

# Calculation of average molecular descriptions of heavy petroleum hydrocarbons by combined analysis by quantitative <sup>13</sup>C and DEPT-45 NMR experiments

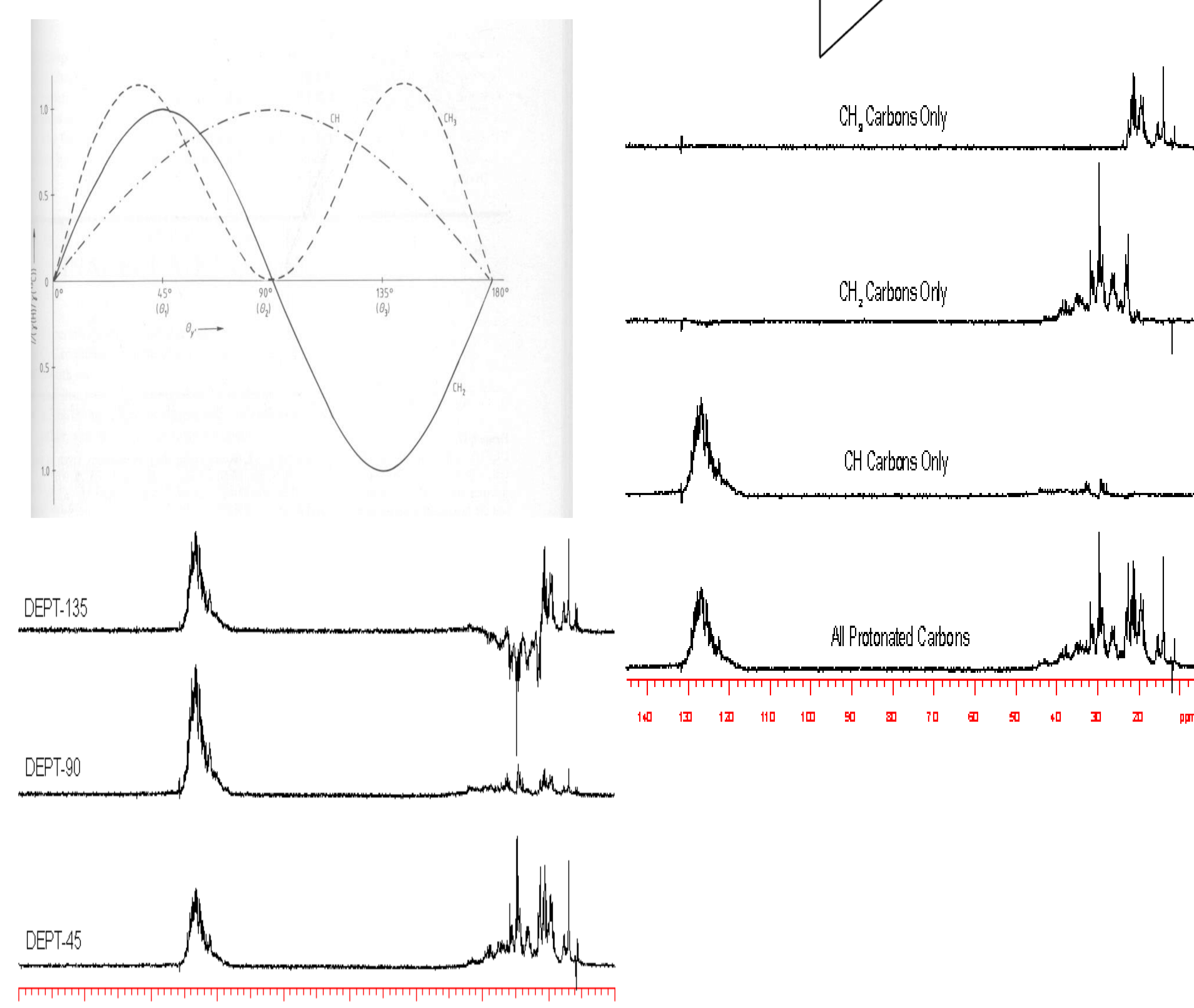
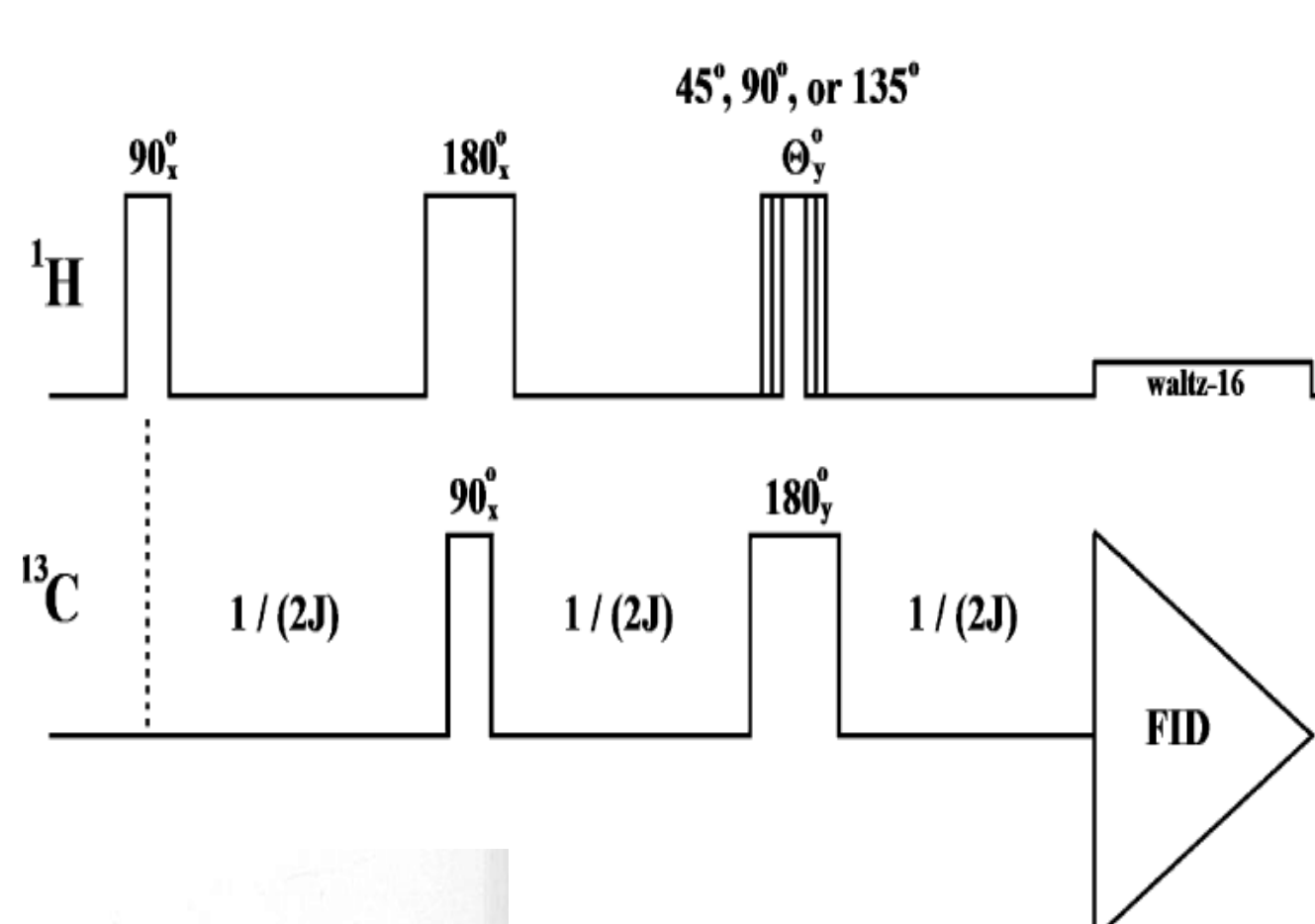
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## Overview

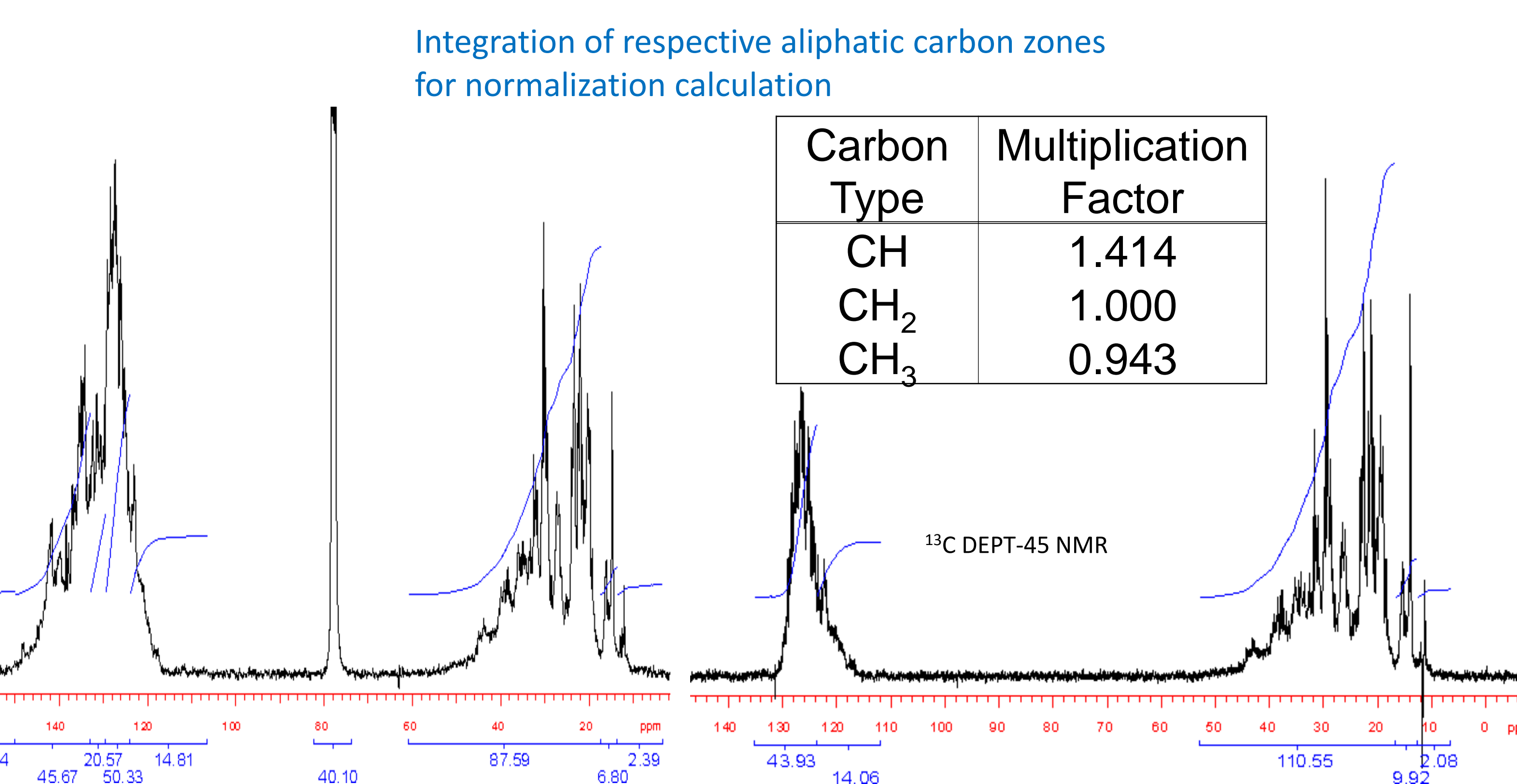
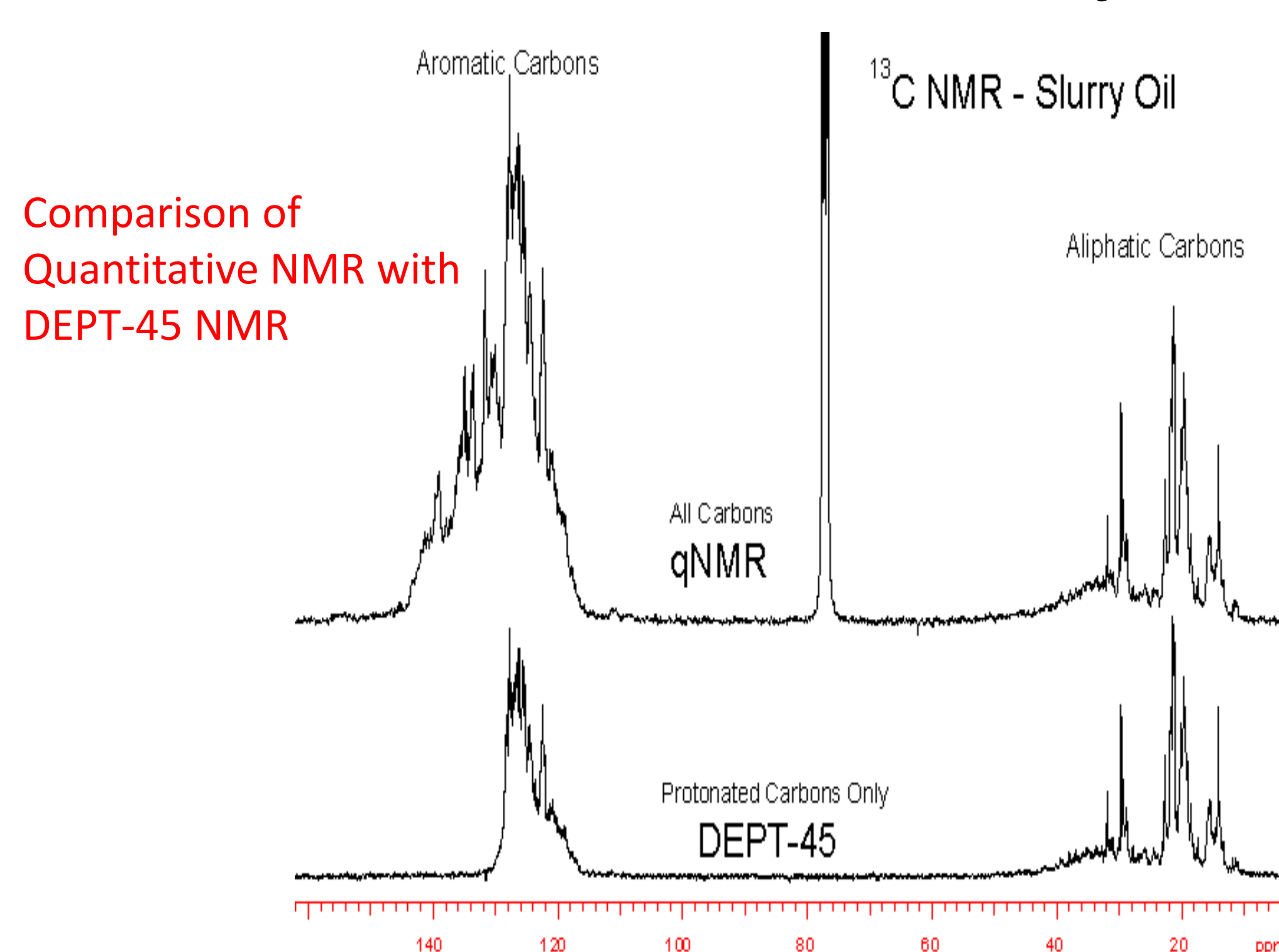
Over the years much debate has centered around the validity and accuracy of NMR measurements to accurately describe the sample chemistry of heavy petroleum materials. Of particular issue has been the calculated size of aromatic ring systems that in general seem to be underestimated in size by NMR methods. This underestimation is principally caused by variance in chemical shift ranges used by researchers to define the aromatic carbon types observed in the <sup>13</sup>C NMR spectrum, in particular the bridgehead aromatic carbons that can be shown to overlap strongly with the protonated aromatic carbons. The ability to discern between bridgehead aromatic carbons and protonated carbons in the 108-129.5 ppm region of the spectrum is key in the derivation of molecular parameters that properly describe the "molecular average" carbon structure present in the sample. Utilizing methodologies developed by Pugmire and Solum<sup>1</sup> for the solid-state <sup>13</sup>C NMR analysis of coals and other carbonaceous solids we have developed a liquid-state <sup>13</sup>C NMR methodology that allows the relative quantification of overlapping protonated and bridgehead aromatic carbon signals to be determined. The NMR experiments involve the combined analysis of both quantitative <sup>13</sup>C single pulse excitation which observes "all carbons in the sample" and DEPT-45 which observes only the protonated carbons in the sample. Though the DEPT-45 results are not quantitative across all carbon types (CH, CH<sub>2</sub>, and CH<sub>3</sub>) due to polarization transfer differences, the technique is well enough understood that simple multiplication factors allow the relative absolute intensities of the different carbons to be determined. An additional aspect of the experiments is the addition of a standard material (Polyethyleneglycol (PEG) polymer) that allows the calculation of the absolute percentage of the carbons that are observed by the <sup>13</sup>C NMR technique. This allows the relative amount of bridgehead carbon to be calculated by direct comparison of the aromatic region with the standard signal intensity. The average ring system sizes derived from these NMR experiments tend to be several ring systems larger than has been calculated in previous studies. In asphaltenes for example the ring systems are 5-7 rings in size rather than the 3-4 rings reported previously<sup>2</sup>. The ring sizes determined by this new combined NMR method are in agreement with FTICR-MS and fluorescence measurements<sup>3-6</sup>.

## DEPT Experiment

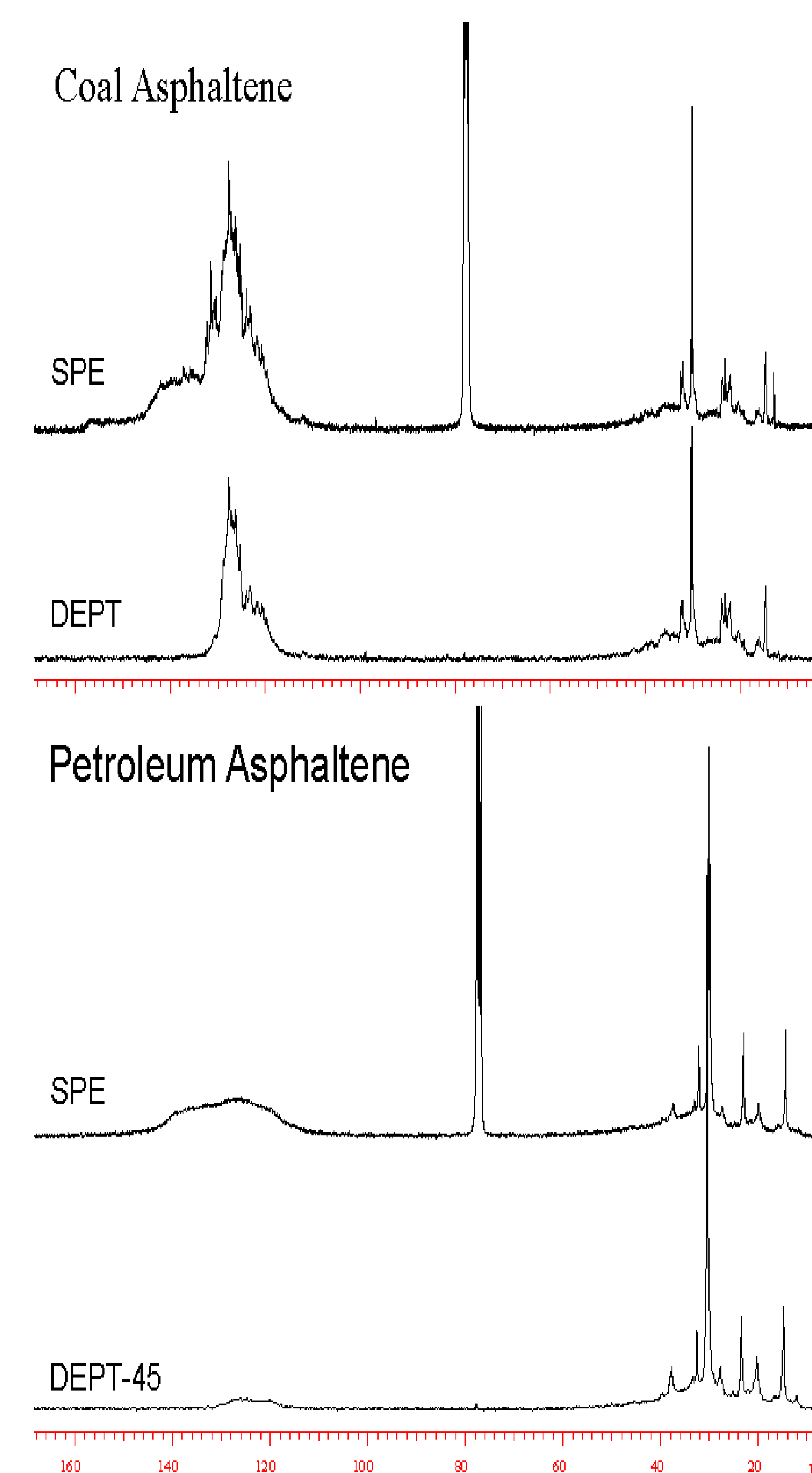


	CH peak intensity	CH <sub>2</sub> peak intensity	CH <sub>3</sub> peak intensity	Relative noise level
θ° <sup>1</sup> H pulse:	sinθ	2sinθcosθ	3sinθcos <sup>2</sup> θ	
s1. 45° <sup>1</sup> H pulse:	n	0.707	1.060	1.0
s2. 90° <sup>1</sup> H pulse:	2n	0	0	1.414
s3. 135° <sup>1</sup> H pulse:	n	0.707	-1.060	1.0

## <sup>13</sup>C NMR Analysis



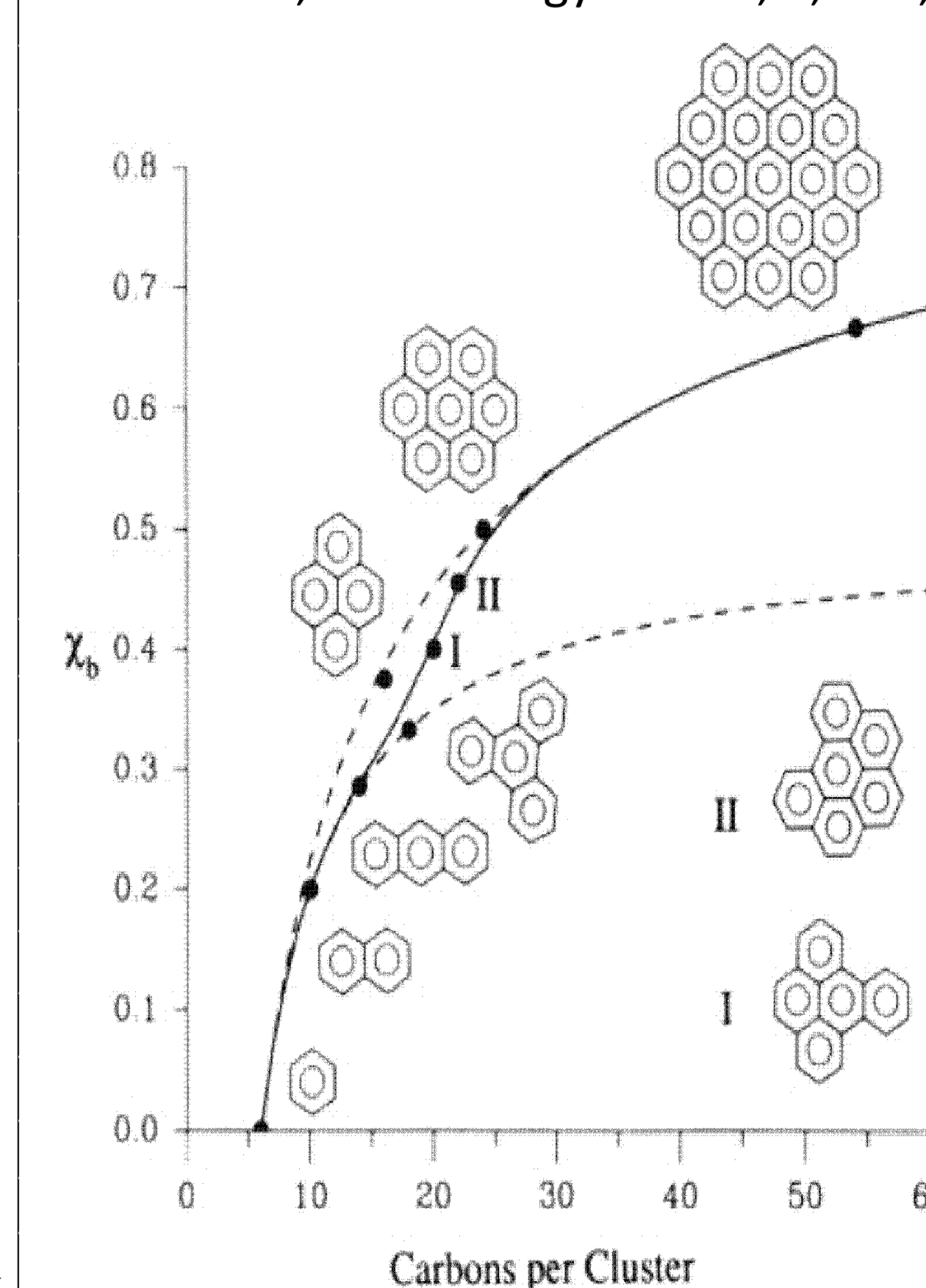
## Examples



## Carbon Chemical and Molecular Parameters

Parameter	Shift Range (ppm)	Description	Calculation
F <sub>a</sub>	90-240	Carbon Aromaticity	
F <sub>a</sub> <sup>+</sup>	90-165	Aromaticity - not including Carbonyl/Carbonyl	F <sub>a</sub> <sup>+</sup> = F <sub>a</sub> - F <sub>a</sub> <sup>C</sup>
F <sub>a</sub> <sup>C</sup>	165-240	Carboxylic and Carbonyl Carbon	
F <sub>a</sub> <sup>CO</sup>	185-240	Carbonyl - Ketone, Aldehyde	
F <sub>a</sub> <sup>COO</sup>	165-185	Carboxylic - Acid, Ester, Amide	
F <sub>a</sub> <sup>P</sup>	150-165	Phenolic Aromatic Carbon	
F <sub>a</sub> <sup>S</sup>	135-150	Alkyl-Substituted Aromatic Carbons	
F <sub>a</sub> <sup>H</sup>	90-165	Protonated Aromatic Carbon	DD Aromatic - F <sub>a</sub> <sup>H</sup> = F <sub>a</sub> <sup>H</sup> M <sub>0</sub> G
F <sub>a</sub> <sup>N</sup>	90-165	Non-Protonated Aromatic Carbon	F <sub>a</sub> <sup>N</sup> = F <sub>a</sub> <sup>+</sup> - F <sub>a</sub> <sup>H</sup>
F <sub>a</sub> <sup>B</sup>	90-165	Bridgehead Aromatic Carbon	F <sub>a</sub> <sup>B</sup> = F <sub>a</sub> <sup>N</sup> - F <sub>a</sub> <sup>P</sup> - F <sub>a</sub> <sup>S</sup>
F <sub>al</sub>	0-50	Total Aliphatic Carbon	
F <sub>al</sub> <sup>O</sup>	50-90	Oxygenated Aliphatic Carbon	
F <sub>al</sub> <sup>H</sup>	22-50	Protonated Aliphatic Methylenes and Methine	DD Aliphatic - F <sub>al</sub> <sup>H</sup> = F <sub>al</sub> <sup>H</sup> M <sub>0</sub> G
F <sub>al</sub> <sup>M</sup>	0-22	Methyl Carbons	F <sub>al</sub> <sup>M</sup> = F <sub>al</sub> - F <sub>al</sub> <sup>H</sup>
X <sub>b</sub>		Mole fraction of Bridgehead Carbons	X <sub>b</sub> = F <sub>a</sub> <sup>B</sup> / F <sub>a</sub> <sup>+</sup>
C		Carbons per Aromatic Cluster	See Figure 24 - C is calculated from X <sub>b</sub>
σ + 1		Average Number of Alkyl Attachments	σ + 1 = (F <sub>al</sub> <sup>P</sup> + F <sub>al</sub> <sup>S</sup> ) / (F <sub>a</sub> <sup>+</sup> × C)
P <sub>0</sub>		Fraction of Intact Bridges and Loops	P <sub>0</sub> = (F <sub>al</sub> <sup>P</sup> + F <sub>al</sub> <sup>S</sup> - F <sub>al</sub> <sup>M</sup> ) / (F <sub>al</sub> <sup>P</sup> + F <sub>al</sub> <sup>S</sup> )
B.L.		Bridge and Loop Alkyl Attachments	B.L. = P <sub>0</sub> × (σ + 1)
S.C.		Terminal Alkyl Side Chains	S.C. = (σ + 1) - B.L.
M <sub>w</sub>		Average Molecular Weight of a Cluster	M <sub>w</sub> = 12.01 C / (F <sub>a</sub> <sup>+</sup> × %C/100) %C from Elemental
M <sub>c</sub>		Average Molecular Weight of Attachments	M <sub>c</sub> = (M <sub>w</sub> - 12M <sub>0</sub> G) / (12(1-M <sub>0</sub> G)C) × (σ + 1)

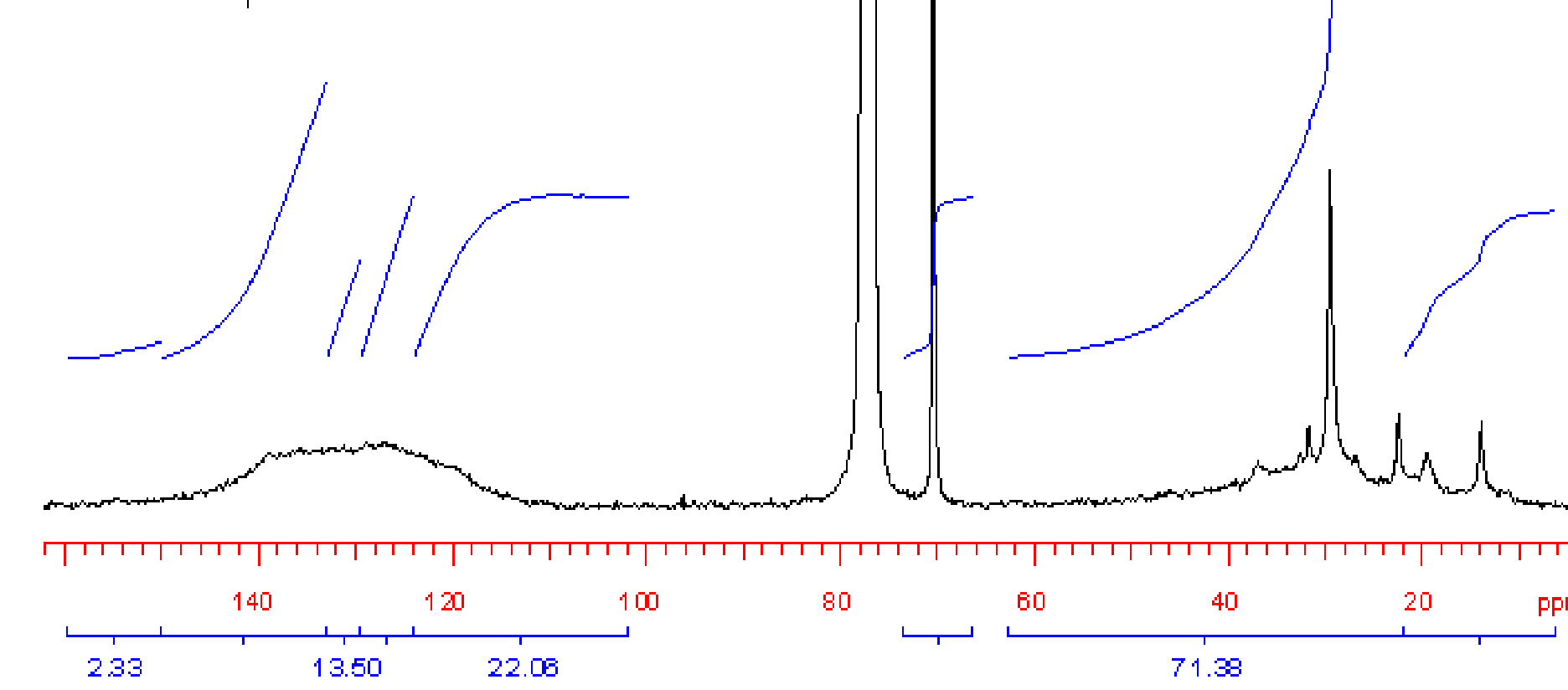
Relationship between mole fraction of bridgehead carbons X<sub>b</sub> and aromatic cluster size (C). From Solum, et al. Energy & Fuels, 3, 187, 1989.



Aggregation estimation by qNMR internal standard technique. PEG acts as a carbon content standard allowing observed carbon to be calculated as well as acting as the DEPT normalization standard.

## Petroleum Asphaltene

PEG = 54.5% C  
Asphaltene = 80.3% C  
Weighted Amounts of Each in Solution  
A simple ratio calculation allows % of asphaltene carbons being observed in the NMR experiment to be calculated.



Carbon NMR Parameter	Slurry Oil	VGO	Petroleum Asphaltene	Coal Asphaltene	Pyrolyzed Coal Extract
Carboxyl Carbon % (F <sub>a</sub> <sup>C</sup> )	0.00	0.00	0.00	0.00	1.13
Carbon Aromaticity % (F <sub>a</sub> )	57.76	37.48	53.49	51.86	87.23
Carbon Aromaticity (No CO) % (F <sub>a</sub> <sup>+</sup> )	57.76	37.48	53.49	51.86	87.23
Carbon Aliphaticity % (F <sub>al</sub> )	42.24	62.52	46.51	48.14	11.64
Phenolic Aromatic C % (F <sub>a</sub> <sup>P</sup> )	0.41	0.67	1.03	0.71	6.43
Substituted Aromatic C % (F <sub>a</sub> <sup>S</sup> )	19.94	15.22	19.29	19.89	22.55
Bridgehead Aromatic C % (F <sub>a</sub> <sup>B</sup> )	23.17	12.14	30.77	28.34	44.95
Protonated/Hetero Aromatic C % (F <sub>a</sub> <sup>H</sup> )	14.24	9.46	2.41	2.92	13.30
Non-Protonated Aromatic C % (F <sub>a</sub> <sup>N</sup> )	43.52	28.02	51.08	48.93	73.93
Methyl Aliphatic C % (F <sub>al</sub> <sup>M</sup> )	13.31	13.18	9.37	9.27	5.25
Methylene/Methine C % (F <sub>al</sub> <sup>H</sup> )	28.92	49.34	37.15	38.87	6.39
X <sub>b</sub>	0.401	0.324	0.575	0.546	0.515
C - Carbons per Aromatic Cluster	19.7	16.5	31.9	28.4	25.7
No. Aromatic Rings per Cluster (linear-cata)	4.4	3.6	7.5	6.6	5.9
No. Aromatic Rings per Cluster (globular-pen)	5.3	4.2	9.6	8.4	7.5
No. Aromatic Rings per Cluster (Average 50/50 per/cata)	4.9	3.9	8.5	7.5	6.7
Clusters per 100C	2.93	2.28	1.68	1.83	3.39
Total Substitutions per Cluster (Alkyl + Phenolic)	6.94	6.98	12.11	11.28	8.55
Carboxyls per Cluster	0.00	0.00	0.00	0.00	0.33
Phenols per Cluster	0.14	0.29	0.61	0.39	1.90
Alkyl-Substitutions per Cluster	6.80	6.68	11.50	10.89	6.65
Average Length of Substitutions	2.08	3.94	2.29	2.34	1.55
P <sub>0</sub> - Fraction of Intact Bridges and Loops	0.35	0.17	0.54	0.55	0.82
B.L. Intact Bridges and Loops per Cluster	2.40	1.19	6.53	6.20	7.00
S.C. Terminal Side Chains per Cluster	4.54	5.79	5.58	5.08	1.55
M <sub>w</sub> - Mw of Average Aromatic Cluster	410.6	558.7	681.1	619.6	385.89
M <sub>d</sub> - Average Mw B.L. and S.C.	25.1	51.8	25.7	24.3	10.8

- 1) Pugmire et al., Energy & Fuels, 3, 187, 1989.
- 2) Sheremata et al., Energy & Fuels, 6, 414, 2004.
- 3) Badre et al., Fuel, 85, 1, 2006.
- 4) Sharmar et al, Energy & Fuels 16, 490, 2002.
- 5) Groenzin and Mullins, "Asphaltenes, Heavy Oils and Petroleomics, Ch. 2.
- 6) Rodgers and Marshall, "Asphaltenes, Heavy Oils and Petroleomics, Ch. 3.