

ACTA UNIVERSITATIS UPSALIENSIS
*Comprehensive Summaries of Uppsala Dissertations from
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321

**ELECTRONIC SPUTTERING OF
ORGANIC SOLIDS**

David Fenyő



UPPSALA 1991

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Doctoral dissertation at Uppsala University 1991

ISBN 91-554-2738-3

ISSN 0282-7468

Abstract

Fenyő, D., 1991. Electronic Sputtering of Organic Solids. Acta Univ. Ups., *Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science* 321, 32 pp. Uppsala. ISBN 91-554-2738-3.

The mechanisms of ejection of material from organic solids following impact of ions in the electronic stopping regime has been studied experimentally and theoretically. The velocity distributions of ejected large intact molecular and fragment ions were measured. A continuum mechanical model and a computer code for molecular dynamics simulations of the ejection process were developed. The yield and velocity distribution of the ejected material were studied as a function of different incident ion parameters such as energy deposition and angle of incidence, and as a function of material properties such as cohesive energy and sample film thickness. Craters in the solid, created during single ion impacts, were also investigated.

It is concluded that different ejection mechanisms have to be invoked in order to describe the ejection of different species. Atoms and small molecules can be ejected directly during dissociation of excited molecules or during evaporation from the volume energized by the incident ion. Larger thermally labile molecules are preferentially ejected by the cylindrical pressure pulse formed during ion impact. The trajectories of ejected hydrogen ions, created within a short time after the passage of the primary ion, are altered by Coulomb interaction with the short lived positively charged track, created at ion impact.

David Fenyő, Division of Ion Physics, Department of Radiation Sciences, Uppsala University, P.O. Box 535, S-751 21 Uppsala, Sweden.

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Graphic System, Stockholm, 1991

This thesis is based on the following papers:

- A. *Sputtering by Fast Ions Based on a Sum of Impulses*
R. E. Johnson, B. U. R. Sundqvist, A. Hedin and D. Fenyő,
Physical Review B40 (1989) 49.
- B. *Molecular Dynamics Study of Electronic Sputtering of Large Organic Molecules*
D. Fenyő, B. U. R. Sundqvist, B. R. Karlsson and R. E. Johnson,
Physical Review B42 (1990) 1895.
- C. *Radial Velocity Distributions of Secondary Ions Ejected in Electronic Sputtering of Organic Solids*
D. Fenyő, A. Hedin, P. Håkansson and B. U. R. Sundqvist,
International Journal of Mass Spectrometry and Ion Processes 100 (1990) 63.
- D. *On the Mechanism of Formation of Alkali Cation Adducts in Plasma Desorption Mass Spectrometry of Biomolecules*
P. Demirev, D. Fenyő, P. Håkansson and B. U. R. Sundqvist,
Organic Mass Spectrometry 26 (1991), in press.
- E. *On the Ejection of Hydrogen Ions from Organic Solids Impacted by MeV Ions*
D. Fenyő, P. Håkansson, B. U. R. Sundqvist and R. E. Johnson,
In manuscript
- F. *Computer Experiments on Ejection of Material from an Amorphous Solid due to a Local Expansion*
D. Fenyő,
In manuscript

I was responsible for most of this work including both development of computer programs for simulations (Paper B, E and F) and performance of experiments (Papers C, D and E). Paper A is a development of a model by R.E. Johnson. Although the main part of this work was performed by him, I have actively taken part in developing the model and writing the paper. Paper D was based on an idea by P. Demirev but I was involved in all portions of the study.

Parts of the work in this thesis has also been presented by myself at the following international conferences:

11th International Mass Spectrometry Conference, 29 August- 2 September 1988, Bordeaux, France. Poster presentation.

A Molecular Dynamics Study of Electronic Sputtering of Organic Solids,

D. Fenyő, B. U. R. Sundqvist, B. R. Karlsson and R. E. Johnson,

Advances in Mass Spectrometry 11b, ed. by P. Langevialle, Heyden & Sons, 1989.

2nd International Workshop on MeV and keV Ion and Cluster interaction with Surfaces and Materials, 5 - 8 September 1988, Orsay, France. Oral presentation.

A Molecular Dynamics Study of Electronic Sputtering of Organic Solids,

D. Fenyő, B. U. R. Sundqvist, B. R. Karlsson and R. E. Johnson,

Journal de Physique 50 (1989) C2-33.

5th International Conference on Ion Formation in Organic Solids, 18 - 21 June 1989, Lövånger, Sweden. Poster presentation.

Radial Velocity Distributions in Electronic Sputtering of Organic Molecules,

D. Fenyő, A. Hedin, P. Håkansson, R. E. Johnson and B. U. R. Sundqvist,

Proceedings ed. by A. Hedin, B.U.R. Sundqvist and A. Benninghoven, John Wiley & Sons, Chichester, 1990, p. 33.

13th International Conference on Atomic Collisions in Solids, 7 - 11 August 1989.

Århus, Denmark. Poster presentation.

3rd International Wangerooze Workshop on the Physics of Small Systems, 11 - 15 September 1989. Spiekeroog, FRG. Oral presentation.

Electronic Sputtering of Large Organic Molecules,

D. Fenyő, A. Hedin, P. Håkansson and B. U. R. Sundqvist,

Proceedings ed. by E.R. Hilf, W. Tuszynski, World Scientific, Singapore 1990.

Interaction of Charged Particles with Solids and Surfaces, NATO-ASI, 6 - 18 May 1990, Alicante, Spain. Poster presentation.

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Introduction

Ion and atom beams can be used in a variety of ways both for material analysis [1] and for material modification [2]. The process in which an incident energetic particle deposits energy in a solid near its surface, thereby leading to material ejection, is called sputtering. Depending on whether the energy deposition process is dominated by collisions with target electrons or by collisions with target nuclei the process is termed electronic or nuclear sputtering, respectively.

In nuclear sputtering three different regimes have been observed in correlation with the energy deposited by the primary particle [3]. At low energy, ejection can occur when a target atom receives enough energy to escape the solid in a direct 'knock on' collision with the incident ion. At higher primary ion energy the recoiling target atoms acquire sufficiently high energy to be able to displace other target atoms from their lattice sites, resulting in collisions cascades. In the linear collision cascade regime the cascades, created by an incident ion, do not spatially overlap [4], but in the 'thermal spike' regime, on the contrary, there exists a large overlap between different collision cascades created by the same incident ion [5].

The phenomenon of electronic sputtering, on the other hand, is less well understood. It has found two major applications so far: in astrophysics where fast ion erosion of condensed gas solids has been studied [6], and in chemistry and biochemistry where electronic sputtering has been used for generation of gas phase ions of involatile biomolecules [7]. Fast ion bombardment of thin films of organic solids consisting of e.g. small proteins (see Figure 1.1) causing electronic excitations and ionizations in the solid, leads to ejection in the gas phase of large intact biomolecules in different charge states. This phenomenon has been exploited to construct ion sources for mass spectrometers, thus allowing precise determination of the molecular mass of involatile organic molecules [8]. Substantial efforts have been made to describe the basic mechanisms involved [9].

The aim of the studies described in this thesis was to investigate the ejection mechanism operating in electronic sputtering of organic solids by incident ions. A brief introduction to the theory is presented in Section 2. The methods employed in the studies, both experimental and theoretical, are presented in Sections 3 and 4. In Section 5 the results of the investigations are summarized and discussed. Proposals for the continuation of these investigations are discussed in Section 6.

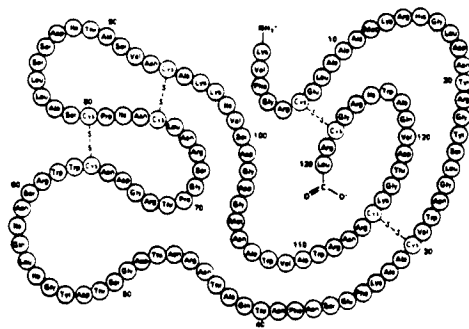


Figure 1.1 Lysozyme ($C_{610}H_{946}N_{192}O_{184}S_{10}$), a protein purified from hen egg-white.

Grau, teurer Freund, ist alle Theorie,
und grün des Lebens goldner Baum.
Goethe

2.1 Energy Loss of Ions in Solids

An ion that penetrates a solid loses energy mainly in collisions with target nuclei (nuclear stopping) or target electrons (electronic stopping). The variations of the energy loss per unit path length of ^{127}I in an organic solid as a function of primary ion energy are shown in Figure 2.1. The major variations of the energy loss can be understood within the framework of the semi-classical atomic model according to Bohr. For ions having a velocity much lower than the velocity of target electrons (roughly given by $v=v_0Z_2/n$, where v_0 is the Bohr velocity and Z_2 is the nuclear charge), the energy loss will be dominated by collisions with target nuclei screened by electrons. The energy loss in collisions with electrons is small because there is a possibility for the orbit of the electrons to change adiabatically due to their large velocity and the long collision time. For increasing primary ion velocity the nuclear stopping first increases because the cross section for collisions increases due to decreased screening. As the primary ion velocity increases further the nuclear stopping decreases because the collision time decreases. Since the screening changes slowly with velocity, the interaction can be roughly described by the Rutherford cross section using effective charges at higher velocities.

The electronic stopping dominates when the magnitude of the ion velocity is larger than the velocities of target electrons. The electronic stopping will also reach a maximum, which is higher in magnitude than that of the nuclear stopping since the electron mass is smaller.

For the case when the ion velocity is high enough for the target electrons to be treated as individual scatterers, an expression for the electronic stopping was derived in 1913 by Bohr [10],

$$-\frac{dE}{dx} = \frac{4\pi Z_1^2 e^4 n}{mv^2 (4\pi\epsilon)^2} \cdot \ln \left(\frac{2mv^2}{I} \right) \quad (2.1)$$

where m is the electron mass, Z_1 the atomic number and v the velocity of the projectile. The material is described by the electron density n and the ionization potential I . The derivation is performed by treating the collisions classically and considering only collisions with an impact parameter smaller than va_0/v_0 , where a_0 is the Bohr radius. For larger impact parameters the collision time will be long and the energy transfer can be neglected. A quantum mechanical justification of Equation 2.1 was later presented by Bethe using the first Born approximation [11]. The secondary electrons, i.e. electrons of the solid which are liberated in collisions with the primary ion, will affect the solid away from the ion trajectory by depositing their energy. Thus, energy will be deposited in direct ion-electron collisions in a region within the Bohr adiabatic radius (a few Ångström) from the ion path, called the infra track. The region in the solid within the penetration range of the secondary electrons is called the ultra track (radius of a few hundred Ångström) [12]. The energy deposited by the secondary electrons in the ultra track is roughly proportional to the inverse square of the distance from the ion path [13].

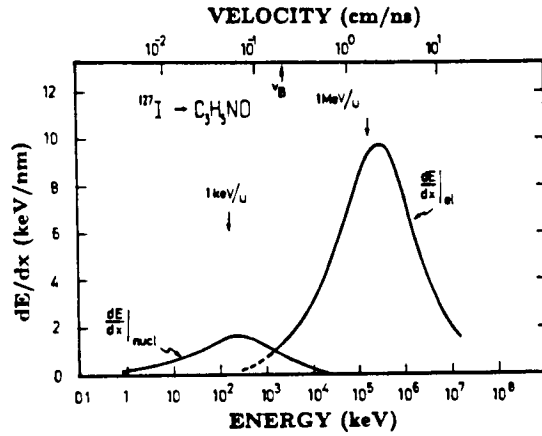


Figure 2.1 The stopping power of ^{127}I in $\text{C}_3\text{H}_5\text{NO}$ as a function of energy.

Equation 2.1 is based on the assumption that an ion collides with one electron at a time. A way to treat collective excitation is to consider the ion passing through a material described by its dielectric function. The polarization of the material due to the charge of the incident ion and the resulting retarding force can be calculated and gives the energy loss [14].

More generally, an expression for the electronic stopping cross section can be written [15],

$$-\frac{dE}{dx} = \frac{4\pi Z_1^2 e^4 n}{mv^2 (4\pi\epsilon)^2} (L_0 + Z_1 L_1 + Z_1^2 L_2 + \dots) \quad (2.2)$$

where L_0 , L_1 and L_2 are independent of Z_1 . L_0 contains the Bethe term and shell corrections as well as relativistic corrections. A non-zero L_1 gives rise to the so called Barkas effect which has been interpreted as a polarization of the electron cloud of the material by the penetrating ion and explains the difference in stopping power between a particle and its antiparticle [16]. This was first calculated for classical harmonic oscillators [17] and recently using the second order Born approximation on a spherical harmonic oscillator model [18]. Finally L_2 is the Bloch correction [19].

A very simple summarizing picture is: immediately after the passage of an ion, having a velocity for which electronic stopping is dominant, the material is left with a track of excitations and ionizations around the ion trajectory and the surrounding material is irradiated with secondary electrons created in the ion-electron collisions. In a conductor the deposited energy will be swiftly delocalized but in an insulating material these local excitations can survive for a sufficient long time that their energy can be converted into kinetic energy of atomic and molecular motion.

2.2 Conversion of Electronic Excitations into Atomic Motion

A considerable part of the discussion concerning electronic sputtering has been focused on how the electronic excitation energy deposited along the primary ion trajectory is converted into kinetic energy of atomic motion. Generally conversion into considerable atomic motion is only possible in materials in which fairly long-lived localized electronic excitations can exist, i.e. in nonconducting materials. The first and most easily understood conversion mechanism is the Coulomb explosion model suggested by Fleischer *et al.* in order to explain why MeV ions produce etchable tracks in insulators [20]. This model was later employed by Haff to electronic sputtering [21]. The model states that ion-target electron collisions will create a region around the ion trajectory that is depleted of electrons, i.e. an infra track of positive repelling charges is formed. If the conductivity of the material is low enough the Coulomb repulsion has sufficient time to cause significant atomic motion before the region is neutralized (Figure 2.2). However, it has been claimed that even insulators may not have large enough neutralization time to allow a Coulomb explosion to transfer significant momentum to target atoms, due to enhanced conductivity in the highly excited region of the ion track [22].

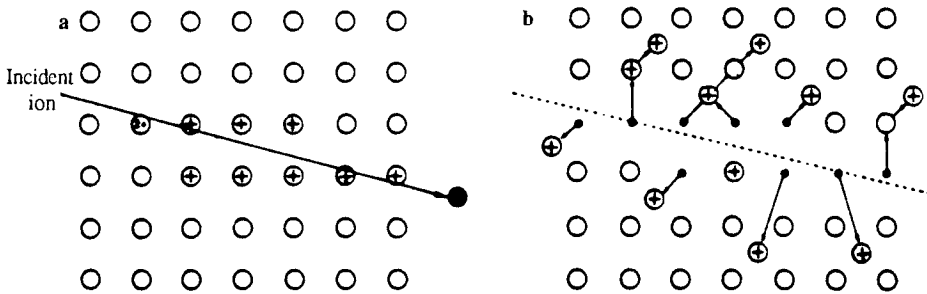


Figure 2.2 The ionizations produced by the incident ion (a) can be converted into expansion of the solid through Coulomb repulsion between positive ions (b) [20].

Another channel for energy conversion into atomic motion is through electronic excitation of a chemical bond to a long-lived repulsive state and the subsequent separation of the molecule [22, 23] (Figure 2.3a). An additional possibility involves vibrational excitation of chemical bonds which will lead to larger separation between the atoms because of the anharmonicity of the interatomic potential (Figure 2.3b). Possible pathways of vibrational excitation include secondary electron-molecule collisions [24] or electronic excitation decay [9]. All these mechanisms (extensively discussed in Reference 9) give rise to atomic motion by causing an expansion of the solid around the ion trajectory.

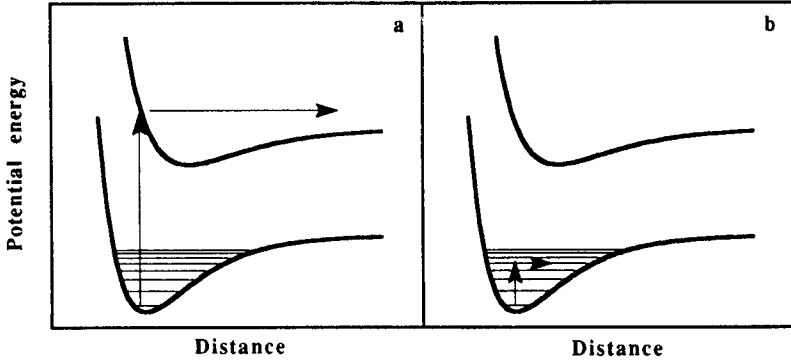


Figure 2.3 Two further examples of how electronic excitation can be converted into expansion of the solid: a) repulsive decay and b) vibrational excitation.

2.3 Ejection of Material at a Surface

A complete description of electronic sputtering would require the solution of the time dependent Schrödinger equation for a large number of interacting particles. For a simpler analytical description of the ejection process a continuum mechanical model of the energy and momentum flow in the material can be used together with an ejection criterion. The fluid dynamic picture that is outlined in Paper A and Reference 25 gives such a description. It is assumed that the energy flow is described by the diffusion equation,

$$\frac{d\epsilon(r,t)}{dt} = \nabla \cdot [\kappa(\epsilon) \nabla \epsilon(r,t)] - \frac{\epsilon(r,t)}{\tau} + (\text{source terms}) \quad (2.3)$$

where $d/dt = (\partial/\partial t + \mathbf{v} \cdot \nabla)$ is the material derivative, ϵ the local energy density, κ the diffusivity and $1/\tau$ the rate of energy flow into internal degrees of freedom. The choice of the source terms is usually based on the arguments in paragraph 2.2. Fast ions penetrate deep into the solid and when the ions are in charge state equilibrium the energy loss will be approximately constant in the region near the surface. Consequently the source terms are assumed to be cylindrically symmetric around the ion path and independent of the axial coordinate. It is also assumed that contributions from different parts of the solid are linearly additive. The momentum flow is assumed to be described by Navier-Stokes equation,

$$\rho_m \frac{d\mathbf{v}}{dt} = -\nabla P + \mu \nabla^2 \mathbf{v} + \rho_m \mathbf{B} \quad (2.4)$$

together with the continuity equation,

$$\frac{\partial \rho_m}{\partial t} = -\nabla \cdot (\rho_m \mathbf{v}) \quad (2.5)$$

where \mathbf{v} is the local velocity, ρ_m the molecular mass density, μ is the coefficient of viscosity, \mathbf{B} is the body forces per unit mass and P is the local pressure which is related to ϵ through an equation of state. For a complete description the Equations 2.3-5 should be solved simultaneously together with an ejection criterion. Since this is a complex problem different approximations are made.

The most commonly used approximation considers only Equation 2.3. In the framework of the so-called thermal models the energy density (temperature) at the sample surface is calculated as a function of time and ejection is regarded as evaporation through the surface which is described as a potential step. Several models of this type have been suggested to explain experimental results on electronic sputtering of organic solids [26, 27, 28].

Another approach [A, 25] is to first solve 2.3 in order to obtain the energy density $\epsilon(r,t)$ and then to substitute $\epsilon(r,t)$ into 2.4. If the dissipation of momentum and the body forces are disregarded 2.4 can be rewritten by using $P=\beta\epsilon(r,t)$ and the momentum given to a volume element in the solid during time τ will be

$$p(r) = \int_0^\tau \left[-\frac{\beta}{n_m} \nabla \epsilon(r,t) \right] dt \quad (2.6)$$

where β is a constant depending on the material and n_m is the molecular number density. The expression in the square brackets of equation 2.6 can be regarded as a force exerted on the material due to the energy gradient. A part of the solid is considered to be ejected if it obtains a momentum normal to the surface larger than a critical momentum (p_c) given by the cohesive energy of the material. In this picture the ejection is caused by a pressure pulse which is due to the energy gradient developed during ion impact.

When the energy density is high the contributions from the different parts of the solid can not be added linearly. This case has to be treated according to the formalism of hydrodynamic shock waves [29-33]. As a cylindrical shock wave propagates through the solid the energy density will decrease and eventually an energy density is reached for which the different contributions can be added linearly. Thus, at high energy densities an inner region has to be treated according to the shock wave formalism and the outer region can be treated as described above.

To summarize, the ejection of material from organic solids following ion impact can roughly be described as evaporation from the energized region close to the ion track or as volume ejection due to the pressure pulse further away from the ion track. Both processes occur and their relative importance depends on both primary ion and target material parameters. Pressure pulse ejection is favoured for ejection of intact large organic molecules because of their thermal lability.

2.4 Ionization and Neutralization of Ejecta

Close to the ion trajectory a lot of secondary ions are created but the energy density here is high which will lead to the destruction of large organic molecules. Thus, ejection from that volume is dominated by low mass fragment ions. Further away from the ion path, from where intact molecules can be ejected by the pressure pulse, the solid is irradiated with fast δ -electrons which can lead to ionization of molecules. The implications of this mechanism have been investigated in the ion track model [34]. It has also been suggested that for some organic solids there are preformed alkali metal ion-molecule complexes, already present in the solid before the incident ion deposits its energy [35]. Another possibility is that chunks of material, ejected by the pressure pulse, could be charged due to statistical charge fluctuation and molecular ions could be produced either by

dissociation or evaporation [36, 37]. It has also been proposed that charged fragments or alkali metal ions may react with neutral molecules in the gas phase close to the surface and form protonated or cationized molecular ions [38]. In Paper D the origin of cationized molecular ions is discussed.

An atom or molecule which is ionized can be neutralized again before leaving the solid. For example, an ion which is created inside the solid far away from the surface has a large probability of being neutralized in one of the collisions it will suffer on its way to the surface. Even ions created at the surface may be neutralized if they have a low escape velocity [39]. Also neutralization due to gas phase collisions with other ejected molecules could be important.

Computer Simulations

Harsh criticism from its opponents and exaggerated claims from its proponents are frequent in discussions of computer simulations.
D.P. Jackson [40]

In paragraph 2.3 a continuum mechanical description of the ejection of material due to the passage of a fast ion through a solid was presented. Another approach is to regard the solid as composed of particles. As a quantum mechanical treatment is impractical the motion of the particles is described by classical mechanics; using either Lagrange's equations of motion or Newton's equations of motion,

$$m_i \frac{d^2 \mathbf{x}_i}{dt^2} = \mathbf{F}_i(t) \quad i = 1..N \quad (3.1)$$

where m_i is the mass and \mathbf{x}_i the position of particle i . The force, $\mathbf{F}_i(t)$ acting on a particle i , is obtained from the potential energy function,

$$\mathbf{F}_i(t) = -\nabla_i V(\mathbf{x}_1(t), \mathbf{x}_2(t), \dots, \mathbf{x}_N(t)) \quad (3.2)$$

When only two body interactions are considered and all particles are equivalent, Equation 3.2 can be written as:

$$\mathbf{F}_i(t) = -\sum_{j \neq i} \nabla_i V(\mathbf{x}_i(t), \mathbf{x}_j(t)) \quad (3.3)$$

When the number of interacting particles is large Equation 3.1 can only be solved approximately. The idea is to replace the differential operator in time with a difference operator. The time step in the difference operator should be chosen in such a way that the total energy fluctuations of the system become small. There are several different algorithms which have been employed [41, 42]. In this study, the Verlet algorithm [43] was chosen because it is known to be one of the most simple and yet stable algorithms. It may be derived from Equation 3.1 by using a time centred difference operator:

$$\frac{d^2 \mathbf{x}_i}{dt^2} \rightarrow \frac{\mathbf{x}_i^{n+1} - 2 \cdot \mathbf{x}_i^n + \mathbf{x}_i^{n-1}}{\Delta t^2} \quad (3.4)$$

which gives the recursion formula for the positions,

$$\mathbf{x}_i^{n+1} = 2 \cdot \mathbf{x}_i^n - \mathbf{x}_i^{n-1} + \frac{\Delta t^2}{m_i} \cdot \mathbf{F}_i^n, \text{ where } \mathbf{x}_i^n = \mathbf{x}_i(n \cdot \Delta t) \text{ and } \mathbf{F}_i^n = \mathbf{F}_i(n \cdot \Delta t). \quad (3.5)$$

The velocity can be obtained from

$$\mathbf{v}_i^n = \frac{\mathbf{x}_i^{n+1} - \mathbf{x}_i^{n-1}}{2\Delta t} \quad (3.6)$$

An obvious advantage of molecular dynamics simulations is that the position and velocity for all particles are obtained as a function of time. From these it is possible to calculate quantities which are more directly comparable with experimental results.

For quantitative agreement with experiments the shape of the interatomic potential can be very important and since the first molecular dynamics studies a great deal of effort has been exerted in order to obtain realistic interatomic potentials. The interatomic potential may be modelled by either calculations from first principles or assuming a simple analytic potential shape and determining its parameters by fitting macroscopic properties. A large amount of work has been done on computer simulation of nuclear sputtering [44] and usually pair potentials are used. It has also been demonstrated that many-body potentials calculated from the embedded atom model [45] are necessary in some cases. The motion of atoms in a single protein has been studied by molecular dynamics [46, 47] but to calculate the motion of all atoms in an assembly of a large number of proteins, which is necessary for electronic sputtering, is very time consuming. Therefore, in this thesis the smallest unit was assumed to be a protein and the organic solid was built up by these units which interact through Lennard-Jones potentials. The effect of an impinging ion was taken to be expansion of the proteins (see Paragraph 2.2) inside a cylinder around the ion trajectory, i.e. the potential between expanded molecules was changed (Figure 3.1). The motion of the particles were calculated using 3.3 and 3.5. An example showing the ejection of molecules from the solid is presented in Figure 3.2 [B, F, 48]. Computer experiments were performed to investigate the dependence of the yield and velocity distribution of ejected particles as well as the shape of the crater in the sample, on parameters such as deposited energy, angle of incidence and sample thickness.

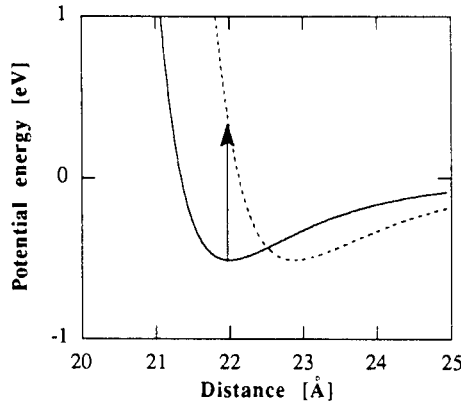


Figure 3.1 The potential energy as a function of distance for two nonexpanded molecules (solid line) and two expanded molecules (dashed line).

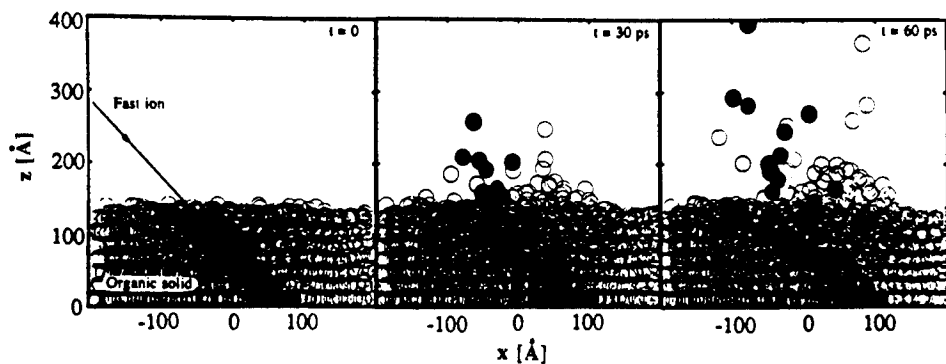


Figure 3.2 The sample 0, 30 and 60 ps after the expansion of the molecules in the ion track. Expanded and nonexpanded molecules are shown as solid and open circles, respectively.

Experimental Methods

Il faut travailler.
Pasteur

4.1 Sample Preparation

The simplest way to obtain a thin film of an organic solid is to deposit a droplet of a solution of organic molecules on a backing and let it dry. More sophisticated methods, e.g. electrospray [49], are needed in order to obtain a sample film with properties favouring ejection of intact ionized large molecules. This method gives an organic solid with a rough surface. Smoother surfaces and better control of the sample film thickness is achieved by utilizing the spin coating technique [50]: i.e. a droplet of the solution is deposited on a rotating substrate. For studies of large organic molecules the most successful method has been adsorption to a polymer surface, usually a nitrocellulose film [51] prepared by either electrospraying or spin coating.

The technique of preparation of Langmuir-Blodgett films [52] allows even better control of the sample parameters. A submonolayer of amphipatic sample molecules is deposited on a water surface and the surface is compressed slowly until a monolayer is formed. The sample molecules have their hydrophilic end in the water and their hydrophobic end towards the ambient. By taking a solid through the water surface and keeping the surface pressure constant a monolayer can be transferred to the solid. Several layers containing different types of molecules can be deposited on top of each other if desired.

4.2 Sample Characterization

Important properties characterizing the sample film are thickness and surface roughness. The film thickness and refractive index can be estimated by ellipsometry, an optical method using reflection of polarized light [53]. The polarization change of an elliptically polarized monochromatic light beam due to interference as it is reflected by the transparent organic film on top of the reflecting substrate is utilized to calculate the thickness and the refractive index of the film. The accuracy of the method is good for films in the thickness range 10-100 nm, being a few tenths of a nm. For thinner films the continuum model has a more limited applicability and the method is less accurate. Information about the surface roughness on the nm scale can be obtained from atomic force microscopy [54]. A naive

description is that the force between the tip of a needle and the surface is measured. As the needle is swept over the surface it is adjusted in a direction normal to the surface by means of a piezoelectric crystal to keep the force constant and a picture of the surface is obtained. Measurements on spin coated films of nitrocellulose show that the surface roughness is better than a few nm [55].

4.3 Identification of Ejecta

In most studies of electronic sputtering of organic solids the ejected *ions* have been analyzed by time-of-flight mass spectrometry. Observables like ion yield and velocity distributions have been measured. Investigation of the ejected *neutrals* is much more difficult and only a few results have been presented so far [56]. In these measurements the ejected biomolecules were collected on a surface which was subsequently analyzed by amino acid analysis. A possible experimental set up for analysis of the ejected neutrals by time-of-flight may include laser post-ionization [57].

In time of flight mass spectrometry the ions ejected from the sample are first accelerated in an electric field, then they are allowed to drift in a field free region and finally reach a detector. The flight time of each ion is measured and from that the mass of different ions can be calculated. In the experiments described in this thesis, the source of MeV primary ions was the tandem accelerator at the The Svedberg Laboratory at Uppsala, Sweden. Before hitting the target the primary ions pass through a thin carbon foil and the ejected electrons were used to generate a start pulse [58]. The secondary ions were detected with a micro channel plate to produce a stop signal. A time of flight spectrum was obtained using a time to digital converter (TDC).

Two pairs of deflection plates were placed in the field free region (Figure 4.1) giving an electrostatic field perpendicular to the spectrometer axis in order to measure radial velocity distributions. The measurements were performed by collecting mass spectra for different voltages applied to the deflection plates (Figure 4.2-3). As both the beam spot on the sample and the collimator in front of the stop detector had a finite size the measured velocity distribution will be a convolution of the initial velocity distribution and the resolution function of the spectrometer which can be calculated from the acceleration voltage and the geometry. The results presented are all distributions of component of the velocity along the x-axis [C, D, E]. An elegant but more complicated method, which works for low mass ions where the background is low, has been used by others to measure velocity distributions along both the x- and y-axis simultaneously with a position sensitive detector [59].

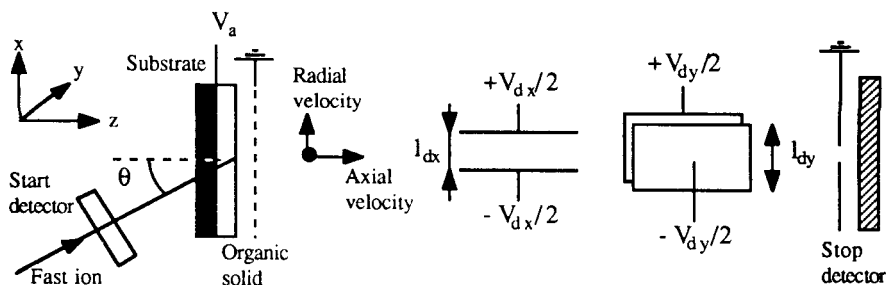


Figure 4.1 The time of flight mass spectrometer.

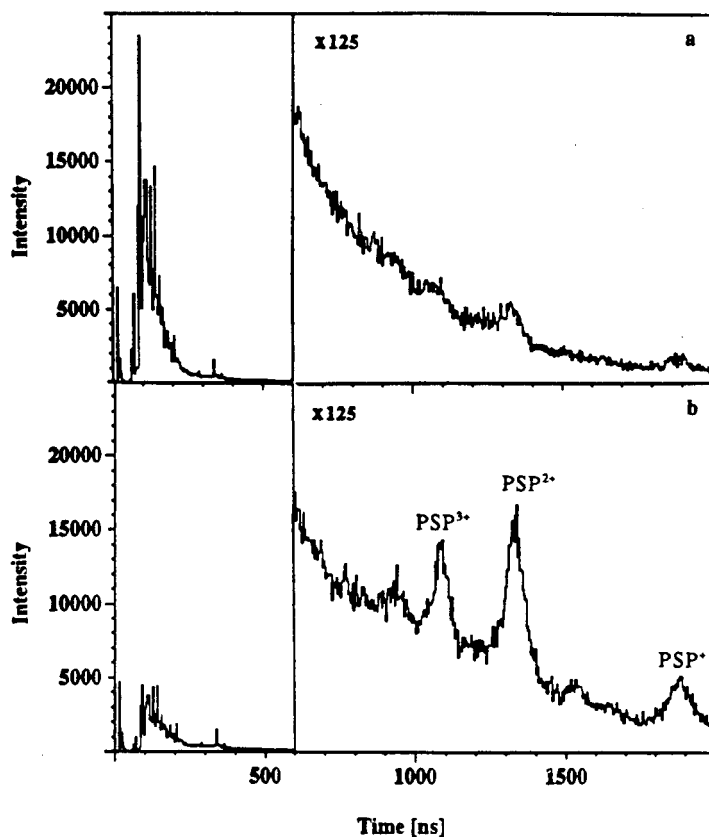


Figure 4.2 Positive time of flight mass spectra obtained by bombarding a sample of pancreatic sphasolytic peptide (PSP, 11 711 u) adsorbed to nitrocellulose with 72.3 MeV $^{127}_{144}\text{I}^{+}$. The voltage (V_x) on the deflection plates in the x direction was (a) +80 V and (b) -60 V, giving high yield of fragment ions and molecular ions, respectively.

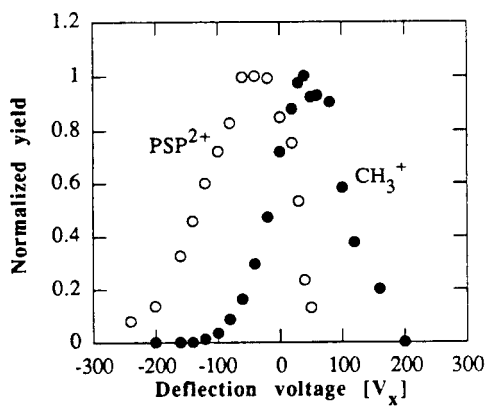


Figure 4.3 The yield of doubly charged pancreatic sphasolytic peptide (PSP^{2+}) and that of CH_3^{+} , as a function of the voltage applied to the deflection plates.

Summary of Results

A continuum mechanical model of the ejection process in electronic sputtering of organic solid by energetic ions is described in Paper A. Classical dynamics simulations of particle ejection following MeV ion impact is discussed in Papers B and F. Experimental results on radial velocity distributions of ejected ions, including intact peptide ions (protonated as well as attached with alkali metal cations) and light ions (H^+ , CH_3^+), are presented in Papers C, D and E. Here the results of Papers A-F are briefly summarized.

5.1 Ejection

5.1.1 Ejected Intact Large Organic Molecules

Results from the continuum mechanical model [A, 25] and the molecular dynamics simulations [B, 48] demonstrate that the total ejection yield varies as the deposited energy to the third power (Figure 5.1). This dependence on the deposited energy is a consequence of the pressure pulse ejection of a volume having an extension in each dimension proportional to the deposited energy. The results of the only reported experiment investigating the total yield of intact organic molecules [60] are in agreement with the results of the simulations and the continuum mechanical model.

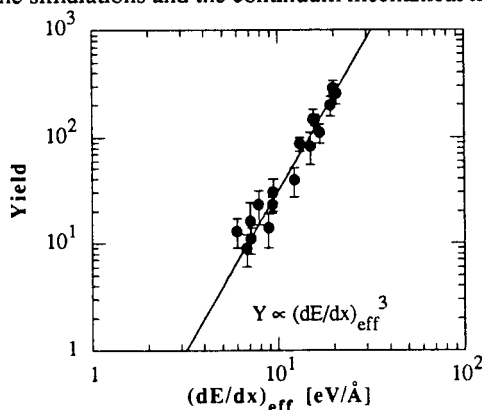


Figure 5.1 Molecular dynamics simulations of the dependence of the yield on $(dE/dx)_{eff}$ together with the predictions of the continuum mechanical model.

The radial velocity distributions of ions of intact large organic molecules are characterized by the cylindrical geometry of the pressure pulse created by an incident MeV ion, i.e. ejected ions will acquire an impulse perpendicular to the primary ion path. The distribution of momentum of particles ejected from the sample surface for different incidence angles following from the continuum mechanical model is presented in Figure 5.2. These results are in qualitative agreement with both molecular dynamics simulations [B, 61] and experiments on radial velocity distributions of molecular ions of proteins [C, D, 59, 61-63].

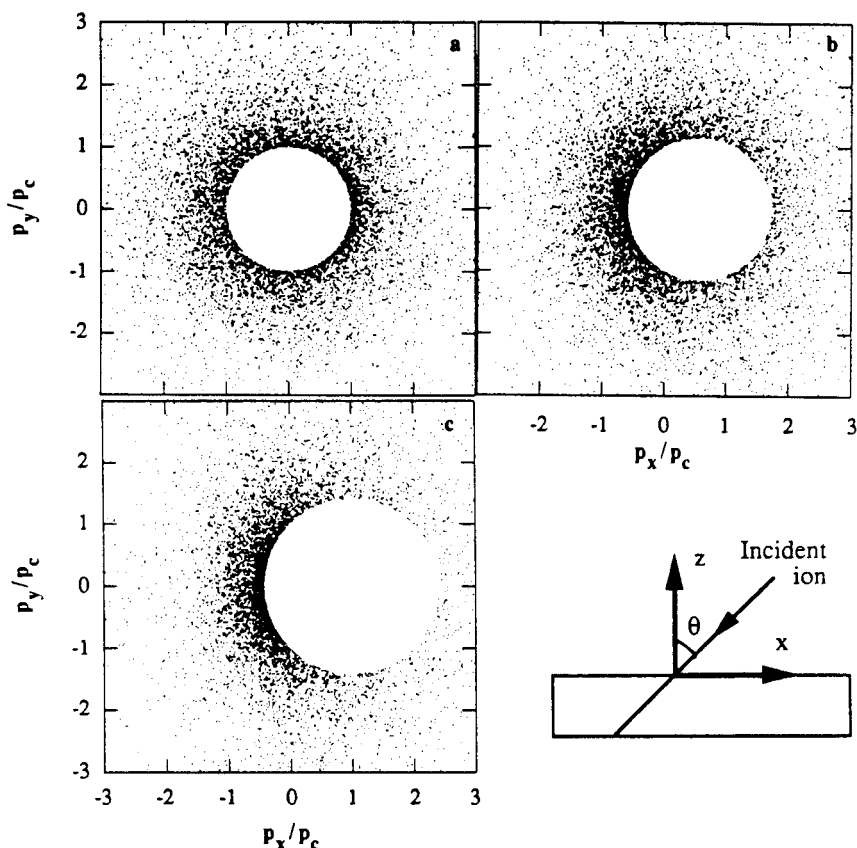


Figure 5.2 Monte-Carlo simulations of the distribution of momentum along the sample surface of particles ejected from the sample surface using Equation 8 in Paper A for different incidence angles: a) 0°, b) 30° and c) 45°.

5.1.2 Ejected Fragment Ions

Light fragment ions such as CH_3^+ , H_3O^+ and CN^+ , unlike the large intact organic molecular ions, are ejected preferentially from a part of the solid having a high energy density and the ejection mechanism is therefore different. On the average most light fragment ions are ejected in a direction normal to the surface and their radial energy distributions are independent of their mass and the sample thickness [C, E]. This indicates that a thermal description of the ejection process can be applicable for the ejected fragment ions.

The hydrogen ions behave differently than other fragments in the sense that the width of their radial velocity distribution increase with sample thickness [E]. This indicates that the interaction with the short lived positively charged track must be taken into account for a description of the ejection of the hydrogen ions.

5.2 Crater Formation

An example of the contour of a simulated crater showing a typical pile up of material at its edges is shown in Figure 5.3. Large variations in crater size and shape are obtained in the simulations due to the statistical nature of the sputtering process. The continuum mechanical model predicts a hemispherical crater for normal incidence. Indications of crater formation in organic solids after MeV ion impact have been given by experiments with Langmuir-Blodgett films of fatty acids. In that case molecular ions are ejected not only from the sample surface but also from a depth of 100-200 Å [64-66]. It has yet not been investigated whether the craters formed in the sputtering process, as indicated by experiment and theory, are healed by the thermal motion of the surrounding material or if these craters still exist a long time after the ion impact.

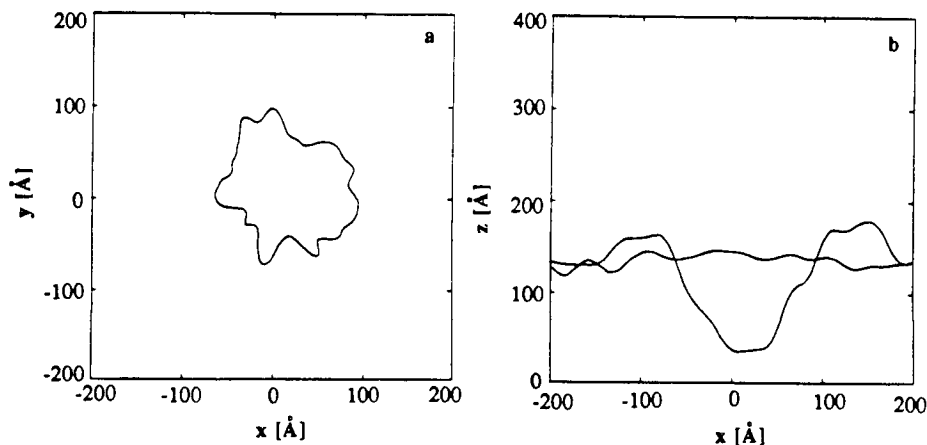


Figure 5.3 An example of a simulated crater induced by a fast heavy ion incident normal to the surface seen from above (a) and from the side together with the surface before ion impact (b).

Concluding Remarks

Der Vorgang der Induktion besteht darin,
daß wir das *einfachste* Gesetz annehmen,
das mit unseren Erfahrungen in Einklang
zu bringen ist.
Dieser Vorgang hat aber keine logische sondern
nur eine psychologische Begründung.
Es ist klar, daß kein Grund vorhanden ist,
zu glauben, es werde nun auch wirklich der
einfachste Fall eintreten.
Wittgenstein

6.1 Conclusions

Results have been summarized from experiments, computer simulations, and a continuum mechanical model, all examining the sputtering of organic molecules due to MeV ion impact. The qualitative agreement between these results has caused a coherent picture of the sputtering event to emerge (Figure 6.1).

At the time of ion impact, energy is deposited in the form of excitations and ionizations in the infra track. The secondary electrons from ion-electron collisions in the infra track, deposit their energy in the ultra track and the infra track is left with a net positive charge. The deposited energy cause an expansion of the solid and a cylindrical pressure pulse is created. Atoms and small molecules can be ejected directly from the infra track during dissociation of larger molecules. For H^+ this seems to be the dominating ejection mechanism. However, the escape velocity of H^+ is altered by the Coulomb interaction with the positively charged infra track. Other light fragment ions can be evaporated from near the ion trajectory where the energy density is high. Intact large thermally labile organic molecules, on the other hand, are ejected preferentially by the pressure pulse from a region further away from the track where the energy density is low enough not to cause destruction. The ejected molecules can be both neutral and charged. The probability that an ejected intact large molecule is charged depends both on its distance from the ion trajectory and the surface. Closer to the ion path, where the energy density is higher, ionization is more probable. Molecules ejected from deep down in the solid have a higher probability to be neutralized in collisions with other particles than those ejected from close to the surface.

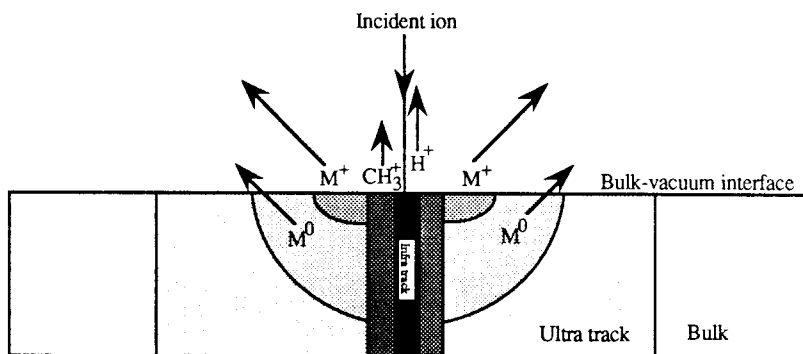


Figure 6.1 Schematic drawing of an ion impact showing the ejection of fragment ions (e.g. H^+ and CH_3^+) as well as neutral intact molecules (M^0), and charged (radical, protonated or attached with alkali metal cations) intact molecules (M^+).

6.2 Outlook

MeV ion induced desorption is a simple, useful way of forming ions from involatile proteins for mass spectrometry studies. To improve this technique, electronic sputtering of organic solids should be examined in further detail. Several avenues of research remain to be exploited in order to further increase the understanding of this phenomenon. It would be useful to have more experimental data on the yield and velocity distributions of neutral ejecta in order to facilitate comparison between data and predictions of simulations and theory. Direct observation of the predicted craters and measurements of their actual shapes by atomic force microscopy would also be desirable. Computer simulations should be performed to investigate the possible mechanisms of conversion of electronic energy into atomic motion. For example, it should be possible to test how efficient Coulomb explosion and expansion of proteins is in initiating molecular motion. In particular it is important to study in more detail how the pressure pulse is formed in the solid. Furthermore, a model of ionization which can explain why the dependence of the yield on energy loss for positive and negative ions differ from that of the neutral molecules, would be important.

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Acknowledgments

First of all I would like to express my sincere gratitude to my supervisor Bo Sundqvist for his invaluable support as well as for his inspiring and stimulating ideas. I am grateful to Per Håkansson for his patience when teaching me experimental physics. For guidance through the theoretical part of the work I am indebted to Bob Johnson. I also want to thank Bengt Karlsson and Orlando Tapia-Olivares for stimulating discussions. Sten-Erik Lindqvist and Erik Wistus are gratefully acknowledged for help with preparing Langmuir-Blodgett films. Special thanks to Allan Hedin, Plamen Demirev, Ib Koersner, Mehran Salehpour, Curt Reimann, Gunnar Brinkmalm, Johan Kjellberg, Judit Kopniczky and all others at the laboratory.

A handwritten signature in black ink, appearing to read "David", followed by a stylized flourish.

Uppsala, April 1991

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Distributor:
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Stockholm – Sweden

ISBN 91-554-2738-3
ISSN 0282-7468