

Entropic Processes in Heavy Ion Induced Desorption of Biomolecules Applied to Peptides

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Introduction

The heavy-ion-induced desorption of organic molecules has proved effective to produce excessive yields of undamaged large organic molecules, even if they are as fragile as polypeptides, polysaccharides or DNA-strings up to any mass. Contributing to elucidate the physics of this unique process is the aim of this contribution. By that we hope that on the long run theoretical model calculations of the process will help to optimize the experimental setup thus serving the wide open field of applications in biochemistry and pharmacy. In addition, learning about a complex physics phenomenon may give independent additional information to the physics of the touched fields.

The process itself is started by shooting a heavy ion (the physicists prefer to use a heavy-ion accelerator, the applications are more easy with fission fragments of the Californium isotope 252) on a thin film target. The ion has to be as fast as the bound electrons of the target atoms, and thus much faster than any target atomic oscillations. This will be discussed in contrast to the FAB-mechanism, where the "fast atom bombardment" is actually also an ion which is however an order of magnitude slower than in PDMS. Thus PDMS serves the target initially with a localized track where on a very short time scale an excessive amount of energy is depo-

* Supported by Bundesministerium für Forschung und Technologie

sited, high enough to serve a large area with the energy required for desorption of a large number of molecules. It is to learn the transient mechanism in order to gain quantitative predictions. In contrast FAB with its much lower energy deposition stirs up the solid around the ion track, giving rise to local excitations of atomic motion thermalizing and thus yielding a burst of highly excited fragmenting molecules around the ion track.

The difference of the processes resemble the difference between desorption by a very short pulse of a very intense laser beam as compared to the ordinary gentle laser desorption. However, they differ from the MeV-ion-induced desorption by the scale in space. In laser desorption macroscopic areas of the material are irradiated. Thus the whole process here may be described macroscopically by an excitation of a mechanical shock wave leading to desorption in unirradiated areas versus local excitation of the bonds, thus leading to desorption of individual molecules. Thus the yields in laser desorption should be enhanced by increasing the power and shorten the pulse independent of the frequency for high-power laser desorption, while for the gentle case tuning the frequency is the relevant parameter. For both processes we refer to the paper of Grottemeyer in this volume. We will therefore call the PDMS as well as the high power laser desorption "entropic" in contrast to the more "thermal" processes, referring to that entropic processes in general are characterized by short time excessive energy input, where the relevant free energy is dominated by the number of outgoing channels accessible by the process, in contrast to thermal processes where the final distribution of energy about all existing states has to be studied.

Molecular binding

Compared to any intramolecular atomic motion the time of quasi-elastic scattering of electrons passing an atom is extremely short [1, 2]. The time-dependent quantum mechanical perturbation theory of intense but short interaction with a quantum-mechanically bound atom tells us immediately that the deposited energy is proportional to the number of exit channels $\rho(\epsilon)$ accessible within the interaction time δt . The break-up probability of an atomic bound is thus proportional to

$$\int d\varepsilon \rho(\varepsilon) M_{0\varepsilon} \exp\{-a\tau_\varepsilon\} \exp\{-\varepsilon\delta t/h\}$$

where t_ε is the relaxation time of the exit state ε , and $M_{0\varepsilon}$ a reduced matrix element.

The information to put into our model, which we need most urgently from the chemists, is therefore the level density of all the bond types existing in a sample of the molecules of our interest. This is in contrast to FAB, where the separation energy is the parameter of prior interest.

Level density and separation energy are properties well known for v.d.Waals-bonds (large $\rho(\varepsilon)$, small $\Delta\varepsilon$) and covalent bonds (small $\rho(\varepsilon)$, large $\Delta\varepsilon$). Thus both an "entropic" as an "energetic" calculation yields qualitatively the same: v.d.Waals-bonds are more easily broken than covalent bonds (however the ratio is much smaller).

The peptidic and glycosidic bindings are therefore of special interest, since they show a relatively strong binding compared to their relatively large level density (due to a rich variety of possible rearrangements of the bond area after break up). This becomes evident in PDMS, where peptidic and glycosidic bonds survive by a good chance as compared to v.d.Waals bonds, but break much more easily than equally strong covalent bonds. From experiments using different oligosaccharides we read off that for each v.d.Waals bond broken we get an 8% chance for glycosidic bond to break (for FAB it is about 50%).

For an interpretation of experimental spectra there are two predictions to be learned from the theoretical model:

- for a branched polypeptide each peptide-bond has the same breakup chance in PDMS, while in FAB each end-chain bond is less likely broken
- a large molecule adsorbed to a surface will be easily desorbed even when it is lying "flat" on the surface, bound by numerous v.d.Waals-bonds, since any of these bonds is broken easily and thus will contribute to the molecular momentum. In contrast to this situation in FAB molecules "standing up" will be favorately desorbed since their chance to escape is controlled by $\exp\{-n\Delta\varepsilon/kT\}$ (n = number of surface bonds, T = Temperature).

From the distribution of the kinetic energy of the molecules one can get informations relevant for improving the model calculation. The distribution looks individually for any desorbed species "Maxwellian" (although a global temperature value cannot be found) with a kinetic temperature in the range of 10^4K (internally the molecules are quite cold, however). Identifying this by the kick-time $\delta t = h/T_{\text{kin}}$ we find a time comparable to the Rydberg - time h^3/me^4 , characterizing the time required for an electron to pass one atom.

Electronic excitation

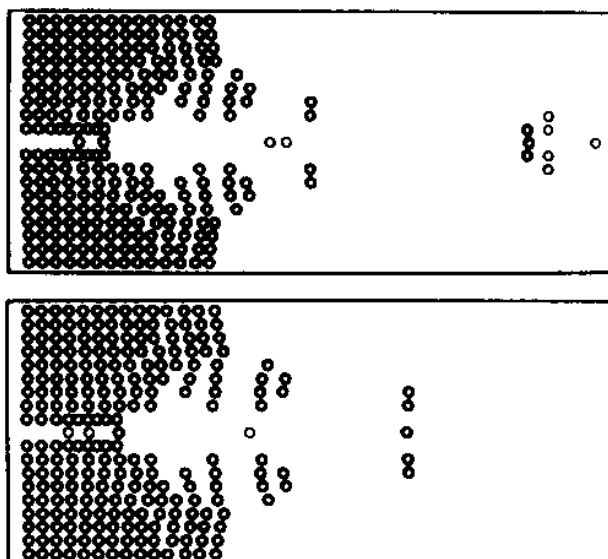
Even without a deeper study of the different electronic processes which transport energy at last to any degree of freedom existing in condensed matter, the coupling strength between electronic and mechanic degrees of freedom indicates that there exists an intermediate period where electrons are thermalized but "hotter" than the molecules (unbalanced electron and lattice temperature). This assumption is used in different models [1, 3] and is justified by the behaviour of the electrons excited by the projectile: the high-energy part (δ -electrons) is set free with a wide range of motion and (initially) weak coupling to other electrons, while the slower electrons distribute the energy they received by numerous scattering events with other electrons within a relative short range around the ion track. Additionally plasma oscillations are produced which contribute to the "heating up" of the electron system in being damped [4] (a publication about a study of these processes is in preparation).

The subsequent development of the electron system is assumed as described in [3]: an excited region which is cooling off at its cylindrical boundaries mainly by Auger-processes. This configuration, of course, allows the "entropic" excitation of molecules as well as other processes proposed to carry energy from the electrons to the lattice, such as the mechanism described by Sundqvist and Williams [5] or the one described in [3]. However, in our calculations we used the "entropic" approach which leads to intermolecular forces comparable to those found in [3].

Computer simulation and results

When molecular forces produced by the initial excitation processes are found, maybe using an excitation model as quoted in [3] or [5], the resulting molecular motion remains to be calculated. Bittensky and Parilis assume a shock wave to be formed and use the continuum approximation for its description [6]. The continuum approximation is a powerful tool, but when we are also interested in the lower-energy transition region (starting with low projectile charge) we will find situations where the mechanic energy may be concentrated to dimensions comparable to those of the molecules of the target. In order to account for the finite size of the molecules, and since the nonlinear character of the interatomic forces will require numerical iteration methods soon or later, we used a simple first-order iteration algorithm for a calculation of coordinates and momenta of the molecules. The calculations were performed in one dimension and assuming cylindrical symmetry (rectangular incidence of the projectile).

Figure 1: motion of molecules 0.5 and 1 picoseconds after projectile impact (10^4 eV/nm)



In our calculations we are interested mainly in the total yield and the depth under the target surface contributing. So intramolecular processes were neglected. This is, by the way, no restriction required by the method used here: the theory developed by Lucchese et al. [7] could be applied additionally, in order to get information about ionization and fragmentation. In the numerical program we keep track on "electronic" and "lattice"-heat; this might be ex-

tended to the detailed observation of special molecular degrees of freedom.

Qualitative results are shown in fig. 1, which was calculated for a Valine target bombarded by a projectile producing an energy loss of 200 eV/A. A calculation of the total (neutral + ions) yield in dependence of the energy loss gives the curve shown in fig. 2. The proportionality $Y \sim (dE/dx)^2$ is reproduced as found in previous calculations using the continuum limit [3], but for lower energy losses obviously desorption stops below some threshold value. An interpretation of this result within the context of our model is that electronic energy dissipates too fast for the molecules to react to forces existing only for a very short time. Even fragmentation of molecules does not change the fact that no "half atoms" are desorbed, as implied by continuum models. The energy threshold found here reproduces the experimental observation that lower-charge projectiles are not capable for producing the same desorption effects as heavy ions, even if both values may differ quantitatively.

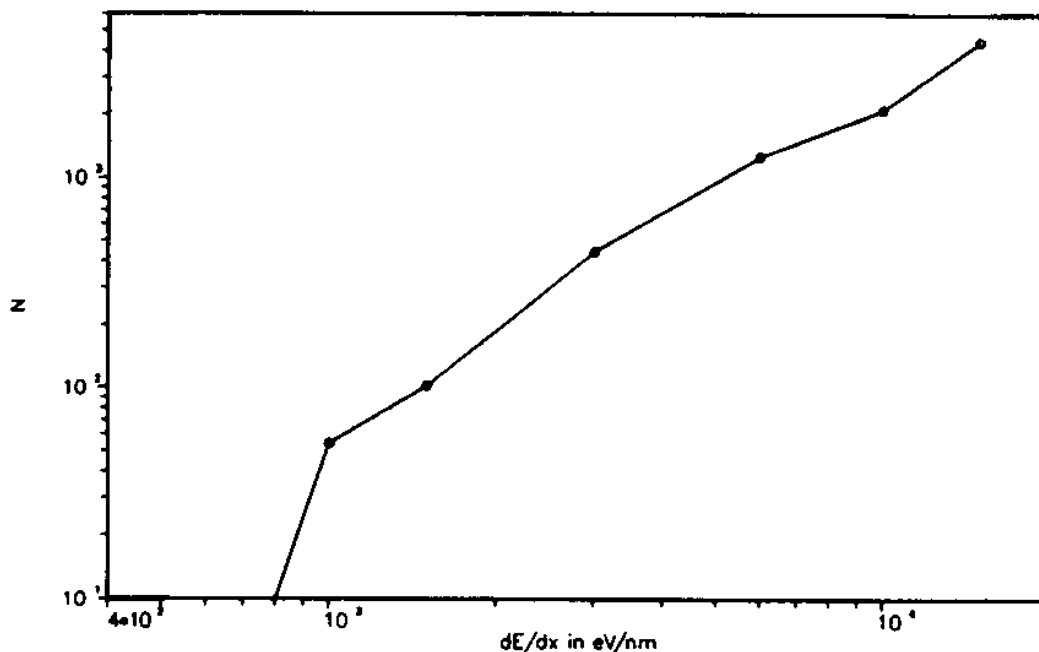


Figure 2: dependence of the total desorption yield of electronic energy loss

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British Library Cataloguing in Publication Data Available

ISBN 0 471 92062 2