Laser Desorption Single-Photon Ionization of Asphaltenes: Mass Range, Compound Sensitivity, and Matrix Effects

Hassan Sabbah,[†,‡,§,*] Andrew E. Pomerantz,[∇] Manfred Wagner,[#] Klaus Müllen,[#] and Richard N. Zare[§]

[†]Université de Toulouse, UPS-OMP, IRAP, Toulouse, France
[‡]CNRS, IRAP, 9 Av. colonel Roche, BP 44346, 31028, Toulouse Cedex 4, France
[§]Department of Chemistry, Stanford University, Stanford, California 94305, United States
[∇]Schlumberger−Doll Research, Cambridge, Massachusetts 02139, United States
[#]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

ABSTRACT: Molecular-level characterization of petroleum asphaltenes is important for addressing reservoir concerns such as connectivity and flow assurance. Laser desorption single-photon ionization mass spectrometry (LDSPI-MS) has emerged as a favored technique for asphaltene analysis, because of its ability to detect these samples with minimal artifacts from fragmentation, aggregation, and multiple charging. However, questions persist regarding the sensitivity of LDSPI-MS to different components of asphaltenes, the molecular weight range detectable with the technique, and the importance of matrix effects. We present LDSPI-MS mass spectra of mixtures of model compounds and asphaltenes in various matrices to assess the significance of these effects. We observe that LDSPI-MS has comparable sensitivity for all studied model compounds and for asphaltenes, including compounds with molecular weight exceeding 1500 Da. In addition, only a minimal matrix effect is observed, as expected from considerations of the desorption and ionization mechanisms. The results add confidence to the previous conclusion of an LDSPI-MS study, in particular that (i) 1500 Da represents a maximum molecular weight for asphaltenes and (ii) the lack of fragmentation implies the dominance of island geometries in asphaltenes.

■ INTRODUCTION

Defined by their solubility in toluene and insolubility in heptane, asphaltenes are the most enigmatic component of crude oil. This fraction of petroleum is relevant to several industrial concerns, such as flow assurance[1,2] and reservoir characterization.[3,4] However, a detailed understanding of these processes has historically been impaired because knowledge about the molecular structure and weight distribution of asphaltenes has been lacking and a topic of some controversy.[5] To address this deficiency, several recent experiments have aimed to measure fundamental molecular properties of asphaltenes, such as their molecular mass distribution and dominant molecular architecture.[1,6−11]

Laser mass spectrometry, including laser desorption/ionization (LDI) and two-step laser desorption laser ionization (L2MS), has emerged as a powerful means of assessing both molecular weight and molecular architecture in nonvolatile molecules and mixtures such as asphaltenes.[9−14] LDI experiments employ one laser pulse, typically in the UV or IR wavelength region, to desorb and ionize molecules contained in the solid sample. However, obtaining an artifact-free signal from any sample prepared in this manner requires a careful combination of optimized instrumental parameters. Without such considerations, the resulting spectra can be obscured by excessive fragmentation, plasma-phase reactions resulting in detectable ion clusters, or, worse, the absence of any signal at all.[11] Two-step laser desorption laser ionization mass spectrometry (L2MS)[15,16] addresses these issues by separating both processes temporally and spatially, allowing individual optimization of each. Coupling UV resonance-enhanced multiphoton ionization (REMPI) to laser desorption mass spectrometry has led to successful organic analyses, because it combines selectivity, sensitivity, and rapidity of measurement.[17,18] More recently, vacuum ultraviolet single-photon ionization (SPI) has been proposed as a universal soft ionization method for organic compounds and has been applied to study asphaltenes as well as surfaces, materials, aerosols, drugs, and peptides.[10,19] L2MS with REMPI and especially SPI ionization has been found to detect asphaltenes with minimal fragmentation and without the plasma-phase aggregation often found in LDI, suggesting that L2MS is particularly well-suited for analyzing the molecular composition of asphaltenes.

Previously,[10] we measured the laser desorption single-photon ionization mass spectrometry (LDSPI-MS) mass spectra of model compounds and asphaltene samples. The results suggested that asphaltenes have a wide range of molecular masses, peaking at ∼700 Da and extending to a maximum of ∼1500 Da. In addition, model compounds with island geometries displayed fragmentation patterns similar to asphaltenes, whereas model compounds with archipelago geometries displayed fragmentation patterns distinct from asphaltenes, suggesting that asphaltenes are dominated by island geometries. To gain further confidence in these results, it must be demonstrated that LDSPI-MS does not suffer from some potential artifacts common in mass spectrometric
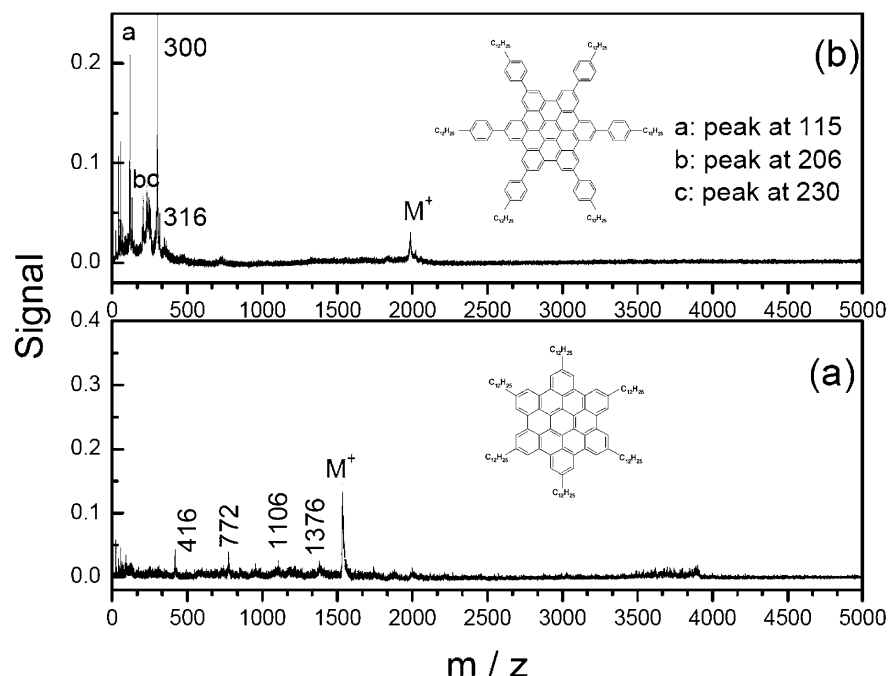
Figure 1. LDSPI-MS spectra of two model compounds with molecular weights of >1500 Da. Their mass spectra were recorded using identical experimental conditions: (a) model compound A and (b) model compound B.

analyses of complex mixtures, including limitations on the detectable mass range, variations in sensitivity to different components, and the significance of matrix effects on the desorption and ionization processes.

The purpose of the current work is to explore the effect of those potential artifacts on the LDSPI-MS analysis of asphaltenes. Here, we apply LDSPI-MS to six families of model compounds including polyaromatic hydrocarbons (PAHs), alkylated PAHs, N-substituted PAHs, O-substituted PAHs, S-substituted PAHs, and porphyrins. We compare the LDSPI-MS detection sensitivity of these model compounds over a range of molecular weights, within individual chemical classes, across different chemical classes, and diluted in various matrices. The results suggest that LDSPI-MS has an approximately uniform sensitivity to all the aromatic species studied, with a mass range extending beyond 1500 Da, and with minimal matrix effects.

■ EXPERIMENTAL SECTION

Model Compounds. Model compounds selected for this work were chosen to have structures as similar as possible to proposed components of asphaltenes. For example, asphaltenes are believed to be a complex mixture with an average H/C ratio around 1.1:1 but containing many molecules with H/C ratios far from that average value.[5] Model compounds selected for this work cover a range centered about that average value, spanning the range from 0.5:1 to 1.42:1. In addition, model compounds with LDSPI-MS fragmentation behavior inconsistent with asphaltenes were excluded from this work.[10] All model compounds used in this work were purchased from Sigma–Aldrich (St. Louis, MO), except for the two alkyl-substituted PAHs with molecular weights of 1532 and 1986 Da. The synthesis of these two model compounds were achieved according to well-known synthesis procedures.[20,21]

To prepare the samples for mass spectrometric analysis, model compounds were dissolved to 1 mg/mL solutions in toluene. Equimolar mixtures in solutions were prepared by using an appropriate volume of each their components. From each solution, a 20 μL drop was spotted onto a glass sample platter. These samples were

introduced into the system via a vacuum interlock, after allowing 1 h for the toluene to evaporate under ambient conditions.

Two-Step Laser Desorption Laser Ionization Mass Spectrometry. The L²MS has been described in detail elsewhere,[15,22,23] and this section provides a brief description of the apparatus. The sample is introduced into the instrument via a vacuum interlock, then the instrument is evacuated to a pressure of $\sim 2 \times 10^{-7}$ Torr and the sample is positioned within the extraction region of the mass spectrometer. The sample is allowed to outgas for $\sim$30 min within the instrument to reduce the background signal. A pulse of infrared (IR) light from a CO_2 laser (λ = 10.6 μm; Alltec GmbH, Model AL 882 APS) is used to desorb neutral molecules via very rapid heating.[24] The pulse is focused to a spot (50-μm diameter) on the sample surface using a Cassegrainian microscope objective (Ealing Optics, 15×). Localization of the laser radiation onto a small area of the sample and the low pulse energy of the output of the CO_2 laser combine to cause desorption of exclusively neutral molecules with minimal decomposition.

During a time delay of 25 μs, the neutral molecules desorbed from the sample surface form a plume in the mass spectrometer's extraction region. The delay time is sufficient for the plume to expand into collision-free conditions in the vacuum. This plume is intersected perpendicularly by the VUV output of a pulsed F_2 excimer laser (λ = 157 nm; Coherent, Inc., ExciStar XS 200) to ionize the constituent molecules. The photon energy (7.89 eV) is sufficient for SPI of aromatic organic species. SPI does not require resonant absorption to an intermediate electronically excited state and is thus a universal ionization technique for any molecule with an ionization potential below the photon energy.[19]

Upon creation of the ions, they are mass analyzed using a home-built reflectron time-of-flight mass spectrometer (TOF-MS) employing a modified Wiley–McLaren geometry.[25] With this setup, only positive ions are detected. The mass resolution of this instrument is approximately one mass unit at m/z 300.

■ RESULTS AND DISCUSSION

LDSPI-MS mass spectra of various mixtures of asphaltenes and model compounds are presented to evaluate performance regarding: detectable molecular weight range, sensitivity to different components, and matrix effect. Their mass spectra
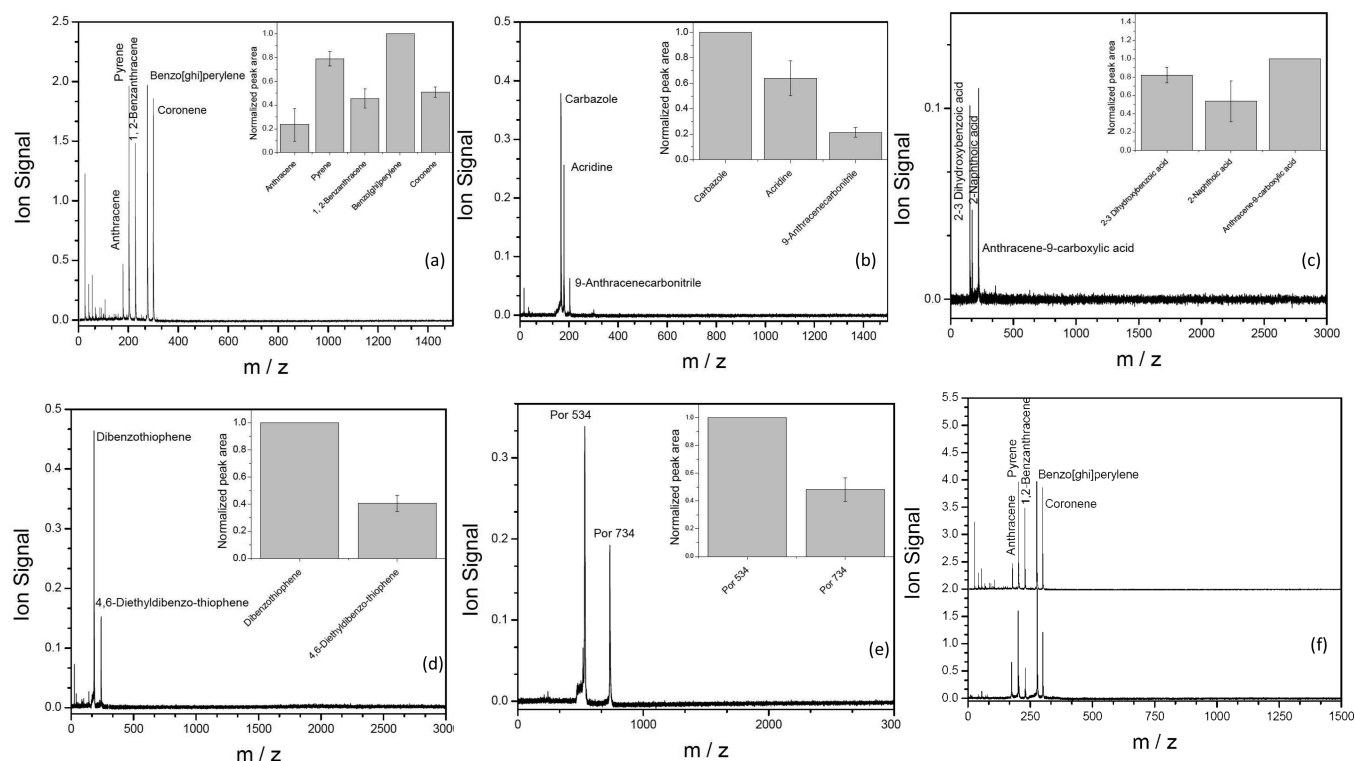
Figure 2. LDSPI-MS spectra of five mixtures of different chemical classes: (a) mixture of PAHs, (b) mixture of N-substituted PAHs, (c) mixture of O substituted PAHs, (d) mixture of S-substituted PAHs, (e) mixture of porphyrins, and (f) mixture of PAHs. All mass spectra here were recorded using identical experimental conditions. The inset graphs represent the PA of each model compound present in a particular mixture. The PA is proportional to the LDSPI-MS sensitivity of each compound. The PAs were normalized to a maximum of 1. The error bars in the inset graphs represent one standard deviation after repeating each experiment three or four times.

were recorded using identical experimental conditions (5 mJ/pulse for desorption; 1 mJ/pulse for ionization).

Molecular Weight Range Observable by LDSPI-MS. Figure 1 presents LDSPI-MS mass spectra of two alkyl-substituted polycyclic aromatic hydrocarbons (PAHs) with molecular weights of 1532 and 1986 Da. To simplify, we will call these model compounds A and B, respectively. The singly charged parent ions (M^+) are observable in both mass spectra, as shown in Figure 1. No aggregates are detected for these two compounds. The spectrum of compound A contains four peaks at masses below the parent ion, originating likely from fragments or impurities. These peaks each have small peak heights, relative to the parent ion, with the peaks areas even smaller because peak width increases at higher m/z. According to the nitrogen rule, for compounds containing no nitrogen (such as these alkyl-substituted PAHs), low mass peaks at odd mass generally result from fragmentation while low mass peaks at even mass generally result from impurities. The low mass peaks for this compound occur at even mass ($m/z = 416$, 772, 1106, and 1376), suggesting that they result from small levels of impurity rather than fragmentation. In particular, among the most likely fragmentation pathways for this compound would be cleavage alpha or beta to the fused ring system, producing the odd-mass ions $C_{12}H_{25}^+$ (mass = 169 Da) or $C_{11}H_{23}^+$ (mass = 155 Da), neither of which are observed. Similarly, the low mass peaks found in the spectrum of compound B occur predominantly at even mass, suggesting that they are also impurities.

These observations demonstrate that the molecular weight range accessible by LDSPI-MS without the formation of significant fragments, multiply charged species, or aggregates

extends beyond 1500 Da. This conclusion is similar to the one obtained previously for different classes of aromatic model compounds.[12]

Sensitivity of LDSPI-MS to Different Compounds. *1. Model Compounds within a Chemical Class.* Five samples were prepared to test the detection sensitivity of LDSPI-MS to aromatic species within chemical classes. They were composed of equimolar mixtures of compounds of the same chemical class. The classes include PAHs, N-substituted PAHs, O-substituted PAHs, S-substituted PAHs, and porphyrins. To simplify, we will call the two porphyrins compounds 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine and 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine Por 534 and Por 734, respectively. Figure 2 presents the mass spectra of each of these mixtures. Each peak is labeled by the model compound's name. An inset graph is included to represent the normalized peak area (PA) of each model compound present in the mixture, normalized to the largest PA in the mixture. The error bars in the inset graphs represent one standard deviation after repeating each experiment three or four times. The normalized PA of the different peaks is proportional to the sensitivity of LDSPI-MS to these compounds. All studied compounds within a chemical class are detected with almost uniform sensitivity (within a factor of 5) and with no trends with respect to molecular weight.

Some of these mixtures also give peaks at m/z below 150. The intensity of these peaks is poorly reproducible, as shown in Figure 2f presenting replicate measurements of one of the mixtures. In this figure, the peaks corresponding to compounds in the mixture reproduce well, while the peaks below m/z 150 reproduce poorly. This result suggests that the peaks below $m/$
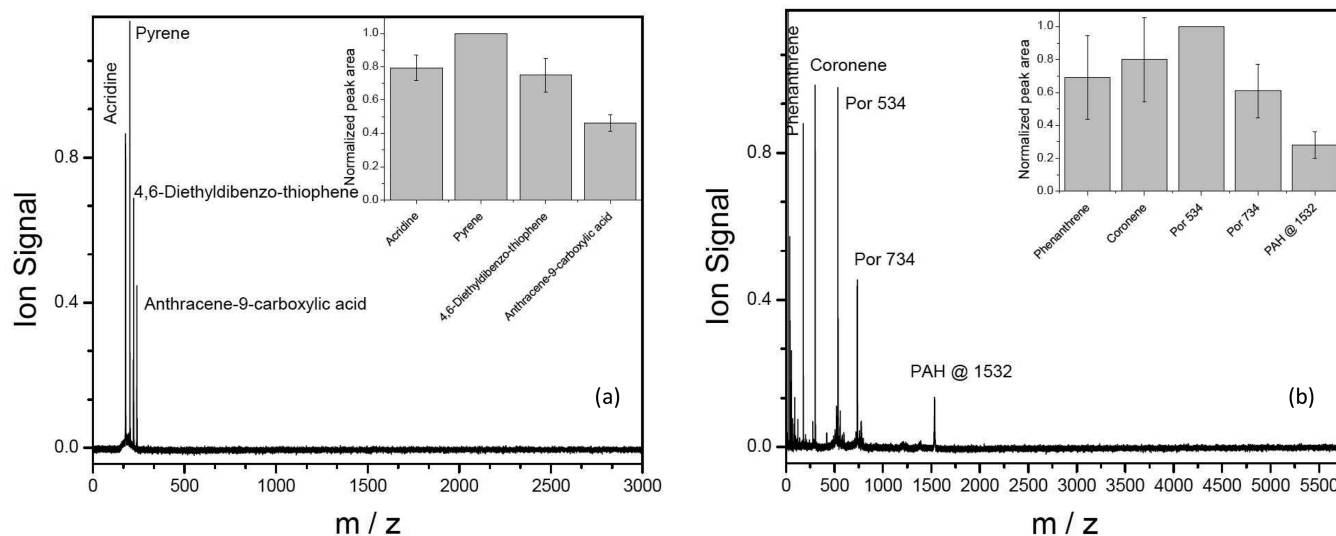
Figure 3. LDSPI-MS spectra of two mixtures composed of model compounds from different chemical classes: (a) mixture of PAHs and heteroatom-substituted PAHs, and (b) mixture of different chemical classes which spans a mass range of 178−1532 Da. All mass spectra here were recorded using identical experimental conditions. The inset graphs represent the PA of each model compound present in a particular mixture. The PA is proportional to the LDSPI-MS sensitivity of each compound. The error bars in the inset graphs represent one standard deviation after repeating each experiment three or four times.

z 150 are not fragments but instead backgrounds resulting from stray laser light ionizing residual organic compounds in the vacuum chamber.

2. Model Compounds across Different Chemical Classes. Two samples were prepared to test the detection sensitivity of LDSPI-MS to model compounds across chemical classes. The first one is an equimolar mixture of PAHs and heteroatom-substituted PAHs. The second one is an equimolar mixture of PAHs, porphyrins, as well as compound A, and it spans a mass range from 178 Da to 1532 Da. Figure 3 presents the LDSPI-MS mass spectra of these mixtures, and the PA of each compound is displayed in the inset. Both graphs of Figure 3 demonstrate that LDSPI-MS has similar detection sensitivity across chemical classes (within a factor of 3). Similarly, there is no observed trend to particular classes of molecules being detected with greater sensitivity than others. Moreover, Figure 3b shows that the LDSPI-MS detection sensitivity is mostly constant for molecular weights in the range of 178−1532 Da. The comparable detection sensitivity of LDSPI-MS to multiple compound classes stands in contrast to other ionization techniques, for example, electrospray ionization where the sensitivity varies by orders of magnitude between polar and nonpolar compound classes.

*3. Asphaltenes and a Model Compound.* One sample was prepared to test the detection sensitivity of LDSPI-MS to model compounds and asphaltenes. The sample is a mixture of asphaltenes and porphyrin with a molar ratio of 2:1 (molar ratio calculation made with the assumption that the asphaltene molecular weight is 750 Da, the mass at which the L²MS molecular-mass distribution peaks). Figure 4 presents the LDSPI-MS mass spectra of this mixture and the inset shows the normalized peak areas of the asphaltenes and porphyrin. Considering the molar ratio of the mixture (2:1), the calculated PA of asphaltenes is divided by a factor of 2. This plot demonstrates that LDSPI-MS has similar detection sensitivity to asphaltenes and to the porphyrin (within a factor of 2.5). Taken together, Figures 2−4 suggest that LDSPI-MS has a comparable sensitivity to all studied model compounds and to a
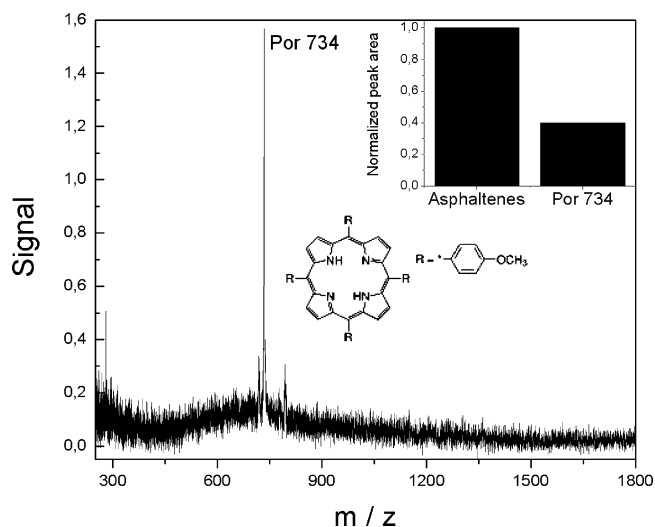
Figure 4. LDSPI-MS mass spectrum of a mixture of asphaltenes and a porphyrin with a molecular weight of 734 Da. The molar ratio of the mixture is 2:1 asphaltenes/porphyrin. The inset graphs represent the PA of asphaltenes and Por 734. The PA is proportional to the LDSPI-MS sensitivity of Por 734 and the average LDSPI-MS sensitivity of asphaltenes. The PAs were normalized to a maximum of 1. LDSPI-MS has similar sensitivity to model compounds and a complex mixture such as asphaltenes.

typical component of the complex mixture of asphaltenes, covering the full mass range found in asphaltenes. While it is possible that there are individual components of asphaltenes not detected by LDSPI-MS, these results suggest that the majority of components of asphaltenes are detected by LDSPI-MS with comparable sensitivity.

Matrix Effects in LDSPI-MS. The matrix effect in mass spectrometry refers to the sensitivity with which a particular compound in a mixture is detected as a function of the composition of the rest of the mixture (referred to as the matrix); ionization techniques where the sensitivity to a
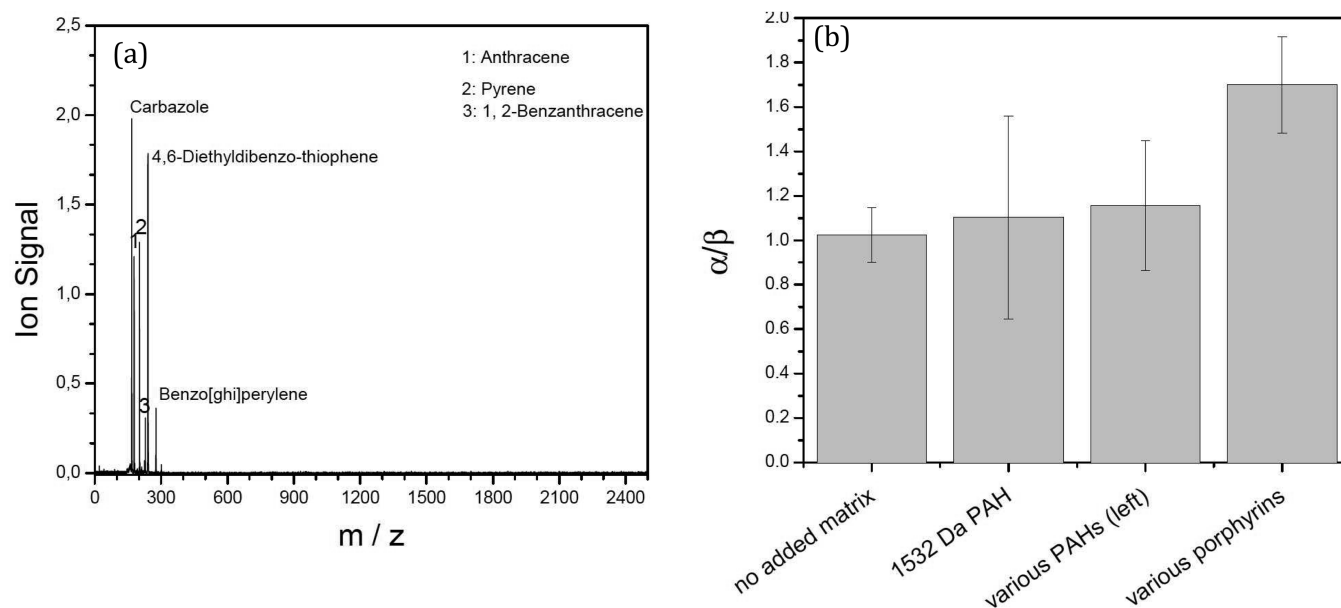
Figure 5. (a) LDSPI-MS mass spectrum of carbazole and 4,6-diethyldibenzo-thiophene within a matrix of PAHs. (b) The PA ratio α/β of the two compounds as a function of the used matrix. The error bars in the inset graphs represent one standard deviation after repeating each experiment three or four times. LDSPI-MS minimizes matrix effect (almost-constant α/β ratio).

particular compound depends strongly on the composition of the matrix are considered to have a large matrix effect. Four samples have been prepared to test the detection sensitivity of LDSPI-MS to two heteroatom-substituted PAH model compounds (carbazole and 4,6-diethyldibenzo-thiophene) within different matrices. These samples each contain a different matrix, including: no added matrix (neat), a matrix of compound A, a matrix of PAHs, and a matrix of porphyrins. Figure 5a shows the LDSPI mass spectrum of these two compounds in a matrix of PAHs; mass spectra acquired with the other matrices are similar and not shown. To assess the importance of matrix effects in LDSPI-MS, the PA of each model compound in each matrix is calculated, and Figure 5b shows the ratio of the peak areas of the two model compounds for different matrices. The relative detection sensitivity of these two model compounds is almost the same for the four matrices (within a factor of 1.7), suggesting that matrix effects in LDSPI-MS are minimal.

The small matrix effect found in LDSPI-MS contrasts the pronounced matrix effect that can be found in atmospheric pressure ionization schemes such as atmospheric pressure photoionization (APPI), atmospheric pressure chemical ionization (APCI), and electrospray ionization (ESI), and that difference can be understood by considering the ionization mechanisms. Atmospheric pressure ionization techniques involve placing ions in a high-pressure environment, causing the ions to suffer many collisions. These collisions lead to ion–molecule and other reactions, resulting in a distribution of ions potentially different from that produced initially. For example, positive-ion APPI mass spectra typically contain abundant peaks from protonated species, resulting from reactive collisions in which a proton is transferred from a charged molecule to a neutral molecule.[26] The relative intensity of peaks in the mass spectra thus are determined not only by the abundance of the compounds in the mixture and by their cross sections for photoionization or chemical ionization but also by interactions between components in the sample, in particular, the rate constants of these reactions. These ionizations techniques have

significant matrix effects because interactions between compounds influence the peak heights.

In contrast, the desorption and ionization steps in LDSPI-MS do not involve interactions between components in the sample. In LDSPI-MS measurements of asphaltenes, the asphaltene sample is deposited as a thin layer on a glass platter. The IR pulse used for desorption is mostly transmitted through the sample and absorbed by the platter, with desorption resulting from energy transfer from the platter to the sample.[27] Thus, desorption results not from interactions between different components of the sample but from interactions between the sample and the platter. After desorption, the plume expands into a vacuum before the ionization pulse is fired. Once ions are created, the pressure is low such that the ions do not undergo collisions, so interactions between different components of the sample do not influence the ionization process.

■ CONCLUSION

Laser desorption single-photon ionization mass spectrometry (LDSPI-MS) is known to be a powerful ionization technique for analysis of asphaltenes because it is mostly free of complications from aggregation, fragmentation, and multiple charging. Here, we investigate the effects of other potential experimental artifacts in LDSPI-MS analysis of asphaltenes: the sensitivity of the technique to different molecules, the detectable mass range, and the matrix effect. It is found that LDSPI-MS has comparable detection sensitivity to model compounds (polyaromatic hydrocarbons (PAHs), O-substituted PAHs, N-substituted PAHs, S-substituted PAHs, alkyl-substituted PAHs, and porphyrins) and asphaltenes, both within and between chemical classes. In particular, the detection sensitivity for compounds with molecular weights of >1500 Da is similar to the detection sensitivity for compounds with molecular weights of <1500 Da, and no trends between detection sensitivity and molecular weight are observed for the studied molecular weight range. In addition, matrix effects in LDSPI-MS are found to be minimal, with the relative sensitivity to different molecules mostly independent of

matrix; the lack of matrix effects is expected from mechanistic considerations, as interactions between different molecules in the sample are not involved in the desorption and ionization processes (in contrast to atmospheric pressure ionization techniques). Previous LDSPI-MS results suggests that (i) 1500 Da represents an upper limit to the asphaltene molecular weight distribution and (ii) island geometries dominate asphaltenes.[9−11,22] However, confidence in those results was limited at the time, because the effect of experimental artifacts such as varying sensitivity to different components of the mixture, limited detectable molecular weight range, and matrix effect were poorly constrained. The results of this work suggest that those artifacts minimally impact LDSPI-MS of asphaltenes, therefore increasing confidence in the earlier results.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: + 33-5-6155-6443. E-mail: hassan.sabbah@irap.omp.eu.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Klein, G. C.; Kim, S.; Rodgers, R. P.; Marshall, A. G. Mass spectral analysis of asphaltenes. I. Compositional differences between pressure-drop and solvent-drop asphaltenes determined by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2006**, *20*, 1965−1972.

(2) Klein, G. C.; Kim, S.; Rodgers, R. P.; Marshall, A. G.; Yen, A. Mass spectral analysis of asphaltenes. II. Detailed compositional comparison of asphaltenes deposit to its crude oil counterpart for two geographically different crude oils by ESI FT-ICR MS. *Energy Fuels* **2006**, *20*, 1973−1979.

(3) Betancourt, S. S.; et al. Nanoaggregates of asphaltenes in a reservoir crude oil and reservoir connectivity. *Energy Fuels* **2009**, *23*, 1178−1188.

(4) Pomerantz, A. E.; Ventura, G. T.; McKenna, A. M.; Canas, J. A.; Auman, J.; Koerner, K.; Curry, D.; Nelson, R. K.; Reddy, C. M.; Rodgers, R. P.; Marshall, A. G.; Peters, K. E.; Mullins, O. C. Combining biomarker and bulk compositional gradient analysis to assess reservoir connectivity. *Org. Geochem.* **2010**, *41*, 812−821.

(5) Mullins, O. C.; Sheu, E. Y.; Hammami, A.; Marshall, A. G. *Asphaltenes, Heavy Oils, and Petroleomics*; Springer: New York, 2007; p XXI.

(6) Hortal, A. R.; Hurtado, P.; Martinez-Haya, B.; Mullins, O. C. Molecular-weight distributions of coal and petroleum asphaltenes from laser desorption/ionization experiments. *Energy Fuels* **2007**, *21*, 2863−2868.

(7) Hortal, A. R.; Martinez-Haya, B.; Lobato, M. D.; Pedrosa, J. M.; Lago, S. On the determination of molecular weight distributions of asphaltenes and their aggregates in laser desorption ionization experiments. *J. Mass Spectrom.* **2006**, *41*, 960−968.

(8) Martinez-Haya, B.; Hortal, A. R.; Hurtado, P.; Lobato, M. D.; Pedrosa, J. M. Laser desorption/ionization determination of molecular weight distributions of polyaromatic carbonaceous compounds and their aggregates. *J. Mass Spectrom.* **2007**, *42*, 701−713.

(9) Pomerantz, A. E.; Hammond, M. R.; Morrow, A. L.; Mullins, O. C.; Zare, R. N. Asphaltene molecular-mass distribution determined by two-step laser mass spectrometry. *Energy Fuels* **2009**, *23*, 1162−1168.

(10) Sabbah, H.; Morrow, A. L.; Pomerantz, A. E; Zare, R. N. Evidence for Island Structures as the Dominant Architecture of Asphaltenes. *Energy Fuels* **2011**, *25*, 1597−1604.

(11) Pomerantz, A. E.; Hammond, M. R.; Morrow, A. L.; Mullins, O. C.; Zare, R. N. Two-step laser mass spectrometry of asphaltenes. *J. Am. Chem. Soc.* **2008**, *130*, 7216−7217.

(12) Karas, M.; Bachmann, D.; Bahr, U.; Hillenkamp, F. Matrix-assisted ultraviolet laser desorption of non-volatile compounds. *Int. J. Mass Spectrom. Ion Processes* **1987**, *78*, 53−68.

(13) Karas, M.; Hillenkamp, F. Laser desorption ionization of proteins with molecular masses exceeding 10 000 Da. *Anal. Chem.* **1988**, *60*, 229−2301.

(14) Hurtado, P; Gámez, F; Martínez-Haya, B. One- and two-step ultraviolet and infrared laser desorption ionization mass spectrometry of asphaltenes. *Energy Fuels* **2010**, *24*, 6067−6073.

(15) Kovalenko, L. J.; Maechling, C. R.; Clemett, S. J.; Philippoz, J. M.; Zare, R. N.; Alexander, C. M. O. Microscopic organic analysis using two-step laser mass spectrometry: application to meteoritic acid residues. *Anal. Chem.* **1992**, *64*, 682−690.

(16) Morrical, B. D.; Fergenson, D. P.; Prather, K. A. Coupling two-step laser desorption/ ionization with aerosol time-of-flight mass spectrometry for the analysis of individual organic particles. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 1068−1073.

(17) Dobson, R. L. M.; D'Silva, A. P.; Weeks, S. J.; Fassel, V. A. Multidimensional, laser-based instrument for the characterization of environmental samples for polycyclic aromatic compounds. *Anal. Chem.* **1986**, *58*, 2129.

(18) Zimmermann, R.; Heger, H. J.; Kettrup, A.; Boesl, U. A mobile resonance-enhanced multiphoton ionization time-of-flight mass spectrometry device for on-line analysis of aromatic pollutants in waste incinerator flue gases: First results. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 1095.

(19) Hanley, L.; Zimmermann, R. Light and molecular ions: The emergence of vacuum UV single-photon ionization in MS. *Anal. Chem.* **2009**, *81*, 4174−4182.

(20) Fechtenkötter, A. Ph.D. thesis, Mainz, Germany, 2001.

(21) Stabel, A.; Herwig, P.; Mullen, K.; Rabe, J. P. Diode-like current−voltage curves a single molecule-tunneling spectroscopy with submolecular resolution of an alkylated, periconsensd hexabenzo-coronene. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1609−1611.

(22) Sabbah, H.; Morrow, A. L.; Pomerantz, A. E.; Mullins, O. C.; Tan, X. L.; Gray, M. R.; Azyat, K.; Tykwinski, R. R.; Zare, R. N. Comparing laser desorption/laser ionization mass spectra of asphaltenes and model compounds. *Energy Fuels* **2010**, *24*, 3589−3594.

(23) Hahn, J. H.; Zenobi, R.; Zare, R. N. Subfemtomole quantitation of molecular adsorbates by two-step laser mass spectrometry. *J. Am. Chem. Soc.* **1987**, *109*, 2842−2843.

(24) Cowin, J. P.; Auerbach, D. J.; Becker, C.; Wharton, L. Measurement of fast desorption-kinetics of d₂ from tungsten by laser-induced thermal desorption. *Surf. Sci.* **1978**, *78*, 545−564.

(25) Wiley, W. C.; McLaren, I. H. Time-of-flight mass spectrometer with improved resolution. *Rev. Sci. Instrum.* **1955**, *26*, 1150−1157.

(26) Purcell, J. M.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G. Speciation of nitrogen containing aromatics by atmospheric pressure photoionization or electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *J. Am. Soc. Mass Spectrom.* **2007**, *18*, 1265−1273.

(27) Maechling, C. R. Infrared Laser Desorption: Mechanisms and Applications. Ph.D. Thesis, Stanford University, Stanford, CA, 1995.