Mg valence electrons. For example, 1 keV Ne will travel ~ 15 Å in 10^{-14} sec. The decrease of f^+ at small R_c (large θ) may be due to vacancy transfer by the electron capture from the Mg $2p$ shell, a mechanism proposed[17] to explain the anomalous Al $2p$ Auger emission induced by He^+ and Ne^+ ions. At these large θ (small R_c), the component of the Ne velocity perpendicular to the surface is small and additional neutralization may result by electron transfer from the surface.

Upon chemisorption of oxygen, there is a large decrease ($\approx 75\%$) in the Ne^+ ion fraction, which correlates with the near disappearance (Fig. 2) of autoionization electrons. The Mg recoil peak is not observed in the TOF spectra of the oxidized surface (Fig. 1), showing that Mg atoms are shadowed by the surface oxygen. Scattering of Ne from oxygen does not produce Ne $2p$ excitations since it is the O $2p$ electrons which are promoted into the $4f\sigma$ MO; these electrons can contribute to the observed background increase in the electron spectra of Fig. 2. Oxidation also produces a band gap in the valence electron states and a change in the work function of the Mg surface which inhibits resonant neutralization to excited Ne states,[18] as indicated by the decrease in the photon yield and increase in f^+ compared to that of soft Ne-Mg collisions.

In summary, our results show that the anomalously large ion fraction (up to $\sim 70\%$) of Ne^+ scattered from Mg surfaces originates in the autoionization of doubly excited $Ne^{**}(2p^4 3s^2)$ formed as a result of the violent Ne-Mg collisions. This is a newly identified mechanism which can account for the high ion yields observed from certain ion/surface scattering systems. We suggest that similarly long-lived autoionizing states may play an important role in determining the ion yields in ion scattering spectrometry, secondary ion mass spectrometry, and photon- and electron-stimulated desorption from surfaces.

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*Permanent address: Centro Atómico Bariloche, 8400 San Carlos de Bariloche, Río Negro, Argentina.

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[13]For small values of the ratio of the inelasticity Q to the primary energy E_0, the SS peak is displaced with respect to its value for elastic scattering by the energy loss

$$\delta E = \frac{Q}{1+\gamma} \frac{\cos\theta}{(\gamma^{-2}-\sin\theta)^{1/2}} + 1 ,$$

where γ is the projectile to target mass ratio and θ is the scattering angle. This expression is readily derived from considerations of energy and momentum conservation.

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