Atmospheric pressure single photon laser ionization (APSPLI) mass spectrometry using a 157 nm fluorine excimer laser for sensitive and selective detection of non- to semi-polar hydrocarbons

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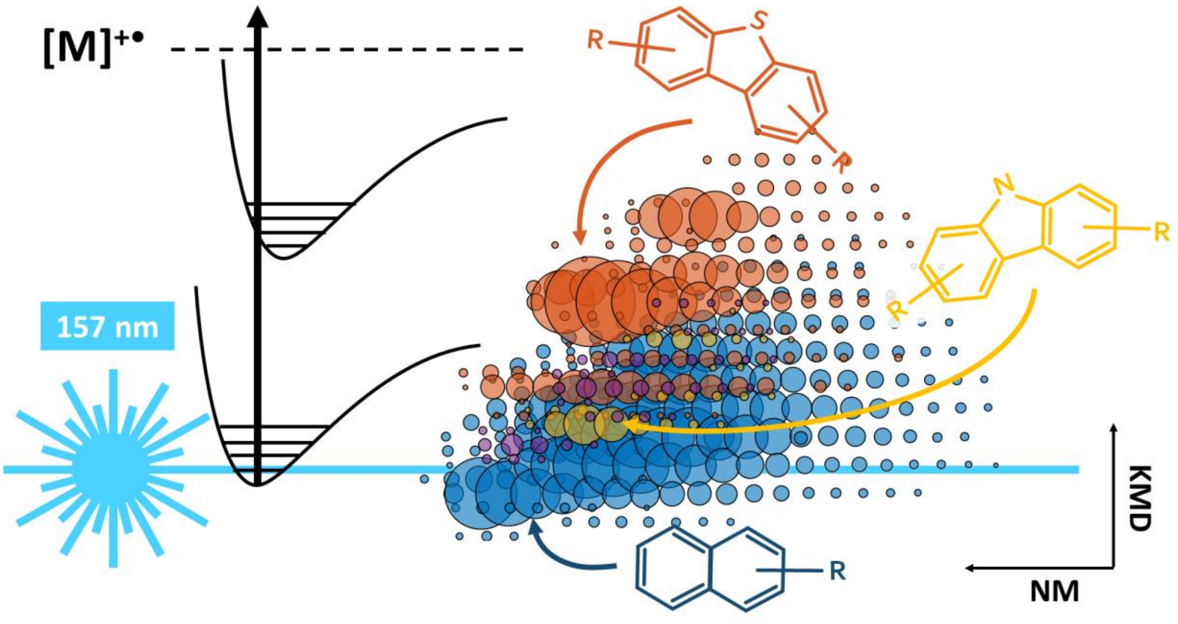

Abstract

Atmospheric pressure single photon ionization (APSPLI) mass spectrometry utilizing a fluorine excimer laser (157 nm, 7.9 eV) is presented for the first time. For evaluation and optimization, polycyclic aromatic hydrocarbon (PAH) standard mixtures were used. The presented technique allowed for the selective ionization of semi- to non-polar compounds in a single photon ionization process using VUV photons. Molecular radical cations were found as base peak, whereas protonated species were almost absent. Although the ionization chamber is flushed by pure nitrogen, remaining oxygen and water traces caused unwanted oxidized ionization artifacts. Installation of water and oxygen filter cartridges significantly reduced the abundance of artifacts. For evaluating complex mixture analysis, APSPLI was applied to characterize a light crude oil. In addition to aromatic hydrocarbons, APSPLI allowed for the sensitive ionization of sulfur-containing aromatic constituents (PASH). A comparison of APSPLI to atmospheric pressure laser ionization (266 nm, 4.7 eV) revealed the additional compositional space accessible by the single photon process. APLI, conducted with UV radiation, is mainly restricted to PAH analysis. APSPLI overcomes this limitation and PAH and PASH, which often occur simultaneously in complex mixtures, can be detected. This novel ionization concept is envisioned to have a high analytical potential further explored in the future.

Introduction

With the introduction of electrospray ionization (ESI) in the early 1990s, atmospheric pressure ionization (API) techniques have become prevalent in various mass spectrometric research and application fields. In the following two decades, a multitude of ionization techniques has been introduced[1]. The extensive development of API is primarily driven by the wide introduction of high-resolution mass spectrometric platforms enabling the direct infusion of sample material without time-consuming pretreatment and motivates the development of selective ionization lowering matrix effects.[2]

High-resolution mass spectrometry has proven to be a powerful approach to characterize complex organic mixtures.[2] High-resolution at the *m/z*-dimension enables the separation of isobaric species, whereas the high mass accuracy allows for direct chemical conclusions by attributing elemental compositions. The application of selective ionization techniques, chromatographic coupling, or tandem mass spectrometry, further add chemical information.[3] In contrast to vacuum ionization techniques, API offers operational simplicity and collisional-cooling. However, analytical drawbacks, such as combating ionization mechanisms and, thus, drastic matrix effects may be observed. Moreover, ionization artifacts can occur, including clustering, solvent-adducts, and oxidation.

Atmospheric pressure photoionization provides low matrix effects and is able to ionize a broad compositional space, *i.e.*, entirety of compounds with a certain distribution in mass, structure, and chemical functionalities.[4–6] In classical direct infusion experiments, dopants are added to enhance the ionization yield.[7,8] Nonetheless, low sensitivity for certain compound classes or the occurrence of both protonated and radical cations complicates analysis and interpretation. Consequently, atmospheric pressure laser ionization (APLI) mass spectrometry was developed and first reported by Benter and co-workers in 1999.[9] Laser-based ionization drastically increases the photon density and creates a defined timing and space/geometry for the ionization event. Schiewek et al. introduced evolved gas analysis APLI, in terms of GC-APLI-MS, in 2007 and reported detection limits as low as 5 ng/l for chrysene.[10] Schrader and co-workers extended this work and presented detection limits of 2 µg/l for benzonaphtothiophene on an ultrahigh-resolution mass spectrometric system.[11] In the following decade, APLI by 248 nm (KrF-excimer laser)[12] and 266 nm (4th harmonic of Nd:YAG solid-state laser) was deployed for the chemical characterization of various petroleum-derived materials[13–16], combustion aerosols[17], emerging environmental contaminants and pollutants[18–21]. Furthermore, the usage of specific dopants or derivatization techniques was studied.[22,23]

Vacuum laser ionization can be divided into single photon ionization (SPI) and resonance enhanced multi-photon ionization (REMPI).[24,25] SPI realized by VUV photons can be referred to as universal ionization technique ionizing any component with an ionization energy lower than the applied photon energy. Resonance-enhanced multi-photon ionization (REMPI) operated at UV-wavelengths exhibits an excited state selectivity and is particularly selective and sensitive towards many aromatic constituents. APLI at UV-wavelengths is driven by a two-photon process comparable to the REMPI process, where the absorption of one photon leads to an excited state and subsequent ionization by absorption of a second photon generating a radical cation.[23] Polycyclic aromatic compounds are efficiently ionized by REMPI/APLI.

In this study, for the best of the author's knowledge, laser ionization mass spectrometry utilizing VUV laser light under atmospheric pressure is reported for the first time. For this purpose, a fluorine excimer laser operating at 157 nm (7.9 eV) is applied. This technique will be able to trigger single photon ionization pathways in contrast to the common APLI approaches and is therefore referred to as APSPLI. In classical APLI, contrary to PAHs, sulfur-containing polycyclic aromatic hydrocarbons (PASHs) show low ionization cross sections due to the short lifetime of the excited state in the REMPI process. Because of the single photon process in APSPLI, we could obtain high ionization cross sections even for PASHs. In this proof-of-concept study, we introduce APSPLI by analyzing PAH standard mixtures and petroleum-derived, highly complex materials. The analytes are subjected to the ionization source by gas chromatographic and thermal analysis hyphenation removing the influence on the ionization from the solvent. Therefore, ionization characteristics, such as the generation of ionization artifacts and the occurrence of radical/protonated species, can be directly discussed.

Experimental

Material

Two different standards of various polycyclic aromatic hydrocarbons, named A4 and M3, were used for evaluation, optimization, and validation purpose of the APSPLI setup (Table S1 and Table S2). Briefly, the standard consisted of 14 (A4) and 25 (M3) PAHs (self-made from the respective chemicals supplied from Sigma Aldrich, Darmstadt, Germany, in analytical grade purity). Concentrations in the standard ranged between 0.3 to 5 mg/L. The applicability of APSPLI for the description of complex organic mixtures was evaluated with a light crude oil (CPC Blend from Kazakhstan, Gunvor Raffinerie Ingolstadt GmbH). This specific crude oil sample was already investigated by comprehensive gas chromatography mass spectrometry in literature.[26]

Method

All analyses were carried out on a Bruker Apex II ultra Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a 7 Tesla superconducting magnet. A commercial GC-APCI II source (Bruker Daltonics, Bremen, Germany) was modified for atmospheric pressure laser ionization. This modification was realized by exchanging the glass viewports at the leftand right-hand side (rectangular to the sample and mass spectrometric inlet) with magnesium fluoride windows (MgF_2-VUV-window, laser polished, 25±0.2 mm diameter, 2±0.1 mm depth, Korth Kristalle GmbH, Altenholz, Kiel). A schematic representation of the system can be found in Figure 1 (photographic scheme in Figure S1). For ionization, the 157 nm radiation emitted by a fluorine excimer laser (Compex Pro F2, Lamda Physik AG, Göttingen, Germany) daily refilled with fluorine gas (4.99±0.15 v-% fluorine in helium, Air Liquide, Hamburg, Germany) was used with a beam diameter of 7 mm clipped by a cylindrical aperture. A laser repetition rate of 10 Hz was used. Laser power was between 25 and 43 mW (20 ns pulse width, pulse energy 2.5 – 4.3 mJ) measured after the transmission through the ion source by a VUV sensor (PEM 24K VUV, Laser Optics Scientific Instruments, RBM R. Braumann GmbH, Langenbach, Germany). The concentration of remaining oxygen and water inside the ionization chamber was reduced by installing water (Gas Clean GC/MS Filter, CP17973, Varian Technologies, Palo Alto, CA, USA) and oxygen filter cartridges (SGT Oxygen Filter, Scientific Glass Technology, Sgt Middelburg B.V., Middelburg, Netherland).

The beamline between the exit port of the laser and the ion source window was enclosed by a plastic tube with common vacuum flange connectors and was sealed with O-rings. The beamline is flushed with several liters per minute of dry nitrogen (purity > 99.999 v-%) to prevent significant attenuation of the laser beam due to absorption of the VUV photons by oxygen or water.

Gas chromatographic analyses were performed on a CP 3800 system (Agilent, former Varian Technologies, Palo Alto, CA, USA) equipped with a programmable temperature vaporizer (PTV) injector. A 5%-phenylmethylsilicone column (Restek, Bad Homburg, Germany) with a length of 30 m, 320 µm inner diameter and 0.1 µm film thickness was used for separation. Helium (99.999 v-% purity) was used as carrier gas with a constant head pressure of 2.1 (Method 1) and 0.7 bar (Method 2). The temperature ramp of the GC oven was as following: Method 1 – hold for 3 min at 30 °C, raise to 300 °C with 5 K/min and hold 5 min, Method 2 – hold for 3 min at 30 °C, raise to 320 °C with 5 K/min and hold 2 min. The PTV injector equipped with a straight inlet liner was kept 1 min at 65 °C and then raised with 100 K/min to 300 °C held for 5 min. For thermal analysis, a thermobalance (TG 209, Netzsch Gerätebau GmbH, Selb, Germany) was used. The samples were heated from 20 to 600 °C in an aluminum crucible under nitrogen atmosphere (99.999 v-% purity) after 2 min initialization at 20 °C with a heating rate of 10 K/min. Further details on the gas chromatographic [27] and thermogravimetric [28] hyphenation can be found elsewhere. For both cases, the transferline was kept at 280 °C.

One µL of the PAH standard mixtures was injected for GC analysis. The light crude oil was diluted by a factor 1000 (1000 v-ppm) in dichloromethane and 1 µL of the diluted sample was injected into the PTV injector for GC analysis. For thermogravimetric analysis, 1-5 mg of the sample material was directly placed in the aluminum crucible.

The mass spectrometer was operated in positive ion mode. The nebulizer gas flow rate (a gas stream supporting the GC effluent) was varied between 1.5 to 6 l/min and the dry gas flow (a gas stream from the mass spectrometer inlet side) was set to 3 l/min with a temperature of 220 °C. Mass spectra were recorded from *m/z* 100 to 1,000 with a transient length of approximately 2 s, resulting in a resolving power of roughly 260,000 at *m/z* 400.

Data analysis

General evaluation and *m/z*-calibration of the mass spectrometric data were carried out in Bruker Data Analysis 5.0 (Bruker Daltonics, Bremen, Germany). Internal *m/z*-calibration of the petroleum-derived sample materials was performed using a list of alkylated PAH and PASH species covering the complete mass range. After peak picking (≥S/N 9), the data were exported.[27,28] The exported data were processed by self-written MATLAB algorithms (MATLAB R2019b). The following elemental composition boundaries were deployed: *m/z*-error 2 ppm, $C_{6\text{-}100}H_{6\text{-}100}N_{0\text{-}2}O_{0\text{-}5}S_{0\text{-}2}$. Root-mean-square-errors (RMSE) of below 0.5 ppm were found.

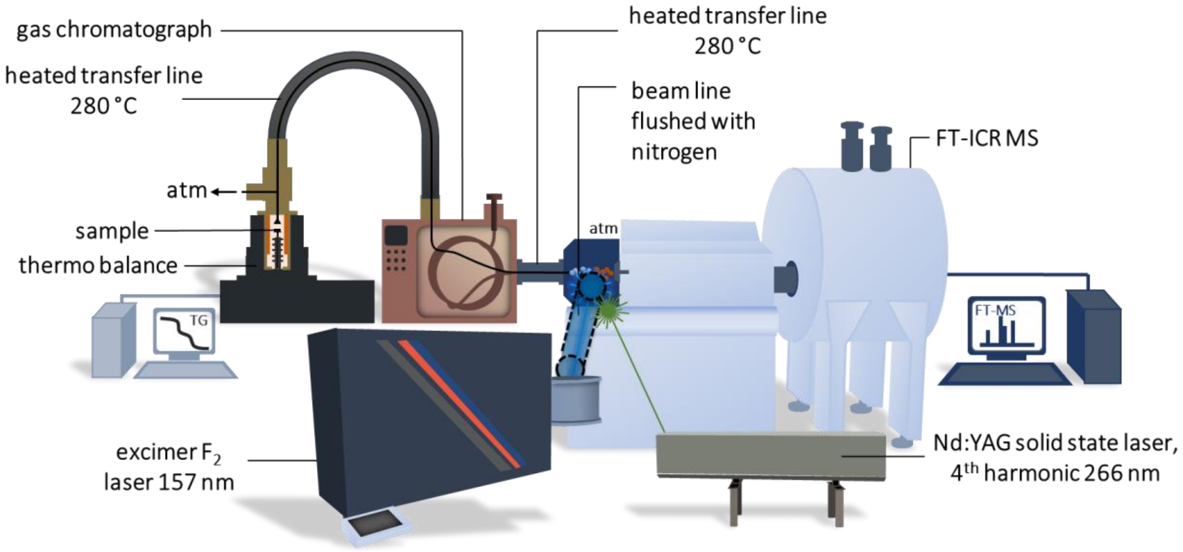

Figure 1: Atmospheric pressure single photon laser ionization (APSPLI) setup using a fluorine excimer laser (157 nm). The Nd:YAG laser operated at the 4th harmonic (266 nm) for APLI is also depicted.

Results and Discussion

Polycyclic aromatic hydrocarbon standard

The fluorine excimer laser (157 nm) for single photon ionization at atmospheric pressure was evaluated and optimized with PAH standard mixtures subjected by gas chromatographic separation to the ionization chamber. All PAHs with an ionization potential (IP) lower than the photon energy of the F_2 laser (7.9 eV) were detected (Figure 2), with the radical cation being the most prominent signal. Naphthalene (IP 8.12 – 8.15 eV), acenaphthylene (IP 8.12 eV), biphenyl (IP 8.16 eV), and methyl eicosanoate (IP > 10 eV) were not observed due to their higher ionization energies.[29] These findings indicate that the ionization process is solely realized by direct single photon ionization and not by multiphoton ionization or chemical reaction cascades.

Without further adaption of the commercial API source, detection limits in the sub-ppb level can be estimated for the GC coupling. The high sensitivity is suggested to result from the very high photon density in the laser beam compared to the divergent light of classical krypton discharge lamps deployed for APPI. For species below a double bond equivalent (DBE) of 10 (3-ring PAHs), the sensitivity drastically increases with increasing aromaticity. A slight trend of increased sensitivity can be observed for the PAHs with three to seven conjugated aromatic rings. Nonetheless, for those analytes, the overall normalized response was within one order of magnitude. The FTICR-MS platform is optimized for the transmission of species with a $m/z > 150$, which will also partially affect the response of the smaller PAH. In classical vacuum REMPI, the ionization cross-section and, thus, mass spectrometric response varies drastically with the isomeric structure.[30,31] For the presented APSPLI approach the behavior is similar to vacuum SPI.[32]

As noticeable from Figure 2, APSPLI provides a very low and nearly absent chemical background noise as a clear advantage. Chemical noise complicates data interpretation and could cause matrix effects or ionization suppression.[27] The low background noise in APSPLI is caused by the selective ionization process for compounds with an ionization potential lower than 7.9, which excludes *e.g.* siloxanes eluting from GC columns at higher temperatures. Interestingly, larger aromatic species PAHs can also be found as doubly charged (z=2) species, such as indeno[1,2,3,*c,d*]pyrene ($C_{22}H_{12}$, *m/z* 276, DBE 17) (Figure S2).

Comparable to APPI conducted with a krypton discharge lamp (124/117 nm emission), oxygen is a critical parameter when using VUV-light for ionization under atmospheric pressure conditions. Oxygen and moisture in the ionization chamber substantially impact the ionization characteristics and lead to an unwanted formation of oxidized ionization artifacts. The formation of those artifacts is a drawback of APSPLI. By absorbing a VUV photon, oxygen or water molecules are photolyzed into oxygen or hydroxyl radicals. Oxygen radicals may subsequently combine with intact oxygen molecules forming highly reactive ozone (O_3).[33] Ozone readily reacts with organic constituents, creating oxidized products. Nonetheless, the occurrence of oxidized species as an ionization artifact was also reported for atmospheric pressure chemical ionization.[27] In the first optimization step, this influence can be minimized by careful flushing and heating the ionization chamber for several hours prior usage.

Figure 3 a and b compare pyrene ionized by APSPLI with an oxygen concentration of approximately 200 ppm and 10 ppm. High oxygen levels yield in a high content of oxidation artifacts with the mono-oxidized radical cation ($C_{16}H_{10}O^{\bullet+}$) as intense as the molecular ion ($C_{16}H_{10}^{\bullet+}$). Even a series of multiple oxidized species, up to $C_{16}H_{10}O_3^{\bullet+}$, and the respective protonated species were observed. This intense reaction cascade increases the spectral complexity drastically and hinders chemical interpretation. Nonetheless, a reduction of the oxygen concentration by a factor of approximately 20 to the low ppm-level completely changes this picture and leads to a drastic reduction of ionization artifacts. The molecular ion is the base peak, and the mono-oxidized species was found with an abundance of around 10 %. Other ionization artifacts were almost absent. Moreover, Figure 3 c shows the effect after deploying a software filter in the mass spectrometric processing using the automated elemental composition attribution and removing the signals attributed to the CHO_x-class.

Oxygen and water concentration of the nebulizer gas have a high impact on ionization artifacts. Consequently, the water and oxygen level in the ionization source was reduced by the installation of water and oxygen filter cartridges for the nebulizer nitrogen gas supply. A reduction of the abundance of oxidized ionization artifacts by a factor of two to four to approximately 10 % was achieved for the PAHs covering three- to seven-ring aromatic structures (Figure S3). The presence of multiply oxidized ionization artifacts was largely reduced. It can be found that installing either the water or oxygen filter slightly reduces the oxidation artifacts, but the combination of both filter cartridges gave the best results and was used for all further investigations. Some PAHs are very prone to oxidation, such as acenaphthene, for which the abundance of the oxidized species could only be reduced to approximately 35 % of the molecular radical cation.

Laser ionization techniques allow controlling the timing and the position of the ionization event. Three different positions for the laser beam were investigated (Figure S4): 1) beam position near the GC effluent capillary, 2) beam position in the middle between GC effluent and MS inlet, and 3) beam position in front of the MS inlet. The highest intensities for the molecular radical cations of the respective standard compounds were found for 1) and 2), whereas the abundance is up to five-times lower for ionization close to the MS inlet (Figure S5). These findings can be explained by the flow conditions in the ionization chamber. Analytes subjected to the source are diluted in the source volume and, thus, concentration of the neutral molecules is highest at the sample inlet and lowest at the mass spectrometry inlet. More interestingly, the position affects the absolute abundance more drastically than it changes the proportion of oxidized species. Position 1) and 3) revealed comparable strengths of oxidation. Positioning the laser beam close to the sample inlet was found to be the optimized location.

In chromatographic hyphenation, ionization artifacts can be further removed from the data set by intelligent processing algorithms tracing the time-resolved signal (extracted ion chromatogram) of the molecular ion and corresponding oxidized species.[27] With this combination of chromatographic and mass spectrometric information, a non-targeted investigation of complex organic mixtures containing oxygenated species is feasible. Species not containing oxygen, such as CH-, CHS-, and CHN-class compounds, can be sensitively characterized.

Complex mixture analysis

Evaluation of the APSPLI approach for the chemical description of complex organic mixtures was performed on a light crude oil (CPC Blend), which was subjected to APSPLI by gas chromatography and thermal analysis.[27,28] Although the separation power of thermal analysis is much lower compared to gas chromatographic hyphenation, almost the same compositional space could be detected indicating low matrix effects for APSPLI. Figure 4 a) shows the survey diagram, with insets of the total ion chromatogram (TIC) and base peak chromatogram (BPC), which reveals the characteristic, complex pattern of the petroleum-derived material.

The CH-class was found as the most dominant compound class. Nonetheless, also CHS_1-, CHO_1-, CHN_1 and CHS_1O_1-class constituents were detected with considerable abundance. Predominantly, radical cations were detected (Figure S6). This beneficial characteristic of APSPLI allows simplifying the immense isobaric complexity of the investigated crude oil, yielding 5-10 signals per nominal mass. In contrast, APPI using a Krypton-discharge lamp (10/10.6 eV) commonly generates protonated and radical cations to the same extent, which would yield > 15-20 signals per nominal mass.

For the PAH standard mixture measurements, oxidation was found as a considerable ionization artifact. For the light crude oil, however, the abundance of the complete CHO-class was found to be below 4 % (attributed raw data). Furthermore, the DBE distribution of the CH-class was found to be Gaussian-shaped, whereas the CHO-class revealed an entirely different non-uniform pattern of the DBE histograms (Figure S7). The same can be found comparing the CHSO- and CHS-class DBE distributions. If we assume comparable oxidation for all CH/CHS-class compounds, the CHO/CHSO-class should reveal the same or a comparable DBE distribution shape. Surprisingly, the Gaussian-shaped DBE distribution is not found for the CHO/CHSO-class, and certain values dominate the pattern. This discrepancy suggests that only a lower percentage of the CHSO- and CHO-class might result from oxidation in the ionization source. Based on this hypothesis, we can suggest that artificial in-source oxidation might be only pronounced to a certain extent.

Sulfur-containing aromatic and polyaromatic hydrocarbons (PASH), such as thiophenes and benzothiophenes, but also oxygenated and halogenated PAHs, are generally poorly detected by REMPI/APLI because of their low ionization cross-sections due to intersystem crossing (ISC). With APPI conducted with Krypton-discharge lamps (10/10.6 eV), those compound classes are primarily detected as a mixture of odd and even species due to complex reaction cascades, but generally with good sensitivities. Accordingly, the presented APSPLI approach allowed the efficient ionization of PASHs as well, which were found as the second most abundant compound class. In the average mass spectrometric response (Figure 4 b) a series of CHS_1-constituents with a DBE of 9 (tentatively dibenzo- and naphthothiophenes) can be found as high abundant homologous alkylation series with $C_{16}H_{16}S_1$ as base peak. Comprehensive gas chromatographic analysis (GCxGC with electron impact MS) with minimal analytical bias and universal ionization of the same light crude oil revealed semi-quantitatively dibenzothiophenes (~1 %) and benzothiophenes (< 1 %) as dominant sulfur-containing constituents.[26] For APSPLI, benzonaphthothiophenes (CHS_1-class, DBE 12), hardly detected at all with the GCxGC, were detected as the second most dominant aromatic core structure for the CHS_1-class. In contrast to GCxGC, even CHS_2-class species were detected by APSPLI (Figure S8).

APLI, in the following referred to as APMPLI, due to the multi-photon process at atmospheric pressure, ionizes PAHs with high sensitivity and selectivity, but is not capable to efficiently ionize a variety of heteroatom-containing PAHs. Figure 4 c) and d) compares the compositional space of the compounds ionized by APSPLI (157 nm) and APMPLI (266 nm). A strong variation of the ionization cross-section of several orders of magnitude between different compound classes is given for APMPLI.[25] This strong variation in ionization response hinders direct quantification. Certain chemical classes with very low ionization cross-section, *e.g.*, due to short-lived intermediate states, might not be detected at all. In contrast, APSPLI broadens the observable compositional space and aside from the CHS-class, nitrogen-containing constituents are found. The Kendrick mass defect plots (Figure 4 c)/d)) emphasizes the additional information of APSPLI by giving access to further compound classes and a broadened compositional space of semi- to non-polar constituents. Particularly, heteroatom-containing compounds were detected with good ionization yield compared to classical APLI.

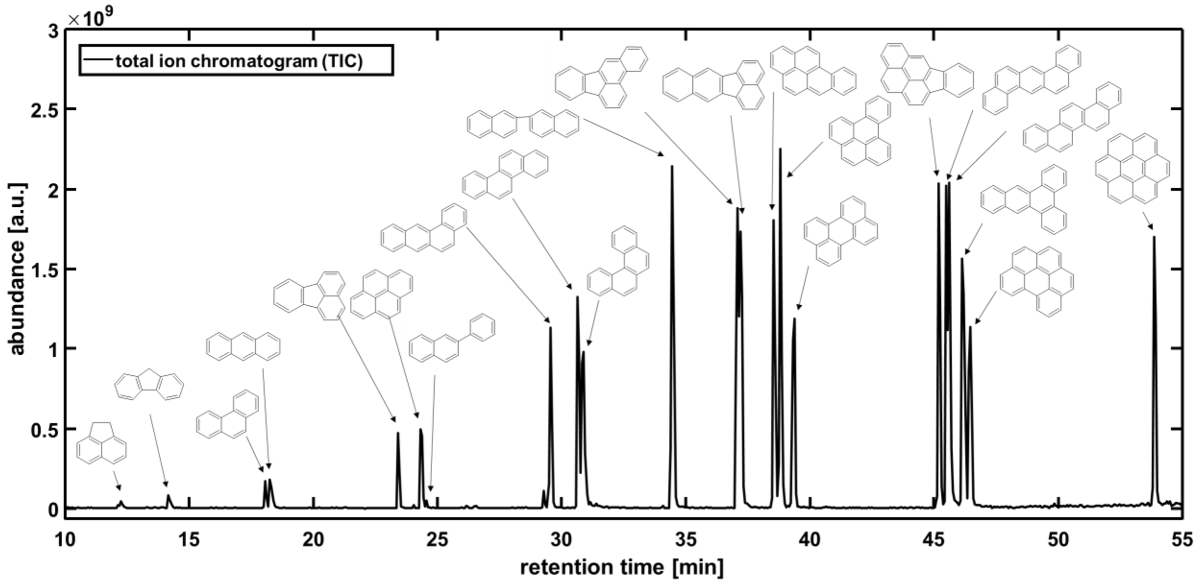

Figure 2: Gas chromatographic separation of the M3 PAH standard mixture ionized by APSPLI (157 nm). All constituents could be detected, except naphthalene, biphenyl, acenaphthylene, and methyl eicosanoate, because of their higher ionization energies than 7.9 eV.

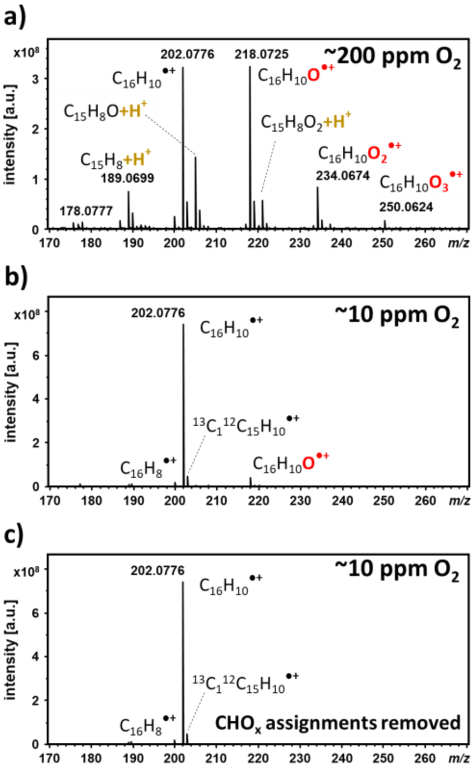

Figure 3: Pyrene ($C_{16}H_{10}$, *m/z* 202) subjected to 157 nm APSPLI by thermogravimetry coupling. The pattern of the molecular ion (radical ions, odd-electron configuration), quasi-molecular ion (protonated species, even-electron configuration), and oxidized artifacts are depicted. a) at 200 v-ppm, b) at 10 v-ppm oxygen (after installation of an oxygen- and water-filter, and c) after additional deploying a software filter in the processing removing the signals attributed to the CHO_x-class.

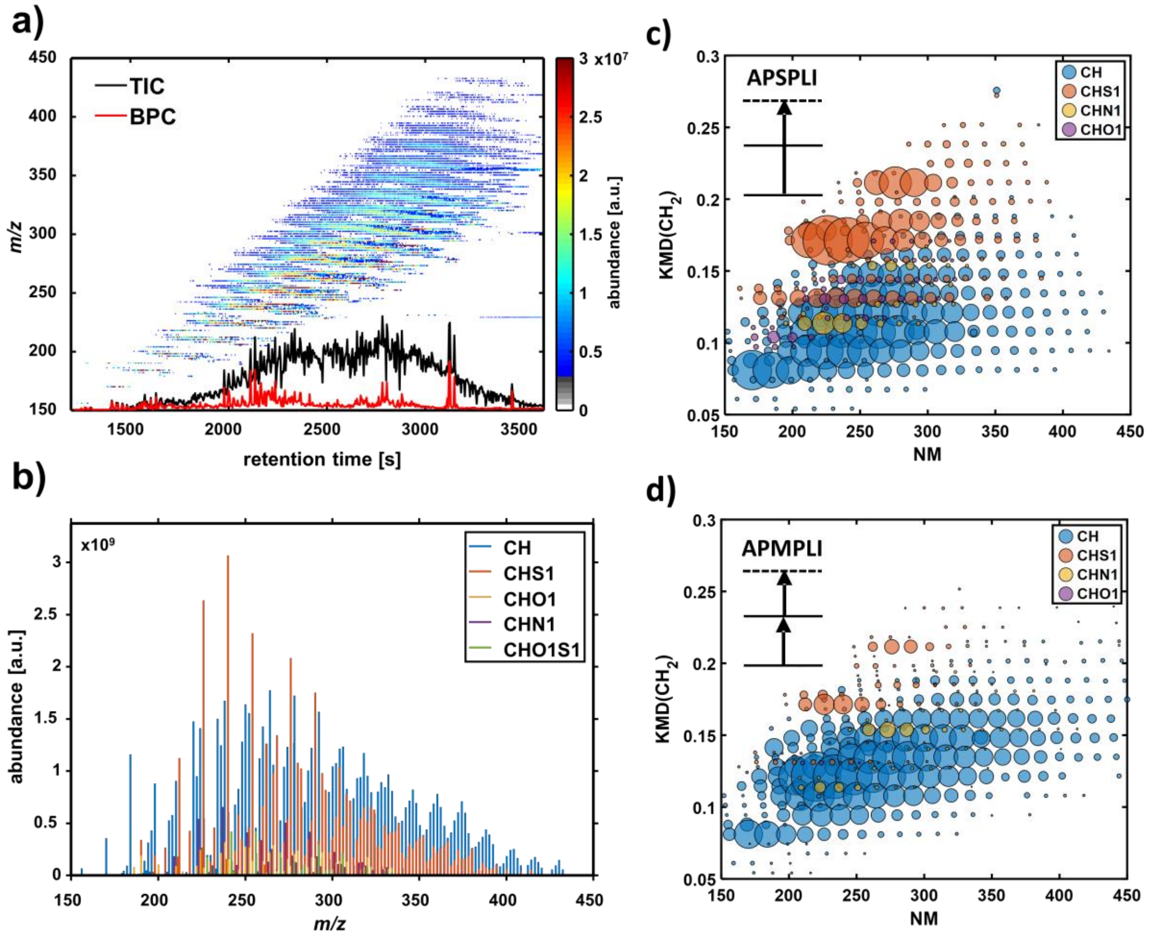

Figure 4: GC-APSPLI at 157 nm of a light crude oil: a) Survey diagram (time versus *m/z*) with total ion count (TIC) and base peak chromatogram (BPC) as inset, and b) average mass spectrum color-coded according to the attributed compound class. Kendrick mass defect (KMD) diagrams of the light crude oil analyzed by thermal analysis coupled to FT-ICR MS: c) Deploying APSPLI (157 nm) and d) APMPLI (266 nm). NM – nominal mass, CH – hydrocarbon class C_xH_y, CHS_1 – hydrocarbons with one sulfur as heteroatom $C_xH_yS_1$, CHN_1 – hydrocarbons with one nitrogen as heteroatom $C_xH_yN_1$, CHO_1 – hydrocarbons with one oxygen as heteroatom $C_xH_yO_1$.

Conclusion

We could present the first application of laser-based VUV-radiation for the ionization at atmospheric pressure (APSPLI) in high-resolution mass spectrometry. For this purpose, a fluorine excimer laser operating at 157 nm was installed at an FT-ICR MS.

Based on the evaluation with PAH mixtures, we could show the selective and sensitive ionization of constituents with an ionization potential below the photon energy of 7.9 eV. An ionization process driven by single photon ionization is clearly proven, which results predominantly in molecular radical cations and low abundance of protonated species. This feature significantly reduces the spectral complexity. Nonetheless, residual oxygen and water in the ion source atmosphere were found to cause unwanted oxidized ionization artifacts, which could be reduced by increasing the flow rate of the nitrogen gas purified by water and oxygen filter cartridges and by ionizing the analytes at the position near from the ionization chamber inlet.

APSPLI could successfully be applied for the characterization of petroleum-derived material. CH-class and CHSx constituents were found as the dominant compound classes and the CHN-class was found with increased sensitivity compared to APLI. Hence, APSPLI was found to be able to ionize compounds from a broad compositional space overcoming the limitations of classical APLI, which is mainly restricted towards PAH analysis. APSPLI overcomes this constraint and PAH and PASH, which often occur simultaneously in complex mixtures, can be detected. Future studies will focus on the optimization of ionization conditions and geometry with the motivation for a drastic reduction of oxidation artifacts. The high sensitivity may help in the characterization of low concentrated mixtures, such as emerging pollutants or carbonaceous aerosol emissions. Moreover, this novel ionization technique could be applied to other research areas, such as to life sciences, *e.g.*, metabolomics, or for studying biofuels and other new feedstocks. From an instrumental perspective, the compositional space accessed by APSPLI will be further broadened by deploying laser technologies with even shorter wavelengths.

Acknowledgment

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Supplemental Material

The Supporting Information is available free of charge at XXX

> Table S1 and Table S2 list the composition and concentration of the PAH standard mixtures. In Figure S1 a photographical setup of the APSPLI is shown. Figure S2 exhibits APSPLI mass spectrum of indeno[1,2,3,*c,d*]pyrene. Figure S3 shows the effect of deploying an oxygen-, a water-filter, and both filter types for purification of the nebulizer gas supply. Figure S4 gives a scheme of the laser beam position. Figure S5 reveals the effect of the different ionization positions on the radical cation abundance. Figure S6 displays the compound class distribution of the light crude oil ionized by APSLI. Figure S7 depicts the double bond equivalent pattern of various compound classes ionized by APSPLI. Figure S8 shows the Kendrick mass defect plot and an enlargement to a single nominal mass for the light crude oil investigated by GC coupling.

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