**Further Insights into the Structure and Chemistry of the Gilsonite Asphaltene from a
Combined Theoretical and Experimental Approach.**

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Submitted to

Fuel

December 2014

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Abstract

Gilsonite is a natural fossil resource, similar to a petroleum asphalt high in asphaltenes. Asphaltenes are a class of organic compounds operationally defined based on their solubility in organic solvents, and as a result there is wide range of potential compositions and structures that can fit into this class. Specific compounds are challenging to propose due to its complexity. A sample of the asphaltene derived from the Gilsonite deposit was characterized by Fourier transform infrared spectroscopy, Raman spectroscopy, and high-resolution transmission electron microscopy. The high intensity of the 1600 cm^{-1} infrared peak, which corresponds to a C=C stretching vibrational mode of the aromatic carbons also found prevalent in other asphaltenes, is likely a characteristic asphaltene feature. The high intensity can be explained by the stack structure and/or by polycyclic aromatic infrared transitions with a high dipole moment derivative. The nanosize stack structure was validated by the electron microscope and diffraction patterns, giving inter-sheet distances of 2.54 and 3.77 Å, respectively. Complementary calculations using density functional theory suggest a specific island-type polycyclic aromatic molecular model, with the calculated vibrational modes consistent with all of the characteristic peaks in the infrared spectrum. The method combining theoretical and experimental can be extended for more specific asphaltene molecular structure identifications.

Highlights

- Combined computational and experimental approaches to characterize asphaltenes.
- 1600 cm^{-1} IR peak with large intensity identified as a characteristic asphaltene feature.
- Nanosize stack moieties found by TEM and SAED.
- An ‘island’ molecular model validated by experimental and calculated spectra.

Keywords

Gilsonite, asphaltene, vibrational spectroscopy, transmission electron microscopy, density functional theory

Introduction

The world uses more than 90 Mt asphalts every year, among which about 60-70% is used for road paving, 10-20% for waterproofing and anticorrosive materials, and 10-20% for other industrial applications [1]. Gilsonite is a well-known natural deposit of bituminous asphalt primarily located in the Black Dragon and Bonanza area in the eastern Utah basins and has been of wide interest and use [2]. It can be in liquid or solid form, possibly originating from protein transformations and biodegradations [3]. Solid gilsonite is known for its high content of asphaltene [4]. Asphaltenes, usually derived either from coal or from petroleum vacuum distillation residues, are wide-spread, and a class of compounds that are defined by their solubility, *i.e.* insoluble in n-heptane and soluble in toluene [5]. GilsoniteTM is produced with a fair degree of quality control so as it has consistent properties. It is a useful substance in which to study asphaltenes, to compare with the petroleum asphaltenes, and further understand their chemistry and structure.

There have been numerous studies to understand asphaltene components and their structures utilizing a range of analytical methods based on references cited therein [6,7]. Progress is being made, with a broad range of studies being carried out to develop asphaltene molecular models [8-13]. Raman and infrared (IR) spectroscopy are complementary techniques for observing molecular vibrations based on polarizability and dipole moment changes, respectively. Raman spectroscopy is useful in identifying structures with both long-range order and short-

range order and has been applied to asphaltene characterization [14]. Alkyl chain content derived from IR spectra has been quantitatively related to insolubility [15]. Transmission electron microscopy (TEM) has been used to determine asphaltene microstructure and micelle size [16], providing a size range limit for asphaltene molecules. Computational methods were applied to probe possible structures and to compare with experimental nuclear magnetic resonance spectra and Raman spectra, and the highest occupied molecular orbital-lowest unoccupied molecular orbital gap was related to observed optical spectra [17-20]. The actual asphaltene composition covers a wide span of molecules from low to high molecular weights, and various core structures. Different conditions such as the origin of the asphaltene, separation solvents, analytical methods, etc. result in assignment variations. A structure that is likely to be one of the many possibilities for asphaltene candidates is easy to propose; yet its verification requires independent experimental evidence to prove its existence or exclude the possibility. In this work, we use both experimental and computational methods to provide a more accurate basis for asphaltene chemical identification.

Experimental Section

Materials. The sample used in this study was an asphaltene fraction from the Gilsonite deposits in the Bonanza area in eastern Utah supplied from a commercial source. The sample preparation using column distillation, n-heptane precipitation, toluene filtration, and drying, were all done by the source who provided the sample. No further treatment was performed.

Spectroscopy. Fourier transform infrared spectra (FTIR) were acquired on a Thermo Nicolet 870 spectrometer in transmission mode. The solid sample was ground with anhydrous KBr powder and hydraulically pressed to form a grey opaque pellet. Before taking the sample spectrum, an IR spectrum of a blank KBr pellet window was taken as the background. The

spectrum was collected with a resolution of 4 cm^{-1} from 4000 cm^{-1} to 400 cm^{-1} for 100 scans using a deuterated triglycine sulphate detector.

Raman spectra were taken on a WiTec CRM200 Raman spectrometer equipped with a charge-coupled device as the detector. The laser beam wavelength used was 532 nm; the power was approximately 15 mW concentrated on the sample with a 100x objective lens. Prior to sample measurement, a Si wafer was used for the alignment and instrument calibration test. A 600 g/mm dispersion grating was used for the measurements. The ground sample particles were then placed on a glass slide and packed to about 1 mm in thickness. Each spectrum was taken as an average of 20 scans with an exposure time of 2 s at each scan.

Microscopy. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were done on a FEI CM200 to search for the presence of any crystalline structures in the asphaltene. The solid samples were ground to micro-particle sizes and suspended in methanol, followed by coating on a copper grid (Holey Carbon Film on 300 mesh copper, from Electron Microscopy Sciences). The measurements were at a 200 kV emission voltage (electron wavelength λ of 2.74 pm) and a 10^7 magnification to the imaging plates used a 2k×2k CCD camera with an image resolution of about 2.4 Å. The camera length was calibrated using an evaporated Al film at the same lens current and emission voltage. The electron diffraction pattern was then processed using the ProcessDiffraction program [21].

Computational Methods. The geometries were optimized using density functional theory (DFT) with the hybrid B3LYP exchange-correlation functional [22,23] and the 6-31+G(d,p) basis set [24]. The geometries were also optimized using the semi-empirical PM6 molecular orbital method and the vibrational frequencies were calculated at both levels [25]. These

electronic structure calculations were done with the Gaussian09 program system [26]. Spectral broadening was added by giving each line a Lorentzian line shape with a 5 cm^{-1} line width.

Results and Discussion

FTIR and Raman Spectra. The solid Gilsonite asphaltene sample's main Raman shifts and IR vibrational peaks are labeled in Figure 1(a). These spectra are similar to asphaltene spectra observed and assigned by other researchers [14,18,27]. This indicates that Gilsonite asphaltene should have similar basic structures as that of asphaltenes from other sources, as evidenced by the similarities in their Raman and infrared spectra. In our earlier work on heavy oil analysis, it was noticed that certain heavy oil FTIR peaks such as the ones at 1390 cm^{-1} and 1600 cm^{-1} have an unusually high intensity and the extra intensity may correspond to asphaltene contribution [28]. A comparison of transmission FTIR spectra for the asphaltene and heavy oil, which is a mixture of saturates, aromatics, resins, and asphaltenes, corroborates this statement as shown in Figure 1(b). When the spectra are normalized with respect to the 2920 cm^{-1} C-H stretching peak, in the asphaltene IR spectrum, the 1600 cm^{-1} peak is significantly more intense than that of the heavy oil with an asphaltene fraction. This indicates that the prominent 1600 cm^{-1} peak observed in many heavy oil and asphaltene IR experiments should be partly assigned to an asphaltene characteristic peak, whose intensity is stronger than that of many aromatic molecules. However, the structural reason leading to the increased intensity has not yet been uncovered.

In the petroleum literature, these two peaks are usually assigned as C=C stretching and C-H bending modes, respectively [29]. Although the band at $\sim 1600\text{ cm}^{-1}$ is not unique to asphaltenes as many aromatics may have peaks around this value, their intensities are not always as strong. Very few aromatic substances if any in the IR database have a similar spectrum as that of asphaltene [30]. Most of them have peaks around these wavenumbers, but at the same time,

have very intense peaks at other wavenumbers that do not match the asphaltene spectrum. It is still challenging to find a model that has all the peak locations and peak intensities that match the asphaltene spectrum; however, the 1600 cm^{-1} intensity can be used as a guide to screen models.

Besides the 1600 cm^{-1} peak, a broad shoulder to the lower wavenumber region at 1375 cm^{-1} is prominent in Figure 1. In many reports for carbonaceous materials, there are similar characteristic peaks close to the two observed peaks, e.g. 1587 and 1362 cm^{-1} in the FTIR spectrum for ground graphite [31], and the G (1580 cm^{-1}) and D (1350 cm^{-1}) bands in the Raman spectra for charcoals, carbon fibers, and soot [32-36]. The G band can shift to higher wavenumbers when the graphite crystal size becomes smaller, and the D band results from the small crystallinity of graphite, symmetry-breaking at the edges, or nanometer size disorders [33,35]. Bouhadda *et al.* also observed the G and D bands in the Raman spectra of an asphaltene, but did not attribute them to asphaltene characteristic bands [14]. In their report, the D band was deconvoluted with different assignments to estimate asphaltene molecular dimensions, and one of them was related to non-crystal carbon black, which is a graphite-like, quasi-crystalline species [37]. Besides the 1600 cm^{-1} and 1350 cm^{-1} peaks, there is a small peak around 2730 cm^{-1} in the IR spectrum, which is apparent in both the heavy oil and asphaltene IR spectra. A low broad “hum” near this region exists in the Raman spectrum (Figure 1(a)). As a comparison, a second-order of zone-boundary phonons peak named 2D has been reported for glassy carbon [38]. From these similarities, one explanation for the prominent 1600 cm^{-1} peak observed in many heavy oil and asphaltene IR experiments is that the intensity is contributed by structures similar to the well-known Yen’s ‘asphaltene micelle’, or qualitatively described as a ‘graphite-type stack’ [39], which may arise from the intermolecular attractions between asphaltene molecules through “aromatic planes” [40].

The full width at half maximum (FWHM) of the peaks in the Raman spectrum (Figure 1(a)) are about 170 cm^{-1} for the 1600 cm^{-1} peak and 270 cm^{-1} for the 1350 cm^{-1} peak, respectively. The FWHMs are greater than those for single crystal graphite [33]. The difference may arise from the low crystalline quality of stack domains in asphaltene, with larger amounts of plastic deformation or disorder, besides instrumental resolution differences. In addition, it could be due to a broader range of compounds with varying amounts of different types of C=C bonding which would broaden the peak.

HRTEM. Ultrafine random oriented nanocrystalline structures were found in some of the asphaltene particles on the TEM grid as shown in Figure 2. The contrast interface of the darker region and the brighter region corresponds to possible phase boundaries between the polycrystalline structures and the amorphous materials or some structures at a different zone axis. In addition, crossing fringes seem to exist in one grain. This is a validation of the previous FTIR hypothesis that quasi-crystalline stacks might exist in this asphaltene. The upper left corner and in the middle of Figure 2(a) of the HRTEM image, lattice fringes of ~ 2.54 , 3.77 , and $10.90\text{ \AA}$ spacings are noticeable, of which the former two are consistent with reported asphaltene layer dimensions of $2.1\text{--}5.3\text{ \AA}$ measured by XRD [41], while the one at $10.90\text{ \AA}$ is not very clear but might be due to the nanocrystalline boundaries of stacked layers. Overall, the results suggest a stack layer number of between 2 and 5. The spread range of these lattices is a few tens of nanometers as seen in the dark region in Figure 2(a), which reflects the agglomeration size of these nanocrystallites. The spacing of $3.77\text{ \AA}$ is close to but a little greater than the reported distance of $3.55\text{--}3.70\text{ \AA}$ for graphite [42,43]. Thus the stack is similar to a graphite sheet, but different in that it contains steric distortions due to peripheral alkyl groups on the stacked polycyclic aromatics, or some other type of small clusters of fused rings, such as porphyrins,

which are known to self-assemble and form stacked structures [2,40]. Separation of these stack domains is difficult and poses a challenge in the analysis of the FTIR assignments in terms of the 1600 cm^{-1} peak intensity. The straight rather than round lattice spacings indicate that they are more likely to be sheet-stacked nano-clusters and not other allotropic structures (i.e. diamond, or fullerene-like species). Among the micro-particles tested, some are amorphous and not all particles show diffraction rings, as given in Supplementary Data A, Figure S1. The TEM image reflects the size of asphaltene micelles in agreement of the size range as found by others, and the crystalline region corroborates the view that the asphaltene may tend to form stack domains [27].

An SAED ring pattern for the HRTEM and its analysis is shown in Figure 2(b) and (c). Peaks in Figure 2(b) correspond to the diffraction rings in Figure 2(c). Three peaks or rings are observable. The weak intensities are due to the small amount of crystalline material. The peak at 2.34 Å is of lower indices than the peak at 1.35 Å, and may correspond to the 2.54 Å lattice fringes domains in Figure 2(a). The value variation is due to the spatial resolution limit when finding and scaling the fringes in the HRTEM image. The spotty Debye rings instead of points or continuous lines in Figure 2(c) can also be due to different asphaltene crystalline stacking patterns or amorphous species of short-range order. More studies are needed to conclude whether these values can account for the aromatic sheet distances in an asphaltene cluster crystalline moiety. Overlapping of other lower indices with the direct beam is possible and makes it difficult to determine the lattice constant.

Molecular Modeling. The infrared spectrum from an electronic structure calculation can be helpful in interpreting the observed spectra, as there are unlikely to be actual reference materials for the assignments. As discussed earlier, the high intensity of 1600 cm^{-1} IR peak is likely an asphaltene characteristic feature. The stack structure may have caused this high

intensity, as corroborated by Raman experiments and TEM observations of carbonaceous materials. However, this relatively prominent and high intensity 1600 cm^{-1} peak is not observed in many aromatic IR spectra so it is difficult to find the correct molecular model. As the IR intensity is proportional to a dipole moment derivative, this suggests the presence of a substituent on the aromatic ring leading to an enhanced dipole derivative, which was suggested by other researchers by the observations using ^{15}N nuclear magnetic resonance for the same source material Gilsonite [2]. This feature in the IR spectra can be a potential indicator for use in probing asphaltene markers, and as a benchmark for screening the electronic calculation of specific asphaltene molecules used to model asphaltene.

Following on studies supporting an ‘island’ type structure as a dominant asphaltene structure [12,44], a heuristic model was constructed as shown in Figure 3 (structure as given in Supplementary Data A, Table S1), which contains 4 fused rings in the molecule with 1 N heteroatom. Its H:C ratio is about 1.34 similar to the average Gilsonite asphaltene’s ratio (Supplementary Data A, Table S2). Its calculated IR spectrum is close to the experimental observed Gilsonite IR spectrum, and has a molecular weight of 401 Da. The double bond equivalence (DBE) of the model molecule is 11. The maximum dimension of the molecule is about $15\text{ \AA}$, and the cross section thickness is about $3\text{ \AA}$, which is also within the lattice spacing as observed in the HRTEM image in Figure 2.

The vibrational spectra of a set of molecules with fused poly-aromatic rings from 4 to 10 have been calculated to help interpret the Gilsonite FTIR spectrum (Supplementary Data A, Figure S2). The intensity of the asphaltene characteristic peak 1600 cm^{-1} is not directly proportional to the number of rings. Among the investigated models, more core rings do not necessarily lead to a more intense peak at $\sim 1600\text{ cm}^{-1}$ (Supplementary Data A, Figure S3).

However, future investigations in screening the listed thousands of candidates are necessary to unveil this correlation.

4. Conclusions

Gilsonite asphaltenes are similar with other petroleum source asphaltenes, having a polar core and tend to interact and form aggregates or macromolecules not seen in simple liquids. A short-range ordered structure was observed by TEM and SAED, forming stack domains. The intense IR vibrational band at 1600 cm^{-1} is identified as a feature peak of asphaltenes and serves as a benchmark for the calculation of vibrational spectra using electronic structure methods. This intense IR peak may be explained by two reasons: the stack structure as observed by TEM and/or the presence of polycyclic aromatics with a large dipole derivative as calculated by DFT. Island-type structures are possible in Gilsonite asphaltene. One model compound with a heteroatom and four rings provides a good calculated spectral match with the Gilsonite asphaltene's experimental IR spectrum. Further work with in-depth analysis using computational chemistry to validate the molecules observed by other experimental tools such as mass spectrometry can be extended to provide more possible asphaltene compound candidates.

Acknowledgements

This work was supported by the U.S. Department of Energy, under contract DE-NT-0005663 to the Colorado School of Mines and by the DOE Office of Basic Energy Sciences, Geosciences program (DE-SC0009362). The authors appreciate the HRTEM measurements by Dr. Gary Zito and ICP-OES tests in Prof. James Ranville's lab. K. Li thanks the Fundamental Research Funds for the Central Universities (22A20154009). D. A. Dixon thanks the Robert Ramsay Chair Fund of The University of Alabama for partial support.

243 **In Memoriam** of Dr. Michael Batzle, who was a geophysicist and a great scholar to have
244 worked with.

245 **Appendix A. Supplementary Material**

246 Supplementary data associated with this article can be found, in the online version, at
247 www.fuel.org.

248 **References**

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249 **Figures Captions**

250 **Figure 1.** (a) Raman (top) and transmission FTIR (bottom) spectra of the solid Gilsonite
251 asphaltene; (b) FTIR spectra of the solid Gilsonite asphaltene (red line, shaded, same spectrum as
252 in (a)) and heavy oil (Canadian, 434 m, black line), both normalized to the peak at 2920 cm^{-1} .

253 **Figure 2.** (a) HRTEM image; (b) the intensity distribution of an electron diffraction pattern, K is
254 the inverse of lattice spacing; and (c) an electron diffraction pattern of one Gilsonite asphaltene
255 particle, camera length 150 mm.

256 **Figure 3.** (a) Transmission FTIR spectra of Gilsonite asphaltene (same as in Figure 1), and (b)
257 calculated IR spectrum for model $\text{C}_{29}\text{H}_{39}\text{N}$ with a scaling factor of 0.9404.

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260 **Figure 1.**

Figure 2.

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264 **Figure 3.**