

## The long wavelength optical absorption of asphaltenes analyzed by molecular orbital singlet ( $S_0$ )-triplet ( $T_1$ ) calculated transitions and optical spectroscopy

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Previous molecular orbital calculations [1-4] of the singlet-singlet transitions have shown that polycyclic aromatic hydrocarbons (PAHs) with 4-10 fused rings account for the center electronic band positions for bulk asphaltenes. The primary determinants in optical absorption band location are shown to be the size and geometry of PAHs. Large PAHs are shown to exhibit optical properties exhibited by asphaltenes and crude oils. However, the rapid declining electronic absorption at wavelengths exceeding 600 nm is shown to be consistent with the presence of a few large ring systems. The very small electronic absorbances for very low energy are found to fall outside of the absorption profile of large hydrocarbon PAHs.

The electronic absorption and emission spectra of petroleum asphaltenes are distinct and characteristic; indeed, asphaltene "color" is one of the canonical properties of asphaltenes. Moreover, each  $\pi$  electron has a fixed oscillator strength; thus, each aromatic carbon, nitrogen, and sulfur is represented in the absorption spectrum. Nevertheless, these spectral origins have not previously been thoroughly explored.

In the present work we address the very low absorbances for asphaltenes. We consider that the long wavelength absorption or small electronic absorbances for very low energy transitions might correspond either to the lowest singlet-triplet spin forbidden transitions of the dominant population of 7 FAR (fused aromatic rings) PAHs in asphaltenes or to the lowest singlet-triplet transition of the large PAHs. To verify this we have calculated the lowest singlet-triplet transitions for systems with 4FAR to 11FAR. The energy of the transition singlet-triplet has been obtained by subtracting the total energy of the  $S_0$  state (basal state) from that of the excited triplet ( $T_1$ ) state at the respective optimized geometries. All the calculations, including geometry optimizations, were carried using the high level quantum DFT (density functional theory) approach with the self-consistent generalized-gradient GGA and the Perdew-Wang 91 exchange-correlation potential (DFT GGA-PW91) with a DNP basis set (triple numerical basis set) with a radial cut off of 3.0 Å, as implemented in the DMol3 code. All experimental excitation energies for comparison with the calculations were taken from the literature. For the transition  $T_1$  states, the 0-0 excitation energies in solution are used because excitation energies in the gas phase are not

available. There is a good agreement between the theory and the experimental values.

We find that the large PAHs (9FAR to 11FAR) present a singlet-triplet transition that goes from around 600 nm to as high as 11000 nm. The singlet-triplet transition of 7FAR goes from around 500 to 1600 nm. The PAHs with a high carbon ratio (that is, the ratio of carbon atoms in isolated double bonds versus aromatic sextet rings), with a high content of carbon atoms in isolated double bonds, present the lowest electronic absorbances. The heavy atoms like sulfur in the PAH provide some degree of spin forbidden transition. The results for the calculations will be presented and discussed as well as the implications in asphaltene optical transitions.

### References

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