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Advances in Laser- and Lamp-based Photoionization High Resolution Mass Spectrometry

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Photoionization schemes have been extensively explored in both vacuum and ambient ionization mass spectrometry. In ambient ionization, atmospheric pressure photoionization (APPI) development has largely stalled, and atmospheric pressure laser ionization (APLI) remains niche. However, photoionization provides unique control over ionization characteristics and structural selectivity based on light-source wavelength. Uncommon vacuum and ambient laser/lamp-based ionization techniques are presented, offering diagnostic insights at high-resolution mass spectrometry with confident elemental composition attribution.
To expand the photoionization toolbox, atmospheric pressure single photon ionization (APSPLI) using a fluorine excimer laser and Xenon lamp APPI have been explored. [1,2] Compared to standard APLI (266 nm), APSPLI showed increased ionization for aromatic compounds with heteroatoms, while Xenon-APPI demonstrated minimal background signal.
In seeking a robust portable platform, vacuum photoionization Orbitrap mass spectrometry has been realized by deploying aromatic-selective multiphoton ionization (REMPI). [3] Online field studies have shown reliable operation under harsh conditions, recording complex emission patterns with sub-ppm mass accuracy [4]. Facing the diversity in energy transition matrices featuring various oxygen functionalities, derivatization with gas chromatographic pre-separation was evaluated. We find that the silylated species can be well ionized with REMPI. More interestingly, introducing the unique isotopic pattern of Silicon resulted in narrow mass splits. Even in complex mixtures, this characteristic isotopic fine structure could be resolved and used for increased confidence in molecular attribution. [5]
For further structural insights, a custom setup with adjustable-wavelength APLI has been built. Therefore, an optic-parametric oscillator (OPO) was used to investigate wavelength-dependent ionization characteristics in the range of 213-300 nm. Insights into the ionization behaviour of standard compounds allowed us to find structurally diagnostic patterns, with significant redshifts for alkylation or broader absorption bands for larger aromatic moieties. The first correlation of this standard library with the results from petroleum matrices indicated isomeric information. [6]

Literature:
[1] Rüger et al., *Analytical Chemistry*, **2021**, 93, 3691–3697; [2] Neumann et al., *JASMS*, **2023**, 34, 1632–1646; [3] Kösling et al., *Analytical Chemistry*, **2021**, 93, 9418–9427; [4] Kösling et al., *Analytical Chemistry*, **2022**, 94, 16855–16863; [5] Vesga-Martínez et al., *JASMS*, **2024**, 35, 3242–3255; [6] Etscheidt et al., *Analytical Chemistry*, **2025**, 97, 676–685

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