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Theoretical study of swift molecular ions specularly reflected from solid surfaces under glancing angle of incidence

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Abstract

We develop a theoretical model to study grazing scattering of fast diatomic molecular ions from a solid surface, based on the dielectric response formalism within the specular reflection model, where the plasmon pole approximation for dielectric function is employed to describe the single-particle and the collective excitations of the electron gas at the surface. Evolution of the bound-electron densities at the constituent ions of a molecule in the course of scattering is described by an approach similar to recent implementation of the Brandt–Kitagawa model for single-ion surface grazing scattering. We solve numerically the equations of motion for the constituent ions and obtain the ion scattering trajectories in the presence of Coulomb explosion modified by the surface wake potential, for the initial molecular-axis orientations in either random directions or along the beam. Vicinage effect on the total energy loss is discussed on the basis of analyzing the position-dependent stopping powers of individual ions and the interferences in the electron excitations of the substrate.

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1. Introduction

Owing to rapid progress in the development of ion sources, swift molecular and cluster ions have become available in wide ranges of energies for use in the implantation technology, materials modification and surface analysis. Ever since Brandt et al. [1] have demonstrated experimentally the existence of the so-called vicinage effect in the energy loss of molecular hydrogen ions in solid carbon, the interaction of swift cluster and molecular ions with solids and solid surfaces has attracted increasing attention [2,3]. In analogy

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with grazing scattering of atomic projectiles [4,5], when a molecular ion approaches a solid surface at a glancing angle, it is subject to the attractive dynamic image force and to a short-ranged repulsive force due to atoms located in the first surface layer. However, new physical processes are expected to take place due to the molecular, or vicinage effect. For example, one of the most typical processes is Coulomb explosion of the incident molecule, which is triggered by stripping of its binding valence electrons due to the interaction with the substrate, resulting in a separation of the constituent ions on a time scale of several femtoseconds. This period matches the duration of the close projectile-surface interactions under typical grazing-scattering conditions, thereby indicating that the vicinage effect will be substantial.

First experimental measurements of Coulomb explosion in grazing scattering were performed by Susuki et al. [6] for MeV H_2^+ and HeH^+ on a clean SnTe surface. Similar experiments were performed by Winter et al. [7], in which clearly resolved Coulomb explosion patterns in the energy spectrum of the dissociated fragments were obtained for H_2^+ on Si and W surfaces. Numerical simulations, performed by Susuki et al. [8,9] in conjunction with their experimental measurements, suggested that almost all molecular ions were dissociated during scattering, and that a pronounced alignment of the internuclear axis took place in directions parallel to the surface.

The vicinage effect is also manifested in the energy losses of the molecular ions during grazing scattering, showing important differences in comparison with the scattering of isolated ions under identical conditions, as a consequence of the interference in the electronic excitations in the surface by the spatially correlated molecular constituents. For example, in the experiment on grazing scattering of MeV H_2^+ on SnTe, the energy loss measurements showed a positive vicinage effect [10], where increased losses of the molecule were a consequence of the positive interferences. On the other hand, in the dielectric models, negative interferences for the molecular projectiles moving at lower velocities are often responsible for lower energy losses in comparison with isolated projectiles.

Moreover, the charge state of the molecular projectiles made of heavier atoms may also play important role during the interaction with the target, which is regarded as the vicinage effect in charge states. For example, negative vicinage effects were reported for the energy losses of fast N_2^+ and O_2^+ ions in thin carbon foils [11]. It was shown that mutual reduction of the effective charges of the constituents in such projectiles was responsible for lower energy losses, as well as for slower Coulomb explosion of the molecular ions, when compared to the same molecular projectiles with the charge states corresponding to the isolated ions at the same speed [12,13].

In the present contribution, a theoretical model based on the dielectric response theory and the specular reflection model is formulated to describe the grazing scattering of fast molecular ions from solid surfaces, with the special attention paid to the role of charge states in the Coulomb explosion and the energy losses during scattering. Unless otherwise indicated, atomic units (a.u.) will be used throughout.

2. Theoretical model

Being only concerned with the homo-nuclear diatomic projectiles, we assume that the internuclear axis is parallel to the surface plane, in accord with the corresponding experimental and theoretical findings [7,8]. A coordinate system is placed in the scattering plane, with the x-axis along the direction of the parallel component of the projectile velocity $\mathbf{v}_\mathbf{k}$, and the z-axis perpendicular to the surface. The scattering center ($x = 0$, $z = 0$) is placed at a target-atom nucleus in the first atomic plane, such that the region z^0 z $r_d < 0$ is occupied by the electron gas of the bulk of the solid, where r_d is the average atomic radius of the target. The notations $\mathbf{r} = (\mathbf{R}, z)$, $\mathbf{k} = (\mathbf{Q}, k_z)$ and $\mathbf{v} = (\mathbf{v}_\mathbf{k}, v_z)$ will be used, where $\mathbf{R}$, $\mathbf{Q}$ and $\mathbf{v}_\mathbf{k}$ represent components parallel to the surface. With typical angles of incidence being of the order of milliradian, we may assume that the total molecular ion velocity $\mathbf{v}$ $\mathbf{v}_\mathbf{k}$. In analogy to the approach developed for heavy-ion grazing scattering [5], the charge state of the molecular ion can be expressed as

$$
\begin{aligned}
{}_{\mathrm{ext}}(\mathbf{r};t) &= \tfrac{1}{4}\pi Z_1 \left[\rho_n(\mathbf{R}-\mathbf{R}_1-\mathbf{v}t)-\rho_n(\mathbf{R}-\mathbf{R}_1-\mathbf{v}t)\right]\delta(z-z_0) \\
&\quad +\tfrac{1}{4}\pi Z_1 \left[\rho_n(\mathbf{R}-\mathbf{R}_2-\mathbf{v}t)-\rho_n(\mathbf{R}-\mathbf{R}_2-\mathbf{v}t)\right]\delta(z-z_0),
\end{aligned}
\tag{1}
$$

where Z_1 is the atomic number of the projectile, $(\mathbf{R}_1, z_0)$ and $(\mathbf{R}_2, z_0)$ are the position vectors of the leading and the trailing ions, respectively, with the internuclear vector $\mathbf{R}_0 = \mathbf{R}_1 - \mathbf{R}_2$. Here, $\rho_n(\mathbf{R})$ is the two-dimensional electron distribution, previously developed in a modification of the Brandt and Kitagawa (BK) statistical model [14].

As the molecular ion approaches the surface, in addition to the dynamic image force and the repulsive force from surface atoms, there also exist bare Coulomb force and the dynamic interaction force between the constituent ions, resulting in a wake-modulated Coulomb explosion. Thus, following the procedure in [15], we obtain the trajectory of the center of mass (x_0, z_0) from

$$
\frac{dz_0}{dx_0} = \sqrt{1 - 2\frac{U_p(z_0) + U_s(z_0) + U_w(z_0;\mathbf{R}_0)}{E}};
\tag{2}
$$

where $E = M_c v^2/2$ with $M_c = 2m$ being the molecule mass, whereas the equations of motion for the relative position $\mathbf{R}_0$ and the relative velocity $\mathbf{u}$, are as follows:

$$
\frac{d\mathbf{R}_0}{dx_0} = \frac{\mathbf{u}}{v};
\tag{3}
$$

$$
\frac{d\mathbf{u}}{dx_0} = \frac{1}{vm}\left[\mathbf{F}^{(a)} + \mathbf{F}^{(w)}\right].
\tag{4}
$$

In the above, $U_p(z_0)$ and $U_s(z_0)$ are the sur-

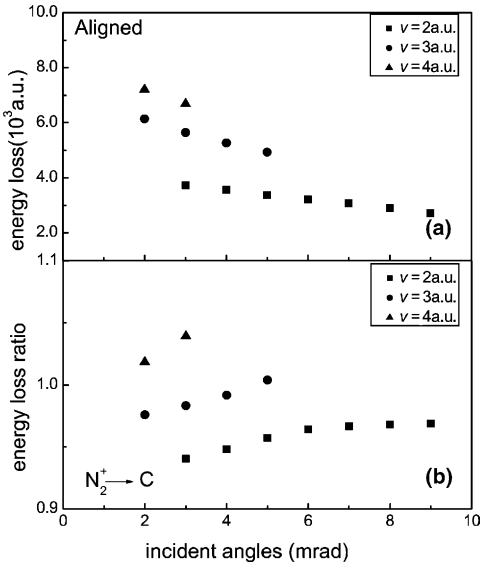

Fig. 3. The dependences of (a) the total energy loss and (b) the energy loss ratio on the incident angles for N_2^b ions grazingly scattered from C surface at velocities $v = 2$, 3 and 4, for the molecular axis aligned in the direction of motion.

and to the resulting weakening of the interference effects [11–13]. So, in comparison with the calculated results for H_2^b [15], the energy loss ratios for N_2^b are reduced here and remain around one. In particular, comparison of the parts (b) in Figs. 2 and 3 shows that we have a negative vicinage effect in the case of the aligned molecular axis, with the energy loss ratio less than one for speeds $v = 2$ and 3. This appears to be consistent with the discussion in [2,3], where more pronounced negative interferences have been predicted in the vicinage effect for lower projectile speeds and for the aligned molecular axes. Therefore, one may conclude that three factors, namely, the partial stripping of the constituent ions, the low projectile speed, and the alignment of the molecular axis, all work to reduce the enhancement of the energy loss due to the vicinage effect for a heavy-molecule grazing scattering on solid surfaces.

4. Summary

Based on the dielectric response theory and the specular reflection model, we have formulated the equations of motion for grazing scattering of a swift N_2^b ion from a C solid surface, with the molecular axis parallel to the surface. We have calculated the molecule scattering trajectory and the evolution of the inter-nuclear distance during Coulomb explosion for both the case of the molecular axis aligned in the direction of motion of the molecule, and the case of randomly oriented axis in a plane parallel to the surface. The vicinage effect on the energy losses of N_2^b has been evaluated by means of the position-dependent stopping power, and discussed in terms of the incident angles and the projectile speeds.

In analogy with the situation concerning the molecular ions moving through solid foils, we also find that, owing to the partial stripping of valence electrons, the vicinage effect is generally weaker for the heavier projectiles, such as N_2^b in comparison with H_2^b, even though the absolute energy losses may be greater for heavy projectiles. In particular, we find that, in the case of swift molecular ions with randomly oriented axes, the molecular energy loss is always larger than that for two independent ions, whereas a negative vicinage effect occurs when the molecular ions are slower and when their internuclear axes are aligned in the direction of the center-of-mass motion.

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