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Electronic Absorption Edge of Crude Oils and Asphaltenes Analyzed by Molecular Orbital Calculations with Optical Spectroscopy

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Previous molecular orbital calculations have shown that polycyclic aromatic hydrocarbons (PAHs) with 4–10 fused rings account for the center electronic band positions for bulk asphaltenes. Here, this work is extended to cover low-energy electronic transitions of crude oils and 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. Furthermore, these results are consistent with the observed Urbach spectral profiles. The rapidly declining electronic absorption at wavelengths exceeding 600 nm is shown to be consistent with the presence of a few large ring systems. Measurements of concentration and temperature independence of crude oil and asphaltene optical spectra imply that potential contributions to their coloration from charge-transfer and potential free radicals are not significant. Nevertheless, the very small electronic absorbances for very low energy are found to fall outside of the absorption profile of large hydrocarbon PAHs. Future work is indicated to account for addressing these very low absorbances for asphaltenes.

Introduction

Upon seeing a crude oil, the first striking property one notes is its coloration. Figure 1 is a dramatic demonstration of the color differences one obtains with different crude oils. A striking aspect of the crude oils displayed in Figure 1 is that they were obtained in a single column of oil, thus exhibiting huge compositional grading. Figure 1 is rotated on its side to represent the crude oils vertically as they appear in the formation. This amazing collection shows that crude oil coloration varies continuously and, furthermore, based on this continuity, one might expect the same mechanism to account for the coloration of various crude oils, whether light or dark. Nevertheless, the origin of crude oil coloration is not transparent. In an organic mixture such as crude oils or asphaltenes, it is reasonable to expect that coloration is in part related to the constituent polycyclic aromatic hydrocarbons (PAHs). However, this fact has not been sufficiently edifying for crude oils and asphaltenes because, until recently, the nature of crude oil and asphaltene PAHs has been obscure. Fortunately, the origin of crude oil and asphaltene coloration and the nature of their PAHs have recently been clarified.

Several fundamental issues must be addressed when exploring crude oil and asphaltene coloration. First, it must be established whether the optical properties of asphaltenes do or do not reflect a continuum with respect to lighter crude oil components. If indeed the asphaltene optical properties are found to grade continuously with other crude oil components, then the corresponding chemical explanation of asphaltene coloration should also reflect this continuum. Second, it is necessary to consider the impact of PAHs on crude oil and asphaltene coloration. For

example, the largest PAH (graphite) is known by many school children to be the actual black colorant in their “lead” pencils. At the other limit, for light condensates, individual absorption bands of one- and two-ring aromatics can be resolved. However, for asphaltenes, the characterization of PAHs has proven complex. If indeed PAHs are proposed as being the primary vehicle to yield crude oil and asphaltene coloration, then it must be established (i) that explicit PAH candidates are consistent with corresponding optical and other properties and (ii) that other mechanisms to induce coloration are unlikely to apply.

Asphaltenes^{1–3} have been enshrouded in mystery ever since they were defined. The solubility classification of asphaltenes (e.g., toluene soluble, *n*-heptane insoluble) obfuscates their chemical resolution; nevertheless, this classification should not be denigrated by those expecting greater chemical clarity because this definition captures the most aromatic component of crude oil, a useful objective. In addition, recent work indicates that this definition of asphaltenes captures those chemical components of crude oil that undergo aggregation in crude oil.⁴ Nevertheless, the lack of chemical clarity of asphaltenes has led to ample speculation about potential contributing molecular components. The molecular weight of asphaltenes had been a significant controversy. Fortunately, this issue has largely subsided: asphaltenes are relatively small molecules with average molecular weights being ~750 g/mol.^{1,5–8} Of course, asphalt-

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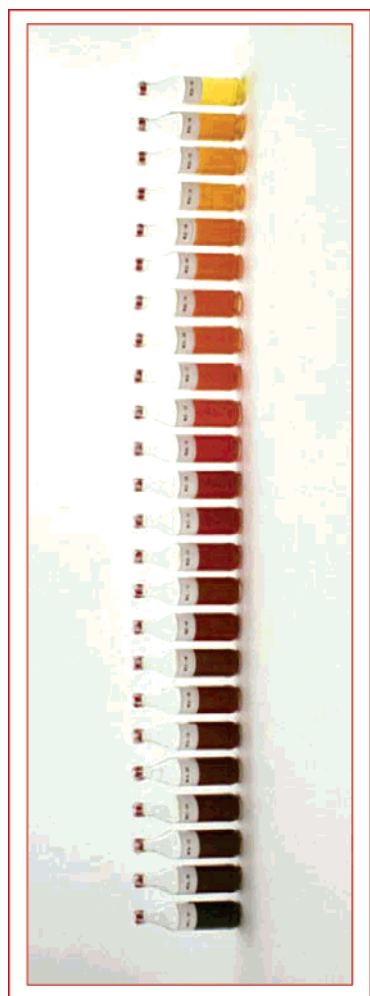


Figure 1. Crude oils from a single column of oil in an oil reservoir. Large coloration differences are noted. Huge vertical compositional grading is evident. [Courtesy of Hani Elshahawi, Dan McKinney, Shell Exploration and Production Company].

enes are a complex mixture so widths of distributions are always of interest. The nature of asphaltene PAHs has also been difficult to clarify. Proposed asphaltene PAHs have spanned an enormous range including molecules with ~ 20 fused rings with either percondensation (three fused rings share a bridgehead carbon) or catacondensation (no carbon atom is shared by three rings). Note that small observed molecular weights preclude such large ring systems. At the other extreme, recent proposed asphaltene molecules and their PAHs purport evidently *colorless* molecules with one, two, and three fused ring systems forming the bulk of asphaltene PAHs.⁹

Our approach here is to analyze the ubiquitous optical absorption data of asphaltenes in terms of molecular orbital (MO) calculations. We look for systematics in the optical absorption data to guide our thinking as to likely crude oil and asphaltene chromophores. We develop involved MO methods to treat large numbers of PAHs as well as distinct classes of

PAHs. In a previous publication, we used this strategy to explore the most probable PAH size for asphaltenes.¹⁰ By examining the optical absorption and fluorescence emission profiles of asphaltenes, we find that petroleum asphaltenes most probably have seven fused rings in their PAHs. The width of the distribution is roughly 4–10 fused rings. This result is in close agreement with direct molecular imaging by two methods, scanning tunneling microscopy (STM)¹¹ and high-resolution transmission electron microscopy (HRTEM).^{12,13} These results are also in close accord with all results measuring asphaltene molecular diffusion constants, for example, by time-resolved fluorescence depolarization.^{5–7} These results are in agreement with the number of aromatic ring systems found by ultrahigh-resolution mass spectrometry;⁸ however, this technique has not yet differentiated whether these ring systems are fused. This result is also in agreement with the analysis of ^{13}C NMR spectra of asphaltene fused ring systems.¹⁴

The electronic absorption edge of many materials is described by the Urbach tail. The Urbach absorption edge, first measured in silver halides of importance for photographic emulsions, is an exponential decline of the optical absorption at the absorption edge and is related directly to the number of absorber sites with the corresponding band gap.^{15,16} Specifically, the absorption edge (Urbach tail) is given by

$$A = C \exp\left(\frac{h\nu}{E_0}\right) \quad (1)$$

where A is the optical absorption, C is a constant for the system, $h\nu$ is the photon energy, and E_0 is the Urbach decay width. For semiconductors and the like, the Urbach decay width $E_0 = kT$ where k is Boltzmann's constant and T is temperature. That is, thermal excitation of optical absorber sites lowers the band gap by exactly the thermal excitation energy.^{17–19}

Both crude oils^{17,18} and asphaltenes^{17,19} exhibit the Urbach tail in the optical absorption edge. For black oils, asphaltenes can contribute significant coloration but not light scattering (in the absence of flocculation).²⁰ However, with the coloration of nearly colorless condensates, the coloration results from *n*-heptane-soluble components.¹⁷ Figure 2 shows that the Urbach tail for condensates, black oils, and heavy oils exhibit the same slope. Similar slopes and thus Urbach decay widths are obtained for crude oils and asphaltenes as shown in Figure 3.^{17–19} Consequently, asphaltenes indeed do exhibit an extension of the coloration of crude oils; it is likely that the same phenomenology applies for light absorption of condensates through asphaltenes.

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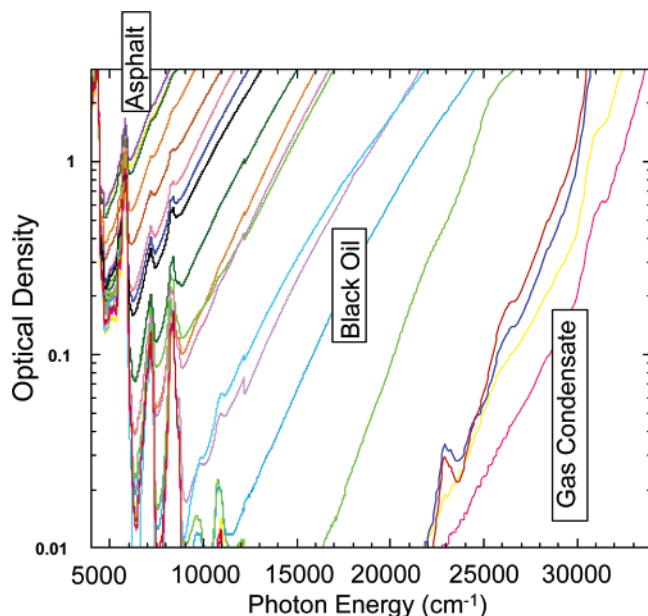


Figure 2. Electronic absorption edge of all crude oils exhibit the same slope when plotted on log(OD) vs photon energy. This “Urbach” behavior is due to the exponentially decreasing population of larger PAHs at the electronic edge for any given crude oil.

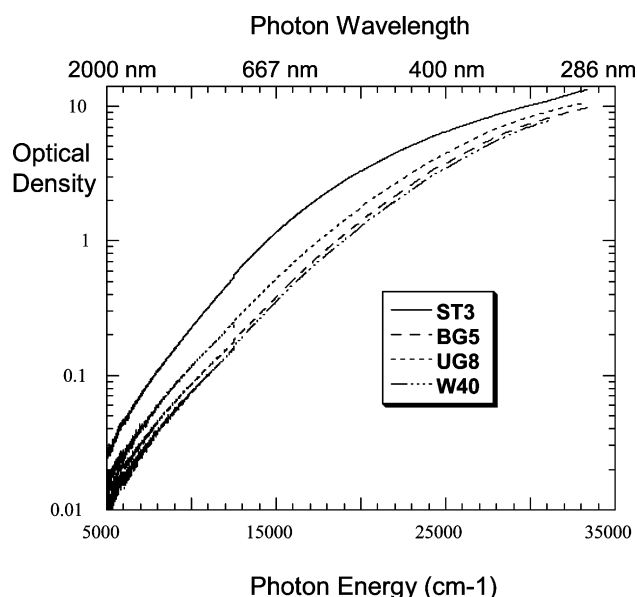


Figure 3. Asphaltenes exhibit the Urbach behavior as well. For asphaltenes, small and rapidly declining ODs are noted at ~ 600 nm, indicating rapidly declining populations of the corresponding chromophores.

The Urbach decay width of crude oils from gas condensates to very heavy oils is 2162 cm^{-1} .¹⁸ For asphaltenes, the Urbach width is $\sim 2800\text{ cm}^{-1}$.¹⁹ Obviously, The Urbach phenomenon in crude oils and asphaltenes does not result from thermally excited PAHs as these decay widths would correspond to ~ 3000 K. Instead, the Urbach tail for crude oils and asphaltenes results from the distribution of the PAH population in crude oils and asphaltenes. Consider a hypothetical for pedagogic purposes, that asphaltenes only contained one-, two-, and three-ring aromatics—no others. Then the asphaltene spectra would show no visible absorption and significant UV absorption. The exact type and distribution in asphaltene of these one-, two-, and three-ring aromatics would give the resulting asphaltene UV absorption spectrum (again with colorless or white spectra in the visible).

In fact, asphaltenes are deeply colored in the visible and even near-infrared. It is a central feature of this paper that large PAH ring systems exhibit corresponding optical absorption in these long wavelength regions. Furthermore, as shown previously¹⁰ and examined further herein, within a given class of PAHs, increasing numbers of fused rings leads to red-shifted optical absorption profiles. This is a consequence of a quantum particle-in-a-box familiar in freshman quantum mechanics, so this is not a shocker. We then note that the exponential decline of long wavelength optical absorption in crude oils and asphaltenes corresponds to an exponential decrease in PAHs with increasing numbers of fused rings. As noted above in the pedagogic example, the exact type and distribution in asphaltene of these PAH aromatics would give the resulting asphaltene optical absorption spectrum. In addition, note that this exponential decline in large PAHs for asphaltenes occurs in the long wavelength side of the absorption profile. This corresponds to PAHs larger than those at the centroid of the PAH population. As noted above, this centroid for asphaltenes is seven-ring PAHs.¹⁰

We consider an explanation consistent with earth science processes that give rise to crude oils and asphaltenes as to how an exponential decline occurs for PAHs with increasing numbers of fused aromatic ring systems—and furthermore, how this process relates to the Urbach formalism—a well-known result in thermal physics considerations. We consider the consequences of the thermal process known to produce the PAH population in crude oils and asphaltenes. For example, immature kerogen is much lighter in color than mature (heated) kerogen. Why? Kerogen diagenesis and catagenesis yields the thermal production of larger PAHs (many fused rings) with their longer wavelength absorption or “redder” from bluer, smaller PAHs (few fused rings). We contend that the characteristic color of crude oil results from the distribution of PAHs that have been created in the thermal process of kerogen catagenesis. The spectral location of the edge depends on the size of the PAH where an exponential decline in population takes place. For asphaltenes, the edge of the Urbach tail might correspond to PAHs with 10 rings while for gas condensates, this optical absorption edge might correspond to three-ring PAHs. In such a circumstance, the optical absorption edge of asphaltene would occur at ~ 650 nm while for the gas condensate it occurs at 350 nm. Indeed, the measurement of asphaltene molecular size versus electronic band gap supports this picture.^{5–7}

At the risk of gross simplicity in this pedagogic treatment, we compare the thermal processes driving the production of chromophores in crude oils and asphaltenes to the mundane process of toasting white bread. Initially, the bread lacks chromophores in the visible. Upon toasting, the bread becomes somewhat yellow, then tan, and then brown. If the toaster remains on too long, then the bread becomes black (in the visible). These colors are the colors one notes in crude oils: clear, yellow, tan, brown, and black. Figure 1 shows all but the clear type (some condensates). If the toaster is left on for a few weeks, one would end up with a char approaching graphite—which is an infinitely large PAH from the molecular point of view. Thus, in toasting bread, we are producing large PAHs from small ones and generating something akin to the Urbach tail. We are proposing the same process applies in crude oils and asphaltenes.

Finally, why is the Urbach decay width for asphaltenes somewhat larger than for crude oils? That is, the optical spectrum is somewhat flatter (smaller increase at shorter wavelengths) for asphaltenes. In crude oils, there are single ring

aromatics such as toluene, two-ring aromatics, etc. These small aromatics absorb only at short wavelengths. They give rise to a significant increase in absorption in the short wavelength region. In contrast, in the isolation of asphaltenes, single-ring aromatics such as toluene are removed. Likewise with almost all two-ring aromatics. In other words, the asphaltenes are deficient in small ring systems¹⁰ in comparison to crude oils. Consequently, at short wavelengths, there is no increase in optical absorption from these small (missing) chromophores. Thus the spectral profile of asphaltenes is flatter than for crude oils—which equivalently gives a larger Urbach decay width for asphaltenes. We also note that ref 17 provides a more in-depth analysis of the Urbach tail for crude oils and asphaltenes.

Systematic MO calculation methods have been developed to enable a very large number of compounds to be analyzed accurately.^{21,22} These results have proven that the Clar representation of PAHs^{23–25} is accurate and applies to PAHs relevant to asphaltenes.^{21,22} The Clar representation treats PAHs as being composed of (stable) aromatic sextets and (less stable) isolated double bond carbons.^{23–25} In particular, we characterize the PAHs in terms of the ratio of carbon atoms in isolated double bonds to those in aromatic sextets.¹⁰ The MO results have shown that the stability and the optical properties of PAHs depend primarily on the number of fused rings in a PAH as well as the fraction of sextet carbon. Other factors such as detailed PAH geometry are also important. Most importantly, the MO method relies on the determination that the asphaltene PAHs are dominated by sextet carbon but are not entirely sextet carbon.^{26,27} This result is not surprising, the PAHs which are dominated by sextet carbon are stable. In addition, there are numerous PAHs of this type.

In our previous work comparing MO calculations of PAHs with optical properties of asphaltenes,¹⁰ the objective was to determine the PAH size (number of fused rings) that corresponds to the centroid of the asphaltene electronic bands; the HOMO–LUMO bands to be precise. For any given PAH, the HOMO–LUMO band is the lowest energy allowed electronic transition and corresponds to exciting an electron from the *highest occupied molecular orbital* to the *lowest unoccupied molecular orbital*. In addition to the centroid of the asphaltene bands and the corresponding PAHs, the width of this distribution was also of interest. The Urbach tail, where optical absorption decreases exponentially, was used as the long wavelength edge to constrain the MO calculations. At longer wavelengths, there is little electronic absorption, thus little corresponding molecular population.

To constrain the short wavelength side, we used the fluorescence emission spectra of asphaltenes.¹⁰ That is, we needed to find the smallest PAHs in asphaltenes that are present in significant numbers. As discussed above, small PAHs (e.g., few

fused rings), have high-energy electronic transitions. The transitions overlap excitation of highly excited states of large PAHs. Thus, optical absorption in the UV cannot be used easily to gauge the population of small chromophores. However, fluorescence emission can be used. It is well-known that fluorescence of PAHs generally corresponds to the HOMO–LUMO gap. Furthermore, at short wavelengths, the fluorescence quantum yields are large; thus fluorescence is not problematic here.²⁸ Fortunately, the wavelengths where fluorescence quantum yields fall correspond to the Urbach tail where optical absorption can be used to track corresponding molecular population. Finally, at short wavelengths, there is no reduction of fluorescence lifetimes of asphaltenes *in dilute solutions* as compared to maltenes. Thus there is little intramolecular fluorescence quenching.²⁹ Of course, in concentrated solutions, intermolecular interactions reduce asphaltene fluorescence quantum yields and fluorescence lifetimes.^{28,30,31} The center of the asphaltene electronic transitions was found to correspond to PAHs with seven fused rings. The full width half-maximum (fwhm) was found to range from 4 to 10 fused aromatic rings. It was also noted that only a single fused ring system (or occasionally two) can fit in an asphaltene molecule given the known molecular weights and alkane carbon content.

In this report, we extend our previous work on the PAH composition of crude oils and asphaltenes to the long wavelength absorption edge—essentially in the Urbach tail. In particular, we establish that PAHs do exist, which have the requisite optical properties commensurate with the low-energy HOMO–LUMO gap of the red asphaltene chromophores. The lowest energy electronic transitions of these PAHs are shown to be determined largely by both the number of fused rings and the fraction of sextet carbon in the corresponding PAHs. Furthermore, these PAHs are seen to be only slightly larger than PAHs that are present in high concentration in asphaltenes. Experiments are performed to search for other potential contributors to the absorption profiles of light and heavy crude oils. The systematic lack of temperature or concentration effects in crude oil and asphaltene coloration suggests that other contributing mechanisms such as charge-transfer complexes or free radical electronic transitions are not significant for crude oils and asphaltenes. Nevertheless, the very lowest energy electronic transitions of asphaltenes that are of very low absorbance fall outside the largest hydrocarbon ring systems examined. It is noted that these transitions correspond to a tiny fraction of the asphaltene molecules. Possible origins of these bands are discussed.

Theory

The theoretical methods used herein have been described previously.¹⁰ The geometry optimization of the PAH systems was done by performing force field-based minimization using the energy minimization panel in Cerius2 version 4.6 and the COMPASS (Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies)^{32,33} consistent force field as

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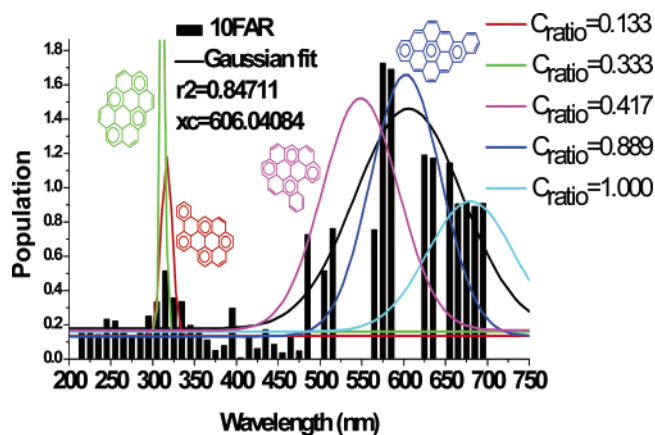


Figure 4. Electronic absorption band locations for PAHs of 10 fused aromatic rings as determined by molecular orbital calculations. Some ring geometries and corresponding absorption bands are shown.

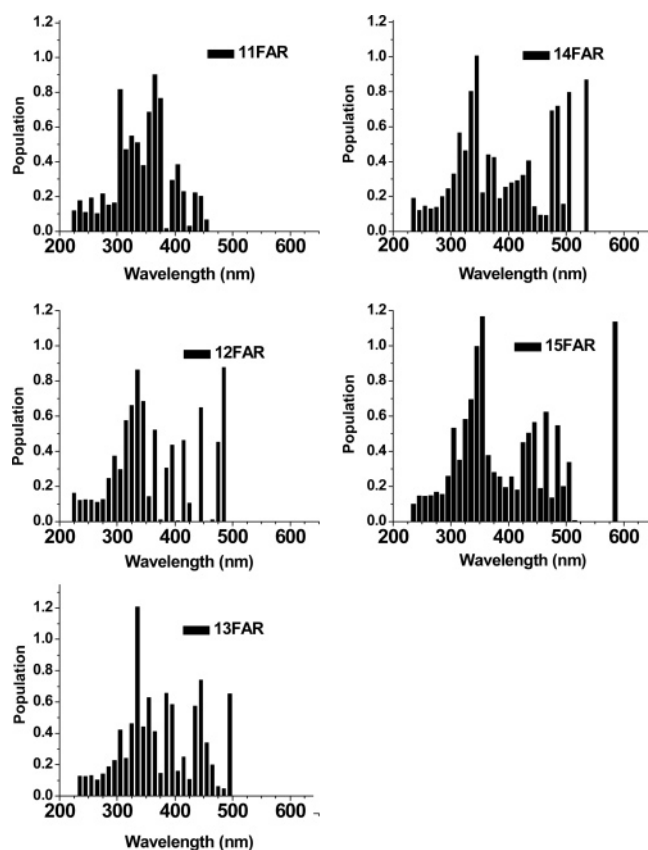


Figure 5. Electronic absorption band locations for PAHs with 11–15 fused aromatic rings (FARs). The corresponding ring systems have an atomic ratio of isolated double bond to aromatic sextet carbon in the range of 0–0.2778. Increasing numbers of fused rings lead to spectral red shift.

it is provided in the Cerius2 package.³⁴ This type of minimization or geometry optimization is a molecular mechanics simulation where the laws of classical physics are used to predict the structures and properties of molecules. The COMPASS force field (FF) has been tested and validated extensively against experiment for many organic molecules. It is an *ab initio* FF that enables accurate and simultaneous prediction of gas-phase properties (structural, conformational, vibrational, etc.) and condensed-phase properties (equation of state, cohesive energies, etc.) for a broad range of molecules and polymers.^{33,34}

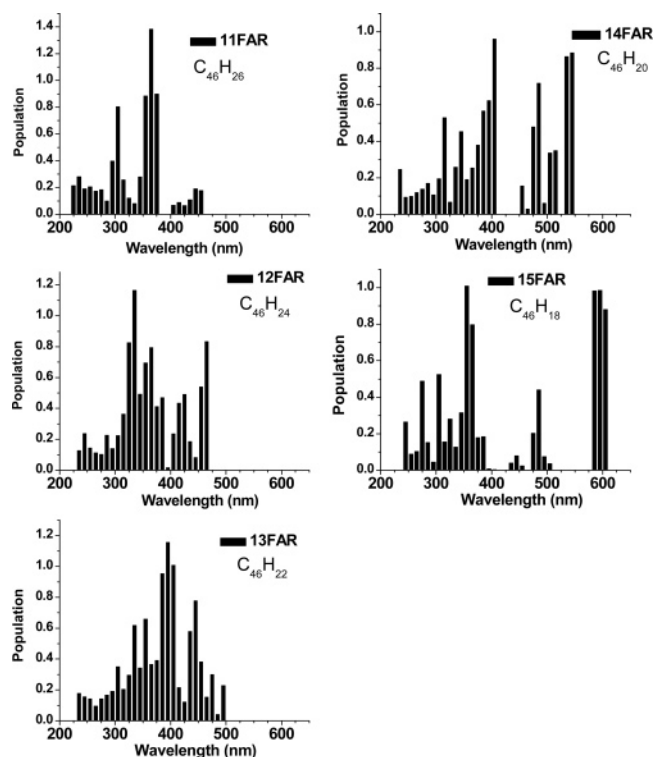


Figure 6. Electronic absorption band locations for PAHs with 11–15 fused aromatic rings (FARs). The corresponding ring systems have an atomic ratio of isolated double bond to aromatic sextet carbon in the range of 0.2778–0.5333. Increasing numbers of fused rings lead to spectral red shift.

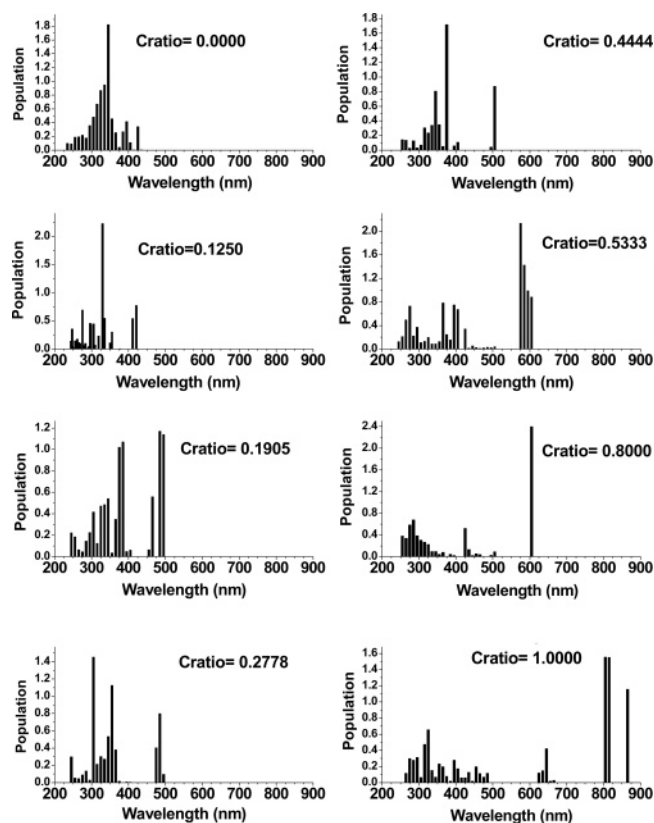


Figure 7. Electronic absorption band locations for PAHs with 15 fused aromatic rings (FARs). Increasing the ratio of IDB carbon leads to a spectral red shift.

In a previous studies,^{21,22} we carried out the validation of the best combination of theoretical methods (optimization

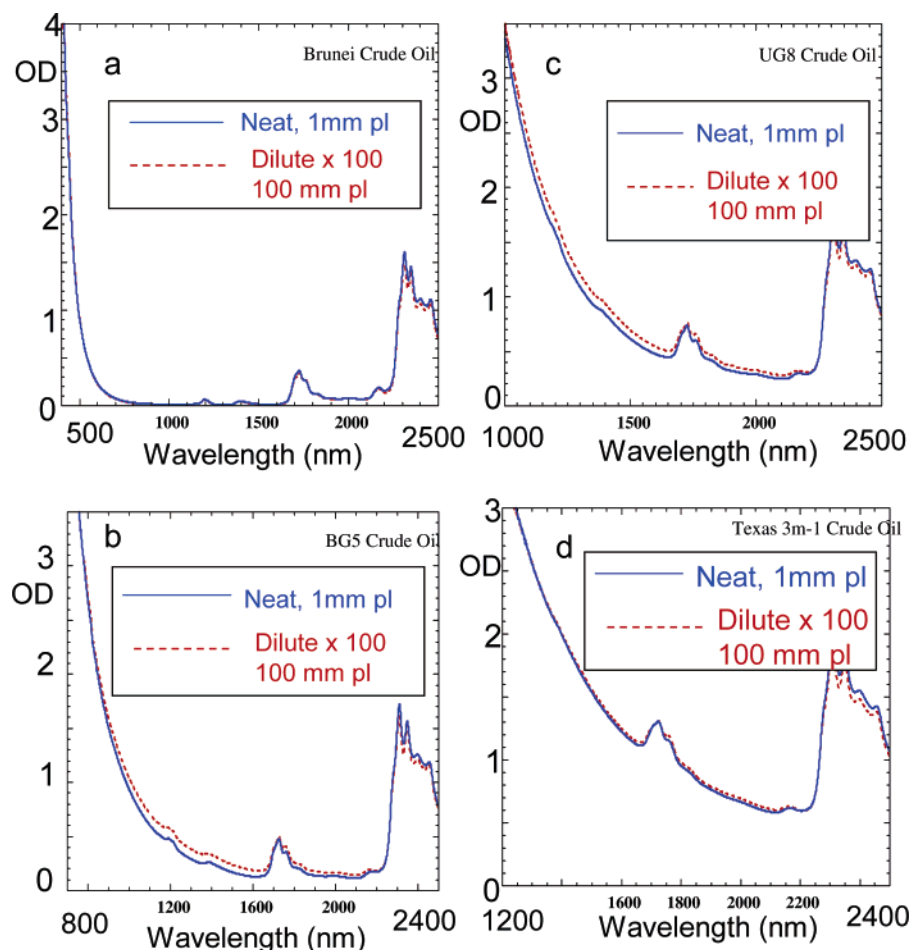


Figure 8. Crude oils, whether light or heavy, do not exhibit any nonlinear dependence of coloration vs concentration. Potential contributors to crude oil coloration that would show nonlinear concentration dependencies such as charge-transfer complexes are not found. Coloration of crude oils from PAHs is corroborated.

method//excited states calculation method and optimization method//single point calculation method) that agree better with the experimental fluorescence emission data of PAHs. Thus, to find the best method for the geometry optimization of the structures we tested three different methods: (1) using COMPASS FF-based minimization; (2) using the semiempirical PM3 method, and (3) using density functional theory and the B3LYP functional. The excited electronic states (including the frontier orbital $\pi-\pi^*$ transition) were calculated using also different methods: (1) the semiempirical electronic structure method ZINDO/S, (2) the semiempirical PM3 method, (3) using a single-point calculation at the Hartree–Fock (HF) self-consistent field level, (4) using a single-point calculation with density functional theory (DFT) and the B3LYP functional, and (5) using the time-dependent density functional theory TD–DFT to calculate the transition energy. We concluded that the best agreement between theory and experiment is observed for the case of the FF//ZINDO calculations.²² Thus, in the present study the excited electronic states of the PAH systems were calculated using the ZINDO/S³⁵ method as it is provided in the Gaussian 98 package³⁶ and using the COMPASS FF geometry optimized structures.

As stated before, we characterize PAHs in terms of the ratio of carbon atoms in isolated double bonds (IDB) to those in aromatic sextets. For example, naphthalene with its two IDB and single aromatic sextet has a carbon atom ratio of IDB/sextet of 2/3. Asphaltenes, from both petroleum and coal, have been

shown to have a value of this IDB/sextet ratio to be roughly 1/3. In both the original formulation of the Clar theory²³ and its several later variants, sextets of π -electrons are located in particular hexagons of the benzenoid molecule, indicating domains of increased π -electron contents and/or local aromaticity. The Y-rule^{24,25} for constructing Clar-type aromatic sextet formulas for benzenoid molecules was used for locating aromatic sextets in pericondensed benzenoids. Here we show a typical analysis employed for large PAHs. Figure 4 shows the results for MO calculations of PAHs consisting of 10 fused aromatic rings (FARs) with various values of IDB/sextet ratios. These calculations capture the lowest energy electronic transitions and all electronic transitions in the spectral range shown. Forty-

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eight different PAHs were analyzed for the preparation of Figure 4. The height of the solid, vertical black bars is determined by the sum of the calculated UV–vis intensity for all the compounds that fall in the investigated wavelength range divided by the number of occurrences that fall in that given 10 nm wavelength range, which is represented by the black bar. The continuous spectrum is an incoherent, integrated, smoothed spectral prediction (Gaussian fit). The black curve represents the Urbach tail, while the colored curves are the best Gaussian fit that represents the population versus wavelength for the different systems that present the same carbon ratio (ratio of IDB/sextet).

The excited states of a total of 338 PAH systems have been calculated with different carbon ratios. The total number of systems calculated (PAHs and PACs) for each FAR family is: 11 FARs 42 systems; 12 FARs 36 systems; 13 FARs 90 systems; 14 FARs 85 systems; 15 FARs 85 systems. PACs, polycyclic aromatic compounds, are PAHs with heteroatoms.

Experimental Section

All spectral were collected on a Cary 5 UV–visible near-infrared spectrometer from Varian, Inc. The concentration studies were performed by comparing the spectrum from a 1 mm path length sample of a given crude oil (using a standard 1 mm cuvette) with a 100 mm path length sample of the same crude oil diluted by a factor of 100. The 100 mm cuvette was held in the spectrometer by a custom sample holder. With such a long path length, some beam walk-off with concomitant reduction of throughput can occur. In addition, the imaging optics of the spectrometer are perturbed by having a 100 mm long cell. This can give rise to subtle problems as well in spectral comparisons. Thus, subtle differences in baseline were sometimes observed, but this effect is very small.

The temperature studies were performed in a custom temperature cell. A 2 mm brass annulus spacer was placed between two sapphire windows giving a 2 mm sample path length. An O-ring was placed inside the brass annulus to seal the crude oil sample. The crude oil was placed inside the volume defined by the O-ring. A small gas cap was used to prevent extreme pressure build-up during the heating cycle. The gas cap was kept out of the optical beam to prevent spectral artifacts, which would have been very obvious if present. This arrangement did mean that we do not know the precise pressure on the crude oil sample during the heating cycle. The gas cap allowed the liquid to undergo thermal expansion in the cell during the heating cycle. We do not know the pressure inside the cell during heating but it was not high enough to cause noticeable compression. The initial pressure is one atmosphere. The charge-transfer complex was made with pyrene and tetracyanoquinone, both obtained from Aldrich Chemical and used without purification.

Results and Discussion

Figure 5 plots the spectral results for five different PAH ring systems, 11–15 rings where the range of the carbon ratio (IDB/aromatic sextet) varies between 0.0 and 0.2778. These ring systems have an IDB/sextet ratio smaller than expected for the bulk of asphaltenes. For larger numbers of fused aromatic rings (FARs), the absorption spectra are seen to shift toward long wavelength. This is the expected result in accord with the standard quantum particle in a box. As the size of the box gets bigger, the wavelength becomes longer, shifting lower both energies and energy transitions.

These larger ring systems segway naturally to the smaller PAHs found to account for the bulk of the asphaltene optical absorption, which are PAHs with 4–10 fused rings.¹⁰ Many properties of asphaltenes are seen to change continuously from maltenes. Moreover, many asphaltene properties change continuously within different solubility cuts of a bulk asphaltene.

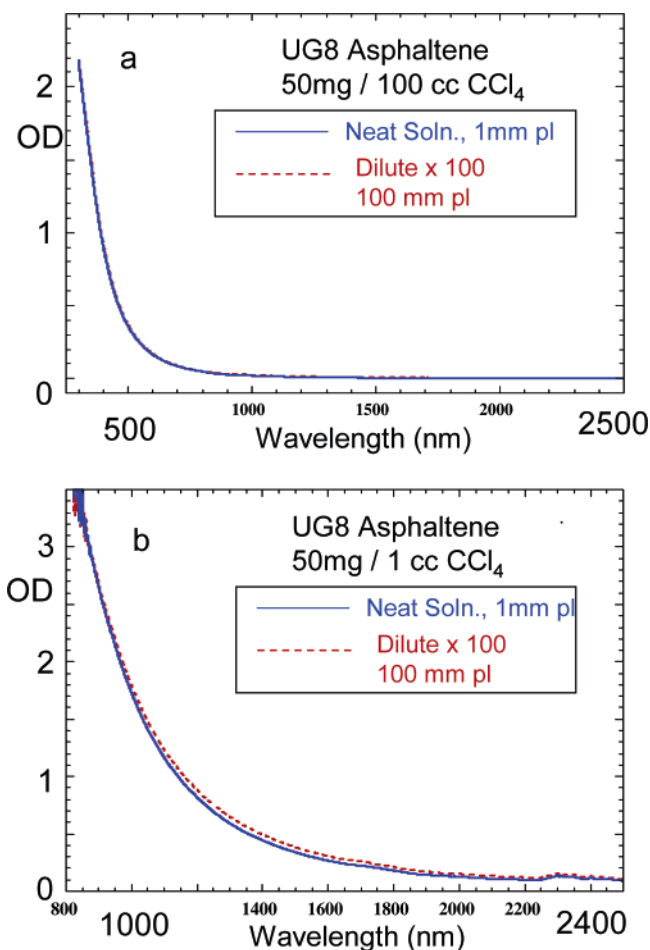


Figure 9. Asphaltenes also do not exhibit any nonlinear dependence of coloration vs concentration. Potential contributors to crude oil coloration that would show nonlinear concentration dependencies such as charge-transfer complexes are not found. Coloration of asphaltenes from PAHs is corroborated.

For example, asphaltene molecular size as determined by time-resolved fluorescence depolarization (TRFD) exhibits systematic trends from resin to asphaltene^{5–7} and within five solubility fractions obtained using *n*-heptane/toluene mixtures from a single asphaltene.^{5,37}

Figure 6 plots electronic transitions for the same number of fused aromatic rings but for a larger ratio of IDB/sextet carbon. The range for Figure 6 is the IDB/sextet ratio of 0.2778–0.5333. This range includes the bulk of the asphaltene ratio (~ 0.33). This figure also shows the red shift with larger numbers of rings, similar to Figure 5. In addition, comparison of Figures 4 and 5 shows that large IDB/sextet ratios are associated with red shifts in electronic transitions. This result is standard within the Clar formalism.^{21–25}

Figure 7 shows the red shift with increasing IDB/sextet ratio for a single number of fused aromatic rings, 15. Figure 7 also shows that these large PAHs exhibit optical absorption in the range where asphaltenes show small and rapidly declining optical absorption, that is at ~ 600 nm. PAH absorption bands are often 50–100 nm wide; these bands extend into the Urbach region. These large ring systems are known to be present in small concentrations in asphaltenes.^{5–8} It follows that the optical absorption bands of these large 15-ring PAHs contribute little to the optical absorption of asphaltenes. Furthermore, beyond

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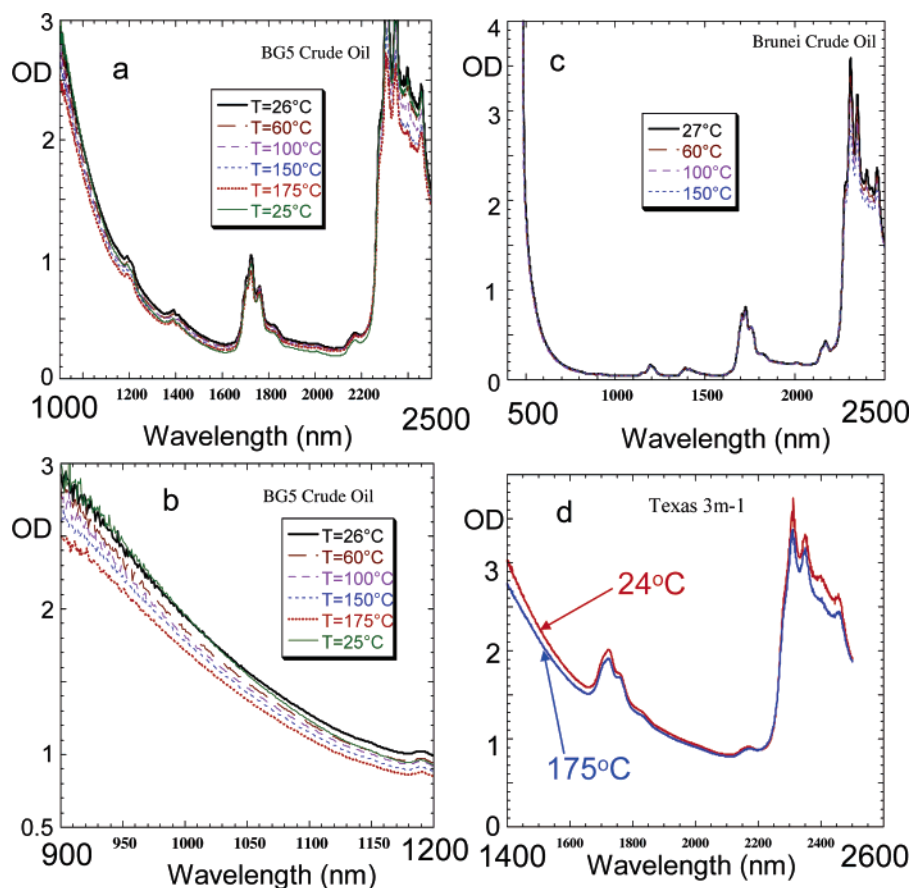


Figure 10. Only temperature dependence of crude oil coloration is the trivial and reversible thermal expansion effect of the bulk sample. Coloration specifically association with complex formation is ruled out.

600 nm, the asphaltene optical absorption drops precipitously corresponding to the lack of any larger PAHs in asphaltenes.

The above analysis concludes that the long wavelength edge of asphaltene absorption results from large PAHs. This also applies to the electronic absorption edge of crude oils with significant asphaltene content. It is important to check whether other excitation processes are likely to contribute significantly to this absorption. Other potential excitation processes include charge-transfer or free radical electronic excitation, which would likely still be associated with PAHs. Charge-transfer complexes are weakly bound and tend to be strongly affected by changes in concentration. Free radical concentrations in asphaltenes are known to be dependent on temperature and likely on the state of asphaltene aggregation.¹⁴ Thus changes in concentration would give rise to nonlinear changes in optical absorption if free radical excitations were responsible for long wavelength electronic transitions of asphaltenes and crude oils.

Figure 8 plots the variation of the optical absorption edge with a factor of 100 change in concentration for a range of crude oils, light to heavy. These crude oils span coloration in the short-wavelength visible through near-infrared. A nonlinear effect which would be expected from charge-transfer complexes or free radicals contributing significantly to asphaltene (or crude oil) optical absorption would show up as the neat and dilute curves not overlaying for a particular sample. A path length $\times 100$ longer was used for the samples diluted by $\times 100$. Figure 8 shows that these curves overlay. Independent of the weight of the crude oil, there is no change in the absorption edge upon $\times 100$ dilution. The very small differences noted in some of the spectra are likely due to walk-off effects and imaging effects of the optical beam in the 100 mm path length cell. The lack of any concentration effect on the electronic absorption edge

of all crude oils including heavy oils implies that charge-transfer complexes and free radicals do not contribute significantly to the corresponding electronic absorption. The fact that all crude oils show the same invariance is consistent with PAHs being responsible for the bulk of electronic absorption in the UV–visible NIR spectral range. This result is consistent with the MO analysis above. Similarly, Figure 9 plots the lack of any nonlinear effect on the optical absorption spectral of asphaltene solutions of differing concentrations. The observation applies in the visible where the absorbances are large as well as the near-infrared where the absorbances are low (so 100 times higher concentrations are needed to observe optical absorption).

Figure 10 plots the effect of temperature on optical absorption. Only subtle, yet reversible effects are noted as a function of temperature increase. The three oils plotted in Figure 10 span a large range of weight and coloration; none show much temperature effect. Typical thermal expansion coefficients for dead crude oils are on the order of $10^{-3}/^{\circ}\text{C}$; exact values for the crude oils of Figure 10 were not determined. Figure 10 shows that an increase in temperature of 150 $^{\circ}\text{C}$ yields a 15% reduction in optical density (OD). Figure 10b, an expansion of a portion of the spectrum in Figure 10a, shows this 15% OD reduction most clearly. This is the expected magnitude of density thus OD reduction for a thermal expansion coefficient of $10^{-3}/^{\circ}\text{C}$. As with the dilution studies above, there is no suggested nonlinear change in electronic absorption with temperature increases of 150 $^{\circ}\text{C}$. Again, the suggestion is that crude oil coloration is not impacted by aggregation or complex formation which are known to be dependent on temperature and concentration.

In contrast, Figure 11 plots the concentration dependence of a standard charge-transfer complex, TCNQ, with pyrene. Figure 11a plots their individual spectra. Figure 11b shows the

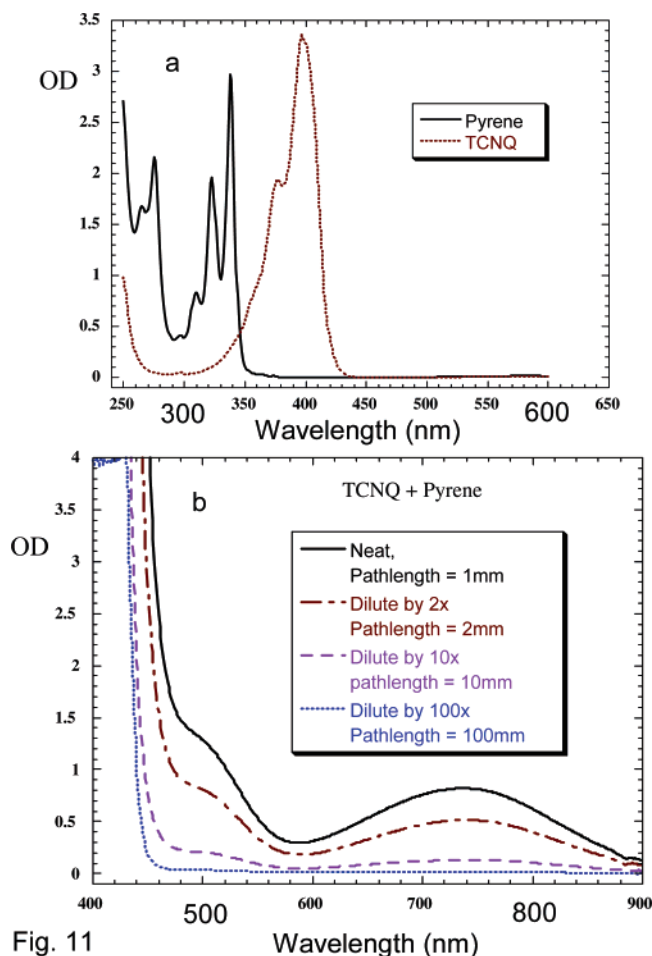


Fig. 11 Large, nonlinear concentration dependence of coloration of a standard charge-transfer complex between TCNQ and pyrene.

absorption of their charge-transfer complex; there is a large nonlinear reduction in absorption for dilute conditions as the charge-transfer complex dissociates at low concentration. For these spectra, a reduction in concentration is accompanied by an increase in path length—as done with the crude oils. Evidently, crude oil spectra give no indication of containing charge-transfer complexes at least with detectable optical impact.

At very high asphaltene concentrations, electronic absorption is seen in Figure 8 into the near-infrared (NIR). Rather large PAHs are examined here and do not exhibit absorption at these very long wavelengths. In addition, the transitions examined here are so-called allowed. It is possible that these very low energy and very weak transitions in asphaltenes are due to forbidden transitions such as $n-\pi^*$ or spin forbidden transitions. Both of these types of transitions are strongly affected by the number and geometry of fused aromatic rings. Work is ongoing to investigate these effects.

Conclusions

MO calculations combined with various optical measurements is a productive way to probe asphaltenes. PAHs with increasing numbers of fused aromatic rings and with decreasing sextet carbon fraction are seen to be characterized by longer wavelength transitions. Previously, PAHs with seven fused rings with a range of 4–10 rings were seen to characterize the bulk of HOMO–LUMO bands of asphaltenes. This work shows that increasing ring size results in longer wavelength transitions. In addition, there is small and rapidly declining electronic absorption for asphaltenes where PAHs with 15 fused rings absorb. The suggestion is that there is a very small number of ring systems with this large number of rings and very little molecular population with larger rings. The lack of any concentration dependence or nontrivial temperature dependence of crude oil and asphaltene coloration in any spectral range indicates that aggregation, charge-transfer complexes, and even free radicals do not play a significant role in establishing crude oil coloration. The very low and very weak asphaltene electronic transitions in the NIR region may be due to forbidden transitions that we have not yet investigated.

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