Theoretical study of multiple ionization of diatomic molecules by ion impact

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Abstract. In the present work we calculate multiple ionization cross sections, as a function of the orientation of the molecular axis with respect to the ion beam, for impact of highly charged ions on N$_2$ and O$_2$ molecules. We use different approaches to obtain the single ionization probabilities that are necessary to compute these quantities into the Independent Electron Model. The influence of the molecular orientation on differential cross sections is analyzed. An adequate description of existing data is obtained.

1. Introduction
Electron emission from atoms and molecules by impact of ions has been a matter of active research in the last decades [1–2], due to its interest in different areas like atmospheric, plasma and biological physics. In the present work we will focus our attention on multiple ionization of simple multielectronic diatomic molecules.

The recent development of new experimental facilities has allowed to obtain an almost complete mapping, in the momentum space, of the aggregates resulting from the collision [3]. Moreover, at high enough impact velocities the collision time is much smaller than the vibrational and rotational ones of the molecular target, and so it can be assumed that the spatial orientation of the molecule remains fixed during the projectile–target interaction [4]. It offers the possibility to make a detailed analysis of the emission spectra as a function of the molecular orientation.

Molecular orientation effects were studied for CO targets in collisions with multiply charged projectiles [5]. The molecule was assumed to be composed by two atoms at the equilibrium internuclear distance and the Independent Electron Model (IEM) approximation was employed [6]. Single ionization probabilities were included in the calculations of multiple ionization by considering a binomial distribution. They were determined using two different approximations: i) supposing that they have an exponential dependence on atomic impact parameters (referred to the C and O centers) and where fitting parameters were determined from experimental single ionization cross sections, or ii) using atomic classical trajectory Monte Carlo (CTMC) calculations. A good description of experimental single differential cross sections was obtained for double ionization in the case of 96 MeV/u Ar$^{14+}$ impact [7]. Further work was performed using the Statistical Energy Deposition (SED) model, where it is assumed that in a first step part of the kinetic energy of the projectile is transferred to the target electrons and in a second step they are ejected in a number proportional to the volume of the available phase space [8–9]. The model was applied to study multiple ionization of N$_2$ targets by impact of highly charged Xe ions.

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In the present work we will concentrate on the case of homonuclear N\textsubscript{2} and O\textsubscript{2} molecular targets. The main aspects of the models here employed are given in the following. The straight line version of the impact parameter approximation is employed in the calculations and atomic units are used except where otherwise stated.

2. Theory

Let us consider a molecular target with \( c = 2 \) centers, each one of them composed by \( n_c \) orbitals with \( N_{n_c} \) equivalent orbital electrons. The \textit{exclusive} probability for \( q \)-fold ionization of the target can be obtained by using the expression:

\[
P_q(\vec{b}) = \sum_{q_1,\cdots,q_n=0}^{N_1,\cdots,N_n} \prod_{j=1}^{n} \prod_{k=1}^{c} P_{kj}((\vec{b}_j))
\]

(1)

where the sub–index \( n = n_1 + n_2 \) indicates the total number of target orbitals. The probability \( P_{kj}(\vec{b}_j) \) to ionize \( q_{kj} \) electrons of the \( kj \)–orbital, is given by [10]:

\[
P_{kj}(\vec{b}_j) = \frac{N_{kj}!}{(N_{kj} - q_{kj})!} p_{kj}(\vec{b}_j) [1 - p_{kj}(\vec{b}_j)]^{N_{kj} - q_{kj}}
\]

(2)

In equations (1) and (2), \( \vec{b} \) and \( \vec{b}_j \) are the impact parameter vectors with respect to the center of mass of the molecule and to the \( j \)–molecular center, respectively, and \( p_{kj} \) the single ionization probability per electron corresponding to the \( kj \)–orbital, which will depend on the theoretical model employed.

The differential cross section for \( q \)-fold ionization, as a function of the molecular orientation polar angle \( \theta \), is obtained as:

\[
\sigma_q(\theta) = \frac{d\sigma_q}{d\theta} = 2\pi \sin \theta \int_0^{2\pi} \int_0^{\infty} P_q(\vec{b}) \, b \, db \, d\varphi
\]

(3)

In the present work, two theoretical models are employed for the calculation of \( p_{kj} \).

2.1. The CDW–EIS model

Highly charged projectiles produce strong fields that must be considered when choosing the initial and final wavefunctions. To do this, probabilities for ionization of each one of the molecular centers are calculated using the Continuum Distorted Wave–Eikonal Initial State (CDW–EIS) approximation [11–12]. Initial Roothaan–Hartree–Fock (RHF) bound orbitals [13] are distorted by a projectile continuum eikonal phase in the entry channel and Coulomb effective target continuum wavefunctions are distorted by a projectile continuum factor in the exit channel.

2.2. The exponential model (EM)

In the exponential model \( p_{kj} \) has the exponential form:

\[
p_{kj}(b_j) = P_{0kj} e^{-b_j/R_{kj}}
\]

(4)

where \( R_{kj} \) is the mean radius of the \( kj \)–atomic orbital and \( P_{0kj} \) is obtained by fitting of the single–electron total cross section per orbital electron obtained using equation (4) to the CDW–EIS cross section. The radius \( R_{kj} \) in equation (4) is selected according to a Hartree–Fock calculation [14] or by employing the prescription \( R_{eff} = n_{kj}/\sqrt{2\varepsilon_{kj}} \), with \( n_{kj} \) the orbital–principal quantum number and \( \varepsilon_{kj} \) the corresponding RHF orbital energy [13]. When probabilities \( p_{kj}(b_j) \) are larger than unity, the unitarization procedure proposed by Sidorovich and Nikolaev [15] is used.
3. Results and discussions

In figures 1 and 2, ionization differential cross sections $d\sigma_q/d\theta$ are shown for the cases of impact of 5.9 MeV/u Xe$^{18+}$ beams on N$_2$ and O$_2$, respectively. The cases of charge multiplicity $q = 6, 10$ are presented. The projectile is considered as an effective nucleus of charge $Z = 18$ in order to take into account the screening produced by the projectile electrons. Experimental results [8,16] are represented as histograms. Calculations obtained employing the CDW–EIS model and the two versions of the EM described above are shown. Sine distributions which correspond to isotropic dependence of the cross sections differential with the molecular orientation are also included. All theoretical results are normalized to the same area as the experimental histograms. The qualitative behavior corresponding to experimental and theoretical results for the cases $q = 6$ or $q = 10$ is different, both for N$_2$ and O$_2$ targets. The better description of experimental data is obtained when the CDW–EIS model is used. CDW–EIS cross sections are also in very good agreement with previous theoretical SED results [8] for the N$_2$ case. EM results are only in qualitative agreement with experiments.
Orientation effects can be explained in terms of the effective impact parameters that contribute to the multiple ionization reaction [8]. As we are dealing with highly charged projectiles, in principle, the electron emission process should be dominated by impact parameters larger than the size of the molecule (large encounter collisions). It seems to be the case for $q=6$, for which weak dependences with the molecular orientation are obtained. However, as the ionization multiplicity increases the momentum $K$ transferred by the projectile to the molecular target must also increase, so the impact parameters $b \sim 1/K$ that dominate the reaction become smaller (close collisions). For an orientation of the molecule perpendicular to the momentum of the incident particle, and for a given projectile trajectory, the number of electrons found by the projectile will be smaller than for other molecular geometries. It gives a qualitative explanation of the orientation dependence observed both theoretically and experimentally. Moreover, according to the molecular description as two-separated atoms, the anisotropy appears to be more pronounced for the $\text{N}_2$ target case.

4. Conclusions
CDW–EIS and EM models have been used in the independent electron approximation to study multiple ionization of homonuclear diatomic molecular targets by highly charged ions. The influence of the molecular orientation on differential cross sections for different ionization multiplicities is analyzed. CDW–EIS results, which include the presence of the strong projectile field in the entry and exit channels, are in very good agreement with experiments and with previous SED calculations.

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