Photoionization Workshop Report

"Photoionization – Between Vacuum and Atmospheric Pressure"

68th ASMS Conference on Mass Spectrometry and Allied Topics (2020 REBOOT)
Wednesday, June 3rd, 2020, Zoom web meeting
Organized by: Sven Ehlert, Matthias Lorenz and Luke Hanley

Approx. Attendance: 45 people

Organizational matters

- Next year's interest group coordinators will be Matthias Lorenz and Luke Hanley, assisted by **Christopher Rüger** (christopher.rueger@uni-rostock.de).
- The interest group supports the oral session "Fundamentals: Photoionization and Photodissociation" for the ASMS 2021
- The interaction with the attendees was difficult. The Q&A tool is not the best for the workshop as fundament for a discussion. Our main target is to bring the people together. The poll function is a nice feature, but just as an addition. If, by what reason ever, it will be necessary to repeat the online version, it would make sense to allow the attendees the oral communication.

Content:

Agenda for the session

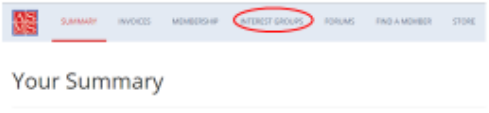
- Brief introduction and session business
  - Introduction to new co-chair: Luke Hanley
  - Call for new workshop co-chair volunteer(s)
  - Call for session coordinator volunteer(s)
- APPI/APLI Application
  - Dr. Christopher Rüger (University of Rostock, Germany)
- New PI Application (Single Particle MS)
  - Prof. Ralf Zimmermann (Joint Mass Spectrometry Centre, Germany)
- Discussion & miscellaneous
  - Presentation of new PI book

Call for volunteers

- Wanted: volunteer(s) for next year's workshop co-chair to work with Matthias and Luke to create the 2021 ASMS Conference workshop for the Photoionization Interest Group
  - Three-year tenure, responsible for planning and delivering the workshop only (no input or control over the oral session, selection of oral talks, or selection of posters)
- Wanted: volunteer(s) for next year's Photoionization & Photodissociation main conference session coordinator/chair
  - Responsible for planning and delivering the main conference session only (no input or control over the workshop session)
  - Workshop co-chairs can recommend oral session coordinator

Other business

- Please review your ASMS profile to ensure that you have Photoionization selected as an interest area
  - Some issues with members' interests being wiped during the platform migration last year
- Please sign up to the ASMS Forums area and participate in the Forum discussions
  - Login > My Account (top right corner) > Forums (top middle)



ATMOSPHERIC PRESSURE PHOTO AND LASER IONIZATION (APPI/APLI) – ASPECTS ON COMPLEX MIXTURE CHARACTERIZATION

Christopher P. Rüger[1,2], Anika Neumann[1], Johann Le Maître[2,3,4], Julien Maillard[2,3], Ralf Zimmermann[1], Carlos Afonso[2,3], Pierre Giusti[2,4]

[1] Joint Mass Spectrometry Center Rostock & Munich – JMSC, Germany

[2] International Joint Laboratory - iC2MC: Complex Matrices Molecular Characterization, France

[3] University of Rouen, COBRA Laboratory, France

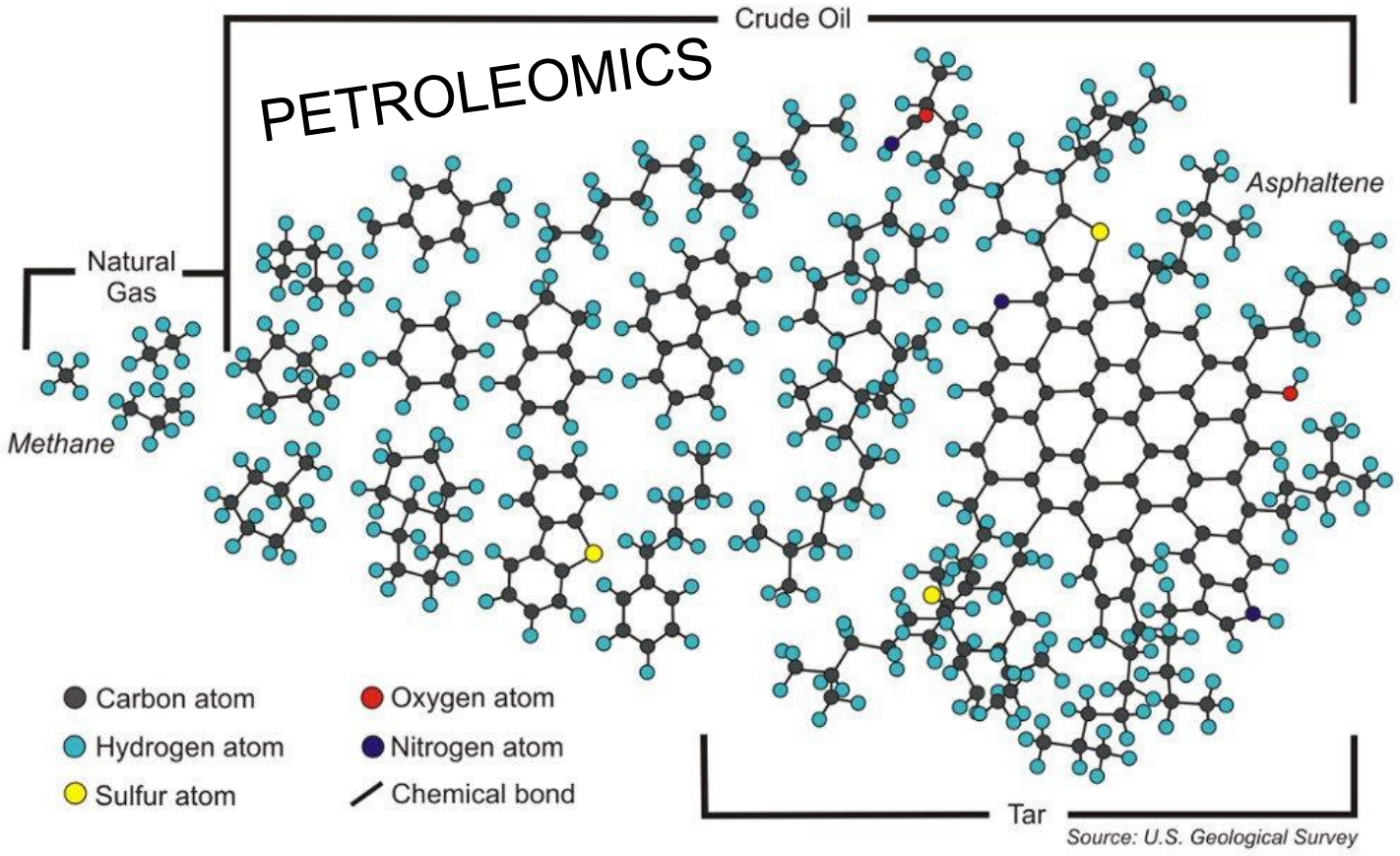
[4] TOTAL Refining & Chemicals, Total Research & Technology Gonfreville, France

Annual conference of the American Society for Mass Spectrometry (ASMS), digital reboot – 03.06.2019

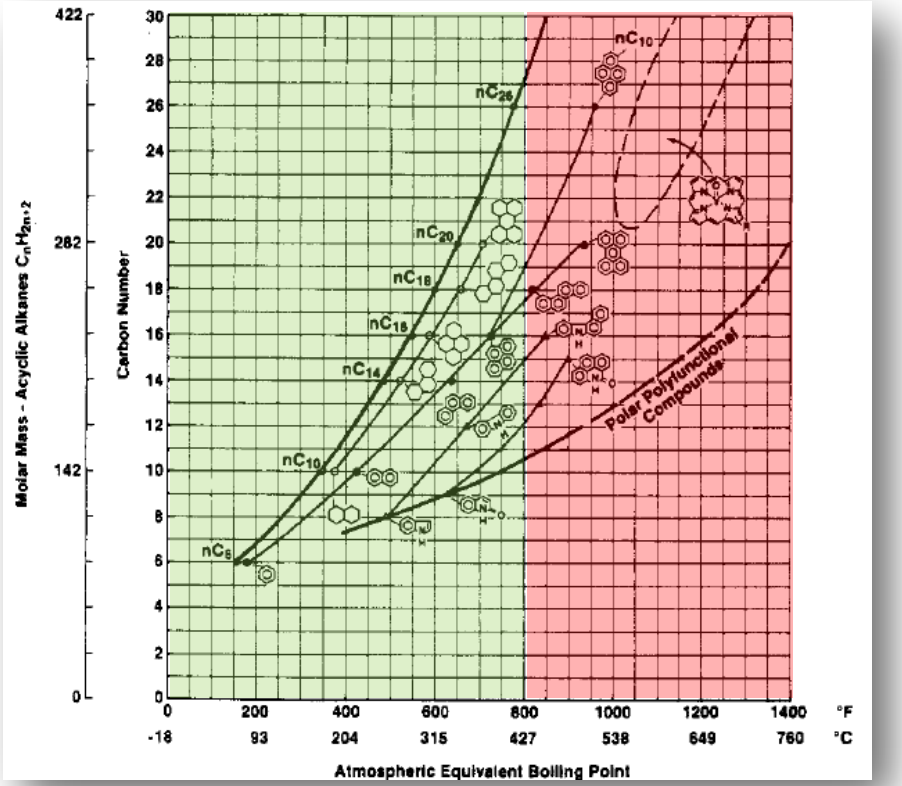
RAPID 5-10 MIN OVERVIEW

- Defining the Playground – Complex Mixture Analysis
- Atmospheric Pressure Photo and Laser Ionization
- The Key: High-resolution Mass Spectrometric Instrumentation
- Selected Application Examples and Conclusion
- Questions and Future Whishes

CHALLENGES IN COMPLEX MIXTURE ANALYSIS - PETROLEUM COMPLEXITY



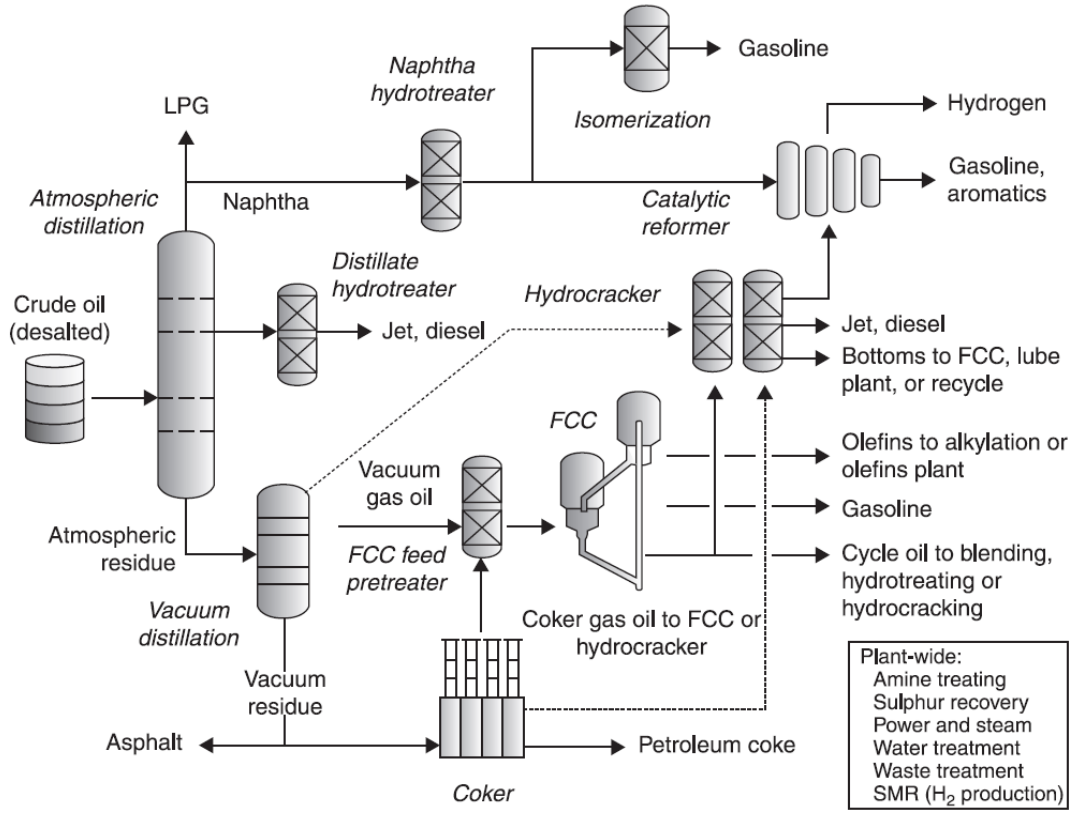
GC/GCxGC-MS accessible

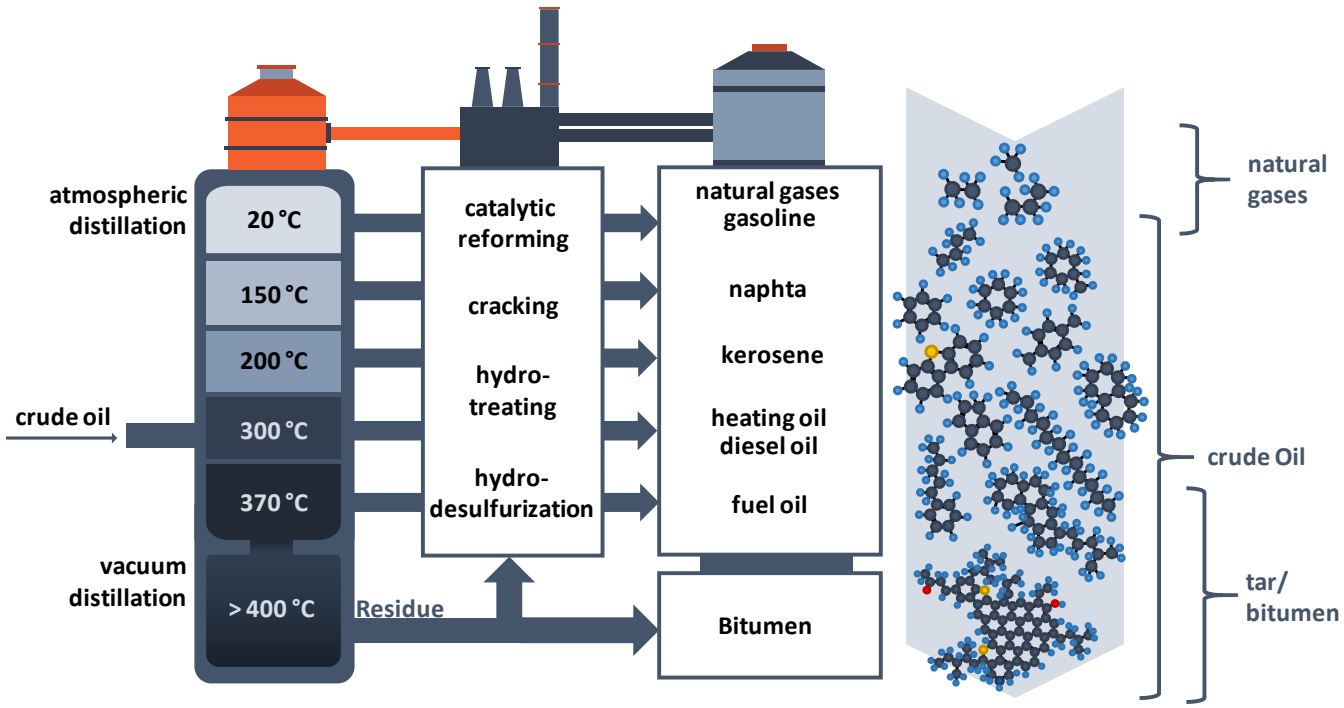


Challenging heavy fractions

→ wide range of chemical functionalities, m/z-range from < 100 up to > 1000,
mostly **CHNOS** and some metals (**Ni, V, Fe**), tremendous isobaric and isomeric complexity

MOTIVATION AND APPLICATION CONTEXT: PETROLEUM COMPLEXITY

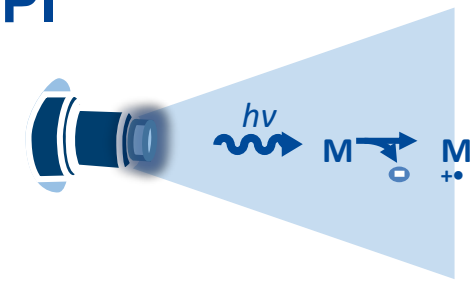




→ wide variety of processes and reaction schemes (distillation, thermal/catalytic conversion, etc.)

INSTRUMENTATION – ATMOSPHERIC PRESSURE PHOTO/LASERIONIZATION

APPI



Single photon ionization (APPI)

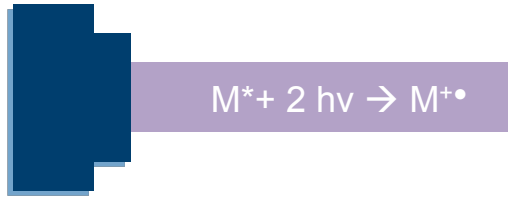
→ universal

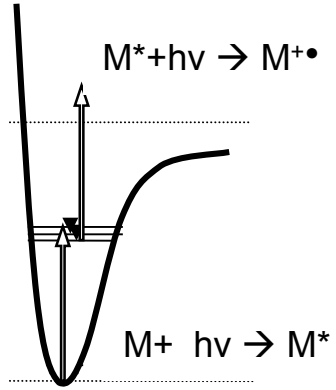
	type of UV lamp and photon energies	Compounds	Ionisation energy [eV]
IINERT		N_2	15,6
		H_2O	12,6
		Acetonitril	12,2
		O_2	12,1
	Argon (11.2 eV)		
IONISATION		Methanol	10,8
		Isopropanol	10,2
		Hexan	10,1
	Krypton (10.0 and 10.6 eV)		
		Heptan	9,9
		Aceton	9,7
		Pyridin	9,3
		Benzol	9,2
		Toluol	8,8
	Xenon (8.4 and 9.6 eV)		
		Naphthalin	8,1
		Anthracen	7,4

APLI

Multiphoton ionization (APLI)

→ high selective and sensitive for aromatic compounds

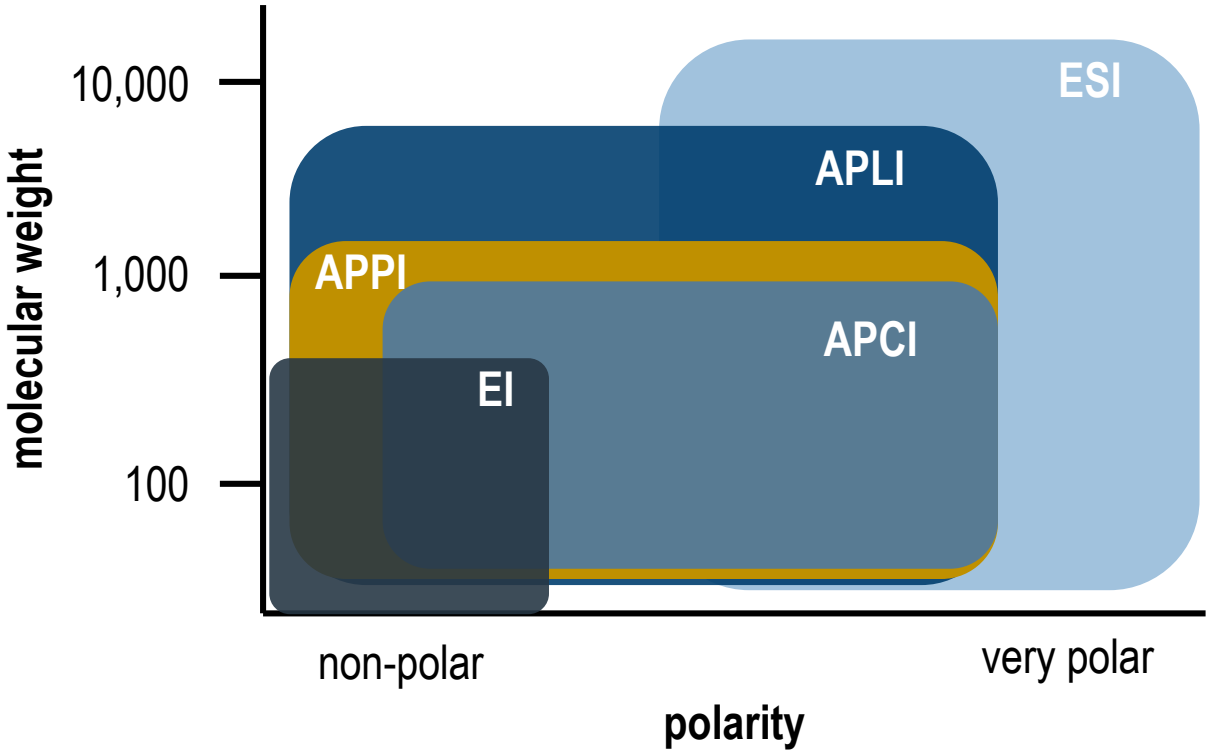




WHY THE EFFORT?

INSTRUMENTATION – ATMOSPHERIC PRESSURE PHOTO/LASERIONIZATION

ADDRESSING DIFFERENT PARTS OF THE CHEMICAL SPACE!



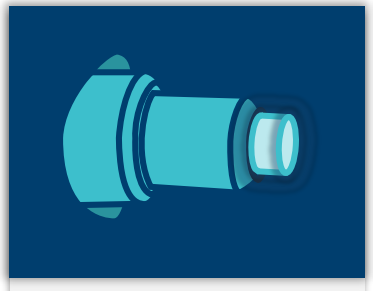
INSTRUMENTATION – ATMOSPHERIC PRESSURE PHOTO/LASERIONIZATION

ADDRESSING DIFFERENT PARTS OF THE CHEMICAL SPACE!

APCI

polar, semipolar compounds (particularly oxygen species)

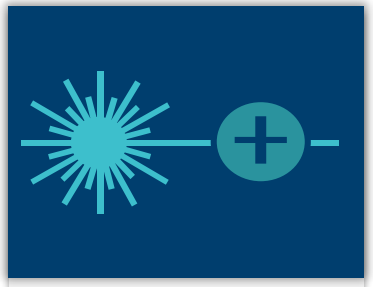
liquid or gaseous sample introduction



APPI

semipolar, non-polar compounds (particularly sulfur species)

Liquid or gaseous sample introduction



APLI

polyaromatic hydrocarbons only

gaseous sample introduction (at Univ. Rostock)

ESI

polar compounds

direct liquid injection method

INSTRUMENTATION – HIGH-RESOLUTION MASS SPECTROMETRY

University of Rostock – ultra-high resolution mass spectrometry laboratory

Ionization techniques

- Electrospray ionization (ESI), Atmospheric pressure chemical ionization (APCI)
- **Atmospheric pressure photo ionization (APPI), Atmospheric pressure laser ionization (APLI)**, Laser desorption ionization (LDI)

Coupling techniques

- Gas chromatography (GC)
- Thermal analysis (TA)
- Liquid chromatography (LC)

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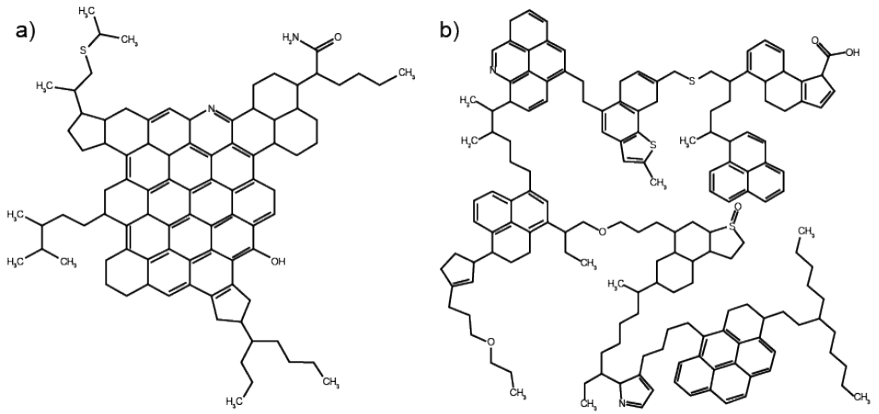
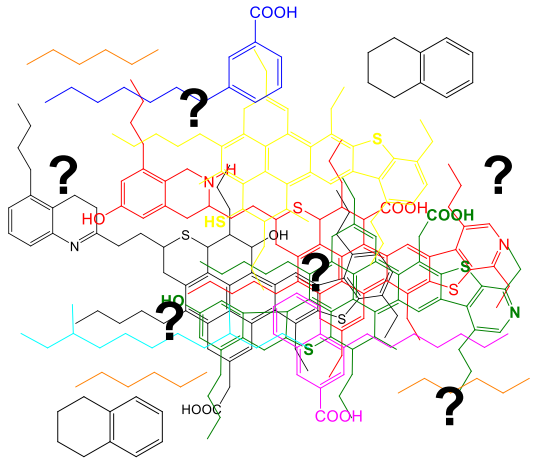
SELECTED APPLICATION EXAMPLES AND CONCLUSION

Asphaltenes

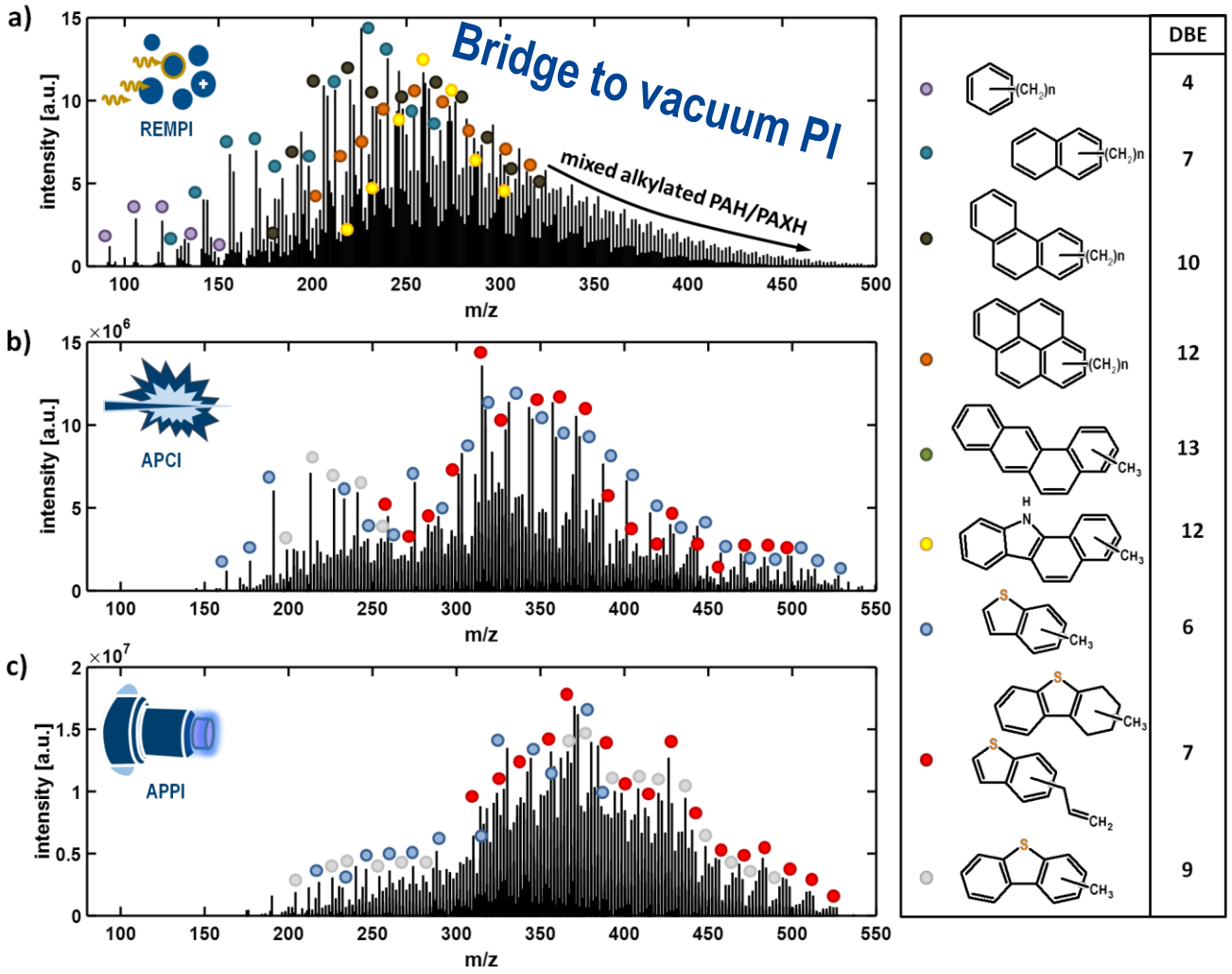
- wellbore deposition (pressure drop and plugging)
- clocking, flocculation, fouling and pipeline blocking
- flow instability and composition changes
- catalyst poisoning/deactivation
- corrosive properties
- the key is managing the precipitation and deposition: **“flow assurance”** → **chemical description** to develop directed strategies

“the cholesterol of oil“

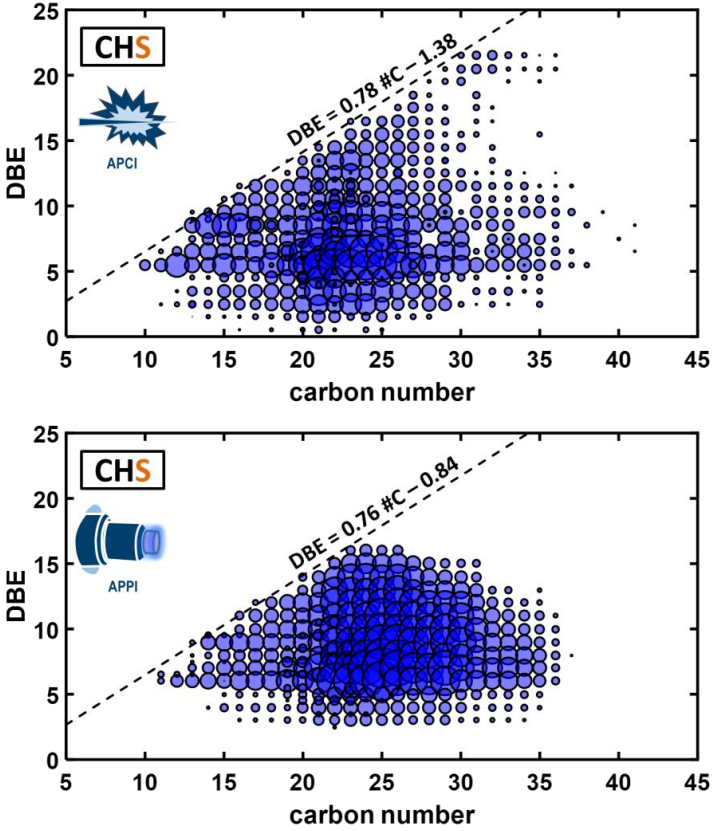




SELECTED APPLICATION EXAMPLES AND CONCLUSION

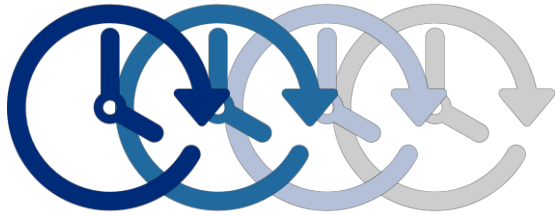


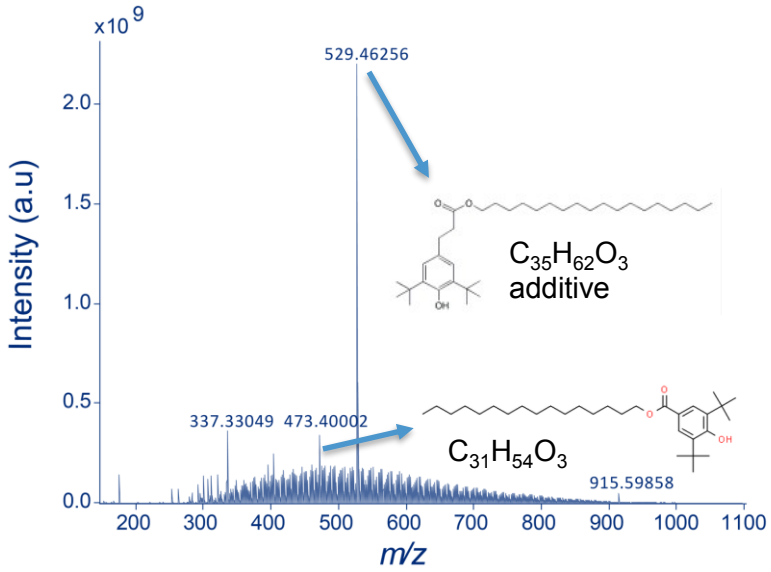
- alkylated aromatic structures with 2-4 rings as major motive CH- and CHS-species as major contributor to APCI and APPI

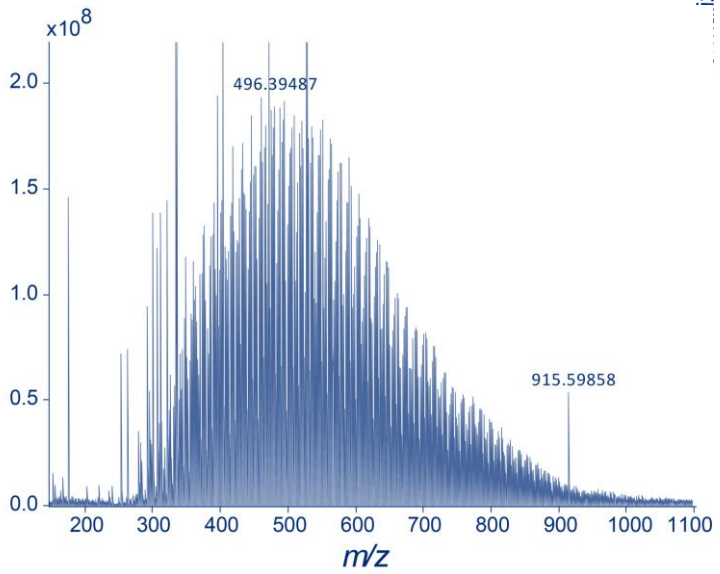


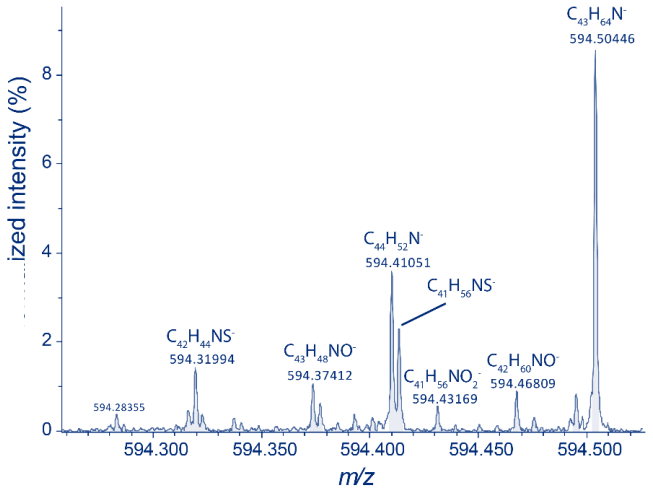
SELECTED APPLICATION EXAMPLES AND CONCLUSION

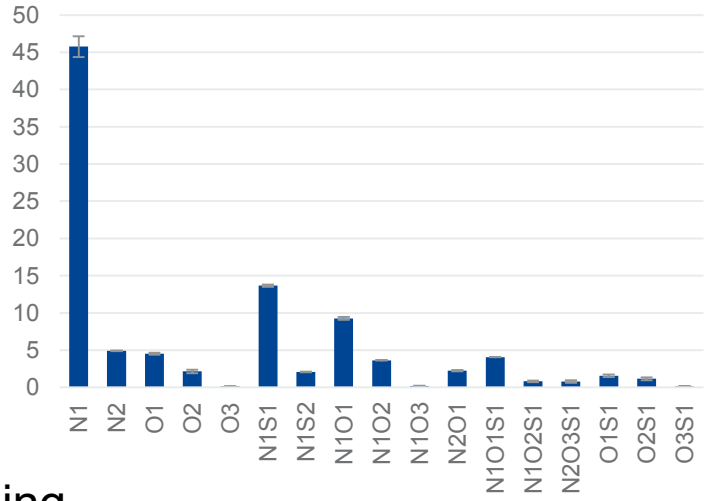
Bitumen Analysis
Electrospray Ionization









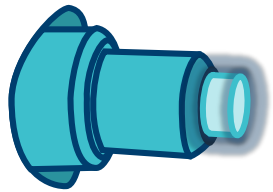


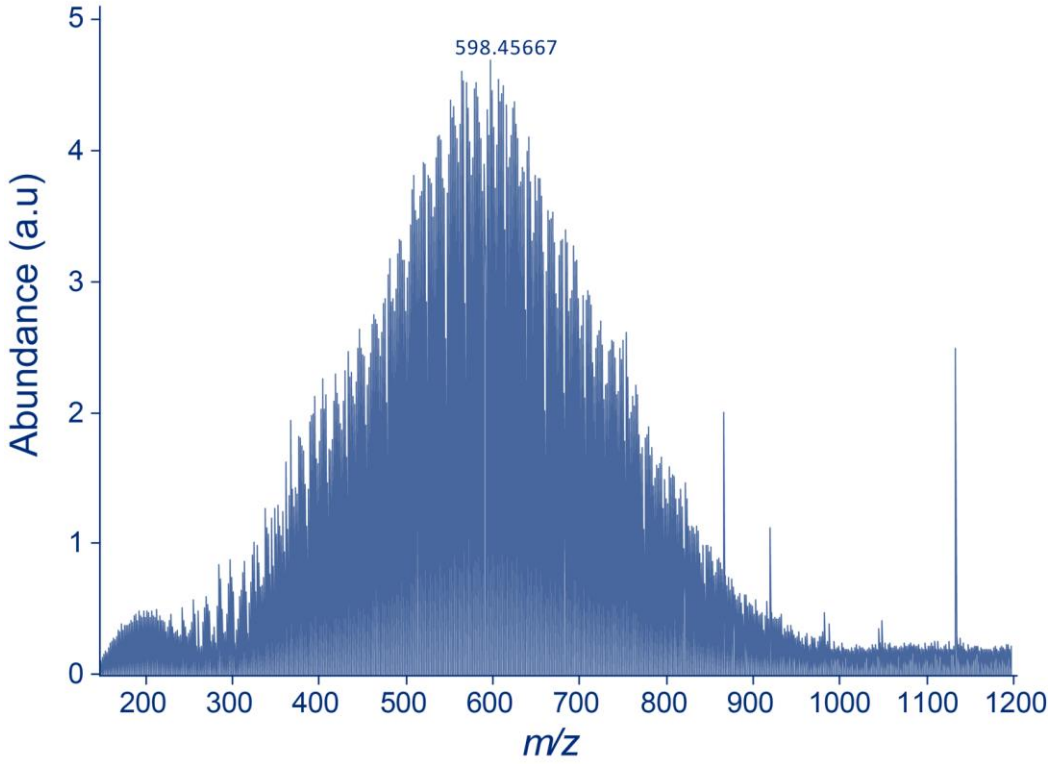
→ polar-constituents formed during the aging can be tracked but

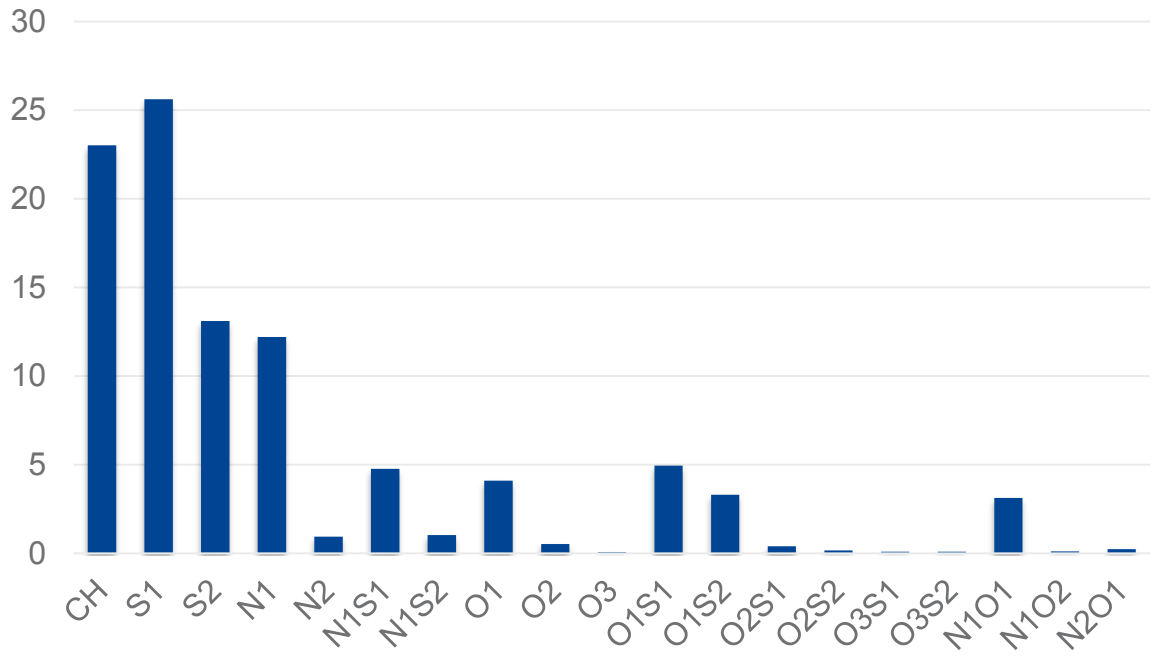
for detailed mechanistically insight certain chemical space might be missing…

SELECTED APPLICATION EXAMPLES AND CONCLUSION

Atmospheric pressure photoionization complementing the picture

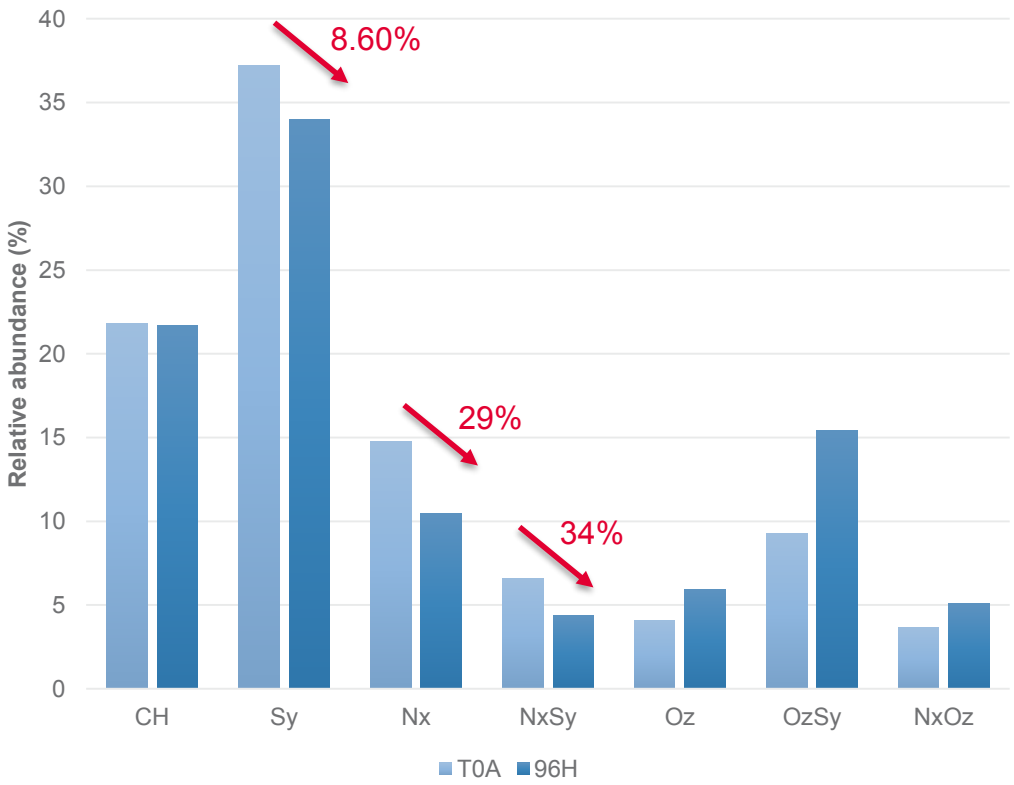


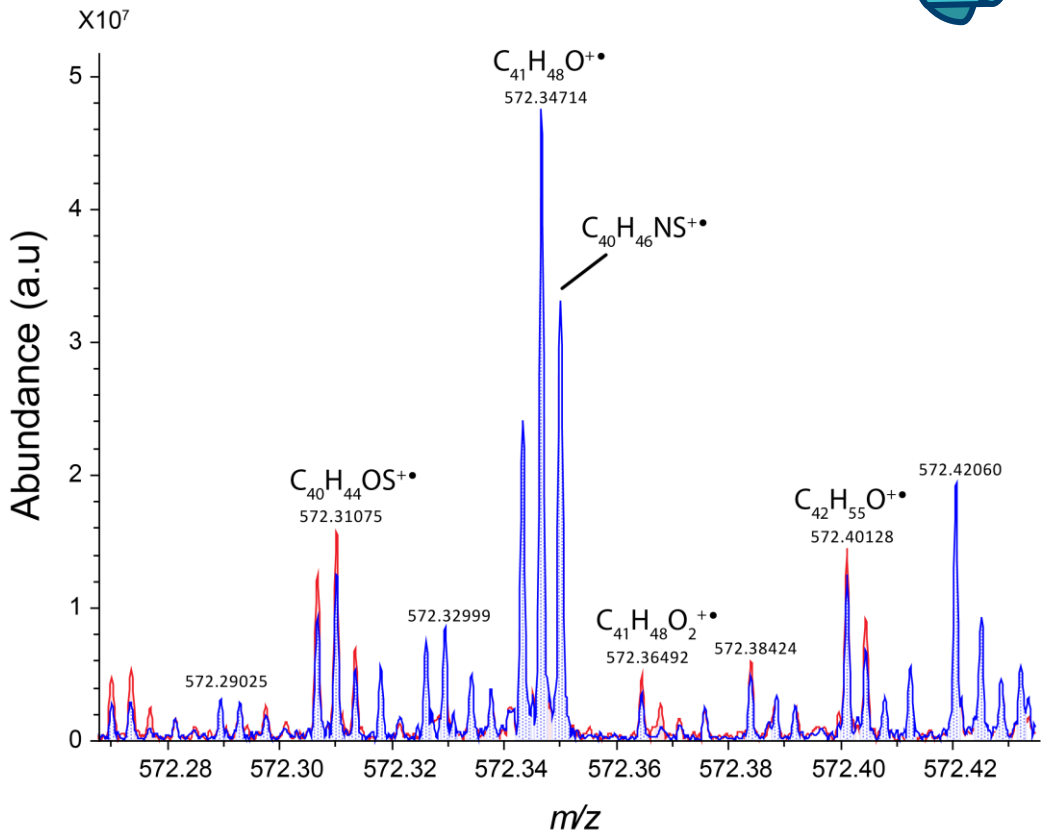




SELECTED APPLICATION EXAMPLES AND CONCLUSION

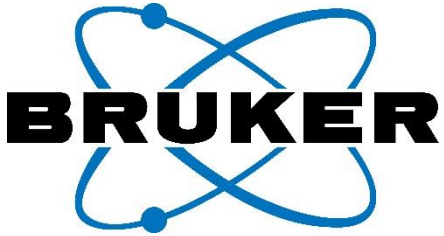
Atmospheric pressure photoionization

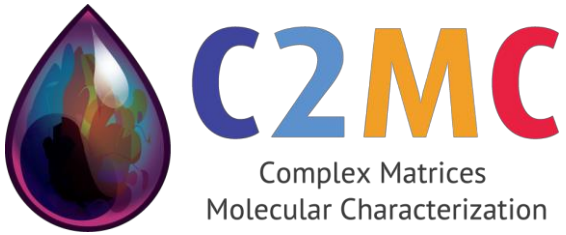




→ information on the CH/CHS_x-class constituents completing the picture

ACKNOWLEDGMENT





Complete team of:

International Joint Laboratory Complex Matrices Molecular Characterization- iC2MC

Joint Mass Spectrometry Centre Rostock and Munich - JMSC

Thank you for the attention!

christopher.rueger@uni-rostock.de

QUESTIONS AND FUTURE WHISHES

Questions

- APLI in routine laboratories – when do we have easy commercial solutions for a broader market?
- How do we develop standard routines and procedures for APPI – which dopants, sample preparation, calibrants and quantification strategies?
- Next level APLI – What does new light sources, such as modern Excimer solutions, offer for MS technology? How does repetition rate and variable light sources, e.g. OPO, help for complex mixtures?
- Can we induce isobaric and isomeric specification by specific ionization properties?

Request and future demands

- ionization of saturates beyond the GC/GCxGC accessible range

  → lubrication oils, waxes, polymer degradation, etc.
- pushing atmospheric pressure ionization (APPI) into sensitive quantification for complex mixtures

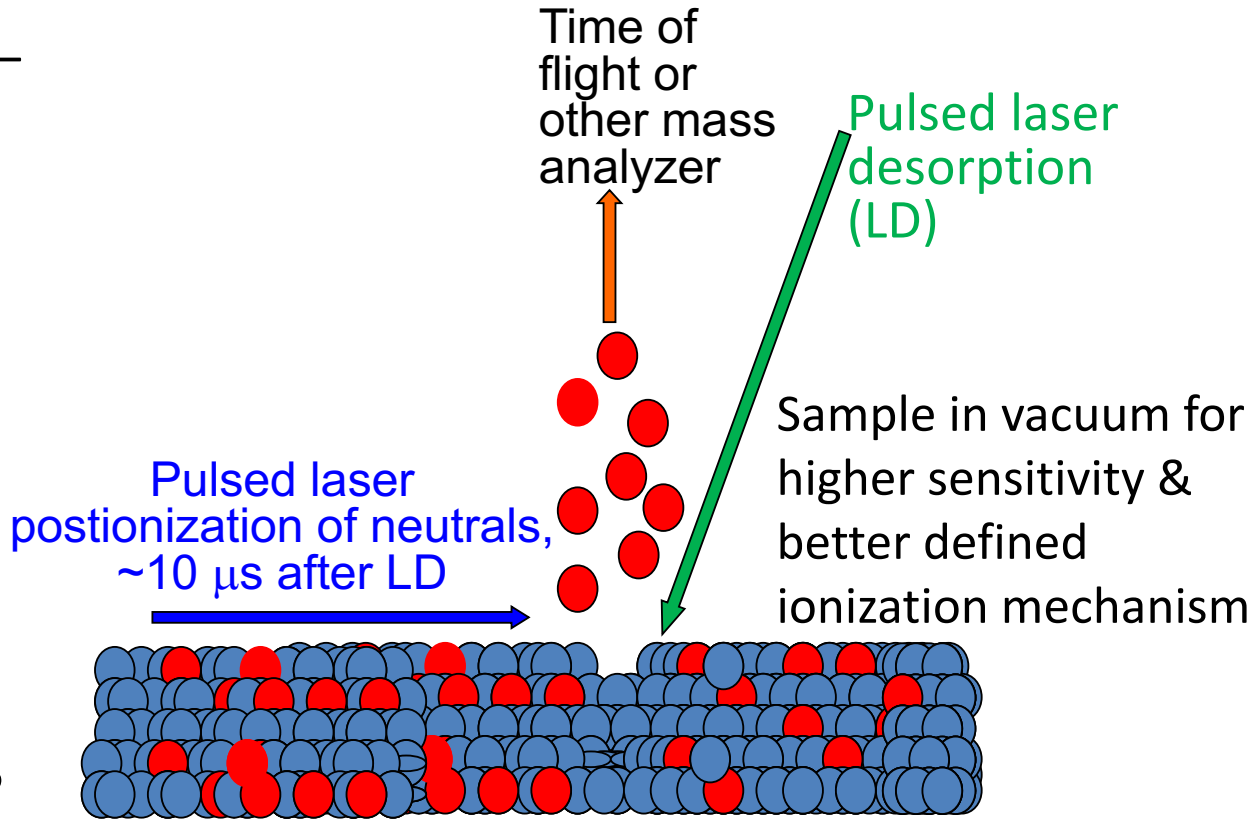
Laser Desorption Combined with Laser Postionization for Mass Spectrometry

Annual Review of Analytical Chemistry, Vol. 12: pp. 225-245
https://doi.org/10.1146/annurev-anchem-061318-115447

Luke Hanley, Raveendra Wickramasinghe, and Yeni P. Yung

ASMS 2020 Reboot Workshop – Photoionization –
Between Vacuum and Atmospheric Pressure

Prof. Luke Hanley
Department of Chemistry
chem.uic.edu/profiles/luke-hanley

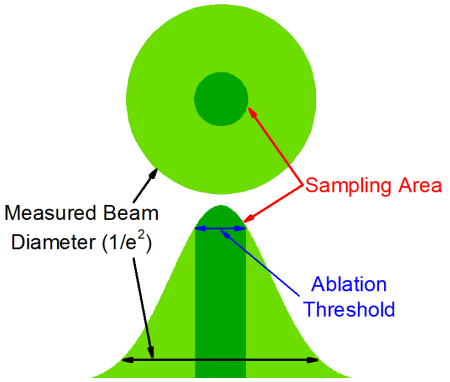


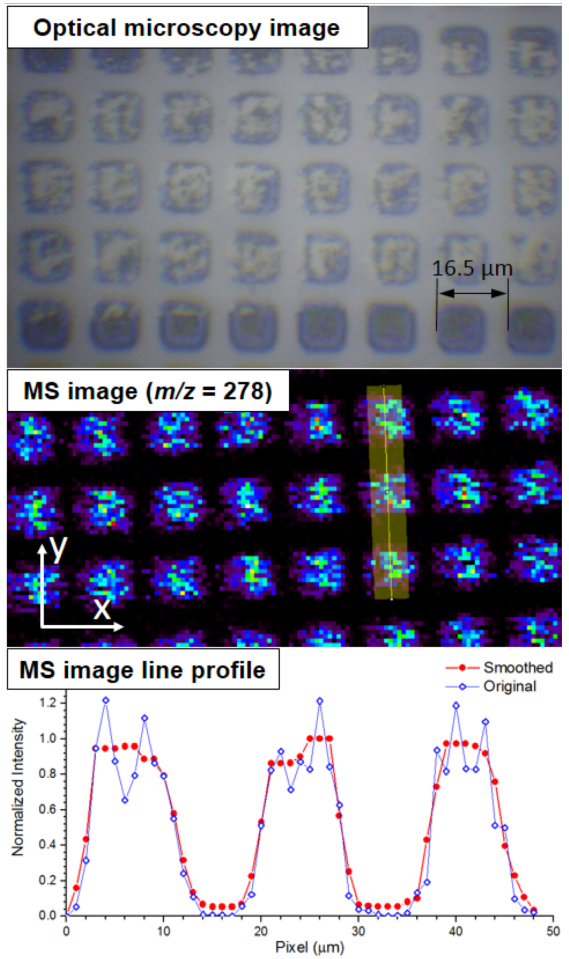
For vacuum laser PI with secondary ion (neutral) MS
→ Gilmore, **Ibid.**, p. 201

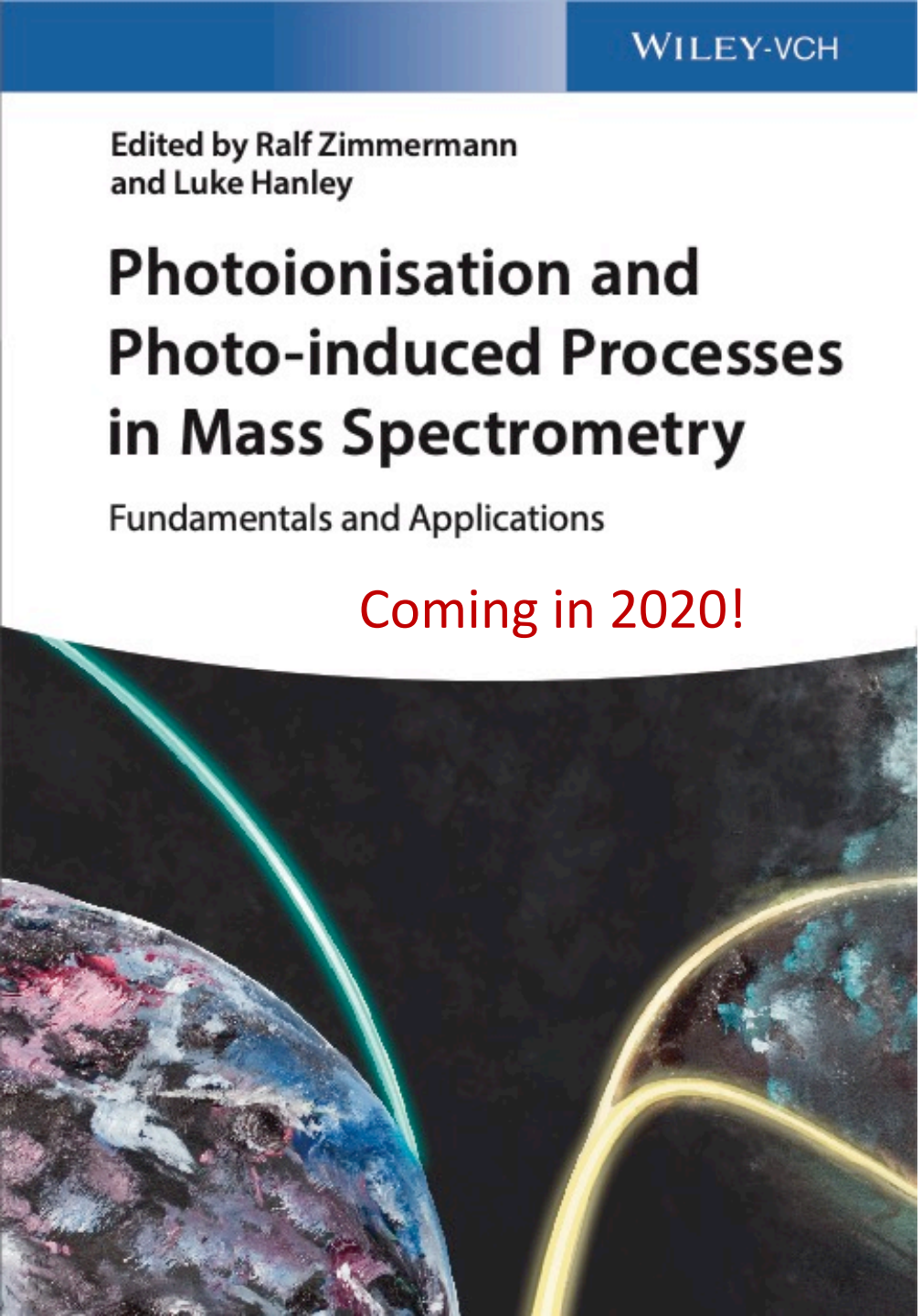
Laser PI for Sub-micron MS imaging

- Direct ion formation limited during laser desorption /ablation (i.e., MALDI) or ion sputtering (i.e., SIMS)
- Detect abundant neutrals with laser PI
- Enhanced signal increases lateral resolution →
- Sub-micron MS imaging made possible by laser PI
- My group is using laser PI for MS imaging analysis of geological & astrological samples

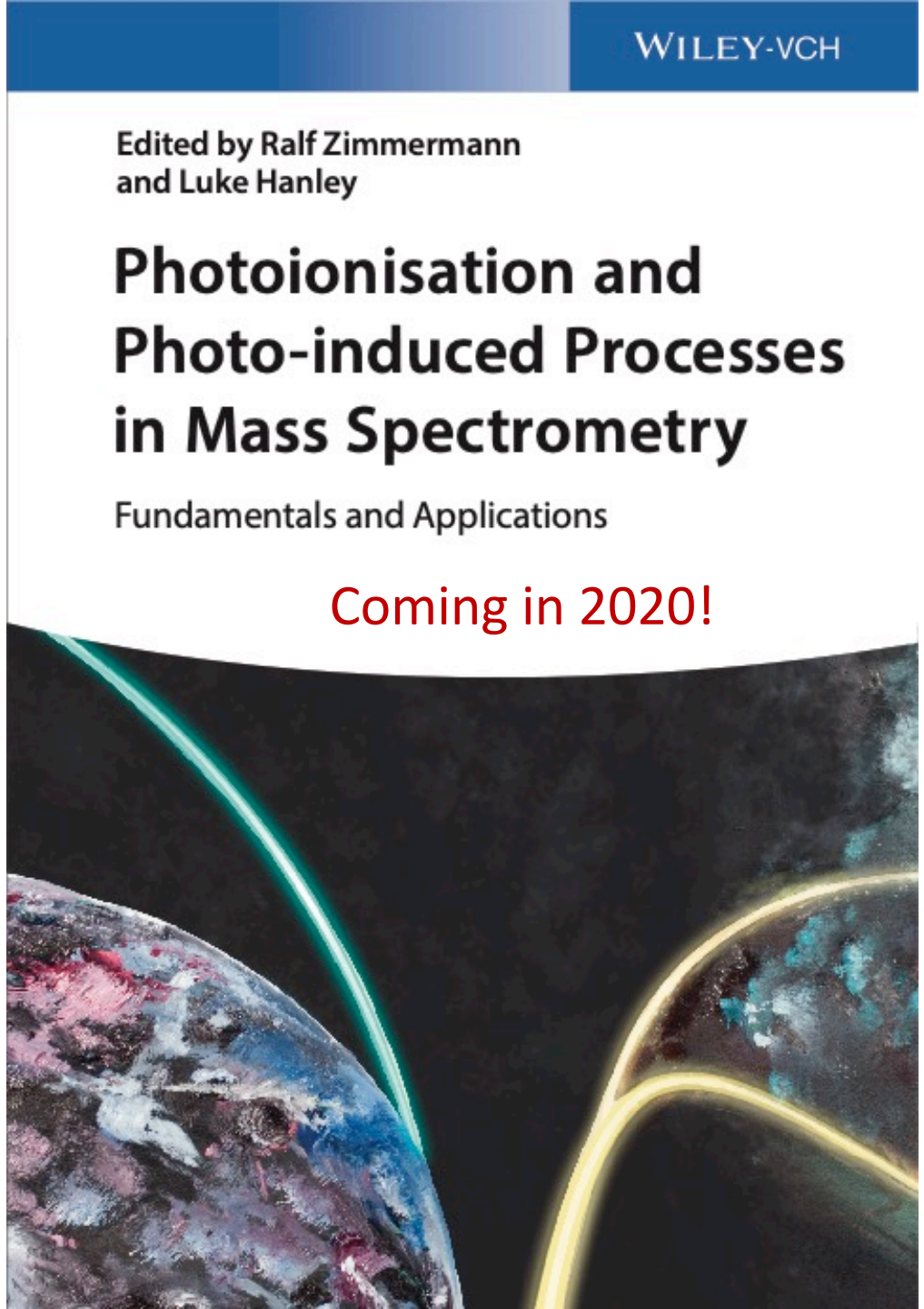
Cui,… Anal Chem 87 (2015) 367 →







- 1: Fundamentals & Mechanisms of Vacuum Photoionization (Passig, Zimmermann & Fennel)
- 2: Fundamentals and Mechanisms of Resonance-Enhanced Multiphoton Ionization (REMPI) in Vacuum & Application in Molecular Spectroscopy (Boesl & Zimmermann)
- 3: Analytical Application of Single-Photon Ionization (SPI) MS (Steibel, Czech & Zimmermann)
- 4: Analytical Application of REMPI-MS (Steibel & Zimmermann)
- 5: Probing Chemistry at Vacuum Ultraviolet Synchrotron Light Sources (Wilson & Fei Qi)
- 6: Resonance Ionization MS: Fundamentals & Applications Including Secondary Neutral MS (Savina & Trappitsch)



- 7: Ultrashort Pulse Photoionization for Femtosecond Laser MS (Pieterse, Gross & Hanley)
- 8: Photoionization at Elevated or Atmospheric Pressure: Applications of APPI and LPPI (Kauppila & Syage)
- 9: Fundamentals of Laser Desorption Ionization (Donnarumma, Murray & Hanley)
- 10: Applications of LDI & Laser Desorption/Ablation with Postionization (Yung, Donnarumma, Murray & Hanley)
- 11: Laser Ionization in Single-Particle MS (Passig & Zimmermann)