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Universal scaling for biomolecule desorption induced by swift heavy ions

G. Szenes *

Department of General Physics, Eötvös University, 1518 Budapest, P.O. Box 32, Hungary

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Abstract

A thermal activation mechanism is proposed for the desorption of biomolecules. Good agreement is found with the experiments in a broad range of the electronic stopping power. The activation energies of desorption U are 0.33, 1.57 and 5.35 eV for positive, negative and neutral leucine molecules, respectively, and 2.05 eV for positive ergosterol molecules. The desorption of valine clusters is analyzed. The magnitude of the specific heat shows that the internal degrees of freedom are not excited up to the moment of desorption. The effect of irradiation temperature and of ion velocity on the desorption yield is discussed on the basis of the author's model. The scaling function derived in the model for the desorption of biomolecules is applied also to the sputtering of SiO_2 and $U = 0.42$ eV is obtained.

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Keywords: Electronic sputtering; Leucine; Thermal spike; Thermal activation; SiO_2

1. Introduction

It was about 30 years ago that Macfarlane and Torgerson observed that intact molecules are desorbed when biologically important large molecules are bombarded by energetic ions [1]. It was clarified that there was a correlation between this effect and the electronic stopping power S_e of the bombarding ions. Up to now, it is an unsolved problem how these large molecules can survive the bombardment without damage. Later experiments provided another surprise: the desorped intact molecules had kinetic energies above 10 eV [2]. These unexpected results attracted the attention of many scientists and excellent experiments were performed in a number of laboratories. Reviews of the most important previous experiments were published in [3–5]. Information about recent results can be found in [6,7]. Many theories have been published but even the mechanism of desorption has not been identified unambiguously [5,8,9].

* Tel.: +36 1 372 2821; fax: +36 1 372 2811.
E-mail address: szenes@ludens.elte.hu

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Recently, we applied our thermal spike model to this problem and derived a scaling function for the desorption which had a much more general validity than any previously proposed one [10]. We showed that the desorption of biomolecules was a uniform process for the molecules in various charge states and were able to draw conclusions with respect of fine details of the structure of the desorped cluster molecules [11]. In this paper we briefly review the main results and present new applications of the model. We discuss the effect of the specific ion energy E and the irradiation temperature T_{ir} on the desorption yield Y and show that our approach can be applied to the sputtering of inorganic molecules as well.

2. Experiments on biomolecule desorption

We showed in [10] that the desorption yield of intact biomolecules can be described by the following function:

$$Y_\omega = B_\omega S_e \exp\{-A_\omega/S_e\}, \quad (1)$$

where ω denotes the charge state and A_ω and B_ω are constant for the given molecule. Eq. (1) is valid for small amino acid molecules (valine) and large biomolecules (bovine insulin) in a range of S_e exceeding an order of magnitude. In Fig. 1 the experimental data of Hedin et al. are shown who measured the desorption of positive, negative and neutral amino acid leucine molecules (MW = 131) [12]. The samples were prepared by the electrospray method and they were irradiated by C, O, S, Ni, Br, and I beams of 0.61 MeV/nucleon specific energy at room temperature. We present the experimental data in a $\ln(Y_\omega/S_e) - 1/S_e$ plot in Fig. 1 where the experimental results are well described by Eq. (1) for molecules in various charge states. Please note that Y of neutral molecules is about 10^3–10^4 higher than Y of charged molecules. We also show the experimental data of Hakansson et al. [13] on ergosterol $C_{28}H_{44}O$ with MW = 397. The irradiations were performed by I, Cu, S, O, C and Li ions between $E = 0.12$ and 0.5 MeV/nucleon. Seemingly, Eq. (1) describes well the desorption of ergosterol as well.

Ion-induced desorption experiments were also performed by Hakansson et al. on amino acid valine samples prepared by the electrospray method. The irradiations were performed with various ion beams of the same velocity ($E = 0.71$ MeV/nucleon). The desorption of positive clusters of n valine molecules $(nV + H)^+$ were observed up to very high values of n [4]. The results are shown up to $n = 4$ in Fig. 2. The data of Brandl et al. on the desorption of $(V - H)^-$ ions are also shown for comparison [14]. Eq. (1) provides again a good description of the results.

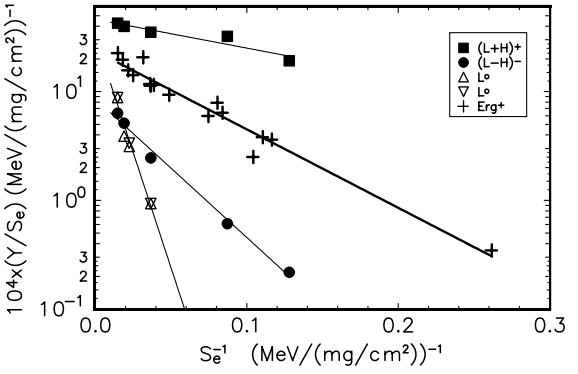

Fig. 1. Variation of the desorption yield Y with the electronic stopping power for positive $(L + H)^+$, negative $(L - H)^-$ and neutral L^0 leucine molecules [10]. The Y is multiplied by 5×10^3 for L^0. The results for positive ergosterol ions Erg^+ are also shown [11].

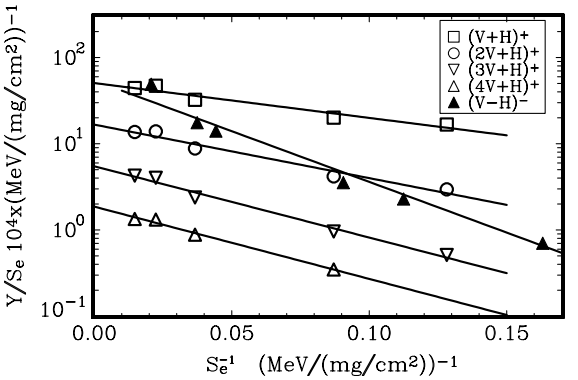

Fig. 2. Variation of the desorption yield Y with the electronic stopping power for valine cluster ions [12]. The results on negative valine molecular ions are also shown [13].