

Ionization of Organic Molecules by Fast Molecular Ion Bombardment

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The bombardment of organic samples by the ionization products of trimethyl-pentaphenyl trisiloxane was found to have a strong effect on the sputtering yield of molecular parent ions of thermally labile compounds. For the tetrasaccharide stachyose an order of magnitude higher yield was obtained with fast molecular ion than with fast Hg atom bombardment. This difference decreased from tetra to disaccharides and was smallest for arginine.

Secondary ion mass spectrometry (SIMS) is of growing interest for the analysis of thermally labile organic compounds [1–5]. In this ionization technique, secondary molecular parent ions such as $[M+H]^+$ or $[M+Na]^+$ ions are produced by bombardment of sample layers with atomic ions or neutral atoms ("fast atom bombardment" [5, 6]) of some keV energy. Up to now a number of elements such as Ar, K, Xe, Cs and more recently also Hg [7] have been applied as primary bombarding particles. With increasing mass from Ar to Hg a significant increase in the yield of molecular parent ions has been observed.

This phenomenon of a collision induced desorption of parent ions of organic molecules cannot be explained by linear collision cascades but has to be attributed to the formation of a "spike", i.e. a dense cascade in which all atoms of a cascade volume are in motion [8]. Since the bombardment with molecular ions favours spike formation [8], the use of fast molecular ions instead of fast atoms or atomic ions may lead to a further increase in the yield of secondary molecular parent ions. Enhanced sputtering by diatomic molecules as compared to the sputtering yield of two atoms of the same velocity is well established [9]. Following this line we have chosen the ionization products of larger molecules to examine the effect of fast molecular ion bombard-

ment on the ionization of thermally labile compounds.

In this note we report first promising results on the use of fast molecular ions as primary particles for SIMS of bioorganic compounds. The molecular ion beam of some keV energy was generated by the ionization of the diffusion pump fluid trimethyl-pentaphenyl trisiloxane (DC 705) in a discharge. To this end the siloxane was introduced into a commercial saddle field discharge tube (Ion Tech Ltd.) developed for the production of a fast Ar or Xe beam in conventional fast atom bombardment mass spectrometry. Using Ar or Xe a high degree of neutralization of keV ions occurs by resonant charge exchange reactions in a collision region. However, for the ionization products of the siloxane such neutralization reactions should be negligible because of the lack of resonance in charge exchange between the neutral molecules and most ions leaving the discharge region. This conclusion can be derived from the electron impact mass spectrum of the siloxane in which the parent ion peak is very weak. In this spectrum the base peak at m/z 531 is formed by $[M-CH_3]^+$ ions. A few further abundant fragments are observed between m/z 197 and 453. It is probable but has not yet been checked that under the applied conditions of a low gas pressure in the source of about 10^{-3} Pa or less the fragment ion of mass 531 is also the main component of the fast ion beam.

A voltage of 7 kV was applied to the discharge tube. The intensity of the ion beam was between 3 and $10 \mu A$ depending on the pressure in the source. The beam was directed onto the target surface at an angle of 60° with respect to the normal direction. A quadrupole filter was used for analysis of the secondary ions.

The oligosaccharides used in this study were mixed with NaI in a 10/1 ratio of the weights and dissolved in methanol. The sample solutions were deposited on the target by adding a larger amount of glycerol.

In order to get an estimate of the relative yield between fast molecular ion bombardment and atom bombardment similar experiments were performed with Hg using again the saddle field Ion Tech source. For Hg a voltage between 3.5 and 4 kV was

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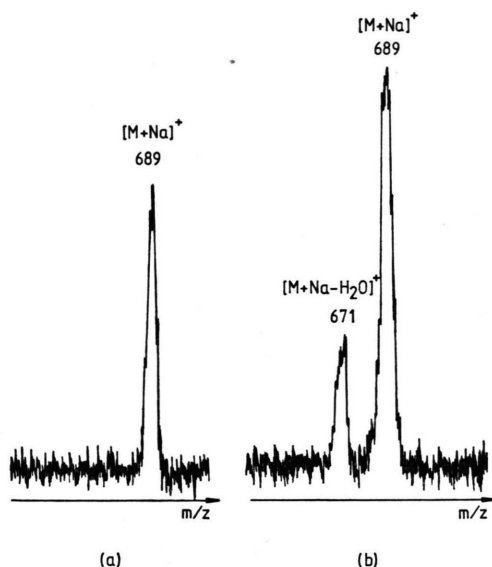


Fig. 1. Secondary ion signals of stachyose recorded by a quadrupole mass spectrometer at low resolution and obtained by bombardment of a mixture of stachyose, NaI and glycerol (a) with a fast Hg beam of about 40 μ A and 3.6 kV and (b) with a fast molecular ion beam of about 3 μ A and 7 kV. The fast molecular ions are produced by ionization of trimethyl-pentaphenyl trisiloxane in a discharge.

applied to the source and the resulting beam current was between about 30 and 40 μ A.

The most striking effect of fast molecular ion bombardment was observed for the tetrasaccharide stachyose: As shown in Fig. 1 the yield of the $[M+Na]^+$ ion of stachyose is an order of magnitude higher following bombardment with the siloxane ions than with Hg atoms if the difference in the beam current is taken into account. This enhance-

ment in the yield of the $[M+Na]^+$ ions was found to decrease strongly from stachyose to sucrose. In the case of arginine the yield of the $[M+H]^+$ ions was about comparable for both modes of secondary ion mass spectrometry. It is interesting to note that bombardment with fragment ions of perfluorotributylamine, whose masses are mostly below m/z 200, resulted in a higher yield of parent molecular ions for arginine and a much lower yield for stachyose as compared to the siloxane ion bombardment.

A second difference in the secondary ion formation is also shown in Figure 1. The bombardment by the siloxane ions gives rise to an enhanced water elimination from the molecules. This effect was also observed with raffinose and may point to a higher thermal loading of molecules in the desorption step. On the other hand some fragment ions resulting from glycosidic bond rupture in the spectra of oligosaccharides became less abundant under conditions of molecular ion bombardment. It has to be added that peaks from the siloxane are also present in the spectra.

Fast molecular ion bombardment appears to be promising for the ionization of larger organic molecules. By selecting primary molecular ions of appropriate size and mass and applying much higher energies than in the present study for the bombardment of samples the number of thermally labile organic molecules amenable to mass spectrometry may be considerably increased.

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