Absolute cross sections for production of molecular dications by electron impact

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Abstract. Molecular dications are important metastable species present in a variety of environments including, but not restricted to, planetary atmospheres and the human body when submitted to radiation. On the other hand, symmetric molecular dications cannot be separated from the cation corresponding to the molecule broken in half (e.g. \(\text{N}_2^{++}\) and \(\text{N}^+\)) in standard mass spectrometers. The DETOF technique allows one to identify the symmetric molecular dication, obtaining absolute cross sections related to their production. Results for dications of molecular nitrogen, molecular oxygen, ethylene and benzene are discussed here, giving emphasis on the mechanisms behind their production. It is seen that, while most metastable molecular dications result from a combination of direct double ionization and Auger-like processes, \(\text{N}_2^{++}\) and \(\text{O}_2^{++}\) represent so-called pure cases, where the dication is produced only by, respectively, double direct ionization or post-collisional Auger-like decay.

1. Introduction

Molecular dications have been the object of many different studies dedicated to their production, stability and subsequent fragmentation [1, 2, 3, 4, 5, 6, 7]. The most interesting aspect of dications is that, while singly ionized fragmentation process produce only singly-charged and neutral species, resulting in low kinetic energy releases (KER), they can dissociate into fragments with high kinetic energy due to Coulombic repulsion [8, 9, 10], leading to KER of the order of tens of eV. Their presence in planetary atmospheres have been predicted by many authors and the KER resulting from their fragmentation can lead to a local increase of the atmospheric temperature, which in turn is directly connected to planetary escape [1, 11, 12].

Although doubly charged molecular ions are possibly a crucial factor for the understanding of physical-chemical processes in energized media [13], such as planetary atmospheres, plasma environments and the human body when submitted to radiotherapy treatments, little is known regarding the absolute cross sections for the dication production in symmetric molecules, due to the intrinsic impossibility of separating moieties with the same mass to charge ratio in a time of flight (TOF) spectrum [1, 14]. As a consequence, they have never been detected in planetary atmospheres yet, although both molecular nitrogen and oxygen are the main components of Earth’s atmosphere, where, on the other hand, \(\text{O}^{++}\) has already been detected [15, 16], showing that double ionization processes are present.

Besides, the mechanisms and pathways for dications formation and possible stability are still not known, raising the question if post-collisional processes play a significant role and, if that
is the case, what would their relevance be for the production of these metastable species. In this work, the following symmetric molecular dications were investigated: nitrogen, oxygen, benzene and ethylene. In order to disentangle the dication from the fragment representing the breakup of the molecule in two identical parts (e.g. $\text{N}_2^{2+}$ and $\text{N}^+$), the well-established Delayed Extraction Time-Of-Flight (DETOF) technique was employed. The DETOF technique allows one to identify different kinetic energy distributions present in recoil ions. Since the fragmented molecules acquire kinetic energy in the fragmentation process, while dications retain their original Maxwell-Boltzmann velocity distribution, the identification of the latter becomes straightforward [17, 18, 19, 20].

A comparison between the production mechanisms of these four molecules and other non-symmetric molecular dications found in the literature show that a combination of direct double ionization and Auger-like post-collisional relaxation are usually present (as, for example, are the cases of ethylene and benzene). On the other hand, nitrogen and oxygen dications are produced by pure processes, where only one mechanism is predominantly present in their formation.

2. Experimental setup

The experimental setup is detailed elsewhere [21], thus only a summarized description is included. It consists mainly of a pulsed electron gun, operating in the 25 to 900 eV energy range, a gas cell and a time-of-flight mass spectrometer. The pressured inside the gas cell is controlled and kept below $5 \times 10^{-4}$ torr in order to ensure a single-collisional regime, the electron beam is collected by a Faraday cup and the recoil ions, after passing through the TOF drift tube, are detected by a Micro-Channel Plate (MCP), allowing therefore absolute cross sections to be obtained. Both the electron beam and an 21 V/mm electrostatic extraction field used to guide the produced positively-charged ions into a TOF drift tube are synchronously pulsed with a frequency of 20 kHz and pulse durations of 50 ns and 100 ns, respectively. This electrostatic extraction field signal and the MCP signal are time-resolved by a time-to-digital converter analyzer in order to produce the TOF spectra, and the overall efficiency of the apparatus is determined by a calibration procedure described before [21].

The DETOF technique is based on this synchronization between the electron beam and extraction field pulses. If the extraction field is turned on exactly after the electrons pass through the interaction region inside the gas cell, all recoil ions produced in a collision would be guided through the collimator at the entrance of the TOF drift tube. On the other hand, if some time delay exists between these two pulses, the fragments after molecular breakup are allowed some free flight time before the extraction field is applied. Thus, species produced with high velocities after fragmentation may leave the collection region and will not be detected - in other words, this time delay works as a velocity selector. This means that consecutive measurements, by systematically and gradually increasing this time delay between the electron beam and extraction field pulses, provide a profile of the kinetic energy distributions present for a single peak in a TOF spectrum. For the particular case of dication production, since a molecular dication does not undergo fragmentation, it retains its original Maxwell-Boltzmann distribution, while all other higher kinetic energy distributions must correspond to the fragmented species with the same mass-to-charge ratio, which acquire momentum in the molecular breakup (e.g. $\text{N}_2^{2+}$ and $\text{N}^+$). This allows the disentanglement between the two different species present in the same peak in the TOF spectra, and since their relative proportions are known, their production absolute cross sections can be obtained. It must be noted that the time-frame of a measurement is in the order of microseconds [18, 20, 21] and, since the metastable lifetimes of all dications discussed here are orders of magnitudes higher than that, we can assume that only a negligible amount of them will dissociate inside the spectrometer before being detected.
3. Results

Absolute cross section values for the molecular dication production of nitrogen, oxygen and ethylene were already published before using the DETOF technique [18, 19, 22, 23]. However, in order to evaluate the predominant mechanisms for their production, the most important property to be analyzed is the dication-parent ion ratio, meaning the ratio between the doubly and singly-ionized non-fragmented molecule, as can be seen in figure 1. It is evident there that the behavior for all three molecules, specially when looking at the high impact energy range of the data, is very different. For nitrogen, the ratio steadily decreases with the increase of the impact energy, while for oxygen, after the increase above the dication threshold up to ∼ 100-200 eV, the ratio remains constant throughout the whole impact energy range. Ethylene, however, seems to exhibit both features: there is a marked decrease with the increase of the impact energy after the maximum value for the ratio has been reached, but above ∼ 500 eV impact energy the ratio reaches a constant value up to the highest impact energy observed here.

It is well known that, at high projectile velocities (with corresponding impact energy $E$), single ionization has a cross section dependency with a $1/E$ trend, while for direct double ionization, meaning the removal of two electrons in the same collisional process, it follows a $1/E^2$ behavior [24, 25]. Therefore, a direct double-to-single ionization ratio should follow a $\sim 1/E$ shape, since it is a comparison from a second order to a first order process. On the other hand, if the dication is produced by a single electron removal followed by a post-collisional Auger-like auto-ionization, the primary collisional process results in a single ionization. In this case, the doubly-to-singly ionized species ratio should be constant, since both cases come from a first order process.

![Figure 1](image.png)

Figure 1. Ratio between dication and parent ion absolute cross sections for nitrogen (red circles - empty symbols [18] and full symbols [22]), oxygen (black squares - empty symbols [20] and full symbols [22]) and ethylene (blue triangles [23]).
In order to investigate this, a further analysis of the behavior of the ethylene dication-to-parent ion ratio is shown in figure 2. Once again the ratio between the dication and its parent ion is shown, but now the ratio between the K-shell ionization cross section from Talukder et al. [26] and our experimental parent ion cross section [23] are also included. A rough estimate of the contribution of both double direct ionization and K-shell ionization followed by Auger decay to the dication formation can be performed using the expression 

$$ R \sim A/E + B\sigma_K/\sigma_{C_2H_4^+} $$

where $R$ is the dication-to-parent ion ratio, $\sigma_K$ is the K-shell ionization cross section from Talukder et al., $\sigma_{C_2H_4^+}$ is the parent ion absolute cross section and $A$ and $B$ are the relative weights of each contribution. Using $A = 2.368$, in order to normalize it to the dication-to-parent ion ratio at 200 eV impact energy, and $B = 0.6$, a reasonably good agreement with the measured ratio is obtained for impact energies above 300 eV, shown in figure 2. This shows not only that both processes contribute significantly to $C_2H_4^{++}$ formation, but also that, since the value for $B$ is below unity, single K-shell ionization followed by Auger decay must also contribute to the fragmentation of the molecule.

![Figure 2](image-url)  
**Figure 2.** Ratio between ethylene dication and parent ion absolute cross sections (blue squares [23]). Theoretical points for a $\sim 1/E$ dependence, where $E$ is the impact energy, normalized with the experimental ratio data at 200 eV impact energy (red circles). Ratio between the data for K-shell ionization of carbon by Talukder et al. [26] and our parent ion experimental data [23] (black triangles). A good agreement between the experimental ratio and the sum of the other two with adequate weights can be reached and is shown as a solid orange line here.

On the other hand, when one looks at the behavior for nitrogen and oxygen dications, shown in detail in figure 3, it can be observed that both molecules do not exhibit these two simultaneously competitive mechanisms. Figure 3 shows, along with the experimental dication-to-parent ion ratio, the K-shell ionization data for nitrogen and oxygen from Tawara et al. [27] and the double ionization fragmentation data (i.e. $N^++N^+$ and $O^++O^+$) from Tian and Vidal [28], all normalized to the parent ion cross section. It can be readily seen that K-shell ionization,
particularly for the oxygen molecule case, is negligible in comparison to the ratios observed. This means that even if a relatively large contribution of post-collisional Auger decay comes after K-shell ionization, this value is still small enough so as to not play a significant role in the dication production. For nitrogen, in particular, it can be seen when comparing to the \( \text{N}^+ + \text{N}^+ \) data of Tian and Vidal [28], whose ratio also present a \( \sim 1/E \) shape, that the main mechanism for producing metastable molecular nitrogen dication comes from direct double ionization (known as TS-2). Auger-like processes involving inner valence shell primary ionization are not energetically (from a molecular orbital’s point of view) allowed, and therefore cannot be present. Thus, nitrogen dication represents a pure double direct ionization mechanism for dication production in the projectile energy range studied.

\[ \text{Figure 3. Ratio between different channels’ described below and the parent ion cross sections as a function of the electron impact energy. Oxygen molecule, black squares: filled symbols - } \text{O}_2^{2+}, \text{ this work; open symbols - } \text{O}^+ + \text{O}^+, \text{ Tian and Vidal [28]); crossed symbols - O K-shell ionization cross section, Tawara et al. [27]. Nitrogen molecule, red circles: filled symbols - } \text{N}_2^{2+}, \text{ this work; open symbols - N}^+ + \text{N}^+, \text{ Tian and Vidal [28]); crossed symbols - N K-shell ionization cross section, Tawara et al. [27]. The data from Tian and Vidal have been multiplied by 0.33 in order to facilitate comparison in the same plot.} \]

Meanwhile, the metastable molecular oxygen dication exhibits a completely different behavior from that of nitrogen. After reaching its maximum value at around 100-200 eV, the dication-to-parent ion ratio remains constant throughout the whole measured impact energy range. This leads to the conclusion that direct double ionization is negligible in comparison to post-collisional auto-ionization processes following single ionization, depicted by the ratio’s constant dependency with the impact energy. It is important to notice as well that not only K-shell ionization of oxygen is negligible when compared to the ratio values, but also that its onset is at a much higher impact energy than what is observed in the present experiment. Therefore, the main mechanism behind metastable molecular oxygen dication production must be inner valence shell single ionization followed by an Auger-like ionization, leaving the molecule in a doubly-charged
state. The interesting question that arises in this case is: why does O\textsubscript{2} not allow double direct ionization as a mechanism for its dication formation?

The final state of an oxygen molecular dication implicates the absence of its two outermost unpaired electrons. The probability of the two outermost electrons being removed in the same collisional process must be so small as to completely suppress this dication formation pathway. A possible explanation is that the molecular $\pi$ orbitals of the unpaired electrons absent in the final dicaticionic state are spatially separated from each other in the oxygen molecule. Therefore, the trajectory of the projectile has to be a very particular one in order to access exclusively these two electrons in order to interact with them, which means that the geometry of the molecule itself suppresses this mechanism [22]. Therefore, it can also be assumed that direct double ionization of other than the two outermost electrons probably results in a fragmented state, as can be seen in figure 3 from the $\text{O}^+ + \text{O}^+$ data of Tian and Vidal. $\text{O}_2^{++}$ is, hence, a pure Auger-like post-collisional auto-ionization following single ionization mechanism for dication formation.

A further evidence for this can be seen when comparing these results with collisions between electrons and O$^+$ [29]. Although the fragmentation channel still dominates, the stable O$^+_2^{++}$ is now produced by direct ionization of the cation, without any geometrical constraint to inhibit the stable dication production. On the other hand, for stable N$^+_2$ ionization [30], the formation of the stable N$^+_2^{++}$ is more probable than its fragmentation, which resembles what was observed [22].

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**Figure 4.** Ratio between dication and its parent ion cross sections as a function of the electron impact energy for different molecules: O$\textsubscript{2}$ (black squares [20, 22]), N$\textsubscript{2}$ (red circles [18, 22]), C$\textsubscript{2}$H$\textsubscript{4}$ (ethylene - blue up triangles [23]), C$\textsubscript{6}$H$\textsubscript{6}$ (benzene - pink stars, present work), NH$\textsubscript{3}$ (gold crosses [31]), ND$\textsubscript{3}$ (green asterisks [31]), CO (purple lozenges [32]) and CO$\textsubscript{2}$ (orange down triangles [33]).

Comparison, in figure 4, of these results with several other molecules - namely benzene (present data), NH$\textsubscript{3}$ (Rejoub et al. [31]), ND$\textsubscript{3}$ (Rejoub et al. [31]), CO (Tian and Vidal [32]) and CO$\textsubscript{2}$ (Straub et al. [33]) - shows that for almost every molecule single and double vacancy production processes (Auger-like post-collisional ionization and TS-2) are competitive.
mechanisms for the dication production. CO$_2^{++}$ and ND$_3^{++}$ data are still inconclusive, but seem to exhibit the same trend. The data for benzene shows that not only benzene dication has a much larger cross section than any other studied dication - meaning it is a much more stable molecule, since after the removal of two electrons the probability that it does not fragment is much larger than for other molecules - but also that the its main dication production mechanisms are exactly like ethylene’s, presented above, with only different weights between them. It must be remembered that benzene has triple the amount of carbon atoms than ethylene, which increases the importance of carbon K-shell ionization. Thus, it is interesting to observe that the only two guaranteed pure mechanisms are, yet, N$_2^{++}$ and O$_2^{++}$.

4. Conclusions
To sum it up, the DETOF technique allows the disentanglement of species with the same mass-to-charge ratio, isolating the dication of a symmetric molecule from its symmetric fragments. Therefore, it became possible now to determine the absolute cross sections for the formation of symmetric molecular dications such as N$_2^{++}$, O$_2^{++}$ and C$_2$H$_4^{++}$ (prior to that, only dications of such molecules could only be measured by looking at hetero-isotopic nuclei, breaking the molecule’s symmetry [14]).

The ratio of dication to parent ion absolute cross sections shows an important aspect of the dication formation - the energy dependence between first (single ionization) and second (direct double ionization) order processes. It is shown that ethylene and benzene, along many other molecules found in the literature, present a contribution of both processes to their dication formation: for low impact energies the direct double ionization dominates, while for high impact energies the dication production comes primarily from post-collisional Auger-like processes. This means that, for most molecules, dications, a doubly-ionized species in its final state, are not negligible in the high projectile velocities regime when compared to the singly-ionized moieties. Also, it must be noted that, since post-collisional processes depend only on the molecular orbital from which an electron was removed in the collision, these processes must be present for dication formation regardless of the projectile (albeit with different cross section values).

Lastly, two cases are very important as benchmarks: (i) N$_2^{++}$, which shows a pure direct double ionization process because inner valence shell Auger-like decays are not energetically allowed and K-shell ionization is negligible in comparison; and (ii) O$_2^{++}$, which shows a pure post-collisional Auger-like decay following single inner valence shell ionization, in which direct double ionization is suppressed due to geometrical reasons. It must be mentioned that these behaviors could only be identified thanks to the DETOF technique, since N$_2^{++}$ and O$_2^{++}$ were not clearly observed prior to that in a TOF spectrum.

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