Soot Formation Process

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Objectives

- Use new experimental approaches that provide insight and new data on the formation of aerosol/soot particles.
- Supply experimental data that can be used to validate theoretical models for soot formation in combustion process.
- Use this data to assist in describing mechanistic pathways.
- Provide fundamental information on electronic structures of PAH's through correlation of experimental chemical shift tensor data with advanced quantum mechanical simulations.

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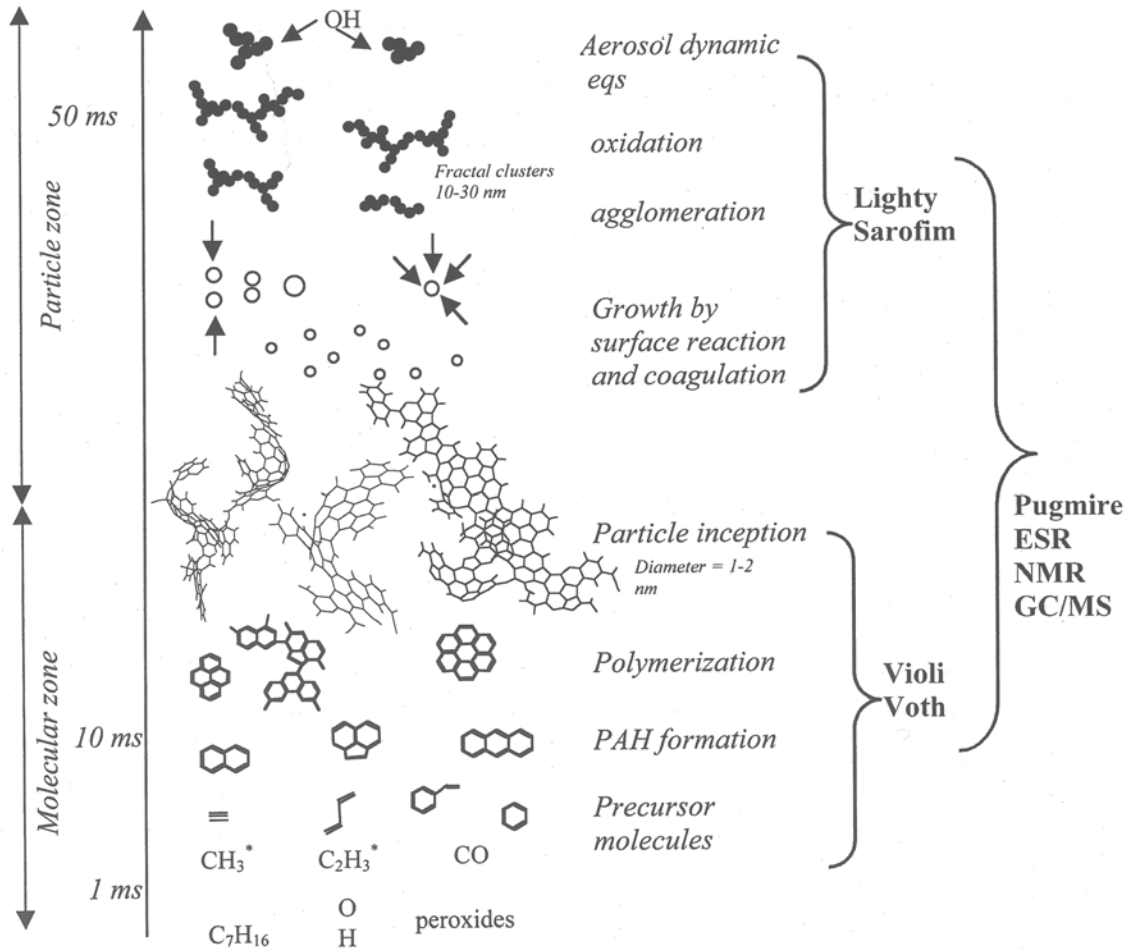
Timescale of Soot Formation



Coagulation & Condensation,

t < 10 s

Intermolecular rearrangements, optical constants etc.

t = ps ~ ms

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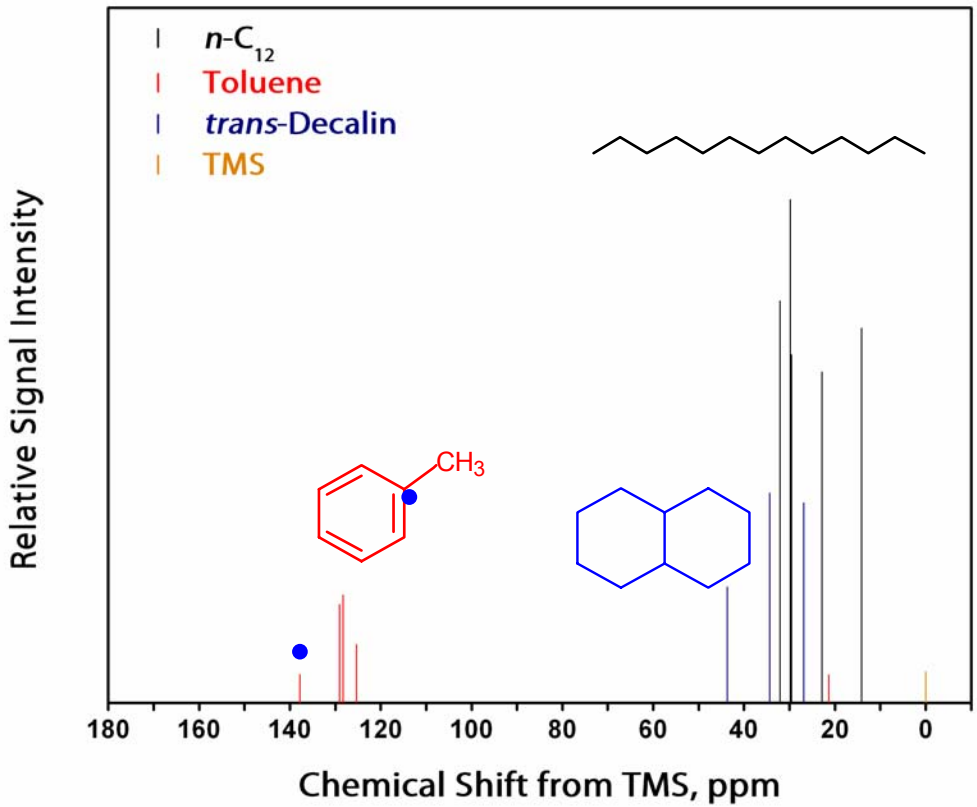
Why Use NMR in Soot Formation Study?

Modern NMR technique have high sensitivity to molecular structure.

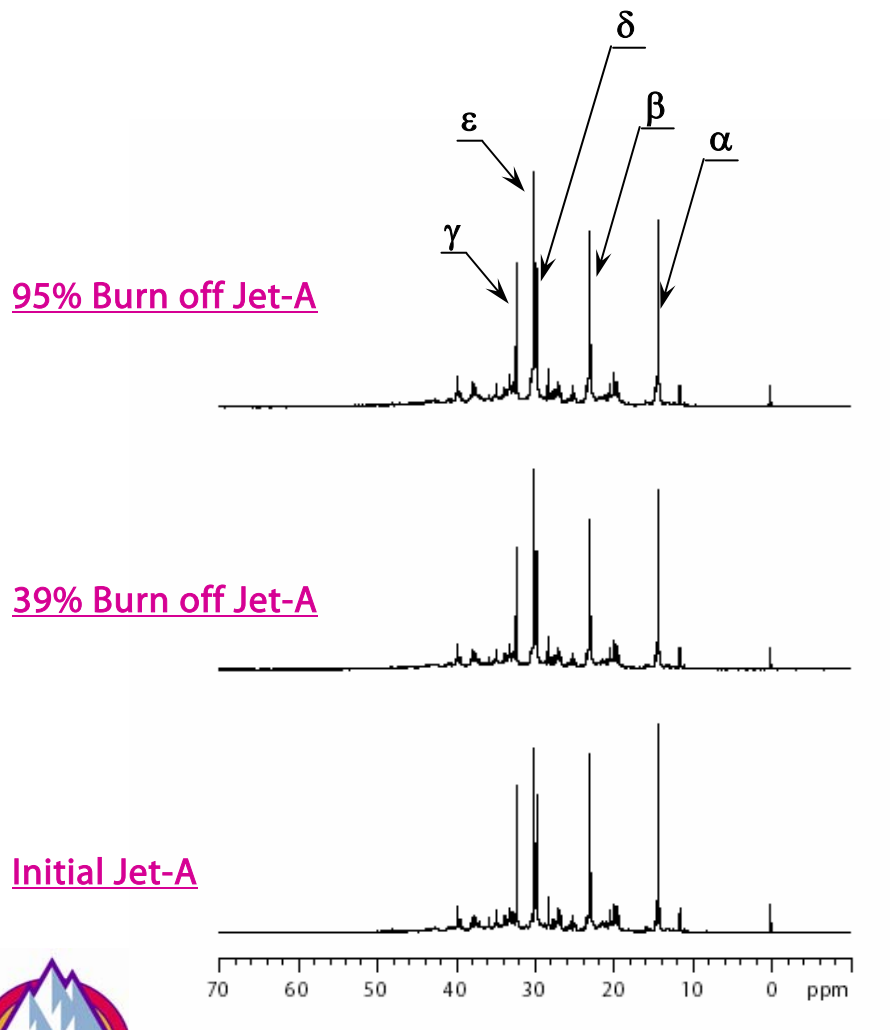
Carbon and hydrogen atoms in different functional groups will have different chemical shifts, which is easily detected with various NMR experiments. This feature makes NMR ideally suitable in soot study.

Applications of NMR techniques, which characterize fuel, soot precursors and their possible structures will be shown.



^{13}C NMR Spectrum of A Sample Fuel Mixture
(n-dodecane, toluene and trans-decalin, 1:1:1 v%)

JP-8 Pool Fire Fuel Study with NMR (1)



^{13}C NMR Spectrum of Liquid Fuel in Batch Experiment

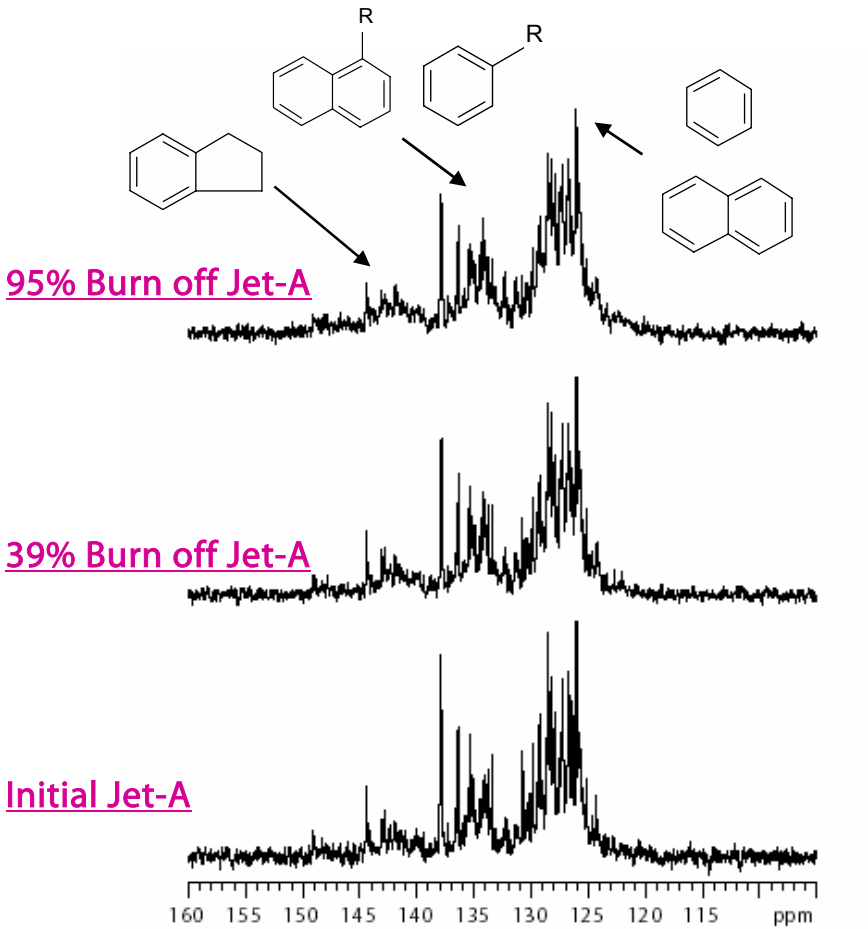
…. C_ε-C_ε-C_δ-C_γ-C_β-C_α

(Assignment scheme for *n*-C12)

α_C/ε_C decreases with burning implying that the aliphatic chain length increases as observed in GC-MS data.

Less cyclic aliphatics are found in burned oil samples, same trend is found in ^{1}H NMR spectra.

JP-8 Pool Fire Fuel Study with NMR (2)



^{13}C NMR Spectrum of Liquid Fuel in a Batch Experiment

No major difference is found

- Aromatics content increases slightly with burning
- Indan like compounds increase as much as 60%

Sample	Aro. C, %[i]	Aro. H, %
Jet-A_B-0	**10.6**	**3.3**
Jet-A_B-39	**11.4**	**3.3**
Jet-A_B-95	**12.2**	**3.2**

Note: i- Aro. C % is the ratio of aromatic carbon atoms to total carbon atoms; ii-Aro. H % is the ratio of aromatic hydrogen atoms to total hydrogen atoms

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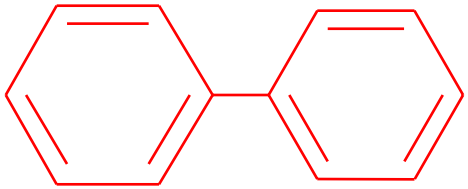
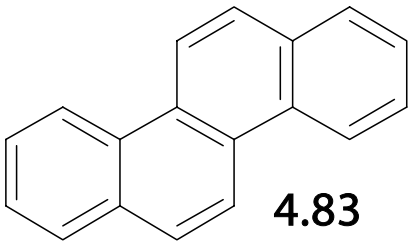
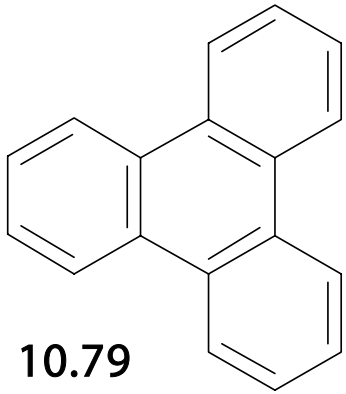


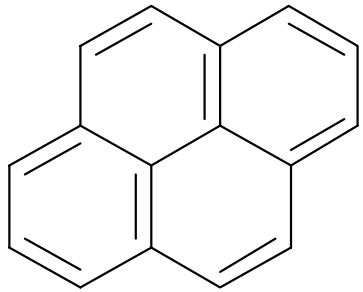
Biphenyl 1365K Aerosol Major Compounds from GC-MS



4.83

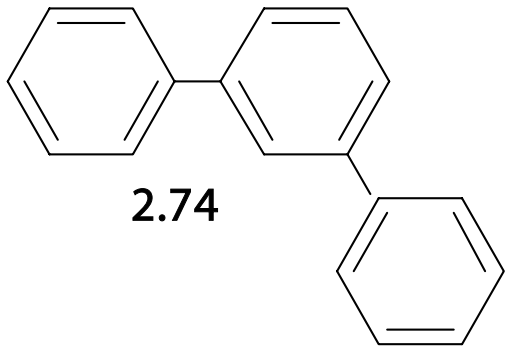


10.79

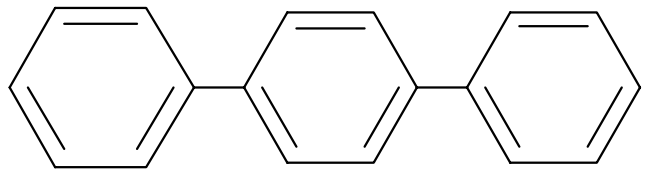


3.94

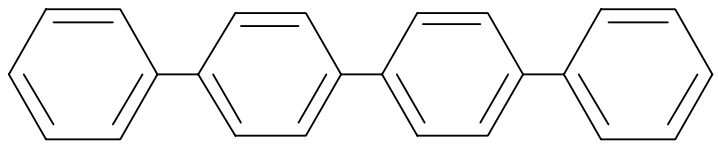
(8.85, 8.81)



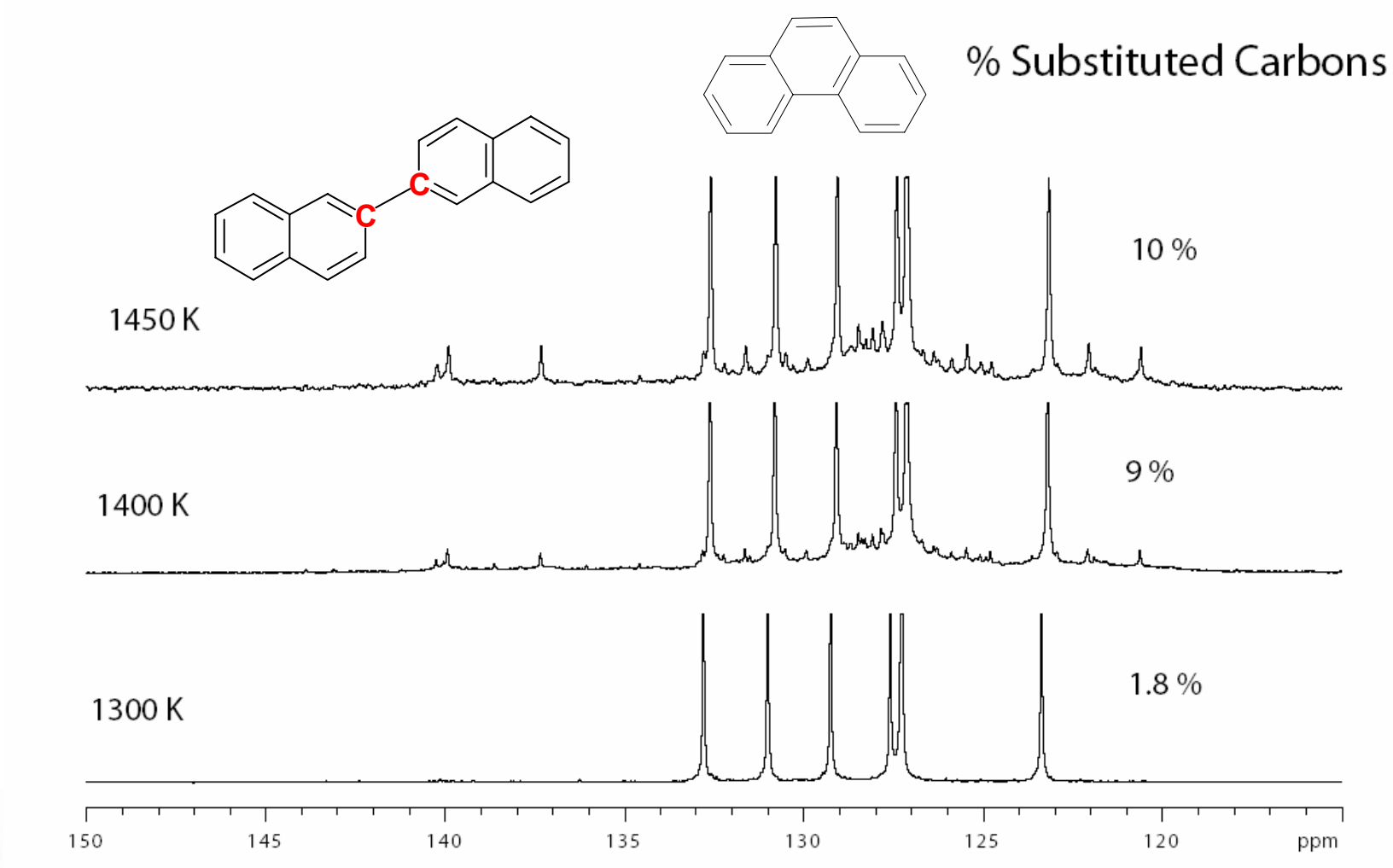
2.74



2.21

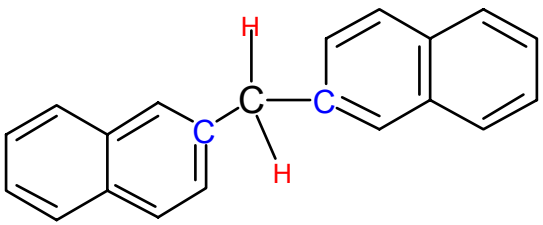


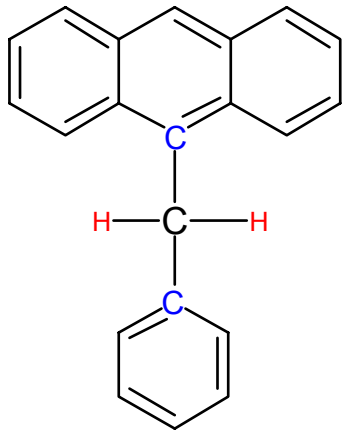
Phenanthrene Tars ^{13}C NMR Spectra

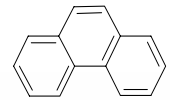


Phenanthrene Tars ^{1}H NMR Spectra

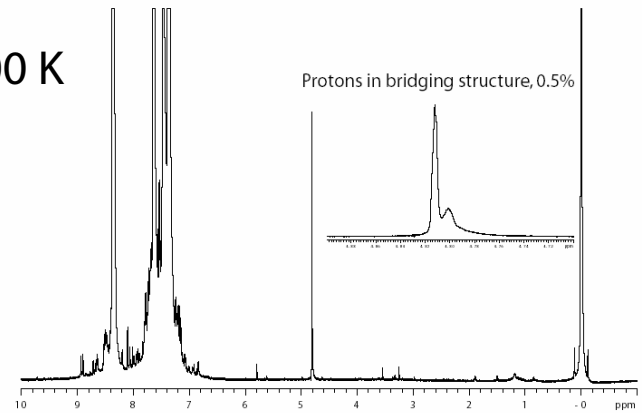
Tar samples of phenantherene heated to 1250 K ~ 1450 K collected in droptube furnace. NMR spectra showed that protons in bridging structure could be formed under this condition. This might suggest start of polymerization. Possible structures of these protons could be:



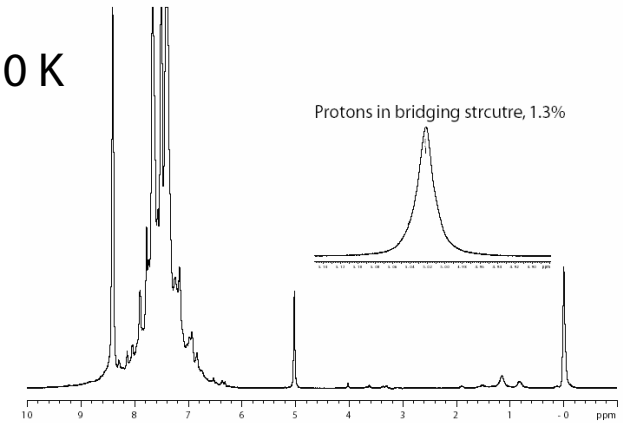




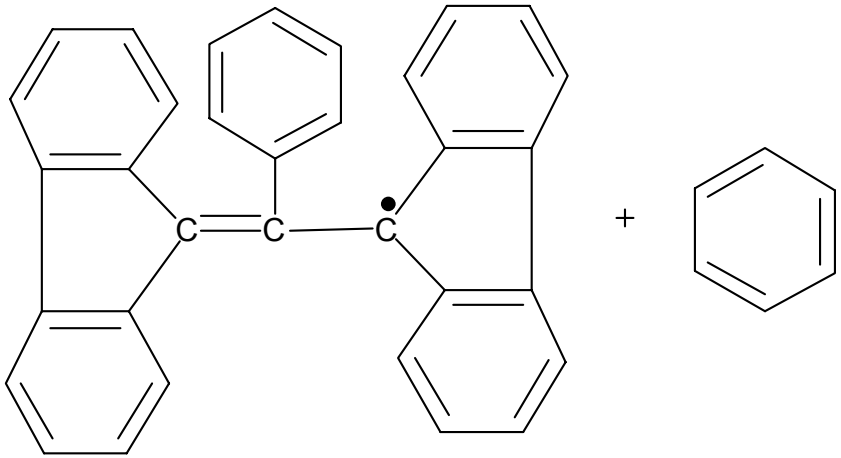
1300 K



1450 K



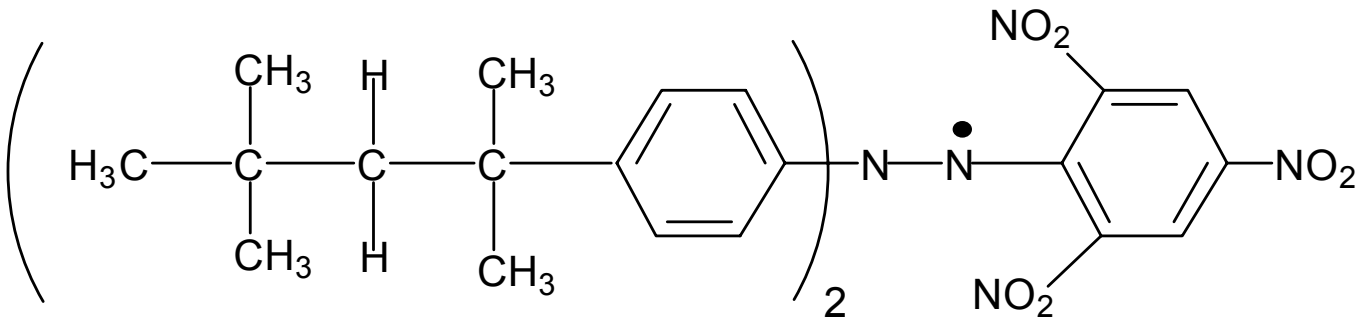
Stable Free Radicals



(a)

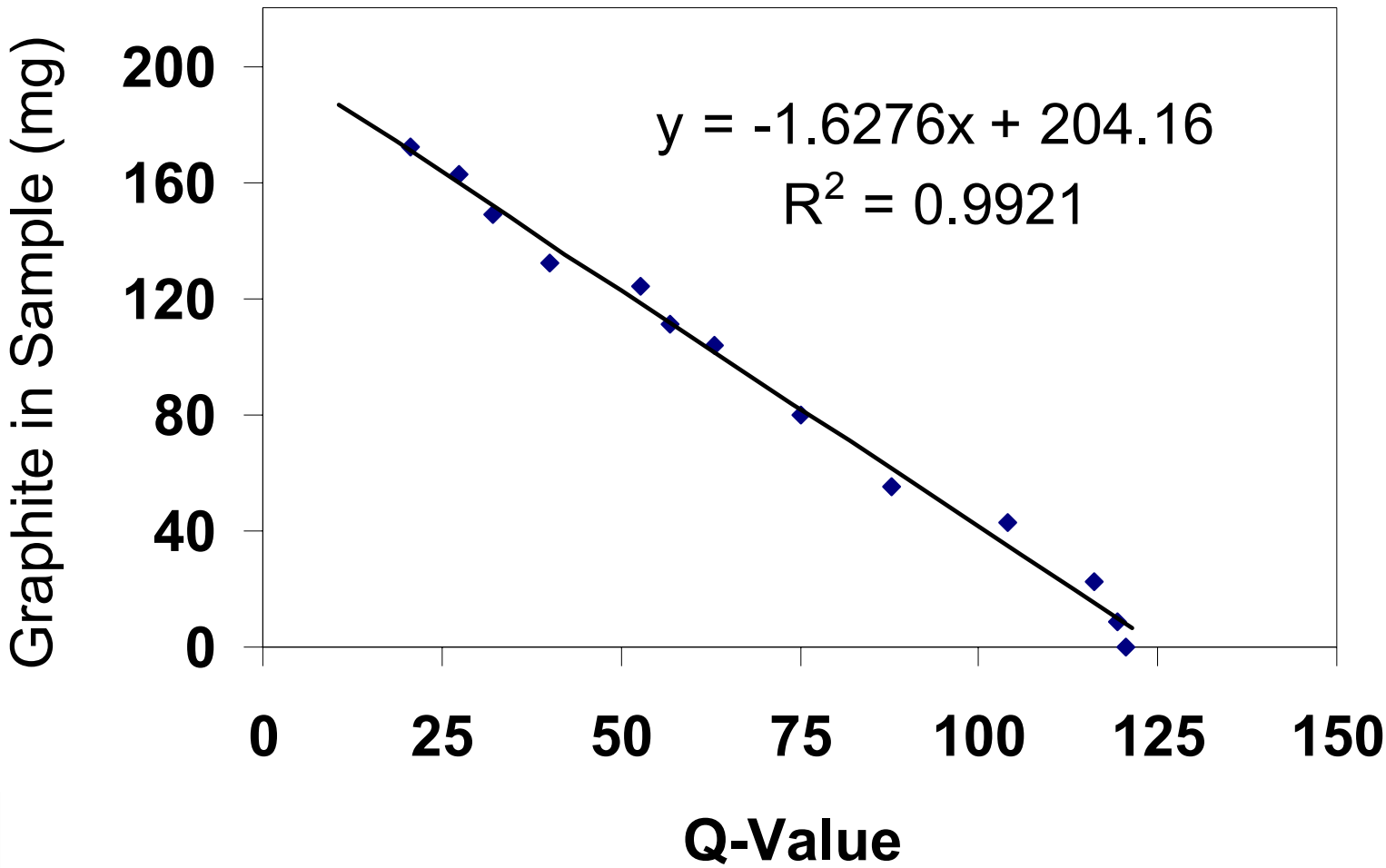
(a) DPPH-2,2-Di(4-*tert*-octylphenyl) -1-picryhydrazyl

(b) BDPA –α,γ-bisdiphenylene-β-phenylallyl complex with benzene (1:1)



(b)

Standard Graphite Curve



Anthracite Coals of Varying Carbon Content

Coal	%C (daf)	ΔQ 100MHz	G.F.	$N_e \times 10^{19}$ spins/g	C_{13} Shift (ppm)	T_{1H} (ms)	$T_{1\rho H}$ (ms)	d_{002} (Å)	ΔH_{pp} (G)	L_c (Å)
LCNN $C_{100}H_{18.7}N_{1.1}S_{0.2}O_{0.8}$	95.7	74	0.148	3.26	120.7	59.2	20.7	3.49	3.76 0.04	59
Jeddo $C_{100}H_{18.7}N_{1.1}S_{0.2}O_{0.8}$	95.2	58	0.112	3.53	121.3	44.3	17.5	3.82	2.61 0.12	70
UAE $C_{100}H_{18.7}N_{1.1}S_{0.2}O_{0.8}$	94.0	8	0.024	4.90	122.9	33.1	12.1	3.60	1.24	85
SUMMIT $C_{100}H_{18.7}N_{1.1}S_{0.2}O_{0.8}$	93.2	4	0.014	2.64	125.3	38.2	5.8	3.61	2.94	71

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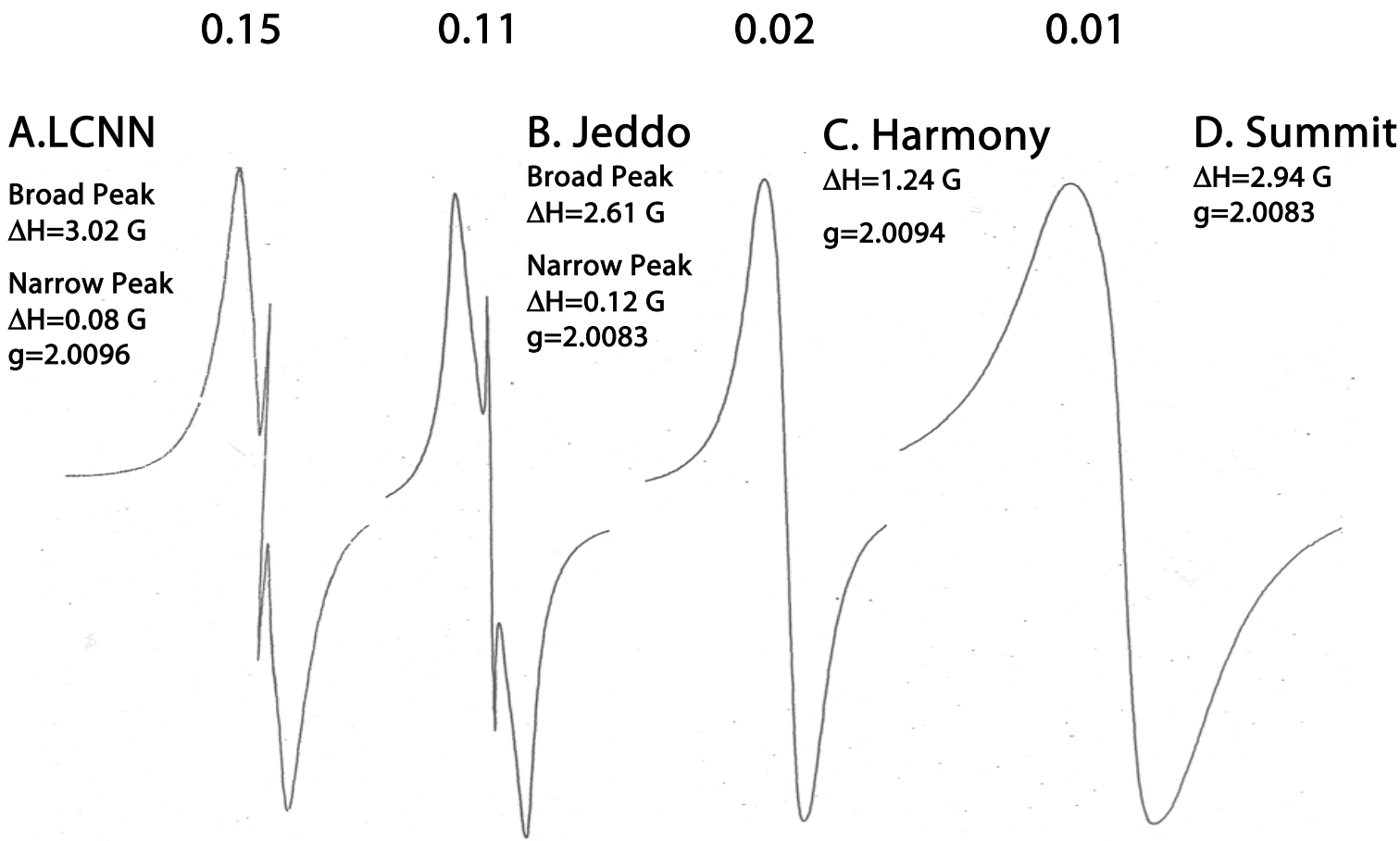
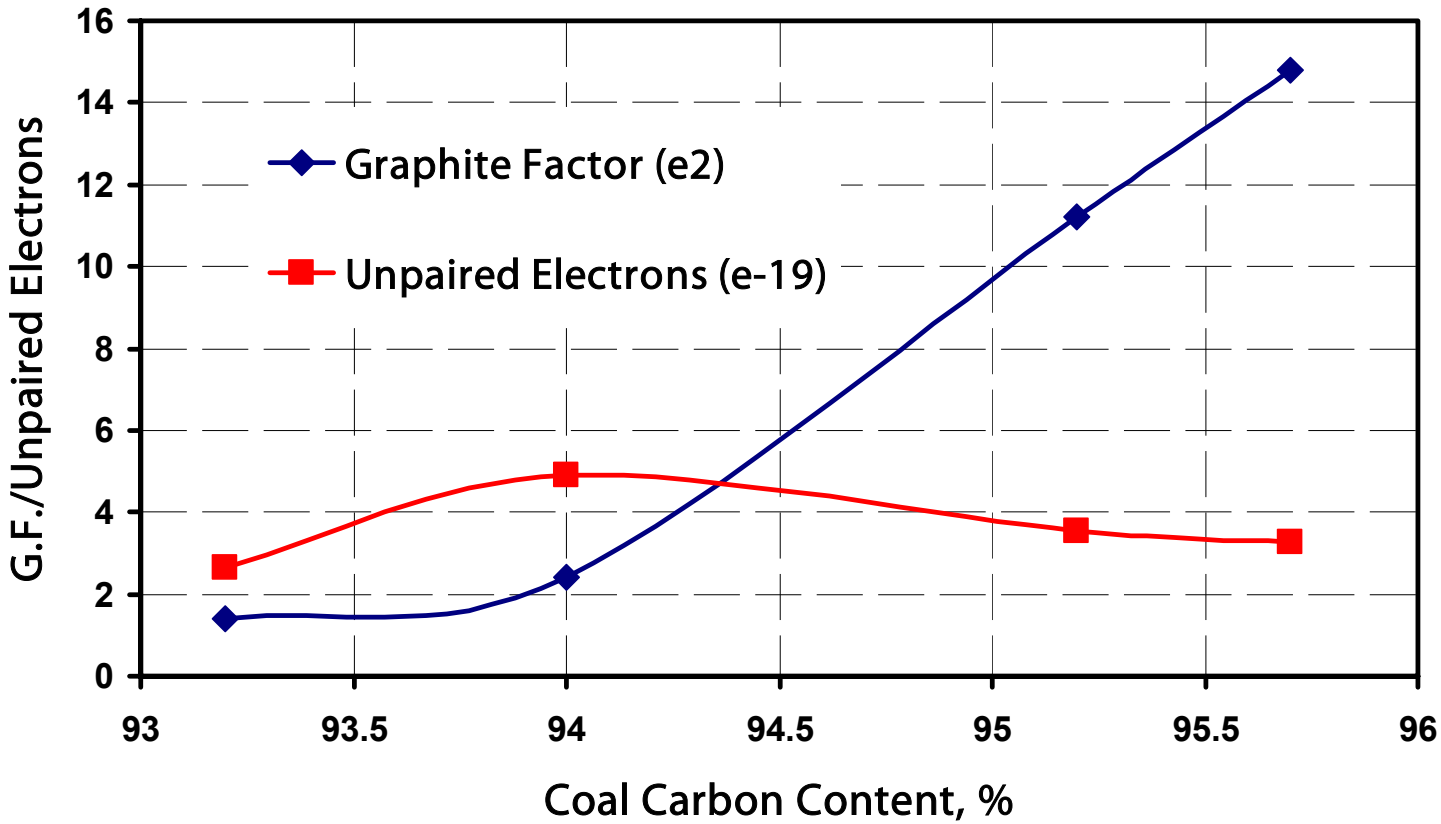
ESR Results of Anthracite Coals

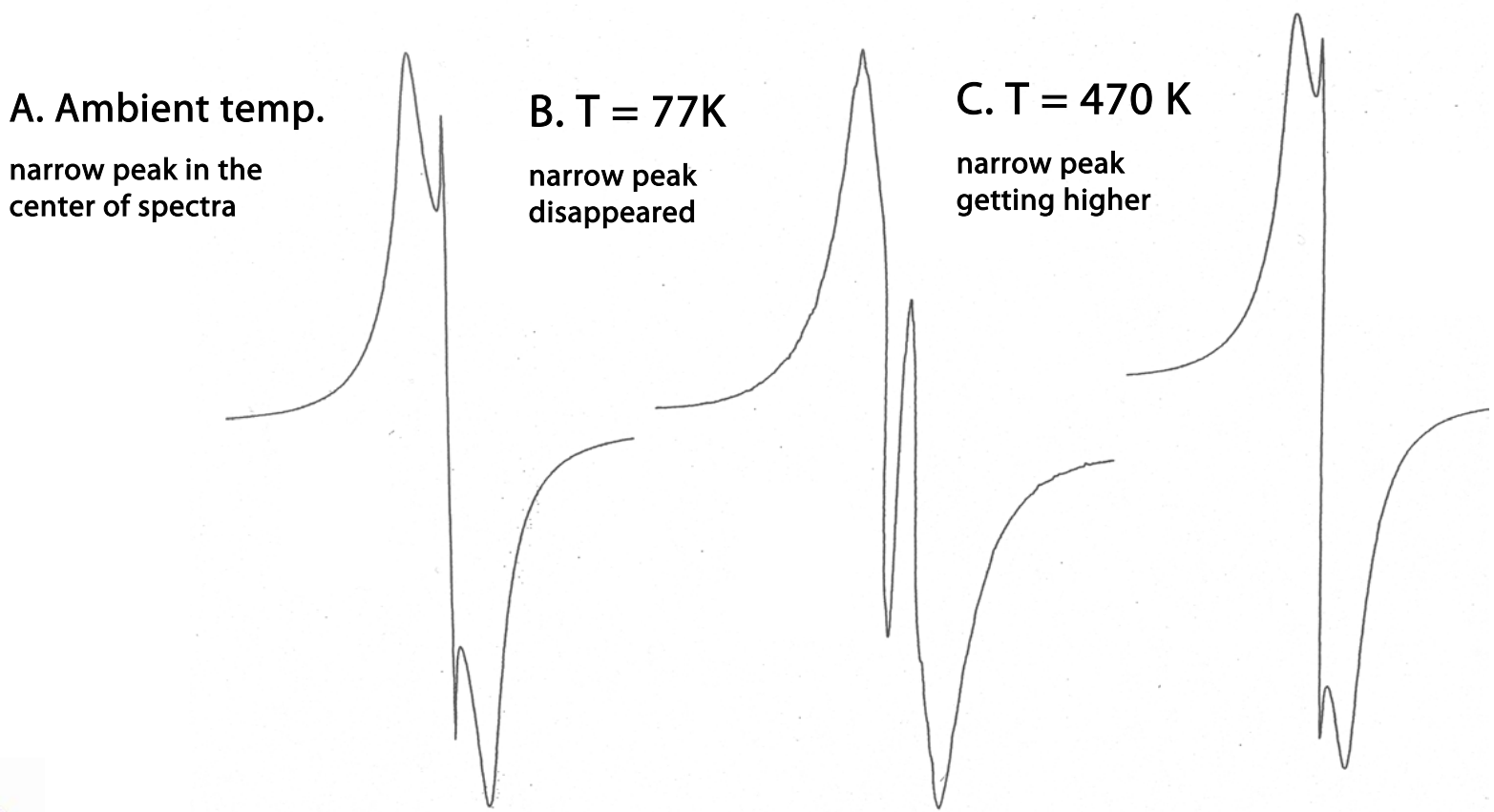
Graphite Factor:



Graphite Factor/Unpaired Electrons Change



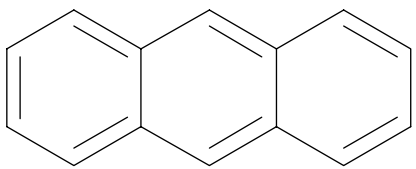
Temperature Effect on ESR Spectra of Anthracene 1400 K Soot Residue

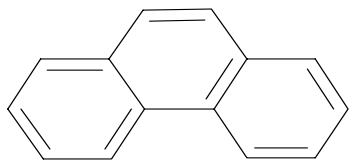


Anthracene & Phenanthrene Aerosol Parameters

	Color	*Graphite Factor*	*$N_e \times 10^{17}$ spins/g*	*Extract (%)[a]*
Anthracene samples				
1250 K aerosol	Yellow	0	3.5	100
1300 K aerosol	Lt. Brown	0	90	96
1400 K aerosol	Black	n/a	980	n/a
1400 K extract	Black	0	1.2	9.6
1400 K residue	Black	0.47	1100	n/a
Phenanthrene samples				
1250 K aerosol	Yellow	0	n.d.	100
1300 K aerosol	Lt. brown	0	0.5	96
1400 K residue	Black	0.09	1300	46
1450 K residue	Fluffy/black	0.57	770	12

a. 24 hr sohxlet extraction in DCM





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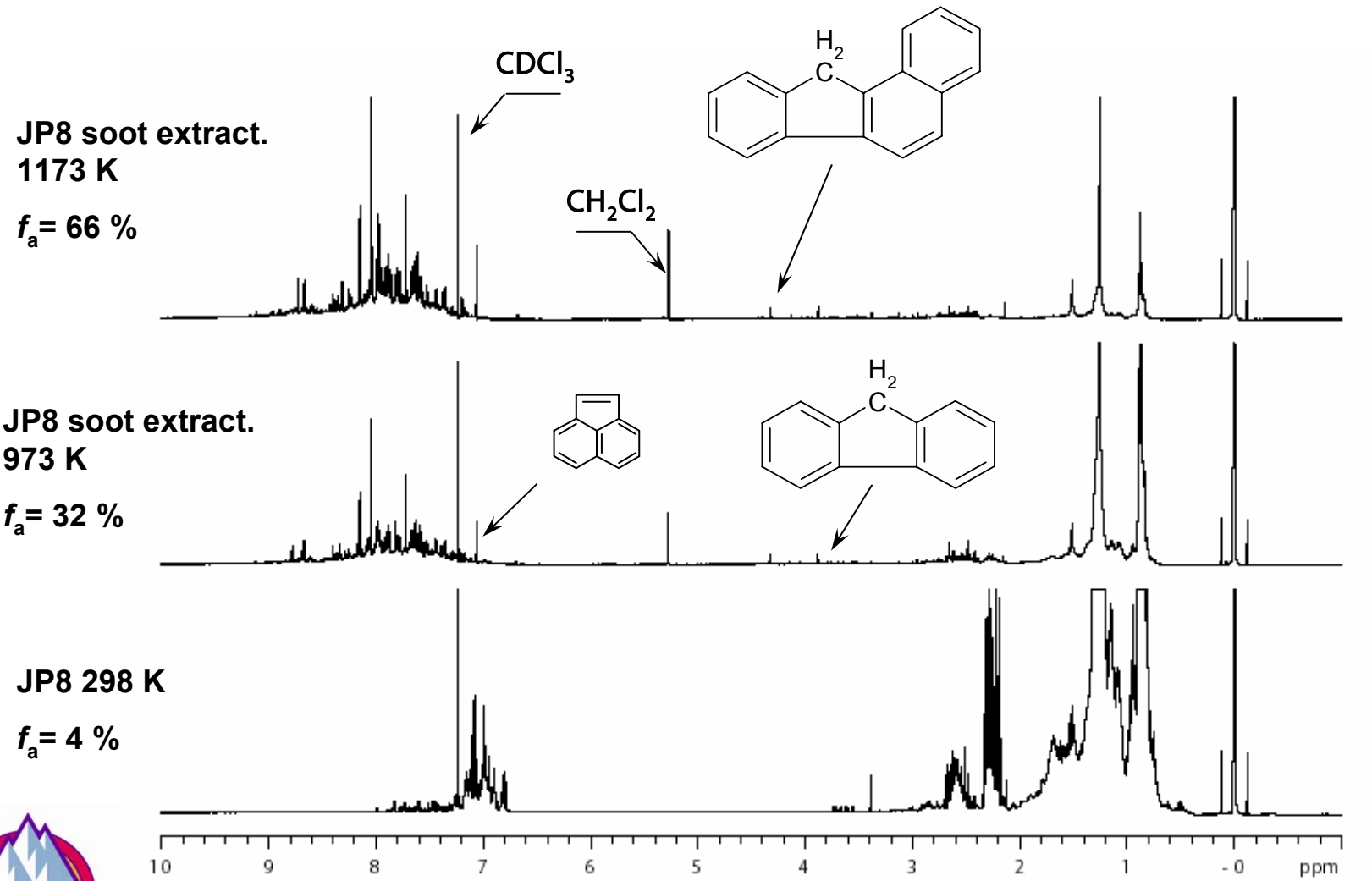
Droptube Soot Extract. Study With NMR

n-C_{12} and JP-8 soot samples are collected in droptube furnace at 973 K and 1173 K. Summary of experiments are listed below. NMR study of the soot extractables showed interesting signs related to soot formation.

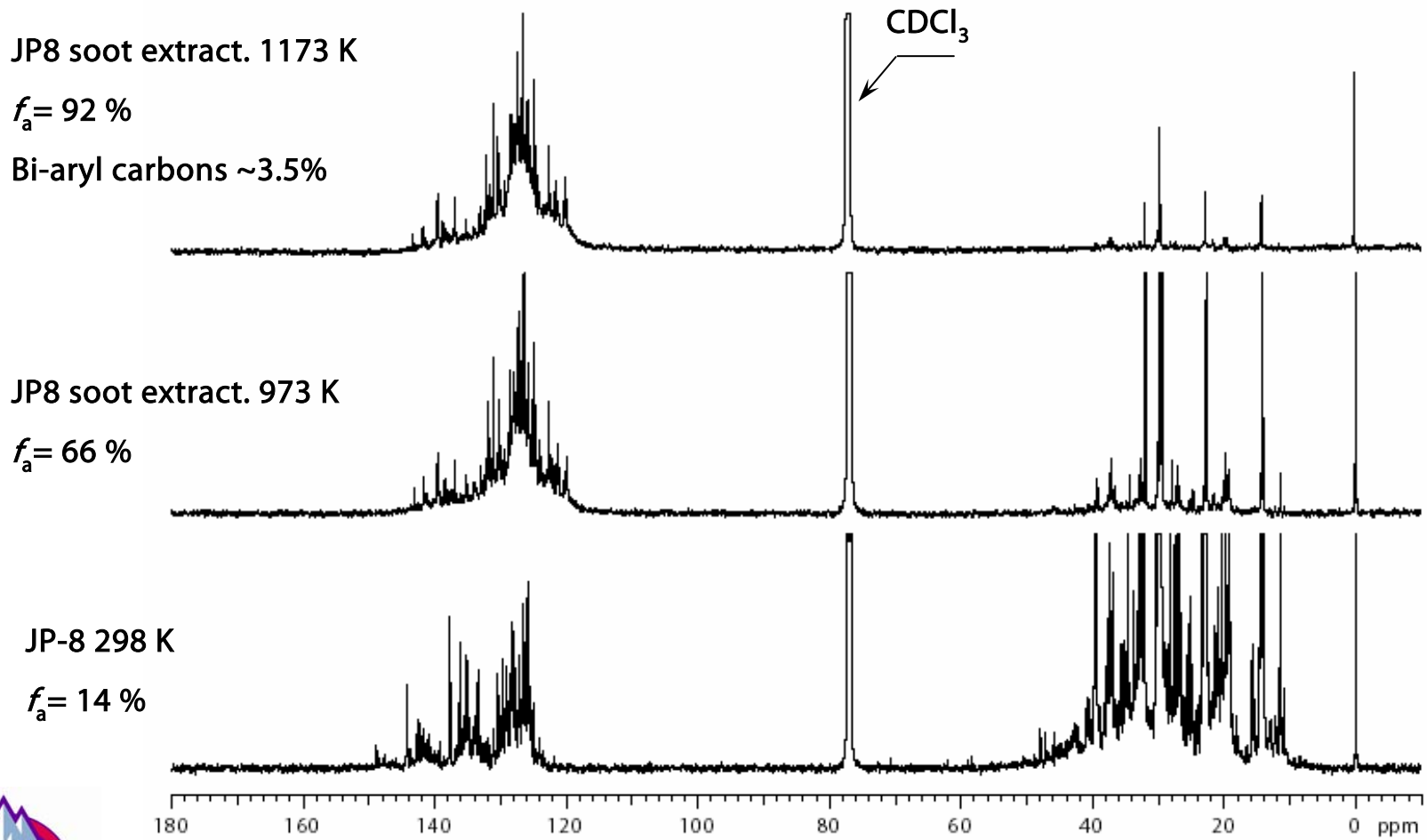
	n-C_{12}		JP-8	
Temperature, K	973	1173	973	1173
Gross Soot Yield, %*	4.5	7.5	8.4	17
Tar Yield, %*	42	30	30	14
$N_e \times 10^{19}$, spins/g (in Residue)	soon	soon	4.53	2.07
Smoke Point, mm	>50		24.5	

*-- Gross soot yield, % = Aerosol mass / Feed mass, Tar yield, % = Extracted tar mass/ Aerosol mass

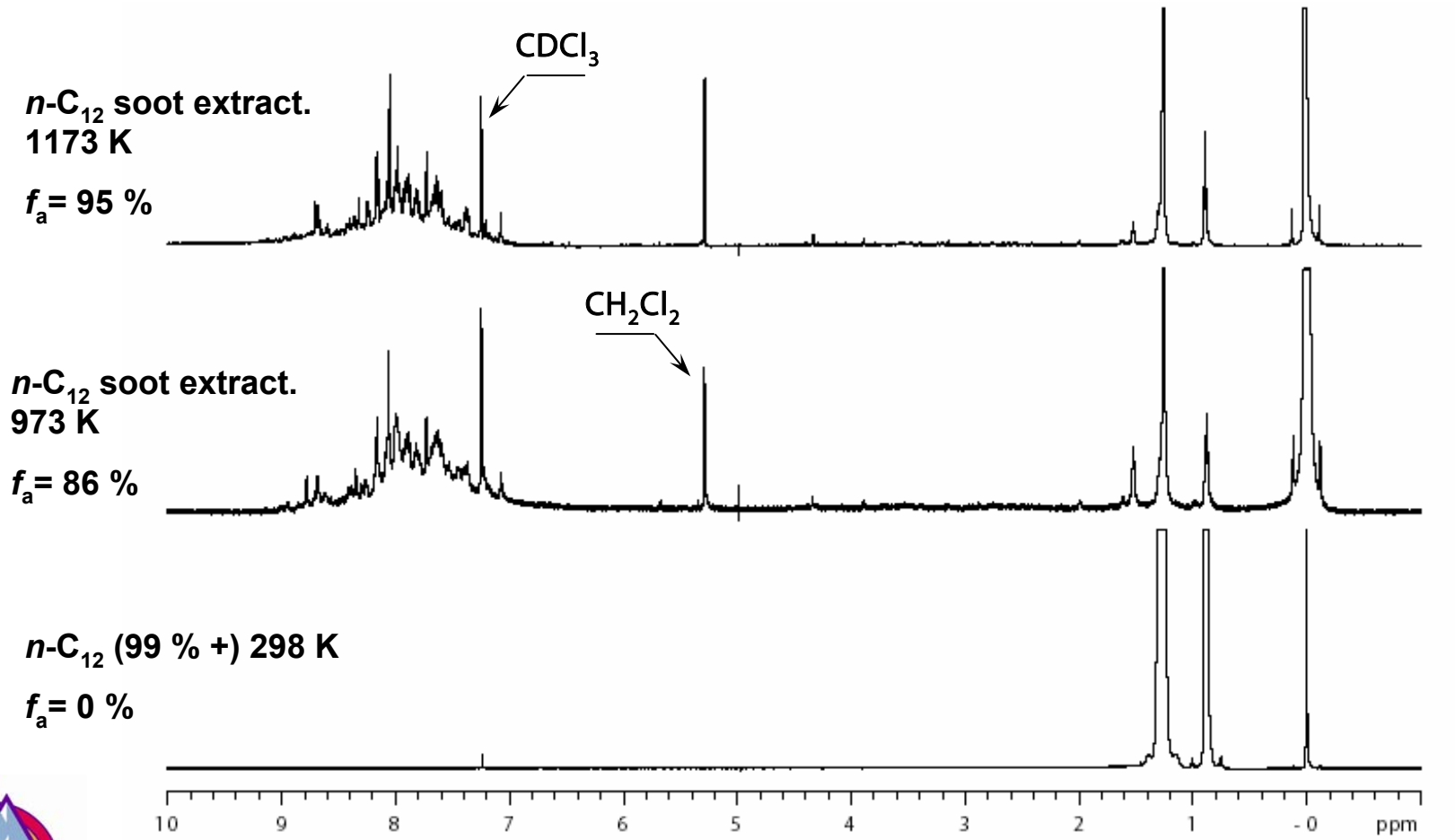
JP-8 Droptube Soot Extraction ^{1}H NMR Spectra



JP-8 Droptube Soot Extraction ^{13}C NMR Spectra



n-C_{12} Droptube Soot Extraction ^{1}H NMR Spectra



n-C_{12} Droptube Soot Extraction ^{13}C NMR Spectra

n-C_{12} droptube soot extract. 1173 K

f_a= 96 %

Biaryl carbons ~4.5%

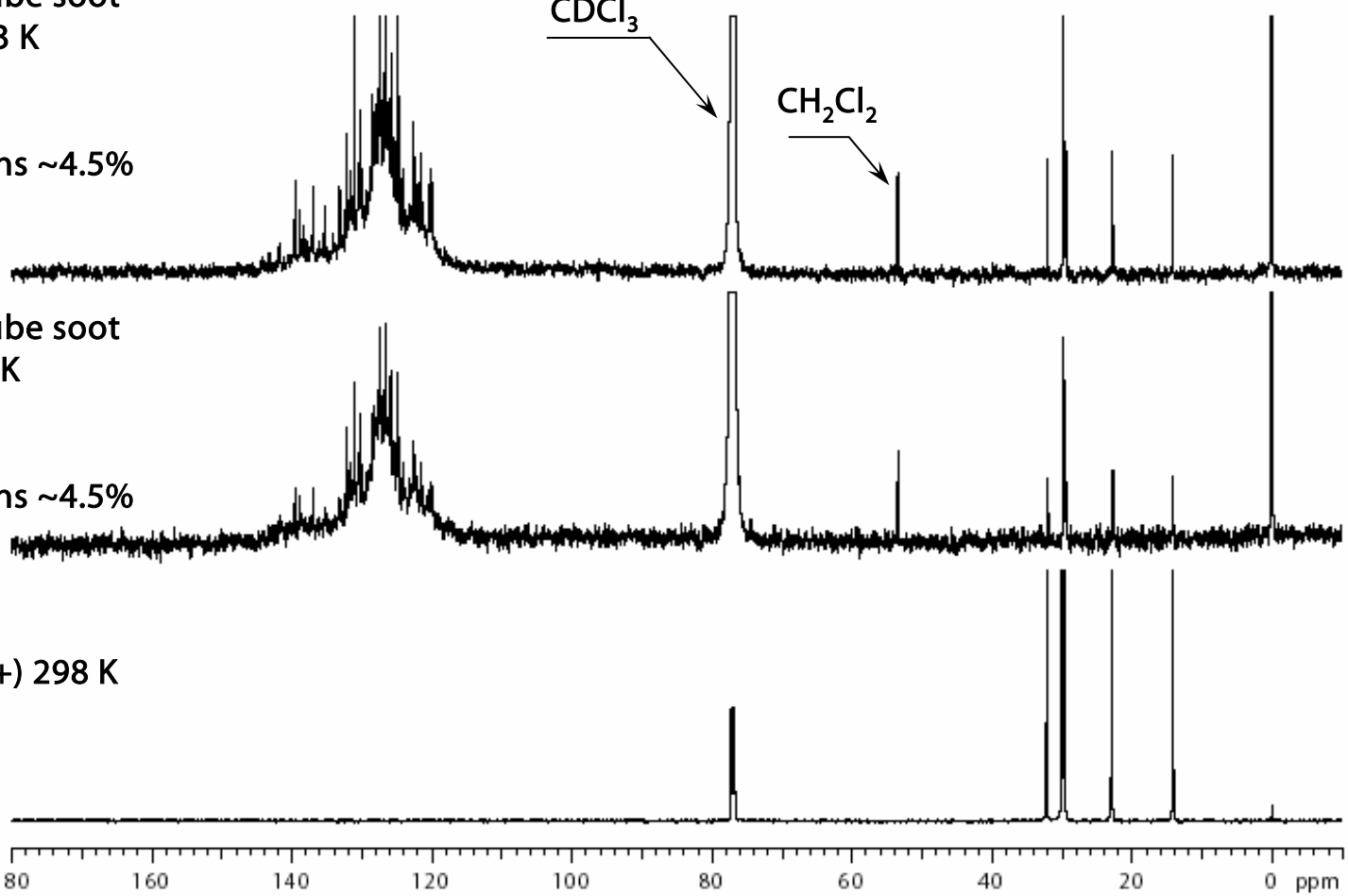
n-C_{12} droptube soot extract. 973 K

f_a= 98 %

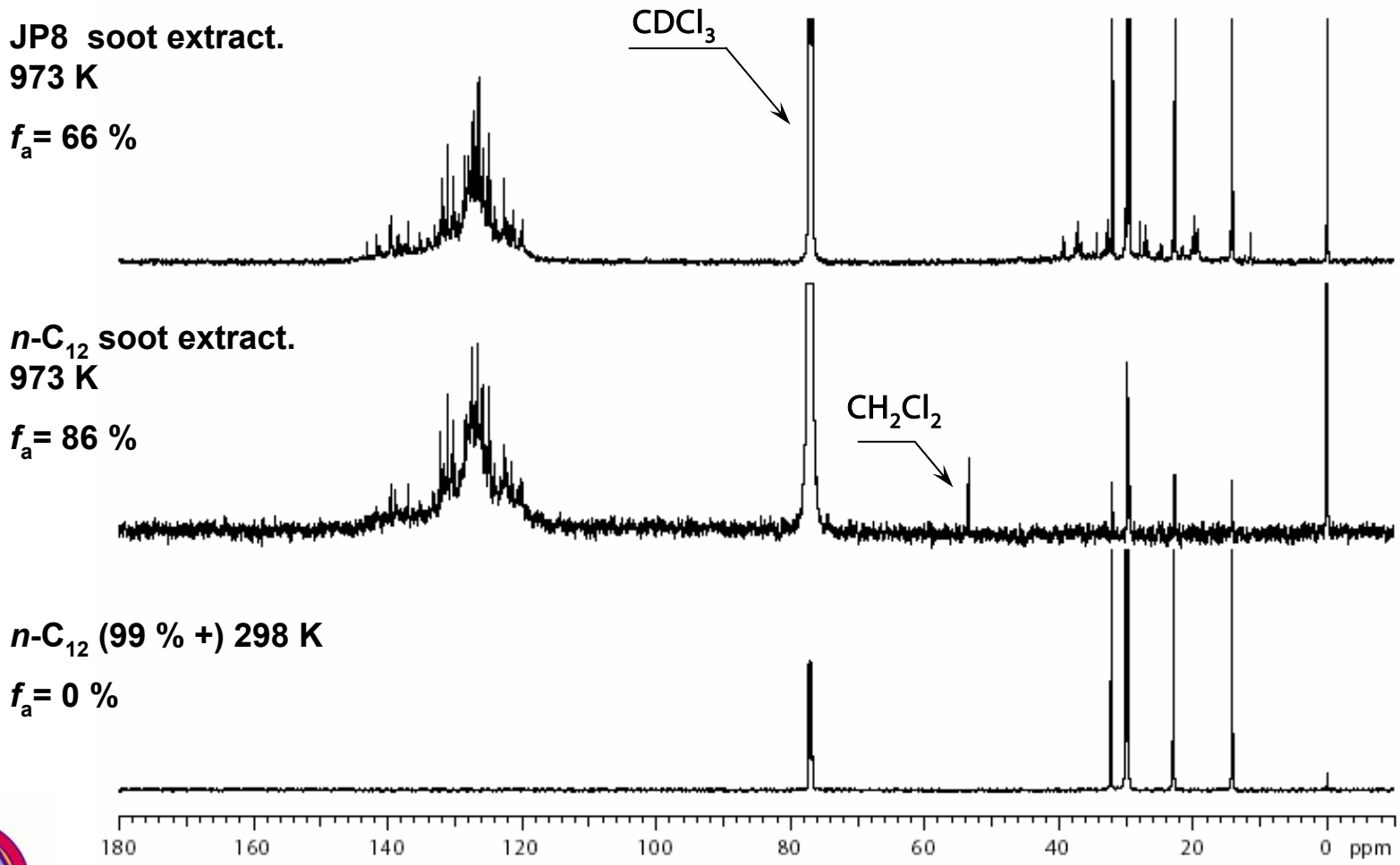
Biaryl carbons ~4.5%

n-C_{12} (99 % +) 298 K

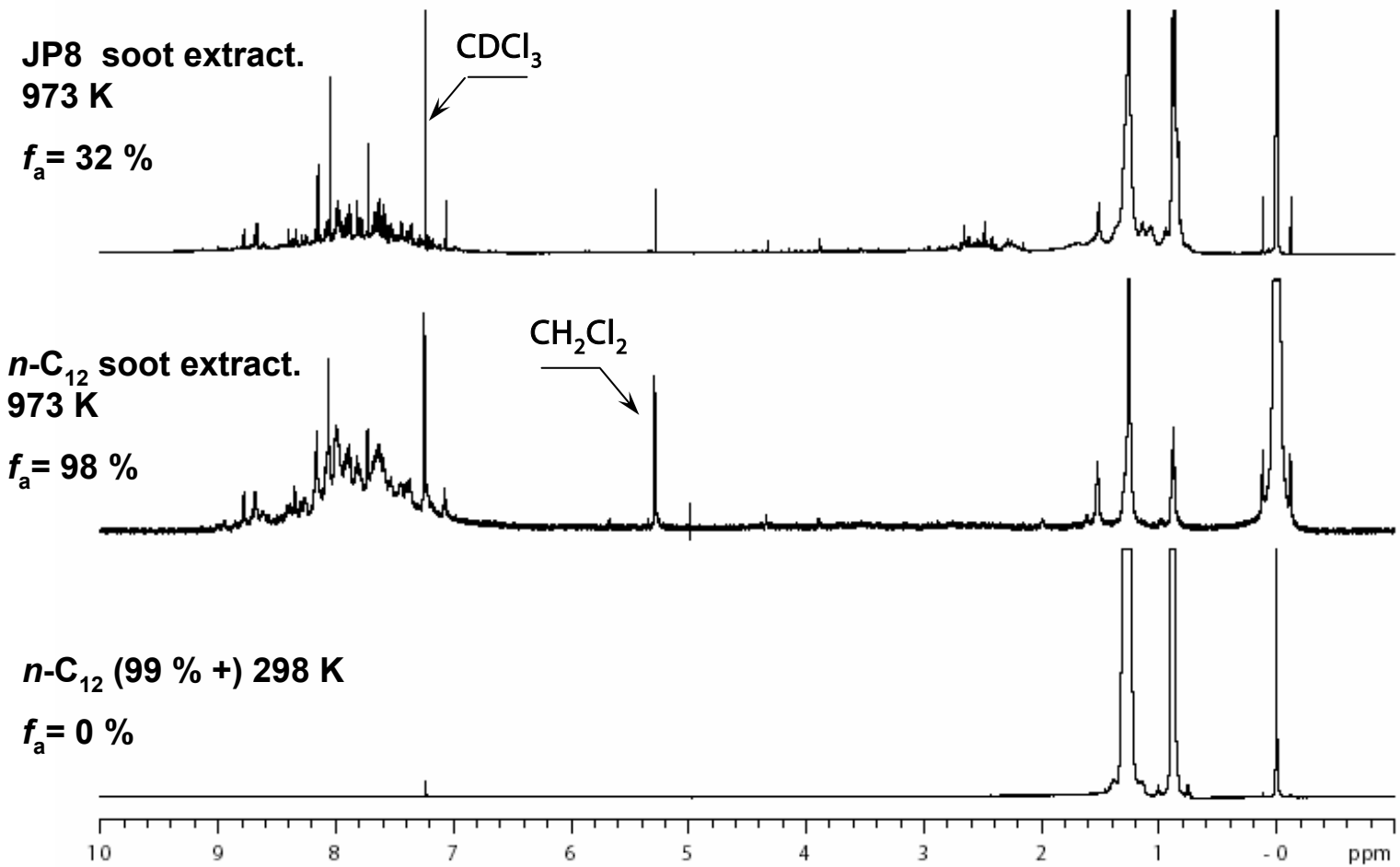
f_a= 0 %



n-C_{12} vs. JP8: ^{13}C NMR Spectra of Droptube Soot Extract.

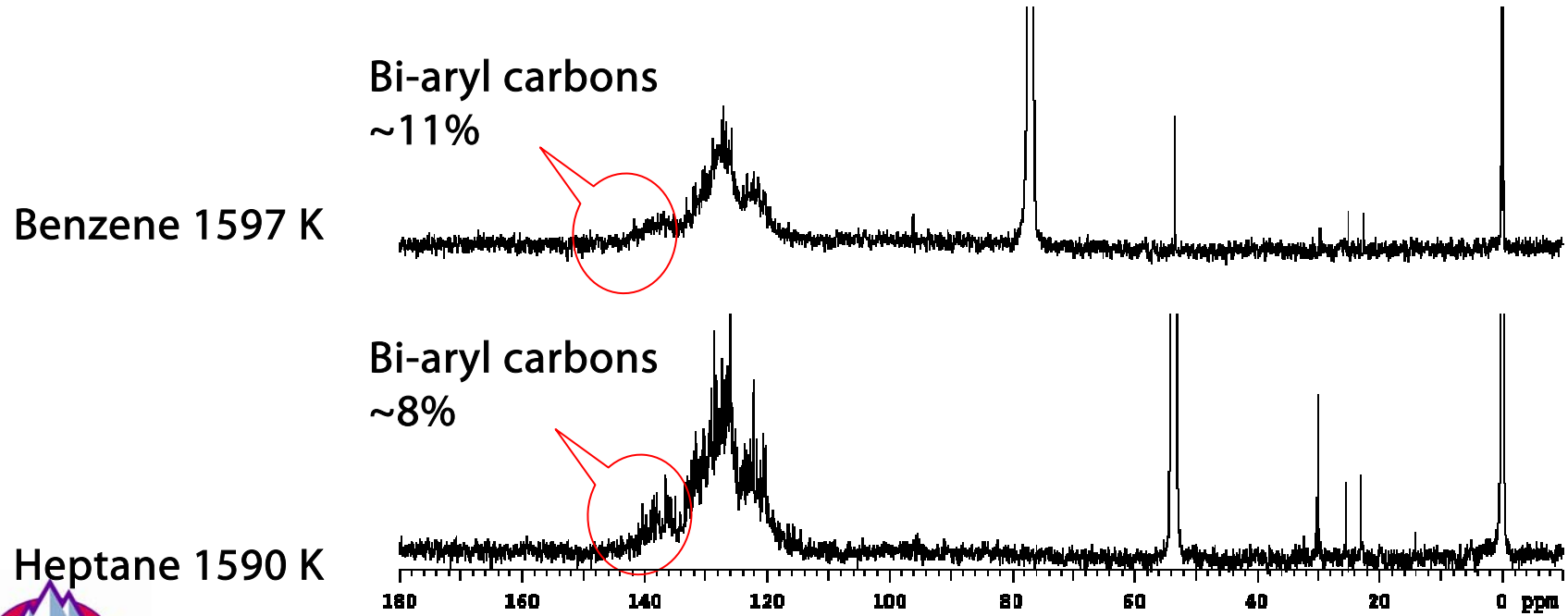


n-C_{12} vs. JP8: ^{1}H NMR Spectra of Droptube Soot Extract.



FFB Soot Extract. Study With NMR (1)

Methyl group found in heptane FFB soot extract. Sample is ~ 0.1%, and not found in benzene sample.



Conclusions

- In the early stages of soot formation the starting material appears to have a significant influence on the intermediate aerosol structures.
- Polymerization reactions that produces alkyl as well as bi-aryl structures play a significant role. These data will be helpful in describing mechanistic pathways.
- A fairly narrow temp. window (100~200K) is observed for conversion of soot precursors into soot material.
- High resolution ^{1}H & ^{13}C spectra complement the solid state NMR data and provide insight to the polymerization reactions and the formation of bridging structures.
- The combination of NMR and MS data has proven to be quite informative.
- Future work will continue on model compounds but also focus on surrogate fuels as well as aerosol samples obtained from pool fires.

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