Carbon K-edge Raman Spectroscopy of Carbonaceous Materials

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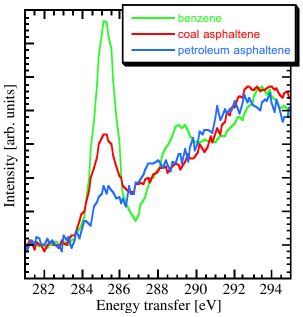
Introduction

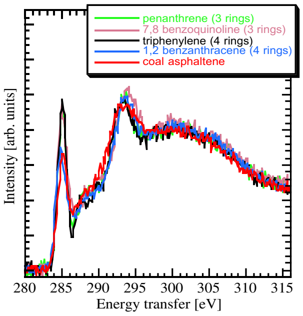
Understanding the complex chemical and physical properties of petroleum asphaltenes is becoming increasingly important due to their inordinate effect on exploitation of deep-sea oil reserves. In order to optimize the use of valuable fossil fuels concomitant plugging of deep-water sub-sea facilities by asphaltene flocculation has to be avoided However, the molecular structure of complex carbonaceous materials such as asphaltene has eluded satisfactory solution. Even the order-of-magnitude of molecular weight of petroleum asphaltenes has been controversial for 20 years, although that now appears to be solved.[1] Recent work is illustrating the strong connection between molecular structure and physical properties of asphaltenes.[2] The size of the fused ring moieties is found to scale with the length of alkane chains in asphaltenes and this governing principle determines the size of the fundamental asphaltene micelle in crude oil. Clearly, asphaltene molecular structure is strongly related to important asphaltene properties. The structures of the fused aromatic ring systems in asphaltenes have been probed by 13C-NMR, fluorescence depolarization, STM, high-resolution mass spectroscopy, and other techniques. A consensus is building that the overall size of the fused ring systems consists of 4 to 10 rings, although some controversy exists here. What is still very much in doubt is the geometry of these ring systems. Are the ring systems similar to pentacene structures, coronene structures, aromatized steroid structures, etc.?

Methods, Results and Discussion

Carbon x-ray absorption spectroscopy offers an excellent probe of these structures. Sulfur XANES studies and nitrogen XANES studies of petroleum asphaltenes provided the most definitive description of the corresponding heteroatom moities contained in asphaltenes.[3,4] However, direct x-ray absorption carbon XANES suffers from various problems. First, the carbon is about 90% of the mass fraction of the samples, leading to strong saturation effects from self-absorption. Electron yield or sample current detection is essentially a surface investigation; asphaltenes are known to suffer surface oxidation. Inelastic x-ray Raman scattering (XRS) uses a hard x-ray probe (>6 keV) and overcomes both these problems. Initial carbon XRS work on asphaltenes showed the enormous promise of this technique.[5] Recent high-quality data obtained at Advanced photon Source beamline 18-ID (Bio-CAT) yield profound insights into asphaltene molecular structures. Figure 1 shows that the 1s-π* resonance in benzene is much larger than that found for petroleum asphaltenes Therefore, the existence of a substantial fraction of benzene rings in petroleum asphaltenes is ruled out by carbon XRS. This has been the subject of conflicting papers, and confirms the optical fluorescence measurements.[6]

Figure 1 also shows that petroleum and coal asphaltenes are different, a fact utilized to elucidate asphaltene structure in other studies. Figure 2 shows that coal asphaltenes are very similar to various 3- and 4-ring model compounds.





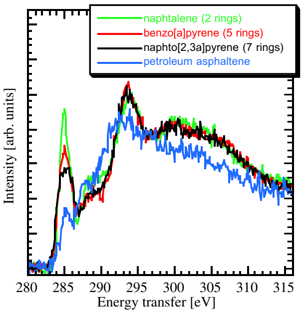


Figure 3 shows the spectrum of petroleum asphaltene compared with those of model compounds with different numbers of fused rings. Larger, asymmetric ring systems tend to produce a smaller 1s-π* transition, which is more similar to the petroleum asphaltenes. It is known that ~50% of petroleum asphaltene carbon is saturated. With more model data a quantitative structure analysis of the fused ring systems in petroleum and coal asphaltenes should be possible. The ease and speed to perform XRS at a facility like 18-ID is a crucial advantage for future applications of this technique.

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