Average Molecular Structure of Gasoline Engine Combustion Chamber Deposits Obtained by Solid-State *13*C, *31*P, and *1*H Nuclear Magnetic Resonance Spectroscopy

Overview

1 > Brief description of a typical carbon-13 NMR Spectrum of a base fuel CCD.

2 > NMR experiments used to obtain total carbon type distribution.

3> Data manipulation to obtain "average molecule" description.

4> "Average molecule" comparisons used to investigate:

i. Structural similarities between CCDs and bituminous coals,

ii. Cylinder-to-cylinder structural variations of CCDs

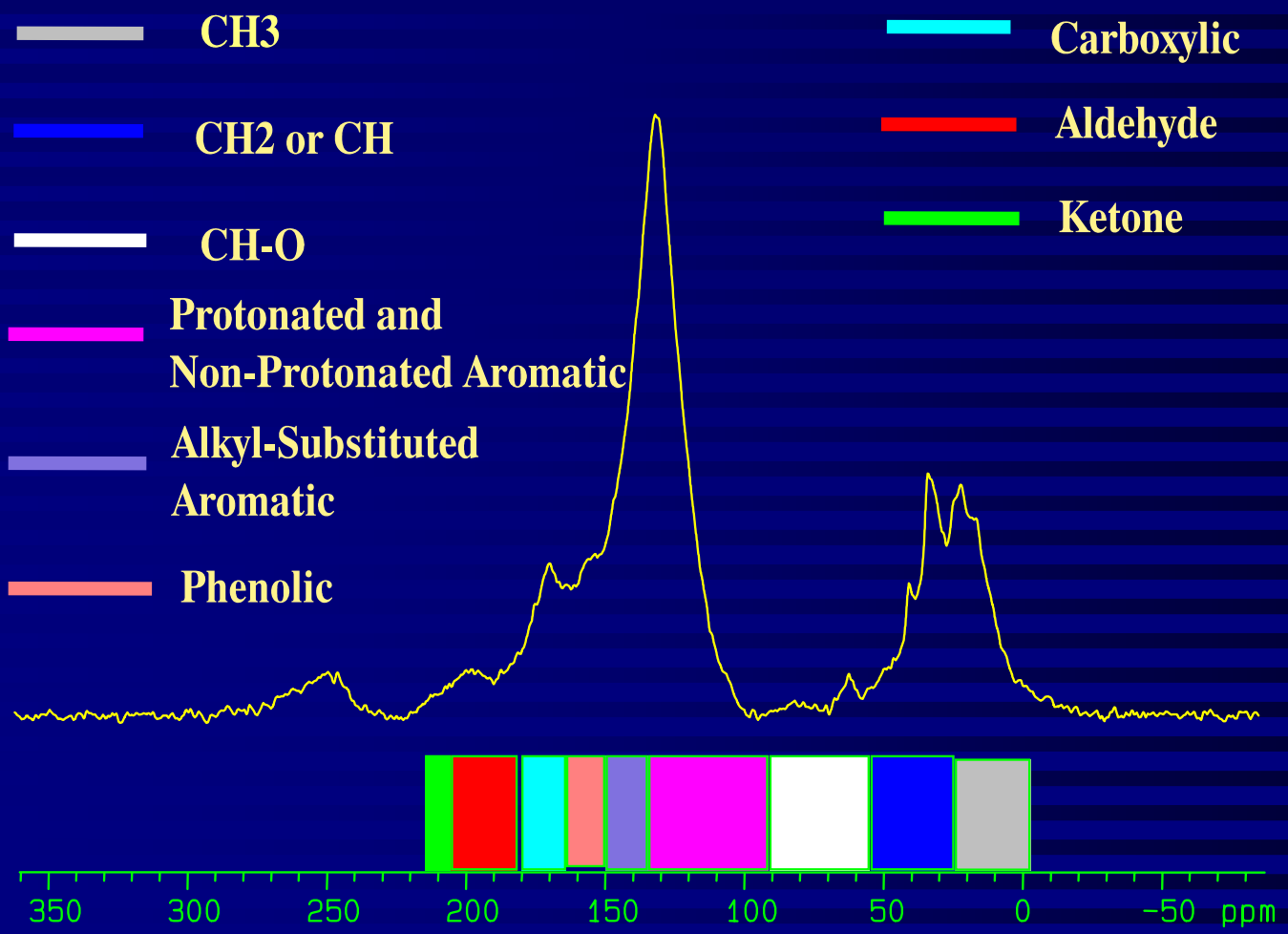
iii. Structuural differences caused by use of different fuels.

5> Honda generator screening test.

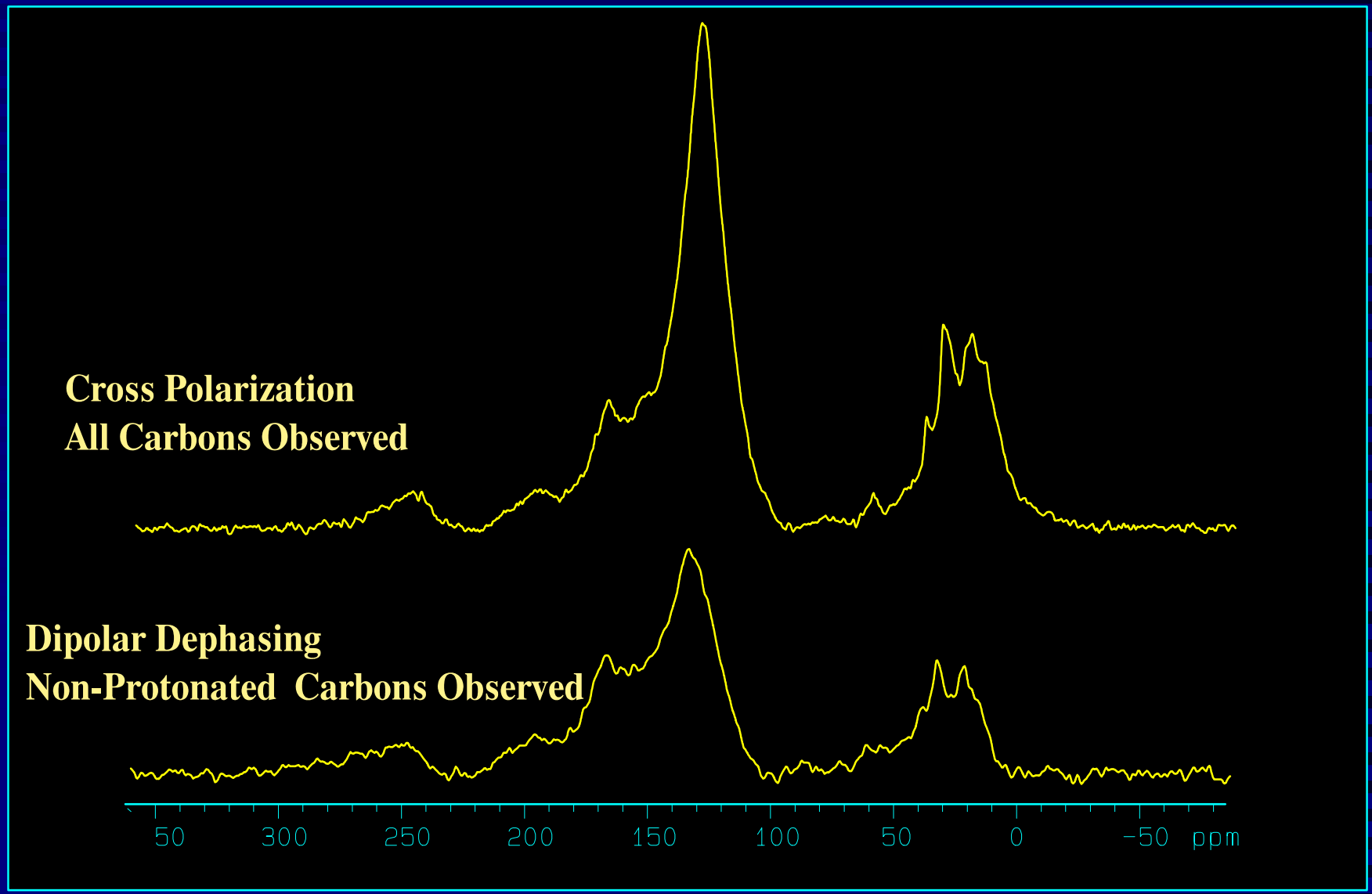
Observation of effects of test and engine modifications.

6> Conclusions and future work.

Regions of Carbon-13 NMR Spectrum Used in the Analysis



Comparison of Experiments Used to Determine Mole Fraction of Bridgehead Aromatic Carbon



NMR Structural Parameters

Description of a Typical 100 Carbons

Parameter	Carbon Type Represented	Typical CCD Values
fa	aromatic/carboxylic/carbonyl	0.77
fa'	aromatic	0.61
faC	carboxylic/carbonyl	0.16
faH	protonated aromatic	0.22
faN	non-protonated aromatic	0.40
faP	phenolic	0.08
faS	alkyl-substituted aromatic	0.16
faB	bridgehead aromatic	0.16
fal	aliphatic	0.23
falH	methylene/methine	0.13
fal*	methyl	0.05
falO	alcohol/ether	0.05

$faB/fa' = 0.26 = X_b$

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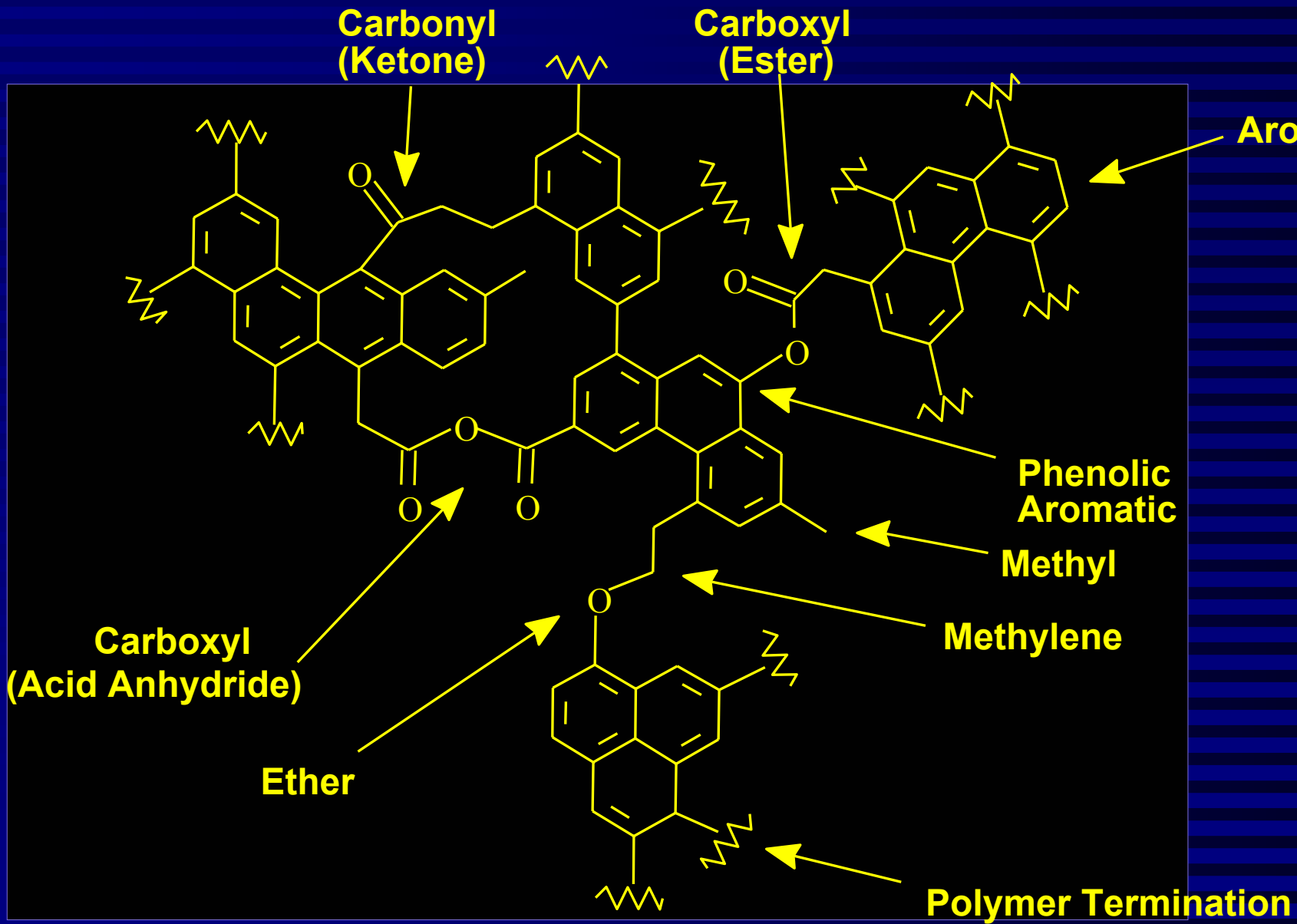
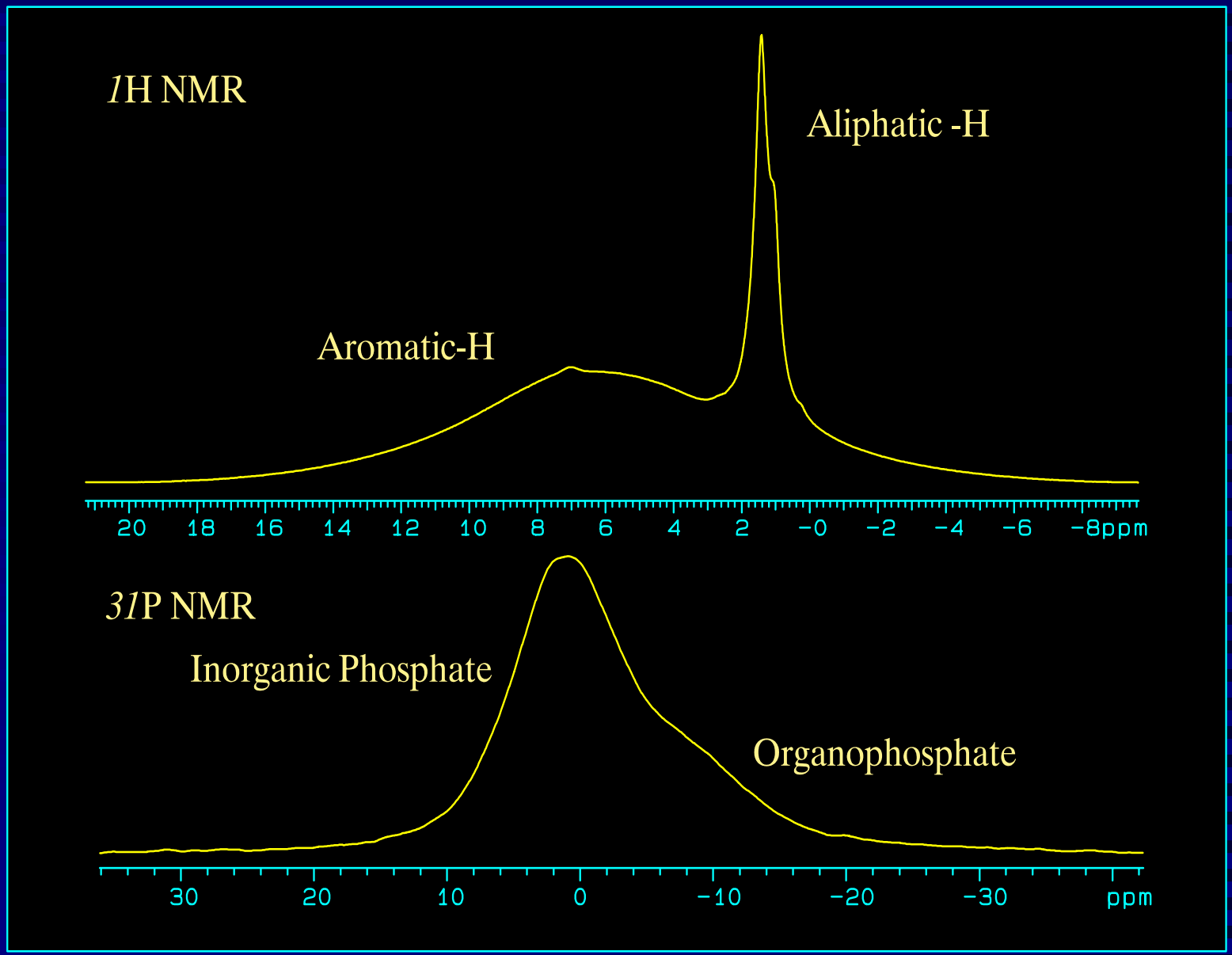
Average Molecular Structure Information Obtained by NMR

Structural Parameter	Description	Typical Value
C	Average # aromatic carbons per cluster	13
(S+1)	Average # attachments per cluster	4.8
Po	Average fraction of intact bridges	0.8
B.L.	Average # of intact bridges per cluster	3.8
S.C.	Average # terminal side chains per cluster	1
Phi-O	Average # phenolic groups per cluster	1.6
Phi-CO	Average # carboxyls per cluster	3.3
n’	Average aliphatic chain length per cluster	1
Mw	Average molecular weight per cluster	303

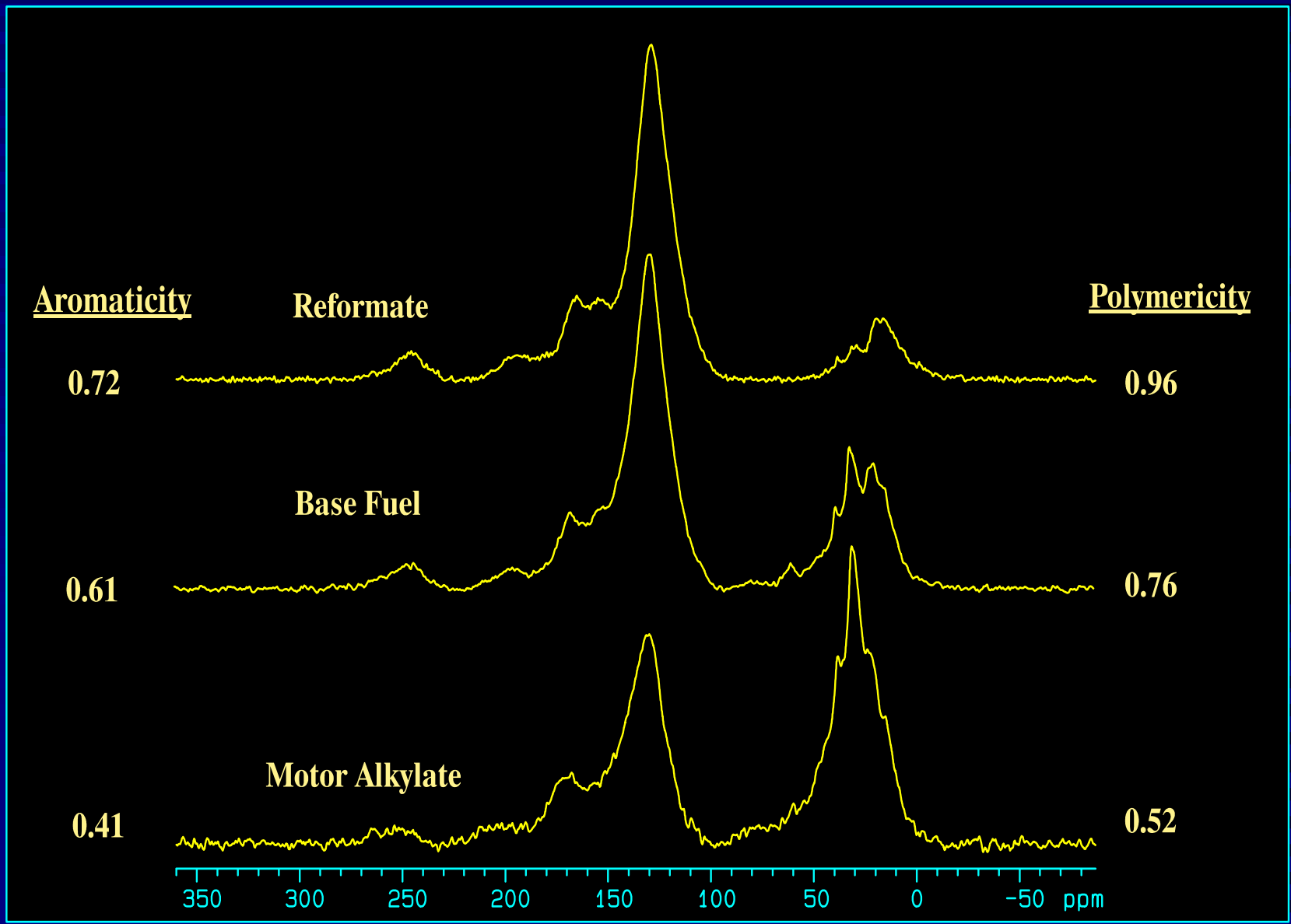
Typical Base Fuel Combustion Chamber Deposit



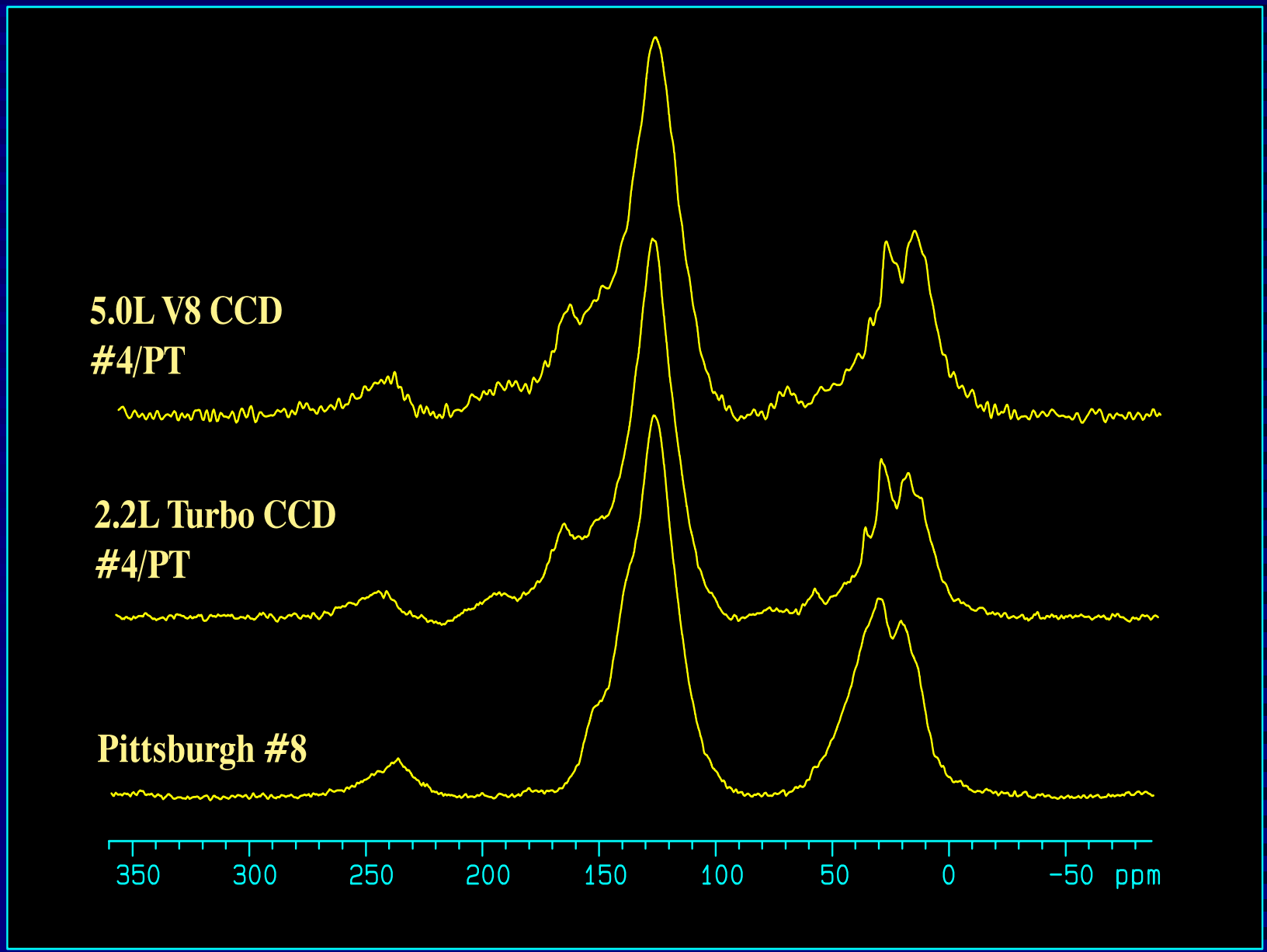
*1*H and *31*P NMR Data of a Typical Base Fuel CCD



Effect of Fuel Composition on CCD Molecular Structure



Comparison of CCD with High Volatile Bituminous Coal



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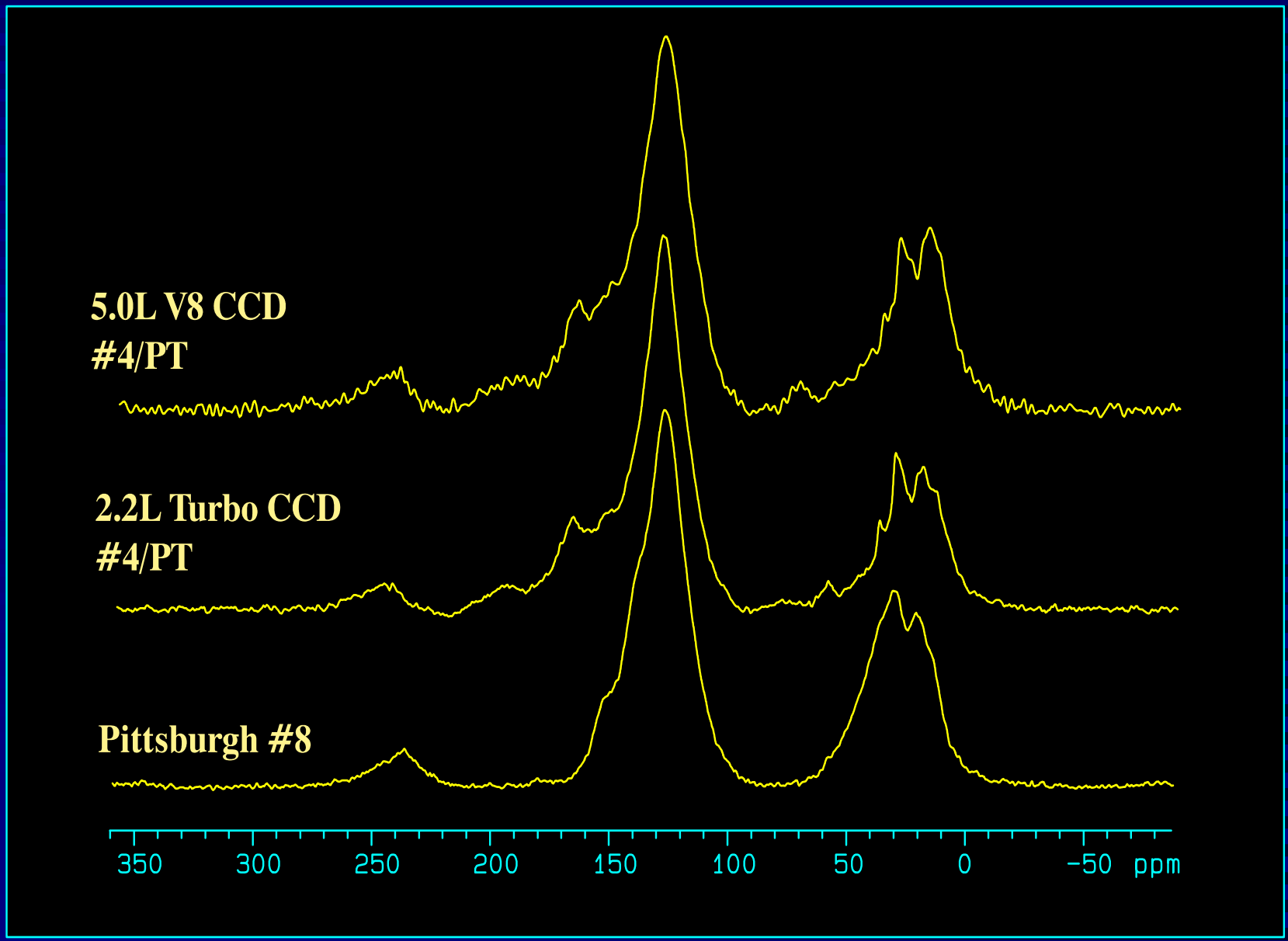
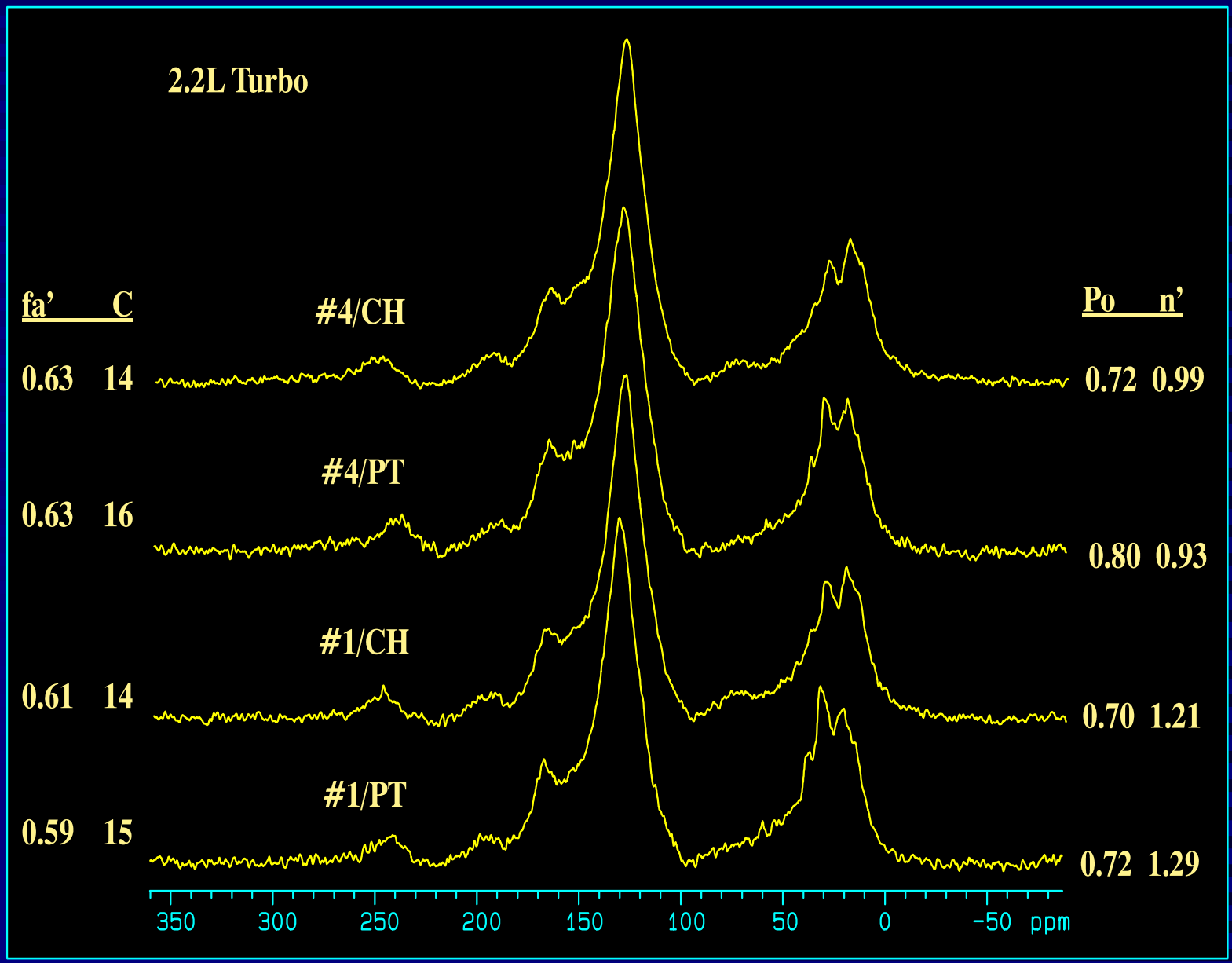


NMR Structural Parameters for Coal and Typical Base Fuel CCDsStructural parameter

Structural Parameter	Pittsburgh #8	2.2L Turbo	5.0L V8
Aromaticity	0.63	0.63	0.61
Carboxyls per cluster	0.53	2.81	3.26
Average chain length	1.84	0.97	0.96
Polymericity	0.72	0.75	0.8
Attachments per cluster	4.82	5.11	4.77
Carbons per aromatic cluster	16	13	13

Cylinder-To-Cylinder Variation of CCD Structure



Honda Generator Test

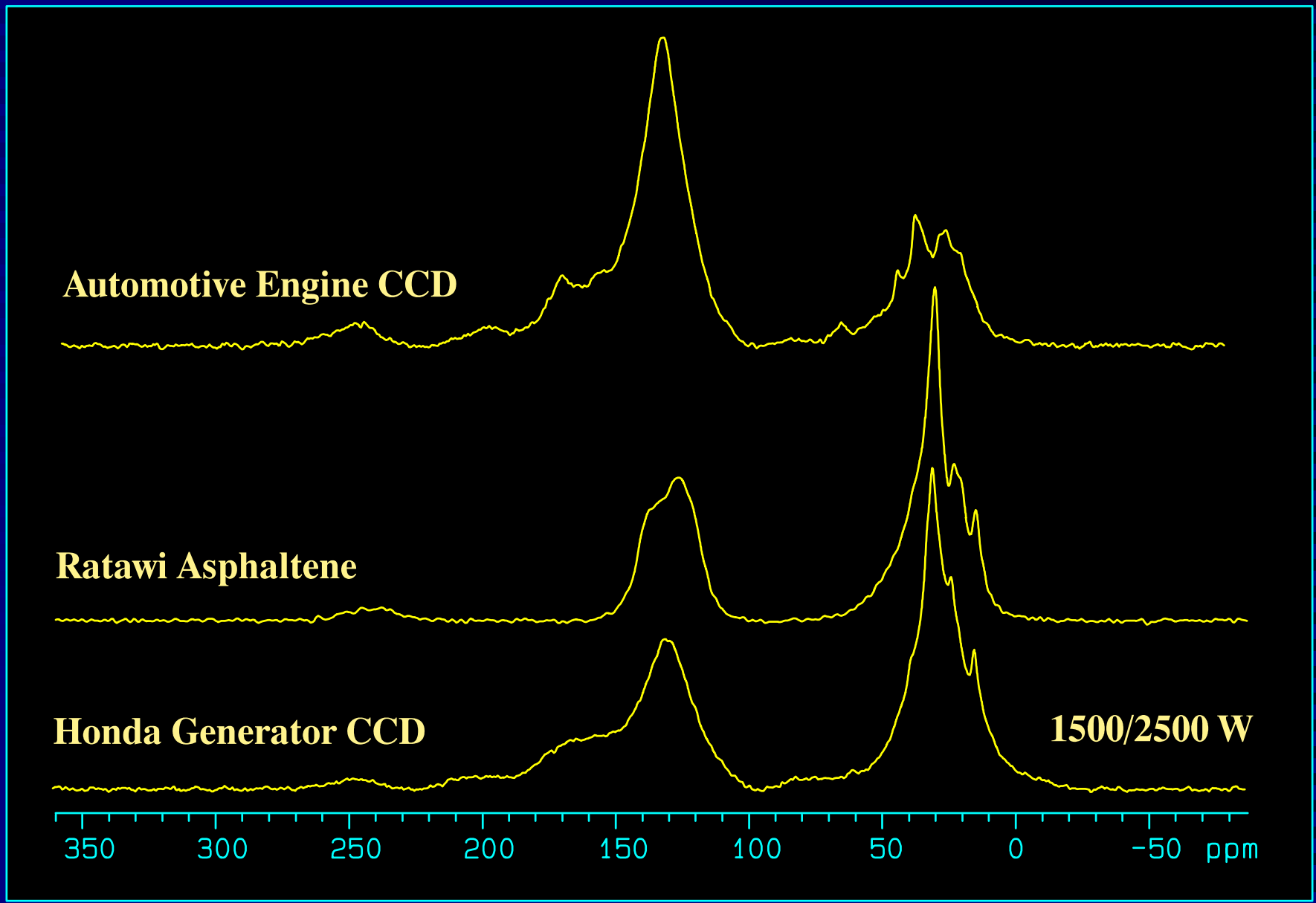
80 hour test

2 load conditions of 1500 and 2500 W

2 hours at each condition

Lube : 10W-40 SF

Comparison of Honda-Generator CCD with Asphaltene



Honda Generator CCDs Produced at 1500/2500 W Test Conditions

Structural Parameter	Honda PT	Honda CH	2.2L Turbo PT
Aromaticity	0.46	0.43	0.63
Carboxyls per cluster	3.8	2.8	2.8
Average chain length	2.24	2.54	1
Polymericity	0.59	0.69	0.75
Attachments per cluster	7.28	5.19	5.11
carbons per aromatic cluster	17	12	13

Modified Honda Generator Tests

80 Hour Tests

Load Condition Modified to Cycle Between 2500 and 4000 W

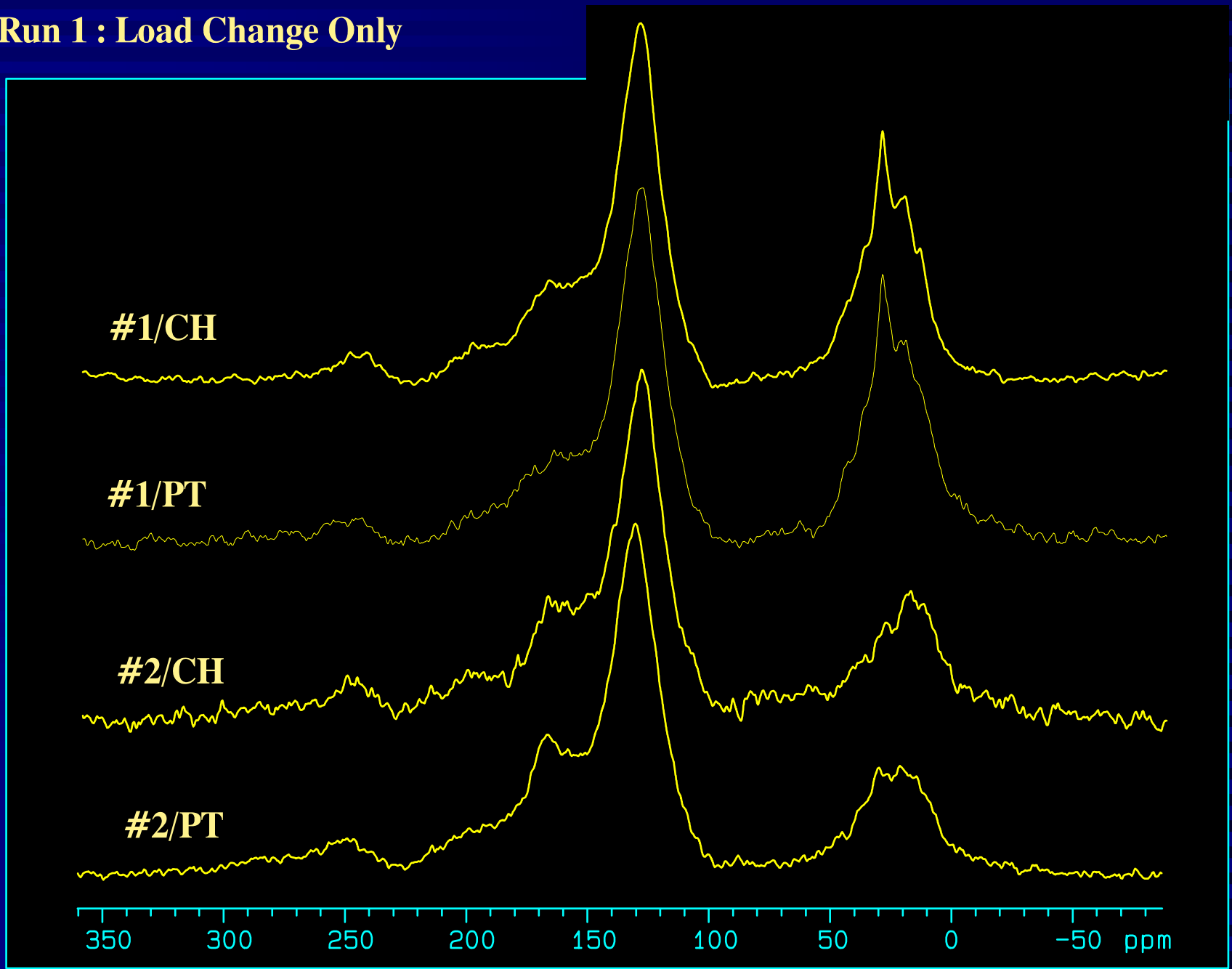
2 Hours at each Condition

Run 1: CCDs generated at this higher load.

Run 2: CCDs generated at higher load and with coolant routing modification.

Honda Generator CCDs Produced at 2500/4000 W Conditions

Run 1 : Load Change Only

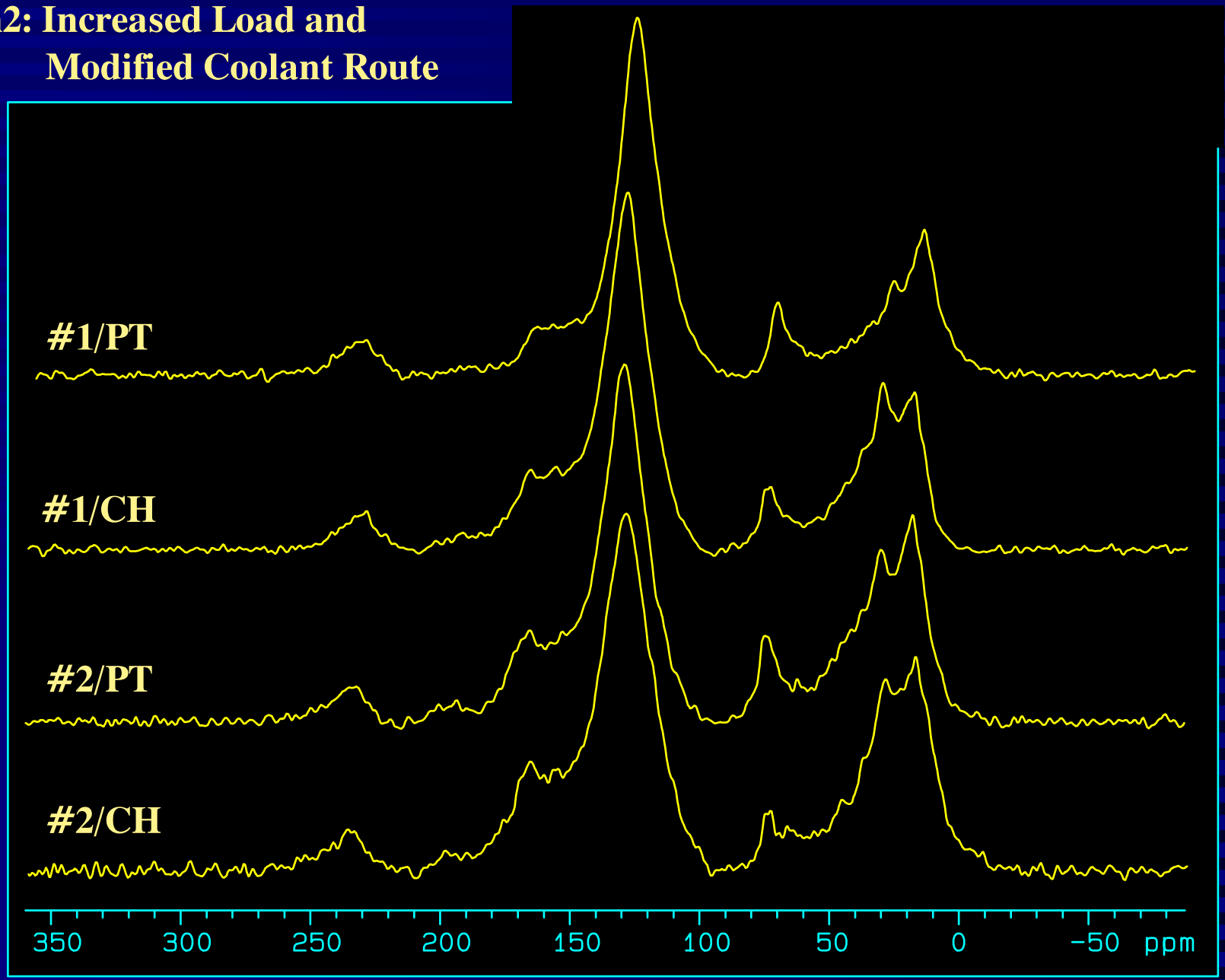


NMR Structural Parameters for Honda Generator CCDs Produced at 2500/4000 W Loads

Structural Parameter	Run 1 PT/1	Run 1 PT/2	Run 2 PT/1	Run 2 PT/2
Aromaticity	0.57	0.66	0.56	0.59
Carboxyls per cluster	1.9	4.1	2	3.1
Average chain length	1.4	0.5	1.7	1.4
Polymericity	0.65	0.86	0.52	0.71
Attachments per cluster	3.08	5.48	5.94	6.65
Aromatic carbons per cluster	9	13	16	18

Honda Generator CCDs Produced at 2500/4000 W Conditions

Run2: Increased Load and Modified Coolant Route



Conclusions

1 > Carbon-13 NMR yields reliable molecular structure information on CCD polymeric backbones.

2 > The Average building block of the polymer backbone is a 2-4 ring polynuclear aromatic, independent of engine test or fuel type.

3 > Large variations in molecular structure can be observed for:

i. different fuel types, and

ii. different combustion environments caused by engine variables such as heat, air/fuel ratio, load, etc.

4 > NMR analysis can be used to monitor the effects of bench test modifications.

Future Work

1 > Correlate "average molecule" data with:

i. Heat capacity

ii. Knock location

iii. Emissions performance

iv. Individual fuel components

2 > Investigate fuel/lubricant interactions leading to deposit formation in the combustion chamber and the crankcase.

3> Observe the effects of additive technologies on the CCD molecular structure.