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***CLUSTER IMPACTS AT keV AND MeV ENERGIES:
SECONDARY EMISSION PHENOMENA***

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CLUSTER IMPACTS AT keV AND MeV ENERGIES: SECONDARY EMISSION PHENOMENA

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Abstract:

Polyatomic projectiles of different types over a broad range of velocities have been used to bombard solid targets. Electron, ion and neutral secondary emissions were measured in experiments at low and high impact velocities. In both nuclear and electronic stopping power regimes, the nonlinear effects which are observed in the secondary emission are characteristics of collective effects induced by cluster impacts. Several recent experiments are described and discussed. Massive clusters like C_{60} at several tens of MeV can now be accelerated to large velocities and large amount of matter containing high mass molecular ions can be emitted in single impacts. The collision with solids of these exotic projectiles is an emerging field and several aspects are discussed in the paper. The experimental results which are presented were obtained at Orsay.

Keywords : secondary emission, cluster at keV and MeV energies, TOF mass spectrometry, ions-solid collisions

Introduction

Polyatomic projectiles are a unique tool for bombarding small areas of a solid by several atoms simultaneously and for depositing large energy densities in the atomic systems of solids. This paper summarizes some experimental results obtained in the last years in the field of collision of polyatomic ions with solid materials over a broad range of incident velocities. The energy which is deposited during the interaction processes with the target atoms as a whole or with their electronic systems may dissipate through various exit channels. For example, the emission of electrons, neutral atoms and molecules, atomic ions, molecular and cluster ions, photons and X-rays can be observed on a short time scale after the collision event (10^{-10} - 10^{-15} s). The material modifications (tracks and defects) that result of the relaxation of the energy may also be investigated, usually a long time after the collision. We will focus mainly on secondary emission from the surface (and the bulk) of the solid target. The rate of emission, the ejectile velocity and angular distribution, the type of structures emitted (molecular ions, clusters...), etc. can be used to probe the projectile solid interaction and the response of the solid to the energy dissipation. In recent years there has been a renewal of interest in collisions of complex ions with solids due to new experimental possibilities. Cluster ion sources have been improved and developed in several laboratories. Many different types of polyatomic ions have been used as incident particles to bombard a surface. One of the most spectacular improvements is probably the production, in the gas phase, of very large stable structures like multiply charged macromolecules with masses well beyond 100000 u. A new very interesting projectile is also the fullerene molecule. Beams of C_{60} from tens of keV to tens of MeV are now available in a few laboratories.

In this broad domain, the fundamental research is closely linked to existing and potential applications. An important application for instance is the detection of massive macromolecular ions. Once massive ions are in the gas phase, the conventional way of detection is to accelerate them in order to generate secondary electrons and ions resulting from a collision with the surface of a solid detector or with an electron or an ion conversion dynode. Experiments providing a detailed study of these types of collisions may result in an improved detection system for which there is actually a growing interest. Other topics in surface analysis, film deposition, micromachining of surfaces and material modifications are subjects which have been reviewed in the proceedings of conferences held in the last years [1-4].

A recent important step in the development of the field was the acceleration, of large clusters and molecules to high velocities with electrostatic type accelerators. The pioneers were Beuhler and Friedmann who accelerated water cluster molecules $(\text{H}_2\text{O})_n\text{H}^+$ ($n \leq 150$) up to energies of 300 keV [5]. The first experiments on secondary ion emission with fast clusters were performed by Thomas et al with hydrogen clusters [6] containing up to 60 atoms at a total energy of 600 keV, and by Salhepour et al [7] with small hydrocarbon clusters at energies in the MeV range. The massive cluster and molecular beams which are now accelerated by tandem accelerators [8-11] to energies of several tens of MeV have considerably extended the field of polyatomic ion impact.

In all regimes of projectile velocity, the simultaneous impact of several atoms on a small surface of a solid induces collective effects which are not present in single ion impact. The experimental phenomena observed in these many body processes are in most cases unexplained by standard theory. The complexity of the interactions is such that theoretical research through molecular dynamic simulation is probably a useful approach to understand the reality. At the present time, the experiments are ahead of theory.

When single atomic ions are used as projectiles, it is usual to consider 2 regimes of velocity which correspond to the two different modes of energy loss processes of a particle in a solid : electronic collisions and atomic collisions. The Bohr velocity v_0 of about 0.2 cm/ns is a value that "separates" the 2 velocity regimes. In fact well beyond v_0 , only the electronic stopping power dominates while well below v_0 , only the nuclear stopping power should be considered. At intermediate regimes of velocity both electronic energy loss and nuclear energy loss are present. With cluster projectiles, the velocity of impact still remains an important parameter but it is more difficult to establish a clear separation in terms of impact velocities. Highly charged massive molecules, clusters and/or « droplets » may have several MeV of energy with a very low velocity. The total energy, energy loss, range of atoms in the solids and the number and nature of the atomic constituents as well as projectile velocities are important and useful quantities to be considered. The energy density per unit volume is a more relevant parameter although it is not easy to quantify ; it is certainly the amount of energy that is locally deposited in the solid that induces, by its fast dissipation, transient conditions of pressure and temperature that are responsible for the spectacular effects created by impact of cluster in all regimes of velocity. A review on collisional sputtering under cluster impact was made by Andersen [12] and some aspects of polyatomic ion impact induced desorption were discussed in a general paper by Demirev [13].

We will first discuss recent results on electron emission from solids bombarded by heavy polyatomic ions (molecular ions) at low impact velocities, regarding a possible electron emission velocity threshold. Secondary ion emission from solid surfaces induced by impacts of the same type of projectile will be also recalled. In a large range of energy per atom ($4 < E/n < 11.000$ keV) gold clusters Au_n were used as projectiles to study the emission of electrons, emission of ions and also the total sputtering from various targets. There is a complete set of data with Au_n clusters. Carbon clusters and C_{60} molecules were also produced at different velocities and used to bombard targets. At low and high energy the C_{60} projectile is an excellent probe for the desorption-ionization of molecules and large biomolecules. Results are presented at the end of the paper.

PART I - Low velocity clusters

1. Secondary electron emission at low impact velocity

The electron emission from solids induced by polyatomic ion impact yields information on the physical processes occurring during (and after) impact. However, the experimental conditions must be very well defined as the electron yield measurements are sensitive to surface and vacuum conditions. Thus, the comparison of electron emission from surfaces bombarded by different projectiles should be made in the same vacuum chamber under the same experimental conditions. In the literature, relatively large differences on electron emission yield are observed in "identical" experiments. We will concentrate mainly on electron emission in the low impact velocity regime where applications for detection of massive molecules are important. A first approximation of the electron emission yield by polyatomic ion projectiles follows the additivity rule $\gamma(A_i)_n = \sum_n \gamma(A_i)$ where A_i is the mass of the atomic constituents,

γ the electron yield per impact and n the number of constituents. Each individual atom is assumed to behave independently. As will be seen later, there are deviations from this rule which imply that the electron emission velocity threshold, V_{th} , for a cluster projectile is smaller than the threshold for the individual constituents. The notion of velocity threshold is related to the sensitivity of detection which can be different in two experimental set ups. In event by event experiments a single electron must be detected with a known probability. A measured threshold is in any case an "apparent" threshold.

Two main mechanisms are responsible for electron emission at low velocity. Potential electron emission (PEE), requires high positively charged clusters approaching a surface, while kinetic electron emission (KEE) depends on the impinging velocity. The potential energy of the projectile is released through Auger electron capture processes and deexcitation. This is a fast process that does not depend on the kinetic energy of the projectile. The PEE of clusters is lowered with respect to multiply charged atomic ions since other modes of energy dissipation can compete with Auger processes [14,15].

In experiments performed by Axelsson et al [16] with large molecules of albumin containing charge states from 34^+ to 84^+ , the increase in the electron emission yield at a constant impact velocity between $3 \cdot 10^4$ m/s and $5 \cdot 10^5$ m/s shows only a small contribution of the incident charge which would correspond, in this velocity range, to a relative contribution of 10 %. Experimentally, no effect is detected by Axelsson et al, in contrast with the results of Mahoney et al [17], obtained with large multiply charged water-glycerol macroclusters in the mass range 10^6 - 10^7 u at lower velocities, around 10^3 m/s. These authors attribute the large electron emission to a potential electron emission ($50 e^-$ per impact for an incident charge state of 170^+ !). Potential electron emission with multiply charged molecular ion at low velocities is an interesting subject which requires more experimental results.

The kinetic electron emission is induced by direct interaction of the projectile with the atoms of the target. The type of bondings in polyatomic projectiles is probably important as shown by K. Toglofer et al. [18]. They have bombarded clean metal surfaces with the projectiles Ne^+_{40} , $(N_2)^+_{30}$ and C_{70} with about the same mass, at the same velocity (around $3 \cdot 10^4$ m/s). They observe lower electron emission yields with projectiles having molecular bonds, as in $(N_2)^+_n$ and C_{70} . One explanation could be that part of the initial kinetic energy would be transformed into internal excitation during the collision time. Delayed electron emission could even occur.

If one considers only the electron emission induced by impact of low velocity molecular projectiles, Beuhler and Friedmann [5] were the first to use large molecular clusters (water clusters striking a copper surface), in the mass range from $3 \cdot 10^2$ to $6 \cdot 10^4$ u. They also used beams of $(C_nH_m)^+$ projectiles and have derived experimental nuclear stopping power $\left(\frac{dE}{dx}\right)_n$ from electron yield measurements. A comparison of secondary electron yields from accelerated water cluster ions with masse up to 50.000 u, striking Al_2O_3 and copper surfaces was

presented several years ago by Beuhler [19]. The range of investigated velocities was from 1 to $4 \cdot 10^4$ m/s. Several tens of electrons were observed per impact, above $3 \cdot 10^4$ m/s. When the electron yield reaches 1 electron per impact ($\sim 10^4$ m/s) the values are not very reliable in this experiment because of the detection by means of a Faraday cup.

Absolute electron yields were measured in the past few years with different projectiles, various electron emissive surfaces and also better sensitivity. One goal was to improve the detection efficiency of large molecular ions.

Bio-molecular ions like LHRH (MW = 1183) and Insulin (MW = 5733) were used as projectiles, to emit electrons from a copper surface in the velocity range of 1.8 to $4 \cdot 10^4$ m/s. The number of electrons was precisely measured by a surface barrier silicon detector [20]. An « apparent threshold » was obtained at about $1.8 \cdot 10^4$ m/s. It is also shown in this work that an average number of 8 electrons is emitted per impact of LHRH at 10^6 m/s. Moshhammer and Matthäus [21] have measured a mean electron number of 9 electrons under impact of an organic molecular ion of mass 2000 at about $5 \cdot 10^5$ m/s on a solid surface of Al_2O_3 . With a cesium iodide surface, a number of 40 electrons was measured under the same experimental conditions.

The most recent results on electron yield measurements at low velocities of molecular projectiles, are the ones from the Manitoba [22] and Orsay [23] groups. Molecular ions with masses ranging from 1000 to 110.000 u were used at velocities varying from $4 \cdot 10^3$ m/s to $\sim 2 \cdot 10^4$ m/s in ref. [20] and from $5 \cdot 10^3$ to $7 \cdot 10^4$ m/s in ref. [23]. The bombarded surfaces were stainless steel and CsI at $\sim 10^{-7}$ torr. From the Manitoba results, the nature of the surface does not seem to play an important role at velocities below 10^4 m/s.

In the « threshold » velocity region (actually below 10^4 m/s), the electron yield (for a given projectile mass) varies as fast as v_p^4 , v_p being the projectile velocity. Above $2 \cdot 10^4$ m/s, the variation of the electron yield γ_e is not as rapid and varies linearly with v as $\gamma_e \propto (v - v_0)$ with $v_0 \sim 1.5 \cdot 10^4$ m/s. Fig. 1 shows the Orsay data in the low velocity region. The γ_e values are systematically smaller than the results of G. Westmacott et al [22]. In these experiments, single electrons are detected and the emission yield is smaller than one electron per impact. Several factors in these event by event experiments can play a role in the absolute measurements, like the determination of the exact number of molecular ions impinging on the surface, and also the detector sensitivity (or efficiency). The difference between the two experiments is not too surprising. The main point is that they both indicate that large mass ions are still detectable at

low velocity by electrons. Fig. 2 shows the reduced electron yield per projectile mass unit γ_e/u as a function of the velocity in m/s and/or energy per mass unit eV/u.

As already mentioned, internal excitation of molecular bonds upon impact with the solid surface give rise to the breaking of bonds that results in a kind of thermoionic electron emission. A free electron would therefore be accelerated before multiplication by the electric field which is used to extract the electrons. In these experiments, other mechanisms, different from the kinetic electron emission, may exist. It must be noted however, that in all experiments related to collisions of large molecules at very low velocities, the total secondary ion yield emitted from a surface by bombardment with large mass ions is always much larger than the electron yield (see later).

With regard to the dependence of the electron yield with mass at a given velocity, a general dependence can be written as $\gamma_e = m^\beta f(v)$ with $\beta \sim 0.7$. Large molecular ions are complex molecules but their basic atomic composition remains the same. There is a sublinear effect of the electron emission with the total mass of organic projectiles.

2. Secondary ion emission at low impact velocity

It has been shown that for low impact velocity of molecular ions, the secondary ion emission is larger than the electron emission [23-27]. Measurements of secondary ion yields [25] with projectiles of mass up to 66.000 show that the total secondary ion yield is always larger than one at velocities above 0.5×10^4 m/s. Wien et al [28] used projectiles with very large masses, up to 2×10^6 u at lower velocity ($\sim 0.06 \times 10^4$ m/s). They also found that the detection efficiency by using ion to ion conversion (with impact on a CsI surface) is close to 100 %. In their experiments the electron yield value was 0.01 per impact. The detection of large species by ion to ion conversion is more efficient than with electrons. Massive projectiles deposit all their energy on a small surface in the very first layers of the solid. The mass spectra of the secondary ions exhibit a large fraction of masses from contaminant layers but secondary ions from the sample material are also clearly visible. The negative secondary ions $(\text{CsI})_n\text{I}^-$, were observed with a large yield in the bombardment of a sample of CsI by molecular ions of Albumin, Insulin and LHRH at 18 keV [29]. Let us recall that the calculated range of a carbon atom, with an energy between 10 and 60 eV, in an organic material varies from 3 Å to ~ 9 Å. A multiply charged macromolecular accelerator (MUMMA) that consists of an electrospray

source and a quadrupole mass filter has been used to produce and accelerate molecular ions in the mass range 1000-66000 u with energies from 10 to 520 keV [30]. At the impact velocities of $\sim 3 \times 10^4$ m/s), the number of secondary ions emitted per impact of insulin, Lysozyme and Albumin projectiles is also larger than one [29].

Intact large secondary molecular ions can also be emitted from solids by impacts of high mass molecules [31] on bio-organic samples. A "massive cluster impact" source was designed by Mahoney et al [31] ; experiments were performed with multiply charged glycerol droplets striking a solid surface (the energy per mass unit of the projectiles is only 0.1-1 eV). Mainly, multiply protonated ions dominate the secondary ion mass spectra and surprisingly, almost no fragmentation is observed. In these experiments with masses as high as 10^6 - 10^7 u most of the projectile energy is deposited over a distance smaller than a sample molecule diameter. The simultaneous impact of a large number of atoms generate a transient pressure that propagates the surrounding molecules without breaking internal bonds. For these soft desorption experiments a shock wave model [32] was proposed to explain the emission phenomena.

Until now highly charged bio-molecules or microdroplets have been used as projectiles at relatively low velocities. In the future, large velocity molecules could be obtained by using very high acceleration voltage. This aspect will be discussed at the end of the paper.

3. Secondary ion emission at intermediate energy of cluster impact (below MeV energy)

The general aspects and the mechanisms of ion sputtering phenomena are similar to the neutral sputtering phenomena. The ionization processes are not very well known and it may be difficult to separate the role of the ionization from the sputtering process itself. It is, however, much easier to measure secondary ions than neutrals and it is also easy to identify the different types of emitted secondary ions with accuracy.

Nonlinear effects in the enhancement of secondary ion sputtering were first observed with dimers of Ne_2 and Ar_2 [33] and small molecules [34]. In 1985, Thomas et al [6] used cluster beams of hydrogen H_n ($3 < n < 23$) to bombard a CsI surface. A large non linear effect was observed. The authors emphasized the potential analytical applications of microcluster beams in secondary ion mass spectrometry analysis (SIMS). SF_6 clusters were later used [35] in SIMS and compared to the sputtering yield of Cs^+ atomic ions. An enhancement factor of

about 20 for positive secondary molecular ions ($m/z \sim 300$) was measured when comparing SF_6 to Cs projectiles between 5 and 20 keV [36]. A comparison of yields of negative molecular secondary ions ($m/z > 80$) using bombardment with SF_5 and SF_6 instead of monoatomic Xe primary ions shows an enhancement of two orders of magnitude [37]. Heavier projectiles as $(\text{CsI})_n\text{Cs}^+$ clusters were later used by the Texas A&M group [38] who obtained data showing yield enhancements. Complex organic and inorganic projectiles ($73 \leq m/z \leq 600$) at energies between 5 and 30 keV as well as Cs iodide clusters were also used at Orsay [39] in event by event coincidence experiments. The advantage of coincidence measurements in these experiments was clearly shown. Each projectile was well identified and quantitative results on secondary ion emission yields were obtained in desorption experiments with organic and CsI targets. A systematic study was performed by the Orsay group with $(\text{Au})_n$ clusters produced by a liquid metal ion source at energies between 5 and 60 keV. A variety of targets was used and several types of secondary ions were observed. A comparison of Au_n and $(\text{CsI})\text{Cs}^+$ clusters as projectiles is presented in this work [40]. Figure 3 shows the emission yield of a small organic molecular ion (phenylalanine) as a function of E/u (energy per mass unit) of Au_n cluster projectiles. The main conclusions of this work are that :

- the number of constituents is an important parameter
- the non linear enhancements of yields are more important for complex secondary ions than for atomic secondary ions.

This is a general finding in cluster collisions with solids. A relative large amount of matter is ejected per impact. As shown later on, the impact of one Au_5 cluster on a gold target generates on the average the emission of about 3000 gold atoms. Here the emitted clusters are identified in mass and the enhancement factors increase when large clusters are emitted by large cluster projectiles. For analytical purposes a cluster ion gun could be an excellent probe for analysis of molecules present at the surface of solids.

A comparison of the emission yield of secondary molecular ions desorbed by molecules of coronen $(\text{C}_{24}\text{H}_{12})^+$, C_{60}^+ , Cs^+ ions, Au^+ and Au_n clusters has been made by Baudin et al [41-42]. It was shown that C_{60} molecular ions at energies between 5 keV and 30 keV are even more efficient for inducing secondary emission than Au_4 projectiles at the same velocity of impact. C_{60}^+ ions and Au_4^+ have about the same mass but they contain a different number of atoms. In the case of C_{60} , the depth of penetration of each atom of carbon in an organic layer is much less than the range of one gold atom. Therefore the projectile energy is deposited closer to the surface with C_{60} , giving rise to a larger emission rate. Fig. 4 shows the variation

of the emission yield of molecules from targets of phenylalanine (mw = 165) prepared by vapor deposition and from Langmuir-Blodgett films of Cd stearate (mw = 285).

A comparison of secondary ion yields from C_{60}^+ projectiles with atomic and polyatomic projectiles at 10-30 keV has also been recently reported by Van Stipdonk et al [43]. It was shown that the secondary ion yield of molecular ions from a phenylalanine target is more than an order of magnitude larger with C_{60}^+ than with Cs^+ projectiles at the impact energy of 20 keV. Molecules with large masses have not been investigated in this work but the enhancement should be bigger for large molecular secondary ions. In these experiments on SI yields with C_{60} projectiles, the C_{60}^+ ions were produced as secondary ions by the passage of fission fragments through an aluminized mylar foil coated by layers of C_{60} material. The double TOF coincidence technique was used. For analytical purpose a reasonably focused beam of mass separated C_{60} ions with energies of 20-40 keV could be developed for SIMS analysis.

PART II - Fast clusters

In the following section, cluster projectiles with energies of several MeV were used in various types of experiments. We describe briefly the methods which have been developed to accelerate cluster ions to high energy.

The production of high energy clusters (MeV) has been described in several recent papers [8-10]. Singly charged negative clusters are obtained by sputtering a target with 20 keV Cs^+ ion from a Cs gun. These cluster ions are accelerated from ground potential to 200 kV before entering an electrostatic accelerator (tandem type). The terminal voltage of the tandem accelerator at IPN can vary from 2 to 14 MV. The negative clusters accelerated to the high voltage terminal collide with N_2 molecules in a gas channel, lose several electrons, and are accelerated again toward the exit of the accelerator as positive clusters. The identification of the cluster projectiles is made by time-of-flight, magnetic analysis and energy measurements. It is obvious that the collisions of polyatomic ions with solids at very large energy produces effects which are not observed in single ion collisions. This is actually a virgin domain of research. We will summarize some of the most recent results, some of them being yet unpublished.

1. Sublinear effects in the electron emission from solids bombarded by fast gold cluster

Recent papers by Baragiola [14] and Fallavier [44] give a review on electron emission by cluster impacts. One of the basic questions is : How does the solid respond to the impact of one atom by comparison to the simultaneous impacts of n atoms in a cluster at the same velocity. A limited number of experimental results exist on this subject and these results are apparently contradictory. A systematic study on electron emission was made by the group from Lyon with light H_n clusters [45,46] striking carbon targets at energies/u from 30 keV/u to several hundred keV/u. Below 200 keV/u the ratio γ_n/γ_1 for a given n was found to be slightly smaller than 1 and slightly larger than 1 at about 200 keV/u. (γ_n is electron yield for a cluster of n atoms and γ_1 the yield for one atom). The mechanisms involved in these « positive » and negative molecular effect are not completely elucidated but the impact velocity plays a crucial role. The target material is of course also an important parameter.

Heavy clusters of Au_n^+ ($1 < n \leq 5$) over a large energy range between 30 keV/atom and 6000 keV/atom were recently used to investigate electron emission from a CsI surface [47]. The ratio γ_n/γ_1 is always smaller than one, and the more atoms in the cluster the less electrons emitted (per atom) upon cluster impact, as shown in Fig. 5. The ratio γ_n/γ_1 decreases with increasing incident cluster energy. The sublinear effect in electron emission is therefore more important at larger energies. The target surface was CsI in a vacuum chamber at 10^{-7} torr. The explanation for this effect is an ionization occurring in the upper shells of the target atoms, in correlation with the electronic stopping power which also increases with energy. When the cluster passes through the CsI crystal, the front atoms of the Au_n projectile ionize and emit an electron from the upper shell. The following and next atom in the same cluster have a much lower probability to eject another electron from the same target atom, because the cross section of double ionization is much smaller. The number of available electrons for ionization by the "last" atoms in the clusters is reduced. Experiments with carbon clusters C_n ($n \leq 10$) recently performed in the same velocity regime also show a sublinear effect in the electron emission yield [48].

The study of electron emission with cluster may be a way to probe the spatial proximity of the atoms in the clusters after a certain distance of penetration.

The electron emission refers to close binary collision mechanisms. The sublinear effects observed with Au_n^+ and C_n^+ clusters indicate that at the entrance side of a foil the atomic

constituents are close to each other. For high velocity clusters, the persistence of the same effect at the exit side of a thin foil means that the separation distance between the atoms is on the order of atomic distances. The variation of this the sublinear effect at the exit side of foils with different thicknesses may hence give information on the radial distance separation of the cluster atoms in the solid.

2. Total emission of atoms (neutrals and ions) induced by gold cluster impacts

The first results on the total sputtering (atoms, molecules) by cluster impacts were obtained a long time ago (see review in ref. [12]). A non linear enhancement of the emission yield was observed for cluster impact by comparison with single atom impacts at the same velocity. The ratio Y_n/nY_1 , expressing the emission yield Y_n induced by a cluster containing n identical atoms over n times the yield for one atom, is larger than one. This was shown for example, with clusters of Sb_2 , Sb_3 at 30 keV/atom, Bi and Bi_2 at 45 keV/atom were used to bombard metallic surfaces as Au or Ag [49,50]. The first data on the non linear effects in the emission yield are from Andersen and Bay who bombarded Ag targets with Te and Te_2 [51].

In order to extend the range of bombarding energy and to observe effects with large size heavy clusters, gold clusters Au_n $1 < n < 5$ have been used to bombard metallic targets of gold, in the energy range from 50 keV/atom up to 800 keV/atom [52]. These experiments are in progress but some preliminary results which are shown in Fig. 6 indicate that there is a strong non linear enhancement (between $n=1$ and $n=5$) in the total sputtering yield of gold atoms over the whole energy range [52]. The experiments were performed at Orsay with the ARAMIS tandem accelerator (2 MV). A thick layer of gold metal was deposited on the quartz oscillator of a micro balance. The decrease of the quartz frequency under the beam impact is directly proportional to the amount of removed material. The results obtained at Orsay with single gold atoms as projectiles are in good agreement with those obtained by Bay et al [53] with a gold target. The Orsay results with Au_2 and Au_3 are however in disagreement with the measurements of ref. [50]. As the size of the Au_n cluster increases, the maximum of the sputtering yield value for a given cluster projectile occurs at lower projectiles velocities. Large sputtering yield value per atom of about 300 are obtained with Au_3 and of about 600 for Au_5 . Therefore several thousand atoms of Au are emitted by Au_n cluster impact $n>4$. The linear collision cascade sputtering theory [54] does not explain these large emission yields. The concept of a spike was introduced to describe a spatial region in the solid where dense collision

cascades take place [55]. The multiple collisions and the overlapping of cascades which are initiated in a solid upon impact of a cluster as Au_n immediately creates spike conditions.. A "thermal spike" model was developed by Sigmund and Claussen [56] and Johnson [57] to reproduce the data on cluster induced sputtering. A poor agreement between theory and experiment was found at low energy (below 100 keV) for the sputtering of Ag atoms by Sb_3 . To reproduce the variation with energy of the sputtering yield of Bi and Ag bombarded by Bi_2 and Sb_n ($n=1-3$), Johar and Thompson [50] have varied the sublimation energy of atoms in their calculation. From a Monte Carlo simulation they conclude that the multiple collisions at the surface layers result in a much reduced surface binding energy, before thermal equilibrium. The density of collisions at the surface would be the relevant parameter. Brunelle et al [52] have used the Sigmund and Claussen model to fit the data on sputtering of gold atoms by Au_n between 30 and 2000 keV/atom. The spike is modeled as a cylindrical volume with a radius ρ (at normal incident angle of the clusters). The secondary emission is assumed to take place from the surface. The emission of ~ 3000 atoms of gold per impact of Au_5 (on the average !) corresponds to a volume of about $10^5 \text{ \AA}^3$ and it does not seem possible that they all evaporate uniformly from the target surface layer. Increasing the radius of the emission area with increasing energy is however a way to take into account the decrease of the energy density as a function of the incident energy and to reproduce experimental data. Experimentally, when the incident energy increases, the sputtering yield increases until a maximum and decreases. The results on total sputtering with gold clusters will be the most complete set of results on the total sputtering of a metallic solid target. The analysis is not yet finished.

There is however a lack of experimental results in the neutral sputtering by cluster impacts. Physical parameters such as velocity and angular distributions of the emitted particles as a function of parameters in the entrance channel (size of clusters, angle of incidence...) are necessary to put constraints for testing the models. Measurements of angular distributions have been recently made at the Niels Bohr Institute [58]. An important observation would be also the emission rate of clusters. The total emission rate does not give enough information. An average value is obtained that does not tell much about possible "special" or "super" events which occur in the collision processes. In a recent paper by Hartman et al [59], the production of clusters in large sputtering events is discussed. Clusters are produced during (or in) events which sputter a large number of atoms. These conditions are fulfilled in almost all collisions by Au_n clusters and it is likely that Au_n clusters are ejected but experimental observations are difficult..

The processes involved in the collision cascades, spikes... induced by cluster projectiles are very complex and analytical models are difficult to use. Numerical simulation are more adapted to complex situations. Simulations can be considered as "virtual" experiments to track the reality. In terms of speed of output predictions and comparison with experiments, molecular dynamic simulations performed with various computer codes will be more and more useful. A review has recently been presented by Shapiro [60].

3. Emission of complex secondary ions induced by fast gold clusters projectiles

Cluster beams of Au_n ($n = 1$ to 4) were used to measure secondary ion emission yields from organic and inorganic (CsI) targets from 4 keV to 10^4 keV per atom [61]. The Au_n clusters were obtained in three different ways, depending on the energy range.

1. From 4 to 50 keV a pulsed liquid metal ion source was used as described in ref. [40].
2. From 20 keV to 3 MeV, a small electrostatic tandem accelerator was used with a maximum voltage terminal of 2 MV.
3. Above 1.5 MeV the 15 MV IPN-Orsay tandem accelerator was used.

These experiments with different beams of Au_n and a large range of incident energies were performed with the same experimental equipment under the same experimental conditions. Here we show results on the secondary ion emission yield of $Cs_2I_3^-$ ($m/z = 647$) emitted by impact of Au , Au_2 , Au_3 , Au_4 . Figure 7 shows the results of the variation of yield as a function of E/u , where the comparison of yields can be made at the same velocity of impact. Similar curves were also obtained for organic molecules [61]. The emission yield by single Au impact is quite low, while clusters give a much higher yield, very much enhanced with Au_3 and Au_4 projectiles. The enhancement is, however, not constant as a function of energy and there is a relative maximum of emission yield with Au_4 at around 60 - 80 keV. This "peak" does not correspond to the maximum of the nuclear stopping power, which is at about 700 keV/atom.

Fig. 8 shows the variation of the nuclear and electronic energy loss ($\frac{dE}{dx}$) as a function of energy for Au projectiles bombarding a CsI material. The increase of SI yields above 1 MeV/atom may correspond to the increase of the electronic energy loss but at lower energies the shapes of the variation of SI yields measured with Au_3 and Au_4 remain unexplained. In the nuclear stopping regime, clusters of Au_4 create a dense collisional zone. The energy density near the surface is the important ingredient for secondary emission. In the emission of complex

ionized structures, two other factors are involved which are the ionization probability and the cluster decay or fragmentation probability. It is known that the impact of Au₄ on a CsI surface generate more electrons than single Au [47] but this cannot explain the surprising yield curve shape since the electron emission increases continuously with the incident projectile energy. An increase in the secondary cluster or molecular ion decomposition rate, at the surface, in the collision of Au₄ with the CsI surface, between 80 keV per atom and 800 keV per atom would give rise to a yield decrease in this energy range and could explain a decrease in the emission of intact clusters. It must be noted that the variations with E/u, of the negative I⁻ ions emitted by Au₂ to Au₄ on the same target exhibits a smooth continuous increase. It is only the complex secondary ions that have a maximum emission yield just below 100 keV/atom.

4. Carbon clusters and fullerene projectiles

Beams of C_n clusters (1 < n < 12) were accelerated by several tandem type accelerators (Orsay (Aramis and the IPN tandem), Erlangen, Seattle, Zurich, Weizmann Institute). Beams of C₆₀ⁿ⁺ have been produced at Orsay and Zurich by the 4 MV and 15 MV tandem accelerators.

It was recently shown that large craters can be formed at the surface of organic samples by impact of C₆₀. Crystals of valine molecules [62] and Langmuir-Blodgett films [63] were examined by atomic force microscopy after irradiation by C₆₀ at 20 MeV. In both materials, craters with diameters larger than 400 Å and 150 Å in depth were observed. In valine crystal the average size of craters corresponds to an emission of matter of 10⁷-10⁸ u. It is therefore not surprising that a large secondary ion yield is observed under impact of such projectiles. In measurements on energy loss of carbon clusters in carbon foils, it was shown that the energy loss by clusters is equivalent (within 5 %) to the sum of the energy loss of each constituents arriving independently [64]. The energy loss of C₁₀ at 0.4 MeV/atom is about 7 keV/nm and is close to the energy loss of ~10 keV/nm by an atomic ion of mass ~100 and energy 100 MeV in an organic sample. Although the energy losses are comparable, the volume of energy deposition is much smaller in the case of clusters because the range of δ electrons produced from the collisions with the solid is also much smaller. The energy density is the key parameter. Figure 9 shows the emission yield of cluster ions of valine molecules ejected from a valine target by C₆₀ at 0.336 MeV/atom and C₁₀ at 0.42 and 2 MeV/atom [65]. The results with fission fragments as projectile are also shown in the same figures. Clusters of molecules up to at least 11 molecules are observed with C₆₀ projectiles while no cluster above 6 molecules is

seen with MeV atomic ions. Quite surprising results were also obtained with pure carbon foils as targets. Very large yields of negative C_n^- ions with $n > 22$ were measured under 20 MeV C_{60} impacts [65]. Single carbon projectiles at the same velocity as 20 MeV C_{60} do not produce any observable carbon clusters (yield smaller than 10^{-5} per impact). Fig. 10 shows the results of the C_n^- yield as a function of the size of the carbon clusters. Measurements of secondary ions were made in the reflection mode and in the transmission mode. In the transmission mode, C_n^- secondary ions are emitted from the exit side of the carbon foil after passage of the C_{60} projectiles through the foil. The experimental reaction chamber containing the targets and the time-of-flight tube is designed for measuring secondary ions emitted from the front side of the target or from the exit side. The bottom of the chamber can rotate by 360° with respect to the incident direction of the beam so that the emitting surface of a foil is the same as in the reflection mode. In the carbon target foil the carbon atoms from the C_{60} projectile are first in close proximity while traveling through the foil. The carbon atoms being rapidly singly or multiply charged tend to separate under Coulomb repulsion and multiple scattering.

The measurements of secondary ion yields at the exit side of a foil can give information on the proximity of the atomic constituents after a certain thickness. If the atoms are very far from each other, the emission yield will be the sum of independent effects induced by each constituent. If they are very close to each other, the collective effects will still be present and a large emission yield will be measured. As an example, Fig. 10 shows the emission yield of C_n^- measured in the transmission mode with a carbon foil thickness of 32 nm. The emission yield by transmission is even larger than by reflection and the yield enhancement is attributed to a charge state increase of carbon atoms at the exit side. In these experiments it was shown that the exit secondary ion yield decreased with increasing foil thicknesses. The secondary ion emission was thus used to probe the spatial proximity of atomic constituents of atomic constituents of a cluster passing through solid material. Large sputtering yields were also observed in the bombardment of $SiO(SiO_2)$ films by carbon clusters C_n ($n = 4-10$) at energies of 300-700 keV/atom [65].

5. High yield of secondary emission of large bio-molecules by fullerene impacts at 20 MeV

High energy atomic ions were used in the past to desorb intact molecules from bioorganic samples. Fission fragments from a ^{252}Cf source were first used by Macfarlane and co-workers [66] who named the method Plasma Desorption Mass Spectrometry (PDMS). For

about 10 years, it was the only method available for producing, in the gas phase, large molecular ions with molecular weight above 10.000 u. Historically, the discovery initiated research in several laboratories on the interaction between MeV atomic ions and solid material. The results described previously with C_n and C_{60} projectiles motivated investigations of biomolecular samples. Samples of Insulin and Trypsin were electrosprayed on nitrocellulose backing and bombarded with 20 MeV C_{60} at a rate of a few hundreds per second. The range of the carbon atoms after the fragmentation of C_{60} molecules at the surface is less than 1 μm in organic material and therefore, the secondary molecular ions can only be emitted from the entrance side of the targets used in these experiments [67]. The TOF measurements of the secondary ions were made in the usual event by event counting mode but the start signal was obtained from H^+ ions emitted with a very high yield by each incident C_{60} projectile. Fig. 11 shows the Trypsin mass spectrum recorded from 10.000 impacts of C_{60} molecules. The emission yield is about 100 times larger than with MeV atomic ions or fission fragments. For example, there is, on the average, more than one molecular ion of Insuline emitted per C_{60} impact. These results demonstrate that depositing a high energy density into a solid induces the ejection of a large quantity of matter that contains also more molecular ions and clusters than with any other types of projectiles. By using different clusters C_n and C_{60} at the same velocity the role of the energy density could be explored in the future. Molecules with masses above 100.000 u could also be investigated.

The impact of very large masses like microdroplets of mass $\sim 10^6$ at 2 MeV [29] also produces large molecules in the gas phase. Unfortunately, the number of emitted molecular ions per impact is not known in these experiments and the exact incident mass and energy of these heavy projectiles are also not precisely known. It is difficult to compare the effects induced by the fast (C_{60}) and the very slow heavy microdroplets. The regime of impact velocity and energy loss mechanisms are also very different. From a practical point of view the production of high energy C_{60} requires sophisticated equipment. A simplification might be achievable in the future.

In the future heavy multiply charged molecules (or multiply charged droplets) could be used as projectiles accelerated to very large energies, in the electronic stopping regime. Their collisions with a solid would deposit locally a very high energy density and would further enhance the effects already seen with the available fast cluster beams.

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Figure 1 - Secondary electron yield γ_e as a function of the energy per mass unit (eV/u, bottom scale) or as a function of the velocity (10^{-4} ms $^{-1}$, top scale) of C_{60} (mw = 720 u), LHRH (mw = 1182 u), bovin Insulin (mw = 5733 u), bovin Trypsin (mw = 23295 u) and bovin serum Albumin (mw = 66430 u) projectile (from ref. [23]).

Figure 2 - Reduced electron yield for Trypsin and Albumin projectiles on a CsI surface. The electron yield is divided by the mass of the projectiles. The fit to the Manitoba data (ref. [22]) is shown for comparison. The line through the Orsay data is to guide the eyes (from ref. [23]).

Figure 3 - Yield variation of secondary ions (M-H)⁺ (mw = 163) from an organic target (phenylalanine) as a function of primary ion energy per mass unit (E/A). The primary ions are gold clusters Au_n^{p+} with n=1 to 5 and p = 1 or 2 (from ref. [40]).

Figure 4 - Yield variation of secondary ions (M-H)⁻ from a phenylalanine target and Cd stearate Langmuir-Blodgett films with projectiles of C_{60}^+ (720 u) and Au_4^+ (788 u) as a function of energy (eV/u) (from ref. [42]).

Figure 5 - Comparison between the experimental and calculated negative electron emission yield γ_n/γ_1 versus Au_n projectile energy $E = 1000-8000$ keV/atom for a CsI surface (from ref. [47]).

Figure 6 - Preliminary results of the sputtering yield per atom of gold atoms emitted from a gold target bombarded by gold clusters Au_n ($n = 1$ to 5). (ref. [52])

Figure 7 - Secondary ion yield of negative atomic ions of I^- (a) and of $Cs_2I_3^-$ (b) from a CsI target bombarded by Au_n clusters (ref. [61]).

Figure 8 - Variation of the nuclear energy loss $(\frac{dE}{dx})_{\text{nuc}}$ and of the electronic energy loss

$(\frac{dE}{dx})_{\text{electr}}$ for Au projectiles into CsI material, as a function of energy (calculated from the TRIM program).

Figure 9 - Yields of molecular cluster ions of valine ($\text{C}_5\text{O}_2\text{NH}_{11}$, mw = 117 u) ejected from a solid film of valine, bombarded by C_{60} projectiles and by fission fragments.

Figure 10 - Measured yields of C_n^- clusters as a function of n with C_{60} projectiles.

- transmission yield : C_n^- are emitted from the exit side of a 32.5 nm carbon foil
- + reflection yield : C_n^- are emitted from the entrance side of a 32.5 nm carbon foil
- ◆ transmission yield after passage of the carbon constituents (from C_{60}) through a 140 nm foil [65].

Figure 11 - Time-of-flight spectrum of large biomolecular ions from a Trypsin solid target (mw = 23295 u) obtained after impact of 10^4 C_{60} ions at 20 MeV (from ref. [68]).