

Comparing laser desorption laser ionization mass spectra of model compounds and asphaltenes

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Defined by their solubility in benzene or toluene, asphaltenes are the most enigmatic component of crude oil. Asphaltene elemental compositions are well known and a consensus is rapidly forming regarding a typical asphaltene molecular mass distribution. However, the description of the asphaltene molecular architecture remains controversial.

Two theories have been proposed to describe the dominant structure of molecules present in asphaltenes: the "island" model and the "archipelago" model. To address this controversy, nine model compounds were synthesized, belonging to both types of models. These compounds were analyzed employing laser desorption laser ionization mass spectrometry (L²MS). This technique consists of desorbing with a pulsed infrared laser beam the solid materials into a gaseous phase with no fragmentation followed by resonance enhanced multiphoton ionization to analyze the PAH content.

The L²MS spectra of each compound were recorded under the same conditions as the L²MS spectra of asphaltenes (Fig. 1). Model compounds were divided into three classes based on their fragmentation behavior in L²MS. The first two classes - "highly fragmented" (Fig. 2.) and "variably fragmented" - exhibit fragmentation behavior inconsistent with that of asphaltenes under the same experimental parameters. Therefore, the eight specific compounds included in these two classes are excluded from being dominant in asphaltenes. The third group - "highly stable" - contains a single model compound having a single, "island-like" aromatic core and exhibits behavior consistent with previously observed asphaltene samples.

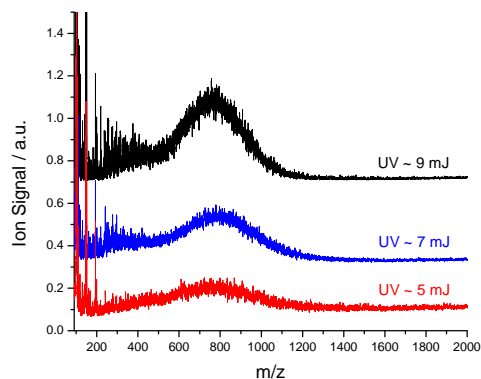


Figure 1: L²MS spectra of BG5 asphaltene powder recorded at different ionization pulse energies. The spectra show no change in molecular mass distribution but the intensity grows with increasing laser pulse energy.

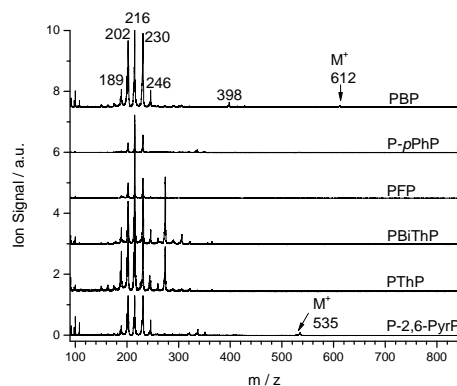


Figure 2: L²MS spectra of six candidate "asphaltene-like" model compounds, from the top: 4,4'-Bis(2-pyren-1-yl-ethyl)-2,2'-bipyridine, 1,4-Bis(2-pyren-1-yl-ethyl)-benzene, 2,7-Bis(2-pyren-1-yl-ethyl)-9,9-diethyl-9H-fluorene, 5,5'-Bis(2-pyren-1-yl-ethyl)-2,2'-bithiophene, 2,5-Bis(2-pyren-1-yl-ethyl)-thiophene, 2,6-Bis(2-pyren-1-yl-ethyl)-pyridine.