Theoretical study of orientation effects in multiple ionization of molecules by fast ion impact

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The dependence of multiple ionization cross section on the orientation of the molecular axis in collisions of fast ions with diatomic and linear triatomic molecules is studied theoretically. The ionization process is described within the statistical energy deposition model. The energy transferred in the collision is calculated within the unitary-convolution approximation by Schiwietz and Grande. The impact-velocity dependence of the orientation effect as well as its dependence on the molecular properties are studied.

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I. INTRODUCTION

Multiple ionization of molecules and the subsequent fragmentation is one of the basic processes that determine the production of slow multicharged recoil ions in fast ion-molecule collisions. It was studied extensively in the last two decades. In spite of the wealth of information available in the literature, some of the features of the fragmentation process are still scarcely studied. For example, in fast ion–molecule collision only a few investigations have been devoted to the angular distributions of the multicharged molecular fragments [1–5]. (Note that in the following we discuss only multicharged fragments and, therefore, rather broad literature devoted to the angular distributions in single and double ionization of hydrogen molecules and other few-electron systems is outside the scope of our discussion.) The knowledge of the angular distributions is important not only for a better understanding of the fragmentation mechanism, but also for practical reasons since anisotropic angular distribution may influence the results of cross-section measurements [4]. For fast collisions with diatomic molecules, the angular distribution of the fragment ions that is measured in experiments is simply related to the dependence of the ionization probability on the orientation of the molecular axis with respect to the ion beam at the moment of collision.

In early investigations, on the basis of simple physical arguments it was expected that the multiple ionization of a diatomic molecule is enhanced when the molecular axis is aligned with ion-velocity direction [1]. In this case the projectile encounters more electrons when it moves with a small impact parameter with respect to both nuclei, which is necessary for multiple ionization. This alignment effect was confirmed in experiment with 19 MeV F\(^{3+}\) ions colliding with N\(_2\) molecules [1]. It was found that the slow N\(^q^+\) fragments with charge \(q\geq4\) were predominantly produced when the molecules were aligned along the beam direction. Later orientation dependence of the multiple ionization cross section for collisions of fast ions with diatomics was studied theo-

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retically on the basis of a simple independent atom-independent electron model [6,7]. The calculations confirmed the above qualitative considerations. It was shown that the probability for multiple ionization is strongly suppressed for molecules oriented perpendicular to the collision direction, the effect being larger for larger degrees of ionization. First systematic experimental study of the orientation effect in multiple ionization was done for He ion collisions with N\(_2\) molecules at the energies 100–300 keV [3,8]. The predicted effect was observed when the total number of ionized electrons was \(n\geq4\). The experimental data compared favorably with the theoretical calculations [8] based on the statistical-energy-deposition model. To the best of our knowledge, there are no investigations of the energy dependence of the effect as well as of its dependence on the properties of the projectiles and the target molecules. Only very recently has first observation of the alignment effect been made for highly charged projectile ions colliding with N\(_2\) and O\(_2\) molecules at very high energy (5.9 MeV/amu) [9].

The lack of experimental information makes reliable theoretical predictions valuable. In the present work we theoretically study the energy dependence of the orientation effect. We compare the results of calculations for various diatomic and linear triatomic molecules. For the calculations we use an advanced version of the statistical energy deposition (SED) model [8,10]. In our previous publications the deposited energy was calculated within the local-density approximation (LDA) as suggested by Lindhard and Scharff [11]. This model is based on the linear-response approximation (the first order of the perturbation theory). Therefore, its application is limited to small projectile charges (\(Z_J\)) and high velocity (\(v\)), i.e., the region where the so-called Sommerfeld parameter \(\kappa=Z_J/v\) is much less than unity, \(\kappa<1\). In order to use the SED model at smaller velocities or for higher projectile charges, we introduce another approximation for calculating the impact-parameter dependence of the deposited energy, the unitary-convolution approximation (UCA), developed by Schiwietz and Grande [12]. In the next section we describe the application of the UCA to ion collisions with molecules and shortly recall the basic ideas of the SED model. In Sec. III the results of our calculations are shown and discussed. Some conclusions are drawn in the last section. Atomic units are used throughout unless indicated otherwise.
II. THEORETICAL MODEL

The physical ideas that constitute the basis of the SED model are very simple. It is supposed that the projectile ion is considered as a classical particle moving along a straight-line trajectory with a certain impact parameter; it collides with the target molecule and at the first stage of the process, transfers part of its kinetic energy to electrons of the molecule. It is known that in the energy range considered (50 keV/amu–10 MeV/amu) the energy loss to the nuclear degrees of freedom (nuclear stopping) is much less than the electronic stopping, thus only electronic excitations are taken into account. In the second stage of the process, after the partners depart from one another, the deposited energy is statistically distributed among all target electrons and the system subsequently emits electrons to reach its final ionization state. The number of emitted electrons is determined by the volume of the phase space available for each of the final states.

We use the formulation of the SED model as given by Russek and Meli [13] and Cocke [14]. Since all formulas necessary for calculating the n-fold multiple-ionization probability \( P_n(E_T) \) for a given energy transfer \( E_T \) are published in those papers (see also [10,8]) we do not repeat them here. We only note that this probability is proportional to the square of some average matrix element of the electron emission, which is parameterized as \( g^n \); the \( g \) factor being considered as an adjustable parameter. In this respect the SED model is a semiphenomenological one. However, as it was shown in [10,8] the parameter \( g \) varies very little from system to system and depends only weakly on energy. The probability of ionization for a certain impact parameter \( \vec{b} \) can be obtained by a convolution with the deposited energy distribution \( w(E_T, \vec{b}) \),

\[
P_n^{(N)}(\vec{b}) = \int dE_T P_n^{(N)}(E_T) w(E_T, \vec{b}).
\]  

Then the total cross section of multiple ionization is

\[
\sigma_n = \int d^2\vec{b} P_n^{(N)}(\vec{b}).
\]

As in [8], we assumed that the deposited energy distribution for each trajectory is Gaussian,

\[
w(E_T, \vec{b}) = \frac{1}{\sqrt{2\pi S(\vec{b})}} \exp\left\{ -\frac{[E_T - Q(\vec{b})]^2}{2S^2(\vec{b})}\right\},
\]

where \( Q(\vec{b}) \) and \( S^2(\vec{b}) \) are the mean energy loss and the energy straggling, respectively, in collision of the projectile ion with the target molecule for a given impact parameter.

In our previous papers [10,8] we calculated the impact-parameter-dependent energy loss and straggling within LDA introduced by Lindhard and Scharff [11] where the stopping was described by the linear-response dielectric-function formalism (see [10] for more details). The main drawback of this method is that it cannot be applied for \( \kappa \geq 1 \) where higher-order corrections to the stopping power are important.

In this paper we have, therefore, used the UCA [12], which incorporates Bloch’s ideas of nonperturbative treatment of the energy loss. The advantage of the UCA, besides its simple mathematical formulation, is that it gives a rather accurate impact-parameter dependence of the energy loss for heavy ions, as was shown by a direct comparison with elaborate coupled-channel calculations [15].

The UCA method has been suggested for ion-atom collisions. However, it can easily be adapted to the case of ion-molecule collisions. Within the UCA the impact-parameter dependence of the energy loss is presented as

\[
Q(\vec{b}) = \int d^2r_T K(\vec{b} - \vec{r}_T) \int dz \rho(\vec{r}_T, z),
\]

where \( \vec{b} \) is the impact-parameter vector (the \( z \) axis is parallel to the projectile velocity \( \vec{v} \), and \( \vec{r}_T \) is the radius-vector component perpendicular to \( z \)) and \( \rho(\vec{r}_T, z) \) is the electronic density of the target. The function \( K \) is

\[
K(b) = \frac{2Z_i^2}{v^2b^2} h(2vb/\eta) \sum_I f_i g(\omega_i b/v),
\]

where \( Z_i \) is the projectile ion charge, \( \omega_i = E_i - E_0 \) are the transition energies, and \( f_i = 2|\langle i|z|0\rangle|^2 \omega_i \) are the dipole-oscillator strengths that fulfill the sum rule \( \Sigma f_i = 1 \). Expression (5) is written for a single electron. If there are several equivalent electrons it should be multiplied by the number of electrons. The functions \( h(x) \) and \( g(x) \) are defined by

\[
g(x) = x^2[K_0^2(x) + K_1^2(x)],
\]

\[
h(x) = \frac{x^2}{2} \int_0^1 dy \ y K_0(x y^2) J_0(x y \sqrt{1-y^2}),
\]

where \( J_0 \) and \( K_0 \) are the ordinary and the modified Bessel functions, respectively. The variable \( \eta \) scales the impact parameter and provides the Bloch correction to the stopping power

\[
\eta = \exp\left[ \kappa \sum_{l=1}^{\infty} \frac{1}{(l^2 + \kappa^2)} \right],
\]

with the \( \kappa \) Sommerfeld parameter. This scaling makes the total energy loss integrated over the impact parameters equal to the Bloch value.

We applied expressions (4)–(7) to the calculation of the stopping of an ion interacting with a molecule. The electronic density of the molecules that enters in Eq. (4) was calculated in the Hartree-Fock approximation using the MOLPRO package of programs\(^1\) [16,17]. The ionization potentials for different states of ionization of the molecules that

\(^1\)MOLPRO is a package of \textit{ab initio} programs written by H. J. Werner and P. J. Knowles with contributions from J. Almlöf, R. Amos, S. Elbert, K. Hampel, W. Meyer, K. Peterson, R. Pitzer, and A. Stone.
TABLE I. Calculated ionization potentials (in eV) used in the SED-model calculations for different states of molecular ionization.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E_3$</th>
<th>$E_4$</th>
<th>$E_5$</th>
<th>$E_6$</th>
<th>$E_7$</th>
<th>$E_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$</td>
<td>15.92</td>
<td>29.79</td>
<td>41.63</td>
<td>54.37</td>
<td>68.13</td>
<td>88.31</td>
<td>97.61</td>
<td>114.6</td>
</tr>
<tr>
<td>$\text{F}_2$</td>
<td>19.36</td>
<td>34.61</td>
<td>65.42</td>
<td>41.26</td>
<td>95.75</td>
<td>77.30</td>
<td>103.7</td>
<td>131.9</td>
</tr>
<tr>
<td>$\text{CO}$</td>
<td>13.31</td>
<td>28.64</td>
<td>39.68</td>
<td>57.84</td>
<td>80.24</td>
<td>71.29</td>
<td>102.1</td>
<td>128.5</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>18.96</td>
<td>31.17</td>
<td>37.54</td>
<td>49.95</td>
<td>82.36</td>
<td>47.36</td>
<td>107.9</td>
<td>76.77</td>
</tr>
</tbody>
</table>

are used in the SED-model calculations [8] have been calculated by the same program as differences between total energies of the ground states of the corresponding ions. The calculated values are presented in Table I.

For the evaluation of the sum over all possible transitions in Eq. (5) we have tested two approximate approaches as suggested in [18]. First, in a rough approximation we replaced the sum over oscillator strengths $\sum_i f_i g(\omega_i b_i / \nu)$ by a single function $g(\omega b / \nu)$ with some average transition energy $\bar{\omega}$ that is considered as an adjustable parameter; it was fitted to obtain a reasonable agreement with the experimental stopping power [19]. Second, we considered each molecular orbital having two electrons as a separate oscillator, and the mean transferred energy $\bar{\omega}_s$ was assumed to be equal to $\alpha \bar{\omega}_s$, with $\bar{\omega}_s$ being the binding energy of the orbital $s$. The calculated binding energies for all orbitals of the considered molecules are presented in Table II. The value $\alpha$ is calculated as [18]

$$\alpha = I_B \exp \left( \frac{1}{N} \sum_s n_s \ln(I_s) \right),$$

where $n_s$ is the number of electrons in the orbital, and the Bethe parameter $I_B \approx 12(\text{eV}) Z_2$ [20], $Z_2$ being the target atomic number. Each orbital contributes independently to the stopping power.

The stopping power of nitrogen gas for $\text{He}^{2+}$, calculated with UCA and LDA are shown in Fig. 1. We see that the best agreement with the experiment [19] is obtained for the UCA calculation made separately for each individual orbital (solid curve). For this calculation we used the Bethe parameter value $I_B = 88$ eV [21]. The calculated curve agrees reasonably well with experimental data for the projectile energies $E \approx 0.2$ MeV or $E/M \approx 0.05$ MeV/amu. We should note, however, that at small energies the electron capture process becomes important. Since it is not included in our model, the results in the low-energy region must be considered with some caution. The simplified approach, with a total electron density and an average energy transfer ($\bar{\omega} = 48$ eV), gives worse agreement with experiment (dotted curve). As is known the LDA (long-dash curve) is not a good approximation for small energies but at large energies $E \approx 0.7$ MeV it describes the stopping power quite well.

For the SED-model calculations of the multiple ionization cross sections, the impact-parameter-dependent energy loss $Q(\hat{b})$ is important. We have, therefore, compared the UCA and LDA calculations of the energy loss for the $\text{He}^{2+} + \text{N}_2$ collision as function of impact parameter for the projectile energy of $E = 10$ MeV. For this energy both model calculations of the total stopping power and experiment are in agreement (see Fig. 1). Figure 2 shows the cuts of the two-dimensional surface $Q(x,y)$ along the $x=0$ line for the two orientations of the molecular axis with respect to the beam. The angle is taken from the direction of the beam. One can see that the LDA results overestimate the energy loss at small impact parameters, in the region near the nuclei, because in

FIG. 1. Stopping power of the $\text{N}_2$ gas for the $\text{He}^{2+}$ ions as a function of the projectile energy. Solid line: the UCA calculation with different mean excitation energies for each molecular orbital (see text). Dotted line: the simplified UCA calculation with a single averaged excitation energy for all electrons $I_B = 48$ eV. Dashed line: the LDA calculation. Crosses ‘‘x’’ represent the experimental data [19].

TABLE II. Calculated electron binding energies $I_s$ (in a.u.) for molecular orbitals. The values marked by an asterisk were used for two orbitals.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$I_1$</th>
<th>$I_2$</th>
<th>$I_3$</th>
<th>$I_4$</th>
<th>$I_5$</th>
<th>$I_6$</th>
<th>$I_7$</th>
<th>$I_8$</th>
<th>$I_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$</td>
<td>15.68*</td>
<td>1.49</td>
<td>0.77</td>
<td>0.63</td>
<td>0.62*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{F}_2$</td>
<td>26.43*</td>
<td>1.80</td>
<td>1.48</td>
<td>0.77</td>
<td>0.82</td>
<td>0.65</td>
<td>0.82</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}$</td>
<td>20.67</td>
<td>11.36</td>
<td>1.54</td>
<td>0.80</td>
<td>0.55</td>
<td>0.64*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>20.65*</td>
<td>11.46</td>
<td>1.51*</td>
<td>0.79</td>
<td>0.74</td>
<td>0.72</td>
<td>0.54</td>
<td>0.72</td>
<td>0.54</td>
</tr>
</tbody>
</table>
the LDA the electron binding energies are neglected. At large impact parameters the LDA results decrease sharply because in this model the energy loss $Q$ is proportional to electron density. The results of the UCA are more appropriate since they take into account the nonlocal effects in the energy loss. In the following calculations of the multiple ionization, we use the UCA model with separate contributions of each orbital as our basic model for calculating the mean energy loss as a function of impact parameter.

The straggling of energy loss $S^2(b)$ is also a function of the impact parameter. Since the straggling is the second momentum of the energy-loss distribution, proportional to the square of the transferred energy, it is mainly determined by close collisions with electrons and, therefore, it has a more local character than the mean energy loss. Thus, for calculations at small and medium impact parameters we have used the UCA model with separate contributions of each orbital as our basic model for calculating the mean energy loss as a function of impact parameter.

The sum in Eq. (9) is approximated by the sum over orbitals $s$ with the average excitation energy $\bar{\omega}_s$ in the same way as the sum in Eq. (5).

III. RESULTS AND DISCUSSION

In this section we present the results of our calculations of the multiple-ionization cross section within the SED model and the UCA for the impact-parameter dependence of the energy loss. Figure 3(a) shows the calculated cross sections of $n$-fold ionization as a function of the number of emitted electrons $n$ for $\text{He}^{2+}$ collisions with $\text{N}_2$ molecules at an energy of 2 MeV. The $g$ factor is chosen to be $g = 0.01$, with the deposited energy calculated in UCA (full lines) and LDA (dashed lines). The cross sections are shown for two orientations of the molecular axis.

$$S^2(b) = \frac{2Z^2}{v^2b^2} \sum_s \omega_s f_s \bar{g}(\omega_bl/v).$$ (9)
FIG. 4. Anisotropy parameter $A$ as a function of the degree of ionization in collisions He$^{2+} +$N$_2$ at several projectile energies.

In order to quantitatively characterize the orientation effect we introduce the anisotropy $A$ that we define as

$$A = \frac{\sigma(\theta = 0^\circ) - \sigma(\theta = 90^\circ)}{\sigma(\theta = 0^\circ) + \sigma(\theta = 90^\circ)}.$$  \hspace{1cm} (10)

This parameter is zero if the cross sections are independent of the molecular alignment; $A \rightarrow \pm 1$ for the other extreme case where the cross section for one of the orientations is much larger than for the other one. The lower panel of Fig. 3 shows the anisotropy $A$ for the considered case as a function of the number of emitted electrons. It has a small negative value at small degrees of ionization but quickly increases to almost +1 for high degrees of ionization indicating the dominant contribution of the molecules aligned with the beam. In the same figure we compare the results of calculations with LDA and UCA for the energy loss. We see that for this high collision energy the results are very close.

In Fig. 4 we study the energy dependence of the anisotropy. The same $n$ dependence of the parameter $A$ as in Fig. 3 is calculated for several collision energies. One sees that with increasing collision energy the onset of the large orientation effect is shifted to larger $n$. Below we try to estimate qualitatively the value of $n$ at which the orientation effect may be observed.

It seems obvious that an orientation effect may exist if some effective range of impact parameters, where the considered ionization is most probable ($b_{\text{eff}}$), is of the order or less than the size of the molecule ($R_e$). Indeed, in the opposite limit $b_{\text{eff}} > R_e$ the ionization occurs at such large distances that small change of the geometry (rotation of the molecule) can hardly be noticed by the projectile. The effective distance at which the ionization of the $n$th electron occurs depends on the strength of the interaction that may be characterized by the parameter $\kappa = Z_i/v$. If $\kappa \ll 1$ the interaction is small and the perturbation theory is valid. In this case the effective range of impact parameters is limited by the so-called adiabatic radius $b_{\text{eff}} < r_{\text{rad}} = v/\Delta E$ where $\Delta E$ is the energy transfer necessary for ionization. For a certain degree of ionization, $r_{\text{ad}}$ increases with velocity and, therefore, the orientation effect should decrease (see below). To estimate $\Delta E$ we note that the $n$th ionization potential of the molecular ion can be roughly estimated by the Coulomb-like expression as $E_n = Z_i^2/2a^2$. Here we have assumed a complete screening of the nucleus by all other electrons and $a$ is some effective principal quantum number of the ionized electron. By fitting this value using the calculated ionization potentials for N$_2$ (see Table 1) we get $a = 2.5$, which does not contradict the expectation that in nitrogen the principal quantum number of the electrons is about 2. Then, to ionize $n$ electrons we need $\Delta E = \sum_{i=1}^{n} E_i = n^2/6a^2$ for large $n$. Using this estimate we get $r_{\text{ad}} = 6a^2v/\Delta E$. The orientation effects may be observed if $r_{\text{ad}} < R_e \simeq 1$. From this condition we obtain the minimal value of $n$ for which we may expect the orientation effect

$$n_{\text{min}} \approx (6a^2v/R_e)^{1/3} \approx 3.3v^{1/3}. \hspace{1cm} (11)$$

This estimate agrees with our observation (see Fig. 4): the degree of ionization at which the strong-orientation effect might be observed increases with increasing velocity. In the case of He$^{2+} +$N$_2$ collisions at $E = 100–300$ keV this estimate gives $n \approx 4$ that does not contradict the experimental observations [3].

In the other extreme case of a strong interaction ($\kappa \gg 1$) the perturbative approach is not valid but we can estimate the minimum degree of ionization using Bohr’s classical approach [22]. According to Bohr the energy transfer from the fast projectile moving at the impact parameter $b$ with respect to an electron at rest is $\Delta E = 2Z_i^2v^2 b^2 = 2\kappa^2b^2$. This energy transfer should be compared with the ionization potential of the $n$th electron. From this we get the constraint for the impact parameter $b_{\text{eff}} \leq \kappa \sqrt{2E_i} = 2\kappa a/n$. As earlier, the effective range of the impact parameters should not be larger than $R_e$. From this condition we estimate the minimum value of $n$ for which the orientation effect may be observed

$$n_{\text{min}} \approx 2\kappa a/R_e \approx 5\kappa.$$  \hspace{1cm} (12)

We see that in the strong-interaction regime, an increase of interaction leads to an increase of $n_{\text{min}}$ at which the effect may be observed.

As mentioned before, the SED model contains one adjustable parameter, the $g$ factor. Up to now we have presented the results for a fixed value of this factor ($g = 0.01$). However, we know that it may be considered constant only at large velocities ($E > 0.5$ MeV/amu). At smaller velocities the $g$ factor increases with decreasing collision energy. In order to investigate the influence of the $g$ value on the anisotropy, we calculated the energy dependence of the cross sections and the anisotropy for different values of $g$. The results are shown in Fig. 5. The influence of $g$ on the anisotropy is most clearly visible at the highest degrees of ionization. Due to its definition, the $A$ parameter is not very sensitive to the $g$ factor in both limiting cases—very small or very large anisotropy. The results shown in Fig. 5 confirm that the orientation effect for a given degree of ionization slowly diminishes with increasing projectile energy, as discussed above.

In Fig. 6 we compare the anisotropy of multiple ionization for several diatomic molecules, homonuclear (N$_2$, F$_2$), heteronuclear (CO), and triatomic molecule (CO$_2$). In the latter case we ignored any bending vibrational modes and considered the molecule as linear. We compare the anisotropy for
three degrees of ionization as a function of the impact energy. All dependencies are similar, and there is no great difference between the molecules considered. This confirms the original idea that the orientation effect is a purely geometric one, and depends only weakly on the intrinsic properties of the molecule.

IV. CONCLUSIONS

We have suggested a different version of the SED model for a description of multiple ionization of molecules by fast ion impact. The deposited energy is calculated within the nonperturbative UCA. At small projectile charge and large velocity the SED-UCA model gives results close to the previously used SED-LDA model [8] where the deposited energy was calculated within the local-density approximation. The new version of the SED-UCA model has the advantage in that it can be used also at smaller velocities and higher projectile charges, i.e., in the strong interaction domain. Using the SED-UCA model we have investigated the orientation effect in the multiple ionization of molecules. We have found that for a given degree of ionization the effect is vanishing with increasing projectile velocity and projectile charge. In two extreme cases of weak and strong interactions we have found conditions at which the orientation effect can be observed. The calculations show that the effect is weakly sensitive to the molecular properties and, for different molecules, displays similar behavior on the projectile energy.

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