

ASS/AE-13-2-I-TH

Cluster-induced desorption/ionization mass spectrometry as a versatile tool to monitor on-surface reactions in-situ

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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 and their reactions on surfaces, which are of growing interest. E.g., the adsorption of porphyrins on various substrates is intensively studied especially with respect to fundamental questions on substrate-mediated reactions [1]; the attachment of biomolecules on surfaces is of interest both from a fundamental point of view as well as with respect to future applications in surface functionalization. For such molecules, a detailed analysis of the chemical composition on the surface and in-situ monitoring of surface reactions would be of high benefit.

Recently, we have shown that desorption/ionization induced by neutral clusters (DINeC) is a soft and matrix-free ion source for mass spectrometry of biomolecules [2,3]. DINeC employs molecular clusters of 10^3 to 10^4 SO₂ molecules; 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 cluster-surface impact. Thus desorption takes place at comparably low cluster energies (< 1 eV/molecule); shattering of 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].

In this contribution, we demonstrate that DINeC can be used for real-time monitoring of surface reactions of larger molecules such as porphyrins and oligo-peptides. The quantitative nature of the method was demonstrated using angiotensin II molecules individually adsorbed on gold substrates by means of electrospray ion-beam deposition [4]. These adsorbates were desorbed and detected as intact molecules down to a coverage of 10^{-13} mol/cm² (0.001 ML); a linear relationship between surface coverage and signal intensity was observed over three orders of magnitude. Real-time monitoring of surface reactions is demonstrated for isotope-exchange experiments with angiotensin II and different types of porphyrins. Dosing D₂O led to a broadening of the isotopic pattern and a continuous shift towards higher m/z values. When the D₂O pressure was chosen high enough, the H/D exchange rate was determined by the exchange process itself. The results were modeled by means of Monte Carlo simulations taking into account reaction and back-reaction of H/D exchange. Several different rate constants could be extracted and are assigned to the different types of functional groups in the respective molecules.

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[3] M. Baur, et al., *Rapid Commun. Mass Spectrom.* 28, 290-296 (2014).

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