Multiple ionization of atoms and molecules impacted by very high-q fast projectiles in the strong coupling regime ($q/v > 1$)*

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In this paper, we present a simple theoretical approach to calculate the multiple ionization of big atoms and molecules induced by very high-q fast projectiles in a strong coupling regime ($q/v > 1$). The results obtained from this approach are in excellent agreement with the available experimental data. A probable scenario of molecular multiple ionization by fast and very high-q projectiles is discussed. The very small computational time required here and the good agreement with the existing experimental data make it a good candidate for studying the multiple ionization of complex molecules under high linear energy transfers.

Keywords: multiple ionization, high-q projectiles, strong coupling regime, model calculation

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1. Introduction

Ionizations of atoms and molecules impacted by ions have attracted much attention both experimentally and theoretically.[1,2] They are fundamentally important in many scientific and technology areas, such as chemical physics, radiation damage to biological tissues, astrophysical plasmas, as well as planetary atmosphere chemical reactions.[3–5]

Theoretically, single-electron processes in many cases have been thoroughly studied. In their early calculations, Senger *et al.*[6,7] adopted the plane-wave Born approximation (PWBA), which starts with the formula for the ionization of atomic hydrogen by proton impact. Later on, Olivera *et al.*[8] used the continuum distorted wave eikonal initial state (CDW-EIS) approximation which can accurately describe the direct single ionization of small molecules by fast ions. Recently, Abbas *et al.*[9] used the eikonal-classical trajectory Monto Carlo (CTMC) method to evaluate single electron capture and the single ionization cross section of water. Most recently, Illescas *et al.*[10] improved the CTMC method with a three-center model potential to study the collisions of protons, He^{2+}, and C^{6+} with water vapor and showed acceptable agreement with existing experimental data.

For multi-electron processes, there are several approaches that are usually used to explain the experimental data. Of them, the most widely used one is the n-body CTMC method,[11] in which the ion trajectories are simulated and the initial momentum distribution of the target electron is assumed. Then, the whole system is evaluated numerically. This method provides a good description of multiple ionization. However, its application to more complex molecules is limited by the time consumed in obtaining good statistical characters. The others are the SCA model[12] and statistical energy deposition (SED) model,[13,14] which can describe the mechanism of multiple ionization in a perturbative regime, where the energy transfer obeys the perturbation law of $(q/v)^2$ by using the independent-particle method (IPM). In a strong coupling regime ($q/v > 1$), however, remarkable deviations from the first-order results have been found.[15–17] Another elaborate theory reported in recent years is the non-perturbative, quantum mechanical approach.[18,19] The calculation shows good agreement with experimental results over a wide range of energy from 20 keV to several MeV in proton–water collision. To the best of authors' knowledge, a non-parameter model for the multiple ionization of atoms and molecules induced by very high-q and fast projectiles ($q/v > 1$) is extremely scarce, where the perturbative methods are not applicable.

From a radiobiological point of view, the multiple ionizations of atoms and molecules impacted by very high-q fast projectiles are closely related to the irradiation effect of biological tissue in high linear energy transfer radiation. It is demonstrated in Cassimi *et al.*'s work[20] that the multiple ionization is expected to be much larger than those for protons and electrons, and what is more, this ionization cannot be deduced from the low-q collisions for the production of charged fragmentations which change dramatically with the increase of projectile charge q. The CDW-EIS model gives a good estimation of single ionization cross section of water, induced by Xe^{44+} beam at 6.7 MeV/u, but multiple ionization cross sections are not predicted. To describe the subsequent biophysical and chemical processes, multiple ionization fractions must be known to simulate the following physicochemical stages.

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Therefore a simple model that can obtain multiple ionization fractions of atoms and molecules impacted by high-q ions in very short time is required.

In the present work, we propose a simple model to calculate the multiple ionizations of atoms and molecules impacted by very high-q fast projectiles in a strong coupling regime. From the comparison between the results obtained from model and the experimental results, we can obtain some useful information about the multiple ionization by fast and very high-q projectiles ($q/v > 1$). Meanwhile, this simple model can provide a convenient way to estimate the multiple ionizations of a far more complex system such as bio-molecules.

The remainder of this paper is organized as follows. In Section 2, the model is presented in detail. In Section 3 our results of atoms and molecules and their comparison with the experimental data are provided. Then, the scenarios of multiple ionization of complex atoms and molecules by very high-q fast projectiles are discussed. Finally some conclusions are drawn from the present study in Section 4. Atomic units are used, unless otherwise specified.

2. Model

In our previous work,[21–24] we used the classical over barrier ionization (COBI) model to interpret the double-ionization of helium in a strong coupling regime. Now, we add an independent-event model (IEVM) and the statistical method to the single-electron probability obtained by COBI to obtain the multi-electron ionization probabilities of complex atoms and molecules.

First, we review the COBI model briefly. The COBI model is based on Bohr–Lindhard's over barrier (OB) model.[25] According to OB, an electron can be released when the Coulomb potential barrier between the projectile and the target nucleus is lower than the electron binding energy. The release distance $R_{\rm r}$, within which the release becomes possible, is given as $R_{\rm r} = Z + 2\sqrt{qZ}/I$, where Z and q are charges of target core and the projectile, and I is the electron ionization energy. If the release occurs within the capture distance of $R_{\rm c}$, which means the electron potential energy in the ionic field of the projectile is larger than its kinetic energy in the projectile frame, then capture will occur. Hence, the capture distance is $R_{\rm c} = 2q/v^2$.

If the electrons are released outside the capture distance, they will not be ionized until they obtain enough kinetic energies to escape. When the projectile approaches the distance $R_{\rm I}$, the Stark energy transferred to the kinetic energy of the released electron is larger than its ionization energy of quasi-molecular state, the ionization will occur. So, the ionization distance $R_{\rm I}$ satisfies the following inequality:

$$\frac{q}{R_{\rm I}} \geq I + \frac{q}{R_{\rm r}}. \tag{1}$$

In brief, electrons released within the capture distance $R_{\rm c}$ will be captured; the others released outside the capture distance will not be ionized until the ion enters into the ionization distance of $R_{\rm I}$. Then, one-electron release, capture and ionization probability for each impact parameter b are given as

$$P_{\rm r} = \frac{2\sqrt{R_{\rm r}^2 - b^2}}{vT}, \tag{2}$$

$$P_{\rm c} = \frac{2\sqrt{R_{\rm c}^2 - b^2}}{vT}, \tag{3}$$

$$P_{\rm I} = P_{\rm r} - P_{\rm c} = \frac{2}{vT}\left(\sqrt{R_{\rm r}^2 - b^2} - \sqrt{R_{\rm c}^2 - b^2}\right), \tag{4}$$

where v is the collision velocity, and $T = 2\pi n^3/Z^2$ is the orbital period of the target electron, n is principal quantum number. Equations (2)–(4) are the obtained single electron ionization and capture probabilities $P_{\rm I}$ and $P_{\rm c}$ for a given atomic orbit.

When we apply the above one-electron ionization probability $P_{\rm I}$ of atomic orbital to the case of molecular orbital, three approximations are adopted. The first approximation is the molecular orientation effect, which has been proved to be obvious in perturbative regime.[26] However, the existing literature[20] indicates that the orientation effect will not exceed a few percent even in the highly charged cases for the collisions in a strong coupling regime. Lekadir *et al.*[27] and Galassi *et al.*[28] also pointed out that the orientation effect is very small and exerts little influence on the collision of molecules with fast ions. We calculate the orientation effect of CO and N_2 impacted by 6.7 MeV/u Xe^{44+} ions and find that even at up to the 8-th ionization, the difference among various orientations is no more than 5%. In the present model the projectile charge is very high, the ionization distance $R_{\rm I}$ is of one to two orders of magnitude larger than the molecular dimension. Thus, atoms of the molecule can be seen as being at the origin of the coordinate. To improve the calculation efficiency and maintain the accuracy, we neglect the orientation effect of molecules.

The second approximation is that our calculation of molecular orbitals is not rigorous solution but several atomic orbitals instead. For the same reason, in the strong coupling regime the ionization distance $R_{\rm I}$ is far lager than molecular size, the fine structure of molecular electron cloud will not play an important role. In the work dealing with single ionizations of DNA and RNA bases impacted by energetic multi-charged ions,[27] the target is described neither by using Bragg's additivity rule nor by adopting the CNDO approximation, but by using the orbitals with corresponding molecular state binding energies instead.

The third approximation is that we use the method of IEVM[29–32] to extract multi-electronic ionization probabilities from single-electron probability. It has been pointed out

that the IEVM is more adequate than usual IPM, because it ignores the variation of considerable ionization potential with the charge state, which leads to wrong probabilities for the high stages of ionization.

Table 1. Calculated values of ionization energy (in eV) for CO and H_2O molecules and molecular ions for different states of ionization.

	1	2	3	4	5	6	7	8
CO	14.05	27.47	40.27	55.12	68.27	86.34	105.41	131.15
H_2O	12.71	28.70	44.08	64.55	84.21	108.91	143.61	169.26

In summary, in present work, atoms of the molecule are all located at the origin of coordinate, outshell electrons are staying at their orbitals with the ionization energy I_i and the period $T_i = \pi \cdot n/I_i$. The ionization energy I_i presented in Table 1 are obtained by employing the quantum chemical Molpro program.[33–35] Then, with the statistical method of multinomial distribution, the relevant q-fold ionization probability can be obtained as

$$P_I^{q+} = \sum_{i,j,\ldots,n} P_{Ii} P_{Ij}, \ldots, P_{In} \prod_{s \neq i,\ldots,n} (1 - P_{Is} - P_{cs}). \quad (5)$$

The cross sections are obtained by integrating the probability $P_I^{q+}(b)$ over all impact parameters as

$$\sigma^{q+} = \int_{-\infty}^{+\infty} P_I^{q+}(b) \cdot 2\pi b \mathrm{d}b. \quad (6)$$

3. Results and discussion

Figure 1 shows the calculated single-electron ionization probabilities of a CO molecule each as a function of impact parameter b. For all stages of ionization the distributions are peaked at $b = 0$ with its largest value of $0.4 \sim 0.7$ and then decrease monotonically to zero with the increase of b. Ionization distance of each MO electron is at an average of 15 a.u. (a.u. is the abbreviation for atomic unit), one order of magnitude larger than the bond length of the CO (1 a.u.). Thus it is appropriate to neglect the orientation and fine structure of the molecule orbital in our model. Moreover, it is clear that the mean value of the ionization probability is not that small, about $0.2 \sim 0.4$. Large ionization probabilities will cause the ionization energy to increase with ionization stage increasing, and then the IEVM will be appropriate.

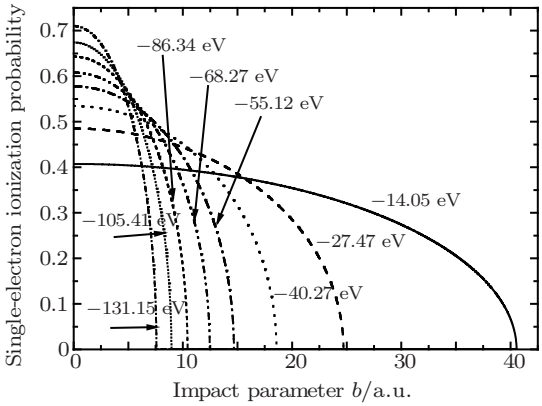


Fig. 1. Plots of single-electron ionization probability for each MO electron of CO molecule to collide with 6.7 MeV/u Xe^{44+} ions as a function of impact parameter.

3.1. Multiple ionization of atoms

In Fig. 2 we report on the calculated relative multiple ionization cross sections each as a function of projectile energy for the Cl^{12+} + Ar collisions. They are compared with the available experimental data (uncertainty is about 25%).[36] The overall agreement is excellent. Double, triple, quadruple five-fold, and six-fold ionization cross sections are about 30%, 15%, 7%, 3%, 1% of the single ionization cross section respectively. For different values of projectile energy, the ratios $R_{q1} = \sigma_q/\sigma_1$ $(q = 1, 2, \ldots, 6)$ are of the same order of magnitude. The ratios are found to decrease very slowly with projectile energy increasing.

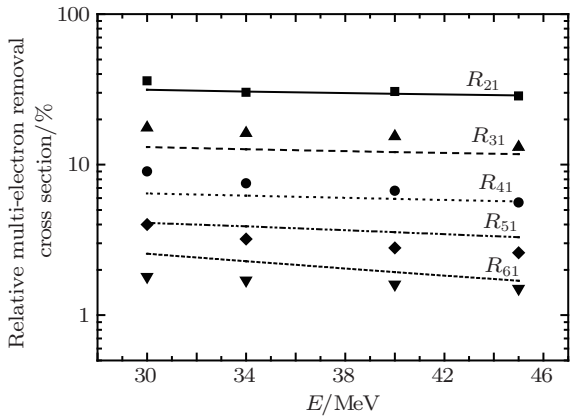


Fig. 2. Relative multiple ionization cross sections each as a function of projectile energy for Cl^{12+} + Ar. The lines represent the model results, and symbols denote the experimental data.

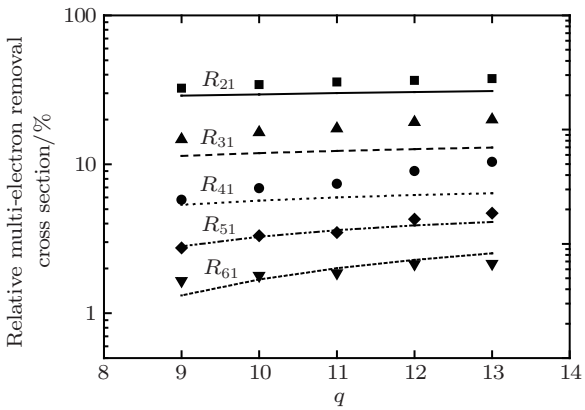


Fig. 3. Relative multiple ionization cross sections each as a function of projectile charge for 34-MeV Cl^{q+} + Ar. The lines represent the model results, and symbols denote the experimental data.

Figure 3 shows the ratios of multiple to single ionization of Ar impacted by 34-MeV Cl^{q+}, each as a function of projectile charge q. It also includes the experimental data of Ref. [36]. It is observed that the double-to-single ratios are

in excellent agreement with the experimental data. For the cases of triple and quadruple ionization, the results are underestimated. The overall agreement is still good. The ratios are found to increase slightly with projectile charge increasing.

The relative multiple ionization cross sections present a weak dependence on projectiles energy E and charge q. We can give a reasonable interpretation to the behavior. For the very high-q projectiles, the release and ionization distance both reach the same asymptotic form of

$$R_{\rm I} = \frac{1}{I}\frac{2q\sqrt{Z}}{2\sqrt{Z}+\sqrt{q}} \overset{q\gg Z}{\longrightarrow} \frac{2\sqrt{qZ}}{I} = R_{\rm r},$$

indicating that

$$P_{\rm I} = P_{\rm r} \approx \frac{2R_{\rm r}}{vT} \propto \sqrt{\frac{q}{E}}.$$

Therefore the ionization probability is determined by the single release probability. Since the single release probability is proportional to $(q/E)^{0.5}$, which is insensitive to q and E, and with the complementary role of $P_{\rm I}$ and $1-P_{\rm I}$ in the multinomial distribution, the very weak q and E dependence of multiple ionization probabilities is expected.

3.2. Multiple ionization of molecules

The calculation result of a H_2O molecule impacted by Xe^{44+} ions is presented in Fig. 4 and compared with the experimental data.[8] It is clear that except for the 8th fold case, the model gives excellent description of the molecular data. We can find that highly charged recoiled ions are copiously produced when they are impacted by fast highly charged Xe^{44+} ions. From single to 8-fold ionizations, the cross sections only drop off from 3×10^{-14} cm^2 $\sim 4\times10^{-14}$ cm^2 to 1×10^{-16} cm^2 $\sim 2\times10^{-16}$ cm^2. Even for 7- or 8-fold ionization, cross sections are still on the order of 1% of single ionization cross section. Totally, the multi-charged fractions contribute more than half of the recoiled ions.

The calculated results of CO molecules impacted respectively by 2.4-MeV/u Ar^{14+} ions[37] and 6.7-MeV/u Xe^{44+} ions[20] are compared with the experimental data in Fig. 5. In general, they are in good agreement with each other. Highly charged recoiled CO ions are copiously produced, and multi-electron removal is found to lead to about 40% of the ionizing events. Note that the slopes of the curves do not increase rapidly with the increase of the recoiled ion charge states. This is quite different from the data and the calculation results in the perturbation regime,[38] where the slope increases quickly with ionization degree increasing. Moreover, one can see that the data of $Ar^{14+}+CO$ and $Xe^{44+}+CO$ collisions do not exhibit a significant difference. The fractions of double and triple ionization cross section are some 20% and 10% respectively; for the 7th fold ionization, the relative cross section is about 1%. The result is somehow contrary to the prediction of the first-perturbative law. The important parameter in perturbative law is $(q/v)^2$, which is about 2 for 2.4-MeV/u Ar^{14+} and 7 for 6.7-MeV/u Xe^{44+}. However, if the perturbative method is valid, such a remarkable difference should show some influence on the relative multiple ionization cross section. But even for the 7th fold ionization cross sections, the difference is still minor.

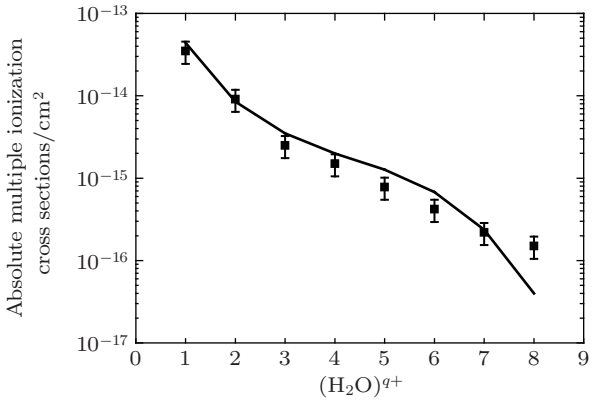


Fig. 4. Absolute multiple ionization cross sections of H_2O molecule for 6.7-MeV/u Xe^{44+} ion impact. The solid curve represents the model result, and symbols denote the experimental data.

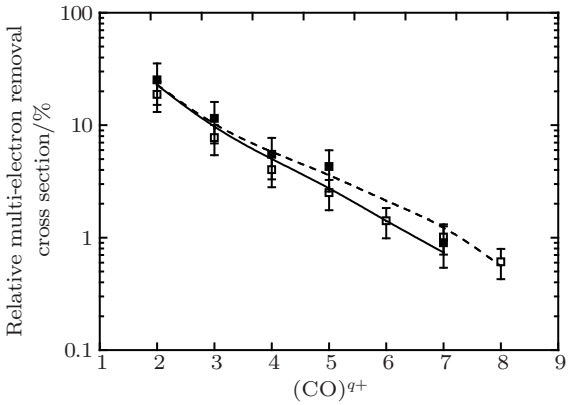


Fig. 5. Relative multiple ionization cross sections of a CO molecule for 2.4-MeV/u Ar^{14+} and 6.7-MeV/u Xe^{44+} ion impact. The lines represent the model results, symbols denote the experimental data (dashed line and open square refer to the $Xe^{44+}+CO$, solid line and solid square indicate the $Ar^{14+}+CO$).

The present model is on the assumption that single-electron release probability is an important parameter in determining the multiple ionization cross sections induced by very high-q and fast projectiles. According to Eqs. (1)–(4), the single electron release probability is proportional to $(q/E)^{0.5}$. The parameter of $(q/E)^{0.5}$ is about 0.38 for 2.4-MeV/u Ar^{14+} and 0.41 for 6.7-MeV/u Xe^{44+}; their difference is small. Furthermore, $P_{\rm r}$ and $1-P_{\rm r}$ will complement each other in the multinomial distribution. So, we can expect that the relative multiple ionization cross sections for 2.4-MeV/u Ar^{14+} and 6.7-MeV/u Xe^{44+} ions will be almost the same.

4. Conclusion

By using the IEVM and the multinomial distribution, our previous work of COBI model is extended to the descriptions

of the multiple ionizations of atoms and molecules induced by very high-q fast projectiles ($q/v > 1$). The available experimental data of atoms and molecules are in excellent agreement with model results. The measurement and model both show that the relative multiple ionization cross sections present a rather weak dependence on q and E. The model assumes that multiple ionization is directly proportional to the single electron release probability $P_r \propto \sqrt{q/E}$, which is insensitive to q and E, with the complementary effect of P_r and $1-P_r$ in multinomial distribution, the relative multiple ionization cross sections will show weak dependence on q and E. Furthermore, systems which have the same parameter of $(q/E)^{0.5}$ almost have the same relative multiple ionization cross sections. This is also proved by the experimental data.

In summary, multiple ionizations of atoms and molecules impacted by very high-q fast projectiles ($q/v > 1$) probably can be seen as sequential release processes occurring at large distances rather than violent binary encounters between projectile and target electrons.

Finally, the main advantage of our model is its simplicity in obtaining the multiple ionization fractions of complex molecules induced by very high-q fast projectiles ($q/v > 1$), providing a convenient way to study the high linear energy transfer (LET) irradiation of biological matter when a rapid computation is required as happens in radiobiology.

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