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# Molecular-Weight Distributions of Coal and Petroleum Asphaltenes from Laser Desorption/Ionization Experiments

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Molecular-weight distributions (MWDs) of asphaltenes extracted from coal and petroleum have been measured in laser desorption/ionization (LDI) mass spectrometric experiments. The dried-droplet and solvent-free sample preparation methods are compared. The coal asphaltenes have a relatively narrow MWD (full width  $\approx$  150 amu) with an average molecular weight of  $\approx$ 340 amu. The petroleum asphaltenes display a broader MWD (full width  $\approx$  300 amu) and are heavier on average ( $\approx$ 680 amu). The LDI spectra also provide evidence for the formation of noncovalent clusters of the two types of asphaltenes during the desorption process. Petroleum and coal asphaltenes exhibit aggregation as do large model polycyclic aromatic hydrocarbons (PAHs) with five or more fused rings also included in the study. Smaller PAHs (pyrene) exhibit less aggregation, especially when alkane-chain substituents are incorporated to the molecular structure. This indicates that asphaltenes possess large PAHs and, according to the relatively small molecular weights observed, that there is a preponderance of asphaltene molecules with only a single fused ring system. The coal asphaltenes present a significantly smaller propensity toward aggregation than their crude oil counterparts. This finding, coupled with the fact that (1) alkanes inhibit aggregation in LDI and (2) petroleum asphaltenes possess much more alkane carbon, indicates that coal asphaltenes have smaller PAHs on average than petroleum asphaltenes. This is further corroborated by the stronger ultraviolet absorbance of the coal asphaltenes at wavelengths shorter than 400 nm.

## 1. Introduction

Asphaltenes are the most enigmatic component of crude oils and in many ways are only now revealing their many mysteries.<sup>1</sup> The difficulty of establishing the chemical structure of asphaltenes originates from their operational definition; e.g., the toluene-soluble, *n*-heptane-insoluble component of crude oil. This broad solubility classification captures various chemical families and contributes to the complexity of chemical analysis. One long controversy in the asphaltene research community has been the size and molecular weight of the asphaltene molecules. The determined molecular weights varied by orders of magnitude, from less than 1000 amu up to above 100 000 amu.<sup>2</sup> Currently, there is strong experimental evidence supporting the fact that asphaltenes are relatively small molecules. Boduszynski used field desorption (FD) ionization mass spectroscopy to obtain a relatively broad molecular-weight distribution (MWD), yielding an average asphaltene weight of  $\approx$ 800 amu.<sup>3,4</sup> Those early mass spectroscopy (MS) measurements are in good agreement with recent FD studies,<sup>5</sup> systematic laser desorption/

ionization (LDI) experiments,<sup>6,7</sup> and electrospray ionization Fourier transform ion cyclotron resonance mass spectroscopy (ESI FT-ICR-MS) measurements.<sup>8,9</sup> Molecular diffusion measurements of asphaltenes based on a variety of techniques also support a mean asphaltene molecular weight of 700–800 amu.<sup>10–14</sup> The much higher molecular weights provided by a set of techniques, such as vapor pressure osmometry and gel-permeation chromatography, are likely to be related to the low critical nanoaggregate and flocculation concentrations of asphaltenes.<sup>14–17</sup>

The LDI technique has evolved rapidly in recent years and is currently capable of providing valuable information about the chemical composition and structure of complex carbon-

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aceous mixtures.<sup>6,7,18–21</sup> However, LDI MS has produced apparently inconsistent results with regard to the MWD of typical asphaltenes. It has been shown that laser power (or more specifically, the surface power density of the laser spot) as well as the surface concentration of asphaltenes are crucial parameters controlling “measured” asphaltene molecular weights.<sup>6,7</sup> Often neither of these parameters are well-controlled. The large operational dependence of the LDI MWD for asphaltenes is traceable to likely noncovalent aggregation of asphaltene molecules in the gas-phase plume created by the laser pulse.

Asphaltene are known to have a strong propensity to aggregate,<sup>14–16</sup> and in fact, flocculation is one of their defining characteristics. The gas-phase aggregation of asphaltenes in LDI experiments may be dependent upon the number of fused rings in asphaltene polycyclic aromatic hydrocarbons (PAHs). If this is the case, then coal asphaltene could be distinguished from crude oil asphaltene. It has been recognized that coal asphaltene have smaller fused ring systems than petroleum asphaltene. Evidence for this is provided by the comparison of the UV–vis absorption and fluorescence<sup>22–24</sup> and the diffusion rates<sup>11,25–27</sup> of the two types of asphaltene and by direct imaging, employing high-resolution transmission electron microscopy.<sup>28</sup> Corroboration of the average number of fused rings in petroleum asphaltene (typically around seven) has been further obtained from ESI FT-ICR-MS.<sup>9</sup> However, these methods cannot yet discern whether the rings are fused.

Examining coal versus petroleum asphaltene is useful to understand the impact of the fused ring system on LDI results. In addition, there is an important underlying issue in asphaltene science that is also addressed by such studies. It has been suggested that, for the bulk of asphaltene molecules, the governing factors controlling solubility (i.e., asphaltene identity) are two familiar chemical concepts: van der Waals attraction (of PAHs) and steric repulsion (from the alkane substituents).<sup>26</sup> This is utilized by the dye industry; to increase dramatically the solubility of standard PAH dyes, alkane substituents are added.<sup>28</sup> Coal and its asphaltene extracts are relatively hydrogen-deficient (in large part that is why coal is a solid). In contrast, petroleum asphaltene have much more hydrogen, nearly all of which is located on alkane substituents. Because coal asphaltene have less steric repulsion from side chains, they must also have smaller ring systems to balance attractive and repulsive forces (van der Waals forces per molecule increase with increasing numbers of fused rings<sup>29</sup>). The need for such balance, which is in turn mediated by the solvent, is inherent to the solubility classification of asphaltene. For example, if attractive forces become dominant (even over solvent–asphaltene interactions),

as occurs when alkane chains are removed by cracking, solubility is lost and coke is formed.<sup>22</sup>

There is one presumption in the above description that assumes that there is a single fused ring system per asphaltene molecule. This assumption is based on fluorescence depolarization studies of asphaltene.<sup>10,11,22,25,26</sup> One might call this asphaltene molecular architecture, single fused ring system surrounded by alkane (and alicyclic) substituents the “island” model. In practice, within the island model, a small portion of asphaltene with more than one fused ring or with no fused rings is considered. There is a popular competing asphaltene molecular architecture, the “archipelago” model, which consists of small fused ring systems cross-linked by alkane chains.<sup>30</sup> If the multiple fused-ring archipelago model dominated the asphaltene structure, then control of intermolecular attractive forces would be mediated by the number of fused ring systems as well as size. There would be no necessity of a tight correlation between the alkane fraction and fused ring size in asphaltene.

LDI experiments on coal versus petroleum asphaltene can help discern whether the island or archipelago model applies. If coal asphaltene exhibit much less gas-phase aggregation than their petroleum counterparts, then the LDI data would indicate that the coal asphaltene have smaller PAHs. Given the relatively small asphaltene molecular weights reported here, large PAHs would mandate the island molecular structure. Thus, the LDI measurements are not simply addressing asphaltene molecular weight but also weigh in on the issue of asphaltene molecular architecture, which is an area of much current interest.

## 2. Experimental Section

**Chemicals.** Asphaltene fractions from a coal and a crude oil are considered in the present work. Here, we use the Iino coal asphaltene and the UG8 petroleum asphaltene, both of which have been studied previously with different techniques.<sup>11–13,25,26,28</sup> The UG8 asphaltene was prepared from a Kuwaiti crude oil using 40:1 *n*-heptane/crude oil precipitation. After 24 h, the resulting precipitated asphaltene was filtered and washed with hot heptane until the heptane was colorless. The solid was then redissolved in a small quantity of toluene and precipitated again using a 40:1 ratio. We have never observed any effect on our data from the second precipitation process. The Iino coal asphaltene sample was prepared as a *n*-hexane extract of Tanito Harum coal. We are indebted to Professor M. Iino (Tohoku University, Japan) for providing us with this valuable coal asphaltene, which has proven so informative here and elsewhere.

Model polyaromatic hydrocarbons (pyrene, pyrene–butanol, benzo(a)pyrene, and coronene; >95% purity) were employed as model molecular systems for the LDI experiments. Several polymeric and biomolecular standards were used for molecular-weight calibration up to 4000 amu. Matrix-assisted laser desorption/ionization (MALDI) measurements were performed with 2,4-dihydroxybenzoic acid (2,4-DHB, 99% purity) as the matrix. All of the above chemicals were purchased from Sigma–Aldrich and used without further treatment, besides that involved in the sample preparation methods described below.

**Sample Preparation Methods.** The samples for the LDI/MALDI measurements were prepared by either the standard dried-droplet method or the solvent-free method.<sup>31,32</sup> In the dried-droplet method, solutions of the asphaltene in toluene were prepared at concentrations ranging from 2 to 400 mg mL<sup>−1</sup>. The samples were then prepared by spotting 20 μL volumes of the solution on the stainless-

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steel sample plate and subsequent evaporation of the solvent in air. In the solvent-free method, a simple mortar and pestle grinding treatment was applied either to the pure asphaltene powder or to a solid mixture with the matrix. This resulted in a fine homogeneous powder that was spread on the sample plate with a spatula. The sample surface was finally gently blown with air to remove the analyte weakly attached to the plate to avoid contamination of the ion source. For the MALDI experiments, a 2,4-DHB matrix/asphaltene molar ratio of 500:1 was employed (as calculated with the average molecular weight measured for the asphaltenes).

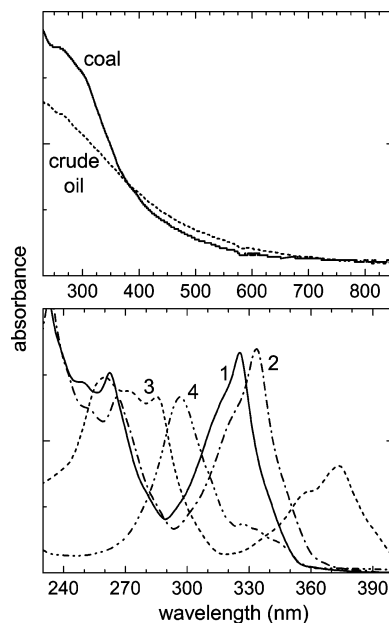
**Instruments.** The UV-vis absorption spectra of the asphaltenes and of the model PAHs were measured in an optical fiber charge-coupled device (CCD) spectrometer (DH2000, Ocean optics).

LDI MS experiments were performed in a customized time-of-flight mass spectrometer (TOF-MS) described elsewhere.<sup>6,7</sup> In brief, the positive analyte ion yield of the LDI process is accelerated toward the TOF tube at 4.2 and 3.5 kV voltages in the repeller and extractor plates of the ion source, respectively. Either continuous (CE) or pulsed (PE) ion extraction was applied. Under PE operation, the ion source voltages are applied in pulses of 7 ms duration, delayed by 1  $\mu$ s with respect to the desorption laser. All of the spectra considered in the present work were obtained in linear TOF detection mode for mass discrimination. The laser radiation employed in the study was delivered by the fourth harmonic (266 nm) of a Nd:YAG laser (Minilite II-Continuum) or by a Nd:YAG/Dye laser system (Brilliant-Quantel/Scanmate-Lambda Physik) tunable in the 270–300 nm range. The present experiments applied laser pulses with energies ranging from 10 to 100  $\mu$ J, focused on the sample with a lens of 25 cm focal length. The mass resolution of the mass spectra was  $W/\Delta W \approx 200$ . The spectra were averaged over 128 laser shots, at 10 shot/s operation, while scanning the laser focus through the sample. The only additional data treatment occasionally performed on the recorded spectra was simple smoothing, without any baseline correction besides the flat zero signal line. In previous studies, the customized apparatus passed a consistency test against two different commercial MALDI equipments.<sup>6,7</sup>

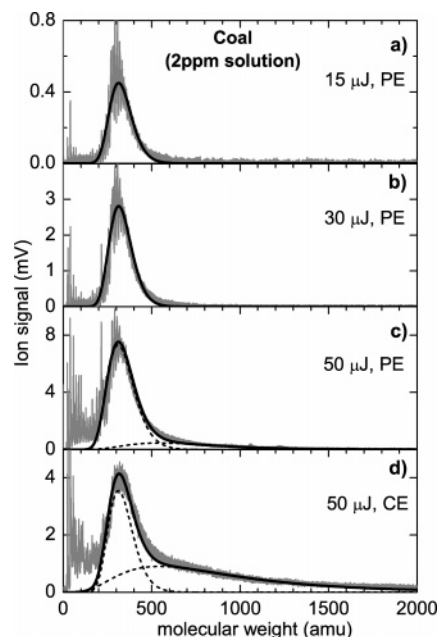
MWDs for the polydispersed asphaltenes were determined from the best fit of the measured LDI mass spectra with a log-normal functionality, as described in previous studies.<sup>6,7</sup> In the cases where the spectra provided evidence for aggregation, separate distributions were employed to fit the contribution from the monomers and the clusters.

### 3. Results and Discussion

The UV-vis (230–850 nm) absorption spectra of the coal and petroleum asphaltenes are shown in Figure 1. The spectra were measured on thin films of the asphaltenes on a quartz plate prepared with the dried-droplet method. The spectra of the two types of asphaltenes have been arbitrarily scaled to have similar absorbances in the long-wavelength region ( $\lambda > 700$  nm). Such scaling also leads to a crossing of the two spectra (i.e., a coincidence in absorbance) at  $\approx 385$  nm. Irrespective of the scaling employed, it is observed that the absorbance of the coal asphaltene increases more rapidly toward the ultraviolet than that of its crude oil counterpart. For instance, the ratio of the absorbances at 250 and 400 nm is  $\approx 3$  for the coal asphaltene in comparison to  $\approx 2$  for the crude oil asphaltene. It is known that the polyaromatic cores of the asphaltenes are responsible for the absorbance in the UV-vis region.<sup>23,24</sup> Hence, the greater absorbance toward the far-UV region of the coal compounds can be attributed to polycondensed arrangements of smaller size on average. It will be shown that this tentative assertion is consistent with the interpretation of the LDI measurements presented in this work. As stated above, a number of previous experimental studies also show that coal asphaltene PAHs are smaller than petroleum asphaltene PAHs.



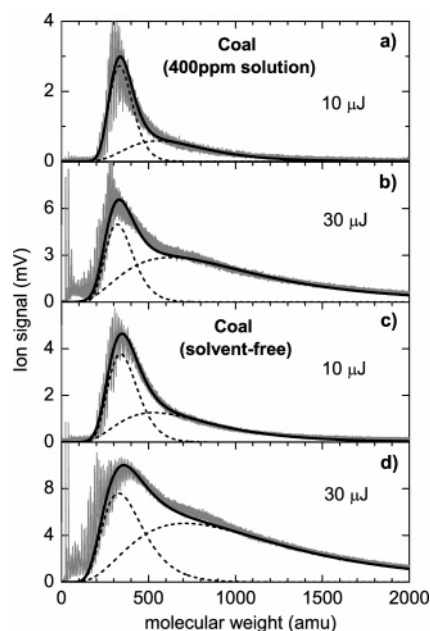
**Figure 1.** (Top) UV-vis absorption spectra of thin films of the coal and crude oil asphaltenes investigated in the present work. The greater absorbance of the coal asphaltenes at the shorter wavelengths can be attributed to the smaller average size of the fused ring systems. The LDI measurements of the two asphaltenes were recorded at 266 nm. (Bottom) UV-vis spectra of the model polyaromatic hydrocarbons explored in the present work (acetonitrile solution): pyrene (1), pyrene-butanol (2), benzo(a)pyrene (3), and coronene (4). The LDI experiments for these PAHs applied laser wavelengths of 266, 266, 285, and 297 nm, respectively. The absorbances of the PAHs are scaled in the plot to have the same value at these wavelengths.



**Figure 2.** LDI spectra measured on dried-droplet samples of the coal asphaltenes with a low average analyte density (20  $\mu$ L of a 2 ppm toluene solution). The laser was operated at 266 nm, with the pulse energies indicated in each panel. The smooth curves correspond to the fit with independent distributions for the monomers and clusters. PE refers to pulsed extraction, which inhibits aggregation. CE refers to continuous extraction, which accelerates molecular ions though plume exacerbating gas-phase aggregation.

Figures 2 and 3 depict a series of illustrative LDI-TOF measurements recorded on dried-droplet and solvent-free samples of the coal asphaltenes. Dried-droplet samples prepared from

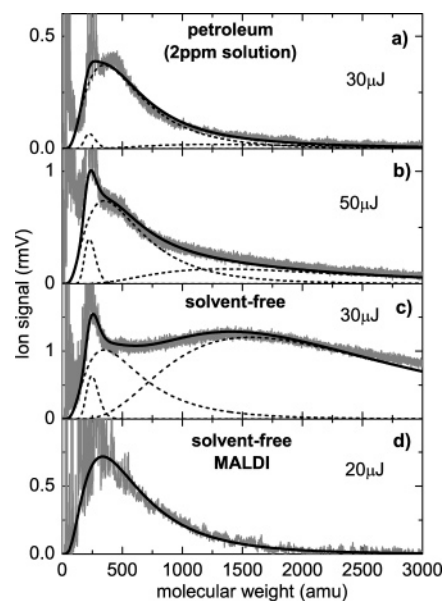




**Figure 3.** Same as Figure 2 for coal asphaltene samples prepared with the dried-droplet method for high analyte density (a and b; 20  $\mu$ L of a 400 ppm toluene solution) and with the solvent-free method (c and d). These spectra were acquired using pulsed ion extraction. Asphaltene clusters formed in the desorption plume are detected in all cases.

diluted toluene solutions of the asphaltene (2 mg/mL) are considered in Figure 2. It has been shown in previous works<sup>6,7</sup> that the small sample concentrations achieved in this way are required to reduce (and eventually avoid) self-aggregation of the asphaltenes in the desorption plume. The LDI spectra of the coal asphaltenes recorded at low energies ( $\leq 30$   $\mu$ J/pulse) of the 266 nm laser display a relatively narrow MWD centered at 300 amu and extending slightly above 500 amu. No trace of cluster formation is observed for this sample at these low laser energies. However, at higher laser energies (50  $\mu$ J/pulse, Figure 2d), an additional broad band emerges in the MWD, which is centered at roughly 600 amu and extends well above 1000 amu. This band becomes significantly more intense under continuous ion extraction in comparison to pulsed extraction. Such collection of heavier compounds is assigned to noncovalent aggregates (primarily dimers and trimers) of the asphaltenes. The enhancement of the aggregation under continuous ion extraction can be attributed to the nucleation around the asphaltene ions produced in the early stages of the desorption process, which are accelerated through a dense plume of neutral asphaltenes.<sup>7</sup> The fact that changing the ion extraction dynamics results in appreciable changes in aggregation strongly suggests that the aggregation occurs in the plume as opposed to aggregates being desorbed from the solid.

Figure 3 shows LDI spectra measured on dense samples of the coal asphaltene. These measurements demonstrate that increasing the asphaltene surface concentration at constant laser power greatly increases aggregation. This again implies that aggregation takes place in the plume and not from an interaction of the laser with the solid. The samples were prepared by either the dried-droplet method from a concentrated toluene solution (400 mg/mL) or the solvent-free method from asphaltene powder. In both cases, the concentration of the asphaltene on the sample plate is at least 2 orders of magnitude greater than for the samples considered in Figure 2. It is observed that for these dense asphaltene samples the broad band associated with the aggregates is detected easily even at low laser energy (10  $\mu$ J/pulse). It must be noted that these spectra use pulsed



**Figure 4.** LDI spectra at 266 nm performed on petroleum asphaltene. All measurements were taken in pulsed ion extraction mode. The samples were prepared either with the dried-droplet method at low average density (a and b; 20  $\mu$ L of a 2 ppm toluene solution) or with the solvent-free method for high sample density (c). d shows a MALDI spectrum on a sample with the asphaltene diluted in a 2,4-DHB matrix under solvent-free conditions. The strong aggregation propensity of the petroleum asphaltenes is inhibited by matrix dilution. The smooth curves are fits to the MWD of the monomers and clusters. Note that two distributions are required for the monomer to account for the narrow band of compounds around 250 amu, on top of the broader distribution of monomers extending above 1000 amu. The distribution of heavier compounds peaking around 1700 amu is associated with asphaltene clusters.

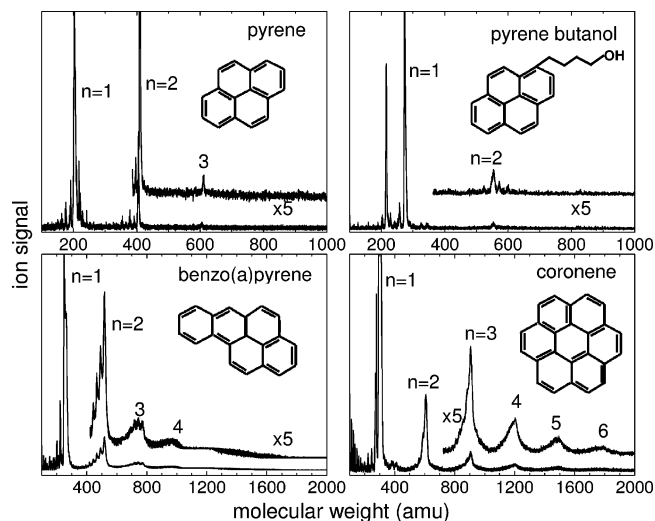
extraction, which suppresses somewhat asphaltene aggregation. These findings corroborate the conclusion of previous works<sup>6,7</sup> that both diluted samples and low laser energies are mandatory to obtain the true MWD of asphaltenes and similar self-aggregating compounds without the interfering signal from clusters. The LDI spectrum of Figure 2a is expected to resemble closely the actual MWD of the coal asphaltenes and yields an average molecular weight of 340 amu.

Similar LDI experiments were performed for the petroleum asphaltenes with the results illustrated in Figure 4. These measurements provide evidence for an enhanced aggregation tendency on the petroleum asphaltenes in comparison to the coal asphaltenes. The sensitivity of these experiments at laser energies below 30  $\mu$ J/pulse was too small to produce spectra with a satisfactory signal-to-noise ratio. This is in contrast to the similar coal asphaltene samples for which good-quality spectra could be obtained at 10–15  $\mu$ J/pulse. The reduced sensitivity for the crude oil asphaltenes can be attributed to their smaller absorbance at 266 nm (Figure 1) and, possibly, to some extent also to the greater cohesion of the petroleum asphaltene material. Consequently, higher laser powers are required to yield comparable plume molecular densities for petroleum asphaltenes as for coal asphaltenes. The LDI spectrum obtained for the dried-droplet sample at 30  $\mu$ J/pulse laser energy (Figure 4a) is expected to approach fairly well the MWD distribution of the asphaltene monomers, although a small contribution from fragmentation and aggregation cannot be discarded. Aggregation effects do become clearly apparent in the spectrum at 50  $\mu$ J/pulse in the form of an enhancement of the ion signal on the high mass tail of the distribution. At this higher energy,

fragmentation of the asphaltenes also induces a significant yield of ions at low masses ( $W < 200$  amu).

The LDI spectrum of the solvent-free sample (Figure 4c) provides particularly clear evidence for an extensive formation of asphaltene clusters in the desorption plume. In this case, the cluster signal dominates the LDI spectrum for masses above  $\approx 700$  amu and virtually obscures the discrimination of the monomeric distribution. This cluster signal is significantly more intense than the one observed in the analogous LDI measurement, with the same laser energy on the solvent-free sample of the coal asphaltene (Figure 3d). This result provides a direct indication of the greater aggregation propensity of the petroleum asphaltenes in comparison to the coal asphaltenes. This aspect is supported by the fact that the LD of the coal asphaltenes is more efficient at a given laser power and can be expected to lead to a denser plume, more favorable for aggregation. Despite that, the coal asphaltenes produce less clusters in LDI.

To obtain reliable MWD for the monomeric species of strongly self-aggregating compounds, such as the petroleum oil asphaltenes, a particularly efficient dilution of the analyte in the sample is required.<sup>6,7</sup> The relatively low average densities attainable with the dried-droplet method, while appropriate for the coal asphaltene, may not suffice to suppress aggregation for the more “sticky” petroleum asphaltenes. Analyte dilution is not easily achieved with the dried-droplet method because of the inhomogeneous precipitation of the asphaltenes upon solvent evaporation, leading to an alternation of domains of partial coverage of the sample plate with micrometric films visible in the form of dark traces.<sup>6,7</sup> Dilution of the asphaltene with organic compounds (e.g., MALDI matrices) or inorganic salts provides a convenient method to circumvent this problem.<sup>7</sup> Figure 4d shows a MALDI spectrum measured on a petroleum asphaltene sample diluted in the 2,4-DHB matrix. This sample was prepared with the solvent-free method and a 500:1 matrix/asphaltene molar ratio. The matrix absorbs at the 266 nm wavelength of the desorbing laser and is expected to partly aid in the ionization of the asphaltenes. Good-quality spectra were obtained in this case at 20  $\mu\text{J}$  laser pulse energy. Increasing the laser energy up to 50  $\mu\text{J}$  did not affect the shape of the MALDI mass spectrum. This weak dependence of the measured MWD on laser energy, once aggregation effects are suppressed by the effective dilution of the asphaltene and up to the limit where fragmentation becomes relevant, has been illustrated in detail in two recent works.<sup>6,7</sup> The finding is relevant because it indicates that the recorded mass spectrum is not significantly affected by ionization efficiency effects among different asphaltene subfractions. This is further reinforced by the fact that the MALDI MWD of Figure 4d is roughly similar to the one obtained with LDI on the dried-droplet sample (Figure 4a), despite the fact that the ionization mechanism may differ, at least partially, in the two types of experiments. It can be noted that a reduction of the ion signal above 1000 amu is appreciated in the MALDI spectrum in comparison to the LDI measurement on the pure sample. This can be related to some residual aggregation present in the LDI spectrum that then vanishes under the MALDI conditions because of the dilution of the asphaltenes in the matrix. The structured ion signal observed on top of the envelope of the asphaltene MWD for molecular weights below 300 amu is associated with the background signal from the matrix and is not considered in the present analysis. The contribution from the matrix to the ion yield can be appreciated from the comparison of the spectra in parts a and d of Figure 4. The average molecular weight obtained for the



**Figure 5.** LDI spectra of model polyaromatic hydrocarbons: pyrene (202.2 amu, 266 nm), pyrene–butanol (274.4 amu, 266 nm), benzo(*a*)pyrene (252.3 amu, 285 nm), and coronene (300.3 amu, 297 nm). The laser wavelength is tuned at an absorption maximum of each compound (Figure 1). A laser pulse energy of 30  $\mu\text{J}$  was employed. All measurements are taken in pulsed ion extraction mode. The extent of in-plume aggregation correlates well with the number of fused rings in each molecule. Clusters made of up to six monomer units are observed for coronene. On the other hand, the presence of the alkane substituent in pyrene–butanol reduces aggregation because of steric effects.

petroleum asphaltenes from the smooth fit to the LDI distribution shown in Figure 4d is 680 amu.

It is particularly encouraging to corroborate the good performance of the solvent-free sample preparation method for the LDI (Figure 3) and MALDI (Figure 4) analyses of asphaltenes.<sup>7</sup> This method has the relevant advantage that it avoids the use of solvents. The solubility compatibility of the analyte and the matrix constitutes a key issue in the MALDI studies of carbonaceous compounds. Moreover, sufficiently heavy carbonaceous molecules typically become insoluble in conventional solvents. This difficulty motivated the introduction of the solvent-free technique.<sup>31</sup>

To compare aggregation tendencies in known model systems, we have run LDI measurements on solvent-free samples of several PAHs. In these experiments, the laser wavelength is tuned at an absorption maximum of each compound (see Figure 1), namely, 266 nm for pyrene and pyrene–butanol, 285 nm for benzo(*a*)pyrene, and 297 nm for coronene. A laser pulse energy of 30  $\mu\text{J}$  was employed for these measurements. Figure 5 shows that PAHs aggregate readily upon desorption under favorable conditions of density and laser power. The intensity and size of the clusters detected increase with the number of fused rings. For example, for pyrene, only the dimer and some trace of the trimer are detected. The butanol-substituted pyrene exhibits even less aggregation in accordance with likely steric hindrance to stacking. This is direct confirmation of what has been argued as the defining intermolecular interactions of asphaltenes, steric hindrance counterbalancing van der Waals attraction.<sup>27</sup> On the other hand, the addition of a fifth fused ring in benzo(*a*)pyrene enhances appreciably aggregation and makes clusters up to tetramers clearly visible in the LDI spectrum. Finally, the largest PAH investigated here, coronene, is seen to produce aggregates containing six monomers.

The increasing trend in the aggregation propensity with the number of fused rings and the similarity of the aggregation of large PAHs and asphaltenes indicate that the asphaltenes possess

large fused aromatic ring systems. Petroleum asphaltenes have much more alkane carbon than coal asphaltenes.<sup>27</sup> It has been shown that alkanes interfere with aggregation in LDI measurements. However, the petroleum asphaltenes exhibit greater aggregation tendencies than coal asphaltenes. When considering the relatively low molecular weights recorded here for asphaltenes, coupled with the large asphaltene PAHs implied by our data, there can only be one (or occasionally two) PAHs per asphaltene molecule.

#### 4. Conclusions

Asphaltene have average molecular weights significantly smaller than 1000 amu. Coal asphaltene have average weights smaller than 500 amu and are significantly lighter than petroleum asphaltene, for which the average weights range typically within 600–800 amu. Petroleum asphaltene have a high mass tail, which falls off rapidly above 1500 amu. These results are in agreement with other mass spectrometric studies and with molecular diffusion measurements of asphaltene. Aggregation of asphaltene in the LDI plume is a strong function of the laser power density, the surface mass density of the asphaltene, the ion extraction process, and even the identity of the asphaltene (optical properties and PAH size). The wide variation of LDI results on asphaltene in the literature is most likely related to the lack of control of these concerns.

Increasing the number of fused rings in PAHs increases the aggregation tendencies. On the other hand, alkane substituents evidently impeded aggregation in the LDI plume. Both petroleum and coal asphaltene exhibit significant aggregation

tendencies; consequently, we conclude that asphaltene possess large PAHs. Petroleum asphaltene suffer from more marked aggregation effects than coal asphaltene, yet petroleum asphaltene have a large alkane fraction with corresponding steric hindrance. Thus, we conclude that petroleum asphaltene have larger PAHs than coal asphaltene. These results are in accordance with many other determinations of the PAH size in various asphaltene. Large PAHs coupled with relatively small molecular weights found here are consistent with the single fused ring molecular architecture of asphaltene (“island” model) and are inconsistent with the alternative cross-linked multiple ring molecular structure (“archipelago” model).

Now that LDI applied to asphaltene is understood along with the main plume processes affecting the measured ion yield the technique can be used to probe the asphaltene molecular weight, molecular structure, and aggregation characteristics. A particularly fruitful approach in this context has been the coupling of the LDI analysis with chromatographic separation techniques.<sup>18–20</sup> The careful determination of reliable MWDs of asphaltene subfractions achieved in this way constitutes a route of tremendous potential for the structural determination of complex carbonaceous systems.

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