

Molecular orientation of asphaltenes and PAH molecules in Langmuir-Blodgett films using Sum Frequency Generation spectroscopy

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The surface activity of Asphaltenes is important for establishing reservoir rock wettability, impacting drainage. Enhanced oil recovery methods that attempt to alter this wettability mandate understanding asphaltene interfacial properties. While many phenomenological interfacial studies with crude oils and asphaltenes have been reported, there is very little known at the molecular level. Sum Frequency Generation (SFG) is an inherently surface specific second order (non-linear) optical technique suited for ambient conditions, thus is ideally suited for interfacial studies of asphaltenes and related model compounds. The SFG signal is proportional to both the IR and Raman transition intensities and the polarization of the input (Vis, IR) and output (SFG) beams can be varied, so the orientation of different functional groups including the aromatic core can be determined at the interface.

We prepared Langmuir-Blodgett films of asphaltenes and several model compounds. Monolayers were transferred onto hydrophilic CaF₂ substrates with the LB method. Model compounds and asphaltenes exhibited both Y (head-to-head, tail-to-tail) or Z type (head-to-tail), with the polar-ends attached to the substrate. Computational quantum chemistry was used to support corresponding band assignments.

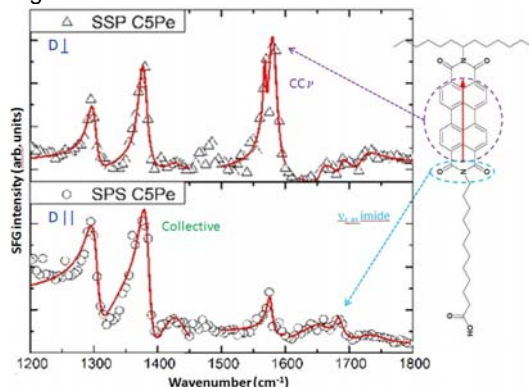


Fig. 1 SFG spectra of the carbonyl-fingerprint region for a 7 layer C5Pe film deposited on CaF₂ substrate.

Fig. 1 shows SFG spectra for a 7 layer C5Pe LB film (Y-type) for SSP and SPS polarizations. SSP (SPS) polarization excites modes with IR transition moments perpendicular (parallel) to the interface. The symmetric and anti-symmetric imide stretches are weak because the Raman intensities are weak, however the CC_v and collective mode are strong in

both IR and Raman, so these are the primary bands seen in SFG. Fig. 2 shows SFG spectra for a 7 layer V-78 LB film (Z-type). Similar to the C5Pe, the ester and ketone are weak in SFG, while the aromatic CC_v mode and collective ring modes are both strong. For the PAH compounds, the dipole moment of the CC_v mode is aligned with the major axis of the PAH molecule, demonstrating that the PAH core is tilted at an angle with respect to the surface normal.

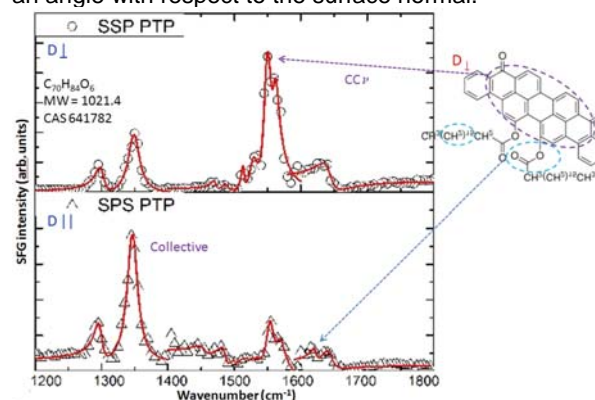


Fig. 2 SFG spectra of the carbonyl-fingerprint region for a 7 layer V78 film deposited on CaF₂ substrate.

Fig. 3 shows SFG spectra for a 7 layer UG-8 LB film (Z-type). In contrast to the model compounds, the asphaltene CC_v mode is strong in SPS polarization but the CH₂ alkane mode is stronger in SSP polarization, thus the orientation of the PAH core is parallel to the interface. This is expected, since the PAH is the site of the greatest molecular polarizability: without other strongly hydrophilic groups, the asphaltene PAH aligns parallel to the interface.

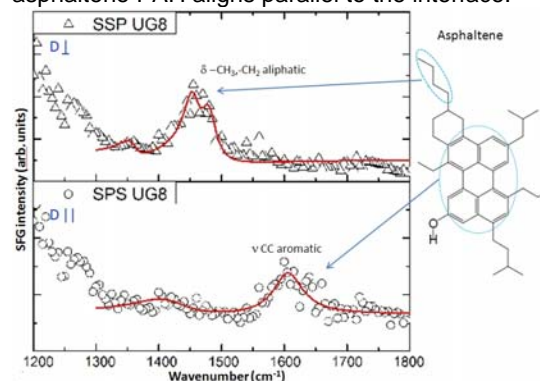


Fig. 3 SFG spectra of the carbonyl-fingerprint region for a 7 layer UG-8 asphaltene deposited on CaF₂.