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## MOLECULAR IMAGING OF PETROLEUM ASPHALTENES BY SCANNING TUNNELING MICROSCOPY: VERIFICATION OF STRUCTURE FROM $^{13}\text{C}$ AND PROTON NUCLEAR MAGNETIC RESONANCE DATA

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### Abstract

Scanning tunneling microscopy (STM) was used to verify the molecular structure of Maya asphaltene which had been derived from combined  $^{13}\text{C}$  and proton nuclear magnetic resonance (NMR) experiments. Petroleum asphaltenes are known to contain large polynuclear aromatic centers with aliphatic sidechains. Average molecular models of Maya asphaltenes were derived using studies which included combined proton and  $^{13}\text{C}$  NMR data to determine total aromatic carbon content and the ratio of peripheral to internal aromatic ring carbons. These parameters permitted estimating the average number of aromatic rings per condensed cluster.

These Maya asphaltenes were imaged by scanning tunneling microscopy (STM) in a dilute solution of tetrahydrofuran on highly oriented pyrolytic graphite. The sizes and structures of the asphaltenes as observed by STM are in reasonable agreement with these average molecular models. We observed asymmetric structures whose largest dimension averaged  $10.4 \text{ \AA} \pm 1.9 \text{ \AA}$  from 24 separate images. The condensed ring portions of three representative NMR derived molecular models yielded an average dimension of  $11.1 \text{ \AA} \pm 1.4 \text{ \AA}$ .

**Key Words:** Scanning tunneling microscopy, nuclear magnetic resonance (NMR), asphaltenes, structure.

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### Introduction

Petroleum resids are generally upgraded to higher value products by hydroprocessing. This process, however, is very demanding because of the highly aromatic nature of the constituent molecules, as well as the high metal and heteroatom content. Most of the problems associated with resid upgrading are attributed to the presence of asphaltenes. Asphaltenes are generally also believed to be the precursors of coke formation during resid processing, limiting the kinetics and economics of the process.

Asphaltene structure has been extensively investigated in the past (Speight, 1991; Herzog *et al.*, 1988; Ravey *et al.*, 1988; Storm, 1991; Sheu *et al.*, 1992; Strausz *et al.*, 1992). These studies have provided a global picture of asphaltene structure, which explains general asphaltene reactivity under thermal and catalytic conditions. Because of various assumptions made in deriving these structures and the dependence of the asphaltene structure on the origin of the crude oil, we performed a detailed study of this particular Maya asphaltene. This work describes a study focussed on Maya asphaltenes, using  $^{13}\text{C}$  and proton nuclear magnetic resonance (NMR) and scanning tunneling microscopy (STM).

### Experimental

#### Asphaltene separation

The asphaltene sample used in this study was obtained by heptane precipitation from Maya vacuum resid. Briefly, the resid was mixed with 44 times its volume of n-heptane and stirred at room temperature for 18 hours under nitrogen atmosphere. The precipitated asphaltene was filtered and dried free of heptane. The asphaltenes were almost completely soluble in toluene and tetrahydrofuran (THF).

#### Scanning tunneling microscopy (STM) analysis

The precipitated virgin asphaltene from the separation procedure mentioned above was diluted in THF to a concentration of 1-5  $\mu\text{g/ml}$  which, at the average

molecular weight for the asphaltenes, corresponds to a submonolayer coverage on an appropriate substrate if agglomeration does not occur. We have employed both freshly cleaved highly oriented pyrolytic graphite (HOPG; Zajac *et al.*, 1994b) and molybdenum disulfide (Zajac, *et al.*, 1994a) which require different imaging conditions but produce comparable results for similar heterofunctional organics. The HOPG was obtained from Union Carbide Corporation (Parma, OH) and a synthetic MoS<sub>2</sub> single crystal was obtained from the Exxon Research Center (Annandale, NJ). Several microliters of the dilute solution were micropipetted on the surface and dried in dry nitrogen. A Digital Instruments (Santa Barbara, CA) Nanoscope II equipped with a side viewing stereo microscope (500X) permitted approach and alignment of the tunneling tip. The tunneling tips are electrochemically AC etched tungsten (250 μm) in 1 M KOH and were subsequently rinsed in distilled water and stored in alcohol. The tunneling conditions were typically 100-600 mV bias voltage ( $V_T$ ) and 0.5-2.0 nA tunneling current ( $I_T$ ). Constant height images were normally obtained since lateral dimensions were of primary consideration.

#### Nuclear magnetic resonance (NMR) analysis

The virgin asphaltene sample was analyzed by <sup>13</sup>C and <sup>1</sup>H NMR in solution on a Varian VXR-300 spectrometer operating at 300 MHz proton frequency. Deuterated chloroform was used as the solvent. The asphaltene sample was completely soluble in chloroform. The solubility was confirmed by filtration through a 1 μm millipore filter that left no residue. The spectral acquisition parameters were set to obtain quantitative spectra. Advanced pulsing sequences were used to delineate chemically distinguishable carbon/proton types, and their distribution was determined by integration of the appropriate signals.

### Results and Discussion

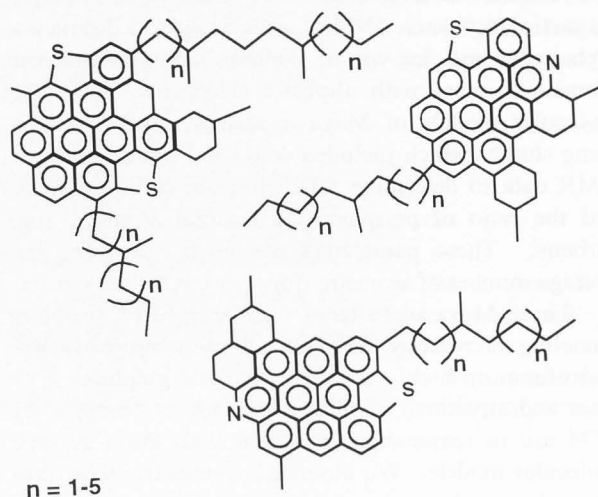
#### Nuclear magnetic resonance (NMR) analysis

The average aromatic cluster parameters for virgin Maya asphaltene (heptane insolubles) were estimated from combined high resolution <sup>1</sup>H and <sup>13</sup>C NMR and atomic hydrogen to carbon ratio (H/C) data. The following is a brief description of the methodology employed to estimate average aromatic cluster size from NMR data and the difficulties inherent in deriving this parameter particularly for asphaltenes.

The average aromatic cluster size for a complex hydrocarbon mixture can be estimated by categorizing all aromatic carbon atoms in three groups: peripheral aromatic carbons attached to protons, peripheral aromatic carbons attached to a saturated or aliphatic carbon, and

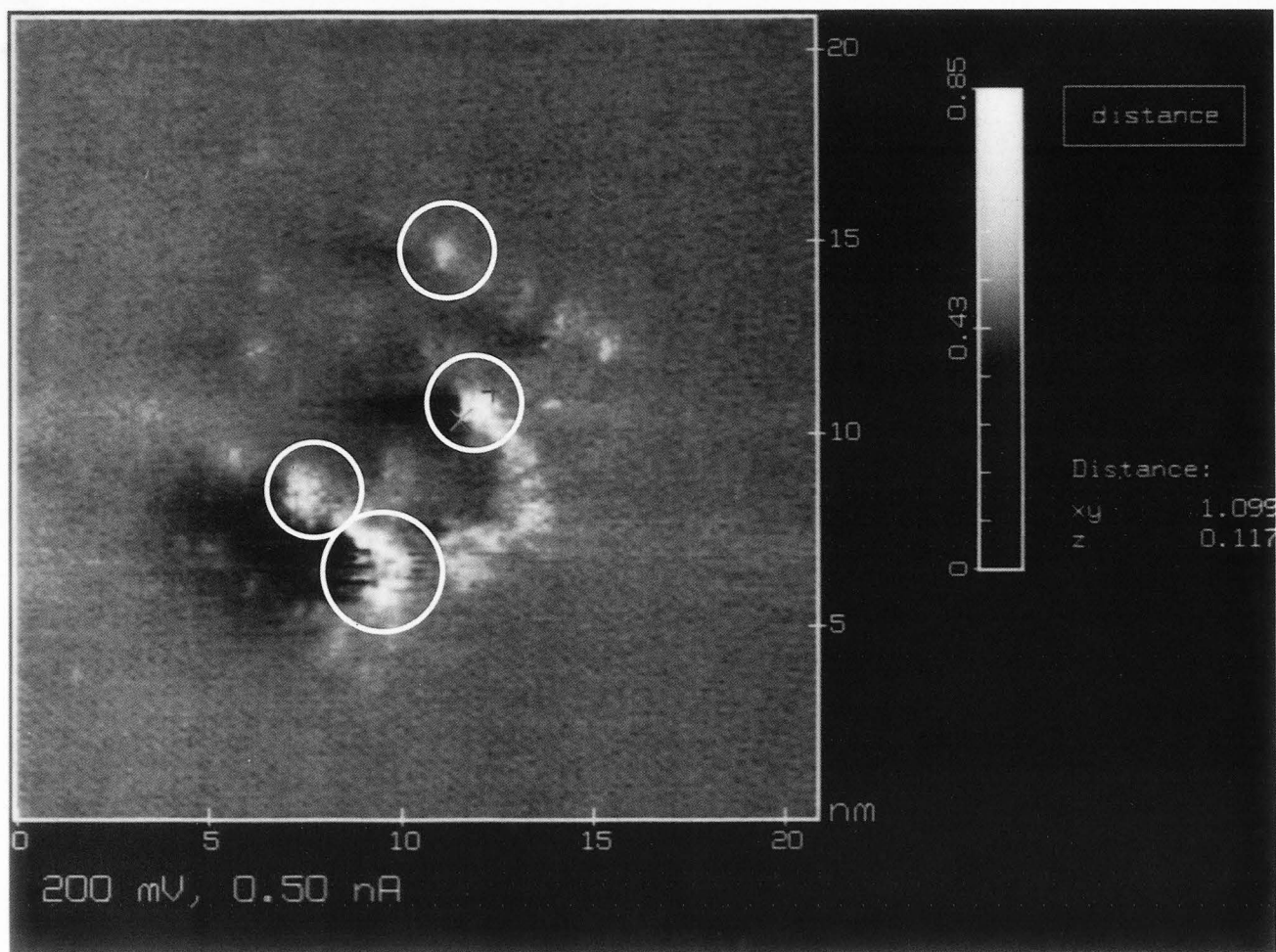
**Table 1.** Carbon and proton types in Maya asphaltene.

Structural Parameter	Maya Asphaltene
Atomic H/C	1.104
Aromatic Protons (%)	13.5
Alpha Protons (%)	17.3
Aromatic Carbons (Ca) (%)	53.3
Attached to Protons	14.9
Attached to Aliphatic	9.3
Internal	29.1
Internal Aromatic/Ca	0.546



**Figure 1.** The <sup>13</sup>C and proton NMR derived average structural units in Maya asphaltene.

internal or bridgehead carbons. While the concentration of peripheral aromatic carbons attached to protons is easily available from the <sup>1</sup>H NMR and atomic H/C data, the distinction between the other two quaternary aromatic carbons is more difficult and relies on the so-called alpha approximation. This approximation states that the H/C of the alpha aliphatic carbons, i.e., the ones directly attached to the aromatic ring, is the same as the H/C of all aliphatic carbons. This approximation has been found to be quite valid for lower boiling point hydrocarbon mixtures, such as gas and oils. Assuming that this approximation holds for asphaltenes as well, concentrations of all three aromatic carbon types can be computed from <sup>1</sup>H and <sup>13</sup>C NMR data. The data obtained on the Maya asphaltene sample from NMR measurements and computed using the alpha approximation are shown in Table 1.



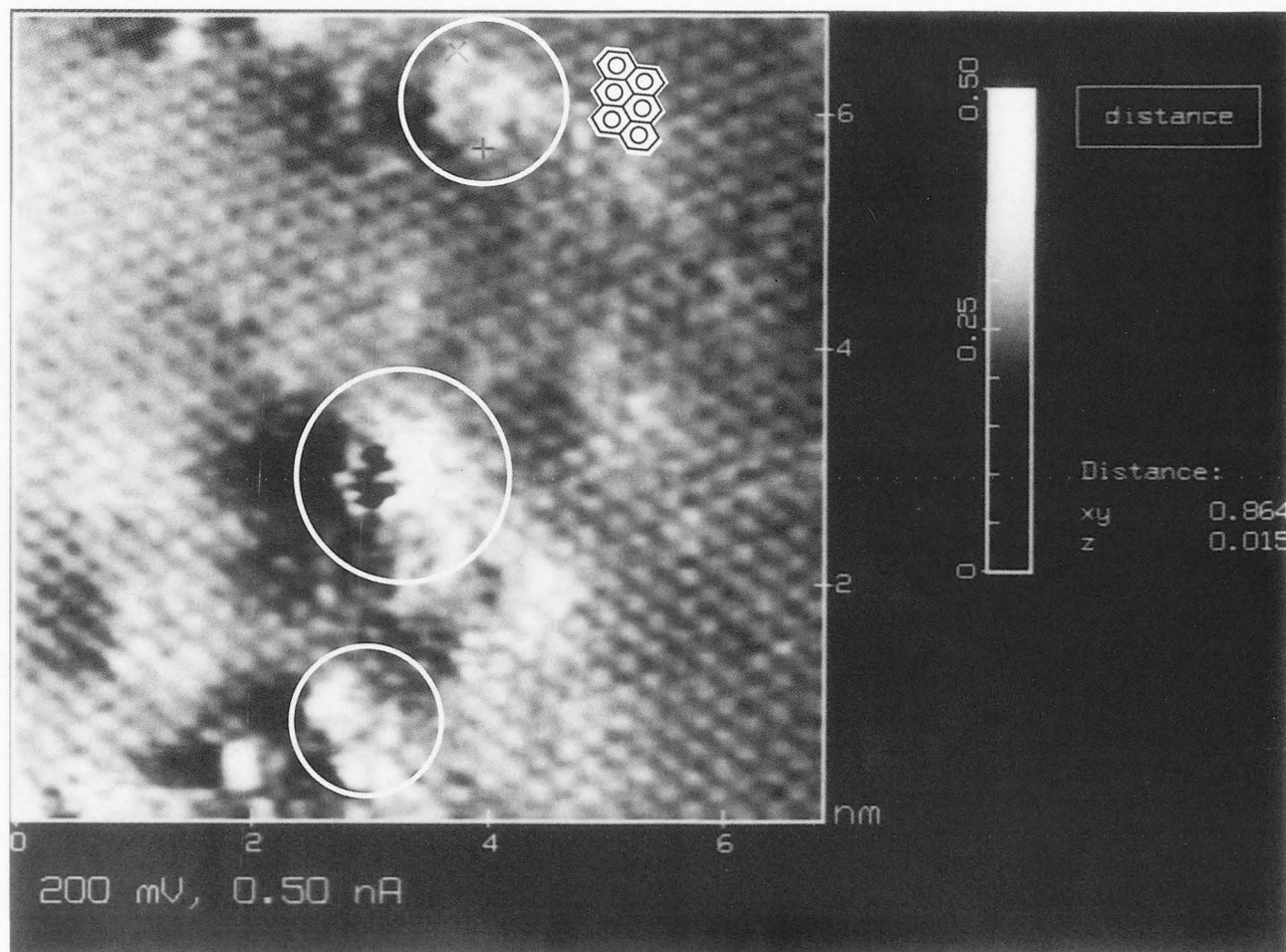
**Figure 2.** A constant current STM image with a  $210 \text{ \AA}$  view of graphite at atomic resolution with a cluster of asphaltenes appearing as bright current spots ( $V_T = 200 \text{ mV}$ ,  $I_T = 0.5 \text{ nA}$ ). Individual adsorbates are circled.

The fraction of total aromatic carbons that are internal (Table 1) is directly correlated to the number of carbons in an aromatic cluster. This correlation is based on a model that incorporates a combined linear and circular aromatic ring condensation to describe the aromatic cluster growth with increasing number of carbon atoms, between the two limiting cases of benzene and graphite (Sethi *et al.*, 1988; Solum *et al.*, 1989). This correlation model applied to the data in Table 1 yields an average number of carbon atoms per aromatic cluster to be approximately 30 (9 condensed rings) for the virgin Maya asphaltenes. Possible structural features of the virgin asphaltene molecule that include cyclic and linear aliphatic carbon atoms are illustrated in Figure 1. Three possible structural units of the virgin asphaltene are shown where the aliphatic side-chains repeat units range from  $n = 1-5$ . Though no direct evidence of the precise structure groups that contain heteroatoms, N, S, O etc., is available, these are assumed to be part of the ring

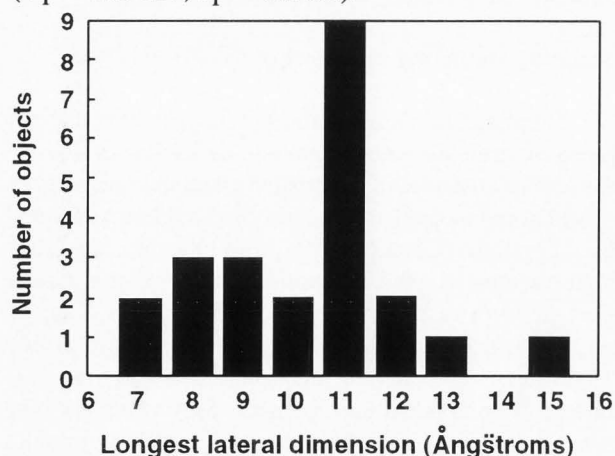
structure, e.g., thiophenic functional groups for S. These NMR derived structural models form the basis of input for the scanning tunneling microscopy study.

### Scanning tunneling microscopy (STM) analysis

Scanning tunneling microscopy is a direct real space probe of structure convoluted with molecular orbital effects. The structure of adsorbates on model surfaces resolved at the molecular level has been applied to a number of systems (Chiang, 1992). For example, the ultra-high vacuum (UHV) adsorption study of coadsorbed benzene with carbon monoxide on Rh(111) (Chiang *et al.*, 1988) and naphthelene on Pt(111) (Hallmark *et al.*, 1991) have resolved the individual aromatic ring features. In an ambient environment, STM studies of the adsorption geometry of alkylcyanobiphenyl on graphite has resolved the individual aromatic groups and alkyl chains (Mizutani *et al.*, 1990; Smith *et al.*, 1990).



**Figure 3 (above).** A constant current STM image with a 68 Å field of view. Three asphaltene regions are arbitrarily circled. The asphaltene at the top which is measured to the right is 8.6 Å across appears to resemble several condensed rings as shown in the schematic ( $V_T = 200$  mV,  $I_T = 0.5$  nA).

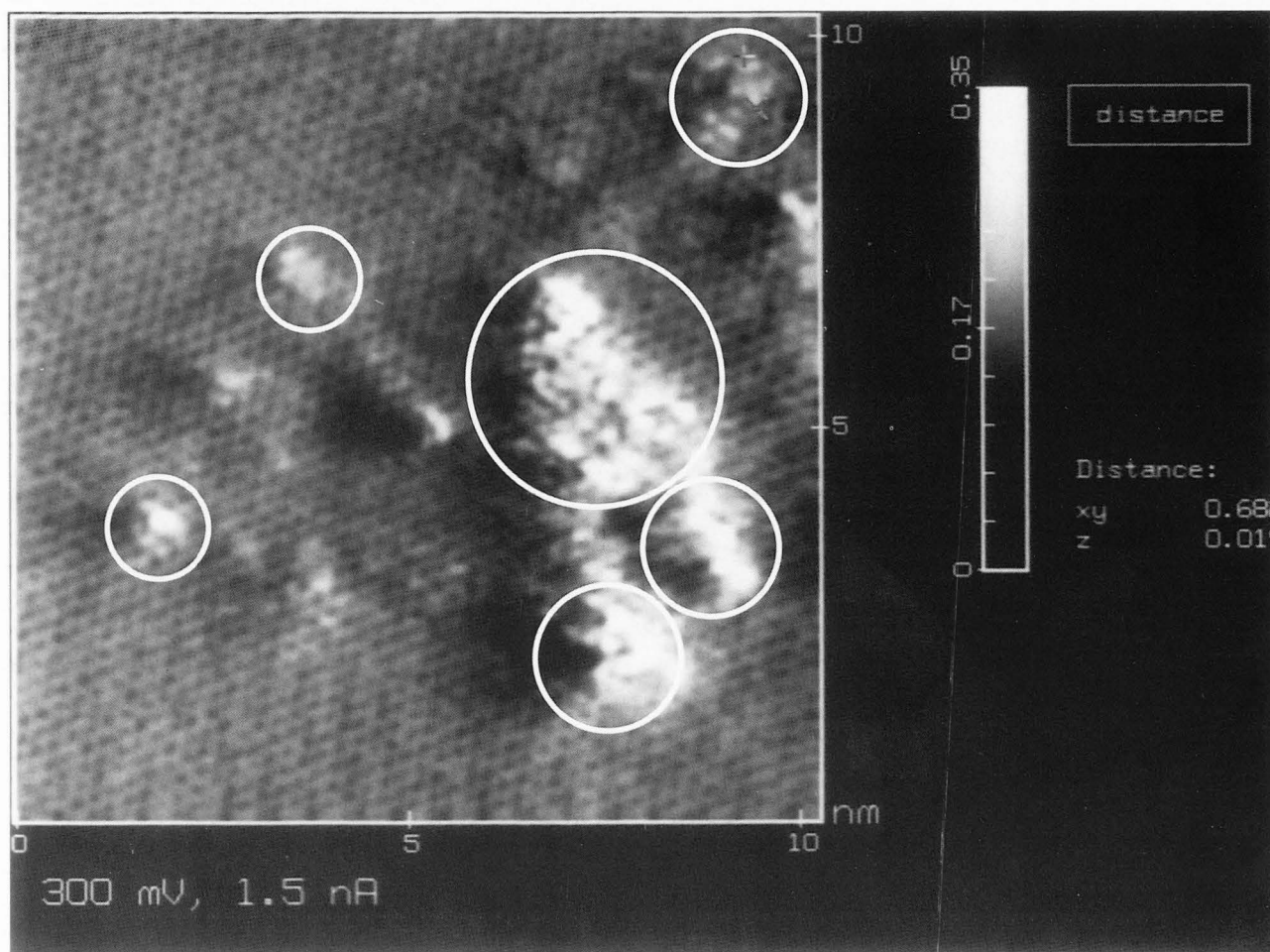


**Figure 4.** A histogram of the distribution of asphaltene sizes observed by STM in Maya asphaltene.

The Langmuir-Blodgett deposition of cadmium arachidate on graphite as viewed by STM shows carbon atom resolution of the alkyl chain (Fuchs, 1988; Mizutani *et al.*, 1988). Macromolecular high resolution STM imaging indicated the symmetry and dimensions of copper phthalocyanine (Lippel *et al.*, 1989) and the aggregate nature of vanadynaphthalocyanine (Manivannan *et al.*, 1993).

Previous STM imaging of Rawati asphaltenes (Watson and Barteau, 1994) at high concentrations ( $5 \times 10^{-2}$  wt%) in pyridine has indicated the self-assembly nature of the alkyl sidechains with large regions of self-assembled asphaltenes. This study was performed in the low concentration regime for the Maya asphaltenes ( $1-5 \times 10^{-3}$  wt%) in order to study the molecular structural units as determined from NMR rather than their intermolecular assemblies.

A typical 200 Å image of a cluster of asphaltenes is shown in Figure 2. The atomically resolved graphite substrate is visible and a group of asphaltenes are observed as the higher contrast white regions. The dimensions are measured from top views of the images as full



**Figure 5.** A 100 Å field of view constant current STM image showing the hexagonal ring resolution of the graphite substrate. A series of smaller asphaltene structural units are visible as is a larger 40-50 Å structure ( $V_T = 304$  mV,  $I_T = 1.5$  nA). Individual adsorbates are circled. The larger structure is arbitrarily grouped as three separate circled regions.

widths of the observed current perturbations. The dark areas to the left of the high contrast asphaltenes are believed to be scanning artifacts. Constant height images were obtained with minimized z-piezoelectric feedback gain and fast scan rate (25-50 Hz). A small finite gain was maintained. As a result, as the tip travels from right to left over a molecular adsorbate, the tip withdraws slightly over the molecule which results in a reduced tunneling current on the opposite side of the molecule from the scan direction. Inspection of the original image data reveals the presence of the substrate image at reduced contrast. A higher resolution STM image of a 66 Å region with several asphaltenes present is shown in Figure 3. The asphaltene indicated in the upper half of the Figure 3 (circled) has a dimension of 8.6 Å and is similar in appearance and size to six condensed aromatic rings. We have arbitrarily circled

several asphaltene structures in Figures 2 and 3. However, we did not exclude other features that appeared in these images from our measurement of a distribution of sizes. The asphaltenes by their very nature are a heterogeneous set of organic molecules varied in functionality and size. An attempt to characterize individual molecular species would be futile because of their heterogeneity. Therefore, we believe it is best to characterize the asphaltenes by means of a measurement of the distribution of sizes observed. A detailed measurement over twenty-four separate entities in approximately ten individual images yields an average full width dimension of  $10.4 \text{ Å} \pm 1.9 \text{ Å}$ . A comparison was made to a random set of ten measurements from the possible NMR-derived asphaltene structural units shown in Figure 1, excluding the aliphatic sidechains. The measurements were made by calibration of the C-C bond length at 1.42 Å and

making several measurements across the condensed ring portion of the three structural units presented. The average NMR dimension derived in this manner is  $11.1 \text{ \AA} \pm 1.4 \text{ \AA}$  for the condensed ring portion of the possible structural models. The reasonable agreement obtained between the NMR structural models and the STM observation argues in favor of the NMR molecular models.

We observed a distribution of sizes for the asphaltenes as shown in Figures 2 and 3; that distribution is presented in the histogram of Figure 4 where we plot the number of observations with the largest observed dimension as shown. We find that the distribution is asymmetric which is consistent with our findings from gel permeation chromatography with a distribution of both small and larger sizes. An example of the heterogeneity in the distribution that we observe by STM is shown in Figure 5 where we find small features in the presence of a larger structure. The larger structure is interesting since it appears to be comprised of three separate structural units which are individually  $< 20\text{-}30 \text{ \AA}$ . It is not clear if the large structure is an aggregate of three smaller units or a single structure connected by aliphatic linkages. Although we do not have clear evidence for the existence of aliphatic side-chains, there is weak fine structure existing in the vicinity of many of the smaller structures that we observe. For example, in Figure 3 the marked region has fine structure to the lower right section of that object. Similarly, in Figure 5, the small bright objects in the center top of the image have weak fine structure connecting these regions. At low bias voltages, aromatic structures would be emphasized and aliphatic regions suppressed, hence, we might be biasing our observations toward the aromatic structures. The appearance of larger structures was not uncommon in our imaging results and is possibly consistent with previous observations of self-assembly of asphaltenes (Watson and Barteau, 1994).

### Conclusions

The  $^{13}\text{C}$  and  $^1\text{H}$  NMR analysis predicts small 6-9 ring condensed aromatic ring structural units with aliphatic side-chains for the virgin Maya asphaltene. The comparison of NMR structural models and STM direct observation reveals an agreement between the distribution of aromatic cluster sizes predicted and observed. The broad distribution ranges from several condensed rings to large macromolecular structures in excess of 30-50  $\text{\AA}$ . This study was performed at very low concentrations ( $1\text{-}5 \times 10^{-3}$  wt%). During hydroprocessing, NMR has shown condensation reactions to occur and the average aromatic cluster size of the residue to grow in size and number (Joseph and Sethi, 1994, unpublished results). One would be tempted to extrapolate to the high

concentration regime where very large aggregates and self-assemblies might dominate and form the basis of coke precipitation during the hydroprocessing process.

### References

- Chiang S (1992). Molecular imaging by STM. In: Scanning Tunneling Microscopy II. Guntherodt HJ, Wiesendanger R (eds.). Springer-Verlag, New York. 181-195.
- Chiang S, Wilson RJ, Mate CM, Ohtani H (1988). Real space imaging of coadsorbed CO and benzene molecules on Rh(111). *J. Microsc.* **152**, 567-571.
- Fuchs H (1988). High resolution STM-studies on graphite and Langmuir-Blodgett films. *Phys. Scr.* **38**, 264-268.
- Hallmark VM, Chiang S, Brown JK, Woll Ch (1991). Real space imaging of the molecular organization of naphthalene on Pt(111). *Phys. Rev. Lett.* **66**, 48-51.
- Herzog P, Tchoubar D, Espinat D (1988). Macrostructure of asphaltene dispersions by small angle X-ray scattering. *Fuel* **67**, 245-254.
- Lippel PH, Wilson RJ, Miller MD, Woll Ch, Chiang S (1989). High resolution imaging of copperphthalocyanine by scanning tunneling microscopy. *Phys. Rev. Lett.* **62**, 171-174.
- Manivannan A, Nagahara LA, Hashimoto K, Yanagi H, Kouzeki T, Ashida M (1993). Imaging of vanadynaphthalocyanine aggregates by scanning tunneling microscopy. *Langmuir* **9**, 771-775.
- Mizutani W, Shigeno M, Watanabe K, Shigo S, Ono M, Kajimura K (1988). Observation of Langmuir-Blodgett films by scanning tunneling microscopy. *Jpn. J. Appl. Phys.* **27**, 1803-1807.
- Mizutani W, Shigeno M, Ono M, Kajimura K (1990). Voltage-dependent scanning tunneling microscopy images of liquid crystals on graphite. *Appl. Phys. Lett.* **56**, 1974-1976.
- Ravey JC, Ducouret G, Espinat D (1988). Asphaltene macrostructure by small angle neutron scattering. *Fuel* **67**, 1560-1567.
- Sethi NK, Facelli FC, Pugmire RJ, Grant DM (1988). Quantitative determination of different carbon types in fusinite and anthracite coals from C-13 nuclear magnetic resonance chemical shielding line-shape analysis. *Anal. Chem.* **60**, 1574-1579.
- Sheu EY, DeTar MM, Storm DA, DeCanio SJ (1992). Aggregation and kinetics of asphaltenes in organic solvents. *Fuel* **71**, 299-302.
- Smith DPE, Horber JKH, Binnig G, Nejo G (1990). Structure, registry and imaging mechanism of alkylcyanobiphenyl molecules by tunneling microscopy. *Nature* **344**, 641-644.

Solum MS, Pugmire RJ, Grant DM (1989). C-13 solid-state NMR of Argonne premium coals. *Energy Fuels* **3**, 187-193.

Speight JG (1991). *The Chemistry and Technology of Petroleum*. Marcel Dekker, New York. pp. 1980-1995.

Storm DA, Barresi RJ, DeCanio SJ (1991). Colloidal nature of vacuum residue. *Fuel* **70**, 779-782.

Strausz OP, Mojelsky TJ, Lown EM (1992). The molecular structure of asphaltene: an unfolding story. *Fuel* **71**, 1355-1363.

Watson BA, Barteau MA (1994). Imaging petroleum asphaltenes using scanning tunneling microscopy. *Ind. Eng. Chem. Res.* **33**, 2358-2363.

Zajac GW, Gallas JM, Alvarado-Swaisgood AE (1994a). Tunneling microscopy verification of an X-ray scattering derived molecular model of tyrosine-based melanin. *J. Vac. Sci. Technol. B* **12**, 1512-1516.

Zajac GW, Gallas JM, Cheng J, Eisner M, Moss SC, Alvarado-Swaisgood AE (1994b). The fundamental unit of synthetic melanin: A verification by tunneling microscopy of X-ray Scattering results. *Biochim. Biophys. Acta*, **1199**, 271-278.

### Discussion with Reviewers

**D.J. Thomson:** How were the sizes of the adsorbates measured? For example, was full width half maximum used? Were the measurements automated or were they performed by eye? How were the individual adsorbates identified? For example, in Figure 2, how are the two features in the center identified as clusters and not as individual adsorbates?

**Authors:** The sizes of the adsorbates were measured from top-views of the images rather than by hand or in cross-section. We felt that the underlying graphite substrate would be useful as an internal scale. Since the current fluctuations represented by the adsorbates on the graphite are highly localized spatially, we believe the full widths are representative of the dimension of the adsorbate. This measurement technique is very similar to that performed on model organic compounds such as ordered liquid crystal molecules (Mizutani *et al.*, 1990).

We identified individual adsorbates by changing contrast between substrate and adsorbate until we could isolate the major components to a given adsorbate from regions nearby which appear to have resulted from "blooming" effects. In this manner of variable contrast, we could assign two individual features in the two regions of the central portion of Figure 2 rather than several single adsorbates.

**D.J. Thomson:** There is still considerable debate about the imaging mechanism when it comes to the imaging of

molecules of this type. Perhaps the authors could add a few sentences about the assumptions they have made in interpreting their images.

**Authors:** We agree that a detailed understanding of the imaging mechanism for molecular adsorbates is currently lacking although several have been advanced. But we must point out that STM studies of model compounds, such as the work of Dr. Chiang (personal communication) and that of ordered liquid crystal molecules (Mizutani *et al.*, 1990), reveals proper molecular dimensions, structural units and symmetries. We have tried to objectively measure dimensions of the adsorbates that we can easily distinguish for a comparison to the structural model derived from the NMR. The only "interpretation" of the images that we permit ourselves is that the current fluctuations we observe are due to the perturbations of the substrate wave-function by the presence of the molecular orbitals of an organic asphaltene adsorbate. We have checked separately the bare substrate and solvent (THF) for impurities which might give rise to similar features without success.

We do agree that ambiguities arise from the complicated structures observed. But we quantified only those features for which no such ambiguity exists.

**P.S. Weiss:** In Figure 2, the right-most circled feature is part of a larger moon-shaped feature. Similarly what about the dark areas? How is it that the authors can assign some features to the molecules and not others?

With regard to Figure 3, the uppermost feature is also part of something larger. How can the authors assign the orientation of the molecules as they do? Once again, what about the dark areas?

In all the images, features of various sizes appear. It is troubling that the authors select features of approximately the "right" size and then analyze the size distributions of the selected features.

**Authors:** As stated in the text, the dark areas to the left of the high contrast asphaltenes are believed to be a scanning artifact. Constant height images were obtained with minimized z-piezoelectric feedback gain and fast scan rate (25-50 Hz). A small finite gain was maintained. As a result, as the tip travels from right to left over a molecular adsorbate, the tip withdraws slightly over the molecule which results in a reduced tunneling current on the opposite side of the molecule from the scan direction. Inspection of the original image data reveals the presence of the substrate image at reduced contrast.

We have arbitrarily circled several asphaltene structures in Figures 2 and 3. However, we do not exclude other features that appear in these images from our measurement of a distribution of sizes. The asphaltenes by their very nature are a heterogeneous set of organic molecules varied in functionality and size. An attempt



to characterize individual molecular species would be futile because of their heterogeneity. Therefore, we believe it is best to characterize the asphaltenes by means of a measurement of the distribution of sizes observed.

**Reviewer III:** For readers who are not NMR experts, it would be beneficial to give a brief explanation of the cluster model and the alpha approximation.

**Authors:** The cluster model relies on the correlation between the ratio of all aromatic carbons that occupy bridgehead position, i.e., junctions of condensed aromatic rings, and the number of aromatic carbons in a cluster. For example, this ratio is zero for benzene that has no bridgehead carbons, 0.2 for naphthalene (2 out of 10 carbons are in bridgehead position), 0.286 for anthracene, etc. Thus, by determining this ratio, one can estimate the aromatic cluster size. This correlation, however, depends upon whether a linear or a circular ring condensation is assumed for the cluster. For instance, this ratio is 0.33 for tetracene with 18 carbons in 4 linearly condensed rings, while a higher ratio of 0.375 exists for pyrene that has fewer carbons (16) but are arranged in 4 circularly condensed rings. To circumvent this ambiguity of the correlation to some extent, a combined linear/circular model was developed that is fully explained in Solum *et al.* (1989). This combined model was used in this work.

In order to determine the fraction of bridgehead carbons, the so called alpha approximation is used. This approximation states that on average the number of hydrogen atoms attached to an aliphatic carbon directly attached to an aromatic ring, i.e., an alpha carbon, is the same as the average number of hydrogen atoms on all aliphatic carbons.  $^{13}\text{C}$  NMR data provides the fraction of total carbon that are aromatic, but does not permit differentiation between the bridgehead and the alpha aromatic carbons.  $^1\text{H}$  NMR data on the other hand allows measuring the total number of hydrogens that are attached to alpha carbons. Using the alpha approximation, one can, therefore, link the information from  $^{13}\text{C}$  and  $^1\text{H}$  NMR to estimate bridgehead carbon population separate from alpha carbons.

**Reviewer III:** Can the authors compare their liquid NMR data with  $^{13}\text{C}$  solid state data? This comparison may provide some information on the reactions that the authors speculate may occur in asphaltenes in solution.

**Authors:** Solid state  $^{13}\text{C}$  NMR spectra of such complex hydrocarbons as asphaltenes lack sufficient resolution to permit the detailed structural analysis as has been attempted here. Also, doubts remain as to the quantitative accuracy of the solids NMR data due to the effects of free radicals and paramagnetic metal impurities. We feel that whenever possible, solution state NMR analysis is to be preferred over solid state especially if one is interested in good quantitative data. The question of comparing solution and solids NMR data to speculate on the chemistry of hydroprocessing is not valid.

**Reviewer III:** How was the content and structure of N, O, and S determined?

**Authors:** The content of heteroatoms was determined using wet chemical methods. The types of structural groups containing these heteroatoms were assumed *vide infra*.