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Correlation between the Total Destruction Cross Section of the Clusters H_n^+ ($5 \leq n \leq 27$) and Individual Total Destruction Cross sections of its constituents H_3^+ and H_2 at 60 KeV/amu.

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Introduction

Hydrogen clusters are molecular aggregates known as clusters of Van der Waals because their cohesion is due to dipolar forces (about 0,1 eV).
Hydrogen clusters can existed in two forms with very different structures: Neutral and charged clusters.

The molecule H_2 is the basic constituent of neutral hydrogen clusters. The interaction H_2-H_2 of Van der Waals ensures the cohesion of the cluster. The liaison is due to the instantaneous electrostatic interaction (the molecule H_2 has no dipolar moment). This interaction of attraction is weak and has a short range because the term dominating, known as dispersion term, evolves in $1/R^6$. Hence one considers a compact structure for the clusters of this type.

For the charged clusters, two additional effects appear: The energies of polarization (the molecules H_2 are polarized) and the delocalization of the defect of electron, whence a greater stability.

The experimental results relating to the production of charged clusters showed that the number of clusters of odd size is very large comparing to the clusters of even size, especially in the production of clusters by electronic impact on a solid hydrogen target [1] or in the supersonic jets [2,3]. The proportion of clusters of odd size is 10^3 to 10^4 times more important than those of even size. That's the reason why we were interested to the clusters of odd sizes. They are represented by a core H_3^+ surrounded of m molecules of dihydrogen, $H_3^+(H_2)_m$ or also written H_n^+ with n=3+2m.

Experiences at The IPNL

First experiments studying the fragmentation of these charged molecular clusters were made at the IPNL-IPM (Institut de Physique Nucléaire de Lyon-Interaction Particule Matière) in France. Clusters H_n^+ (size $3 \leq n \leq 35$) are accelerated at a large speed (~c/100) and collided with the helium gas which correspond to the energy range from 60 keV/amu to 100 keV/amu.

The experiment was carried out in inverse kinematics (clusters are accelerated) which allows the detection of the neutral and charged fragments. Techniques of coincidence used allow to determine the various channels of fragmentation.

Reaction of the collision

$$H_3^+(H_2)_m + He \xrightarrow{60\ keV/amu} \alpha H_3^+(H_2)_k + \beta H_3^+ + \gamma H_2^+ + \delta H^+ + \varepsilon H_2 + \eta H$$

$0 \leq m \leq 16$

Where $\alpha = 0$ or 1 and $0 < k < m$, k natural), β, γ, δ, ε and η are naturals ≥ 0.

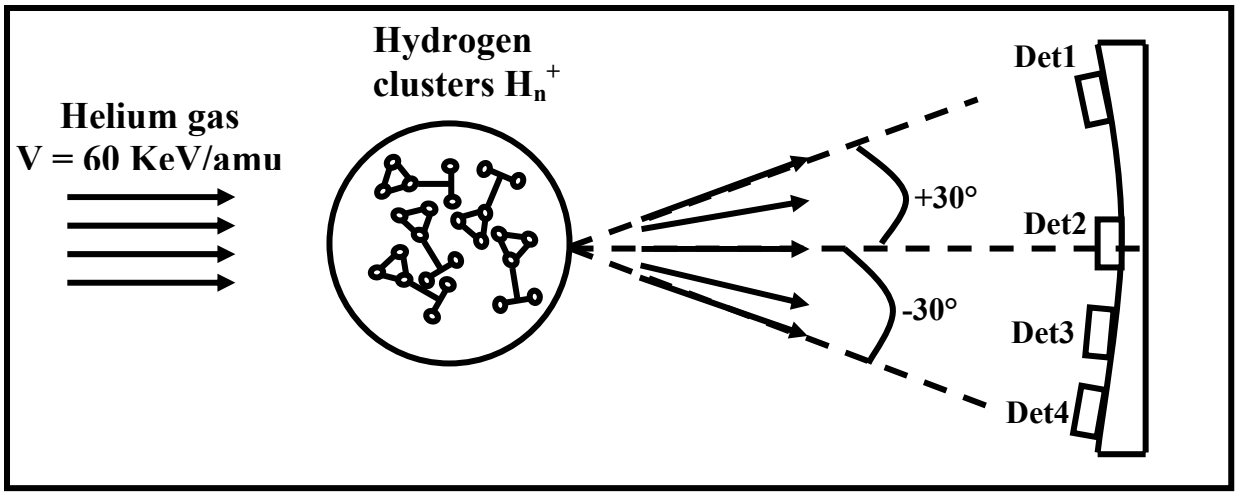


Figure 1: Schematic set-up of the collision between a hydrogen cluster and a helium atom at 60 keV/amu.

Experimental Results

These experiences were carried out for a large range of odd size n ($3 \leq n \leq 35$ in amu). Measurements of the total destruction cross sections of the hydrogen clusters $H_3^+(H_2)_m$ with $0 \leq m \leq 16$ were done by S. Louc [4]. The results obtained (see figure 2) are in a very good agreement with several sets of measurements carried out at the IPNL-IPM between 1993 and 1996 after several assemblies and disassemblings of the totality of the experimental montage. And as expected, the experimental results show that the cross section of destruction increases with the size of the cluster.

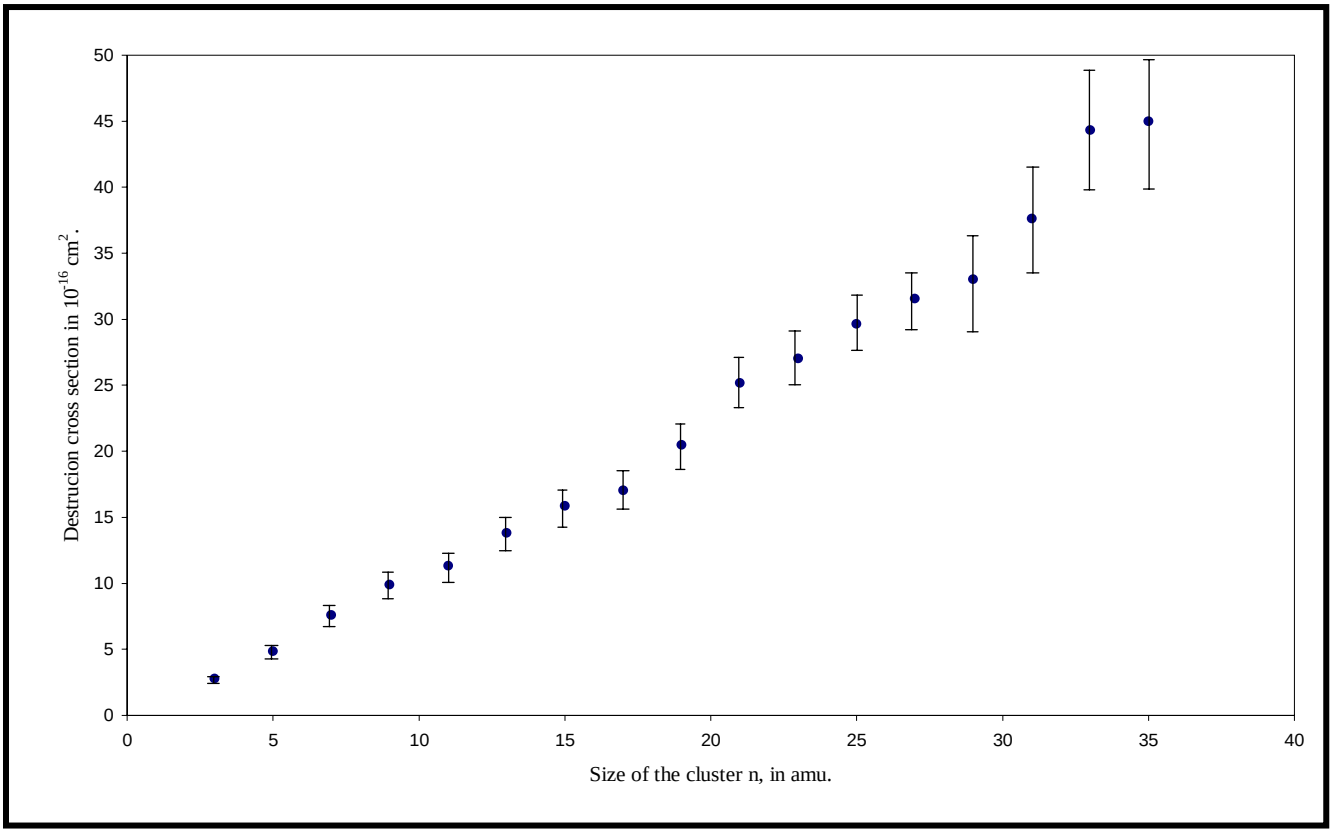


Figure 2: Destruction cross sections of clusters H_n^+ according to their sizes n.

Monte Carlo Simulation

Modelling

Hypothesis for modelling collision of a helium atom with a cluster are based on :

- Electrons are localized on the hydrogen molecules,
- Various electronic states of the molecules are a little beat affected by the interactions ion-dipole or dipole-dipole which ensures the cohesion of the molecular system,
- Electron density is represented by an ellipsoid,

The system is thus treated like a whole of independent molecules (a molecular ion H_3^+ and m molecules of H_2) whose protons' positions are calculated by *ab initio* methods [5].

Our model can be described as "geometrical" in the sense that it doesn't use the Hamiltonian of the system cluster-atom in interaction. Moreover, our simulation is also described as semi-empirical because we use the experimental individual destruction cross sections of both the molecule H_2 and the ion H_3^+ [4,6].

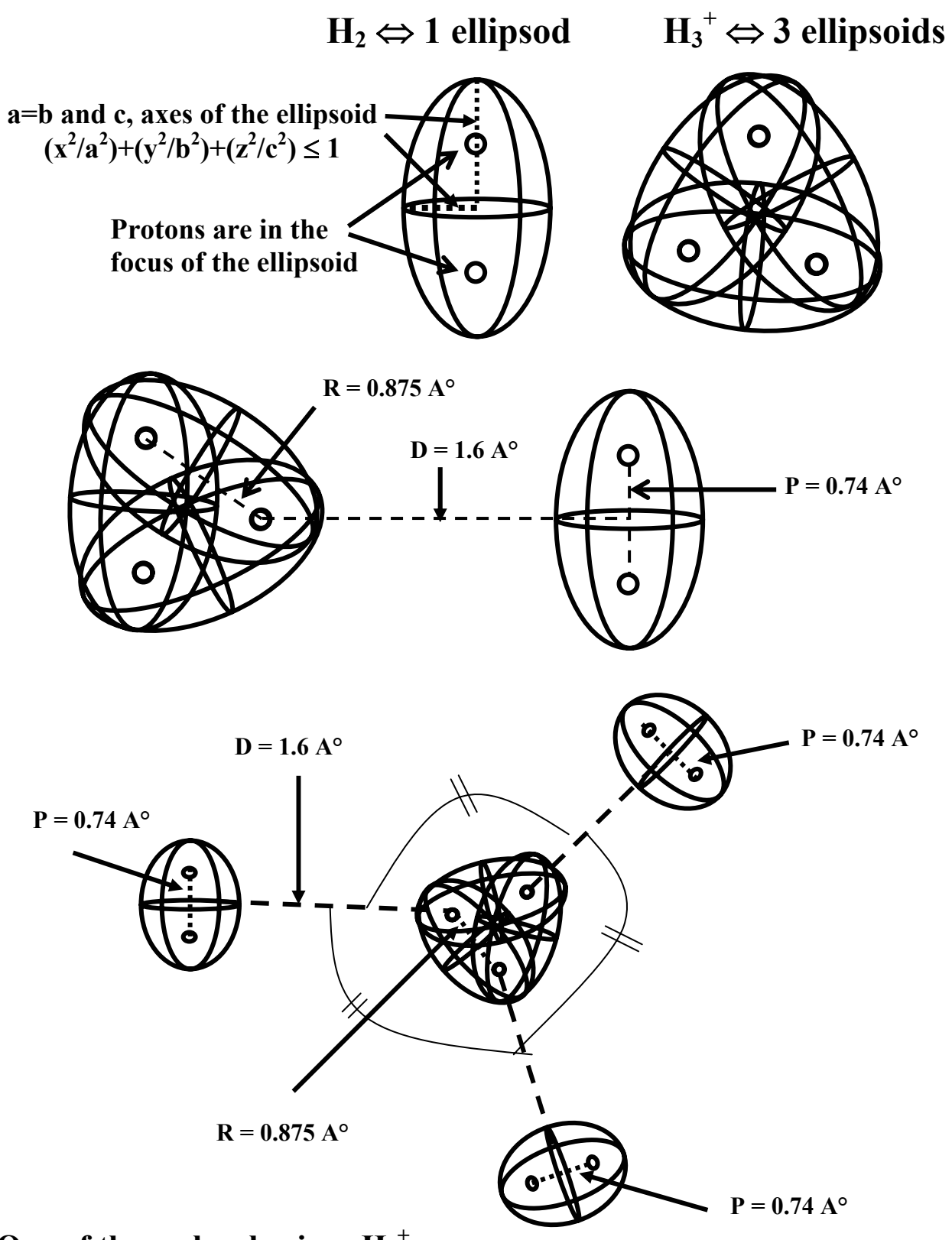


Figure 3 : Figures showing the modelling of the constituents of the hydrogen cluster H_2 and H_3^+ and the example of the clusters H_5^+ and H_9^+.

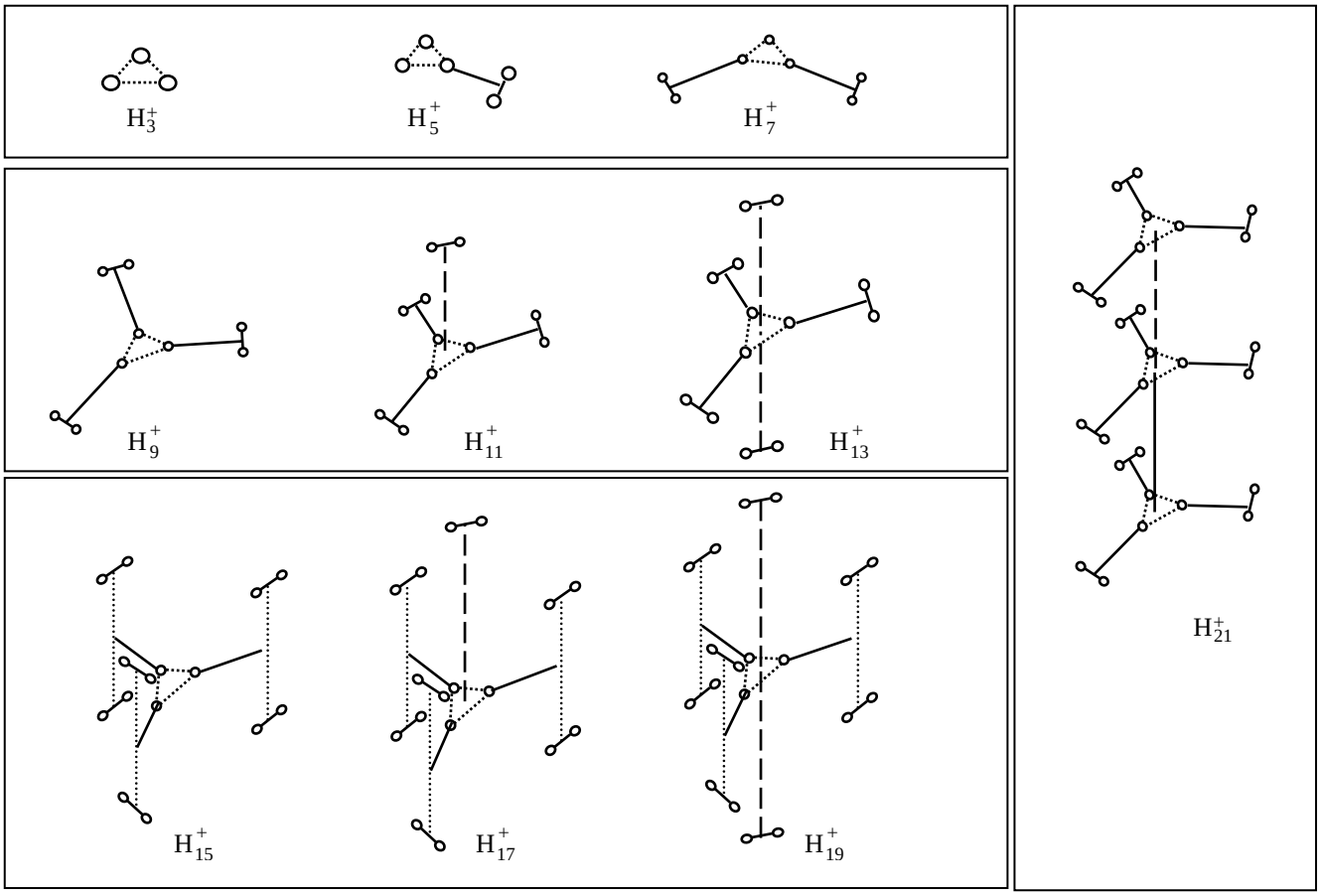
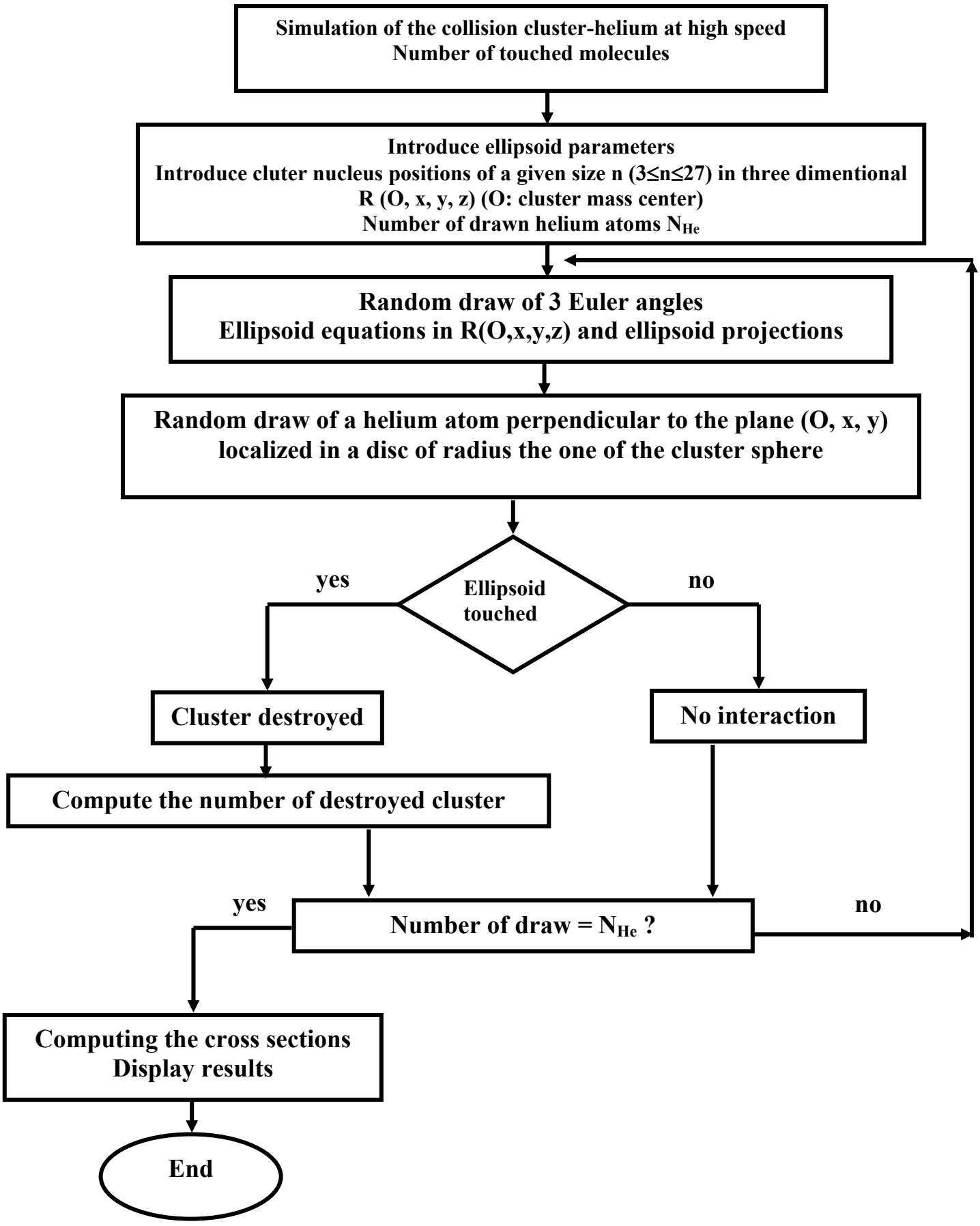


Figure 4 : Geometrical structures of some clusters H_n^+ $3 \leq n \leq 21$.

Theoretical studies of hydrogen cluster ions have been carried out with increasingly regularity over recent years. Yamabe *et al.* [7] confirmed that the $H_3^+(H_2)_m$ (m = 1-4) clusters are dominated by the strongly bound regular H_3^+ triangle on the basis of self-consistent-field (SCF) calculations. Hirao and Yamabe [8] carried out SCF and configuration interaction (CI) calculations on the shell structure of $H_3^+(H_2)_m$ (m = 1-5) clusters and identified m = 5 as being particularly stable. Nagashima *et al.* [9] determined *magic numbers* in the stability of $H_3^+(H_2)_m$ ions at m = 3, 6, 9, 12, and 15 using a classical Monte Carlo simulation and the annealing method. The *ab initio* CI calculations of Diekmann *et al.* [10], however, are consistent with full shells occurring at m = 3, 5, and 9.

By application of SCF and CI methods, Yamaguchi *et al.* [11] calculated the equilibrium geometry of $H_3^+(H_2)$ cluster to have C_{2v} symmetry with one of the atoms in the H_3^+ group bound to the H_2 molecule. The potential energy surface of the cluster has since been modeled by Prosmiti *et al.* [12] using perturbation theory. The geometrical structures and energetics of H_7^+ and H_9^+ have also been calculated by Yamaguchi *et al.* [13] and those of $H_3^+(H_2)_m$ (*m* = 1-6) by Farizon *et al.* [14-17] using an *ab initio* Hartree-Fock (HF) technique. The distance between the protons within the H_3^+ core was reported to be 0.875 Å and that between the protons which form H_2 molecules to be of the order of 0.74 Å. The distance between the H_2 molecules was calculated as 1.6 Å for clusters of size less than or equal to *m* = 3. The larger clusters were described as a nucleation of H_2 molecules around a weakly deformed H_9^+ core. The distance between these additional molecules and the H_3^+ core was calculated to be of the order of 2.8 Å. These results are in agreement with the quantum Monte-Carlo calculations of Štich *et al.* [8, 18] for the cluster sizes *m* = 0, 1, 2, 3, and 12. As expected, the structures derived by Štich *et al.* [18] correspond to a full H_2 shell at *m* = 3.

Organigram


Simulation of the collision cluster-helium at high speed
Number of touched molecules
Introduce ellipsoid parameters
Introduce cluter nucleus positions of a given size n (3≤n≤27) in three dimentional
R (O, x, y, z) (O: cluster mass center)
Number of drawn helium atoms N_{He}
Random draw of 3 Euler angles
Ellipsoid equations in R(O,x,y,z) and ellipsoid projections
Random draw of a helium atom perpendicular to the plane (O, x, y)
localized in a disc of radius the one of the cluster sphere
Ellipsoid touched
yes
no
Cluster destroyed
No interaction
Compute the number of destroyed cluster
yes
Number of draw = N_{He} ?
no
Computing the cross sections
Display results
End

Algorithm description

First we introduce the positions of the protons and also the individual cross sections of destruction, computed empirically, of the ion H_3^+ and the molecule H_2 from which we calculate the characteristic values (a and c) of the ellipsoids of the core of the cluster and the molecule H_2. Then we write the equations of the ellipsoids relative to these two components and which are in the form :
$(x^2/a^2)+(y^2/b^2)+(z^2/c^2) \leq 1$ with a=b because of the symmetry, then we randomly draw a parameter of impact. This latter, noted b having b_{max} as a maximum value, is selected as the radius of a sphere in which the cluster is fixed, it is defined in a plan, it thus describes a disc always compared to the mass center of the cluster, it is also linked to the ellipsoids by the means of an equation of projection of these ellipsoids to which it must make satisfaction to allow or not the destruction of the cluster.

As soon as an ellipsoid is crossed, the cluster is destroyed. The program allows to determine the number and the type of the ellipsoid crossed; in other words the calculation of the number $N_d(H_3^+)$ of destroyed ions H_3^+ and also the number $N_d(H_2)$ of destroyed molecules H_2 and we associate a probability of 2/3 to the crossing of the helium of any of the three ellipsoids of the ion H_3^+ according to the design of this latter. It also allows to compute the number of destroyed clusters and thereafter the computing of the cross sections of destruction. The cross section of total destruction, $\sigma_{destruction}$, is thus calculated by the following relation:

$$\sigma_{destruction}\,(H_n^+) = (\Delta S / N_{He}) \times N_T \times N_d \quad \text{with}$$

$\Delta S = \pi \times (b_{max})^2$: section of the flow,
$N_T = 1$: number of the target,
N_{He} : number of helium atoms,
$N_d = P \times N_d\,(H_3^+) + N_d(H_2)$: number of destroyed clusters,
$P = 2/3$: probability of the crossing of He,
$N_d(H_3^+)$: number of H_3^+ destroyed ions,
$N_d(H_2)$: number of H_2 destroyed molecules.

Before applying the program to any one of the clusters, it was, first of all, tested with the molecule H_2 and then with the ion H_3^+.

Application of the program for the molecule of hydrogen H_2 and the molecular ion H_3^+

Then we apply the algorithm to the components of the cluster and the results we obtained are gathered in the following table:

For the molecule H_2		
	$\sigma_{experience}$ in 10^{-16} cm^2	$\sigma_{simulation}$ in 10^{-16} cm^2
at 50 Kev/amu	3.13 ± 0.42	3.04
at 60 Kev/amu	3.15 ± 0.47	3.09
For the ion H_3^+		
	$\sigma_{experience}$ in 10^{-16} cm^2	$\sigma_{simulation}$ in 10^{-16} cm^2
at 50 Kev/amu	3.35 ± 0.5	3.22
at 60 Kev/amu	2.77 ± 0.42	2.60

The cross sections of destruction $\sigma_{experience}$ and $\sigma_{simulation}$ are in good concord taking into account uncertainties associated to the experimental values.

Application of the program to clusters H_n^+

Calculation by Monte Carlo simulation of the cross sections of destruction of various clusters H_n^+ ($5 \leq n \leq 27$) was made in this same way and then compared to the experimental results.

Comparison between experience and simulation

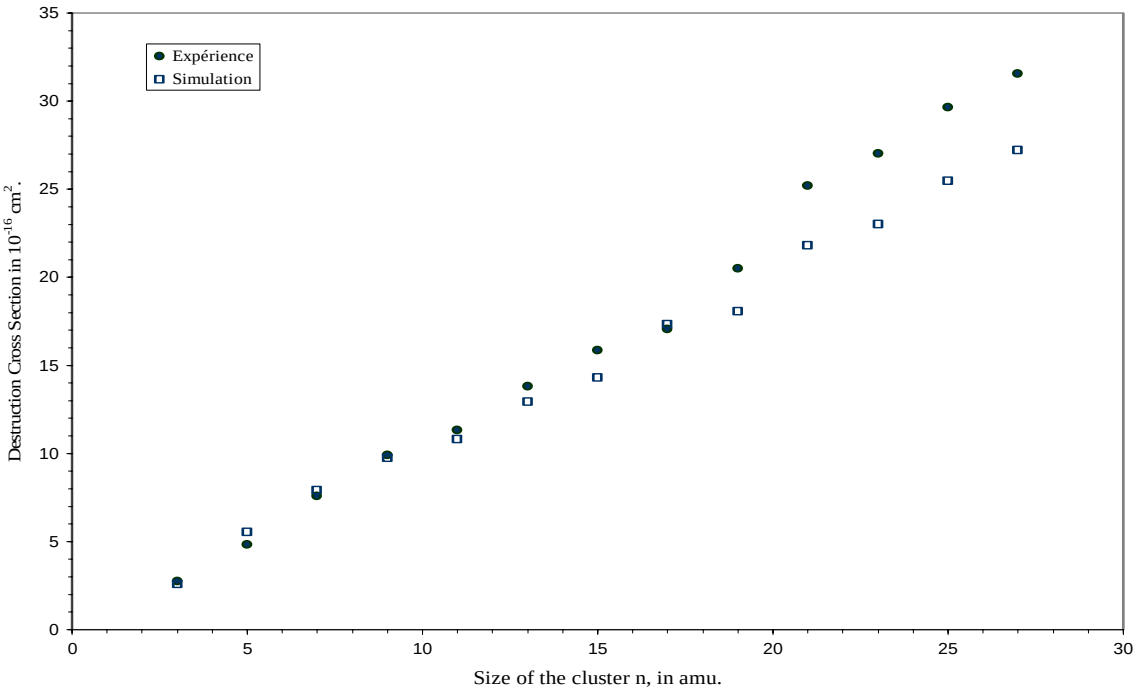


Figure 6 : Evolution of the cross section of destruction of the hydrogen clusters according to their size n.
Comparaison with the model of simulation.

Interpretation of the results

This difference (or gap) noted for large clusters is due to the fact that we didn't use the vibrational excitation cross section of the molecules H_2 in the experimental cross section of destruction which we introduced into the simulation. The fragmentation (or the dissociation) of the cluster can also occur during the vibration of the molecules of dihydrogen of the cluster and which could cause evaporation.

Conclusion and Prospect

The simulation has allowed to show the correlation between the individual destruction cross sections of the components of the cluster and the total cluster destruction cross section. It also showed a linear dependence of the cross section of destruction of the cluster with the size n formulated as the following relation:

$$\sigma_{destuction}(H_n^+) = \sigma_{destuction}(H_3^+) + [(n-3)/2] \times \sigma_{destuction}(H_2)$$

By comparison between experiment and simulation, we noticed that, for the sizes $n \leq 9$, the results of simulation are in agreement with the experimental. However, for the sizes $n \geq 11$, a gap is noted. This can be due to the fact that we didn't take into account the vibrational excitation cross section of the molecule H_2. This vibration could induce evaporation thus fragmentation which appears only for the bigger clusters.

The same program has been applied to the study of the electron capture of the hydrogen clusters on a helium atom at 60 keV/amu. The results will appear in a coming article.

In prospect, we'll be interested to the process of production of an H_3^+ ion during the multi-ionisation of the cluster.

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