

Inner valence-shell vacancy production and molecular fragmentation

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Abstract. Fragmentation of complex molecules is studied linking the fragment-ions to the primary vacancies produced in their molecular orbitals. It is observed that a model based in such association describes well rather complex molecules. Deviations from this model are clear indications that inner valence-shells and double ionization plays a key role in the production of some fragments.

1. Introduction

Most molecules, whether simple or complex, have ionization threshold of the order of 10 eV. Usually, the ionization of the outermost valence molecular orbitals results in the production of the parent molecular ion. As vacancies are produced in more bound valence molecular orbitals, other species of fragment-ions are ejected. The number of orbitals in that outer valence-shell band increases with the size of the molecule and a given fragment ion can be produced from vacancies created in more than one of these orbitals. The fragments produced by this set of outer valence-shells have large cross sections and are, as a rule, induced by single vacancies created by the projectile. Molecular orbitals with binding energies larger than ~ 20 eV, form another set, the inner valence shells. For these more bound orbitals, Auger decay is energetically possible and the molecule can be doubly ionized starting from a simple vacancy created by the projectile. As a consequence of double ionization, the abundances of some charged fragments-ions are increased and additional ionic species are produced. Some of them can be considered as signatures of fragmentation caused by a double ionized molecule.

In this report we focus our attention on how some dynamic features, such as the shape of the cross sections for fragment-ion production as a function of the energy of the projectile, are linked to the production of primary vacancies in the outer or in the inner valence shells. In both cases we will take the water molecule as a benchmark to show that the main dynamic signatures observed in this case can be extended to more complex molecules such as the pyrimidine and pyridazine isomers.

2. Outer valence-shell vacancies

2.1. Water

A particular fragment-ion may be originated from primary vacancies produced on more than one molecular orbital (e.g. H_2O^+ by $1b_1$ and $3a_1$ molecular orbitals) while a primary vacancy produced in a given molecular orbital can give rise to different species of fragment-ions (e.g. $1b_2$). This is illustrated in Fig. 1. The set of observed fragment-ions can be linearly related to the set of molecular orbitals by a fragmentation matrix. The elements of this matrix are obtained empirically using information from the fragment's appearance energies and from the adjustment of fragment-ion production cross sections from the calculated cross sections for vacancy production. They are the same for all projectiles as long



the collision time is much smaller than the fragmentation time. It has been observed that these last cross sections are not particularly sensitive to the method used for its calculation and, in this work, we use the rather general and simple semi-empirical approach as described in references [1-3]. Ref [3] describes the construction of fragmentation matrix in detail. It should be mentioned that some recent attempts have been made to find some fragmentation matrix elements theoretically, as in the case of the $1b_1$ molecular orbital of water [4], but the determination of the fragmentation matrix for any specific molecule is unavailable at present.

The cross sections for the parent molecular ion and for the OH^+ fragment production of water as a function of proton energy is shown in the left panel of Fig.1. The model applied to the outer valence shells describes quite well the overall shape of the cross section curves. In particular, it should be noted that the concavity of the calculated cross section as well as of the set of measured values are both negative, with no apparent point of inflexion.

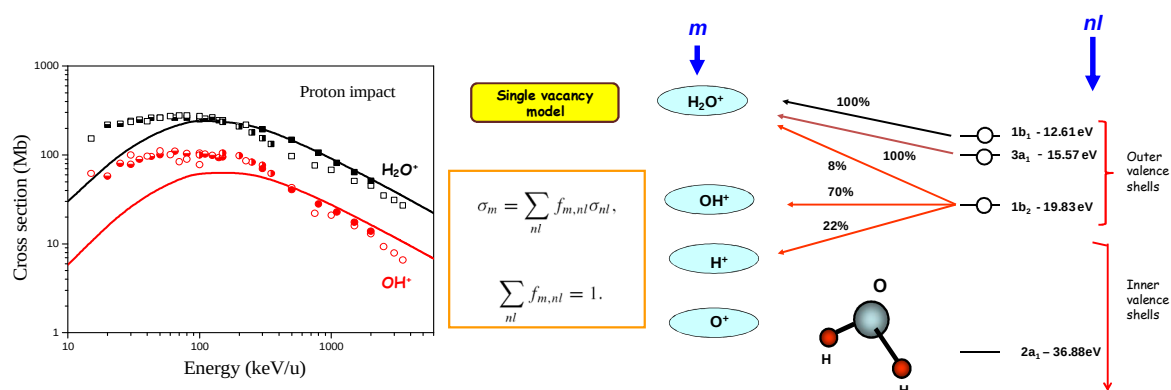


Figure 1. Left panel: H_2O^+ and OH^+ production cross sections from water by proton impact. Calculations (full lines), as described in the text and based on Refs. [1-3]. Experiment: Refs.[5-9]. Right panel: fragmentation fractions associated to vacancies produced in the outer valence-shells of water. It is also shown the relationship - given by the fragmentation matrix $f_{m,nl}$ - between the cross sections for fragment-ion production, σ_m , and that for vacancy production, σ_{nl} .

2.2. Pyrimidine and Pyridazine

Pyrimidine and pyridazine ($\text{C}_4\text{N}_2\text{H}_4$) are two isomers which differ by the relative position of the N atoms in the ring. The number of states in the outer valence-shell is much larger than water so the construction of the fragmentation matrix is much more cumbersome [2,3].

Despite of the need of information about the appearance energies for a large number of fragmentation products, the same methodology applied for the case of water may be used to construct their fragmentation matrix [2,3]. The fragmentation fractions (or fragmentation matrix elements) are depicted in the right panel of Fig. 2. The left panel of Fig. 2 shows the cross sections for some selected fragments of the pyrimidine and pyridazine isomers as a function of the proton energy. Again, the model applied to the outer valence shells describes quite well the overall shape of the cross section curves. The total cross section for ionization of pyrimidine calculated with the simple semi-empirical approach [2], also agrees with more elaborate calculations within the Born Approximation by Champion et al. [10]. It is noteworthy that a simple shift in the position of one N atom in the ring results in very different fragmentation pattern. In particular, the cross sections for ejection of $M=53$ ($\text{C}_3\text{H}_3\text{N}$) differ by almost one order of magnitude for the two isomers. As pointed out in Ref. [11] this finding can be used as a fine marker to identify one or other of these isomers. Further, the cross sections for $M=53$ in pyridazine and $M=51$ in pyrimidine show a clear change in shape for lower energies, at variance with the behavior shown by the other masses in this figure and with the water products of Fig. 1 as well. This fact will be further explored next.

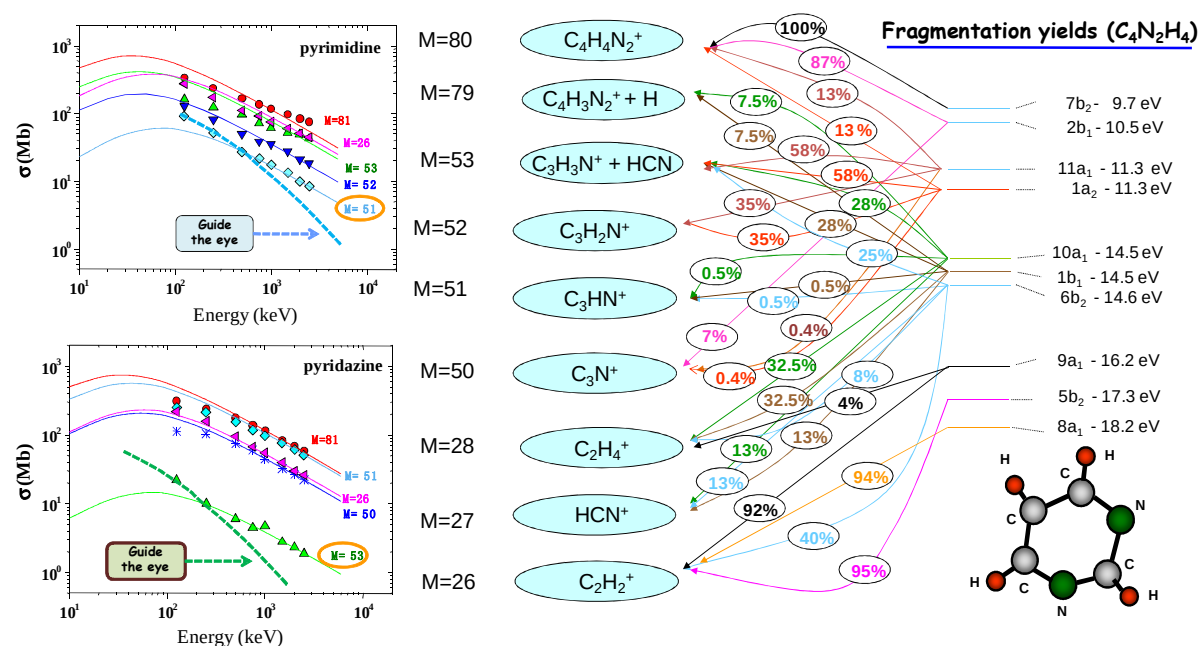


Figure 2. Left panel: Cross sections for some selected fragments of pyrimidine and pyridazine isomers. Calculations (full lines), as described in the text and based on Refs. [1-3]. Experiment: Refs.[2,11]. The dashed lines are to guide the eye and to emphasize the change in the concavity and the presence of an inflexion point, around 200-400 keV, for the products with masses 51 in pyrimidine and 53 in pyridazine. Right panel: fragmentation fractions associated to vacancies produced in the outer valence-shells of pyrimidine.

3. Inner valence-shell vacancies

3.1. Water

The inclusion of orbital $2a_1$ in the fragmentation pathways opens up new alternatives for de-excitation as well as for the identification of more complex dynamics in the production of primary vacancies. The possibility of de-excitation of the orbital $2a_1$ by Auger process opens two possible paths for the relaxation of the water molecule with a vacancy in that state: (i) it may fragment quickly, ejecting a single ionic fragment, as in previous cases or (ii) it becomes doubly ionized by ejecting an Auger electron before fragmenting. In the latter case the fragment-ions species and yields becomes associated to a doubly ionized molecule.

Although giving rise to two ionic fragments, the origin of $O^+ + H^+$ or $OH^+ + H^+$ at high energies is a single vacancy produced in the $2a_1$ molecular orbital. As H_2O^+ is originated from a single vacancy production by the projectile as well, the ratios of $O^+ + H^+ / H_2O^+$ or $OH^+ + H^+ / H_2O^+$ cross sections should tend asymptotically to a constant value at high energies, which is indeed the case. This reasoning was discussed previously by Scully et al. 2006 for the case of electron impact. From these ratios together with the measured single-hit O^+ cross section and the calculated cross section for $2a_1$ vacancy production, the Auger and the prompt yields can be straightforwardly obtained [9]. The complete fragmentation scheme for vacancies produced in all valence shells of water is shown in the left panel of Fig.3.

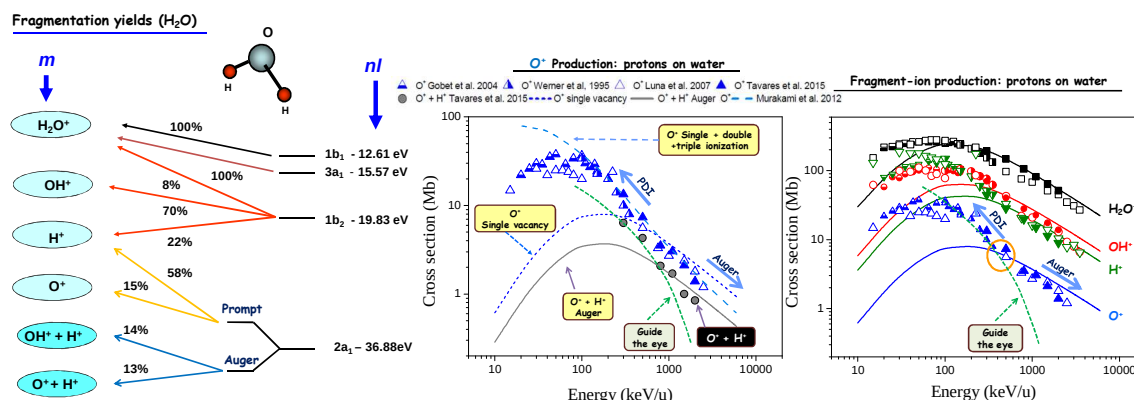


Figure 3. Left panel: fragmentation fractions associated to vacancies produced in all the valence-shells of water. Middle panel: O^+ (triangles) and $O^+ + H^+$ (circles) production by proton impact. Calculations as described in the text and based on Refs. [1-3] and Ref. [13]. Experiment: Refs. [5-9]. Right panel: Cross sections for all fragments of water. Calculations: Refs. [1-3]. Experiment: Refs.[5-9]. The dashed green lines are to guide the eye and to emphasize the change in the concavity and the presence of an inflexion point, around 700-1000 keV.

The total O^+ production comes, at high velocities, from the prompt and Auger branches of the $2a_1$ decay. The middle panel of Fig. 3 shows the model calculations [Refs. 1-3] for both $O^+ + H^+$ and O^+ production cross sections. These curves presents no changes in concavity, in contrast to the experimental data which show a clear inflexion point around 700 – 1000 keV/u. For energies below this point the Projectile Double Ionization (PDI) plays a major role in the O^+ production. The shape of the cross section thus indicates if a particular-fragment ion is mainly produced by a single vacancy or not. The presence of an inflection point is a signature that this particular fragment-ion is produced by double ionization as well, and very much linked to a vacancy produced in an inner valence-shell. If single, double and triple electron removal is considered, as in calculations of Ref. [13], the whole shape of the cross section is well reproduced.

The right panel of Fig. 3 summarizes these findings for water. Outer valence-shells vacancies are linked to fragment-ion production (H_2O^+ and OH^+) dominated by single vacancy in a broad range of projectile energies, with small or negligible contribution from double ionization. The experimental data agrees well with the model calculation for a broad range of projectile energies. Inner valence-shells vacancies are associated with fragment-ion (O^+ and H^+) production divided between single vacancy (prompt) and double vacancy (Auger + PDI) production, with a significant contribution of PDI at lower energies. In this case the experimental data agrees with the single-vacancy model calculations only at high energies. At intermediate-to-low energies a clear increase (inflexion point) of the cross section with respect to the single-vacancy model is observed, indicating that PDI plays an important role in addition to the single vacancy mechanism.

3.2. Pyrimidine and Pyridazine

A very useful finding of our study is that more complex molecules, such as the pyrimidine and pyridazine isomers, behave similarly to water. The more abundant fragment-ions are, as discussed before, associated with single vacancies produced in outer valence-shell orbitals. On the other hand, some less abundant fragments present a clearly different behavior. This was shown in Fig. 2 above for masses 51 and 53 and is shown in Fig. 4 for the fragment-ion with $M=38$. The cross section for production of this fragment presents a clear inflexion point around 1000- 2000 keV. The shape of the cross section for this fragment-ion is an indication that the double ionized parent ion, $C_4H_4N_2^{2+}$,

produced either by Auger decay or PDI, is in the origin of the production of C_2N^+ . Furthermore, this fragment has approximately the same cross section for the two isomers, in contrast with fragments with masses 26 and 51, for example. This is an additional fact to associate that fragment to internal vacancies and to a more violent fragmentation process and, therefore, less sensitive to the details of the outer-shells electronic wave functions that could distinguish the two isomers.

Up to this point, we have considered only protons as projectiles. Protons can be considered unique in providing a clear identification of the mechanisms ruling the production of fragment-ions linked to an inner –valence shell vacancy. The reason for that can be seen in left panel of Fig. 5, where electron impact cross sections were included for O^+ production in water. Indeed, the cross section for electron impact for O^+ production in water do not show any clear inflexion point. The cross section begins to decrease for energies below that at which the PDI begin to become important. In other words, the cross section maximum for electron impact occurs for projectile energy near the proton inflexion point which, because of that, becomes obscured in the electron case.

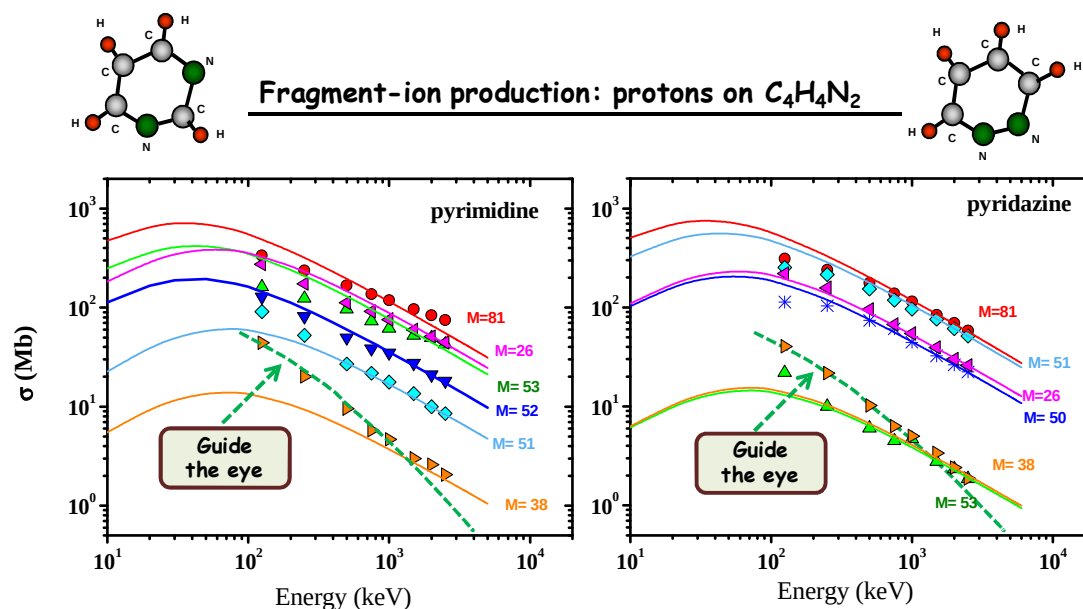


Figure 4. Left panel: cross sections for some fragment-ions of pyrimidine. Right panel: cross sections for some fragment-ions of pyridazine. Calculations (full lines), as described in the text and based on Refs. [1-3]. Experiment: Refs.[2,11]. The dashed lines are to guide the eye and to emphasize the change in the concavity and the presence of an inflexion point, around 1000- 2000 keV, for the products with $M=38$ in both pyrimidine and pyridazine.

The low energy decrease of the electron induced cross section for O^+ production is due to the relatively high ionization potential of the $2a_1$ orbital. In this case it is difficult to identify through a simple visual inspection of the shape of the cross section if some particular fragment-ion (O^+ in this case) is mainly linked to a vacancy in the inner-valence shell.

In the right panel of Fig. 5 the production of $M=38$ by electron impact is also included. In this case, and in contrast with water, the inflexion point is located far (at higher energy) of the cross section maximum for the electron impact and can be well identified. Unfortunately the electron measurements do not go to such higher velocities but, in principle, the signature that the origin of $M=38$ is $C_4H_4N_2^{2+}$ can be done by electron impact as well. The shift of the inflexion point of pyrimidine with respect to water is related to the differences in the energy of the cross section maximum and to the total number of electrons in the molecules, which favours PDI in the pyrimidine case. As a final remark, one should note that some fragments can be produced from several molecular orbitals and just

the appearance energies given by electron impact measurements may not give precise information about the inner-valence shells contributions.

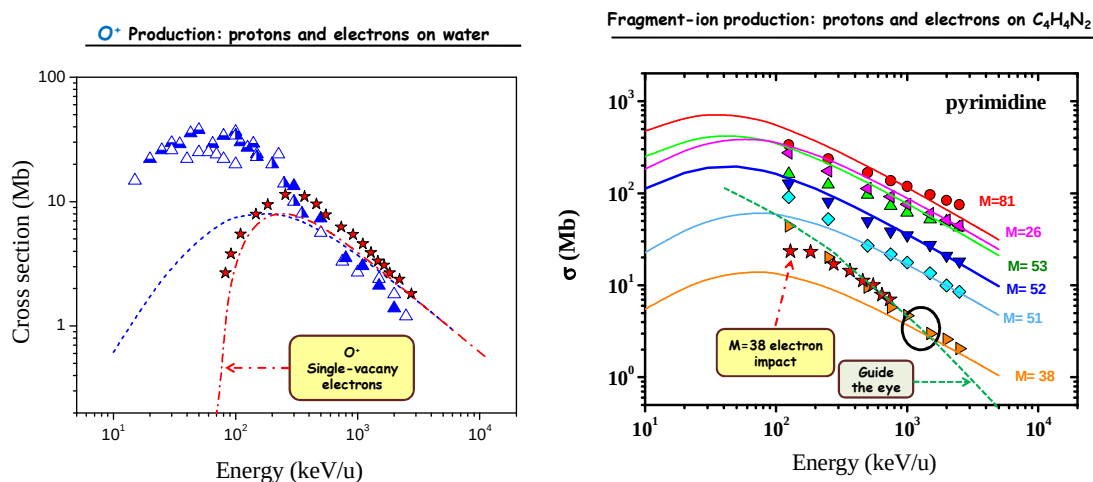


Figure 5. Inclusion of electron impact in the production of O^+ in water, Ref.[14], left panel, and in the production of $M=38$ in pyrimidine, Ref. [2], right panel.

4. Conclusions

For the most abundant fragments, their cross sections can be linearly related, through the fragmentation matrix, to the cross sections for vacancies produced by the projectile in the set of outer valence-shell molecular orbitals. This association is enough to give a quite good description of the shape of fragment-ion cross section for a broad range of projectile velocities. For the less abundant fragments, this scenario gives a good description of the shape of the fragment-ion cross section only at high velocities, with the Auger decay playing a significant role. In this case, these fragments are very much linked to the decay of the double ionized parent ion. Because of that, the single vacancy model fails to give a good description of the shape of cross section at intermediate-to-low velocities where the PDI contributes significantly to double ionization. The PDI contribution increases the cross section somehow sharply at intermediate velocities making to appear an inflexion point in the cross section curve. This inflexion point is a signature that inner valence-shells and double ionization are important players for the production of that particular fragment.

References

- [1] E.C. Montenegro, G.M. Sigaud and R.D. Dubois 2013 *Phys. Rev.* **A87** 012706
- [2] W. Wolff, H. Luna, L. Sigaud, A.C. Tavares and E.C. Montenegro 2014 *J. Chem. Phys.* **140** 064309.
- [3] E.C. Montenegro, L. Sigaud, W. Wolff, H. Luna, N. Ferreira 2015 *Physics Procedia* **66** 39
- [4] J. Suárez L. Méndez, and I. Rabadán. 2015 *J. Phys. Chem. Lett.* **6** 72.
- [5] U. Werner, K. Beckord, J. Becker, and H.O. Lutz 1995 *Phys. Rev. Lett.* **74**, 1962.
- [6] F. Gobet et al. 2004 *Phys. Rev.* **A70**, 062716.
- [8] H. Luna et al. 2007 *Phys. Rev.* **A75**, 042711.
- [9] A.C. Tavares, H. Luna, W. Wolff, and E.C. Montenegro 2015 *to be published*.
- [10] C. Champion, M. A. Quinto, and P. F. Weck 2015 *Eur. Phys. J.* **D 69** 127
- [11] W. Wolff, H. Luna and E.C. Montenegro 2015 *to be published*.
- [12] S.W.J. Scully et al. 2006 *Phys. Rev.* **A 73** 040701R.
- [13] M. Murakami et al. 2012 *Phys. Rev.* **A 85** 052713
- [14] E.C. Montenegro, S.W.J. Scully, J.A.Wyer, V. Senthil, and M.B. Shah 2007 *J. Elec. Spect. Rel. Phenom.* **155** 81.