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Ion Formation from Organic Solids IFOS III

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Ion Formation from Organic Solids (IFOS III)

Mass Spectrometry of Involatile Material

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Editor: A. Benninghoven

With 171 Figures

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Preface

The 3rd International Conference on Ion Formation from Organic Solids (IFOS III) was held at the University of Münster, September 16–18, 1985. The conference was attended by 60 invited scientists from all over the world. Of the 43 papers which were presented, 40 are included in these proceedings.

The aim of IFOS III was to promote the exchange of results and new ideas between scientists actively working in the field of mass spectrometry of involatile materials. Various aspects of the ion formation process – realization and optimization, theoretical understanding and analytical application – were treated, as well as instrumental developments. Some emphasis was placed on recent developments in time-of-flight and Fourier transform ion cyclotron resonance mass spectrometry, and its impact on the mass spectrometry of involatile materials.

The most important goal of the conference was to combine facets of the understanding of the most complex ion formation processes with the many different aspects of its analytical application. The participants came from a wide variety of different fields, including pure and applied physics and chemistry, medicine, pharmacy, and space research.

Finally, on behalf of all the conference participants, I would like to thank Dr. W. Sichtermann and Miss I. Bekemeier for the perfect preparation and technical organization of the conference.

The next conference in this series, IFOS IV, is planned for the autumn of 1987, in Münster.

Münster, January 1986 *A. Benninghoven*

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Part I

^{252}Cf-Plasma Desorption

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Use of Polymer Surfaces for Molecular Ion Adsorption and Desorption

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1. Introduction The desorption of molecules and molecular ions from surfaces as a consequence of excitation by an incident fast or slow particle is a classic example of a good news-bad news scenario. The good news is that organic mass spectrometry has experienced a revolution in development and application. The bad news is that the understanding of the processes involved is still in a state of chaos and there is no evidence that the atmosphere has improved to a level where an orderly evolution of concepts will emerge. Part of the problem is emotional, linked to the personalities and ambitions of those, like ourselves, who are actively promoting a particular variant and model, but another part is related to the complexity of the problem. Unlike studies of atomic and molecular ion emission using highly disciplined surfaces where theory and experiment are sharpened to elegant simplicity, the fragile and reactive nature of the organic molecule makes the study of the emission of their molecular ions a dirty business. One aspect of the high vacuum technology that has made possible a study of adsorbate-substrate interaction is the use of Langmuir adsorption at a solid-gas interface. By careful control of pressure and exposure time, it is possible to lay down adsorbate layers with varying degrees of surface coverage and to study the influence of surface concentration on the desorption-ionization process [1]. It is also possible to perform Langmuir adsorption experiments at a solid-liquid interface. In these studies, solution concentration plays the role of partial pressure in controlling the surface concentration of adsorbate. Rapid removal of the liquid phase after equilibrium has been reached leaves a surface containing adsorbate in a particular state dictated by the conditions of the thermodynamics of adsorption for that particular system. The adsorbate can then be analyzed by a surface sensitive mass spectrometric method. While the adsorbate-substrate system is not as well defined as in gas-solid adsorption, it is a considerable improvement in terms of control over most of the methods used to prepare organic deposits such as electrospraying or solution evaporation. The variables available include solution concentration and temperature, which can yield thermodynamic state function data for adsorption, different surfaces and surface modification to achieve specificity for adsorption, and the influence of the composition of the solution (pH, ionic strength, counter ion) in preparing the adsorbate in different forms (protonated, ion pair, molecular aggregates).

Our first studies in this approach utilized a cation exchange polymer, Nafion, as the substrate, and we were able to demonstrate the feasibility of the method using inorganic and organic cationic species [2]. In the work reported here, we have expanded this approach to include other polymer surfaces and a different modification that transforms the surface to an anion exchange medium [3]. The 252-Cf plasma desorption method was used for mass analysis of the adsorbed layers [4].

2. Adsorption on Polypropylene and Poly(ethylene terephthalate) The standard backing we have used for most of our studies in the past decade is aluminized poly(ethylene terephtalate) (Mylar). Samples of organic molecules are deposited on the metal side of the film and the conducting layer serves as a high voltage equipotential surface for accelerating ions from the surface during the mass analysis. The Mylar film is extremely thin (50 nm) which means that 252-Cf

fission fragments can pass through the film from the back side with minimal attenuation of the energy deposition characteristics of the fast (100 MeV) heavy ions. After our experience with adsorption on Nafion, we became interested in the general application of polymer surfaces as a matrix for molecular ion adsorption,and as a first step we reversed the aluminized Mylar film to determine whether we could obtain a meaningful mass spectrum from the polymer side that would not be distorted by surface charging effects or attenuation of the electric field by the dielectric medium between the Al and the desorption surface. We found that it was possible to obtain mass spectra with a quality very close to that observed using a metallized surface. For Mylar, a fragmentation pattern was observed that could be correlated with the structure of the polymer. Similar measurements using Al-polypropylene films showed that this film could also be used,but no mass spectrum was observed that could be attributed to polypropylene.

The original plan was to use Mylar as a base polymer and to coat the surface with other polymeric materials containing different functional groups. In the first measurement, we carried out adsorption studies with untreated Mylar and polypropylene to establish a base for comparison when the surfaces were coated with other polymers. To our surprise, we found that both Mylar and polypropylene exhibited significant cation exchange behavior in the untreated form. Consequently, our intial study involved the study of the adsorption-desorption character of these polymers. For these studies, Al-polypropylene was used because of the possibility that for Mylar, the cation adsorption sites might be carboxyl groups formed by the cleavage of ester linkages in the polymer. But in the final analysis, there was no discernible difference in the performance of the two polymers in terms of specificity and capacity,and our conclusion was that the cation exchange behavior of these materials was due to impurities chemisorbed on the surface and not related to details of the polymer structure [5].

3. Adsorption of CsI The first solute used in the adsorption studies was CsI in aqueous and ethanol solution. Mass spectra of the adsorbed layer from this solution showed only the presence of Cs^+ ions. There was no evidence for I^- ion adsorption. This meant that the surface of the polymer was negatively charged. Subsequent studies on the origin of the negative charge pointed to the presence of strongly adsorbed Cl^- and OH^- ions on the surface presumably coming from impurities in the polymer and solution and from adsorbed H_2O. A study was made on the influence of solution concentration on the surface concentration of adsorbed species covering a concentration range from 10^{-5} M to 10^{-2} M. Plotting Cs^+ ion intensity (determined by 252-Cf-PDMS) vs. solution concentration, a Langmuir-type adsorption curve was obtained with saturation intensity achieved at 5×10^{-3} M for an ethanol solution. Because of the higher solubility in aqueous solutions, the Cs^+ ion adsorption equilibrium constant was not as large as for ethanol solutions. The 252-Cf-PD spectrum of adsorbed Cs^+ was quite different from an electrosprayed sample of CsI. There were no cluster ions at low concentration,and at high concentration the major cluster ion was Cs_2Cl^+ and not $Cs_2 I^+$ which we have interpreted as indicative of the nature of the adsorption site.

4. Adsorption of Rhodamine 6-G Hydrochloride This species was selected as an example of an organic cation for the adsorption studies. The same type measurements were carried out for this species using aqueous solutions and results were obtained similar to what was observed for CsI adsorption: adsorption of only the cation, a Langmuir-type adsorption with saturation molecular intensity (determined by 252-Cf-PDMS) occurring at 10^{-4} M. Fluorescence and Beer-Lambert absorption at saturation gave evidence for full monolayer coverage at this concentration,which was corroborated by a diminution in the intensity of the peaks due to Mylar in the mass spectrum when this polymer was used. The molecular ion intensity at saturation was essentially the same as for a multilayer electrosprayed sample, indicating that for this species, molecular ions are emitted only from the surface layer. At higher surface coverage, dimer ions of Rhodamine 6-G containing the Cl^- counter ion were observed. These probably are formed in solution at the higher concentration and are adsorbed on the surface in this form.

In order to learn more about the nature of the adsorption interaction, competitive adsorption studies were carried out involving Rhodamine 6-G and CsI. Since both of these species are strongly adsorbed as separate solutes, the adsorption from a binary solution gave information on the competition of these two species for the negatively charged sites. If the site is a small compact region of negative charge, Cs^+ ion adsorption would be preferred because of the dominance of the electrostatic interaction. However, if the negative site has a diffuse charge density, then the combination of electrostatic and polarization forces would favor Rhodamine 6-G adsorption because of the polarizability of the aromatic rings in its structure. The results showed that Rhodamine adsorption dominated even when the molar ratio of Cs:Rhodamine was as high as 4:1. This means that the adsorption site resembles a large polarizable organic anion favoring the adsorption of organic cations even in the presence of high concentrations of alkali metal ions. In later studies, this property was utilized to selectively adsorb organic species from solution in the presence of high salt concentrations.

5. Adsorption of Amino Acids and Leu-enkephalin. After the studies discussed above determined the nature of the adsorption behavior of Mylar and polypropylene, this method of sample preparation was applied to the study of important organic species that were not so strongly basic as Rhodamine as to exist predominantly as a cation in aqueous solution. The simplest of these is the ammonium ion (NH_4^+) which is strongly adsorbed on Nafion and which can be desorbed intact using the fission fragments of 252-Cf-PDMS. However, attempts to adsorb-desorb NH_4^+ ions on Mylar failed. This we attribute to the adsorption site behaving as a strong base capable of deprotonating the NH_4^+ ion. The sulfonate group on Nafion is, by contrast, a weak base (conjugate of a strong acid) so that its interaction with the NH_4^+ ion is essentially electrostatic. The same problem was encountered with simple amino acids, even those that are strongly basic (histidine, tryptophan) which in an acidic aqueous medium are positively charged. With the knowledge from the literature [6] that proteins readily adsorb on polymer surfaces, it became a matter of determining how large a peptide or protein had to be before adsorption took place. We next investigated the adsorption of leu-enkephalin from aqueous solution covering the concentration range previously used in the Rhodamine-Cs studies. From 10^{-5} M to 10^{-3} M there was no evidence for peptide adsorption. But above that concentration, adsorption-desorption of molecular ions was observed. At 10^{-3} M, the spectrum of molecular ions was more intense than that of a multilayer electrosprayed sample. There were also other differences. The dominant molecular ions were M±H ions of nearly equal intensity, and a very low level Na^+ intensity, orders of magnitude lower than the electrosprayed sample of the same material and, overall, a much cleaner spectrum free from peaks due to impurities. In the electrosprayed sample, molecular ions containing single and multiple Na^+ ions were observed. At the onset of the appearance of the molecular ions of this peptide, the dimer ion was also observed. This, coupled with the relatively high solution concentration required to effect adsorption, implies that it is the dimer that is being adsorbed and that the monomer ions are a consequence of the dissociation of a dimer ion during the fast ion-induced desorption process [7].

6. Conversion of Mylar to an Anion Exchange Surface [3] We have now demonstrated that cations can be adsorbed and desorbed from Nafion and Mylar surfaces as a consequence of their negative surface charge. To expand the versatility of the method it would also be desirable to have available a positively charged surface for anion adsorption. We wished also to continue to use Mylar as the base polymer film because of its desirable mechanical properties. We have been able to reverse the polarity of the surface by a new kind of surface modification that involves "dissolving" a hydrophobic molecule into the surface that also contains a positively charged functional group. The molecule chosen for this modification was tridodecylmethyl ammonium chloride (TDMAC). The three dodecyl moieties are long hydrocarbon chains that embed into the Mylar surface when it is solvated with a non-polar solvent system such as toluene-petroleum ether. The molecule attaches strongly and is immobilized when

in contact with an aqueous solution. The quaternary ammonium function extends into the polar phase and functions as an anion exchange site.

7. Adsorption of CsI on TDMAC-Modified Mylar Aqueous solutions of CsI were exposed to a TDMAC-modified Mylar surface. The 252-Cf PD mass spectrum of the adsorbed layer showed a strong I^- ion in the negative ion spectrum plus cluster ions of I containing the TDMA moiety. The positive ion spectrum contained no Cs^+ ions but did show cluster ions comprised of I^- and the TDMA cation. Thus, by modification of the Mylar surface by the adsorption of a hydrophobic quaternary ammonium ion, the polarity of the surface was reversed and the surface was found to have a high capacity for anion adsorption.

8. Concluding Remarks The use of polymer and surface modified polymer surfaces show great promise for selective adsorption and as a means of forming adsorbate layers with different surface concentrations, providing a means of controlling adsorbate states in a manner equivalent to what is used in gas-surface studies. The mass spectrum is a powerful and sensitive analysis for determining not only the kind of species adsorbed but also the surface concentration. In addition, the attenuation of the mass spectrum of the substrate is a confirmational signature for the degree of surface coverage. The versatility of the solid-liquid adsorption equilibrium should provide ample opportunity to develop better sample preparation methodologies.

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Electronic Sputtering of Biomolecules

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1. Introduction

The erosion of surfaces under particle bombardment is called sputtering. For metallic targets, sputtering by elastic collisions between screened nuclei (nuclear sputtering) is the dominating mechanism. This effect is most important at low velocities, i.e. below the Bohr velocity, where nuclear stopping is the main energy loss mode. In insulators, where lifetimes of excited electronic states may be long enough to allow excitation energy to be transferred to atomic motion, sputtering due to electronic processes can occur as well. Sputtering of biomolecules by fast ions i.e. ions with a velocity larger than the Bohr velocity, has been shown to be related to electronic stopping [1,2] and may therefore be called electronic sputtering. Most of the ejected particles in sputtering processes are neutral. As recently shown at Uppsala by Salehpour et.al. [3] that is also the case for electronic sputtering of biomolecules,as will be discussed in some detail below. The analytical application of electronic sputtering of biomolecules is the method invented by Macfarlane and coworkers [4] called ^{252}Cf-Plasma Desorption Mass Spectrometry (PDMS). As fission fragments are fast ions, this method may be described as fast ion-solid sample - SIMS with the time-of-flight technique. One of the most promising developments in the field of PDMS involves the use of samples consisting of adsorbed monolayers or submonolayers of biomolecules on polymer backings [5,6]. In this report, sample application by adsorbing proteins on nitrocellulose is discussed.

2. Yields of intact neutral molecules in electronic sputtering of biomolecules

Almost all studies in the field of electronic sputtering of biomolecules have been concerned with the secondary ions ejected. In the theoretical description of the process the ionization step is a troublesome complication, and therefore experimental data on neutrals ejected are of great interest. Salehpour et.al. [3] have recently developed a method to measure the yield of intact neutral molecules ejected in sputtering of biomolecules. The sputtered particles are collected on a single crystal Si-wafer ($\sim$ 1 cm^2), positioned close to the production target (see fig. 1). A film of biomolecules prepared with the electrospray technique was bombarded with fast ions (90 MeV $^{127}I^{14+}$) from the Uppsala EN-tandem accelerator. The collector was then analyzed in two ways. In the first method the collector was directly transferred in vacuum to a PDMS setup and a low intensity beam (1000 particles/sec) of 90 MeV $^{127}I^{16+}$ was used to make a PDMS-analysis of the

collector surface. With the PDMS method relative yield measurements can be performed. The amount of molecules collected was always less than one monolayer and the sticking coefficient was assumed to be 1.

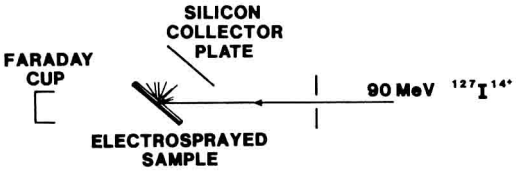

Fig. 1 The principle of the experimental setup used to measure sputtering-yields of intact neutral molecules.

The absolute yields were determined by performing amino acid analysis [7] of the collector. As one monolayer of an amino acid of 1 cm^2 corresponds to about one nanomole, the analysis is performed close to the detection limit of state of the art amino acid analysis. Using the methods described the amino acid leucine (MW 131) was studied with a 100 pA beam of 90 MeV $^{127}I^{14+}$. If one assumes cosθ angular distribution for the ejected molecules, the intact neutral molecule yield was measured to be 1180±280 per incident ion [3]. As the yield of positive (protonated) molecular ions is about 0.1 the neutral to charge ratio for intact molecules is therefore about 10^4. Recently the first method was applied to the peptide LHRH (luteinizing hormone-releasing hormone, MW 1182). In fig 2a the PD-spectrum of positive ions from a Si-collector in that experiment is shown. The protonated molecule can be identified in the spectrum. Also shown is the long flight-time part of the spectrum from a clean collector surface. In fig 2b the PD spectrum of a spincasted LHRH [8] sample is shown. The spincasted film has an estimated thickness of 10Å, i.e. of the order of one monolayer as measured by ellipsometry. The same number of 90 MeV $^{127}I^{16+}$ was used to collect the three spectra. If one assumes that one monolayer is collected in the experiment and the angular distribution is cosθ the "sputter" yield of intact LHRH is about 500.

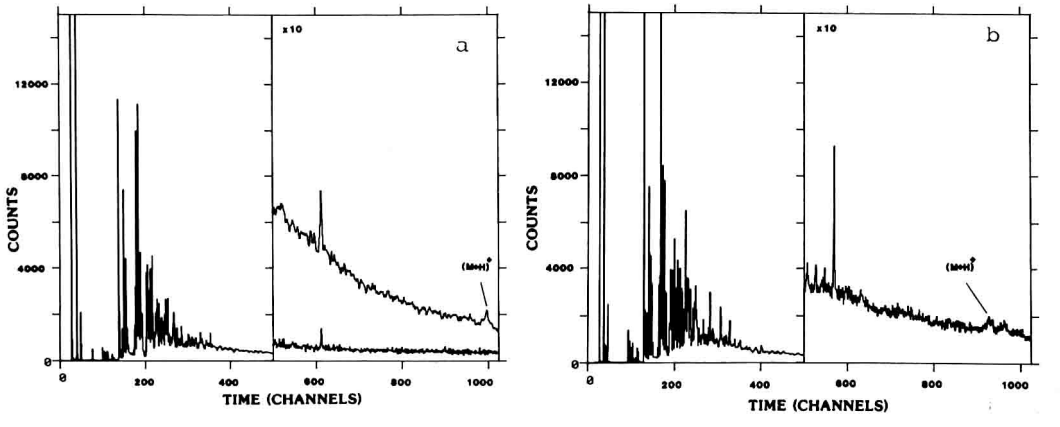

Fig. 2 ^{127}I-PDMS spectrum of positive ions from a Si-collector on which LHRH has been sputter-deposited. Dose: 5.10^{11} ^{127}I (a). The lower spectrum in fig 2a is the spectrum for a pure Si-backing. The corresponding spectrum for an LHRH-spin-casted sample (b).

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