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Excited state distribution of reflected hydrogen atoms at metal surfaces – Development of theoretical models

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ABSTRACT

Numerical methods were developed to study single electron capture by translating hydrogen atoms above metal surfaces. The present method gives predictions for hitherto unknown population distribution of excited species in hydrogen atoms reflected at the metal surfaces. The excited state abundance was calculated for Mo surface. Kinetic energy distribution of the reflected atoms was taken into account with the aid of the Monte-Carlo simulation code (ACAT). Energy distribution associated with the $3d_2$ excited state in reflected neutrals consistently explains peak energy variation with incident energies of Doppler-shifted D_α lines measured by Tanabe et al. Occupation probability of the magnetic sub-levels is obtained to be highly polarized. It suggests strong anisotropy in angular distribution of photon emission from the excited states created via the surface electron capture.

1. Introduction

High-energy (super-thermal) neutral hydrogen atoms are produced by backscattering at metal surfaces. Generally, particle and energy reflection coefficients are larger for metals of larger atomic numbers. Twin-limiter (carbon and tungsten) experiments at TEXTOR [1] clearly showed larger penetration of neutral hydrogen in front of the tungsten limiter. From this experiment, it was inferred that the neutrals reflected at the tungsten surface possessed higher translation velocities into plasmas. Spectroscopic studies identified Doppler-shifted Balmer line emission from high-energy reflected neutrals in plasmas [2]. The line intensity and shape were analyzed taking account of collisions with plasma particles. In the analysis, it has been presumed that the reflected neutrals were initially in the ground state. This naive assumption has been widely adopted, since excited state population in the reflected neutrals was unknown.

The excited states would play characteristic roles in edge plasmas. Photon emission near the surface would be increased by presence of the excited states. Meta-stable excited states with the principal quantum number n have larger ionization and charge exchange cross sections; the ionization cross sections increase approximately as n^2 (electron-impact) and n^4 (proton-impact), and the charge exchange cross sections n^{4-5}. Accordingly, the ionization event per photon should be different from that obtained by assuming no initial population of the excited states.

Excited state population was observed by detecting photon emission from neutrals of an ion beam backscattered at metal surfaces for incident energies of a few keV or higher [3] and lower energies [4]. Some theoretical calculations have been conducted to explain the excited state population in terms of single electron transfer between excited atomic levels and conduction bands of metal surfaces. Burgdörfer et al. calculated $n = 2$ population of atomic hydrogen specularly reflected with grazing angles at gold surfaces [5]. They adopted the kinematic resonance model for the electron transfer associated with nuclear translation parallel to the surface, while adiabatic approximation was used for electronic state evolution associated with the translation along the surface normal. Kato et al. [6] pointed out contribution of non-adiabatic promotion of the translating electron due to the nuclear motion along the surface normal in a simplified one-dimension system; geometry of the electronic system was restricted to the surface normal only. In this work, the previous works were extended to calculate distributions of the excited state population taking account of kinetic energy and angular distributions of backscattered hydrogen atoms. The present electron transfer model gives predictions for the excited state populations of hydrogen atoms translating above metal surfaces with a given velocity and emission angle to the surface normal. With the aid of Monte-Carlo simulation, the excited state distribution in reflected neutrals of a certain energy distribution and the given emission angle are obtained.

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2. Theoretical method

Here, we describe the gist of present theories briefly. More details will be presented else where. Atomic units are used throughout unless otherwise stated.

In this work, the electron transfer is studied by means of the semi-classical theory (electronic transition was treated quantum mechanically, while projectile nucleus motion was represented by classical trajectories). The semi-classical theory is valid as long as the de Broglie wavelength of the projectile is much shorter than the atomic size (≈1 Å). The present calculations were conducted at projectile kinetic energies which met this condition (>100 eV). Once excited hydrogen atoms dive into the metal, electrons at the excited levels are stripped immediately due to the strong screening effect of conduction electrons. Thus, only outgoing part of the trajectory is relevant to the excited hydrogen atoms emitted from the surface. Variation of the projectile velocity due to the image potential of the surface and the electronic transition is omitted, since their energies are much smaller than projectile kinetic energies considered here.

The electron moves under influences of three potentials: the Coulomb attractive potential of a projectile nucleus, the attractive potential well of the target metal surface, and repulsive potential of a pile of electron density at the surface induced by the projectile nuclear charge. The surface potential well was approximated by means of a semi-empirical formula proposed by Jennings et al. [7]. The induced repulsive potential was calculated from the static linear density response function of electrons in the surface potential well [8]. The sum of these three potential energies for Mo is shown in Fig. 1. In the present approximation, only the work function and the Fermi energy (width of the conduction band) specify the interaction with Mo surface.

Electron wave functions in the rest frame of the translating projectile with a velocity $\vec{v} = (v_x, v_y, v_z)$, $\Psi(\vec{r}, t)$, are obtained in the rest frame of the target metal by the Galilean transformation,

$$\Psi(\vec{r} + \vec{v}t, t) = \exp(i\vec{v}\cdot\vec{r} + iv^2/2t)\Psi(\vec{r}, t).$$

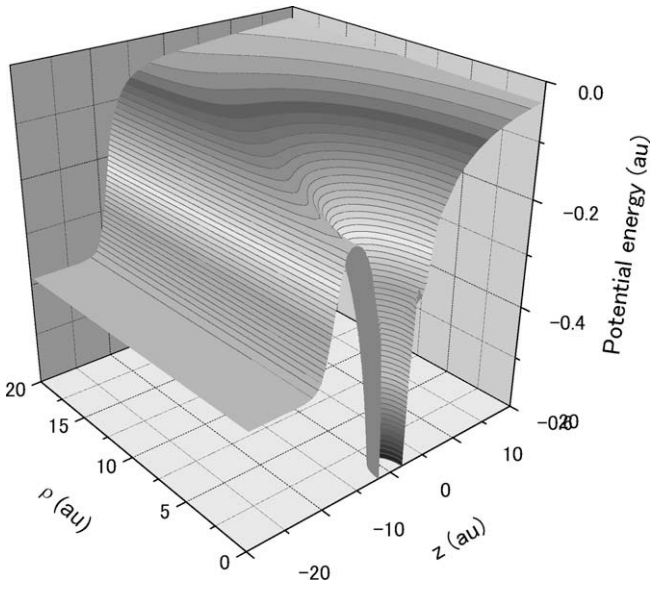

Fig. 1. Potential energy surface for Mo in the cylindrical coordinates $\{\rho, z\}$, the z-axis is set along the surface normal. The potential surface is symmetric under rotation in the polar angle. The origin of the coordinate is at the position of the hydrogen nucleus 10 au above the Mo surface. 1 au (atomic units) of length = 1 Bohr radius and 1 au of energy = 27.21 eV.

The electron translation phase factor $\exp(i\vec{v}\cdot\vec{r})$ represents translation of bound electrons with the projectile in the rest frame of the target, while it represents the Doppler-shift of the Fermi sphere of the surface electrons in the rest frame of the projectile. The Doppler-shift makes apparent population of the surface electrons distributed beyond the Fermi level, and that causes the so-called kinematic resonance electron transfer between higher atomic levels and the surface conduction levels above the Fermi level [9].

Another mechanism contributes populating the higher atomic levels which is non-negligible for higher translation velocities: variation of the electron wave functions associated with the projectile displacement along the surface normal. At each distance from the surface, $D(t) = D(t=0) + v_z \times t$, a different set of local solutions of the time-independent Schrödinger equation is given,

$$\hat{H}(\vec{r}; D)\Phi_\mu(\vec{r}; D) = \varepsilon_\mu(D)\Phi_\mu(\vec{r}; D).$$

At large distances, the solutions are associated to the projectile atomic states and the target electron states of the surface potential well. The variation of the wave functions associated with the projectile displacement can also promote population of the higher atomic levels. It manifests itself in a local propagator of the wave functions in a small sector $[D_i, D_{i+1}]$, $\langle\Phi_\mu(D_{i+1})|\Phi_{\mu'}(D_i)\rangle \times \exp[-i\varepsilon_{\mu'}(D_i)\delta t]$. $\langle\Phi_\mu(D_{i+1})|\Phi_{\mu'}(D_i)\rangle$ is non-orthogonal overlap between the different set of the local solutions obtained at boundaries of the small sector. Thus, the propagation induces transitions between different electronic states μ due to finite off-diagonal elements of the non-orthogonal overlap. This transition can elevate the surface electrons below the Fermi level to the higher atomic levels; we refer to it as the non-adiabatic promotion [6]. It is noted that, for lower translation velocities, de-phased off-diagonal $\mu \neq \mu'$ elements of the overlap are mutually canceled out, and therefore the non-adiabatic promotion is suppressed.

We also note that initial populations of the atomic levels are given depending on the choice of the initial distance, $D(t=0)$. In this work, however, we took the choice of $D(t=0) = 0$ without investigating $D(t=0)$ dependence of final populations of the excited atomic levels. Provided v_z is smaller than the Fermi velocity of target metals, populations of the atomic levels would rapidly equilibrate with those of target conduction levels. In this case, the final population should depend little on the initial population; memory of the initial population would be lost before receding hydrogen nuclei reach the smallest distances wherefrom the electron transfer is truncated. This loss of memory has been observed in the previous calculations by Burgdörfer et al. [5].

3. Result and discussion

Fig. 2 shows state-resolved population of the atomic states formed by the single electron capture from Mo surfaces. In the present calculation, a statistical ensemble was given initially that electronic states below the Fermi level had a uniform population of 1, while the states above the Fermi level had no population. The populations of the excited hydrogen atoms grow as the projectile translation velocity increases, due to the mechanisms of the kinematical resonance and the non-adiabatic promotion. It is noted that at a given translation velocity the excited state populations are smaller for larger emission angles to the surface normal. The de-population may be ascribed to the resonance ionization of the excited neutrals, since the neutrals of the larger emission angles generally stay longer near the surface.

To obtain kinetic energy and angular distributions of backscattered neutral atoms, the Monte-Carlo simulation was conducted using ACAT code [10]. The kinetic energy distributions were calcu-

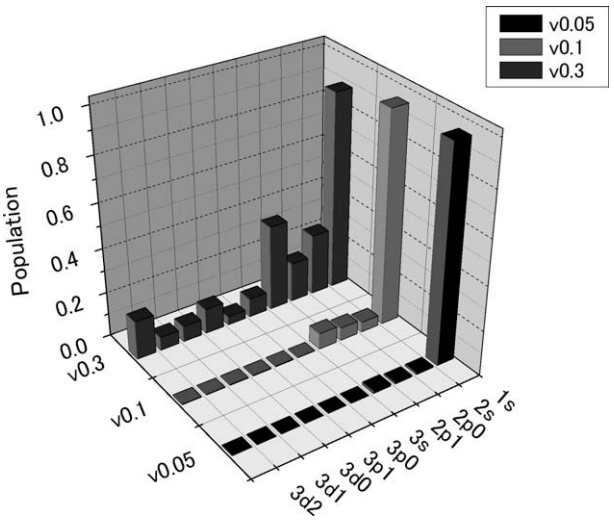

Fig. 2. Population distribution of atomic states after single electron capture by hydrogen nucleus translating outward from the Mo surface with an emission angle of 60° to the surface normal. The population distributions are shown for three translation velocities. The Fermi velocity of Mo = 1.19 au = 2.61×10^8 cm/s.

lated for D atoms reflected at Mo surfaces at incident kinetic energies of 5–25 keV and an incident angle of 60° to the surface normal. The present calculations showed almost uniform distributions below 1 keV and declines for higher energies. A kinetic energy distribution associated with hydrogen atoms of a specific excited state *nlm* is defined as product of the kinetic energy distribution of the reflected particles $f(E_R)$ and the excited state population function of translation energies of the reflected particles $P_{nlm}(E_R)$,

$$\tilde{f}_{nlm}(E_R) = f(E_R) \times P_{nlm}(E_R).$$

The associated kinetic energy distributions are directly related to the Doppler profile of line emissions from the excited states in the reflected neutrals. Fig. 3 shows the associated kinetic energy distribution for $3d_2$ excited states in the reflected neutrals which are coming out at the emission angle of 60° to the surface normal. In the present calculations, the $3d_2$ state has the largest population in the excited states of $n = 3$ manifold. The associated distribution has an apparent peak, although the peak is not seen in the $f(E_R)$. The $P_{nlm}(E_R)$ has a maximum at certain energy independent on the incident energy (about 8 keV for the $3d_2$ state of D atoms reflected to the 60°). Since the $f(E_R)$ is decreasing function at energies where the $P_{nlm}(E_R)$ has the maximum, a maximum of their product always appears below the energy of the $P_{nlm}(E_R)$ maximum. While it is seen that the peak energies and widths of the associated distributions increase with the incident energy, the peak energies have little difference for the incident energies of 10–25 keV. In the same incident energy range and at the same incident angle, Doppler-shift measurements of the D_α line emission from reflected D atoms at the Mo surface were reported that the Doppler-shifts showed a very weak dependence on the incident energy [3]. The present results are therefore consistent with the measurements, although a little discrepancy between the peak energies and the measured Doppler-shifts remains.

Occupation probabilities of excited levels are defined as ratios of excited state populations to the total population of neutrals and ions in the reflected hydrogen atoms. Contribution of $n = 4$ or higher excited states (including ionization states) were neglected in the calculated occupation probabilities. Nonetheless, the present occupation probabilities should not include large errors, since the higher excited states are less populated at projectile energies considered in this paper. The occupation probabilities per incident ion are obtained by multiplying reflection coefficients. Fig. 4 shows the occupation probabilities of excited D atoms reflected to the 60° at the Mo surface. The occupation probabilities are decreasing for higher incident energies, although the populations of the excited states are increasing. It is due to decreasing reflection coefficients with the incident energy. At lowest energies in the figure, the occupation probabilities of some excited states drop. This is ascribed to strong suppression of the excited state population at lower energies. For lower incident energies, the occupation probabilities of the excited states would become smaller regardless of larger reflection coefficients. The suppression of the excited state population has been observed experimentally in decrease of 3 ^{3}P–2 ^{3}S photon emission from surface reflected He atoms for incident energies lower than 30 keV [11]. Due to smaller nuclear mass, for atomic hydrogen the suppression may be apparent at lower energies.

It is seen in the present results that the excited states with the largest magnetic quantum number $\pm m$ have larger occupation probabilities, e.g. $2p_{\pm1}$ states have larger probabilities than $2p_0$ state. The large value of the linear polarization may result from suppression of the resonance ionization of the largest m state (parallel to the surface plane) relative to the $m = 0$ state (aligned along the surface normal chosen as the quantization axis). Anisotropy in angular distribution of photon emission is expected from the polarization. This is a distinct character of the excited states created by the surface electron capture from those excited by collisions with thermal plasma particles. In principle, the excited state created by

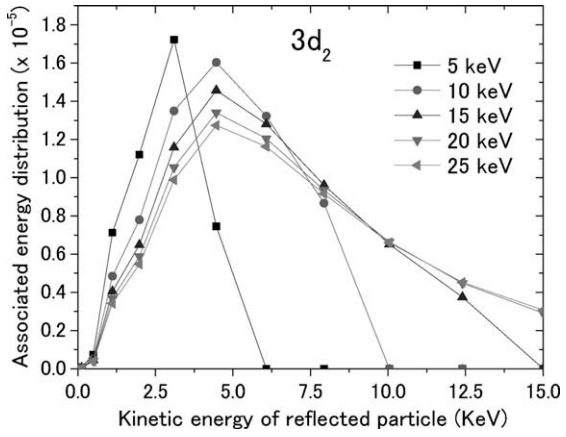

Fig. 3. Associated energy distribution of $3d_2$ state in neutral D atoms reflected at Mo surface with an emission angle of 60° to the surface normal. The distributions are shown for five incident energies in 5–25 keV and an incident angle of the 60°.

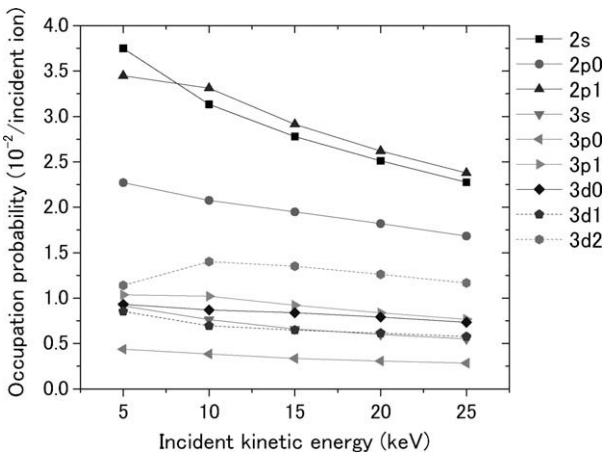

Fig. 4. Occupation probabilities of excited states in neutral D atoms reflected Mo surface with an emission angle of 60° to the surface normal.

the collision with the thermal plasma particles of the isotropic velocity distribution is not polarized. Therefore, the polarization may serve as experimental detection of the excited states created via the surface electron capture in reflected neutrals of edge plasmas.

4. Conclusion

It is challenging to treat electronic excitations in ion-surface interactions based upon the first principle. Earlier studies on the electron transfer between ions and metal surfaces have been undertaken with the aid of simplified interaction matrix elements and/or the adiabatic approximation [5,12–14]. This study is based upon numerical solutions of the time-dependent Schrödinger equation with correct interaction potentials. Earlier works [5] were restricted to the grazing incidence geometry to remedy burdens of considering complicated trajectories of reflected (backscattered) particles at surfaces. This work is an attempt to couple quantum scattering theories and classical Monte-Carlo methods to simulate more realistic reflection dynamics. This work is in progress in a framework of developing integrated simulation codes and precise diagnostics of the plasma–surface interaction.

Acknowledgements

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