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 $\mathbf{v}_{\parallel}$, 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 $z' \equiv z - r_d < 0$ 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 $\mathbf{v} = (\mathbf{v}_{\parallel}, v_z)$ will be used, where $\mathbf{R}$, $\mathbf{Q}$ and $\mathbf{v}_{\parallel}$ represent components parallel to the surface. With typical angles of incidence θ being of the order of milliradian, we may assume that the total molecular ion velocity $\mathbf{v} \approx \mathbf{v}_{\parallel}$. In analogy to the approach developed for heavy-ion grazing scattering [5], the charge state of the molecular ion can be expressed as

$$\rho_{\text{ext}}(\mathbf{r},t)$$
$$= [Z_1\delta(\mathbf{R}-\mathbf{R}_1-\mathbf{v}t)-\sigma_n(\mathbf{R}-\mathbf{R}_1-\mathbf{v}t)]\delta(z-z_0)$$
$$+ [Z_1\delta(\mathbf{R}-\mathbf{R}_2-\mathbf{v}t)-\sigma_n(\mathbf{R}-\mathbf{R}_2-\mathbf{v}t)]\delta(z-z_0),$$
$$(1)$$

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, $\sigma_n(\mathbf{R})$ 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

$$\frac{\mathrm{d}z_0}{\mathrm{d}x_0} = \mp\theta\sqrt{1-2\frac{U_{\mathrm{p}}(z_0)+U_{\mathrm{s}}(z_0)+U_{\mathrm{w}}(z_0,\mathbf{R}_0)}{E\theta^2}},$$
$$(2)$$

where $E = M_{\mathrm{c}}v^2/2$ with $M_{\mathrm{c}} = 2m$ 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:

$$\frac{\mathrm{d}\mathbf{R}_0}{\mathrm{d}x_0} = \frac{\mathbf{u}}{v}, \qquad (3)$$

$$\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}x_0} = \frac{1}{vm}\left(\mathbf{F}^{(\mathrm{c})}+\mathbf{F}^{(\mathrm{w})}\right). \qquad (4)$$

In the above, $U_{\mathrm{p}}(z_0)$ and $U_{\mathrm{s}}(z_0)$ are the surface continuum potential and the surface image potential per ion, respectively [5], whereas $\mp$ correspond to the incoming and the outgoing trajectories. The dynamical image interaction potential $U_{\mathrm{w}}(z_0,\mathbf{R}_0) = (U_{\mathrm{w}}^{12}+U_{\mathrm{w}}^{21})/2$ between the two constituent ions in the presence of surface is given by

$$U_{\mathrm{w}}(z_0,\mathbf{R}_0)$$
$$= \frac{1}{4\pi}\int\frac{\mathrm{d}\mathbf{Q}}{Q}[\tilde{\sigma}_n(Q)]^2\mathrm{Re}\big[F(Q,\omega,z_0',z_0')\big]\cos(\mathbf{Q}\cdot\mathbf{R}_0),$$
$$(5)$$

where $\omega = \mathbf{Q}\cdot\mathbf{v}_\parallel$ and $z_0' \equiv z_0 - r_d$, whereas $F(Q,\omega,z',z_0')$ is previously defined function [5], describing the surface induced response based on the specular reflection model (SRM) [16,17] and the dielectric response theory [18]. In the above, $\tilde{\sigma}_n(Q) = Z_1[q(z_0)+(Q\Lambda)^2]/[1+(Q\Lambda)^2]$ is the Fourier transform of $\sigma_n(\mathbf{R})$, with Λ being a screening length, $q(z_0) = 1 - N(z_0)/Z_1$ the ionization degree, and $N(z_0)$ the number of electrons bound at the ion [14]. Coulomb force between the ions, $\mathbf{F}^{(\mathrm{c})} = 2\mathbf{F}_{12}^{(\mathrm{c})}$, is given by

$$\mathbf{F}_{12}^{(\mathrm{c})} = Z_1^2\left\{\frac{1}{R_0^2}+\int Q\mathrm{d}Q\left[\frac{2(q-1)}{1+(Q\Lambda)^2}\right.\right.$$
$$\left.\left.+\left(\frac{(q-1)}{1+(Q\Lambda)^2}\right)^2\right]J_1(QR_0)\right\}\mathbf{e}_{\mathbf{R}_0}, \qquad (6)$$

where J_1 is a Bessel function and $\mathbf{e}_{\mathbf{R}_0}$ is the unit vector in the direction of $\mathbf{R}_0$. Finally, $\mathbf{F}^{(\mathrm{w})} = \mathbf{F}_{12}^{(\mathrm{w})} - \mathbf{F}_{21}^{(\mathrm{w})}$ is the oscillatory interaction force due to ion wakes

$$\mathbf{F}^{(\mathrm{w})}$$
$$= \frac{1}{\pi}\int\frac{\mathrm{d}\mathbf{Q}}{Q}[\tilde{\sigma}_n(Q)]^2\mathrm{Re}\big[F(Q,\omega,z_0',z_0')\big]\mathbf{Q}\sin(\mathbf{Q}\cdot\mathbf{R}_0).$$
$$(7)$$

As the molecular ion begins dissociating, the Eqs. (2)–(4) will be solved simultaneously to obtain the scattering trajectory and the Coulomb explosion dynamics.

The position-dependent stopping power of the molecular ion with the internuclear separation R_0 can be expressed as

$$S_{\mathrm{mol}}(z_0,R_0) = 2S_{\mathrm{e}}(z_0)+S_{\mathrm{v}}(z_0,R_0), \qquad (8)$$

where $S_{\mathrm{e}}(z_0)$ is the stopping power of an individual ion, whereas $S_{\mathrm{v}}(z_0,R_0)$ is the interference term due to the vicinage effect. One can obtain an analytical expression for the molecular stopping power, as follows:

$$S_{\mathrm{mol}}(z_0,R_0) = \frac{1}{\pi v}\int\frac{\mathrm{d}\mathbf{Q}}{Q}[\tilde{\sigma}_n(Q)]^2(-\mathbf{Q}\cdot\mathbf{v})$$
$$\times \mathrm{Im}[F(Q,\omega,z_0',z_0')][1+\cos(\mathbf{Q}\cdot\mathbf{R}_0)].$$
$$(9)$$

Finally, the total energy loss of the molecular ion is calculated by integrating the stopping power along the center-of-mass scattering trajectory

$$\Delta E_{\text{mol}} = \int_{-\infty}^{\infty} S_{\text{mol}}(z_0, R_0) \mathrm{d}s, \tag{10}$$

with $\mathrm{d}s = \sqrt{\mathrm{d}x_0^2 + \mathrm{d}z_0^2}$, so that the energy loss ratio, $\Delta E_{\text{mol}}/(2\Delta E)$, can be evaluated as a measure of the vicinage effect, with ΔE being the energy loss for a single ion in grazing scattering under identical conditions.

In this work, we use the plasmon pole approximation (PPA) for the bulk dielectric function, $\epsilon(k, \omega) = 1 + \omega_{\text{p}}^2/[k^4/4 + \beta^2 k^2 - \omega(\omega + \mathrm{i}\gamma)]$, which gives an analytical result for the surface dielectric function [18].

3. Simulation results

We consider N_2^+ ions incident on a C surface at a glancing angle. Since the evolution of charge states of the individual constituent ions during grazing scattering is unknown at present, we simplify the simulation by neglecting the influence of the induced wake potential on charge states, and consider the transient charge states to be the same for both constituent ions. For the interaction of fast ions with solid surfaces, the charge exchange processes occur predominantly within the electron gas, so we adopt a picture where the charge state remains unchanged when the ion is outside the electron gas $z_0 > r_d$. The transient charge state effect is then described by a model [19] in which the average number of the bound electrons at each constituent ion can be defined as a function of time from the moment when the molecular ion enters the electron gas. For a projectile with the velocity v, we obtain the number of electrons bound at each ion by means of the path length of the molecular ion in the electron gas, s_{b}, as follows:

$$N(s_{\text{b}}) = N_{\infty} - (N_{\infty} - N_0) \exp(-n s_{\text{b}} \sigma), \tag{11}$$

where N_{∞} and N_0 are, respectively, the number of bound electrons in the equilibrium inside the electron gas and the initial number at the entrance. N_{∞} is obtained from an empirical model [20] dependent on the ion velocity v, which shows a

remarkably good agreement with the experimental data for heavy ions in solids. For the initial charge, we assume $N_0 = Z_1 - 0.5$ for the incident N_2^+ ions. In the above, n is the number density of valence electrons in the substrate ($n = 4 \times 10^{23}$ cm^{-3} for amorphous carbon), whereas σ is the ionization cross section ($\sigma \approx 10^{-17}$ cm^2).

If the internuclear axis is randomly oriented but parallel with the solid surface, we may average the direction of $\mathbf{R}_0$ in Eqs. (5), (7) and (9) over the surface plane, thus obtaining the averaged dynamical interaction potential,

$$\overline{U}_{\text{w}}(z_0, \mathbf{R}_0) = \frac{1}{4\pi} \int \frac{\mathrm{d}\mathbf{Q}}{Q} \times [\tilde{\sigma}_n(Q)]^2 \mathrm{Re}[F(Q, \omega, z_0', z_0')] J_0(QR_0), \tag{12}$$

the wake interaction force,

$$\overline{\mathbf{F}}^{(\text{w})} = \frac{1}{\pi} \int \frac{\mathrm{d}\mathbf{Q}}{Q} \times [\tilde{\sigma}_n(Q)]^2 \mathrm{Re}[F(Q, \omega, z_0', z_0')] \mathbf{Q} J_1(QR_0) \tag{13}$$

and the vicinage stopping power,

$$\overline{S}_{\text{v}}(z_0, R_0) = \frac{1}{\pi v} \int \frac{\mathrm{d}\mathbf{Q}}{Q} [\tilde{\sigma}_n(Q)]^2 (-\mathbf{Q} \cdot \mathbf{v}) \times \mathrm{Im}[F(Q, \omega, z_0', z_0')] J_0(QR_0), \tag{14}$$

where J_0 is the zeroth order Bessel function.

On the other hand, as the molecular ion moves near or in the solid, the internuclear axis, which was initially randomly oriented, will tend to direct itself in the direction of the beam velocity after long interaction time, owing to the alignment effect of the wake forces. Since this alignment effect will definitely have an impact on the stopping power and Coulomb explosion during grazing scattering, we also consider the case of $\mathbf{R}_0$ oriented along $\mathbf{v}$ in the course of scattering, so that $\mathbf{Q} \cdot \mathbf{R}_0 = QR_0 \cos\phi$, $\omega = \mathbf{Q} \cdot \mathbf{v} = Qv \cos\phi$, with ϕ being the polar angle in the $\mathbf{Q}$ plane. The initial internuclear distance of N_2^+ is taken to be $R_0 = 2.117$ a.u., whereas for amorphous carbon we use $v_F = 1.17$ a.u., $\gamma = 0.3675$ a.u. and $r_d = 2.418$ a.u. We suppose that N_2^+ begins to dissociate into two N^+ ions as soon as the charge exchange takes place.

The evolution of the internuclear separation R_0 during Coulomb explosion of N_2^+ on a C surface with the speed $v = 3$ and the incident angle of 3 mrad is shown in Fig. 1 as a function of the distance to the surface z_0. The cases of molecules with randomly oriented axes and with aligned axes, as well as the case of a scattering without the wake forces, are compared with each other in Fig. 1. One can see that the Coulomb explosion is more effective in the absence of wake forces between the constituent ions, but this is manifested only in the outgoing leg of the scattering trajectory, and in comparison with the case of the aligned axis. It also appears that, in the case of randomly oriented axis, the Coulomb explosion proceeds slower in close vicinity of the surface, and that the dynamical attraction of the molecule center of mass to the surface is softer, than in the case of the aligned axis. However, it seems that the relative motion of the constituent ions picks up more kinetic energy in the vicinity of the surface when the axis is randomly oriented in comparison with the aligned-axis case, so that the ballistic separation of those ions at large distances from the surface is faster in the randomly-oriented case than in the aligned case.
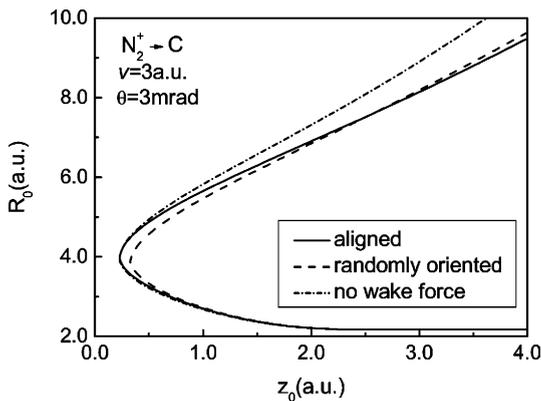
Figs. 2 and 3 depict the incident-angle dependences of the energy losses of N_2^+ specularly reflected on a C surface at several velocities, for the cases of randomly-oriented and the aligned axes, respectively, with the parts (a) in those two figures showing the total energy loss, and the parts (b) showing the energy loss ratio. One can see from the Figs. 2 and 3 that the energy losses decrease with increasing incident angles, mainly due to the shorter interaction times with the electron gas, and due to the absence of the contribution from the inner shell excitations in our model. On the other hand, the energy loss ratio increases with the angle of incidence in both figures. The rates of the changes shown in Figs. 2 and 3 increase with the projectile speed, mostly because more electrons are stripped off the constituent ions due to the more intense charge exchange in the electron gas at higher speeds.

Considering the magnitudes of the energy loss ratios, one expects that less enhancement in the energy loss due to the vicinage effect will take place for the molecules made of heavier atoms, owing to only partial stripping of their valence electrons
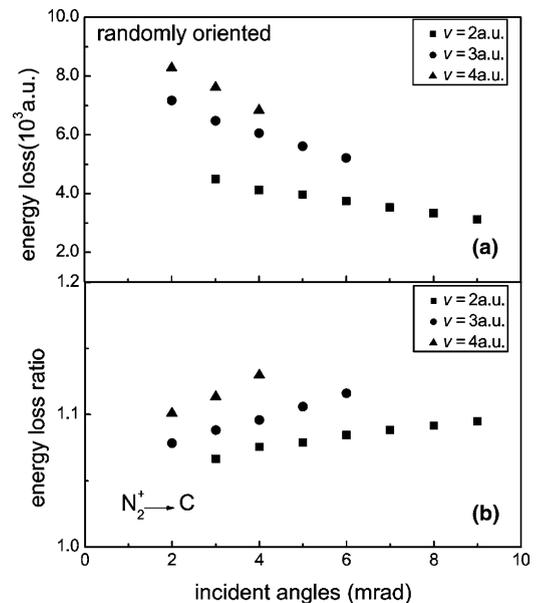

Fig. 1. Internuclear separation R_0 versus distance from the first atomic layer z_0, during grazing scattering of N_2^+ from C surface at the speed $v = 3$ a.u. with the incident angle $\theta = 3$ mrad. Comparisons of Coulomb explosions are shown for the cases of: the molecular axis aligned in the direction of motion (solid line), the molecular axis randomly oriented in a plane parallel to the surface (dotted line), and a grazing scattering without wake forces (dot-and-dash line).

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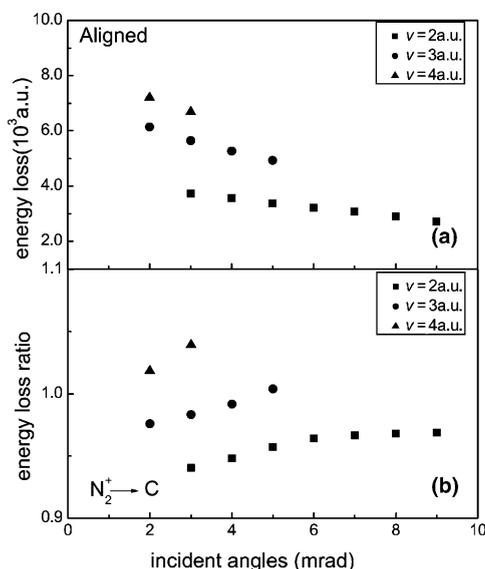
Fig. 3. The dependences of (a) the total energy loss and (b) the energy loss ratio on the incident angles for N_2^+ ions grazingly scattered from C surface at velocities $v = 2$, 3 and 4, for the molecular axis aligned in the direction of motion.

and to the resulting weakening of the interference effects [11–13]. So, in comparison with the calculated results for H_2^+ [15], the energy loss ratios for N_2^+ 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^+ 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^+ 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^+ in comparison with H_2^+, 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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