Two-Step Laser Mass Spectrometry of Asphaltenes

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Defined by their solubility in toluene and insolubility in *n*-heptane, asphaltenes are a highly aromatic, polydisperse mixture consisting of the heaviest and most polar fraction of crude oil.[1] The chemistry of asphaltenes is critically important to many aspects of the exploration and production of conventional crude oil, and asphaltene composition and behavior have been correspondingly scrutinized.[2] Traditionally, asphaltenes are thought to control the phase behavior of oil. More recently, asphaltenes have emerged as an important class of geochemical markers that reflect the geology of oil reservoirs.[1] In the future, the relevance of asphaltenes is poised to increase dramatically, as asphaltenes are present in high concentration ($\sim$15%) in unconventional resources, such as heavy oils and tar sands, which are expected to feature prominently in the world's energy mix in the decades to come.[3] The efficient production of these resources requires a thorough understanding of asphaltene chemistry.

Despite the significant and growing importance of asphaltenes in the world's energy supply, even basic aspects of their chemistry are currently poorly understood. For example, since Boduszynski's initial report in 1987,[4] numerous experimental techniques have been applied to measure the molecular weight distribution of asphaltenes. These experiments have generated a controversy. Reported mean molecular weights range over 2 orders of magnitude for similar samples; recent overviews summarize these different points of view.[1,5,6] Briefly, mass spectrometric measurements with electrospray, chemical, and field desorption ionization, along with fluorescence-based diffusion measurements and electron microscopy experiments that relate molecular size to molecular weight, suggest an average molecular weight in the range of 500−1000 Da. On the other hand, fast atom bombardment and plasma desorption mass spectrometry show a pronounced tail extending at times beyond 10 000 Da, and size exclusion chromatography can give a bimodal distribution containing an intense peak at $>10^6$ Da.

This controversy has not been resolved by studies employing laser desorption/ionization mass spectrometry (LDI). Different groups have reported mean molecular weights spanning 2 orders of magnitude for similar LDI setups and asphaltene samples.[7−11] It has been demonstrated that the measured mass spectrum changes over such a large range as certain experimental parameters, such as laser pulse energy and sample concentration, are varied; higher pulse energy and/or concentration results in heavier measured mass. Two contrasting interpretations of these data have been offered. First, Acevedo et al.[7] and Tanaka et al.[8] report heavy molecular weights (average $\sim$2000 Da), arguing that relatively low laser pulse energy is insufficient to volatilize/ionize the heaviest components of this complex mixture. On similar grounds, Al-Muhareb et al.[9] measured an asphaltene mass spectrum with a maximum $>$50 000

Da and signal extending beyond 200 000 Da. Second, Martínez-Haya and co-workers[10,11] suggest that lighter masses (peak $\sim$500 Da and average $\sim$900 Da) more accurately represent asphaltene molecular weights, arguing that high pulse energy and sample concentration promote aggregation of asphaltenes in the plasma plume produced in LDI. Diluting the asphaltenes in a matrix (MALDI) does not resolve the issue, with different groups reporting widely varying results.[6,10,12]

To clarify this controversy, we report results from a novel experimental approach named two-step laser mass spectrometry (L^2MS), in which the potential for plasma-phase aggregation is eliminated.[13] Performed on a home-built apparatus at Stanford University, L^2MS is a two-color technique in which the laser desorption and laser ionization steps are spatially and temporally separated, and their mechanisms differ fundamentally from those occurring in LDI. In LDI, a UV or near-IR laser pulse strikes a solid surface, initiating multiphoton ionization and desorbing a reactive, high-density plume of charged and neutral particles commonly referred to as a plasma plume.[14] In the plasma, strong ion-induced dipole attractive forces lead to large ion−molecule reaction cross-sections and long-lived complexes, promoting the multibody collisions required for aggregation. In contrast, in L^2MS, the sample is desorbed with 0.1 eV photons from a CO_2 laser (10.6 μm). Because the photon energy is so far below the ionization potential of any asphaltene molecule, multiphoton ionization does not occur and a plume of neutral molecules desorbs; indeed no ion signal is observed by firing only the desorption laser. Attractive van der Waals forces between neutral molecules are too weak to form long-lived complexes, so the plume is unreactive and collisions result in thermalization rather than aggregation.[15] Ionization occurs only after intercepting the plume of neutrals with a pulse of 4.7 eV photons (266 nm), removing an electron from gas-phase species that can undergo (1 + 1) resonance-enhanced multiphoton ionization (REMPI). Gas-phase ionization creates a low-density cloud of charged particles not commonly considered a plasma.[13]

In contrast to those measured by LDI, asphaltene TOF mass spectra determined using L^2MS are found to be insensitive to small changes in experimental parameters. Figures 1 and 2 demonstrate this result for four parameters related to the ones that most strongly influence LDI. These figures show L^2MS mass spectra of the common UG8 petroleum asphaltene, which are characterized by a broad maximum near 600 Da and extend to over 1000 Da. Additionally, a low-intensity series of peaks centered below 100 Da likely results from a small amount of fragmentation. The apparent noise in the spectra is largely the product of partial resolution of peaks at every nominal mass in this complex mixture.

Asphaltene samples are introduced to the mass spectrometer by dissolving them in toluene, spotting 10 μL of that solution onto a glass platter, and inserting the platter into a vacuum chamber. Figure 1a shows asphaltene L^2MS mass spectra measured using solutions

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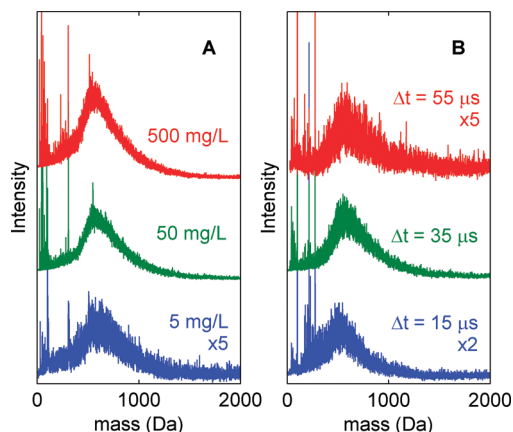‡ Stanford University.

Figure 1. L²MS mass spectra of asphaltenes at different (A) sample concentrations and (B) desorption−ionization time delays.
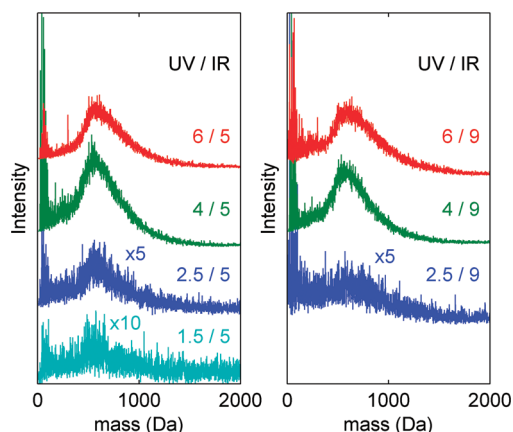

Figure 2. L²MS mass spectra of asphaltenes at different pulse energies. Ionization (UV)/desoprtion (IR) energies are listed in mJ/pulse. UV energies are compared vertically; IR energies are compared horizontally.

with concentration ranging from 5 to 500 mg/L; only negligible differences are observed. In contrast, the most probable mass recorded by LDI shifts by as much as 75% over the concentration range of 0.5−20 mg/L and by 7-fold over the concentration range of 20−400 mg/L.[10] Similarly, Figure 1b shows L²MS mass spectra recorded with varying time delays between desorption and ionization laser pulses. Potentially, species of different mass could spread out spatially in the plume so that the molecular composition found in the small ionization volume at a given time after desorption might not be representative of the distribution of masses found in asphaltenes.[16] Mass spectra recorded at several delay times show negligible differences, thus ruling out that hypothesis. This time delay between the two laser pulses has no analogue in traditional, one-laser LDI.

Perhaps more illustrative, mass spectra presented in Figure 2 show no shift when a range of desorption and ionization laser pulse energies is used. Although absolute pulse energies cannot be compared between the one- and two-laser measurements, relative changes can be: with a similar 2-fold change in laser pulse energy, the most probable mass measured with LDI changes by as much as 80%.[10] The cause of the shift to higher measured mass with increasing pulse energy seen in asphaltene LDI measurements is controversial, with some arguing that the heavier species are not volatilized/ionized unless high pulse energy is applied. That hypothesis appears not to apply here, as similar distributions of compounds are volatilized and ionized in L²MS over the range of

pulse energies investigated. In addition, the invariance of the mass spectrum with pulse energy indicates that fragmentation, which occurs more readily at high pulse energy, is insignificant in L²MS, which is consistent with earlier results.[13]

L²MS desorbs asphaltenes without limitation from low laser pulse energy and eliminates the potential for plasma-phase aggregation. By using a fundamentally different mechanism for desorption/ionization, L²MS bypasses the ambiguities in LDI and resolves the controversy. These data support the hypothesis that LDI asphaltene mass spectra peaking at >1000 Da result from aggregation in the LDI plasma plume.[10,11] L²MS with 266 nm REMPI detection measures an asphaltene molecular weight distribution peaking near 600 Da. This distribution is essentially free from aggregation/fragmentation, although certain limitations exist. For example, this experiment is sensitive only to molecules that absorb 266 nm radiation; this limitation is not expected to be too severe, as aromatic species characteristically absorb at 266 nm and asphaltenes contain ∼50% aromatic carbon.[1]

The techniques presented here may have more general applicability. The ability to measure molecular weight distributions free from aggregation makes L²MS an alternative to MALDI for samples whose propensity to aggregate cannot be overcome by dilution in a matrix. Additionally, the ability to measure accurately the composition of aromatic molecules over a wide range of surface concentrations suggests that L²MS may be especially well suited for studying naturally occurring media whose surface chemistry is influenced by these molecules.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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