

Edited by Ralf Zimmermann
and Luke Hanley

Photoionization and Photo-Induced Processes in Mass Spectrometry

Fundamentals and Applications

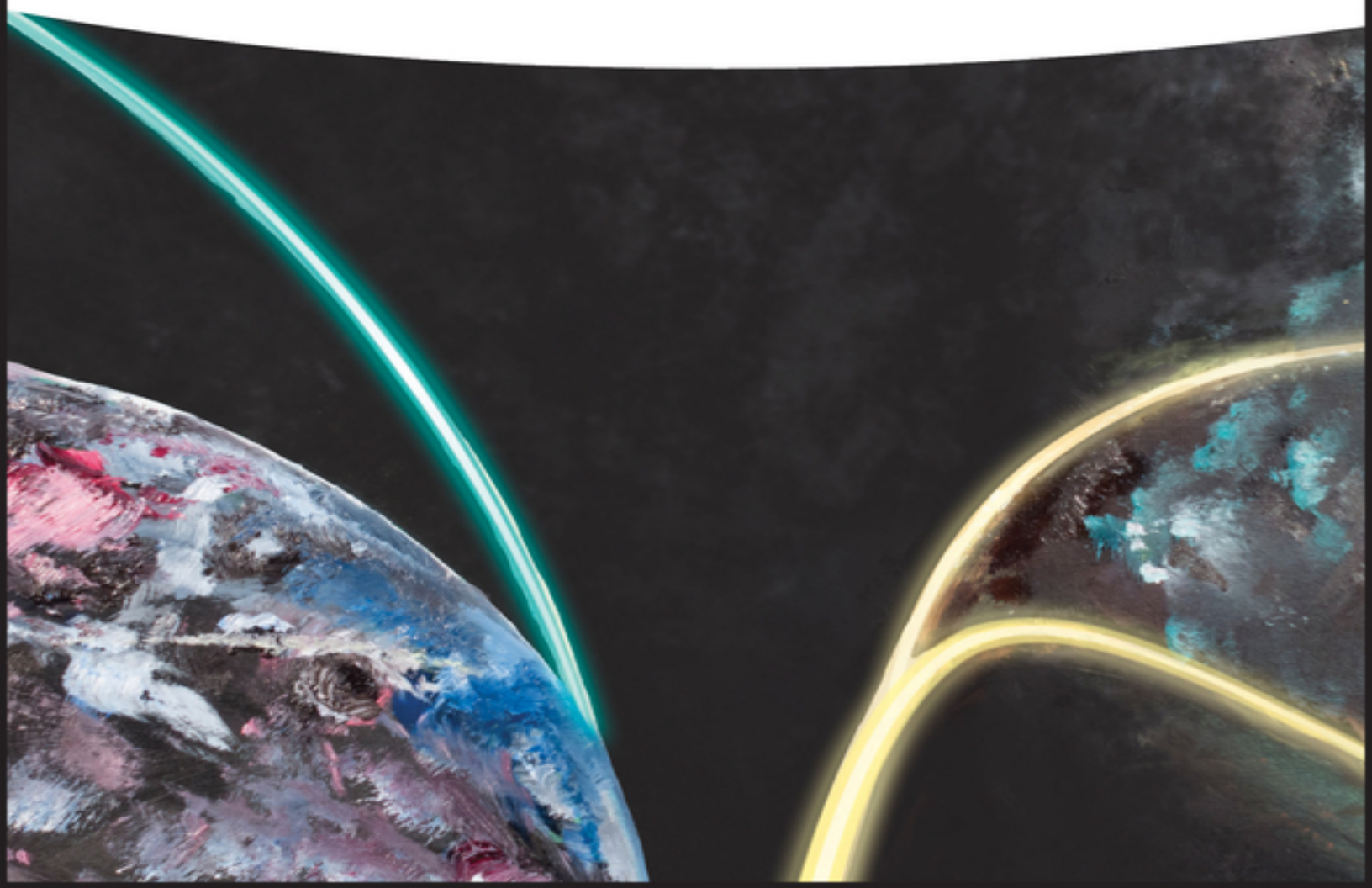


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Cover Images: Courtesy of Jonathan Aldrich, The University of Illinois at Chicago

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Library of Congress Card No.:

applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

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Print ISBN: 978-3-527-33510-7

ePDF ISBN: 978-3-527-68223-2

ePub ISBN: 978-3-527-68222-5

oBook ISBN: 978-3-527-68220-1

Cover Design: Wiley

Preface

The goal of this book is to explain the fundamentals of photoionization (PI) and the associated applications of PI that are playing an increasingly important role in mass spectrometry (MS). The target audience of this book includes practicing scientists, including PhD and MSc students, whose primary interest is in the application of PI to elemental or molecular analysis by mass spectrometry. An overly simplistic analysis provides several motivations for the use of PI in mass spectrometry:

1. Enhance ion yields for specific important compounds of substance classes where other ionization strategies have proven insufficient,
2. Selectively ionize individual molecular structures or classes of molecules from mixtures,
3. Form ions from neutrals with reduced or controlled degree of fragmentation, and
4. Induce desorption or ablation of solids for sampling.

Photoionization comes in different versions and technological realizations, making it somewhat more complicated and thus less popular than standard ionization methods in mass spectrometry such as electrospray ionization and electron ionization. Nevertheless, one goal of this book is to demonstrate how these and other motivations drive the use of PI in MS-based analyses. The editors and authors hope that the readers will use this work as a series of building blocks for future advances in this promising area.

Actually, PI was central to the early development of mass spectrometry and single photon ionization (SPI) remains perhaps the best method for introducing a well-defined amount of internal energy into a molecular ion. Early work in SPI used vacuum ultraviolet (VUV) gas discharge lamps. However, the advent of lasers and the associated nonlinear optical methods made multiphoton ionization (MPI) possible, dramatically expanding PI as a fundamental strategy to probe molecular structure. The continuing improvement of laser technology has also created ongoing opportunities for MS-based applications of PI. For example, MPI via the excimer laser-pumped dye laser was deployed in many early fundamental studies, but was costly, difficult to use, and relatively unreliable. However, the development of smaller and rugged, field-deployable laser sources, such as compact excimer lasers, solid-state lasers as Nd:YAG lasers with integrated harmonic generation, and tunable solid-state lasers such as sealed, Nd:YAG-pumped optical parametric oscillators (OPOs) or Ti:sapphire cavities rendered MPI sufficiently robust for more widespread MS applications.

This interplay between fundamental methods and instrumental considerations has driven the development of analytical applications of PI, so attention is paid here to both considerations. Photodissociation is only discussed here when it occurs in conjunction with PI, such as via the formation of fragment ions from neutral precursors during MPI or SPI. Thus, the burgeoning use of photodissociation of the precursor or molecular ions to form fragment ions for structural elucidation of the former is not discussed here. The fundamentals and mechanisms of low pressure, gas-phase molecular PI for mass spectrometry is covered in [Chapters 1, 2, 5, and 7](#), while molecular atmospheric pressure PI is a topic in [Chapter 8](#). Applications and experimental methods of low-pressure, gas-phase

photoionization mass spectrometry (PIMS) are presented in [Chapters 3, 4, and 7](#). Elemental analysis by PI is covered exclusively in [Chapter 5](#). Processes and applications that include a laser desorption (LD) or direct laser desorption/ionization (LDI) of analytes from the condensed phase are covered in [Chapters 9 and 10](#), while [Chapter 11](#) focuses on the direct analysis of individual aerosol particles using LDI, LD, and PI.

In the following, the content of the book is briefly highlighted chapterwise.

The first chapter entitled *FUNDAMENTALS and MECHANISMS of VACUUM PHOTOIONIZATION*, is serving as an introduction to mechanistic issues common to PI of molecules, atoms, and clusters under vacuum. It provides a fundamental description of light and the interaction of light and matter in the form of photoabsorption on a quantum mechanical level. This includes an excursion in perturbation theory and the dipole approximation and leads to an elucidation of the photon absorption selection rules. Finally, the SPI process, as an absorption in a continuum, nonbound state, is discussed and the most important parameters for SPI, the SPI cross sections and ionization energies, are deducted.

Fundamental aspects of MPI of molecules in the absence of gas-phase collisions are covered in the following chapter, entitled *FUNDAMENTALS and MECHANISMS of RESONANCE-ENHANCED MULTIPHOTON IONIZATION (REMPI) in VACUUM and APPLICATION of REMPI for MOLECULAR SPECTROSCOPY* ([Chapter 2](#)). Here, the theoretical consideration of photoionization processes is extended to MPI processes of molecular species and MPI-based spectroscopy, while multiphoton ionization of atoms is covered in [Chapter 6](#). Different MPI and REMPI processes are presented and a rate equation approach is

used to deduct the influence of molecular physical properties on ionization efficiency. Special REMPI schemes are discussed, which can bypass unfavorable photophysical properties. In the following, MPI-induced fragmentation and dissociation processes are discussed. The application of REMPI for molecular spectroscopy with and without supersonic jet cooling is demonstrated in an exemplary manner via a detailed discussion of the REMPI wavelength spectrum of supersonic jet-cooled biphenylene and some other interesting aromatic molecules. REMPI wavelength spectroscopy, in particular with supersonic jet cooling, reveals the selectivity of the REMPI process that connects high-resolution ultraviolet (UV) spectroscopy to mass spectrometry. The selective ionization of isomeric and isobaric compounds, however, can be extended to the differentiation of isotopomers and – by using a special REMPI technique with circular polarized laser light – even of enantiomers. Finally, in this chapter, REMPI-based photoelectron spectroscopic (PS) techniques such as zero kinetic energy photoelectron spectroscopic (ZEKE-PS) are introduced. The explanation of the fundamental aspects of SPI and REMPI leads to the analytical application of these two PI approaches.

In the beginning of [Chapter 3](#), which is entitled *“ANALYTICAL APPLICATIONS of SINGLE-PHOTON IONIZATION MASS SPECTROMETRY,”* a brief introduction into common VUV-light sources, is given. These can be distinguished as incoherent light sources (“lamp”-based technologies) or coherent light sources (lasers). Also, a brief introduction to the generation of synchrotron light in the VUV range is elaborated (for applications of synchrotron-based SPI, see [Chapter 5](#)). The general setup of SPI mass spectrometry systems with laser- and lamp-based sources is introduced. Depending on the used VUV wavelengths, SPI can be a very soft ionization method,

enabling the detection of the molecular mass fingerprint of complex mixtures. This renders SPI-MS to an ideal approach for direct real time monitoring of complex gas and vapor mixtures. Different applications for online monitoring of combustion and pyrolysis processes are introduced, including online monitoring of gas phases from industrial processes, such as the coffee-roasting and/or the biomass pyrolysis process. Hyphenated instrumental analytical concepts, e.g. gas chromatography (GC) or thermal analysis (TA) coupled to SPI mass spectrometry, are presented and typical results are shown.

[Chapter 4](#), *“ANALYTICAL APPLICATION of RESONANCE-ENHANCED MULTIPHOTON IONIZATION MASS SPECTROMETRY (REMPI-MS),”* gives, in a similar way as [Chapter 3](#) for SPI, an overview of analytical applications of REMPI mass spectrometry. The preferential detection of aromatic analytes by the REMPI process with common laser is emphasized in [Chapter 3](#). An overview on typical fixed-frequency laser lines (excimer lasers or frequency-multiplied, solid-state lasers) is provided along with typical wavelength ranges of tunable laser systems. In the following, several exemplary analytical concepts and applications using tunable and fixed-frequency lasers are presented. The tunable laser sources can be used to focus on specific analytes, which work particularly well with supersonic jet expansion inlet systems. For many applications, however, fixed-frequency wavelength laser and effusive, heated gas inlets can be applied for a useful and often very sensitive “overview” MS-profiling of many aromatic compounds. Exemplary process monitoring applications comprise detection of combustion by-products in flue gases of incineration plants or flavor and roast degree, indicating compounds in coffee-roasting off-gas. Hyphenated instruments connecting gas chromatography or a thermo-optical carbon analyzer (for aerosol loaded

filters) to REMPI-MS devices are discussed. A direct inlet of liquid samples into REMPI mass spectrometry is possible via a membrane inlet or a direct liquid introduction into the ion source. Note that SPI and REMPI processes can be performed in the same MS system. Finally, REMPI under atmospheric conditions is discussed (atmospheric pressure laser ionization – APLI; see also [Chapter 8](#) for SPI-based atmospheric pressure-based ionization).

The application of synchrotron VUV light for SPI-MS-based investigation of combustion and pyrolysis processes is laid out in [Chapter 5](#), *“PROBING CHEMISTRY AT VACUUM ULTRAVIOLET SYNCHROTRON LIGHT SOURCES.”* By direct molecular beam sampling from flames as well as from oxidation or pyrolysis reactors, molecules from the reaction zone can be directly introduced in the mass spectrometer without wall contact. This enables the analysis of stable molecules and intermediates from the reaction zones. The flow reactors and model flame apparatus is often compact enough to be brought to synchrotron light source facilities and can be used for kinetic investigations. Unlike classical VUV sources, the synchrotron light from appropriate beamlines (i.e. equipped with VUV monochromators) exhibit a wide tunability, high energy resolution, and a relatively high photon flux. The identification of individual compounds from isobaric mixture components is possible by photoionization efficiency (PIE) spectroscopy, i.e. the recording of the ion yield as a function of the VUV wavelength. [Chapter 5](#) also presents, an overview on different synchrotron-based PIMS apparatus and analytical results for several reactors and applications.

REMPI of atoms is commonly referred to as “resonance ionization mass spectrometry (RIMS). The RIMS technology and applications are described in the [Chapter 6](#), *RESONANCE IONIZATION MASS SPECTROMETRY*