

Computer Simulations of FHIID

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Abstract

A status report on computer simulations for fast heavy ion induced desorption of biomolecules (FHIID) being presently developed is given. The physical background, concerning the coupling mechanisms responsible for the energy transfer from electronic to molecular degrees of freedom and different excitation mechanisms is briefly discussed. Assumptions on nuclear excitations are checked by analyzing some oligosaccharide-spectra. Qualitative results are presented for a numerical simulation of the desorption by a simple microscopic mechanical model.

Introduction

The most important processes in FHIID occur in the very first nanoseconds after the passing of the projectile and within the space within the distance of few atoms from the path of the projectile. Since this "time-space-region" has not yet been observable in experiments, semi-empirical models being based on later-time experimental data concerning this region are partially speculative. In recent years it has turned out that a lot of relevant processes to occur just there and then cannot be dealt with by just qualitative extrapolation. Our aim is therefore, besides the development of an analytical theoretical description, a numerical study in order to keep track of the complicated processes in space and time where analytical approaches become too complicated.

We also want to investigate how far details in atomic and molecular excitation can really affect desorption yields and spectra. Finally, by evaluation of the equations of motion for atoms or molecules we want to obtain total yields, velocity spectra, fragmentation statistics which can be compared to data from laboratory experiments.

Electronical Excitation

Obviously the initial state of electronical excitation is too complicated to treat the excited region as being homogeneously heated up. For the understanding of a single class of processes on limited energy scales, however, a corresponding approach may be successful. Here we are mainly interested in electronical and nuclear energy loss of secondary electrons and further secondary ionization processes. In contrast to collective degrees of freedom, which seem to transport energy far away, secondary electrons also carry much energy, but are stopped in short distance from the path of the projectile.

Electronical energy loss of electrons depends from energy like

$$d\varepsilon/dx|_e = \alpha/E \cdot \ln(E/I)$$

with $\alpha = 2\pi e^2 n_{At} z_{At}$. If we follow the "track" of secondary electrons produced by the projectile, we will find an inner zone of (cascade-) ionization, a wider extended zone of electronical excita-

tion and an outward zone of nuclear or molecular excitation.

For the purpose of getting a qualitative correct base for mechanical calculations we use for the moment only an average energy value of secondary electrons produced by the projectile, $\langle E \rangle$, instead of the full spectrum of secondary electrons. From the formula describing $(de/dx)_0$ we conclude that for an energy below the parameter I nuclear stopping will dominate, i.e. that in total I will give the order of magnitude of the energy lost by an electron in nuclear (molecular) scattering. Since an electron with an energy below the ionization energy E_1 is no more capable for further ionizing, the mean range of ionization is given by the distance which is required to slow down electrons from the mean energy $\langle E \rangle$ to E_1 . $\langle E \rangle$ is only weakly dependent of velocity and charge state of the projectile; an effective ionization rate dJ/dx is given by $(dE/dx)/\langle E \rangle$.

The mean radii of the zones of electronical excitation (distance for reaching energy γI with $\gamma = \exp\{2/3\}$) and of secondary ionization are calculated by analytical integration of the above formula for $de/dx|_0$ from $\langle E \rangle$ to γI or E_1 , respectively. The mean range r_1 of nuclear excitation is controlled by the positive potential of the ionized core, which hinders electrons with energy I to move farther away than $r_v = r_E \exp\{I/[4\pi e^2 dJ/dx]\}$ (this results from the logarithmic behaviour of cylindric symmetric potentials). Due to the diffusive character of the motion of slow electrons the range of nuclear excitation is taken as $r_N = [r_E^2 + r_1^2]^{1/2}$.

From distinguishing between qualitatively different types of excitation we conclude to different parts of the observed spectra: atomic and multiple ions stem from the innermost zone, while undestroyed molecular ions can be expected to be desorbed from the outer "softly excited" zone. A conclusion from observed yield characteristics to the electronical configuration, on the other hand, requires a knowledge about how molecules are involved in the motion of the material following the initial nuclear excitations. The ratio of fragment yield to undestroyed molecules and of neutral yield to ion yield respectively can give information about electronical excitation processes, but we have to keep in mind that for example the coherent burst of highly excited matter can drive out cold molecules, too. At least in the computer simulations of the final microscopic mechanical desorption we see that instantaneous (on atomic time scales) initially deposited nuclear excitations give rise to a contiguous macroscopic outburst of molecules controlled by the involved sound speeds.

Input and model calculations

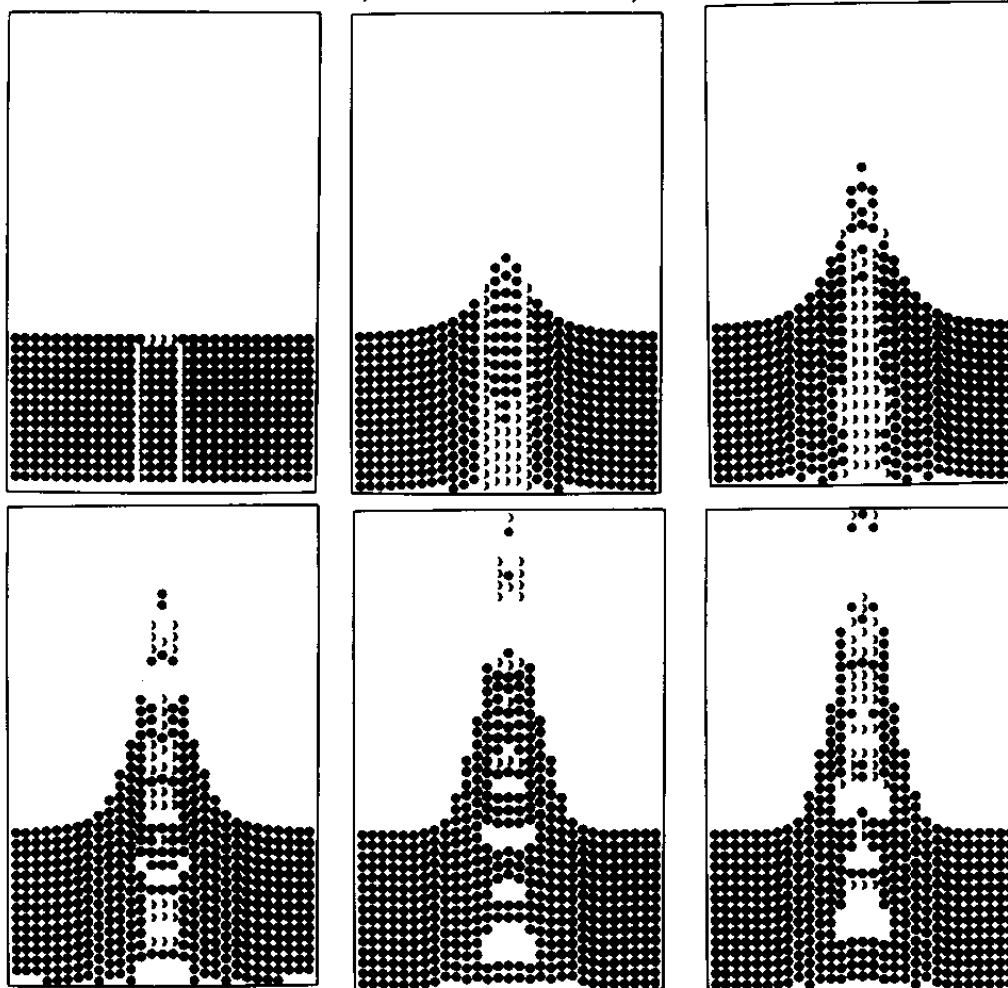
If a process producing molecular motion is found, then the task of evaluating equations of motion remains. In earlier models this problem has been attacked by assuming either individual separation of molecules from the surface, or by macroscopic collective-motion treatment. The aim of those calculations usually is not to give accurate yield predictions, but to test whether a proposed mechanism is reasonable or not. A direct attack on the equations of motion for all molecules involved, on the other hand, has the advantage to bring more information about details to be observed in experiments, such as the shape of the hole left behind after desorption events, or velocity spectra.

Our calculations were performed as a simple evaluation of the Hamilton equations of motion for many-particle-coordinates in first order in time:

$$P(t+dt) = P(t) + F(X) dt \quad \text{and} \quad X(t+dt) = X(t) + (P/M) dt$$

The initial excitation (for the results shown below) was the same as in an earlier paper [1]: a reduction of the attractive part of intermolecular forces proportional to the portion of electrons excited from the valence band within a limited region (corresponding to the zone of electronical excitation). In order to get results comparable to measurements at the IPN (which were the first reason to start our calculations) using Langmuir-Blodgett-molecular targets, we referred to one-dimensional motion perpendicular to the surface only to reflect the extreme anisotropic size of the molecules. The force between molecules touching "head on head" was described by a model

potential consisting of an attractive and a repulsive part¹⁾, while molecules lying "side at side" were assumed to act on each other by friction-like forces only.



The results of the model calculations are at present just snapshots for successive times. For early calculations, see [2]. The formation of "clusters" is enabled both by attractive forces and friction. Since the parameters of friction were taken here one order of magnitude below the potential parameters, energy transport to the side is inhibited.

Entropic excitation

In a somewhat different approach for the initial nuclear excitation by the passing shower of secondary electrons we set off with quasielastic collisions, having the largest cross-section, inversely proportional to their velocity. Since, still, the passing time dt of the secondary electron shower is much less than the atomic oscillation time of the order of picosec, a time-dependent quantum mechanical perturbation may be performed giving the locally deposited energy given to a bond

1) In order to keep numerics stable, we used a non-singular (Morse-) potential, but we found that the type of the potential is not essential to the many-particle-motion, if parameters like molecular spacing, separation energy or sound velocity are kept constant.

which proves to be proportional to its excitation level density times $\exp\{-de \cdot dt\}$, where de is the level spacing. Calculations have been done [2] for the intramolecular v.d.Waals binding.

The collision time in such a process plays the role analogue to the temperature in a quasistationary process. Thus taking as collision time estimate the Rydberg time and converting it to a 'temperature' we gain numbers in the range of those as fitted by McFarlane to his PDMS-Spectra [3]. Detailed calculations for this approach will be given elsewhere [4]. Early qualitative arguments for such a fast energy transfer were given by F.R.Krueger [5] for a model of pure surface excitations.

Tests of the model of nuclear energy deposition have been undertaken using Oligosacharides. The assumption to be checked is whether the energy deposition is proportional to the level-density. Here oligosacharides are especially useful. They consist of a chain of known building blocks loosely bound by a glycosidic bond. This is a covalent bond via an oxygen, but because of the many possible states after break up including hydronization the level density should be high, although much less than for the v.d. Waals binding by which the molecules are bound to each other and to the surface.

The desorption abundancies should show for thermal desorption such as by a FAB induced desorption the following characteristic differences to FHIID. For a thermal excitation we expect the abundance ratio of the full molecule as to one with one building block less to be much smaller than one and in addition to show characteristic odd-even staggering, in that the ratio is larger for molecules with an even number of blocs. These effects may indeed be inferred from recent experiments [6]. In contrast, for FHIID each glycosidic bond has an equal independent probability of breaking up and we get for the abundance ratio z to be related to the break up probability to be $w = \frac{1}{2}[z + 2(n-1)/2]^{-1}$ which readily reflects FHIID-data of oligosacharides measured by the ORSAY group [7] of probes prepared by P.Koell [8], see the figure, where the large surplus yield of undamaged molecules even of a mass in the range of 800 is conspicuous.

The glycosidic breakup comes out here as in all other cases of $n = 2, 3, 4$ to be about 7% of the v.d. Waals binding of the molecules to each other, which we find reasonable in view of the respective level-densities.

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