Adaptive Control-based Femtosecond Laser Post-ionization in Secondary Neutral Mass Spectrometry

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Synopsis Mass spectrometry is an analytical technique, essential for almost all branches of chemistry, providing the mass of molecules or molecule fragments at m/z. To choose a specific mass peak and to increase its intensity is clearly appealing. Such a proof-of-concept method integrates a secondary ion mass spectrometer with a near-infrared femtosecond laser, through a laser pulse shaper, in order to achieve adaptive control post-ionization.

Secondary ion mass spectrometry (SIMS) [1], using primary ions to sputter secondary ions, provides a highly sensitive and comprehensive chemical spatial analysis of almost all solid samples. Different samples result in different secondary ion yields due to the matrix effect, which limits quantification. Moreover, the secondary ions represent only a few percent of the sputtered species, while the majority is neutral, forming a base for secondary neutral mass spectrometry (SNMS). While in SIMS the secondary ions originate from the sputtering/ionization processes at the surface, SNMS uses an external source, usually a laser, to post-ionize the sputtered neutral species.

The laser post-ionization utilizes either resonant or non-resonant mechanisms, with pulses ranging from nanoseconds to femtoseconds (fs), and with visible, ultraviolet or near-infrared (NIR) wavelengths. The NIR fs laser provides an attractive alternative to nonresonant and nospecific post-ionization by increasing the molecular parent ion yield, as well as suppressing molecular fragmentation. The nonspecific post-ionization is based on strong field effects such as multiphoton ionization (MPI) and tunnel ionization (TI), where the processes of multiphoton absorption and potential energy surface bending are operative, respectively.

The SIMS/SNMS primary ions, colliding with tens of thousands eV, deposit a great amount of energy into the sample. The secondary species can be vibrationally and/or electronically excited, which might not influence the SIMS spectra, but can affect the post-ionization. The vibrational excitation can increase a phonon-induced (thermal) desorption / sublimation during SIMS. The electronic excitation can be crucial since the adaptive control-based fs laser post-ionization is dependent on the actual potential energy surface.

Several molecules were chosen for these proof-of-concept experiments, in order to elaborate on the molecular parent ion yield enhancement, the molecular fragmentation suppression, the sublimation effect of the samples, and the excited secondary species.

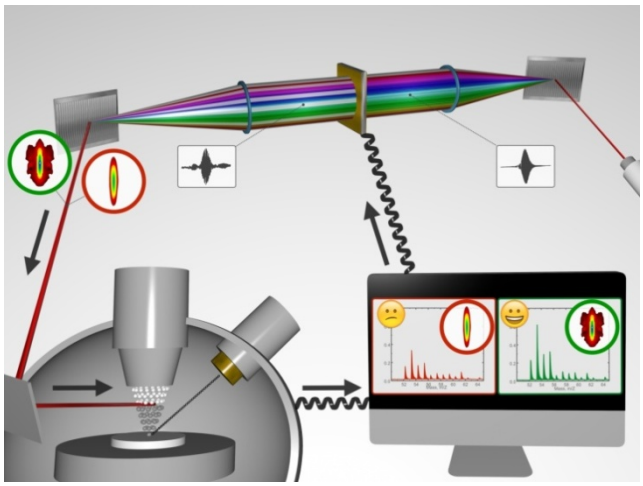

Figure 1. SIMS (lower part, left side) with primary ions sputters the secondary species, which are post-ionized with the laser pulse and then detected. The laser pulse (upper part, right side) is generated and then shaped with the pulse shaper (upper part, middle). The evolutionary algorithm optimizes the mass spectrum (lower part, right side) by changing the pulse phase. The shape is represented with the FROG trace (unshaped and shaped in red and green circles, respectively). The closed loop adaptive control (arrows) consists of SIMS, shaper, and algorithm.

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References

[1] A. Benninghoven, Angew. Chem. Int. Ed. Eng. **1994**, 33, 1023-1043

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