Multi-charged ion-water molecule collisions in a classical-trajectory time-dependent mean-field theory

Alba Jorge, Marko Horbatsch, and Tom Kirchner

Department of Physics and Astronomy, York University, Toronto, Ontario, M3J 1P3, Canada

Abstract

A recently proposed classical-trajectory dynamical screening model for the description of multiple ionization and capture during ion-water molecule collisions is extended to incorporate dynamical screening on both the multi-center target potential and the projectile ion. Comparison with available experimental data for He$^{2+}$ + H$_2$O collisions at intermediate energies (10-150 keV/u) and Li$^{3+}$ + H$_2$O at higher energies (100-850 keV/u) demonstrates the importance of both screening mechanisms. The question of how to deal with the repartitioning of the capture flux into allowed capture channels is addressed. The model also provides insights for data on highly charged projectile ions (C$^{6+}$, O$^{8+}$, Si$^{13+}$) in the MeV/u range where the question of saturation effects in net ionization was raised in the literature.
I. INTRODUCTION

The use and investigation of hadron therapy for the treatment of cancer is a promising field in current biomedical research [1–3]. Even though the use of beams of heavy charged particles to attack the DNA of cancer cells has been known for many years, in the last decade more investigations have been carried out [1]; since 2010 many operational facilities have been opened, eight of them in 2019 [5].

The beams of ions interact with matter in a different way than electromagnetic waves, in the sense that the ions deposit the major part of their energy in the Bragg peak, i.e., at the end of the path they follow, which implies that the energy deposition zone can be adjusted by varying the projectile velocity and charge. Given the amount of water in the human body, the most likely event that occurs is the collision of the ion with a water molecule, which gives rise to different electronic processes such as the ejection of electrons, followed by further ionization or excitation processes [6]. Different mechanisms after the collision can cause DNA damage, such as the creation of secondary electrons and ions, of free radicals or the heating of the medium due to target excitation [7].

The whole picture has to be considered, taking into account the effect of secondary electrons or radicals on the DNA damage [8]. This requires an accurate understanding of the microscopic events, namely the time evolution of the involved ions leading to DNA damage [9]. This implies the need for atomic data such as differential and total cross sections which can then be incorporated in simulation codes [10].

This is the reason why considerable attention is given to the study of collisions of different ions with biomolecules, and to water molecules in the vapor phase for which comparison of experiment and theory is feasible. The main purpose is to obtain a proper atomic database [11] which contains information about a number of electronic processes, such as the fragmentation of the water molecule [12–16], for different projectile ions and impact energies.

Regarding the direct study of basic ion-molecule electronic processes, we find a variety of works dedicated to proton collisions in the literature, both experimentally [17–23] and theoretically [24–28]. This is due to the fact that hadron therapy has been applied mostly with proton beams; however, it is being investigated if the use of other species which could have better physical and radiobiological properties, such as helium (alpha particles), bare carbon or oxygen ions [29], will provide other options. The study of collisions with such ions
is more scarce but it is being developed lately for both low-charge \cite{30,32} and high-charge projectiles \cite{33,37}. The collisions of ions with biomolecules are being investigated as well \cite{38,40}.

In this paper we focus on the multi-electronic processes for ion-water molecule collisions for a variety of projectiles of interest, ranging from the proton to highly charged ions such as Ne$^{10+}$ or Si$^{13+}$. We are interested in analyzing the importance of the many-electron aspect of the water molecule using two lines of attack. In the first one, we look at the importance of the target and projectile potential changes due to the electron removal during the dynamics, by implementing time-dependent mean-field potentials. In the second one, we analyze the repartitioning of the density of removed electrons into the different multi-electronic probabilities, which is usually made through the independent particle model, i.e., trinomial analysis. The trinomial analysis can be problematic, however: the water molecule has three weakly bound molecular orbitals occupied by six electrons. For low-charge projectiles (protons, He$^{2+}$, Li$^{3+}$) the trinomial analysis leads to sizeable transfer probabilities for electron multiplicities that cannot be accommodated on the projectile. Therefore, we also offer an alternative analysis which does not suffer from this problem. Comparison with measurements is performed to interpret the obtained data.

We thus look at low-charge projectiles at intermediate energies, where capture and ionization compete and the effect of dynamical screening on the two centers and the repartitioning approaches are of importance. The goal is a quantitative comparison with available experimental cross sections for many channels.

The saturation problem represents a hypothesis suggested in \cite{41} in order to explain the scaling behavior of the net ionization cross sections for high projectile charges and high impact energies. We also address this problem using the obtained data for both low and highly charged projectiles.

This paper is organized as follows; in Section \ref{sec:II} we explain how we have implemented the time-dependent screening in the classical trajectory method, and the new alternative analysis; Section \ref{sec:III} is dedicated to results and analysis and the paper ends with conclusions and comments in Section \ref{sec:IV}.

Atomic units ($\hbar = m_e = q_e = 4\pi\varepsilon_0 = 1$) are used throughout unless otherwise stated.
II. THEORETICAL METHOD

This work has been implemented using the Classical Trajectory Monte Carlo (CTMC) method [42], where the quantum description of the electron dynamics is approximated by a classical statistical ensemble. The initial condition for this statistical model is a microcanonical distribution $\rho_M = \delta(\frac{p^2}{2} + V_{mod} - E_{MO})$, which is built for each of the molecular orbitals (MOs) in the water molecule. The orbital energies $E_{MO}$ for each of the MOs are chosen as $E_{1b_1} = -0.5187$ a.u., $E_{3a_1} = -0.5772$ a.u., $E_{1b_2} = -0.7363$ a.u., $E_{2a_1} = -1.194$ a.u., $E_{1a_1} = -20.25$ a.u., and every initial ensemble contains $5 \cdot 10^5$ trajectories. The potential $V_{mod}$ for the water ion $\text{H}_2\text{O}^+$ has a multi-center form [24, 43] to account for the two hydrogen and the oxygen atoms assumed to remain in the ground-state geometric arrangement. This potential takes the form:

$$V_{mod} = V_O(r_O) + V_H(r_{H_1}) + V_H(r_{H_2})$$ (1)

$$V_O(r_O) = -\frac{8 - N_O}{r_O} - \frac{N_O}{r_O} (1 + \alpha_O r_O) \exp(-2\alpha_O r_O)$$

$$V_H(r_{H_1}) = -\frac{1 - N_H}{r_H} - \frac{N_H}{r_H} (1 + \alpha_H r_H) \exp(-2\alpha_H r_H)$$ (2)

where $\alpha_O = 1.602$, $\alpha_H = 0.6170$. The parameters $r_O$ and $r_H$ represent the distances from the electron to the oxygen nucleus and the two protons, respectively. The O-H bond lengths are fixed at 1.8 a.u., and the angle between the position vectors for the protons is given as 105 degrees. $N_O = 7.185$ and $N_H = (9 - N_O)/2$ are the screening charges for each of the centers. For each collision event we perform a rotation of the molecule with randomly distributed Euler angles to take into account the possible orientations for the target molecule. For the impact energies we deal with, we can assume that the projectile follows a rectilinear trajectory and the rotational and vibrational degrees of freedom for the $\text{H}_2\text{O}$ molecule are frozen. The collision dynamics is calculated with Hamilton’s equations, and is terminated when the distance between target and projectile gets to 500 a.u.. When the collision dynamics is finished, the mono-electronic probabilities for each MO $j$ are calculated as $p_j^i = n_j^i / n_{j,\text{Tot}}$, where $i$ stands for ionization and electron capture, $n_{j,\text{Tot}}$ is the total number of initial trajectories, $5 \cdot 10^5$ as commented above, and $n_j^i$ is the number of trajectories which end the collision in each inelastic process, calculated with the energy criterion.
A. Target and projectile dynamical response

We study the influence of the dynamical response to the ionization and capture processes in the target and projectile potentials. In ion-atom collisions the response to the electron removal has been investigated (for the target and for the projectile) within an independent particle framework using a time-dependent mean field. In this work we implement such ideas through the use of time-dependent target and projectile potential parameters (such as the screening charge) which depend on the net probabilities for electron removal (target potential) and electron capture (projectile potential).

Many of the theoretical details have already been presented in where dynamical target response was included. The time-evolution is monitored in small time-steps ($\Delta t = 0.05$ a.u.) in the region where the collision happens ($t = -10...20$ a.u., where $t = 0$ a.u. corresponds to the closest approach between the target and the projectile), so that the time-dependent target and projectile potentials are updated on a fine time grid. In the case of the target, the time-dependent screening has been evaluated in the same way as in , i.e., by making the parameters $N_O = N_O(t)$ and $N_H = N_H(t)$ dependent on the net electron removal probability $P_{\text{Removal}}^{\text{Net}}(t)$ from the target. In order to do so, we rename the values $N_O$ and $N_H$ from Eq. (2) as $N_O^c$ and $N_H^c$:

$$N_O(P_{\text{Removal}}^{\text{Net}}) = \begin{cases} N_O^c & P_{\text{Removal}}^{\text{Net}} \leq 1 \\ a \cdot 8(1 - 0.1P_{\text{Removal}}^{\text{Net}}) & 1 < P_{\text{Removal}}^{\text{Net}} \leq 10 \end{cases}$$

$$N_H(P_{\text{Removal}}^{\text{Net}}) = \begin{cases} N_H^c & P_{\text{Removal}}^{\text{Net}} \leq 1 \\ b \cdot (1 - 0.1P_{\text{Removal}}^{\text{Net}}) & 1 < P_{\text{Removal}}^{\text{Net}} \leq 10 \end{cases}$$

where the factors $a = 7.185/7.2$, $b = 0.9075/0.9$ are used to make the piecewise functions continuous.

Regarding the projectile, which enters the collision as a fully stripped ion $A^{Z_p+}$, we have implemented a potential that models each of the ionic states $A^{q+}$ (with $q < Z_p$), using the form [49]:

$$V(r,t) = -\frac{1}{r} \left[ \frac{N(t)}{1 + H(t)(e^{\sigma/d(t)} - 1)} + Z_p - N(t) \right]$$

This potential was proposed in order to deal with neutral atoms and dressed ions, and the parameters $N$, $d$ and $H$, which determine the ionic state of the projectile, are obtained by
Figure 1. Values of $N$, the screening charge of the projectile potential, for the lithium (black circles), carbon (red squares) and neon (green stars) projectiles from [49] as a function of the net capture probability [Eq. (6)].

a modified Hartree-Fock approach. In our calculations, these parameters change according to the net capture probability $P_{\text{Net}}^{\text{Cap}}$ during the collision and therefore become functions of time during the collision. The screening charge parameter $N$ is determined according to:

$$N(P_{\text{Net}}^{\text{Cap}}) = \begin{cases} 
0 & \text{If } P_{\text{Net}}^{\text{Cap}} \leq 1 \\
2(P_{\text{Net}}^{\text{Cap}} - 1) & \text{If } 1 < P_{\text{Net}}^{\text{Cap}} \leq 2 \\
P_{\text{Net}}^{\text{Cap}} & \text{If } 2 < P_{\text{Net}}^{\text{Cap}} \leq Z_p \\
Z_p & \text{If } P_{\text{Net}}^{\text{Cap}} > Z_p
\end{cases}$$

(6)

In Fig. 1 the parametric dependence of $N$ is plotted versus the net capture probability in accord with Eq. (6). As can be seen, we only consider $N$ to go up to $N = Z_p$, which corresponds to the anion with charge -1 when the active electron is captured. Thus, the collision starts with the Coulomb potentials for the fully-stripped ions, a potential which is maintained until the net capture probability $P_{\text{Net}}^{\text{Cap}} = 2 \sum_{j=1}^{5} P_{j}^{\text{Cap}}$ (which ranges from 0 to 10 given the five MOs with 2 electrons each) reaches the value of 1; up to this point the screening charge is 0. From this point, the screening charge starts growing according to two linear functions which describe its dependence on the net capture probability [see Eq. (6)]. In the first range, $1 < P_{\text{Net}}^{\text{Cap}} \leq 2$ the function is built so that for $P_{\text{Net}}^{\text{Cap}} = 2$ we have $N(P_{\text{Net}}^{\text{Cap}}) = 2$. This choice ensures consistency with the previously implemented model for the target. For $P_{\text{Net}}^{\text{Cap}} > 2$ we model the screening charge directly by $P_{\text{Net}}^{\text{Cap}}$, until it reaches the value of the charge $Z_p$ of the considered ion.

The values of $d_i$ and $H_i$ for the different ionic states, $i = Z_p - 1, ..., 0$, can be found in [49]. In the case of these parameters we have implemented piecewise functions as well, using
the values for each ionic state from Table 1 in [49] and interpolating between the integer values.

B. Multinomial analysis for multiple capture evaluation

We use the nomenclature $P_{kl}$, where the integer values $k$ and $l$ stand for the number of captured and ionized electrons, respectively. The impact-parameter dependent probabilities for charge-state correlated channels are computed as in [31],

$$P_{kl} = \sum_{k_1, \ldots, k_5 = 0}^{M_1, \ldots, M_5} \sum_{l_1, \ldots, l_5 = 0}^{M_1, \ldots, M_5} \delta_{k_1, \ldots, k_5} \delta_{l_1, \ldots, l_5} \prod_{i=1}^{5} \left( \begin{array}{c} M_i \\ k_i \\ \end{array} \right) \left( \begin{array}{c} M_i \\ l_i \\ \end{array} \right) \left( \begin{array}{c} k_i \\ k_i + l_i \\ \end{array} \right) \left( p_{\text{cap}}^i \right)^{k_i} \left( p_{\text{ion}}^i \right)^{l_i} \left( 1 - p_{\text{cap}}^i - p_{\text{ion}}^i \right)^{M_i - k_i - l_i} \tag{7}$$

where $\delta_{k,\alpha}$ is the Kronecker delta symbol and $M_1 = M_2 = \ldots = M_5 = 2$ refer to the number of electrons in each MO. Using this nomenclature, we define the single capture probability $P_{\text{Cap}}^1$ and the double capture probability $P_{\text{Cap}}^2$ as:

$$P_{\text{Cap}}^j = \sum_{i=0}^{10-j} P_{ji} \tag{8}$$

The net capture probability can also be defined as

$$P_{\text{Net}}^\text{Cap} = \sum_{j=1}^{10} j \cdot P_{\text{Cap}}^j \tag{9}$$

Equation (7) represents the standard independent electron model (IEM) within which cross sections for multiple processes are computed. As pointed out previously [45, 46], the IEM using the trinomial analysis works well for electron removal of up to about $Z_p$ electrons, with an overestimation of high-multiplicity events. Another problem is that trinomial statistics distributes $N_t$ target electrons over three regions of space: target, projectile and continuum. However, the projectile can only accomodate $Z_p$ electrons (if the creation of a negative ion is considered an anomaly in the sense that it represents a correlated state). Following the work in [25] we construct an alternative system for computing the multi-electronic probabilities, under which the $k$–fold capture with simultaneous $l$–fold ionization processes become:

$$P'_{kl} = \binom{Z_p}{k} p_t^k (1 - p_t)^{Z_p-k} \quad (k \leq Z_p) \tag{10}$$
\( p_l = \frac{1}{Z_p} \sum_{k=1}^{10-l} kP_{kl} \) \hspace{1cm} (11)

where \( p_l \) is a single-particle capture probability while \( l \) electrons are being ionized. Equations (10) and (11) establish that

\[
\sum_{k=1}^{10-l} kP_{kl} = Z_p \sum_{k=1}^{10} kP'_{kl} .
\] (12)

In the case of proton projectiles the single capture probability becomes

\[ P'_{1\text{Cap}} = \sum_{i=0}^{9} P'_{1i} = P'_{10} + P'_{11} + ... + P'_{19} \]

\[ = [P_{10} + 2P_{20} + 3P_{30} + ... + 10P_{10,0}] + [P_{11} + 2P_{21} + ... + 9P_{91}] + ... + [P_{19}] \]

\[ = (P_{10} + P_{11} + ... + P_{19}) + 2(P_{20} + P_{21} + ... + P_{28}) + 3(P_{30} + ... + P_{37}) + ... + 10(P_{10,0}) \]

\[ = P_{1\text{Cap}}^\prime + 2P_{2\text{Cap}}^\prime + 3P_{3\text{Cap}}^\prime + ... + 10P_{10\text{Cap}}^\prime = P_{\text{Net}}^\prime . \] (13)

For the proton case \( P_{2\text{Cap}}^\prime \) is assumed to be zero and the main problem within the IEM, which can give a rather large probability for \( \text{H}^- \) production, and even non-zero probabilities for more highly charged anions, is removed. The transfer ionization probability \( P_{T1}' \), defined as the probability of one electron removal accompanied by multiple ionization, is given by

\[ P_{T1}' = \sum_{i=1}^{9} P_{1i}' = [P_{11} + 2P_{21} + ... + 9P_{91}] + [P_{12} + 2P_{22} + ... + P_{82}] + ... + [P_{19}] \]

\[ = (P_{11} + P_{12} + ... + P_{19}) + 2(P_{21} + P_{22} + ... + P_{28}) + ... + 9(P_{91}) \]

\[ = (P_{1\text{Cap}}^\prime - P_{10}) + 2(P_{2\text{Cap}}^\prime - P_{20}) + ... + 9(P_{9\text{Cap}}^\prime - P_{90}) \] (14)

\[ = P_{\text{Net}}^\prime - i \sum_{i=1}^{10} P_{i0} . \]

In the case of higher-charge projectiles the equations are less straightforward, but can be calculated using the different terms of Eq. (7). In the following section we will analyze the multiple capture results not only in terms of the importance of limiting the electron removal flux by the time-dependent screening during the dynamics, but also as a function of the multi-electronic repartitioning based on Eqs. (10) and (11). We will label the cross sections computed with the usual IEM as \( \sigma \) and those computed with this alternative repartitioning approach as \( \sigma' \).

The cross sections \( \sigma_i = 2\pi \int_0^\infty bP_i db \) follow after integration over impact parameter \( b \).
III. RESULTS AND ANALYSIS

We have performed calculations for the collisions of different projectiles with the water molecule, namely H$^+$, He$^{2+}$, Li$^{3+}$, C$^{6+}$, O$^{8+}$, Ne$^{10+}$ and Si$^{13+}$. We focus on the lower charge-state projectiles to analyze the effects of time-dependent screening. We also study the repartitioning of the capture flux for these systems. The data concerning the highly-charged projectiles is used to shed light on the problem of the saturation behavior of net ionization, which has been posed in [41].

We discuss first the effect of including time-dependent potentials on both the target and the projectile, so that during the dynamics the change of potential parameters is taken into account. In order to compare and evaluate the importance of the screening mechanism, we include calculations with purely static potentials (no dynamical screening), and also the case where only the target response is considered.

We start by comparing our calculations to available measurements for proton-water collisions. In Fig. 2, we show a comparison of total single-electron capture (SC) for this system, as well as for the pure single capture process. We have included two panels for each process so that we can compare the trinomial (standard IEM) and the alternative repartitioning approach for the calculation of multiple processes.

As shown in Eq. (13), the alternative repartitioned version for the single capture cross section simply becomes the net cross section. Therefore, a direct comparison between the two upper panels shows that there are non-negligible differences between the multinomial single capture and the net capture cross section, which imply an important amount of multiple capture to the proton, a known problem within the binomial (or trinomial) IEM. The dynamical screening (in the two approaches) applied during the collision does have an important effect: it is reducing the net capture probability by around 30% at 20 keV with respect to the non-dynamical screening version, but only for the lowest impact parameters, and therefore its effect gets partially diminished when computing the cross section. Still, the results computed with time-dependent potentials do improve the accuracy for low impact energies. Negligible differences are found between the two dynamical screening approaches in the capture process, since the reduction of the target screening charge due to the net electron removal has the effect of lowering the net capture probability to values below one in almost all the cases, and therefore Eq. (6) is never applied. Only for the lowest considered
Figure 2. In the upper panels, the single capture cross section is shown; in the lower panels, we display the cross section for one-electron capture without ionization (i.e., pure single capture), for the collision $\text{H}^+ + \text{H}_2\text{O}$. On the left, calculated within the trinomial analysis, on the right with the alternative repartitioning analysis. Target and projectile dynamical screening (full black line), target dynamical screening (dotted red line), and purely static potential (dashed green line). Experiments, SC: black triangles [17], brown inverted triangles [21]; violet circles [20]. Net capture: orange squares [18]. $\sigma_{10}$: black circles [21]; green squares [20].

impact velocity and only for small impact parameters do we find a region where $P_{\text{Net}}^{\text{Cap}}$ is slightly higher than one when the dynamical screening is applied only on the target, but this region is sufficiently small so that no visible differences can be found between the capture cross sections computed with the two response approaches.

As can be seen in the lower panels of Fig. 2, the effect of repartitioning the one-electron probabilities within the alternative approach for $\sigma_{10}$ does have a negative impact, especially at the lowest energies. As mentioned above, for a process involving electron removal of up to $Z_p$ electrons the IEM should work properly.

By using the measurements for the single capture as well as the $\sigma_{10}$, we can compute ‘experimental’ values for transfer ionization from the measurements in Fig. 2 as $\sigma_{\text{TI}} = \sigma_{10}^{\text{Cap}} -$
σ_{10}. To do so, we create a joint set of data from the different single-capture measurements, and then create a spline function from the σ_{10} sets of points to the single capture data; then we can subtract the two quantities. In Fig. 3 we plot both the IEM and the alternative approach results (as in Eq. (14)) for the transfer ionization process. The improvement with the alternative repartitioning analysis in this case is especially obvious, showing again the underestimation of the single capture cross section in the trinomial analysis, since \( \sigma_{\text{Cap}}^1 = \sigma_{10} + \sigma_{\text{TI}} \), as given previously in Fig. 2.

We focus now on the comparison of results for He^{2+} and Li^{3+} projectiles. In Figs. 4 and 5 we plot the single and double electron capture cross sections, including measurements from [31, 50] and the three sets of CTMC data, computed with the multinomial and alternative analysis models. In the He^{2+} system (Fig. 4), under the IEM trinomial analysis, the inclusion of dynamical screening on the projectile is appreciable and it indeed improves the comparison with the measurements in the region of low impact energy. The total effect of the inclusion of the time-dependent potentials for both target and projectile (relative to including it only in the target) in this region is the increase of the single electron capture cross section and simultaneous decrease of the double capture cross section. When applying the alternative analysis, we find the opposite behavior in the sense that the single capture cross section offers an inferior comparison than for double capture. It is worth noting, however, how the inclusion of dynamical screening is even more noticeable.

For the Li^{3+} case (Fig. 5), the differences between the two time-dependent screening approaches and the purely static potential are negligible for the energies considered, while using the IEM analysis, for the single and double electron capture cross sections. The measurements for this projectile start at an impact energy of 100 keV/u, a region where ionization and capture do not compete anymore and capture is of much less importance compared to the region of experimental values for the He^{2+} projectiles. Within the alternative analysis small differences can be found for the double capture cross section.

Even though we find very similar results for the single capture cross section with and without dynamical screening, the situation does not hold for the σ_{1j} cross sections, as shown in Fig. 6. When no dynamical screening is applied the σ_{10} and σ_{11} are heavily underestimated especially when compared with the good agreement shown by the response data. Therefore, the no-response data predicts higher values of σ_{1j}, with \( j > 2 \), which were not detected in the experiment [31] and are not included in Fig. 6. This applies to both the IEM (trinomial)
Figure 3. Transfer ionization cross sections obtained from subtraction ($\sigma_{TI} = \sigma_{1}^{\text{Cap}} - \sigma_{10}$) using the measurements for single capture [17, 18, 20, 21] and for $\sigma_{10}$ [20, 21], for the collision H$^+$ + H$_2$O. Theory: in the upper panel, the transfer ionization cross section obtained within the IEM ($\sigma_{TI} = \sum_{i=1}^{9} \sigma_{1i}$), in the lower panel computed as in Eq. (14). Target and projectile dynamical screening (full black line), target dynamical screening (dotted red line), and purely static potential (dashed green line).

and the alternative repartitioning model.

With respect to the capture of two electrons, there is an important improvement when computed with the alternative approach, as can be seen in Fig. 5. This better comparison comes from a decrease of the capture flux for this process, which implies also a decrease of the $\sigma_{2j}$ cross sections, as shown in Fig. 6. In this case we find a better comparison with the IEM analysis for the $\sigma_{20}$ process and with the alternative approach for the $\sigma_{21}$ one. It is
Figure 4. Single and double capture cross section for the collisions of He$^{2+}$ with the water molecule are shown in the upper and lower panels, respectively. On the left, calculated within the IEM (trinomial analysis), on the right with the alternative repartitioning analysis. Present calculations: target and projectile dynamical screening (full black line), target dynamical screening (dotted red line), and purely static potential (dashed green line). Measurements: (black bullets with error bars) Ref. [50].

It is worth noting that the most important term for the double capture cross section is the $\sigma_{21}$ one and not the $\sigma_{20}$ term.

We focus now on the ionization process, and therefore the alternative analysis is no longer considered and all the results refer to the IEM trinomial analysis.

If we look at the pure ionization cross sections $\sigma_{01}$ and $\sigma_{02}$ in Fig. 7 the comparison with the CTMC data is poor as expected. The effects of the supression of the high impact parameter probability for ionization, corresponding to low-energy electron emission, as well as its overestimation for very low impact parameters becomes particularly apparent in this case, where no capture channels are considered.

In Fig. 8 we show, for the different projectiles considered here, the percentage contribution of $\sigma_a$ to the total net electron removal cross section $\sigma_{\text{Removal}}$, where we define
Figure 5. Single and double capture cross section for collisions of Li$^{3+}$ with the water molecule are shown in the upper and lower panels, respectively. On the left, calculated within the IEM (trinomial analysis), on the right with the alternative repartitioning analysis. Present calculations: target and projectile dynamical screening (full black line), target dynamical screening (dotted red line), and purely static potential (dashed green line). Measurements: (black bullets with error bars) Ref. [31].

\[ \sigma_a = \sum_{i=1}^{3} i \cdot (\sigma_i^{\text{Cap}} + \sigma_i^{\text{Ion}}) \] and \[ \sigma_{\text{Removal}} = \sum_{i=1}^{10} i \cdot (\sigma_i^{\text{Cap}} + \sigma_i^{\text{Ion}}) \]. The idea behind this presentation is to show where the high-order multi-electron processes (as predicted by theory) are of importance. A minimum in the ratio $\sigma_a / \sigma_{\text{Removal}}$ should be interpreted as an energy zone where the high-multiplicity terms for the electron removal process are of higher importance.

From Fig. [8] it can be seen that the ranges where the multiple ionization and capture processes count the most do not scale simply with $Z_p/v_p$, and for each projectile charge this zone changes. However, we do observe a common trend for all projectiles when $Z_p/v_p$ increases from zero. All curves display a first minimum, located at different $Z_p/v_p$ values depending on the projectile charge $Z_p$. For small $Z_p$ the minimum occurs for $Z_p/v_p < 1$, but for $Z_p = 10$ it moves to $Z_p/v_p \sim 2$. To the right of this first minimum, we find a local
Figure 6. One- and two-electron capture accompanied by 0 and 1 electron-ionization in the collision of Li$^{3+}$ with the water molecule. On the left, calculated within the IEM (trinomial analysis), on the right with the alternative repartitioning analysis. Present calculations: target and projectile dynamical screening (full black line), target dynamical screening (dotted red line), and purely static potential (dashed green line). Measurements: (black bullets with error bars) Ref. [31].

maximum which is then followed by a decrease. In the zone of small $Z_p/v_p$, where all the curves tend to 100% we approach the perturbative regime. With respect to the stationary points, the minimum is related to the zone where the ionization is the dominant process and multiple ionization processes are of highest importance for the total net ionization cross section. For higher values of $Z_p/v_p$ than those shown in Fig. 8 the decreasing trend of the curves is related to the same effect happening for the capture process, a region where ionization is negligible and the high multiple capture terms are of more importance. Quantum mechanical calculations are required in this zone. The local maximum point is related to the regime where capture and ionization processes compete.

Including time-dependent potentials which account for the ionization and capture pro-
Figure 7. Pure single and double ionization cross sections for the collision of Li$^{3+}$ with water molecules. Present calculations: target and projectile dynamical screening (full black line), target dynamical screening (dotted red line), and purely static potential (dashed green line). Measurements: (black bullets with error bars) Ref. [31].

Processes during the dynamics substantially decreases the importance of the highest multi-electronic terms to the net electron removal probabilities, and therefore makes them more consistent with experimental observations.

Having identified the regions where the high-multiplicity terms for the electron removal process are of importance, we look now at the available experimental data for the net ionization cross section. We plot the available measurements in Fig. 9 where the $x-$axis again corresponds to the Sommerfeld parameter $Z_p/v_p$. In the region $Z_p/v_p \lesssim 1$ the saturation behavior should set in. The comparison of the results with and without dynamical screening shows that the net ionization cross section does not change by great amounts (typically a reduction by 30% is observed). This seems reasonable for a global quantity which depends on the geometric distribution of the overall electron density. The comparison with experiments in panel (c) shows the importance of theoretical data to assess the experimental results. As explained above the CTMC net ionization cross sections with dynamical screening are
Figure 8. Percentage of $\sum_{i=1}^{3} i \cdot (\sigma_{i}^{\text{Cap}} + \sigma_{i}^{\text{Ion}})$ with respect to $\sum_{i=1}^{10} i \cdot (\sigma_{i}^{\text{Cap}} + \sigma_{i}^{\text{Ion}})$ in the case of purely static potentials (a), only target response (b) and both target and projectile response (c), as a function of the Sommerfeld parameter, $Z_{p}/v_{p}$ with $v_{p}$ in atomic units. The systems shown are He$^{2+}$ (——), Li$^{3+}$ (−−−), C$^{6+}$ (−·−) and Ne$^{10+}$ (−−−).

expected to approach the correct result from below since the model misses out on low-energy electrons in distant collisions. The Li$^{3+}$ + H$_{2}$O experimental data do not follow the expected trend as a function of $Z_{p}$, i.e., they are too close to the He$^{2+}$ data.

As was shown in Fig 5 of [48], in the singly differential cross sections as a function of the emission angle for the system Si$^{13+}$ ($Z_{p}/v_{p} = 1.027$ a.u.), the high $q$-fold contributions are those which exhibit a more pronounced peak, while the single ionization term shows a more decreasing shape. According to the differential measurements for the O$^{8+}$ projectile from [35, 41] it seems that for increasing values of $Z_{p}/v_{p}$ the ratio between the forward and the middle emission angles decreases, which can also be seen as a less pronounced peak with increasing $Z_{p}/v_{p}$. Therefore, experimentally for increasing values of $Z_{p}/v_{p}$ the high $q$-fold terms lose importance.

The theoretical prediction under the IEM is that the high-multiplicity terms for the ionization process get to be increasingly more important when $Z_{p}/v_{p}$ increases, at least
Figure 9. In panel (a) the available measurements for the net ionization cross section as a function of the Sommerfeld parameter are shown for the following projectiles: H$^+$ (black, [20, 21, 52]), He$^{2+}$ (red, [53]), Li$^{3+}$ (green, [31]), C$^{6+}$, (dark blue, [36, 54]), O$^{8+}$ (light blue, [35, 41]) and Si$^{13+}$ (orange, [36]). The dashed lines connect the points to guide the eye. In panel (b), the equivalent data are given for CTMC results calculated with purely static potentials (dotted line) and both target and projectile response (full line). In panel (c), comparison of the CTMC data results with response is provided with experimental data for which at least three values of $Z_p/v_p$ are known.

up to the point where for each projectile a minimum is reached in Fig. 8. This is due to the repartitioning of the ionized flux within this model, but it still is representative of the collision itself, since the multiple electron ionization comes mainly from small impact parameters. In the case of the measurements what is shown is that for values of $Z_p/v_p \to 1$ the single ionization term is the one which increases in importance. This could be the
reason for the saturation behavior even though, as we have already commented before, it is not directly related to $Z_p/v_p \to 1$ but approaching the first minimum as in Fig. 8. It would be of great interest to have differential measurements for a medium-high charge projectile at both the impact energy where this minimum is reached and somewhere close to it, so that this idea could be confirmed.

IV. CONCLUSIONS

We have implemented a method to take into account dynamical response effects in both the target and projectile potentials in the CTMC description of collisions of different ions with the water molecule. Calculations were carried out over a range of projectile charges $1 \leq Z_p \leq 13$ covering the range of medium to large energies where the CTMC description is deemed reasonable, in order to study their influence on a quantitative level, for specific cross sections, and also to analyze their effect on the general description of multiple ionization.

The target and projectile dynamical response has been shown to yield improvements in the description of electron capture. This shows that it is important to take into account the multiple electronic processes not only through multinomial analysis, but also through the dynamics itself, for systems where a large number of electrons participate. This happens to be the case for $\text{H}_2\text{O}$, as well as for molecules of biological interest, such as DNA and RNA nucleobases.

We have also considered two ways of analyzing the partitioning of the captured flux into the different capture channels, namely the standard IEM trinomial analysis and what we have named the alternative approach, which re-interprets the captured electron probability for a given number of ionized electrons such that only capture of up to $Z_p$ electrons is possible. This addresses a known problem with the IEM, namely the overestimation of the high-multiplicity capture channels. A downside of this analysis is a less satisfying result for the single capture cross section compared to the IEM for $Z_p > 1$. The question of how to properly distribute the captured flux remains therefore open.

In addition, this analysis has allowed us to shed light on the open question of the saturation behaviour for the net ionization cross sections. While on the theory side we find an increase in the importance of high $q$-fold terms, when moving to high projectile charges, the experiments on $\text{Li}^{3+}$-$\text{H}_2\text{O}$ do not corroborate this finding. More experimental work is
clearly needed to address this question.

When comparing CTMC net cross sections as a function of Sommerfeld parameter \( Z_p/v_p \) with available experimental data we observe that the latter follow the theory trend in general, but some inconsistencies remain. Thus, we are calling for additional efforts to determine normalized net ionization cross sections for ion-H\(_2\)O collisions.

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