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Asphaltene Molecular-Mass Distribution Determined by Two-Step Laser Mass Spectrometry[†]

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Two-step laser mass spectrometry (L^2MS) is explored as a technique to measure the molecular-mass distribution of asphaltenes. Unlike widely used laser desorption/ionization (LDI) mass spectrometry, in which a single laser pulse is used to desorb and ionize asphaltenes, L^2MS involves two laser pulses and spatially and temporally separates the desorption and ionization events. This process allows L^2MS to measure the asphaltene molecular-mass distribution free from artifacts resulting from aggregation and insufficient laser power, as occur in LDI. Studies of relevant model compounds show that L^2MS detects these molecules without aggregation (unlike LDI), with only a minimum of fragmentation/multiple charging, and with relatively uniform sensitivity across the relevant mass range; however, the efficiency of the resonant ionization process is sensitive to molecular structure. These data suggest that L^2MS does not suffer from significant mass discrimination in the relevant mass range and that L^2MS provides a slight underestimate of the asphaltene molecular-mass distribution. Petroleum asphaltenes from different geographical origins are found to have similar mass spectra, all showing a peak at every nominal mass under an envelope beginning at 200 units, peaking at 500−600 units, and extending to 1000−1500 units. Coal asphaltenes are found to be considerably lighter and less complex, showing pronounced clusters of peaks separated by 14 units under an envelope beginning at 200 units, peaking at 300 units, and extending to 500 units. These results bring the molecular-mass distribution of asphaltenes as measured by laser desorption mass spectrometry in accordance with many other mass spectrometry and diffusion measurements.

Introduction

Asphaltenes are a fraction of crude oil defined operationally by their solubility in toluene and insolubility in *n*-heptane. This fraction has been studied extensively because of its role in oilfield flow assurance and more recently because of its application as a geochemical marker that can indicate the geologic structure of oil reservoirs.[1−3] From these studies, the elemental composition of asphaltenes has been established and a consensus has been reached that asphaltenes are highly aromatic and polar.[1] Additionally, asphaltenes are known to be a complex mixture containing thousands of distinct molecular formulas.[4,5]

Despite this scrutiny, some fundamental aspects of asphaltene chemistry are still debated. Most strikingly, the average asphaltene molecular mass is still unknown to within an order of magnitude. Over the past 2 decades, several groups have probed the asphaltene molecular-mass distribution with a variety of mass spectrometric techniques, molecular-diffusion-based techniques, and chromatographic techniques. Several recent papers highlight the achievements and criticisms of each measurement.[1,6−12] Mass spectrometric measurements have employed a variety of ionization techniques. In a complex mixture, such as asphaltenes, the use of multiple ionization techniques is essential because the sensitivity of a particular technique varies to an unknown extent over the different components contained in an asphaltene sample; hence, experiments with different ionization techniques measure the molecular-mass distribution of asphaltenes with different biases. Despite great differences in ionization mechanisms, measurements based on field ionization,[13] field desorption ionization,[14] electrospray ionization,[1,11]

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and atmospheric pressure chemical ionization[15,16] all return an asphaltene molecular-mass distribution that peaks in the range of 500−1000 units. However, measurements employing ^{252}Cf plasma desorption and fast atom bombardment ionization show a pronounced tail at times extending beyond 10 000 units.[6,9]

Molecular diffusion experiments measure a diffusion constant, which can be related to a hydrodynamic radius. By calibrating against known compounds, these measurements of molecular size can be related to molecular mass. Four sets of measurements have been performed, each using a different method of detection or measuring a different motion. In this first work of its kind, Groenzin et al.[17,18] used time-resolved fluorescence depolarization to measure the rotational diffusion constant of asphaltenes; the data correspond to an average asphaltene molecular mass of 750 units. Later, Andrews et al.[19−21] used fluorescence correlation spectroscopy to measure the translational diffusion constant of asphaltenes, reporting a similar average molecular mass. The consistency of rotational and translational diffusion constants suggests that internal rotations are not significant. It has been pointed out that these two measurements are sensitive to only the fluorescent fraction of asphaltenes.[7,9,10] Iino et al.[22] used Taylor dispersion to measure the translational diffusion constant of coal asphaltenes. The translational diffusion constant of coal asphaltenes is slightly smaller than the translational diffusion constant of petroleum asphaltenes, consistent with the slightly lower molecular mass of coal asphaltenes. The Taylor dispersion measurements used optical absorption to escape the limitation to fluorescent molecules. Additionally, Freed and co-workers[1,23] used pulsed-field gradient nuclear magnetic resonance (NMR) to measure the translational diffusion constant, which again yielded a similar molecular size. This experiment is not limited to fluorescent molecules but rather is sensitive only to species with a detectable ^{1}H NMR signal.

Size-exclusion chromatography (SEC) separates molecules of different hydrodynamic volumes based on the time they require to elute through a given length of stationary phase. This technique is commonly used in the biological and polymer chemistry communities to characterize molecules of extremely high molecular mass ($>10^7$ units). SEC measurements of asphaltenes return molecular sizes that differ greatly from the sizes measured in diffusion experiments. When *N*-methylpyrrolidinone is used as an eluting solvent, a bimodal distribution of molecular masses is measured, with one peak appearing near 10 000 units and the second peak appearing near 1 000 000 units.[9] It has been suggested that this measurement detects the molecular mass of asphaltene aggregates rather than molecules, because *N*-methylpyrrolidinone is a poor solvent for asphaltenes.[11,24] When tetrahydrofuran (THF) is used as the eluting solvent, the 1 000 000 units peak does not appear.[10] Other difficulties associated with SEC measurements of asphaltenes have been noted.[25]

Laser desorption/ionization (LDI) is a mass spectrometric technique that has produced very controversial data on asphaltenes. In this measurement, solid asphaltenes in a high vacuum chamber are irradiated with an intense laser pulse, causing both desorption of the asphaltenes as well as their ionization; the masses of the ionized species are then analyzed, typically with a time-of-flight mass spectrometer. The controversy arises from the fact that asphaltene molecular-mass distributions differ by orders of magnitude when measured by different groups, with some groups recording average molecular masses of ∼800 units,[26−28] some recording average molecular masses of ∼2000 units,[29,30] and others recording bimodal molecular-mass distributions containing a peak beyond 50 000 units.[31] It has been shown that the measured molecular mass can change over this large range as certain experimental parameters are adjusted.[26−28] For example, the laser pulse energy, the sample concentration on the surface, and the use of continuous versus pulsed ion extraction are all known to influence the experimental LDI mass spectrum. High laser pulse energy, high surface concentration of asphaltenes, and the use of continuous ion extraction all lead to relatively heavy measured asphaltene molecular-mass distributions. Two theories have been advanced to interpret these results: some argue that heavier distributions are recorded with high laser pulse energy because only at high pulse energy are the heavier components of asphaltenes efficiently desorbed and ionized;[29−31] others suggest that these heavy mass distributions result from aggregation in the plasma plume and that aggregation is suppressed at lower laser pulse energy, lower sample concentration, or both.[26−28]

Very recently, two-step laser mass spectrometry (L^{2}MS) has been shown to be capable of measuring the asphaltene molecular-mass distribution without limitation from low laser power or the possibility of plasma-phase aggregation, resolving the controversy created by the LDI measurements.[32] In this contribution, we expand on the use of L^{2}MS to measure accurately the asphaltene molecular-mass distribution. We present L^{2}MS mass spectra of several model compounds, showing the ability of this technique to detect asphaltene-like molecules without any observable aggregation and with only minimal fragmentation. We also study the relative sensitivity of L^{2}MS to a variety of model compounds, which shows no indication of experimental bias toward light or heavy masses in this range. The L^{2}MS spectra of these model compounds are found to be independent of experimental parameters. Additionally, L^{2}MS mass spectra of petroleum asphaltenes from several parts of the world are presented, showing only small differences in their

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molecular-mass distributions. In contrast, coal asphaltenes are found to be considerably lighter and less compositionally complex.

Experimental Section

L^2MS is a mass spectrometric technique that differs significantly from the common laser desorption/ionization (LDI) measurement. The most significant difference between the techniques is that L^2MS is a two-step process, in which the laser desorption and laser ionization steps are separated spatially and temporally, allowing each to be optimized independently. The home-built apparatus used for these measurements has been used previously to analyze samples of cosmogeochemical and environment significance, and a detailed description of the instrument can be found in that literature.[33−41] We provide a brief description of the instrument here, with salient differences from LDI highlighted.

Sample Preparation. Model compounds were purchased from Sigma-Aldrich and used without further preparation. Asphaltenes were extracted from various crude oils by diluting the crude oil 1:40 in *n*-heptane and waiting 2 days for the asphaltenes to precipitate. The asphaltenes were then extracted from the solution by vacuum filtration over a nylon membrane with 0.65 μm pores. The asphaltenes were then dried and dissolved in toluene to eliminate any non-asphaltene species in the crude oil that are insoluble in *n*-heptane (typically inorganic species). The solution of asphaltenes in toluene was then diluted in *n*-heptane and vacuum filtered as before. Finally, the asphaltenes were washed by Soxhlet extraction in *n*-heptane for 2 days. Asphaltenes labeled "UG8" and "BG5" are extracted from Middle Eastern crude oils, while "GOM #1" and "GOM #2" are extracted from crude oils from the Gulf of Mexico. Coal asphaltenes (obtained from Professor Iino, Tohoku University, Japan) are the toluene-soluble, *n*-heptane-insoluble fraction of coal and were prepared similarly.

Prior to introduction into the mass spectrometer, the samples are dissolved in toluene, approximately 10 μL of solution is deposited on a glass platter, and the sample is exposed to air for 15−30 min to allow for the solvent to evaporate. If necessary, a small amount of coronene (300 units) or pyrenebutanol (274 and 215 units) is deposited on the rim of the platter to serve as an internal standard. The platter is then loaded into a high-vacuum chamber via an interlock, allowing for rapid insertion of samples without the need to vent the entire chamber to the atmosphere.

Laser Desorption. Inside the vacuum chamber, the sample is aligned, so that it is irradiated with the focused pulse of light from a CO_2 laser. This pulse of 10.6 μm radiation consists of a 120 ns full width at half maximum (fwhm) Gaussian peak with a 4 μs tail. Typically, 5−10 mJ pulse energy is used, and the beam is focused to an approximately 50 μm spot. The laser light is focused using a Cassegrainian lens, and a dichroic mirror is used to direct visible light to a camera, which is used to align the sample. The sample is mounted on a translational stage and moved between laser pulses, so that a fresh area of sample is exposed to each shot.

The use of a mid-IR photon for laser desorption is a key aspect of L^2MS. With a photon energy nearly 2 orders of magnitude below a typical asphaltene ionization potential, multiphoton ionization does not occur. Therefore, unlike the high ion density plasma plume created in LDI, only a plume of neutrals desorbs in L^2MS. Additionally, the laser fluence is approximately 200 J cm^{-2}, much higher than the 0.5−5 J cm^{-2} commonly used in LDI.[26]

Laser Ionization. Approximately 25 μs after desorption, a second laser pulse is fired to ionize the gas-phase species. In this case, a 5 ns pulse of 266 nm radiation from the fourth harmonic of a Nd:YAG laser intersects the plume at a right angle approximately 2−3 mm above the sample surface. This laser pulse ionizes gas-phase molecules in the desorbed plume of neutrals via (1 + 1) resonance-enhanced multiphoton ionization (REMPI). Because ionization occurs in the gas phase, only a very low density cloud of charged particles is produced, in contrast to LDI, where a relatively high charged particle density plasma plume results from interaction of the laser pulse with a solid surface. Gas-phase REMPI is considered to be a selective technique, because only molecules with appreciable REMPI cross-sections at the ionization wavelength are ionized. In previous studies, this selectivity has been used to detect polycyclic aromatic hydrocarbons (PAHs) in complex mixtures, with the sensitivity to PAHs arising from their large REMPI cross-sections at 266 nm.[38−42] Similar to PAHs, asphaltenes are known to be aromatic; therefore, L^2MS with 266 nm REMPI detection is expected to be sensitive to most asphaltenic molecules. Indeed, despite debate about asphaltene molecular architecture, it is agreed that approximately half of asphaltene carbon is aromatic and the carbon/hydrogen ratio is near unity.[43] Also, molecular orbital calculations demonstrate that PAH structures consistent with much experimental data on asphaltenes all absorb at 266 nm.[44] Nevertheless, differences in REMPI sensitivity among different components of asphaltenes can influence the L^2MS mass spectrum of asphaltenes, and this effect is currently being investigated.

Mass Analysis. Ionization occurs in the extraction region of a modified Wiley−McLaren reflectron time-of-flight mass spectrometer. Ion signals are recorded with a matched set of microchannel plate detectors, amplified, and averaged on a digital oscilloscope. This reflectron mass spectrometer affords a large mass range and a resolution ($m/\Delta m$) of approximately 2000. A typical asphaltene mass spectrum is shown in Figure 1. The mass range of 0−1800 units usually suffices to capture the full tail of the molecular-mass distribution, as shown in Figure 1a. Asphaltenes are a complex mixture containing many components at every nominal mass,[1] and this resolution is sufficient for partial resolution of these peaks. Figure 1b shows an expanded section of the mass range of the spectrum shown in Figure 1a, demonstrating the partial resolution of a peak at every mass. Typically, 100 spectra are averaged together, resulting in a signal-to-noise ratio large enough that these individual peaks can be observed.

Measurements in the time domain are converted to the mass domain through the use of internal standards. Several such standard are commonly employed. First, gaseous toluene-d_8 (100 units) is leaked into the chamber, and its parent ion, isotopologue, and fragments can be used for calibration. Additionally, coronene (300 units) and/or pyrenebutanol (274 and 215 units) deposited on the rim of the platter can also be used as internal standards.

Comparing L^2MS with LDI

L^2MS has recently been shown to resolve an ambiguity in the interpretation of LDI mass spectra of asphaltenes.[32] Briefly, average asphaltene molecular masses recorded by different groups using LDI vary by orders of magnitude. It has been

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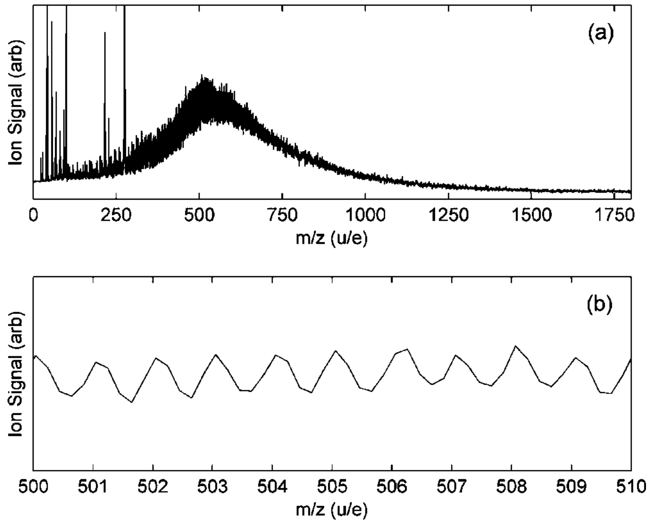

Figure 1. L^{2}MS mass spectrum of UG8 asphaltene. (a) Full mass range, showing the molecular-mass distribution. (b) Zoomed in to cover only the mass range of 500−510 units/e, highlighting the observed complexity of the sample.

shown that the experimentally measured mass spectrum can vary over this large range as certain experimental parameters, such as the laser pulse energy or sample concentration, are changed; high-pulse energy and sample concentration lead to relatively heavy measured masses.[26−28] Two interpretations of these data have been offered: some groups favor the heavier spectra, arguing that high laser power is required to detect the heaviest asphaltenes; other groups favor the lighter spectra, arguing that excessive laser power and/or sample concentration promote aggregation in the plasma plume.

By separating desorption and ionization into two steps, L^{2}MS avoids the ambiguities found in LDI. Because the desorption photon energy is so low, desorption pulse energies much higher than commonly employed in LDI can be used for L^{2}MS, still without producing ions. Because ions are not present in the plume, the strong ion-induced dipole attractive forces required for aggregation are not present; therefore, aggregates would not be expected to form. Additionally, IR laser pulses are often used to break up gas-phase aggregates, further suggesting that aggregates should not be present in the plume (at least for the duration of the desorption pulse).[45,46] After a delay of approximately 25 μs, the UV laser pulse intercepts the plume and ionizes those species that can undergo 1 + 1 REMPI. At this point, the density is so low that aggregation does not occur. Additionally, the ionization process may serve to dissociate any aggregates that happen to exist in the plume; multiphoton ionization has been shown to dissociate approximately 90% of noncovalent aggregates in certain systems.[47]

The success of L^{2}MS is demonstrated by the independence of the measured mass spectra with respect to experimental parameters, in stark contrast to LDI. Figure 2 shows L^{2}MS mass spectra of UG8 petroleum asphaltene recorded over a range of desorption and ionization laser pulse energies. The mass spectrum does not shift with increasing desorption pulse energy, indicating that even the lower pulse energy employed here is intense enough to desorb even the heaviest components of asphaltenes. The fact that the mass spectrum does not shift with increasing desorption or ionization pulse energy is consistent with the lack of aggregation. Additionally, Figure 3 shows that L^{2}MS mass spectra are also independent of the asphaltene concentration and the time delay between the laser pulses. The invariance of the L^{2}MS mass spectra with changes in these four experimental parameters demonstrates that L^{2}MS can record the asphaltene molecular-mass distribution without limitation from aggregation or insufficient laser pulse energy. In particular, the invariance of the L^{2}MS mass spectrum with changing ionization laser power implies that neither aggregation nor fragmentation occurs, in contrast to LDI.[26−28] The fact that heavier compounds do not appear as the desorption laser pulse energy is increased suggests that molecules heavier than recorded here are not present in asphaltenes.

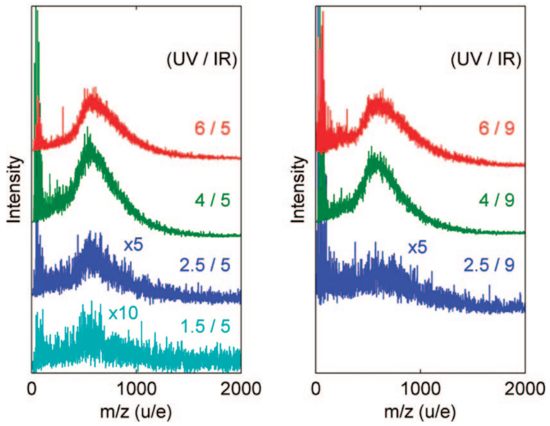

Figure 2. L^{2}MS mass spectra of UG8 asphaltene at different pulse energies. UV indicates the pulse energy of the ionization laser (mJ), and IR indicates the pulse energy of the desorption laser (mJ). Ionization pulse energies are compared vertically, and desorption pulse energies are compared horizontally. The recorded mass spectra are independent of the pulse energy of either laser.

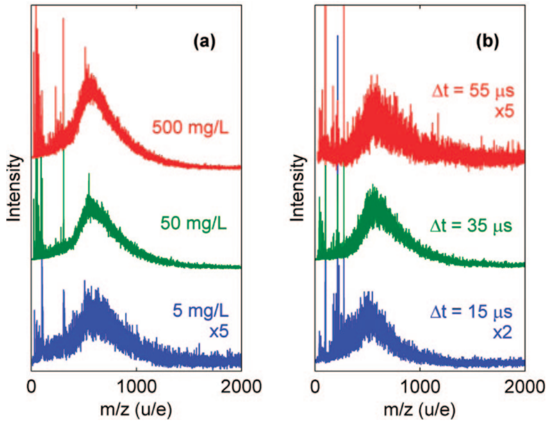

Figure 3. L^{2}MS mass spectra of UG8 asphaltene at different (a) concentrations and (b) desorption−ionization delays. The recorded mass spectra are independent of both the surface concentration and the time delay.

Model Compounds

The mass spectra shown in Figures 2 and 3 demonstrate that L^{2}MS can measure the asphaltene molecular-mass distribution free from limitations arising from aggregation or insufficient laser pulse energy, thus resolving the ambiguities in the LDI measurements. However, there are other potential limitations in this measurement, and they must be addressed to determine how accurately L^{2}MS can measure the true asphaltene molec-

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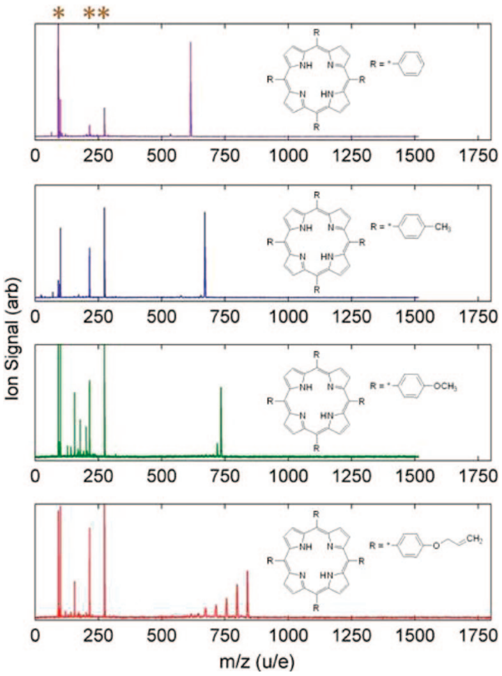

Figure 4. L^{2}MS mass spectra of four porphyrin model compounds. Internal standards at 100, 215, and 274 units/e are marked with an asterisk.

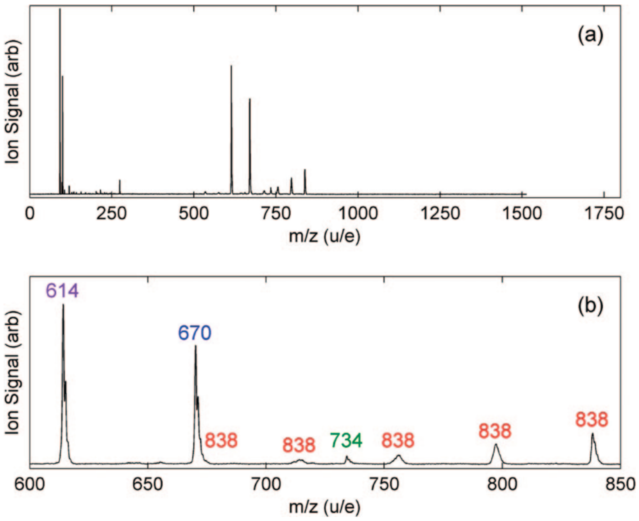

Figure 5. L^{2}MS mass spectra of an equimolar mixture of four porphyrin model compounds. (a) Full mass range, including signals from internal standards at 100, 215, and 274 units/e. (b) Expanded scale in the region of the porphyrin peaks. Peaks are labeled according to their parent ion. A fragment of the 838 unit parent ion is not resolved from an isotopologue of the molecular ion at 670 units.

ular-mass distribution. The limitations are investigated by measuring the L^{2}MS spectra of a series of model compounds, each presenting much simpler spectra that are straightforward to interpret. Four substituted porphyrin structures were selected as model compounds, because these molecules are thought to resemble asphaltenes and are available over a wide range of masses. The four compounds are 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (614 units), 5,10,15,20-tetra-*p*-tolyl-21*H*,23*H*-porphine (670 units), 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphine (734 units), and 5,10,15,20-tetrakis[4-(allyloxy)phenyl]-21*H*,23*H*-porphine (838 units).

Figure 4 shows L^{2}MS mass spectra of these pure compounds. Aside from internal standards (100, 215, and 274 units/e), the largest peak in each spectrum corresponds to the singly charged molecular ion. For the 614 and 670 unit porphyrins, there are virtually no other peaks in the spectra; in other words, the mass spectra are free from fragmentation, aggregation, and multiply charged ions. For the 734 unit porphyrin, some fragmentation does occur, producing a series of peaks in the range of 100−250 units/e. For the 838 unit porphyrin, there is significant fragmentation, but the fragments appear at a mass comparable to that of the molecular ion. Besides the parent ion, the strongest four peaks correspond to the loss of 1−4 units of $CH_2-CH{=}CH_2$, appearing at 41, 82, 123, and 164 units below the singly charged parent ion. These four fragments and the parent ion total 95% of the intensity. For a complex mixture, such as asphaltenes, the loss of low-mass fragments, such as occurs here, makes little difference in mass spectrum, because the fragment peaks will simply overlap the peaks belonging to slightly lighter molecules. Indeed, the mass-weighted average mass of the five largest peaks in the spectrum of the 838 unit porphyrin is 775 units. Therefore, of the four model compounds studied, the largest peak corresponds to the molecular ion in all, peaks at masses above the molecular ion (aggregates) occur in none, and peaks at masses significantly below the molecular ion (fragments or multiply charged ions) appear in only one. These data suggest that L^{2}MS provides very soft ionization. For the remainder of this paper, it is assumed that all detected ions are singly charged.

Table 1. Relative L^{2}MS Sensitivities of Different Porphyrin Model Compounds

porphyrin mass (units)	614	670	734	838
L^{2}MS sensitivity (relative)	100	80	6	84

In addition to soft ionization of individual compounds, accurately predicting the asphaltene molecular-mass distribution from L^{2}MS measurements requires understanding the instrumental response factor for different masses. L^{2}MS signal strength depends upon several factors, including desorption, ionization, and transport though the mass analyzer, all of which are potentially mass-dependent and must be addressed. Desorption in L^{2}MS results from the interaction of the desorption laser with the substrate followed by energy transfer to the analytes, rather than direct absorption of the desorption photons by the analytes.[48] Hence, the absorption is nonresonant, and the IR spectroscopy of the analytes is not expected to contribute to their L^{2}MS sensitivity. Still, some variation in desorption efficiency may exist for different molecules, perhaps because of differences in vapor pressure or intramolecular interactions.[49] Transport through the mass analyzer may not be uniform for all masses, because the reflectron geometry introduces a mass range limitation to the time-of-flight analyzer; however, the mass range cutoff is typically well above the range explored here. Thus, transport through the mass analyzer is not expected to impose too severe of a restriction.[50] Ionization proceeds via a resonant process; therefore, its efficiency may be expected to vary more dramatically from compound to compound. The (1 + 1) REMPI cross-sections are known to vary across even as simple a system as PAHs of different number of rings, although the REMPI cross-sections are similar between alkylated PAHs and their parent, unalkylated molecules.[49]

The sensitivity of L^{2}MS to these four porphyrins was investigated by measuring the mass spectrum of an equimolar mixture of these model compounds. Figure 5a shows the full

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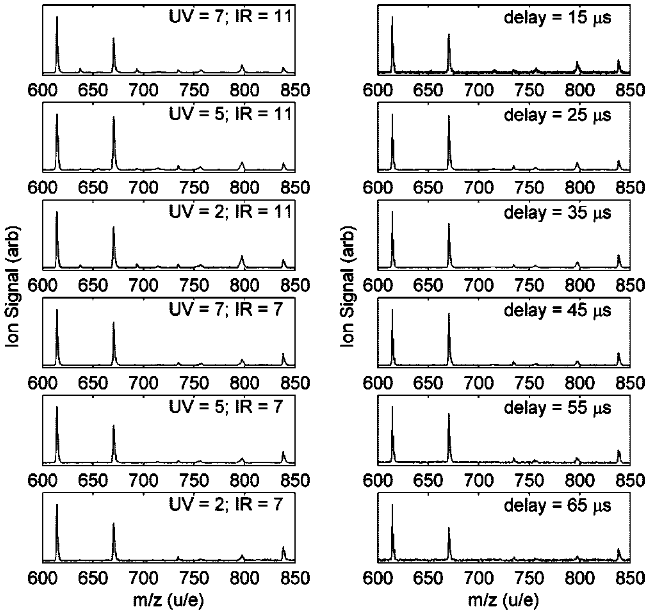

Figure 6. L^{2}MS mass spectra of an equimolar mixture of four porphyrin model compounds at different desorption and ionization pulse energies and desorption−ionization time delays. On the left side, UV and IR indicate the pulse energies of the ionization and desorption pulses in mJ. On the right side, the delay refers to the time between desorption and ionization. All spectra are normalized to the peak at 614 units/e, and in each case, the scale is expanded to focus in on the porphyrin peaks.

mass spectrum of that mixture. As expected, the largest peaks (excluding internal standards) correspond to the parent ions of the porphyrins, and no aggregation is observed. Figure 5b shows the same spectrum expanded to include only the region containing the porphyrin peaks. Each peak is labeled according to its parent ion, according to the spectra of pure compounds shown in Figure 4. The lightest fragment of the 838 unit porphyrin occurs at 674 units and is not fully resolved from the parent ion of the 670 unit porphyrin. The relative L^{2}MS response of the four porphyrins (molecular mass of 614, 670, 734, and 838 units) is 100, 86, 6, and 84, respectively, summing over the fragments of the 838 unit porphyrin (see Table 1). This measurement was repeated with different pulse energies from both lasers and with different desorption−ionization time delays, as shown in Figure 6. These measurements are akin to those shown in Figures 2 and 3 for UG8 asphaltene. Other than minor variations in the extent of fragmentation of the 838 unit porphyrin, there is little difference between these spectra.

In this experiment, the recorded signals are proportional to the relative sensitivity of L^{2}MS to these compounds on a per mole basis. For these model compounds, three of the four give similar responses, while one gives a much smaller response. These data suggest that there is no large change in sensitivity as a function of mass, as is expected for this instrument. However, the sensitivity to individual compounds can vary greatly, as is found here, presumably caused by differences in the REMPI cross-sections. REMPI cross-sections depend upon the photon energy and the shapes and symmetries of many electronically excited potential energy surfaces, and these cross-sections are generally not known for asphaltenic molecules.[51] In earlier work on different samples, it was found that the relative sensitivity to different species can change dramatically with ionization laser pulse energy, presumably because of differences in the spectroscopy of the analytes.[49] For asphaltenes, the measured molecular-mass distribution is independent of the ionization laser pulse energy. This result may be related to the complexity of the asphaltene mixture; because such a large number of compounds contribute to the peak at each nominal mass, differences in their spectroscopy may be averaged out. However, the measured L^{2}MS spectrum of this simple mixture of model compounds is also independent of the ionization power; therefore, such averaging may not be necessary to obtain a reliable molecular-mass distribution. Overall, it is impossible to decouple large changes in mass from changes in structure; thus, the possibility of a gradually changing REMPI cross-section as a function of molecular mass cannot be ruled out. Similarly, the propensity to fragment, although small, also depends upon the molecular structure;[52] for example, the stable $CH_2-CH=CH_2$ radical that fragments off the 838 unit porphyrin is likely not available in asphaltenes, suggesting that asphaltenes may fragment less than the model compounds.

When these measurements of porphyrin model compounds are taken together, they suggest that L^{2}MS can be used to determine an accurate molecular-mass distribution of asphaltenes. Aggregation is never observed in these spectra, and significant fragmentation/multiple charging is rare. None of the steps involved in detection introduce a significant bias toward light or heavy species; therefore, the sensitivity of this instrument appears to be independent of mass over the relevant range. Molecular structure can have a large influence on sensitivity, resulting from the resonant process involved in ionization, although the complexity of asphaltene mixtures appears to mitigate that effect somewhat. Because artificially heavy peaks (from aggregation) virtually never appear and artificially light peaks (from fragmentation/multiple charging) occur rarely, we believe that L^{2}MS provides a slight underestimate of the asphaltene molecular-mass distribution.

Asphaltenes Extracted from Different Sources

Having demonstrated that L^{2}MS can provide an accurate measure of the asphaltene molecular-mass distribution, the L^{2}MS experiment was repeated on asphaltenes extracted from different sources. Figure 7 shows the L^{2}MS mass spectrum of two asphaltenes extracted from Middle Eastern oils (UG8 and BG5) and two asphaltenes extracted from oils from the Gulf of Mexico (GOM #1 and GOM #2). The distributions appear to be similar, with the Gulf of Mexico asphaltenes appearing to have a slightly lower average molecular mass than the Middle Eastern ones. This similarity between petroleum asphaltenes of different geographical origin might be expected, given that petroleum asphaltenes are defined universally as a solubility class of crude oil.

Overall, the L^{2}MS mass spectrum of petroleum asphaltenes shows a single, broad maximum peaking in the range of 500−600 units and tailing out beyond 1000 units. The upper mass limit strongly depends upon the experimental signal-to-noise ratio but likely falls near 1500 units. No indication of molecular masses above 1500 units is observed. The beginning of the molecular-mass distribution is difficult to assess because of the appearance of small fragment peaks, but a reasonable estimate is that the distribution begins near 200 units. The mass spectrum is quite complex, showing a peak at every nominal mass.

Figure 8 compares the L^{2}MS mass spectrum of UG8 petroleum asphaltene with the same spectrum of coal asphalt-

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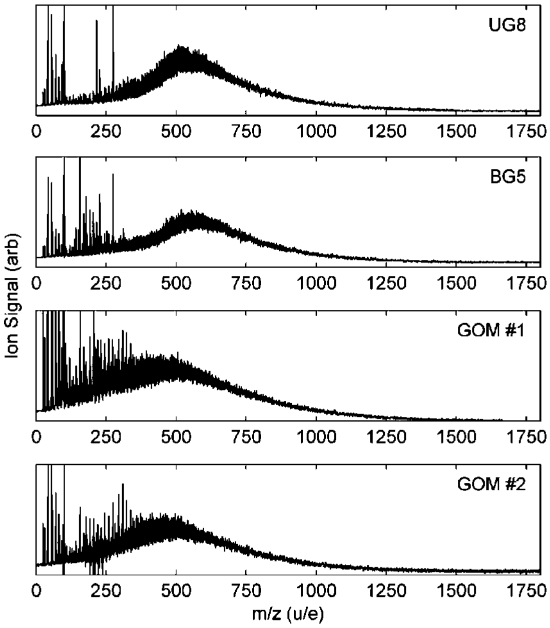

Figure 7. L^{2}MS mass spectra of four petroleum asphaltenes. UG8 and BG5 are extracted from Middle Eastern oils, and GOM #1 and GOM #2 are extracted from oils from the Gulf of Mexico.

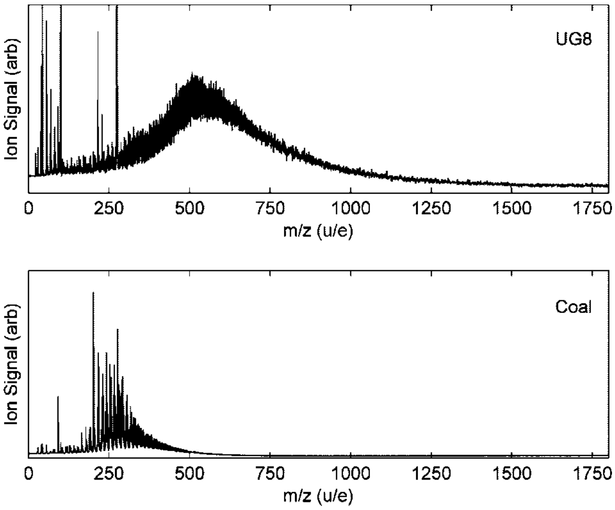

Figure 8. L^{2}MS mass spectra of a petroleum asphaltene (UG8) and coal asphaltenes.

enes. Coal asphaltenes are those components of coal that are soluble in toluene but insoluble in *n*-heptane, and their average molecular mass is thought to be lower than that of petroleum asphaltenes.[18,27,43] Indeed, the L^{2}MS mass spectrum clearly shows that coal asphaltenes are considerably lighter than petroleum asphaltenes. The envelope of the coal asphaltene molecular-mass distribution is a single broad peak starting near 200 units, reaching a maximum near 300 units, and extending beyond 500 units. Additionally, coal asphaltenes appear to be considerably less complex than petroleum asphaltene. The coal asphaltene mass spectrum shows a series of clusters of peaks, with each cluster nearly baseline resolved and separated by 14 units; these 14 unit separations likely correspond to $-CH_2-$ groups in an alkylation series. In contrast, the petroleum asphaltene molecular-mass distribution contains a peak at every nominal mass, resulting in a smooth distribution without any such features.

Conclusions

It has recently been shown that L^{2}MS can provide a measure of the asphaltene molecular-mass distribution free from the effects of aggregation and insufficient laser power that can affect laser desorption/ionization measurements.[32] Here, the technique is considered in more detail to assess its ability to measure accurately the molecular-mass distribution of asphaltenes. Four substituted porphyrin molecules were used as model compounds for studying the ionization and detection processes in L^{2}MS. Aggregation was never observed, and in only one case did significant fragmentation occur. No trend in detection efficiency with mass was observed over the mass range relevant to asphaltenes, as expected from general considerations. However, the detection efficiency can strongly depend upon molecular structure, as a result of the resonant process involved in ionization. Because aggregation appears never to occur and fragmentation occurs rarely, it is concluded that L^{2}MS provides a slight underestimate of the asphaltene molecular-mass distribution.

Petroleum asphaltenes from different parts of the world differ only subtly in their molecular-mass distribution as measured by L^{2}MS. All petroleum asphaltenes investigated here are found to be complex mixtures containing many different components, resulting in the appearance of a peak at every nominal mass in the mass spectrum. The envelope of the molecular-mass distribution for each asphaltene is broad and asymmetric, beginning near 200 units, peaking near 500−600 units, and extending until 1000−1500 units. Coal asphaltenes are found to be considerably lighter and less complex. Instead of a peak at every nominal mass, the coal asphaltene molecular-mass distribution is dominated by a cluster of peaks separated by 14 units. The envelope of the molecular-mass distribution again is a broad asymmetric peak, this time beginning at 200 units, peaking at 300 units, and extending until 500 units.

The question of whether or not the heaviest asphaltene molecules are detected by any mass spectral technique is of fundamental importance to the asphaltene community; lingering inconsistent results from LDI have strengthened this concern.[6−12,26−28] It is imperative that the origin of the high mass findings in some LDI studies be incontrovertibly identified, and moreover, accurate mass spectral results from laser desorption must be obtained. In addressing the concern about detection of the heaviest asphaltene molecules, it is now widely acknowledged that distribution of asphaltene molecular properties form a continuum.[53] This work represents a thorough study of the detection process in L^{2}MS, and no data suggest a large variation in detection sensitivity for different components of this continuum. The L^{2}MS results demonstrate that LDI measurements detecting asphaltene molecular masses well over 1000 units suffer from artifacts because of aggregation and that the correct laser desorption measurement of the asphaltene molecular-mass distribution is consistent with many other mass spectral and diffusion techniques.

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