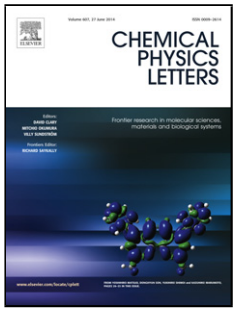

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Author: A. Ballard Andrews Dongxing Wang Katarzyna M. Marzec Oliver C. Mullins Kenneth B. Crozier

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Surface Enhanced Raman Spectroscopy of Polycyclic Aromatic Hydrocarbons and Molecular Asphaltenes

A. Ballard Andrews,[a,*] Dongxing Wang,[b] Katarzyna M. Marzec,[c] Oliver C. Mullins,[a] and Kenneth B. Crozier[b,d,e]

[a]Schlumberger-Doll Research, Cambridge, MA
[b]School of Engineering and Applied Sciences, Harvard University, Cambridge MA
[c]Jagiellonian Centre for Experimental Therapeutics, Jagiellonian University, Krakow, Poland
[d]Department of Electrical and Electronic Engineering and [e]School of Physics,
University of Melbourne, Parkville, VIC 3010, Australia

corresponding author: bandrews@slb.com

Highlights:

- SIOM substrates enable rapid acquisition of SERS spectra of complex mixtures.
- SERS is critical to obtain Raman spectra from asphaltenes because of fluorescence
- We present the first known SERS spectra of individual asphaltene molecules.
- DFT calculations attempt to match spectra with corresponding PAH structures.
- The combination of theory and experiment advances asphaltene characterization.

ABSTRACT: We describe, for the first time to the best of our knowledge, the acquisition of surface enhanced Raman spectra (SERS) of asphaltenes. SERS is an especially sensitive probe for aromatic carbon making it ideal to investigate the enigmatic polycyclic aromatic hydrocarbons (PAHs) of asphaltenes, the heaviest, most aromatic components of crude oil. SERS spectra of a known PAH model compound and of asphaltene samples are compared to density functional theory (DFT) calculations of PAH structures. This combination of experimental and theoretical methods represents an advance in the characterization of asphaltenes and other complex mixtures.

Analysis of complex chemical mixtures is very challenging and requires many diverse methods for proper understanding. Petroleum asphaltenes [1-3] represent one of the most complex chemical mixtures and are only slowly revealing their true nature. Asphaltenes have been subjected to Fourier transform ion cyclotron resonance mass spectroscopy yielding ultrahigh resolution elucidating the elemental composition of individual constituents in the mixture but this is applicable to only part of the asphaltene sample.[4] Laser desorption-laser ionization mass spectroscopy (L2MS), while much lower in resolution, is applicable to virtually all of the asphaltene sample and largely resolves the asphaltenes molecular weight debate [5,6] yielding results in agreement with molecular diffusion measurements of time-resolved fluorescence spectroscopy and fluorescence correlation spectroscopy [7,8] Asphaltenes have been subjected to many sophisticated spectral analysis methods. Sulfur x-ray absorption near edge structure (XANES) and nitrogen XANES methods [9,10] have helped delineate asphaltenes heteroatom chemistry while carbon x-ray Raman spectroscopy has been instrumental in elucidating the aromatic carbon type (within the Clar representation) of asphaltenes [11]. Pump-probe spectroscopy results on asphaltenes with comparison to molecular orbital calculations are consistent with a polycyclic aromatic hydrocarbon (PAH) centroid of seven fused rings [12] in agreement with singlet state spectroscopy and expectations codified in the Yen-Mullins