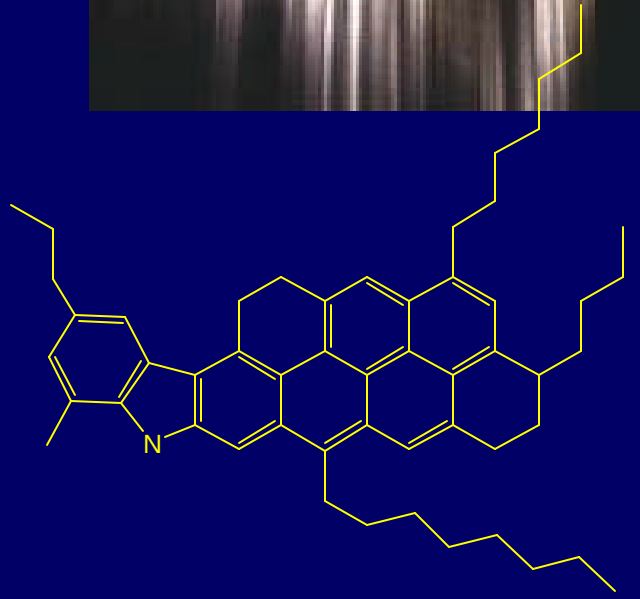
Asphaltenes and Polycyclic Aromatic Hydrocarbons

Oliver C. Mullins
Schlumberger-Doll Research

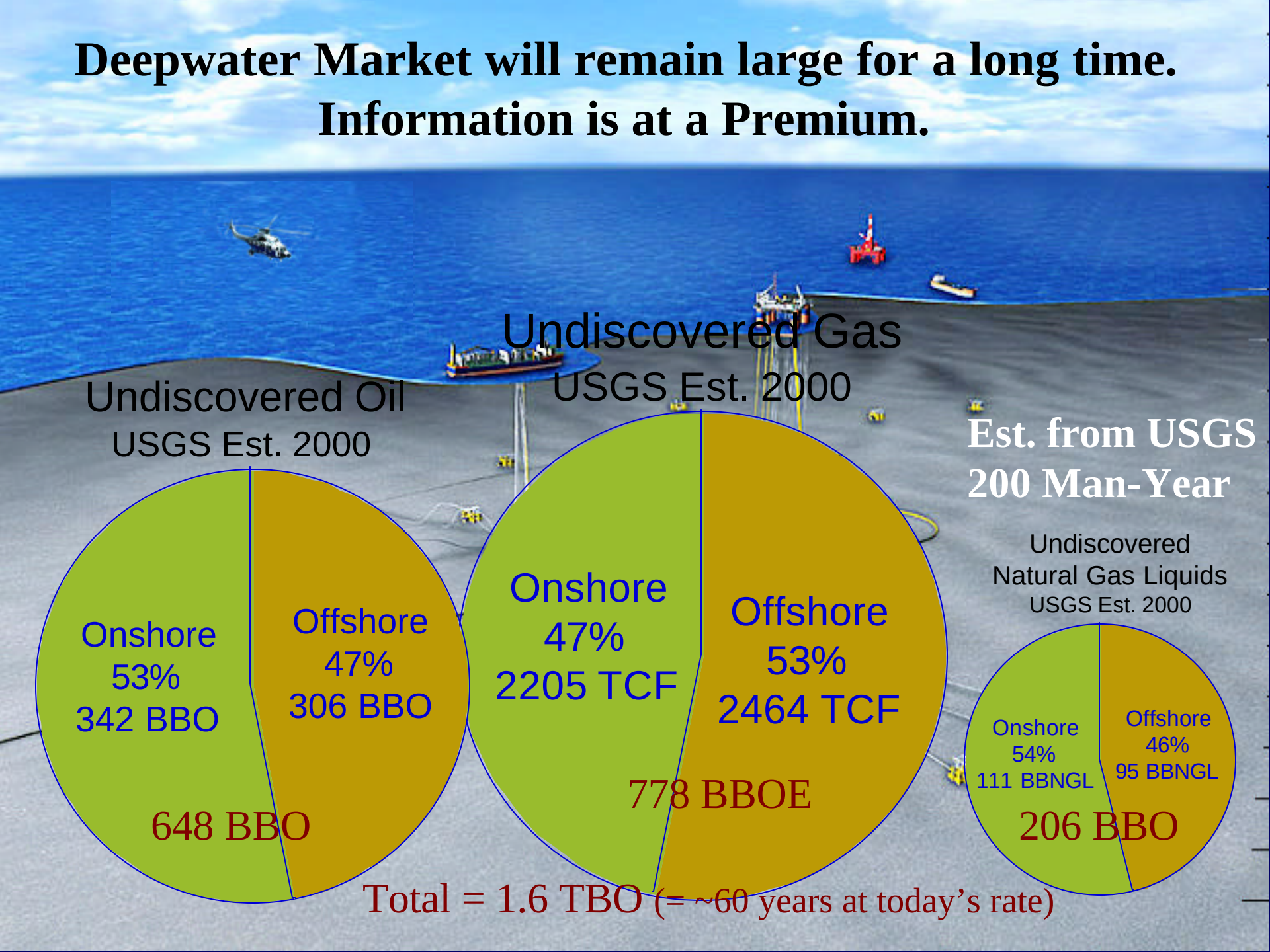
Collaborators:
FLUORESENCE: H. Groenzin, L. Buch
XANES: U. Bergmann, P. Glatzel, J. Fetzer, S.P. Cramer

Outline

1) Why study Crude Oils?
2) Asphaltene Molecular Weight – 25 Year Controversy
3) X-ray
4) Petroleomics
5) Conclusions

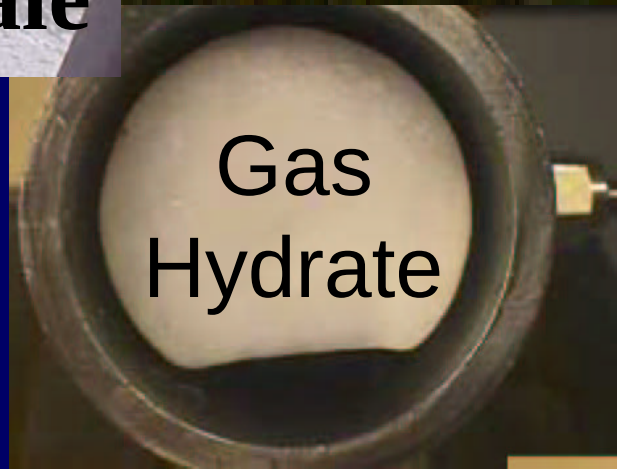


Deepwater Market will remain large for a long time. Information is at a Premium.



Total = 1.6 TBO (= ~60 years at today's rate)

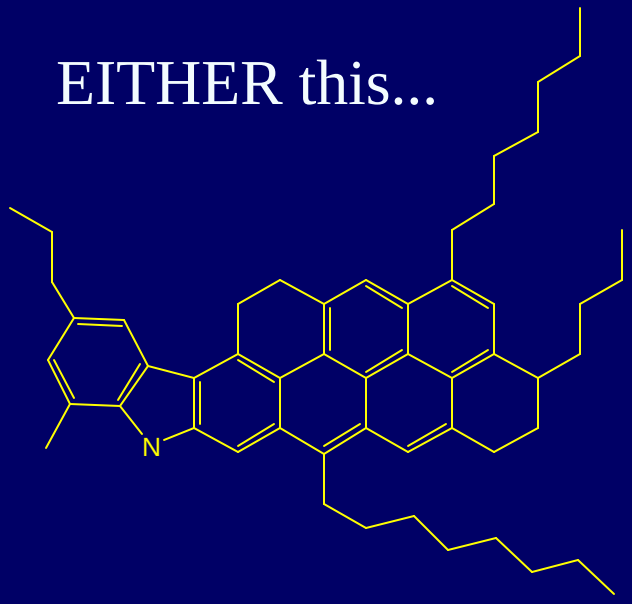
Oil Chemistry affects…



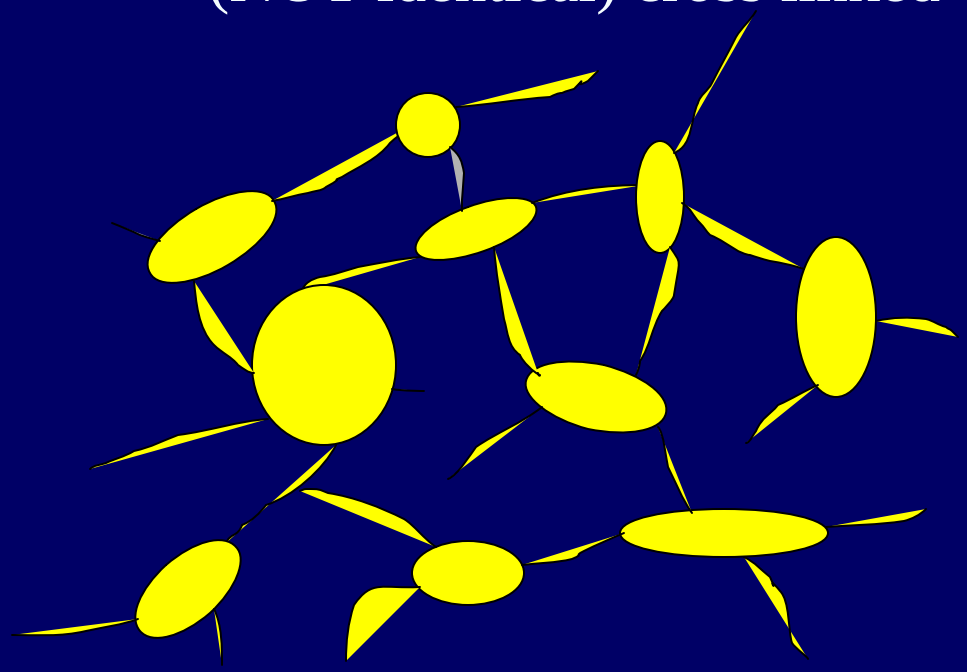
Asphaltene Molecular Structure;
>20 year, x10 fight!

Ring sizes known from STM, HRTEM, 13C NMR,
Consistent with Optics + MO, C XRRS, Solubility

EITHER this...

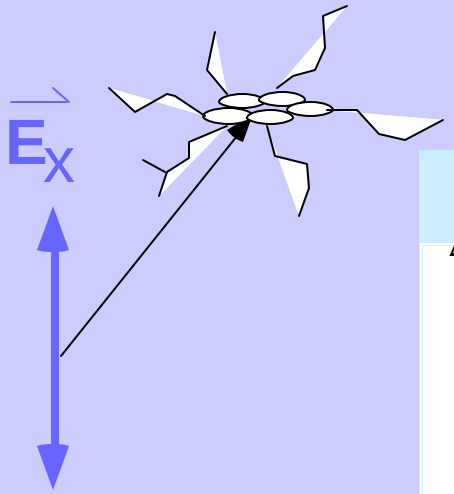


OR... 10 of these
(NOT identical) cross linked

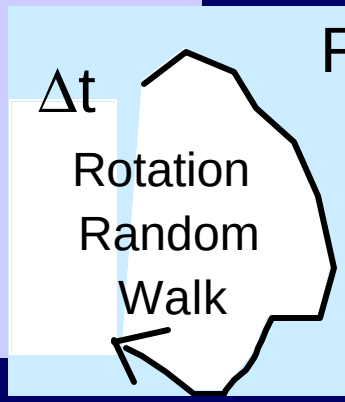


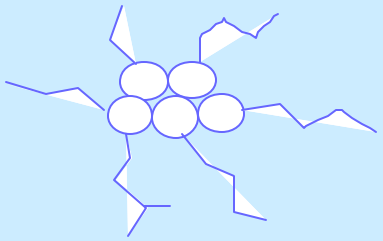
Fluorescence Depolarization

Polarized Excitation

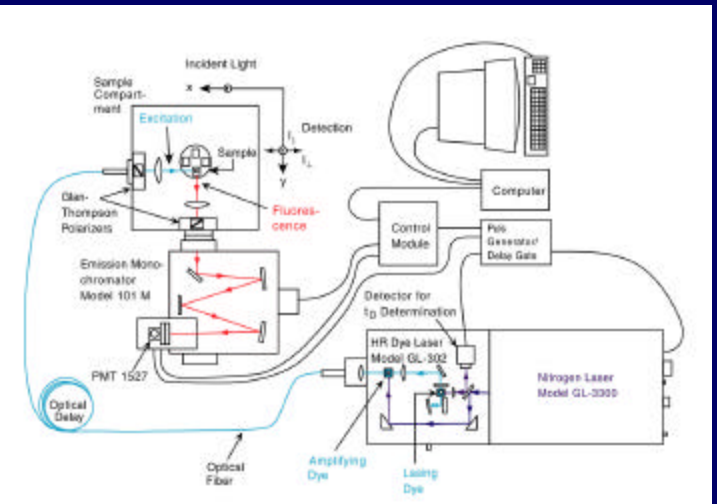


Rotational Diffusion

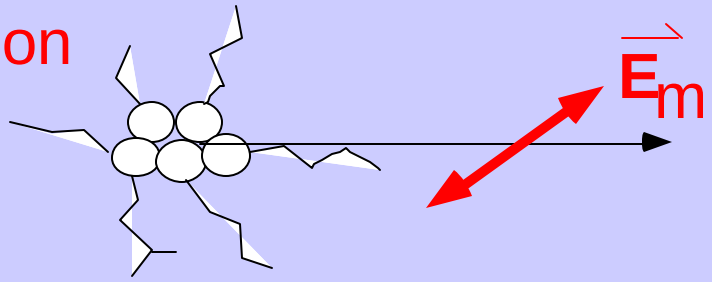




excited molecule

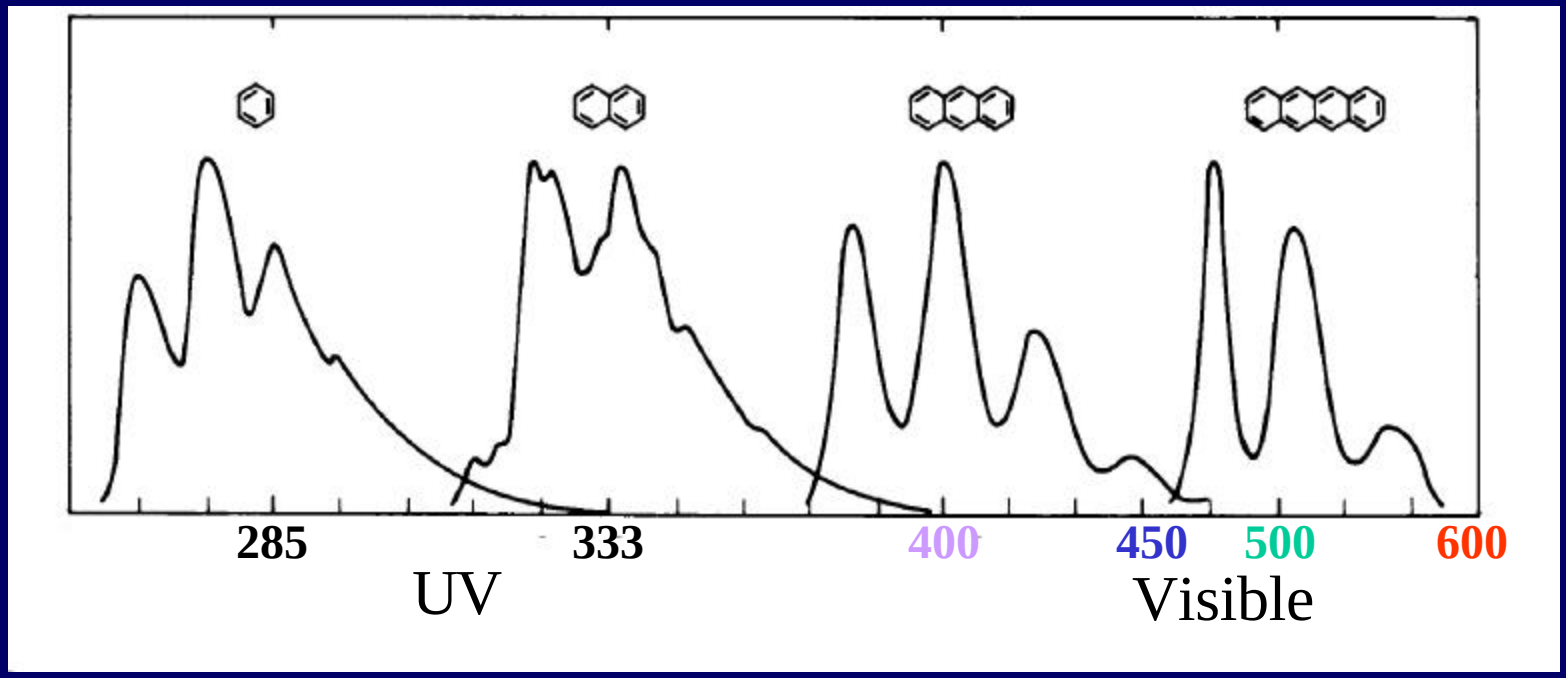


Polarized (in new direction) Emission



Chromophore Selection

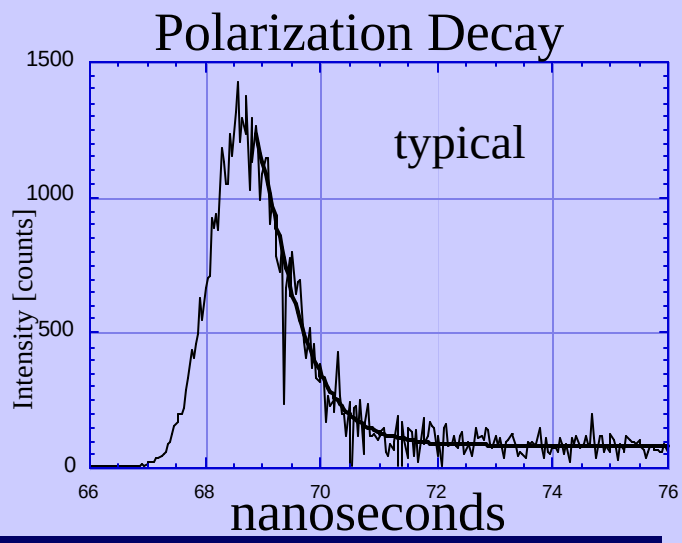
Use Excitation, Emission Wavelength
to Select Chromophore Size

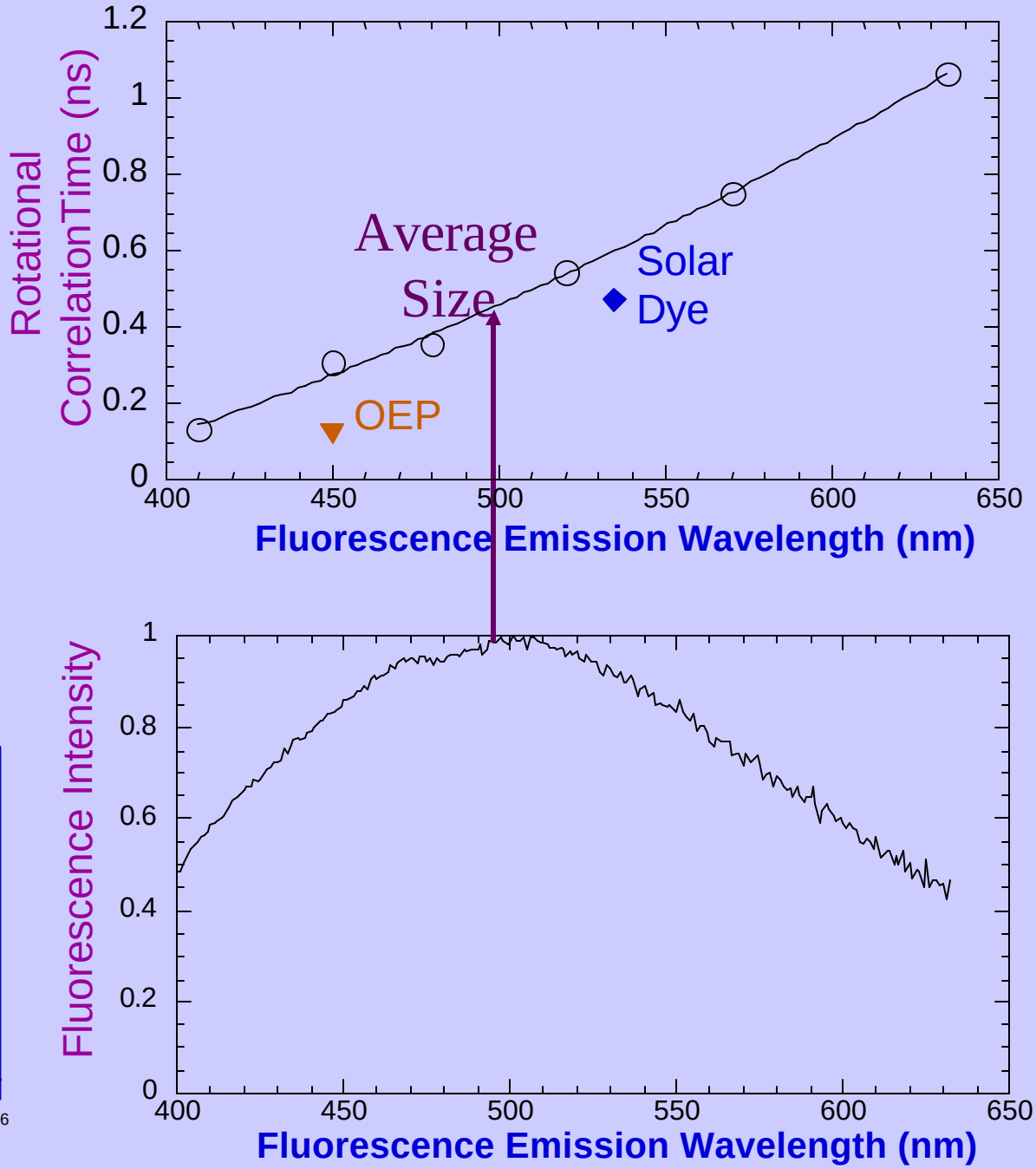


UG8 Asphaltene

H. Groenzin, O.C. Mullins
J. Phys. Chem. A (1999)

H. Groenzin, O.C. Mullins
E&F (2000)
Editor's Choice Article

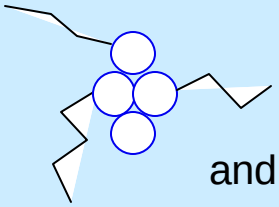




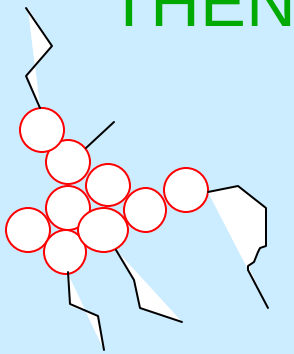
Which Asphaltene Molecule Description?

(This is correct!)

IF

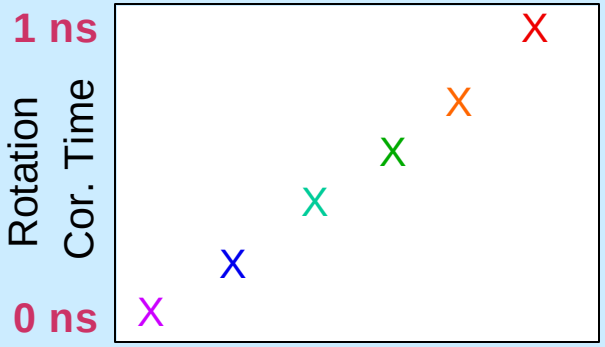


and

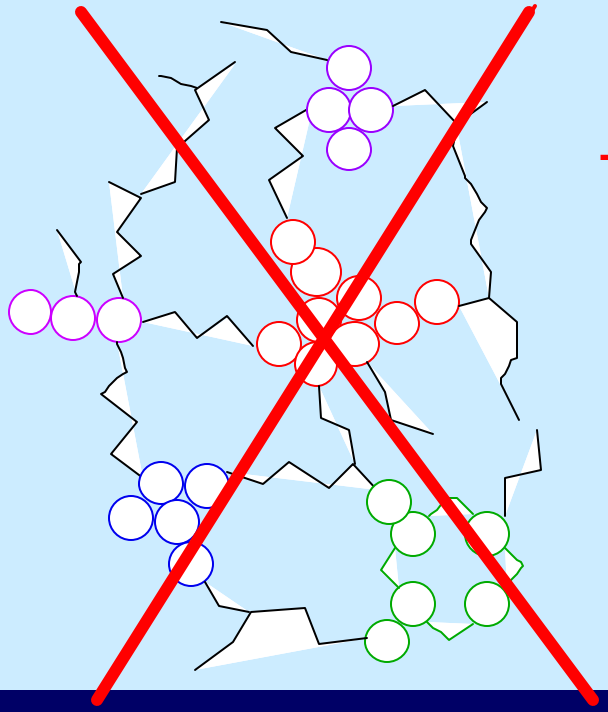


THEN

1) Small Rotation Times
2) Wavelength DEpendent Times

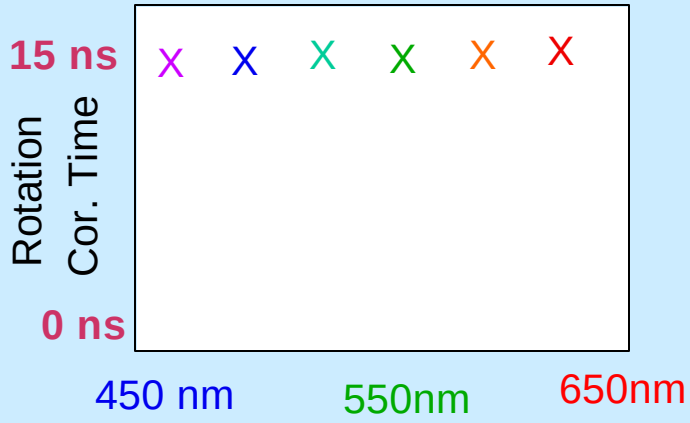


IF



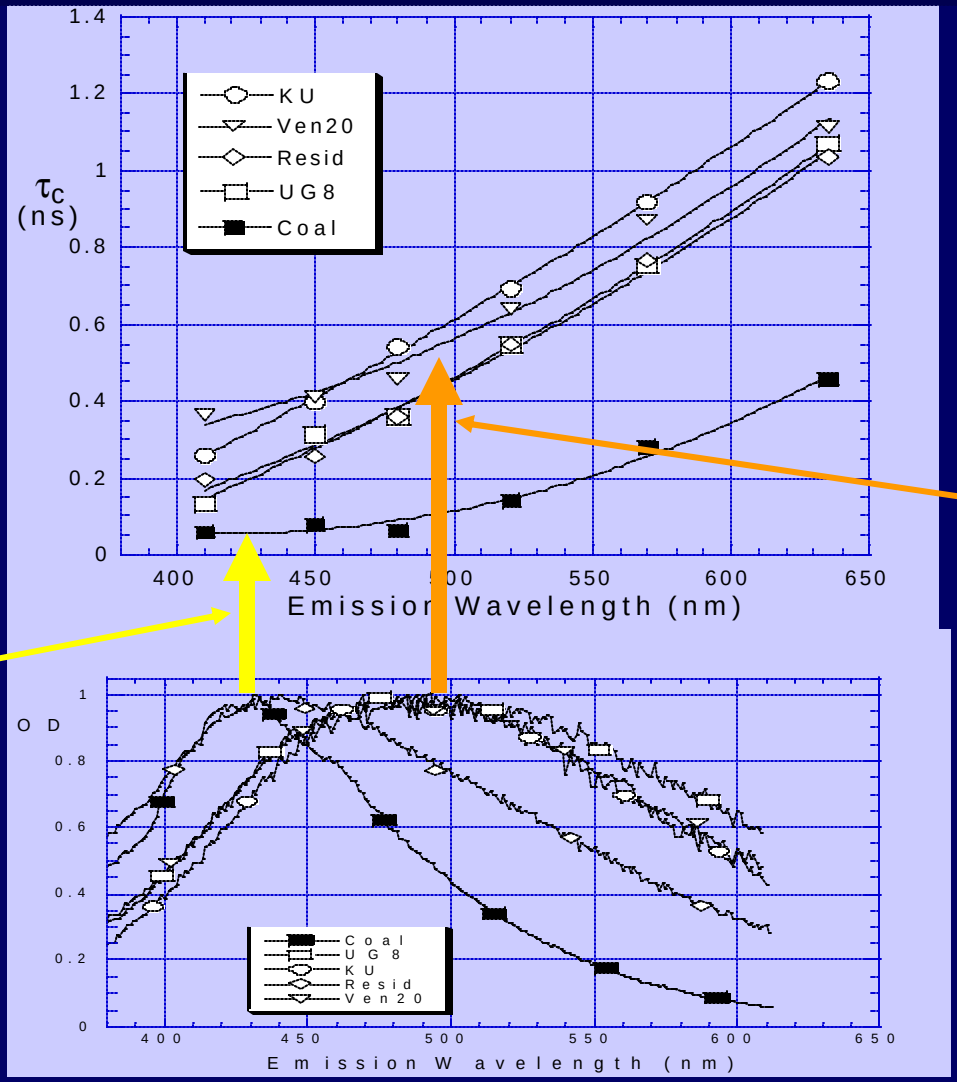
THEN

1) BIG Rotation Times
2) Wavelength INdependent Times



Fluorescence Depolarization

1) Asphaltenes are small!
2) Coal Asphaltenes much smaller than Petroleum Asphaltenes



Coal Asphaltene ~ 500 g / mole

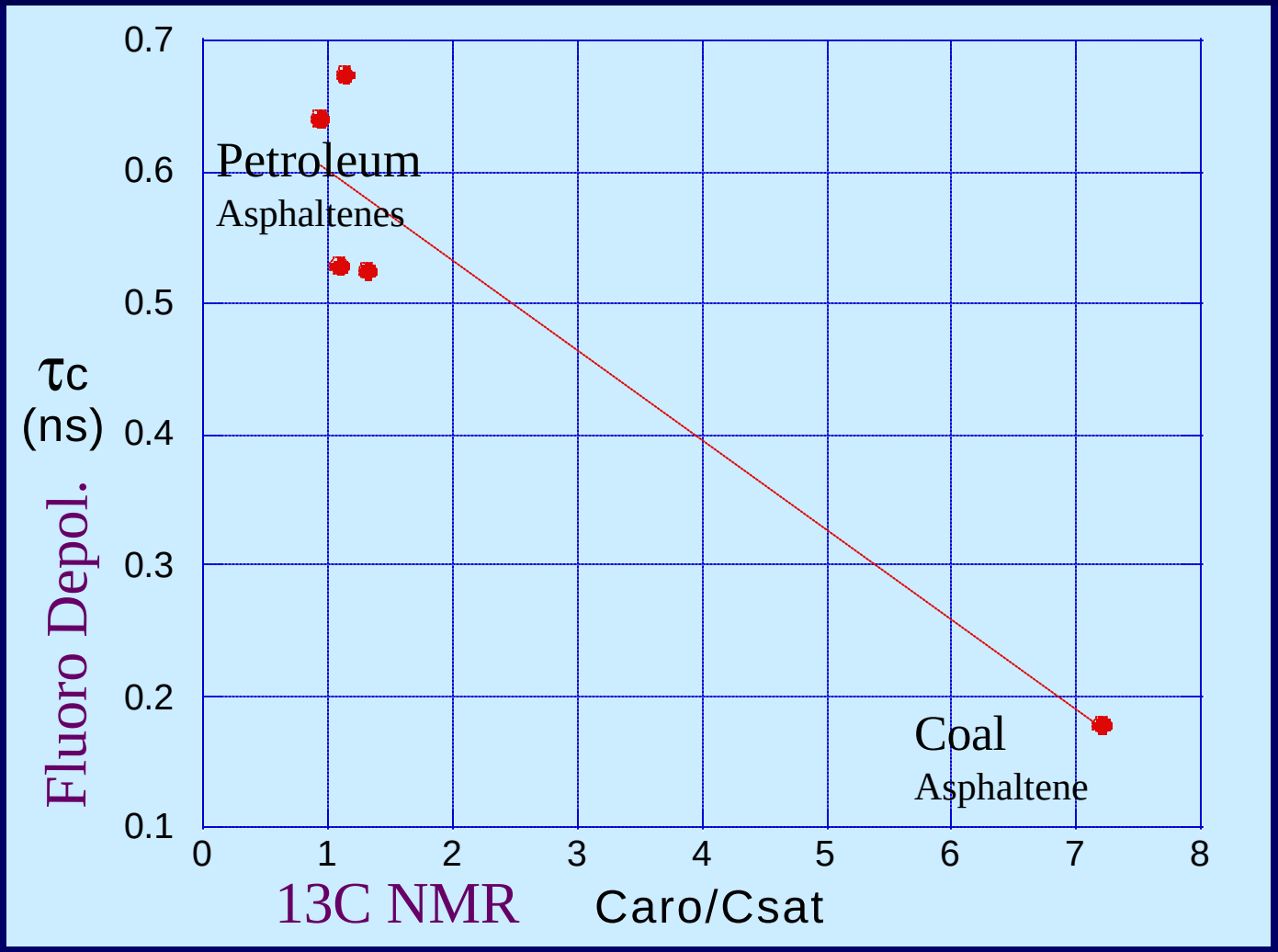
Petroleum Asphaltenes ~ 750 g / mole

E. Buenrostro-Gonzalez, et al, E&F 2001

Asphaltenes

Coal – Small alkane fraction, Small ring systems

Oil - Large Alkane fraction, Large Ring Systems



Asphaltene Solubility:

π-System Stacking vs Steric Hindrance

(Structure to Properties)

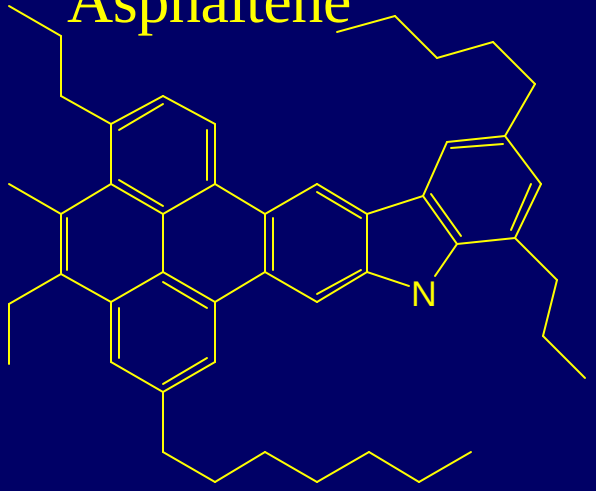
From Petroleum:
Lots-o-Alkane
thus Lots-o-rings
Mol. Wt. 708

From Coal:
Few Alkanes
thus Few Rings
Mol. Wt. 309

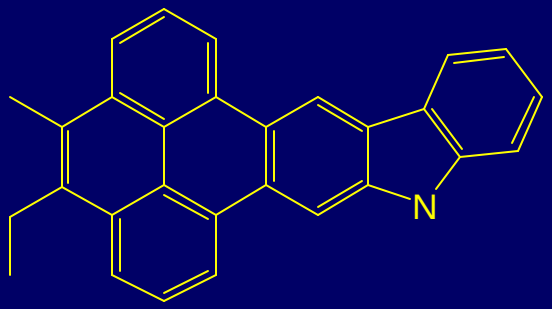
Cracking makes smaller asphaltenes

L. Buch, H. Groenzin, E. Buenrostro-Gonzalez,
S.I. Andersen, C. Lira-Galeana, O.C. Mullins,
Effect of hydrotreatment on asphaltene fractions, Fuel, 82, 1075, (2003)

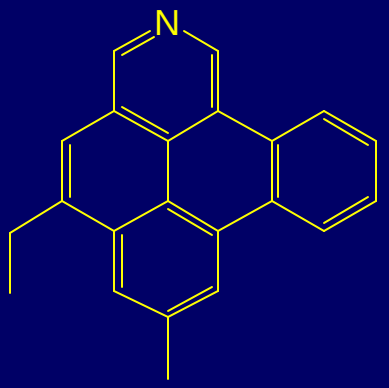
Asphaltene



Coke (insoluble)



Resin



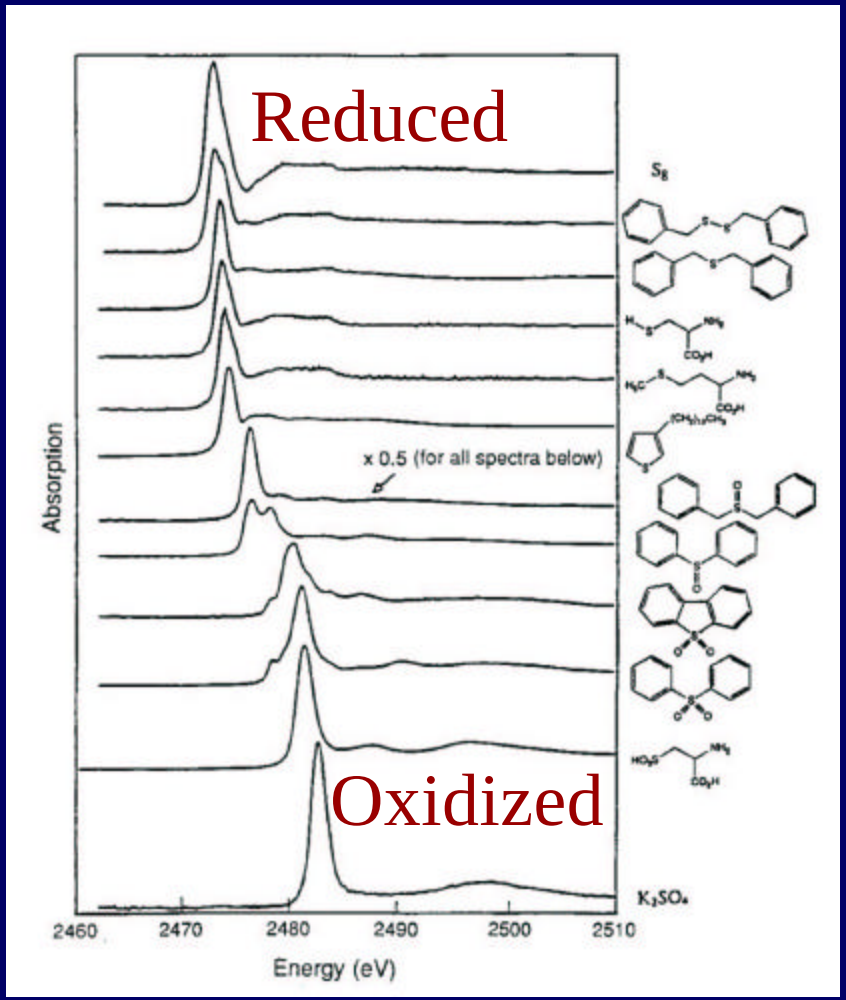
Asphaltene

X-Ray Spectroscopy

Sulfur XANES.

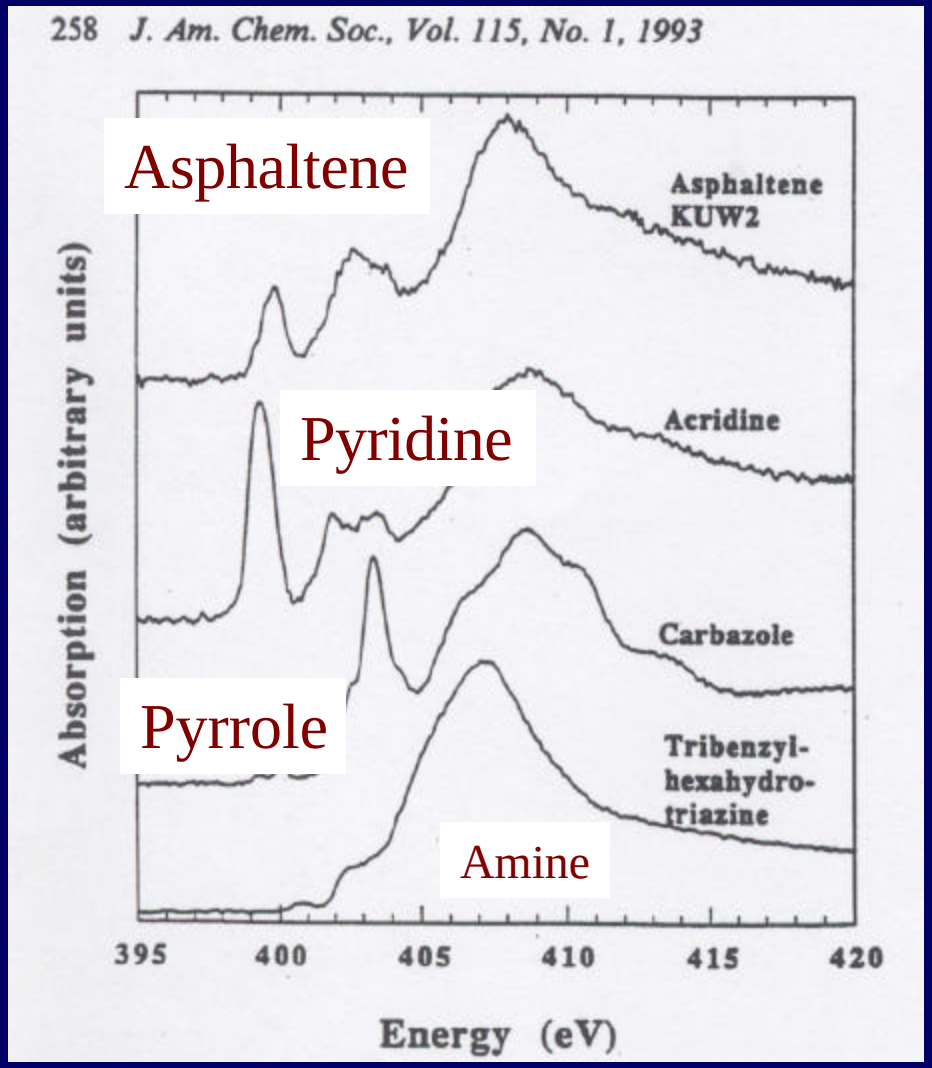
1s-3p → oxidation state

Geoffrey S. Waldo, Oliver C. Mullins, James E. Penner-Hahn, Stephen P. Cramer, Fuel, 71, 53 (1992)



Nitrogen XANES.

1s-π* → Pyrrole or Pyridine

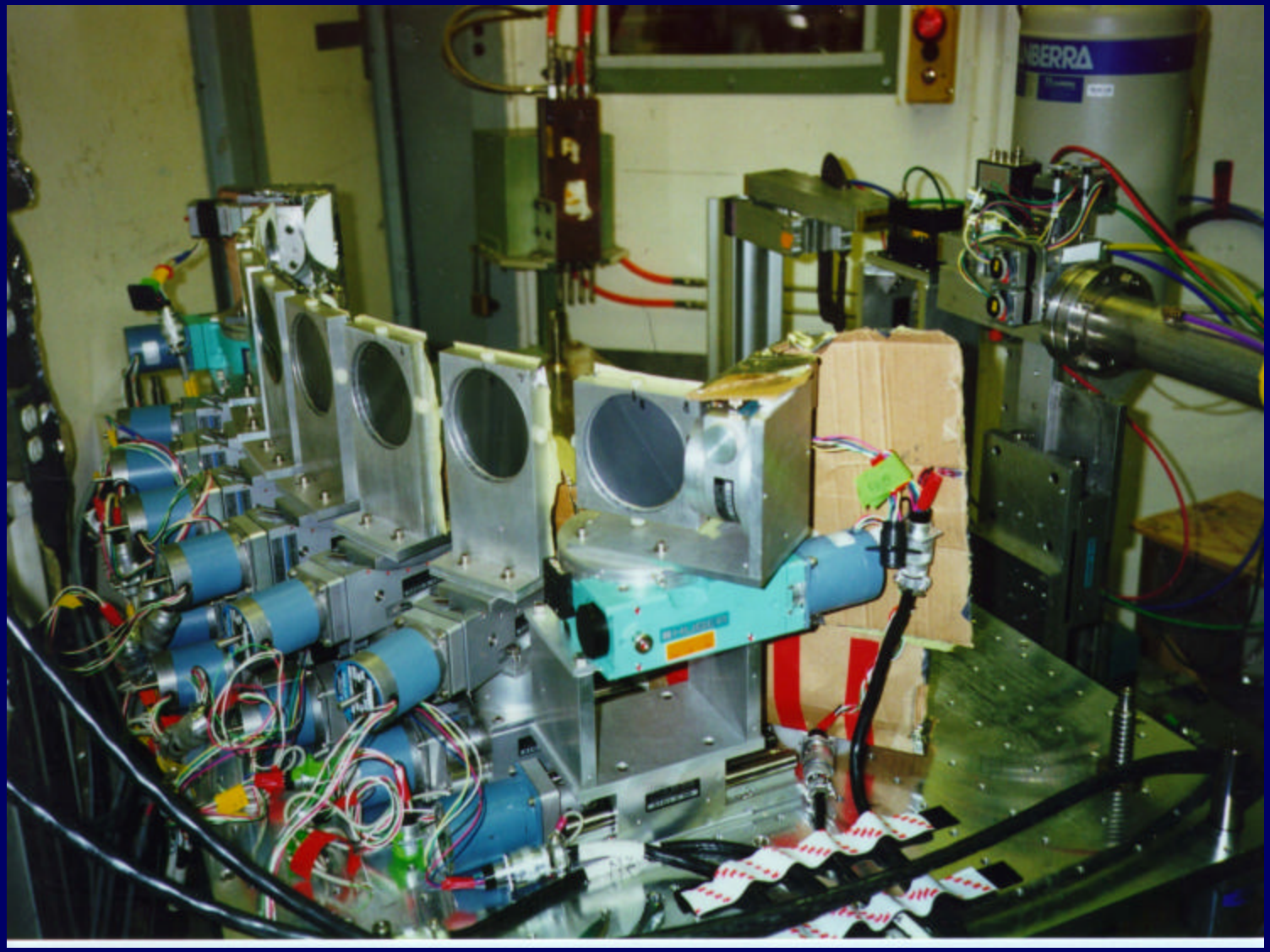


S. Mitra-Kirtley, Oliver C. Mullins, Jie Chen, Jan van Elp, Simon J. George, Stephen P. Cramer, J. Amer. Chem. Soc. 115, 252 (1993)

Carbon X-ray Raman Spectroscopy

Uwe Bergmann et al.

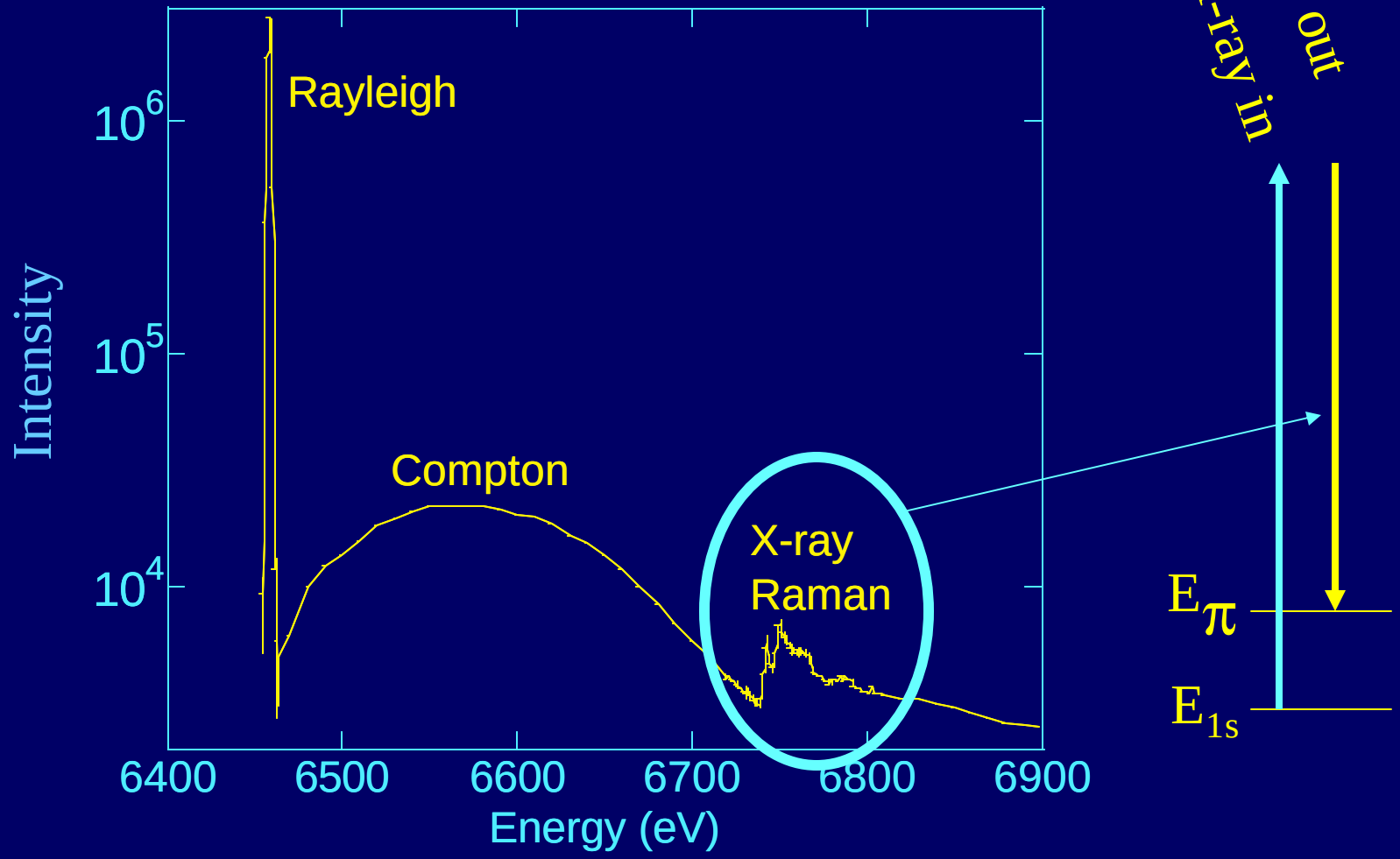
8 – Element X-ray Monochromater



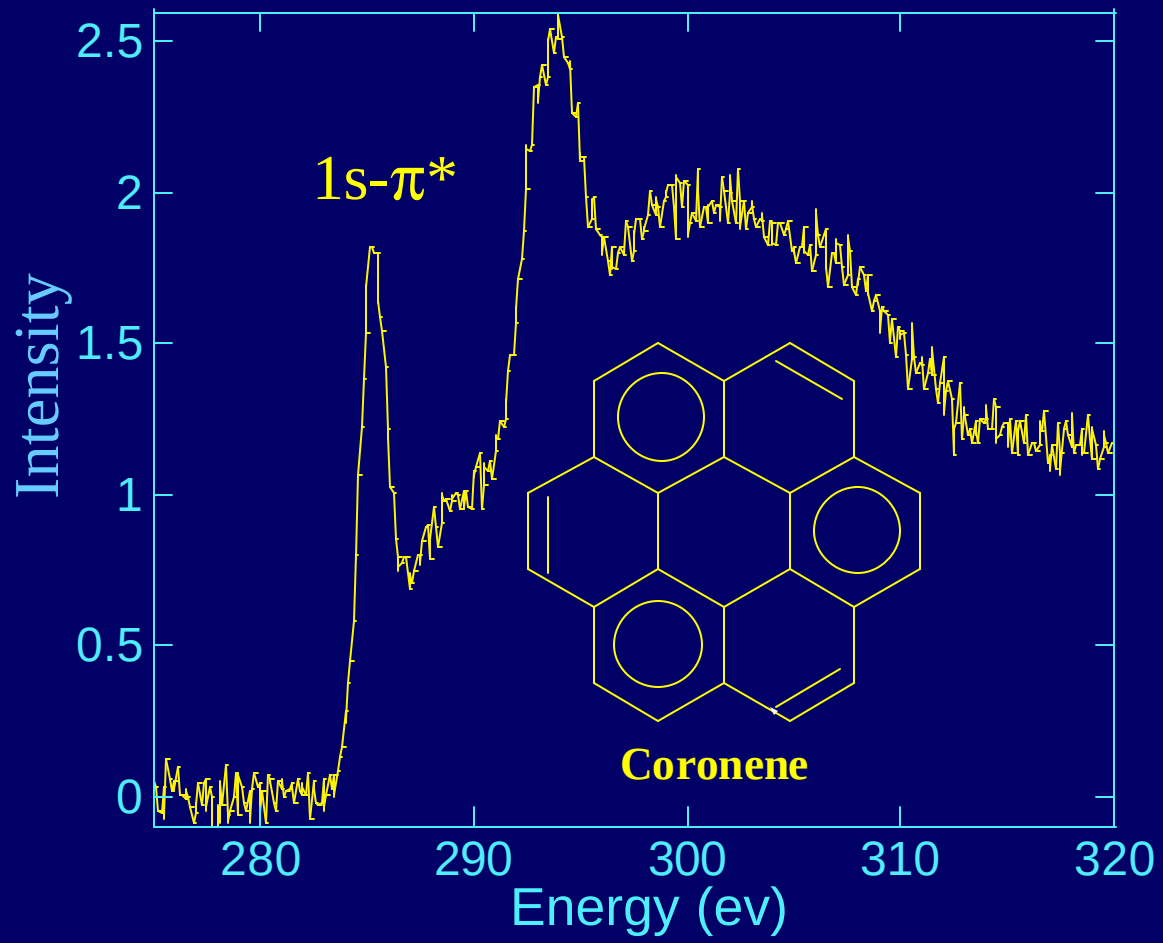
Carbon X-Ray Raman Spectrum

Fix X-ray out, Scan X-ray in

Uwe Bergmann et al.

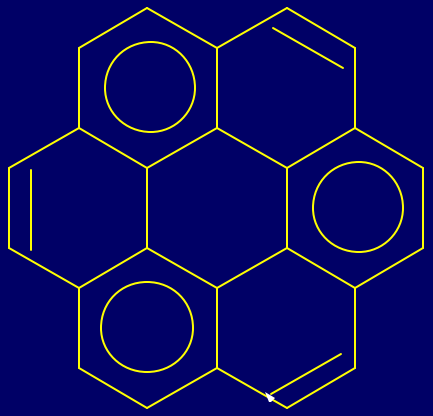


Carbon K-edge Raman Spectrum



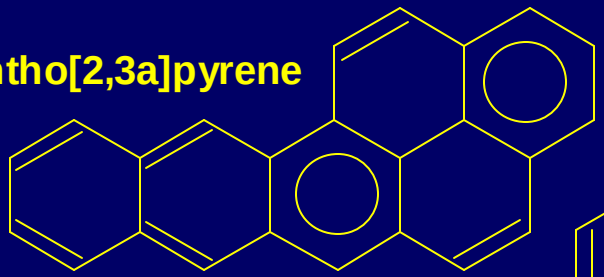
Various PAH's Examined Here

Aromatic sextet- isolated double bond representation

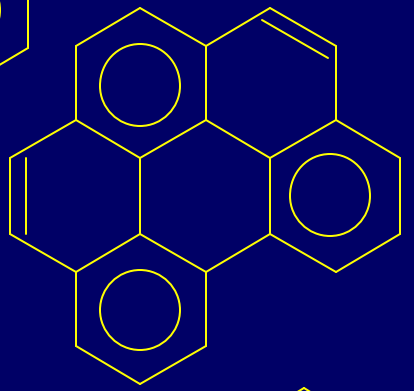


Coronene

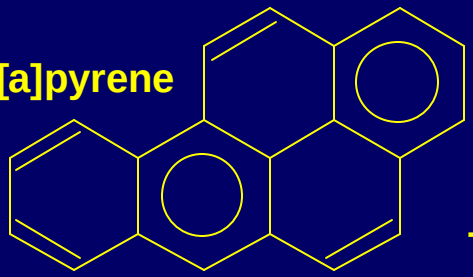
Naphtho[2,3a]pyrene



Benzo[ghi]perylene

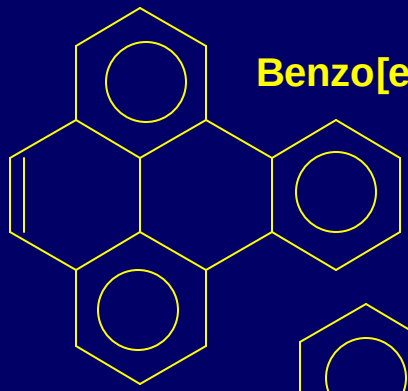


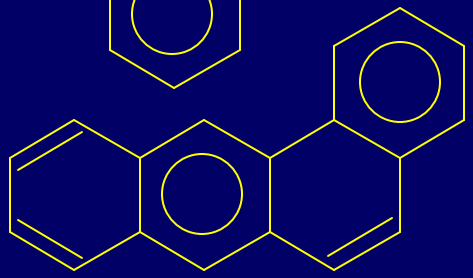
Benzo[a]pyrene



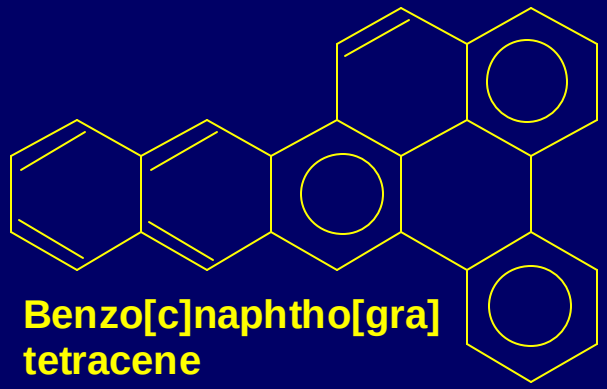
Triphenylene

Benzo[e]pyrene





1,2 Benzanthracene

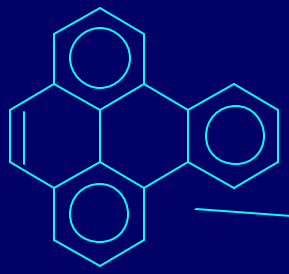


Benzo[c]naphtho[gra] tetracene

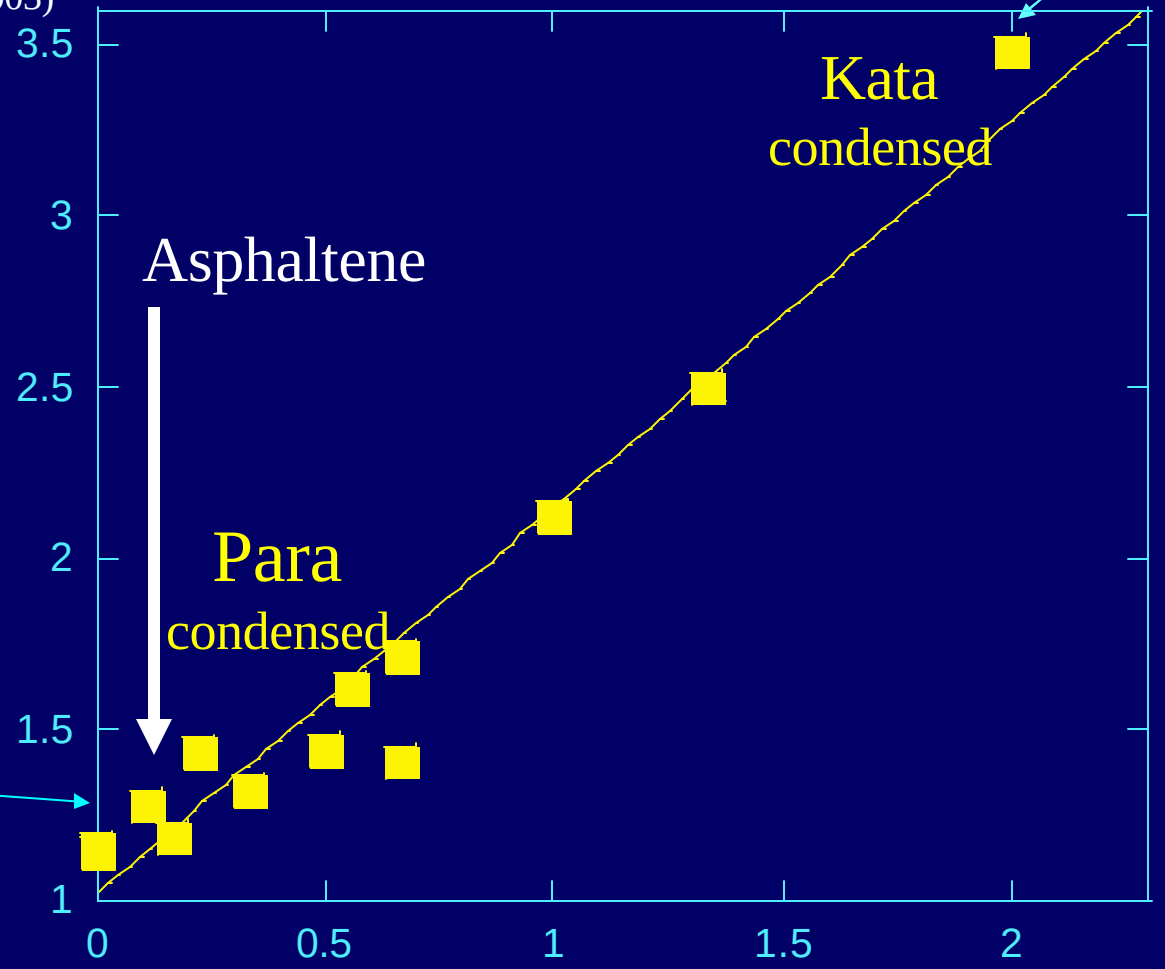
PAH's Structure

U. Bergmann, H. Groenzin, O.C. Mullins, P. Glatzel, J. Fetzer, S.P. Cramer, Chem Phys. Lett. 369, 184, (2003)

Tetracene

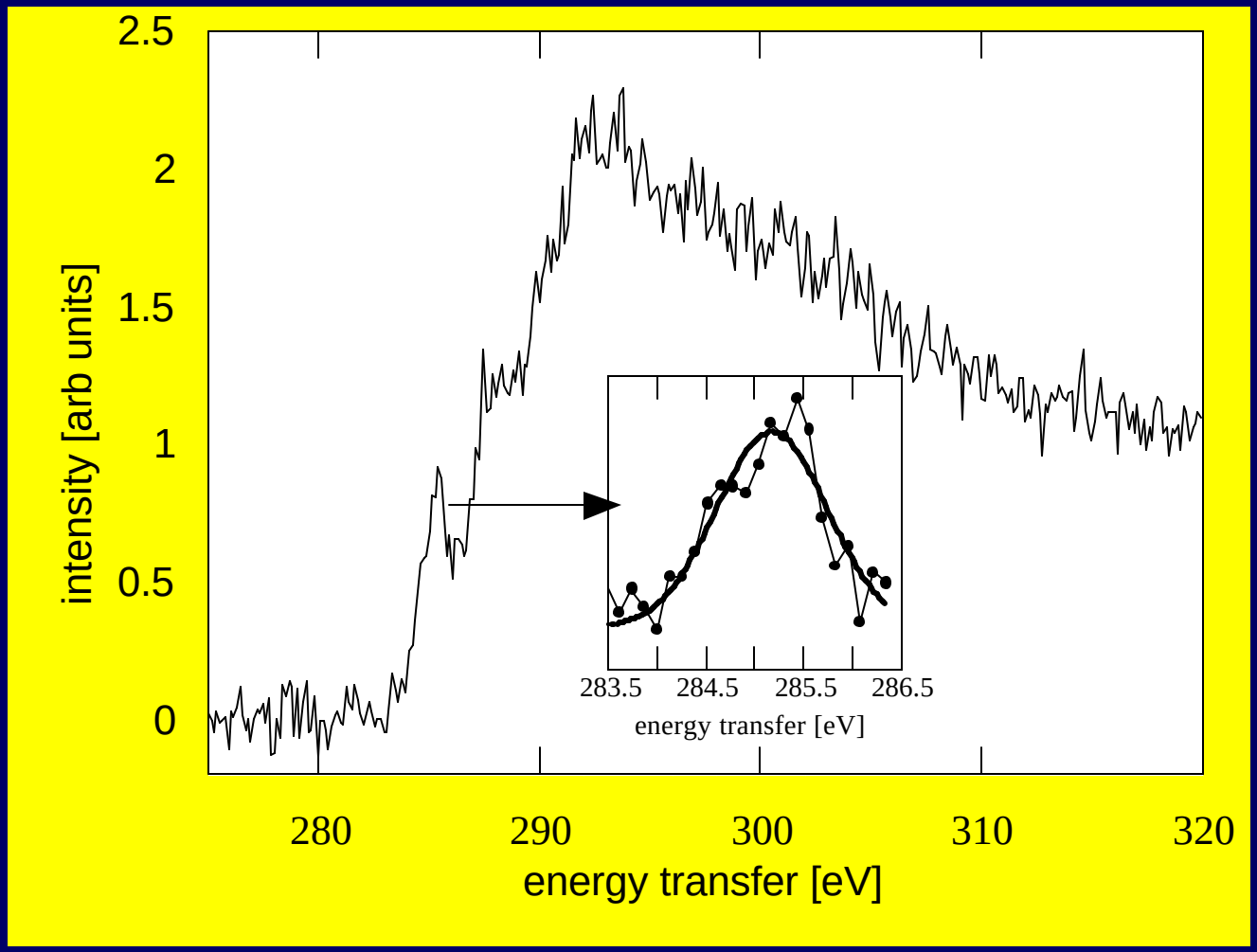


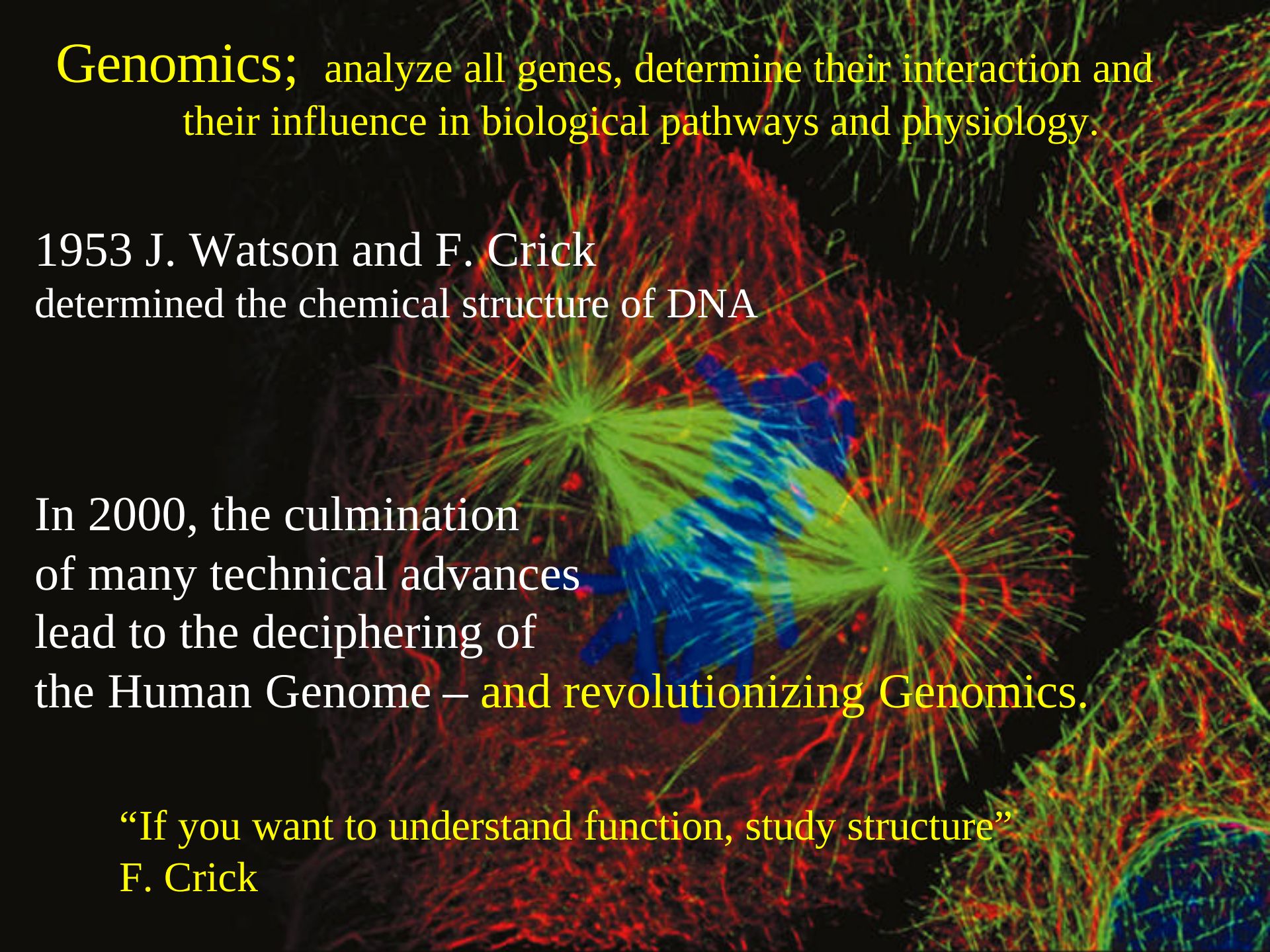
Benzo-e-pyrene



Asphaltenes have Sextet Carbon (Paracondensed)

Asphaltene linewidth ~1.3 eV





Genomics; analyze all genes, determine their interaction and their influence in biological pathways and physiology.

1953 J. Watson and F. Crick
determined the chemical structure of DNA

In 2000, the culmination
of many technical advances
lead to the deciphering of
the Human Genome – and revolutionizing Genomics.

"If you want to understand function, study structure"
F. Crick

September 22, 2003 Genomics

"All the News That's Fit to Print"

The New York

VOL. CLIII . . . . No. 52,614 Copyright © 2003 The New York Times NEW YORK, MONDAY, SEPTEMBER 22, 2003

Genomics Wins !
Petroleomics Enabled !

SOFT ECONOMY AIDS RECRUITING EFFORT, ARMY LEADERS SAY

ALL SERVICES MEET GOALS

Anxiety Over Situation in Iraq Hasn't Hurt Drive to Enlist 100,000, Officials Insist

By ERIC SCHMITT

FORT KNOX, Ky., Sept. 16 — The slumping American economy has proved to be a huge boon to the Army's efforts to recruit the 100,000 enlisted soldiers it says it needs this year to fill its active-duty and reserve ranks, senior Army officials say, so far relieving concerns that the turmoil in Iraq could crimp new enlistments.

All the armed services say they will meet or exceed their recruiting goals for the fiscal year ending on Sept. 30. But many military personnel experts say the Army's efforts are most vulnerable over time because the Army recruits more active-duty and Reserve troops than all the other services combined — 73,800 active-duty and 26,400 Reserve soldiers this year — and it is now fielding about 90 percent of the 180,000 troops in Iraq and Kuwait.

"That's the driver, the economy," said Maj. Gen. Michael D. Rochelle, the head of the Army Recruiting Command here, adding that the chaotic conditions in Iraq have yet to

President Jacques Chirac wi

Bush to Defen Chirac Urges

Theme to Be Curtai Nuclear Proliferati

By DAVID E. SANGER

WASHINGTON, Sept. 21 — dent Bush will tell the United N on Tuesday that he was right t the invasion of Iraq even with

Scientists in Iceland Discover First Gene Tied to Stroke Risk

By NICHOLAS WADE

Researchers in Iceland say they have discovered the first gene that underlies common forms of stroke, a disease that affects more than 600,000 people a year in the United States.

People with a particular version of the gene have a three to five times greater risk of stroke, said the researchers, who are at Decode Genetics, a company based in Reykjavik. This is as large as or larger than known environmental risk factors like high blood pressure, high cholesterol and smoking.

Dr. Kari Stefansson, the chief executive of Decode, said that the new gene makes an enzyme that is a good target for drugs, and that the Roche pharmaceutical company in Switzerland was already testing several such drugs in laboratory rats.

The new gene was identified by a team led by Dr. Solveig Gretarsdottir. The gene had not previously been implicated in stroke, and its detection may open new insights into the mechanisms of the disease. Decode's work, reported today in the journal Nature Genetics, is a "tour de force" and "highly, highly significant for the stroke field," said Dr. Jonathan Rosand, a stroke specialist at Massachusetts General Hospital.

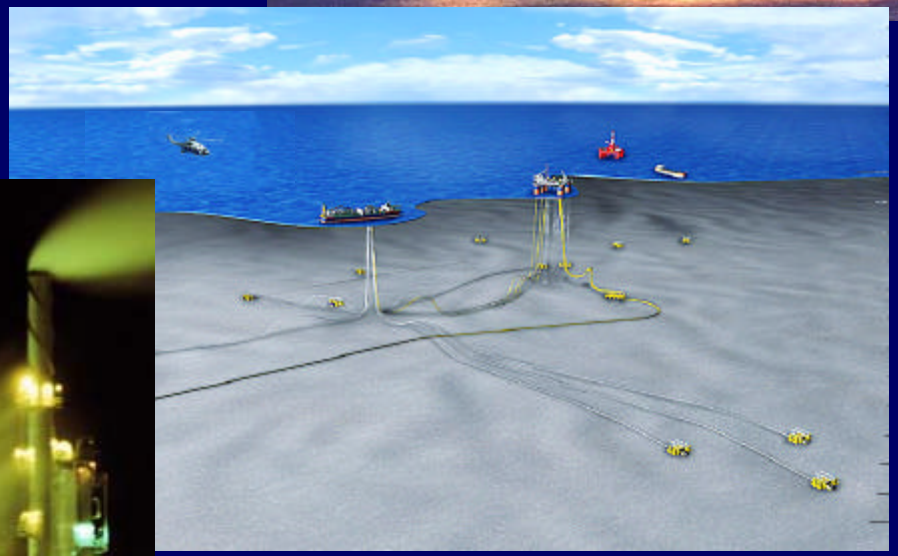
But the study is unlikely to yield new treatments any time soon and

Continued on Page A14

Petroleomics:

The Characterization of All Chemical Constituents of Petroleum, their Interactions and their Reactivity.

Petroleomics: Coined by A. Marshall,
Defined by A. Marshall, O.C. Mullins



Petroleomics:

Composition to Properties

A Marshall, R. Rodgers,

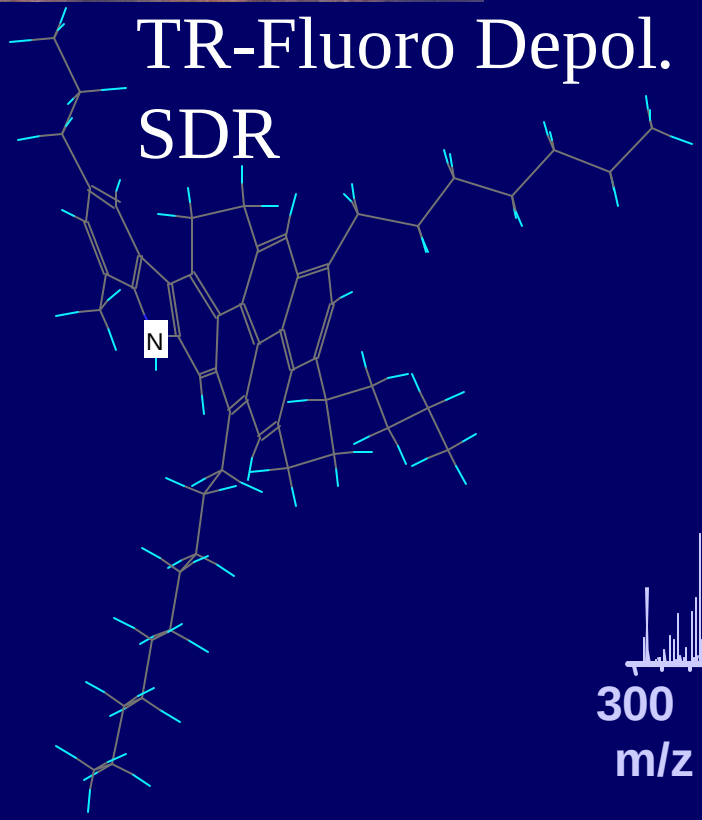
OC Mullins

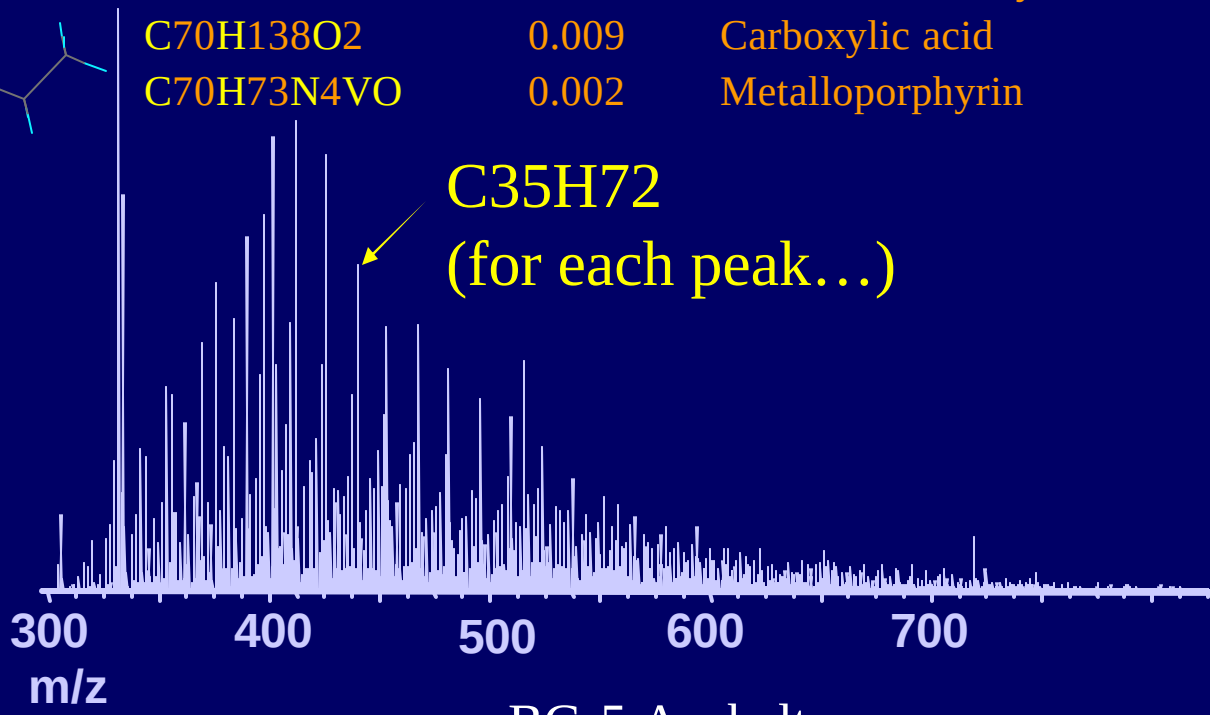
Mass spec of asphaltene: FSU

		Probable
C70H142	0.18	Saturated alkane
C70H134	0.007	Benzy alkane
C70H73	0.012	H-Deficient heavy end
C70H138O2	0.009	Carboxylic acid
C70H73N4VO	0.002	Metalloporphyrin

TR-Fluoro Depol.

SDR





BG-5 Asphaltene

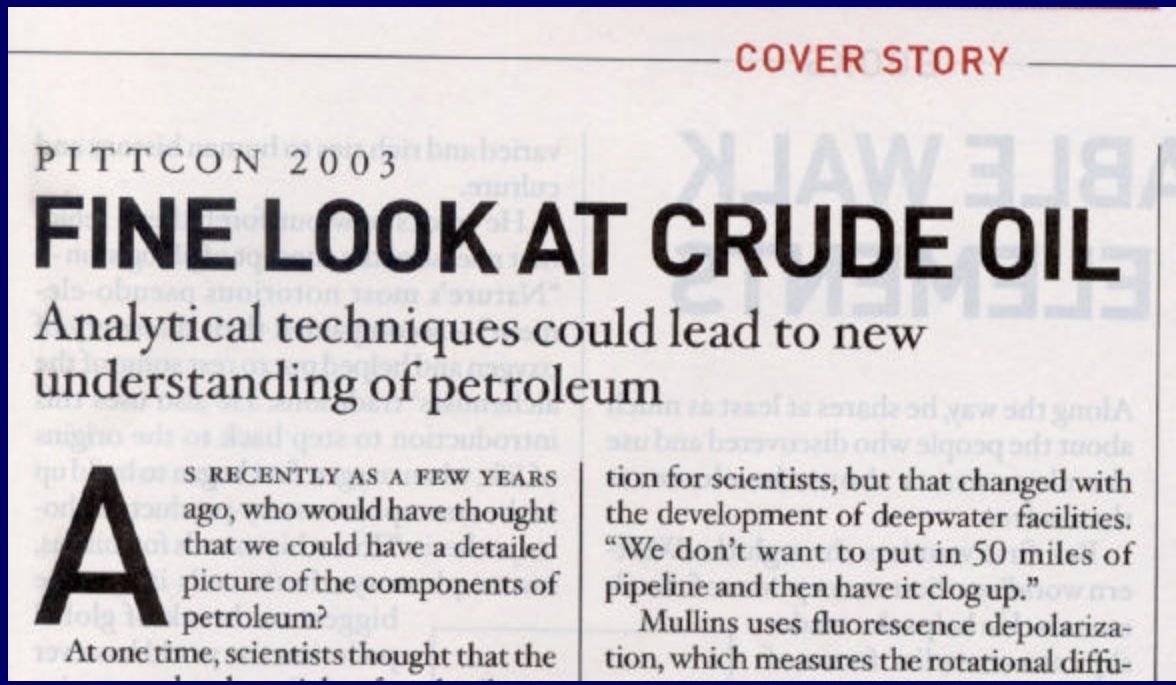
Petroleomics: Composition to Properties

SLB Currently has the best commercial fluid analysis.
but phenomenological….

Florida State U gives
Oil Composition.

We want DOE $
w/ U of Houston
for Dead Oil
Petroleomics.

Endorsement of Chemical Community



COVER STORY

PITTCON 2003

FINE LOOK AT CRUDE OIL

Analytical techniques could lead to new understanding of petroleum

AS RECENTLY AS A FEW YEARS ago, who would have thought that we could have a detailed picture of the components of petroleum?

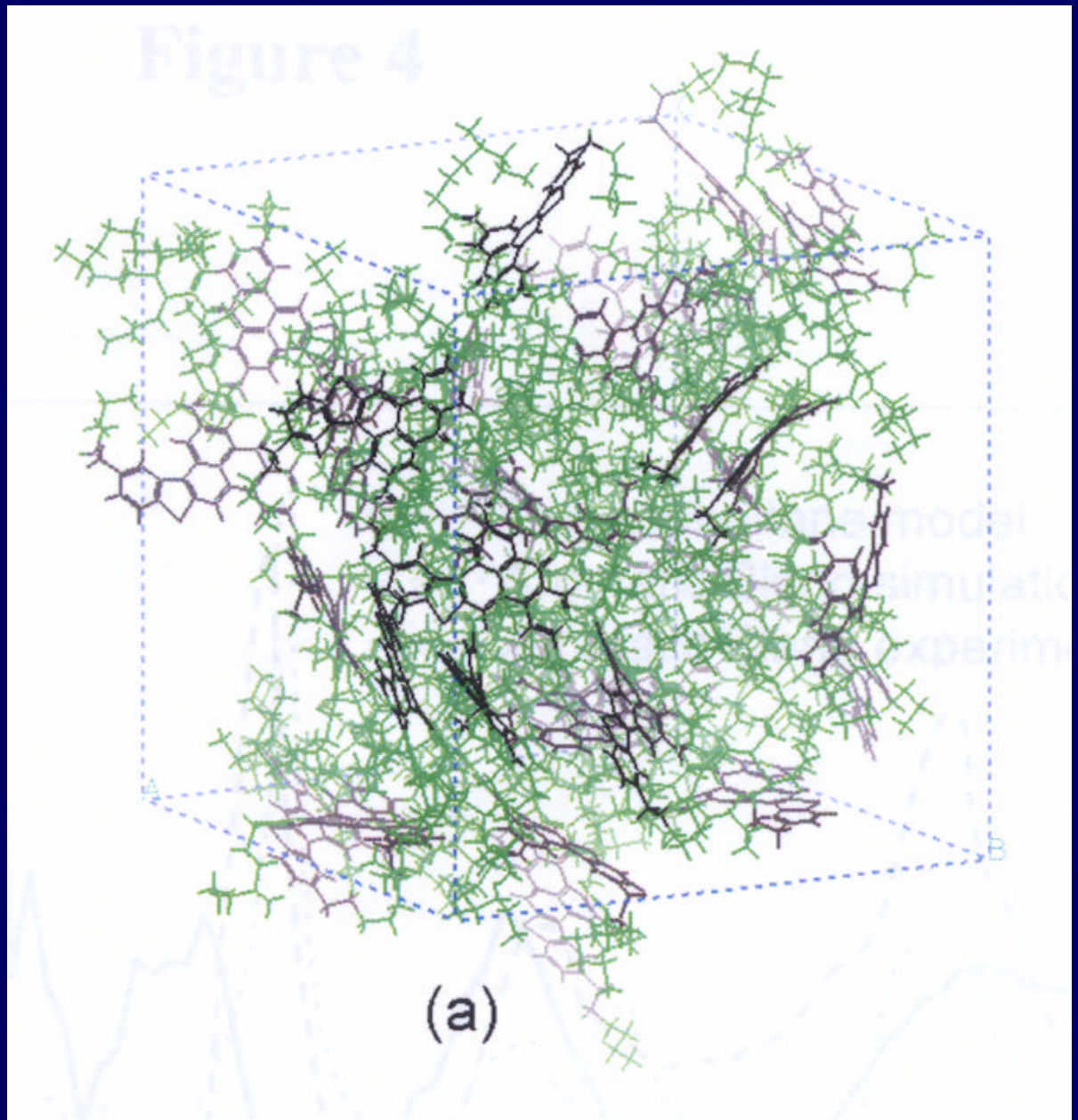
At one time, scientists thought that the

tion for scientists, but that changed with the development of deepwater facilities. "We don't want to put in 50 miles of pipeline and then have it clog up."

Mullins uses fluorescence depolarization, which measures the rotational diffu-

Now we need Chem E's on board.

Asphaltene Structures needed to understand phase transitions.



Conclusions:

1) The study of crude oils and asphaltenes is motivated by efficient resource utilization.

2) Asphaltene molecular weight controversy is ‘over’.

3) X-ray spectroscopy is powerful for molecular structure elucidation of these complex materials

4) Petroleomics - Oil Composition to Properties; is the future of oil analysis.