Molecular fragmentation by electron impact investigated using a time delayed spectroscopic technique.

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Abstract.
A new technique based on time-of-flight mass spectrometry with delayed extraction, in which it is possible to determine the amount of ions with a given energy distribution, is presented. Unlike most techniques designed to measure the energy distribution of molecular fragments, its sensitivity is higher in the low range of the energy distribution, for ions with kinetic energy from thermal energy up to 3 eV. In this progress report we show that this technique is able to open new perspectives for mass spectrometry based on the well established TOF technique, presenting some selected results for collisions of electrons with energy between 15 eV and 400 eV with \( \text{N}_2 \), \( \text{O}_2 \) and \( \text{CHClF}_2 \), which have interesting features involving their low energy fragments.

1. Introduction.
Molecular dissociation is a widespread phenomenon that can produce ions, atoms and molecular radicals that are far more reactive than the original molecule. The usual environment where molecular dissociation occurs generally comprises a molecular medium and some kind of ionizing radiation. Some important and quite distinct examples of this combination are: (i) planetary atmospheres that are constantly irradiated by electrons, cosmic rays or fast ions affecting their molecular inventory [1]; (ii) cancer therapy [2], where the fragmentation of water molecules present in the human body by some ionizing agent can lead to several reactive radicals that can produce local biological damages near the tumor and help the treatment; and (iii) plasma physics, where the environment of ions reacting with each other have many applications, such as the plasma etching of microchips [3, 4] and also in plasma medicine, a new multidisciplinary research field that is showing promising results for new treatments [5, 6].

In this progress report a new technique - Delayed Extraction Time of Flight Spectroscopy (DETOF) - which can be used to study some features of molecular dissociation that are hidden in standard TOF spectrometry is presented. With this technique it is possible to distinguish between fragment ions with the same mass-to-charge ratio taking advantage of the different signatures that these fragments impinge in their energy distributions. As the method uses a TOF spectrometer coupled to a gas cell, it is possible to measure the absolute cross section of the produced fragment ions, which is an important information needed for many applications.

Electron impact measurements with \( \text{N}_2 \), \( \text{O}_2 \) and \( \text{CHClF}_2 \) molecules are presented as examples of the potential of the technique. In principle, it has no restrictions with respect to the projectile...
type or energy, nor the molecular gas species used as target. For that reason, we believe that it has the capacity to uncover some still unknown aspects of molecular fragmentation.

2. Experimental Setup and Methodology.

Briefly, the experimental set-up is based on a TOF spectrometer coupled to a gas cell that keeps the target molecules in thermal equilibrium at room temperature. A pulsed electron gun delivers the electrons towards the gas target and the ions produced are extracted from the interaction region to the TOF tube by applying an extraction voltage. For more details see [7] and [8].

The key feature about the present technique, based in this setup, is that the ion extraction of the recoil ions can be done either immediately after the passage of the electron pulse, or after some controlled delay time. In figure 1-I an example for the $N_2$ molecule is shown: if the extraction occurs after a short delay time ($\Delta t_1$) most of the ions are collected, but, if the extraction is done after a longer delay time ($\Delta t_2$), some of the swift ions leave the extraction region and are not collected.

This variable delay time between the ionization and the extraction events acts as a velocity selector: swift ions leave the extraction region at a small delay time, while slow ions are collected for longer delay times.

For the $N_2$ molecule two different peaks appearing in the mass spectra were studied: the one corresponding to the single ionized parent molecule, $N_2^+$, with mass to charge ratio $m/q = 28$, and the peak with mass to charge ratio $m/q = 14$, which includes the fragment $N^+$ and the double ionized parent molecule $N_2^{++}$. These last two cations are indistinguishable using standard Time Of Flight Spectroscopy. As can be seen in figure 1-I c) and f), the fragment peak clearly decreases much faster with the increase of the delay time when compared with the single ionized parent molecule, since the fragment $N^+$ gains energy in the fragmentation process, while the parent molecule has essentially thermal energy.

In figure 1-II, the experimental data and the results from the modeling of the travel of the ions through the
spectrometer are shown. The modeling is accomplished by integrating the system transmission efficiency \( n_T(v_\perp, t) \) and the ion velocity distribution function \( f(v_\perp) \) over the transverse velocity (with respect to the electron beam) as:

\[
n_{\text{Rec}}(\Delta t) = \int_0^\infty n_T(v_\perp, t)f(v_\perp)dv_\perp
\]  

(1)

Two important factors have to be taken into consideration to describe the transmission efficiency dependence with the perpendicular velocity and the time delay. First we consider the setup’s geometry; where all the ions inside the collimator diameter \( D \) region would enter the TOF drift tube and would be recorded, as if it was an ‘infinite’ electric field extracting the ions. Nevertheless we also consider that the ions are in fact collected by a finite electric field and this interaction affects the ions trajectory depending on their velocities and the delay time. This second factor acts as a correction of the first one, and both trajectories and the dependence with ions energy can be seen in figure 2. This total transmission efficiency \( n_T(v_\perp, t) \) considering both factors described above is shown in blue in figure 2 b), where we have plotted \( n_T(v_\perp, t) \) as function of the ions energy. For this example we used \( \text{N}^+ \) ions with minimum delay time which in our apparatus corresponds to a \( t = 500\,\text{ns} \).

Another important feature of the DETOF technique that it worth to mention is the fact that it is always possible to use the single-ionized parent molecule, that has only thermal energy, to test our analysis and the description of the setup’s transmission efficiency. As the parent molecule has a known energy distribution, Maxwell-Boltzmann’s, the fitting is done with no free parameters: the only variables are temperature, molecule’s mass, collimator diameter and the extraction electric field. All these variables are known, and this is the final test to our methodology and is performed for every new molecule to be studied.

The experimental data is presented in the form \( u/u_0 = n_{\text{Rec}}(\Delta t)/n_{\text{Rec}}(t_0) \), where \( t_0 = 500\,\text{ns} \), which is the minimum delay time possible to achieve with the present apparatus. The single ionized parent molecule \( \text{N}_2^+ \) is very well fitted by a single Maxwell-Boltzmann (MB) energy distribution. The peak for \( m/q=14 \) is fitted by the sum of five different energy distribution functions: one Exponential (Expo), three Gaussians (G) (centered in 0, 8eV, 4eV and 8eV) and one Maxwell- Boltzmann (MB) that corresponds to the contribution from the double ionized parent molecule \( \text{N}_2^{++} \).

In our setup, the best discrimination of the energy distributions occurs for low energy ions, i.e. for the MB and Expo energy distributions, which have 100% transmission efficiency and uncertainties around 7%. For energy distributions centered at higher recoil energies, the efficiency decreases considerably, and the uncertainties are around 20%.

Therefore, we concentrate this progress report on the study of low energy ions produced in the

![Figure 2](image-url)

**Figure 2.** Illustration of the transmission efficiency. a) The ion’s trajectory taken into consideration only the geometry, or ‘Infinite’ electric field approximation, and the real trajectory that takes into account a finite electric field. b) The transmission efficiency as function of the \( \text{N}^+ \) ions energy for the delay time of \( t=500\,\text{ns} \).
fragmentation of some selected molecules by electron impact. The cross-sections for the dications \( N_2^{++} \) and \( O_2^{++} \) production in the ionization of \( N_2 \) and \( O_2 \) are discussed and compared with the available data. As another example, the study of the \( CHClF_2 \) molecule using DETOF spectroscopy shows interesting features regarding its slow fragment, \( CHF_2^+ \), disclosing a non-local contribution to the neutral \( Cl \) production.

3. Measurements of the same m/q ions – Dications \( N_2^{++} \) and \( O_2^{++} \).

Understanding the collision mechanisms that may produce dications, as well as the measurement of the cross section for production of these ions, is of great importance for several areas, as for example in the determination of the ionic inventory of planetary atmospheres. [1] [9]

For the important class of simple, diatomic molecules, the standard Time of Flight Spectroscopy does not allow the distinction between double ionized homoisotopic molecules from other molecular fragments with the same mass-to-charge ratio. Because of that, almost all experiments reporting dication production in this kind of molecules were performed using heteroisotrophic species. [10] [11]. For the \( N_2 \) and \( O_2 \) cases, these measurements were done using their isotopes present in the atmosphere. Due to the small natural abundance of the \( ^{15}N \) and \( ^{17}O \) in the atmosphere, the measurements required long acquisition time and involved relatively high uncertainties.

**Figure 3.** Cross section ratio of \( \frac{N_2^{++}}{N_2^+} \) [7] and \( \frac{O_2^{++}}{O_2^+} \) [12] measurements for homoisotopic molecules \( ^{14}N_2 \) and \( ^{16}O_2 \) compared with previous work from references [10] and [11] that used heteroisotrophic molecules \( ^{14}N^{15}N \) and \( ^{16}O^{17}O \). The solid lines are to guide the eye.

Using the DETOF technique is possible to directly measure the absolute cross section of homoisotopic molecular dications. As shown for the example of \( N_2 \) molecule, the dication \( N_2^{++} \) could be disentangled from the fragment \( N^+ \). The cross section ratio between the single
and the double ionized molecules is shown in figure 3. The comparison between our data [12] with homoisotopic molecules and the previous data with heteroisotopic molecules shows some interesting features. For the $N_2$ molecule our measurement agrees very well with the previous ones. On the other hand, for the $O_2$ case, our data show a clear disagreement with the previous measurements of Márk [10], which is, to our knowledge, the only one reported in the literature to date. This disagreement can be due to the small cross section of the $O_2^{++}$ and the use of correction factors taken from heteroisotopic Nitrogen molecule, which could be a significant source of errors, as remarked in Ref. [10].

Another interesting dynamic characteristic that can be observed in figure 3, is that the cross section ratio for the two molecular ions are, apparently, not parallel for high electron impact energies. The ratio for Nitrogen molecular ions tends to fall for higher energies, which is a typical behavior for double ionization induced by a two-step (double-hit) mechanism. On the other hand, for the Oxygen molecular ions, the cross section ratio does not tend to fall with the increase of electron energy, at least up to our higher measured energy. This behavior is more compatible with a single ionization of an inner vacancy electron followed by a de-exitation through an Auger-like process [13]. Further measurements at higher electron impact energies are needed to corroborate the predominance of this last mechanism.

4. The $CHClF_2$ Molecule, an example for Non - Local Evaporation

The CFC’s (chlorofluorocarbons) are organic compounds that have a wide use in the industry as refrigerants, propellants or solvents which, in the past decades, have been under a worldwide debate due to their contribution to the enlargement of the hole in the Ozone layer. These molecules contain Chlorine and when atomic chlorine is somehow released in the Ozone layer, the following reactions can occur:

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O_3 \rightarrow Cl + 2O_2$$

These feedback reactions can allow a single Cl atom to break a large number of ozone molecules and seriously compromise the ozone layer. [14]

The first CFC’s molecules used in the industry have three or four Chlorine, but lately the industrial CFC’s have their Chlorines atoms replaced by Fluorines or Hydrogens, because with a smaller number of Chlorines, they should cause less harm to the Ozone layer.

The $CHClF_2$ molecule was chosen to be studied because it is still widely used and essentially no information was available about its fragmentation absolute cross sections when impacted by electrons. In our first studies [15] on the fragmentation of this molecule by electron impact we observed that the $CHF_2^+ + Cl^0$ channel contributes up to 40% to the total fragment ions produced. This channel is particularly important because it is the most predominant source for the release of atomic chlorine.

When comparing the measured cross section with a simple theoretical calculation, we observed an indication of a non-local fragmentation, i.e. the fragmentation occurs in a different site from where the ionization occurs. This is illustrated in figure 4. The two main mechanisms suggested
to form the $\text{CHF}_2^+$ ion are: (i) the removal of one electron from Chlorine 3p or, (ii) the removal of one electron from Fluorine 2p.

To further investigate this latter mechanism two complementary measurements were performed. First, we have measured the cross sections for fragment production near the Chlorine ionization threshold (around 13 eV - see figure 5-I). The results are displayed in figure 5-II. The behavior of the cross section ratios between the fragment ions and the parent molecular ion with the electron energy are quite different for the various fragments. In particular, for the fragment $\text{CHF}_2^+$, the cross section ratios show a considerable enhancement above the 2pF threshold (17 eV), indicating that some additional fragmentation channel begins to contribute at this energy.

In figure 5-III, the DETOF experimental data for electron energies of 15 eV and 35 eV are shown as a function of the delay time together with the curve given by the modeling. For the electron energy of 15 eV, and therefore below the 2pF threshold, just one energy distribution is needed to fit the data while, for 35 eV, two distributions with different shapes are required. The Exponential distribution is due the supra thermal fragments that are formed after the removal of one electron from the 3pCl. This fragmentation channel has a very low mean energy. The Gaussian energy distribution, that appears for the 35 eV measurements, is due to a more energetic fragmentation mechanism, related with the electron removal from 2p electron from the Fluorine. As the cross section for both distributions can be independently determined by

\[ f_{\text{Exp}}(E) \]
the DETOF spectroscopy, the above scenario for the Chlorine release can be corroborated by comparing the cross sections found in this way with the model calculation mentioned before. It can be shown that an excellent agreement is achieved. [8]

The identification of a non-local fragmentation mechanism together with the characterization of its energy distribution leads to the conclusion that the use of Fluorine instead of Chlorine molecules in the CFC’s composition is not fully efficient to inhibit the Chlorine release and can also contribute with reasonable efficiency to the depletion of the Ozone layer.

5. Conclusion
The DETOF spectroscopy is a flexible and powerful technique, as shown by the cases described in this report. This new technique allows to obtain absolute cross-section for fragment ions with the same mass-to-charge ratios by distinguishing them using the different signatures impinged in their energy distributions. The cross-section of each energy distribution can be determined and the dynamical behavior of each distribution can be studied varying the projectile energy. The technique is quite comprehensive and can be used to study a wide class of collision systems since it has, in principle, no restrictions regarding the projectile or target molecules used.

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