Cluster-induced desorption/ionization mass spectrometry as a versatile tool for the analysis of complex molecules and their reactions on surfaces

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Desorption/Ionization Induced by Neutral SO2 Clusters (DINeC) is employed as a very soft and efficient desorption/ionization source for mass spectrometry of molecules and their reactions on surfaces. The matrix-free desorption method is based on cluster-surface impact of SO2 clusters at low cluster energy. As a result, fragmentation-free spectra from surfaces composed of or covered with complex molecules such as peptides and proteins are observed. Molecules at a surface coverage as low as 0.1 monolayers were detected; surface reactions such as H/D exchange or thermal decomposition were observed in real-time and the kinetics of the reactions could be deduced.

1. Introduction

Surface analysis techniques cover a wide range of different surface sensitive probes such as photoelectrons, secondary ions, or surface plasmons, which all give valuable information on surface structure or composition. However, the chemical information obtained is still limited. This is especially true when it comes to the investigation of larger molecules on surfaces, which are of growing interest for surface functionalization. E.g., the attachment of biomolecules on various substrates is intensively studied both with respect to fundamental questions on substrate-adsorbate interactions as well as with respect to future applications. For these molecules, a detailed analysis of the chemical composition on the surface, e.g., if the molecules adsorb intact on the surface and which bonds are established, would be of high benefit. Among the standard surface analysis techniques, secondary ion mass spectrometry (SIMS) is widely used for the investigation of surface adsorbates due to its high surface sensitivity and its capability to detect molecular fragments which give information on the chemical entity adsorbed on the surface. A major disadvantage of SIMS is the high degree of fragmentation during ion bombardment; it has been significantly reduced when using molecular clusters as primary ions [1], but still limits its application in various fields.

More recently, we have shown that desorption/ionization induced by neutral clusters (DINeC) is a soft and matrix-free ion source for mass spectrometry of complex molecules on surfaces [2-4].

2. Method

DINeC employs molecular clusters of 10^3 to 10^4 SO2 molecules; during cluster-surface impact, the clusters do not only provide the energy necessary for desorption but, due to the high dipole moment of SO2, also serve as a transient matrix in which the desorbing molecule is dissolved during the desorption process (Fig. 1). Thus, desorption takes place at comparably low cluster energies (< 1 eV/molecule); shattering of

![Fig. 1 Sketch of the DINeC-MS set-up. SO2 clusters are produced via supersonic expansion from a pulsed nozzle. During cluster-surface impact, surface molecules are desorbed and ionized. Molecular ions (red dots) are transferred into the ion trap for mass spectrometry.](image-url)
the clusters during and after surface impact furthermore leads to a rapid redistribution of the system's energy. As a consequence, desorption takes place without fragmentation of the desorbing molecules [2].

The experiments were performed with a commercial ion-trap mass spectrometer (Bruker amazon speed), to which the DINeC ion source was attached. The clusters were generated via supersonic expansion of 3% SO2 in He at 15 bar through a pulsed nozzle ($t_{\text{pulse}} \approx 0.5$ ms, $f_{\text{pulse}} = 2$ Hz). Desorbed ions were transferred into the ion trap via a biased grid, a dual funnel inlet, and several octopolar ion guides.

3. Results

3.1 Fragmentation-free desorption of biomolecules

Typical DINeC mass spectra from an angiotensin II sample are depicted in Fig. 2. As no fragmentation of the desorbed biomolecules is observed, DINeC allows for unambiguous identification of complex biomolecules, in particular when combined with the MS/MS capability of the ion trap in use.

![Fig. 2 Mass spectra as obtained after cluster-induced desorption/ionization from an angiotensin II sample drop-cast on a Si wafer (covered by its natural oxide). The main peaks ([M+H]+, [M-H]-) are assigned to the intact biomolecules; no fragmentation patterns are observed. Dimers ([2M+H]+, arrow) further indicate the soft nature of the desorption process.](image)

3.2 Real-time observation of surface reactions

Whereas mass spectra as those shown in Fig. 2 can be used for the identification of surface molecules, DINeC can be also used to follow surface reactions of these molecules in real time. As an example, Fig. 3 shows the change of the mass spectrum of angiotensin II when heated to 410 K. When the final temperature is reached (Fig. 3b), the spectrum is characterized by an additional peak indicating the loss of a H2O entity ($m/z = 1029$). When keeping the sample at that temperature, further decomposition of the angiotensin II molecules is observed (Fig. 3c), including the loss of one of the terminal amino acid units ($m/z = 932$). Quantitative analysis of the data allows to evaluate the underlying reaction kinetics. Similarly, the kinetics of H/D exchange in peptides has been investigated; different rate constants could be assigned to different functional groups in one molecule [5].

![Fig. 3 Mass spectra as obtained after cluster-induced desorption/ionization from an angiotensin II sample. (a) fresh sample at RT. (b) sample heated to 410 K. In addition to the peak at $m/z = 1047$, which is associated with the intact molecule [M+H]+, peaks at $m/z = 932, 1012,$ and 1029 appear (indicated by arrows). (c) The latter peaks increase and the main peak decreases with time when keeping the sample at 410 K.](image)

4. References

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