



Further insights into the structure and chemistry of the Gilsonite asphaltene from a combined theoretical and experimental approach



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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.

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

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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. 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.

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1. Introduction

The world uses more than 90 Mt asphalts every year, among which about 60–70% is used for road paving, 10–20% for water-proofing 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]. Gilsonite™ 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.

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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, and analytical methods 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.

2. Experimental section

2.1. 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.

2.2. 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 100× 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.

2.3. 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 $2\text{ k} \times 2\text{ k}$ 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].

2.4. 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.

3. Results and discussion

3.1. FTIR and Raman spectra

The solid Gilsonite asphaltene sample's main Raman shifts and IR vibrational peaks are labeled in Fig. 1(a). These spectra are similar to asphaltene spectra observed and assigned by other researchers [14,16,18]. 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 [27]. 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 Fig. 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 [28]. 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 [29]. 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 Fig. 1. In many reports for carbonaceous materials, there are similar characteristic

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