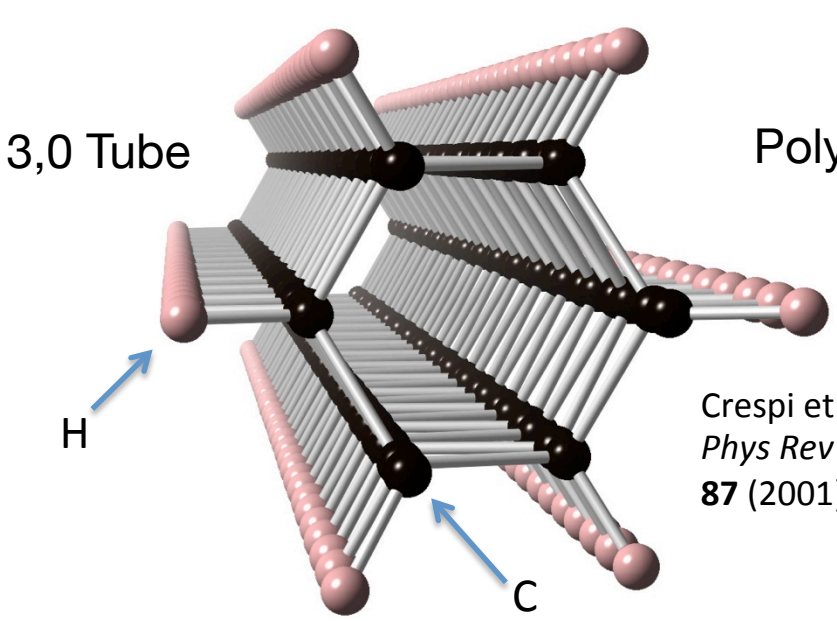
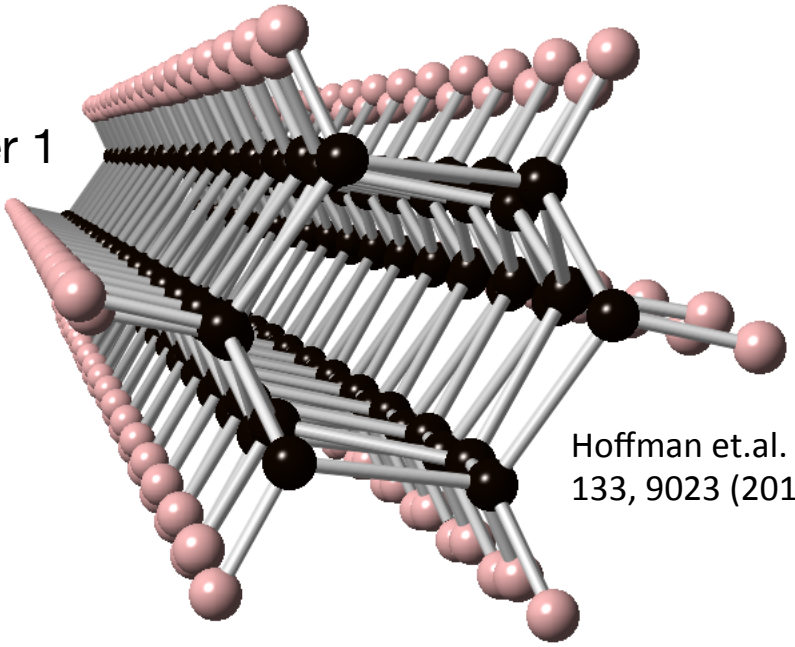


Crespi et.al.
Phys Rev Lett
87 (2001)



Hoffman et.al. JACS
133, 9023 (2011)

Benzene-Derived Diamondoid Carbon Nanothreads

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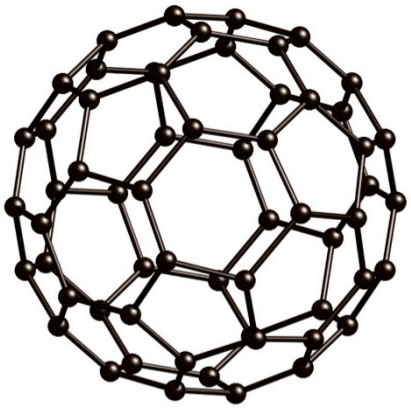
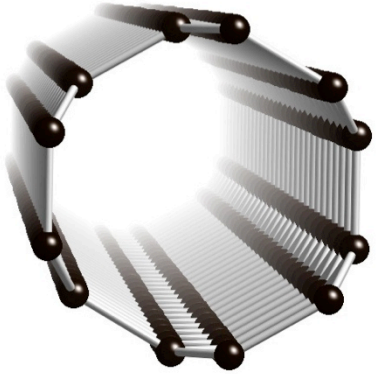
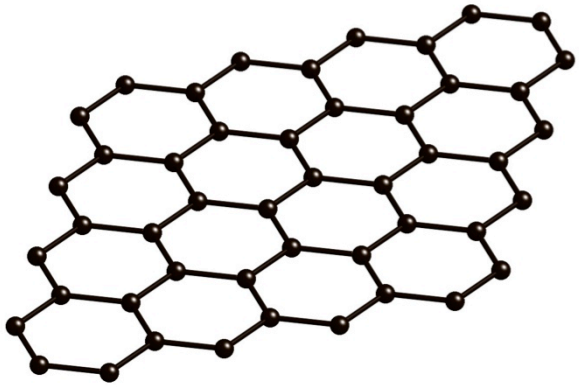
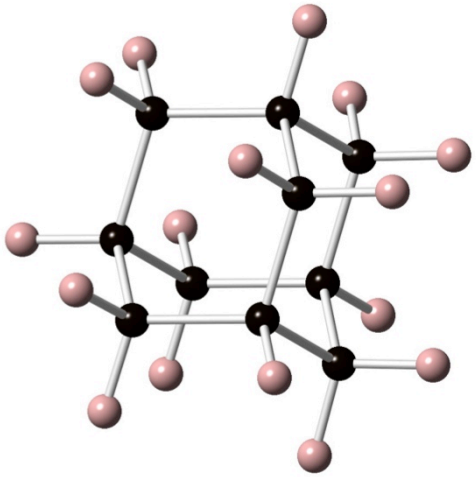
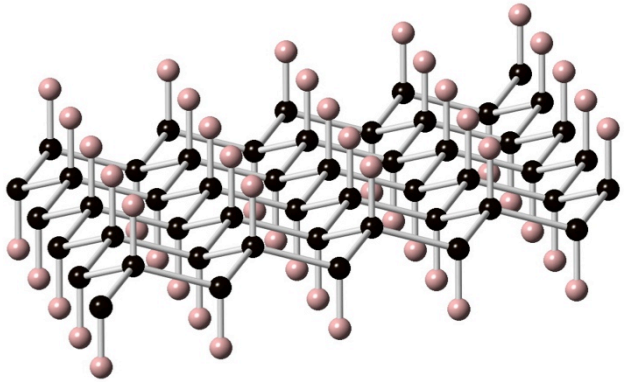
European Spallation Source

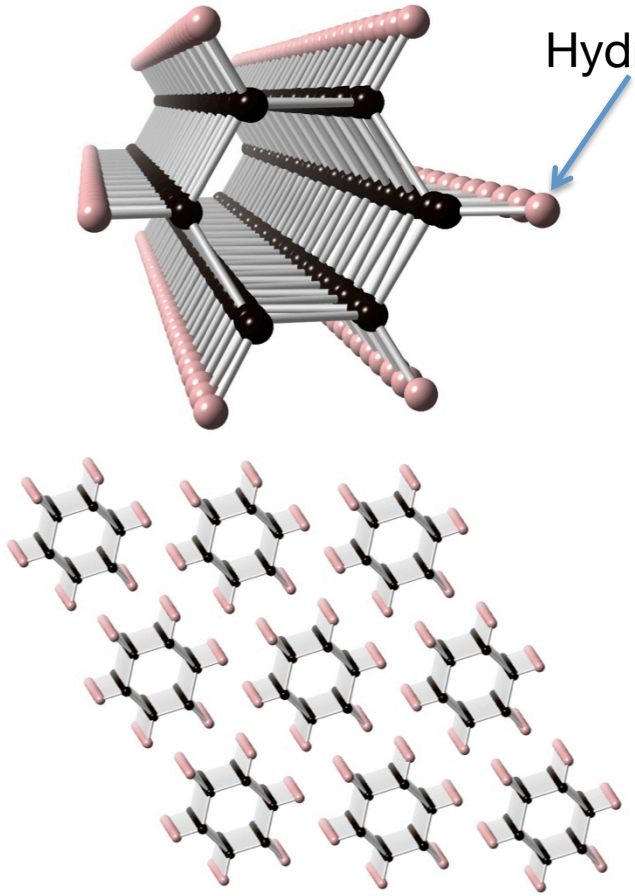
Funding: EFRee DOE Energy Frontier Research Center

Carbon Nanomaterial Dimensionality and Hybridization

	0-d	1-d	2-d
sp^2			
	C_{60}	nanotubes	Graphene
sp^3		?	
	diamondoids		Graphane

sp^3 Carbon Nanotube Theory Predictions

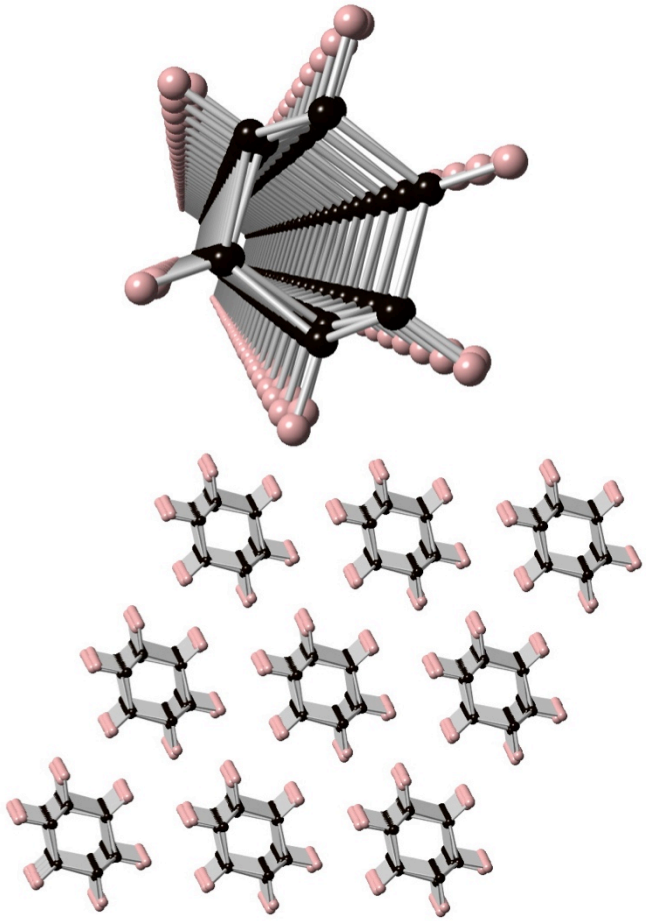
3,0 Tube



First evidence that very small sp^3 carbon nanotubes are thermodynamically stable.

Stojkovic, D. et.al. *PRL* **87**, (2001)

Polymer I

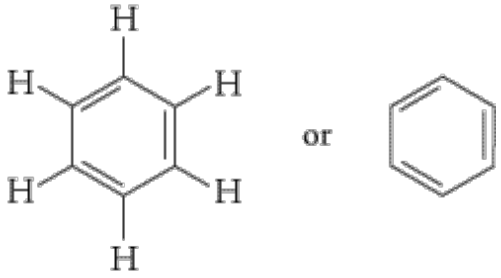


sp^3 tube predicted to form during a high pressure reaction of benzene

Wen, X-D. et.al. *JACS* **133**, 9023 (2011)

Benzene Rapid Decompression: Amorphous Product

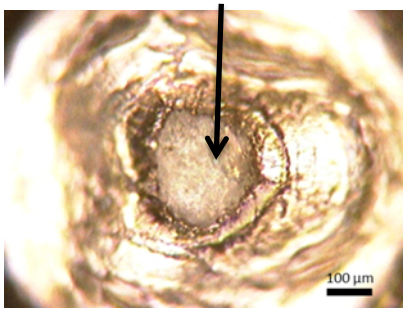
Liquid Benzene



25 GPa

Diamond
Anvil cell

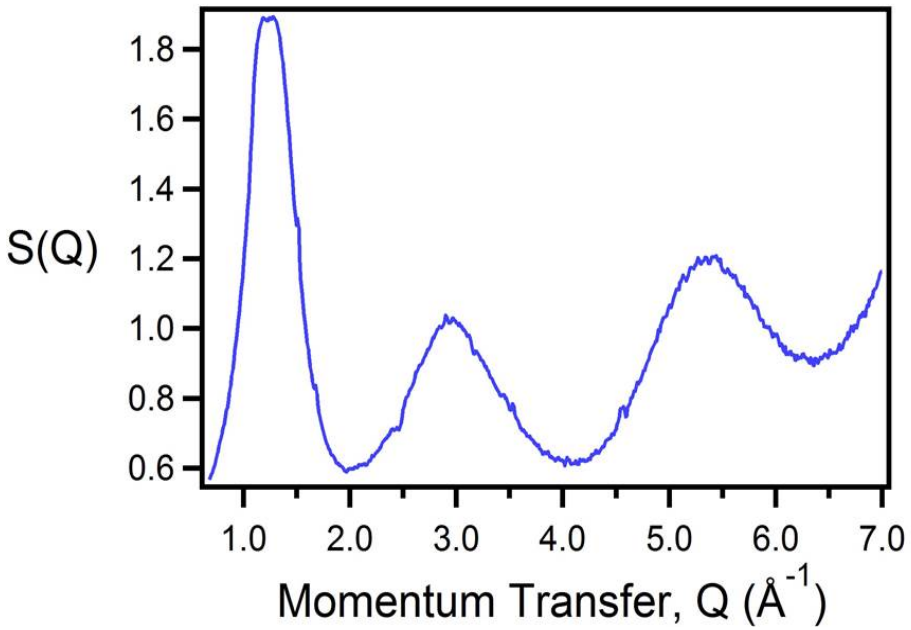
Yellow/white solid



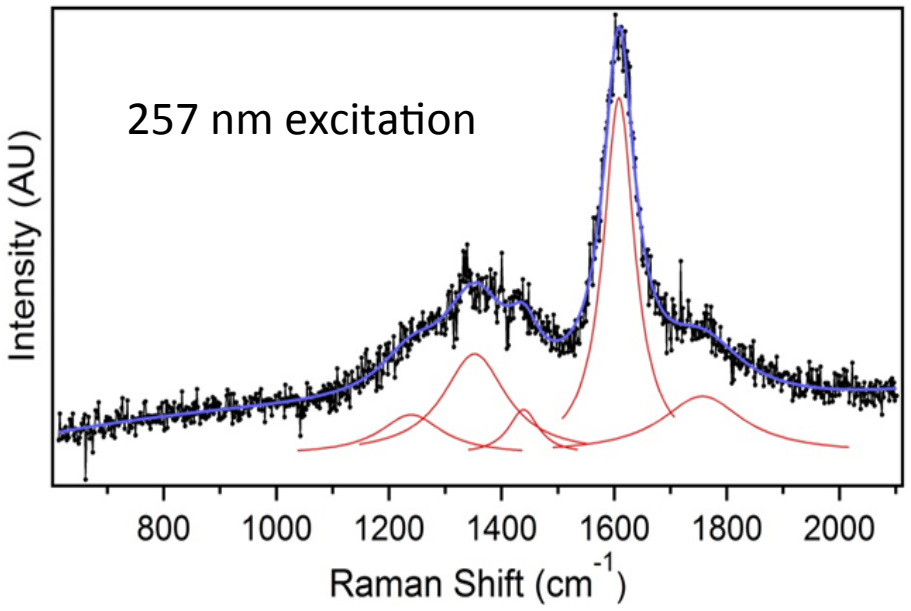
Diamond
anvil cell
gasket after
decompression

Decompression rate ≈12-20 GPa/hr → Broad spectral features

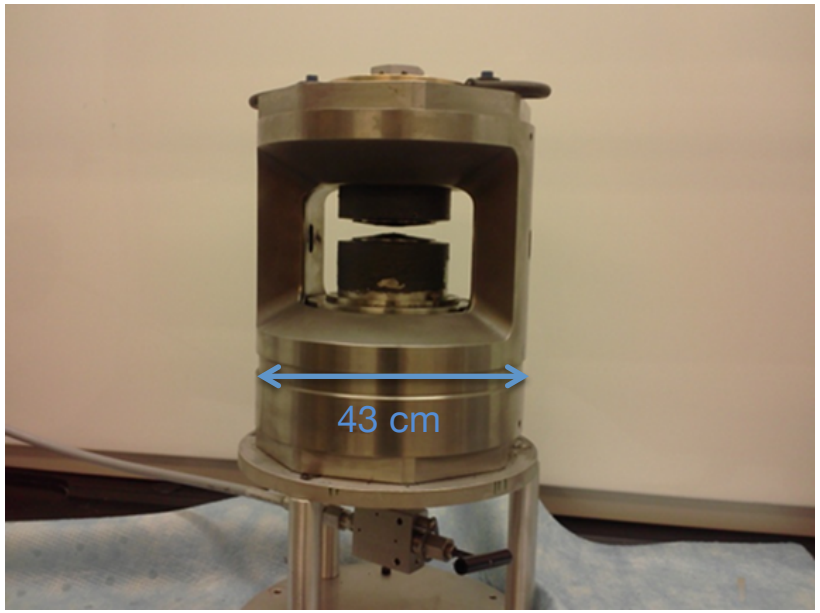
Powder X-Ray Diffraction



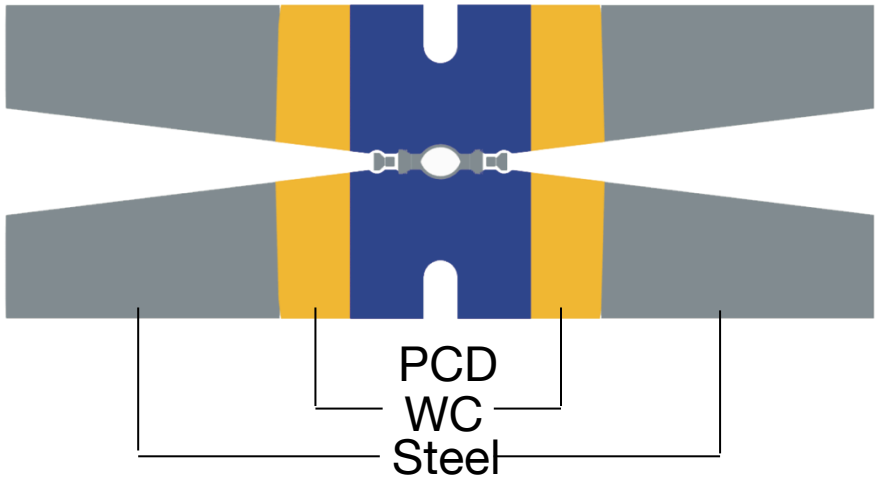
UV Raman Spectrum



Slow Decompression in Larger Volumes

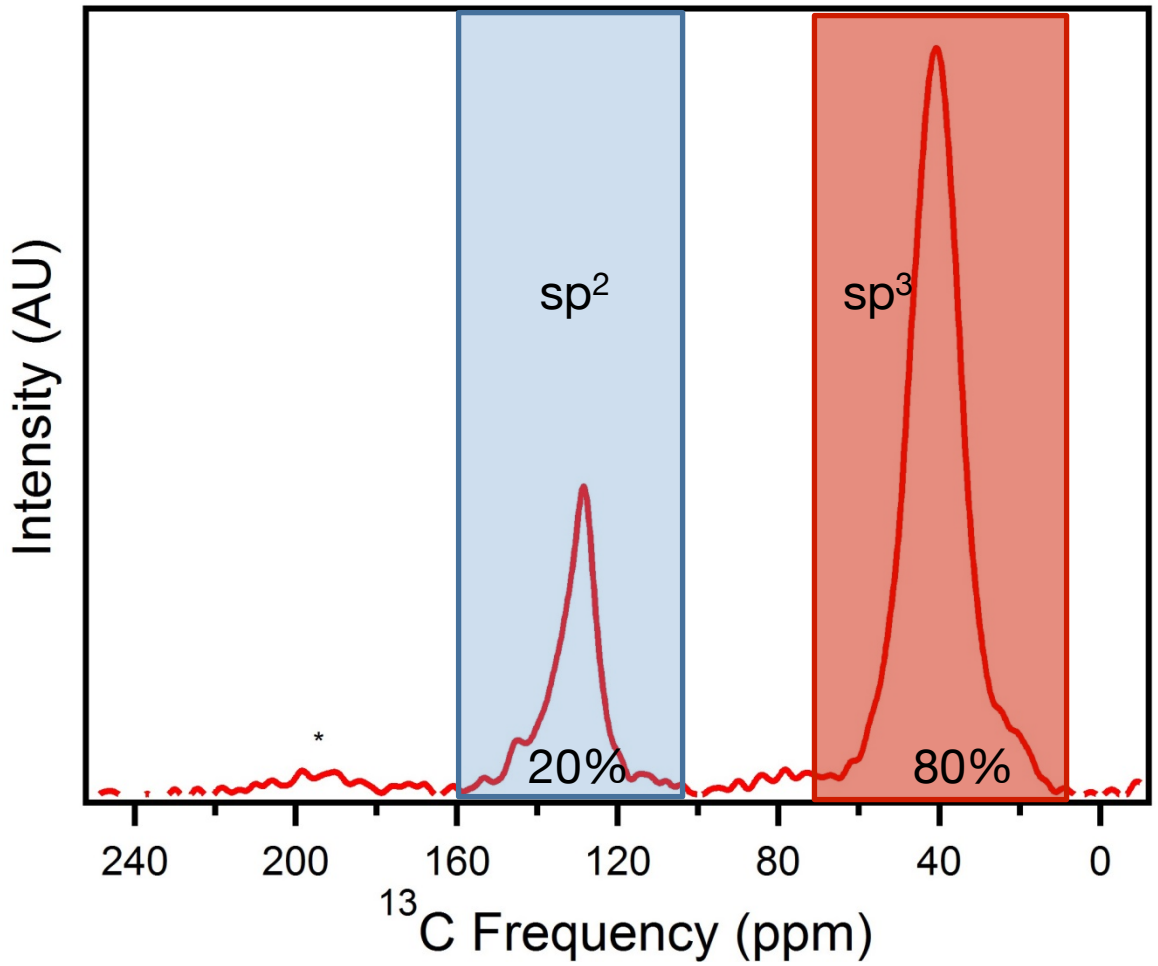


SNAP/ORNL Paris-Edinburgh cell allows for large sample volumes (mg to tens of mg scale).



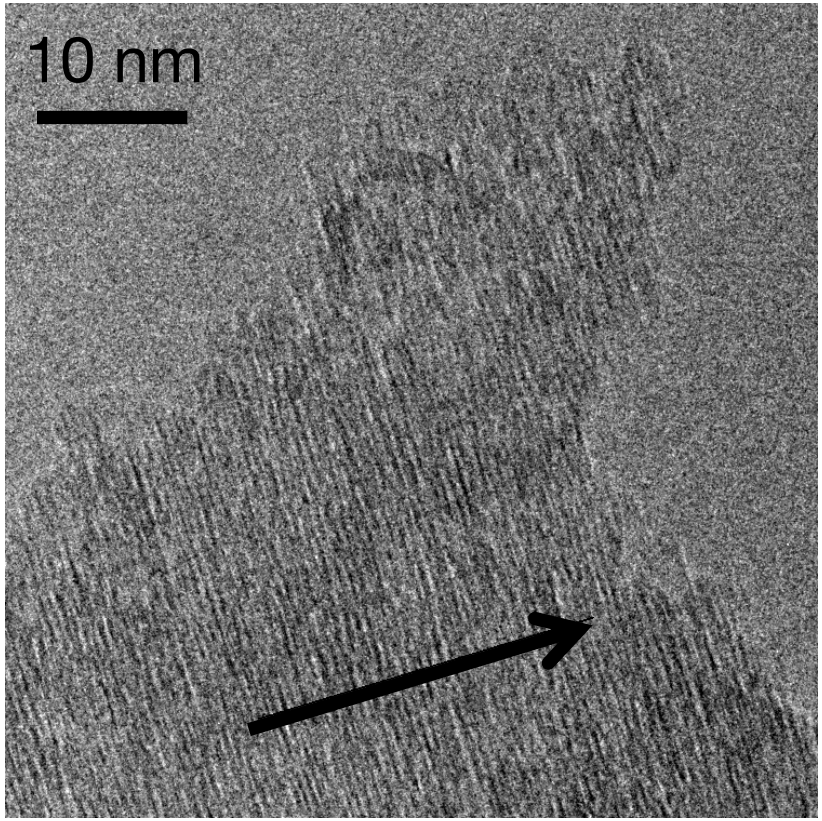
Decompression rate
≈ 2-7 GPa/hr

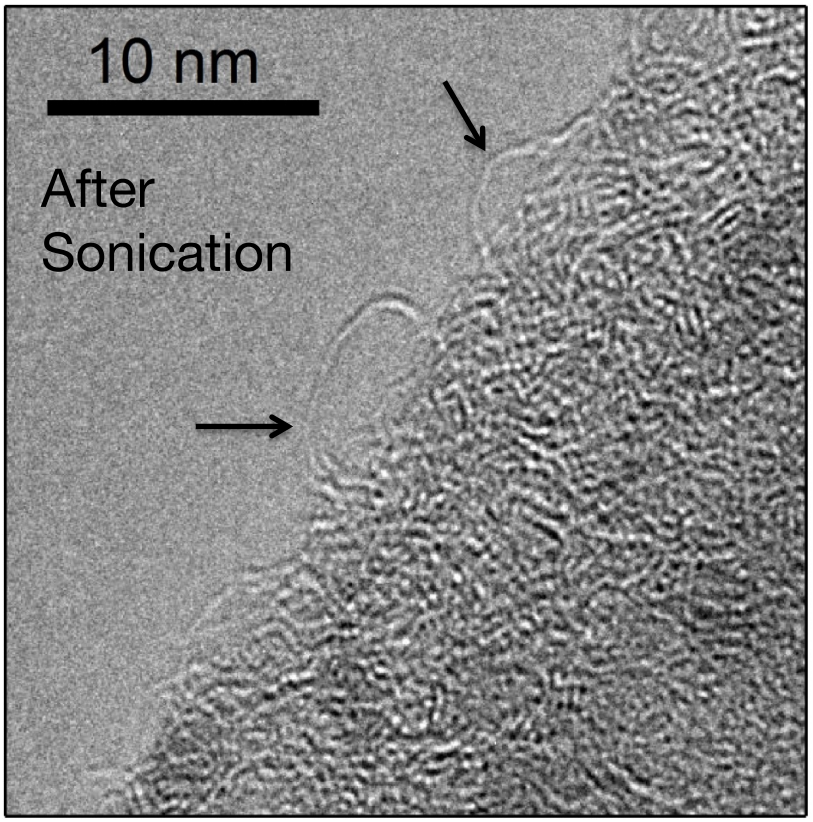
C^{13} Solid State NMR Reveals sp^3 Bonding

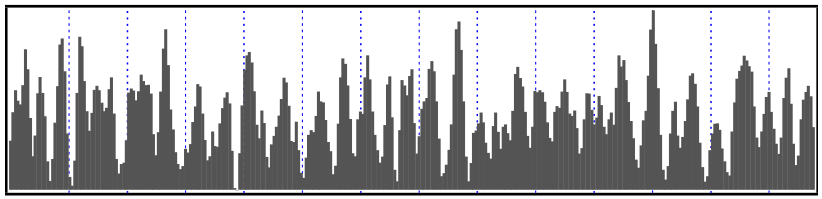


~80 % sp3/ tetrahedral bonding

TEM of Slowly Decompressed Benzene: Nanothreads!





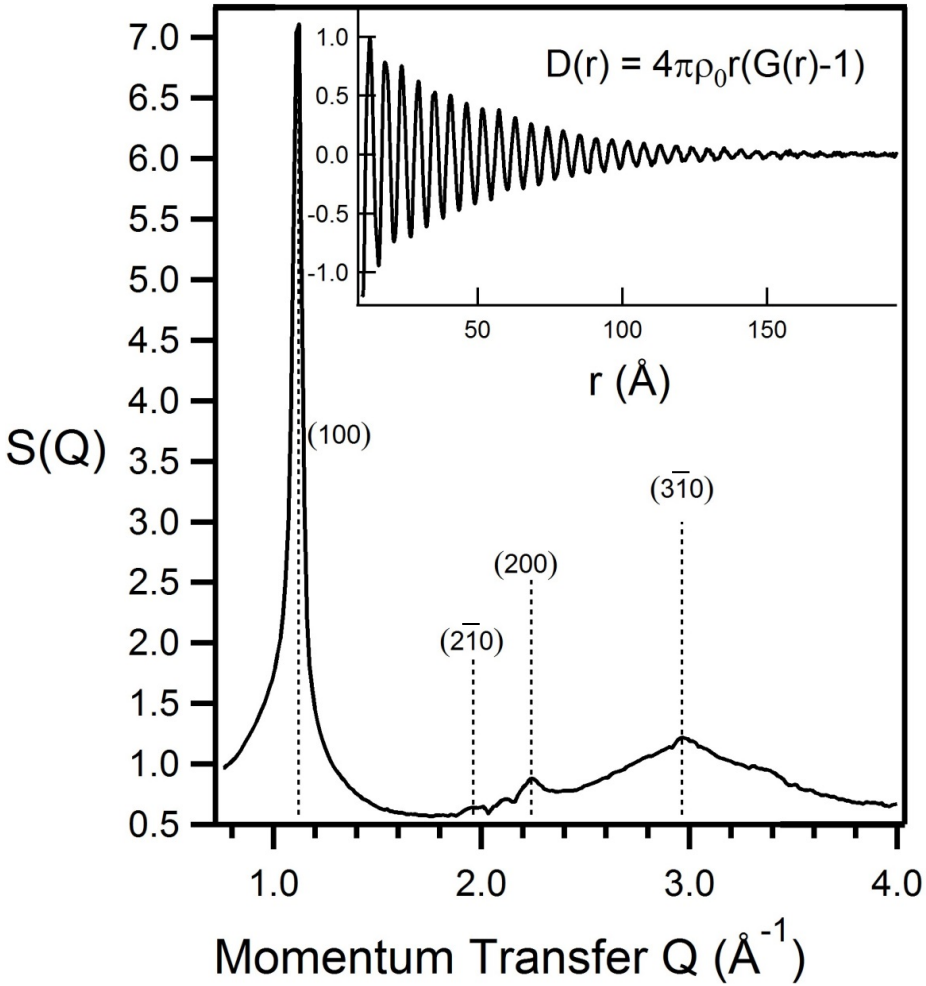


Fitzgibbons et.al., Benzene-derived carbon nanothreads. *Nat. Mater.* **14**, 43-47 (2015)

Crystalline order – striations separated by 6.4 Å .

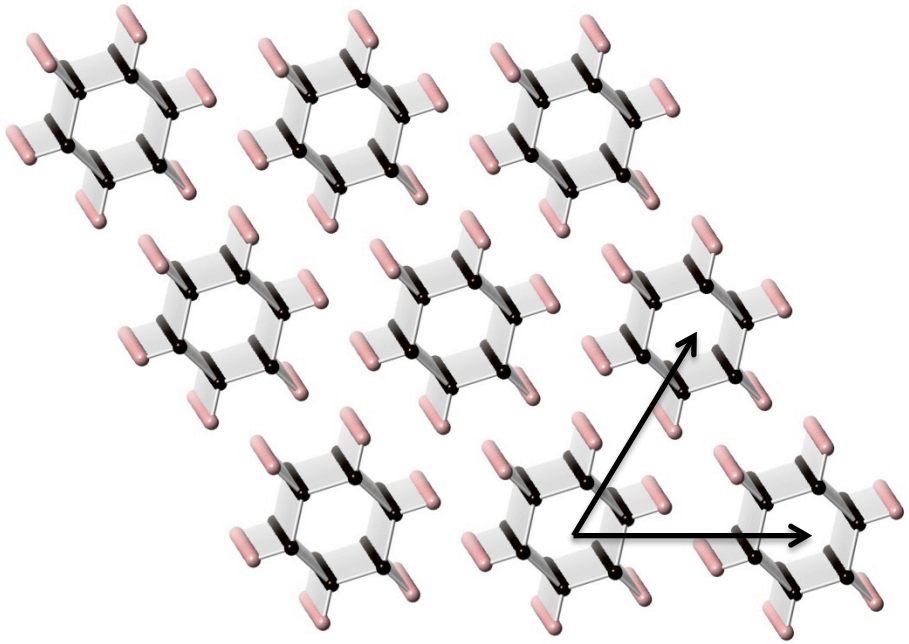
Diffraction Shows Order Too

X-ray Total Scattering Structure Function S(Q)



Q=2π/d

Index Bragg peaks with hexagonal 2-d lattice

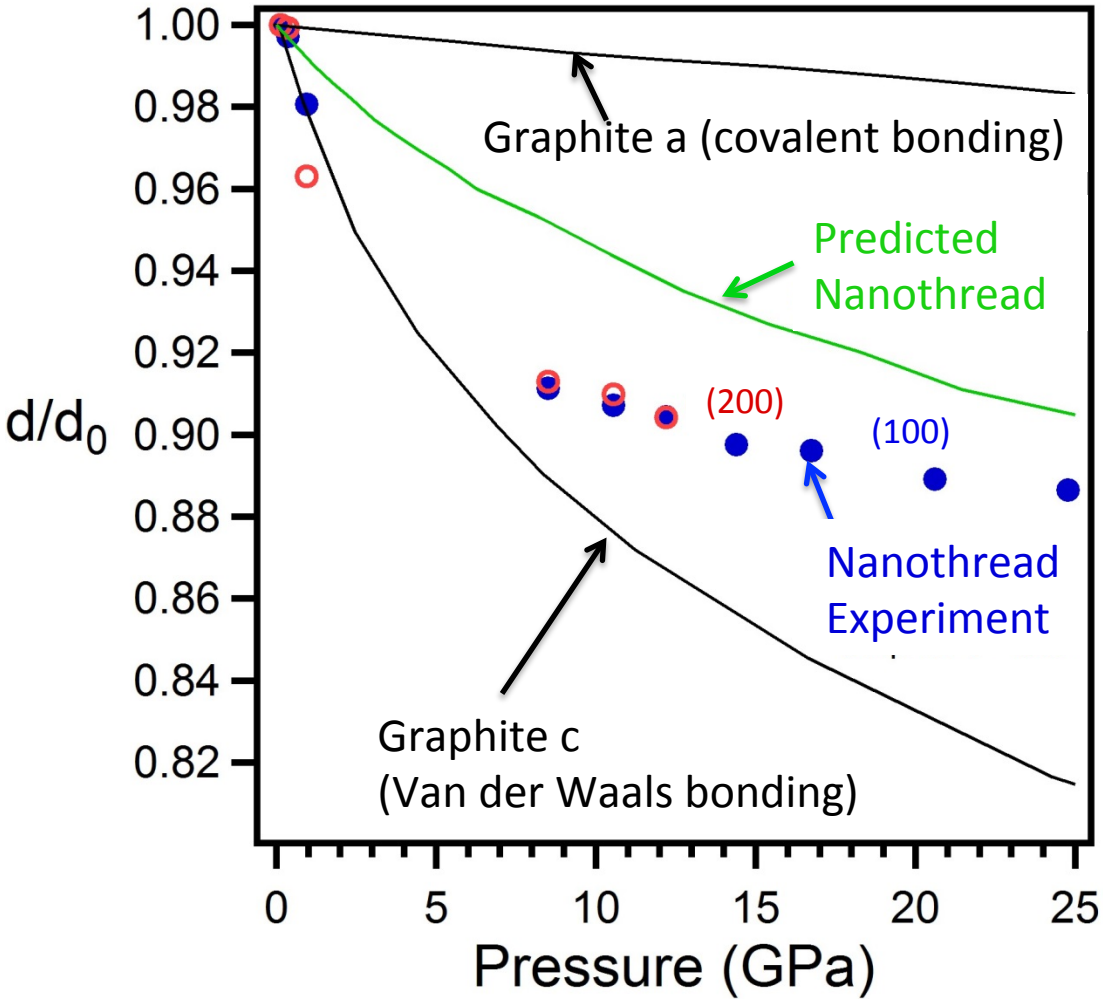


a= 6.47 Å

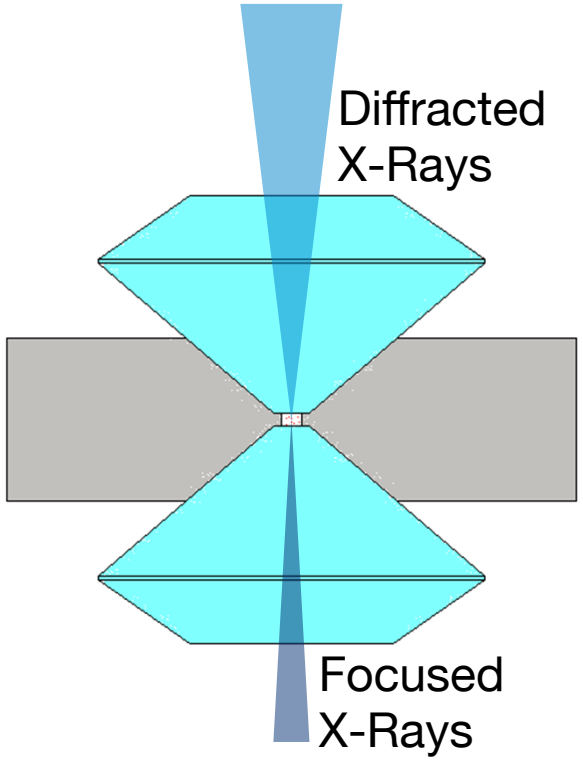
First principles modeling: similar lattice parameter

Weak Inter-thread Bonding

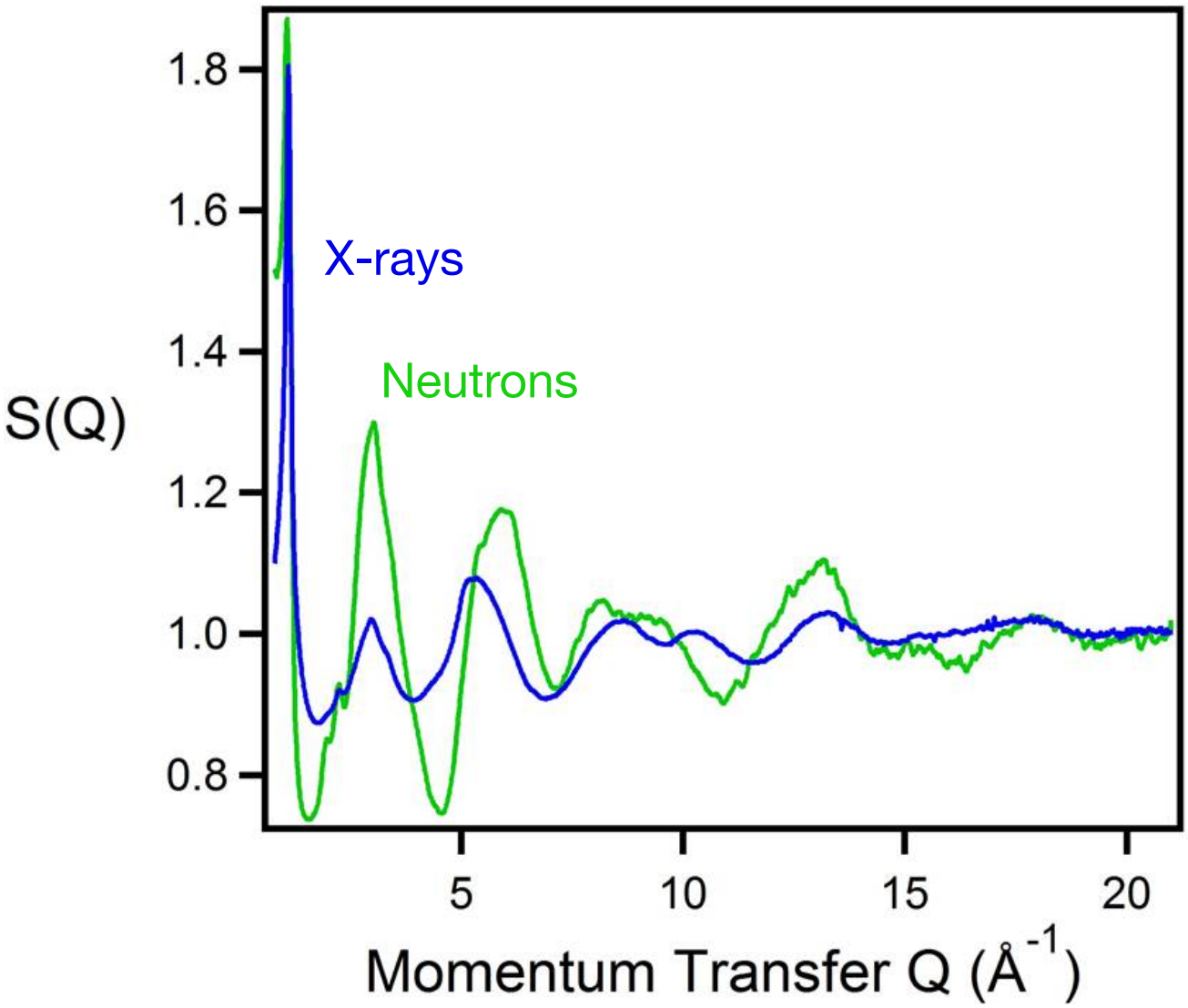
Interplanar spacing vs pressure of nanothread and graphite



HPCAT, APS X-ray diffraction
Nanothread sample loaded in diamond cell



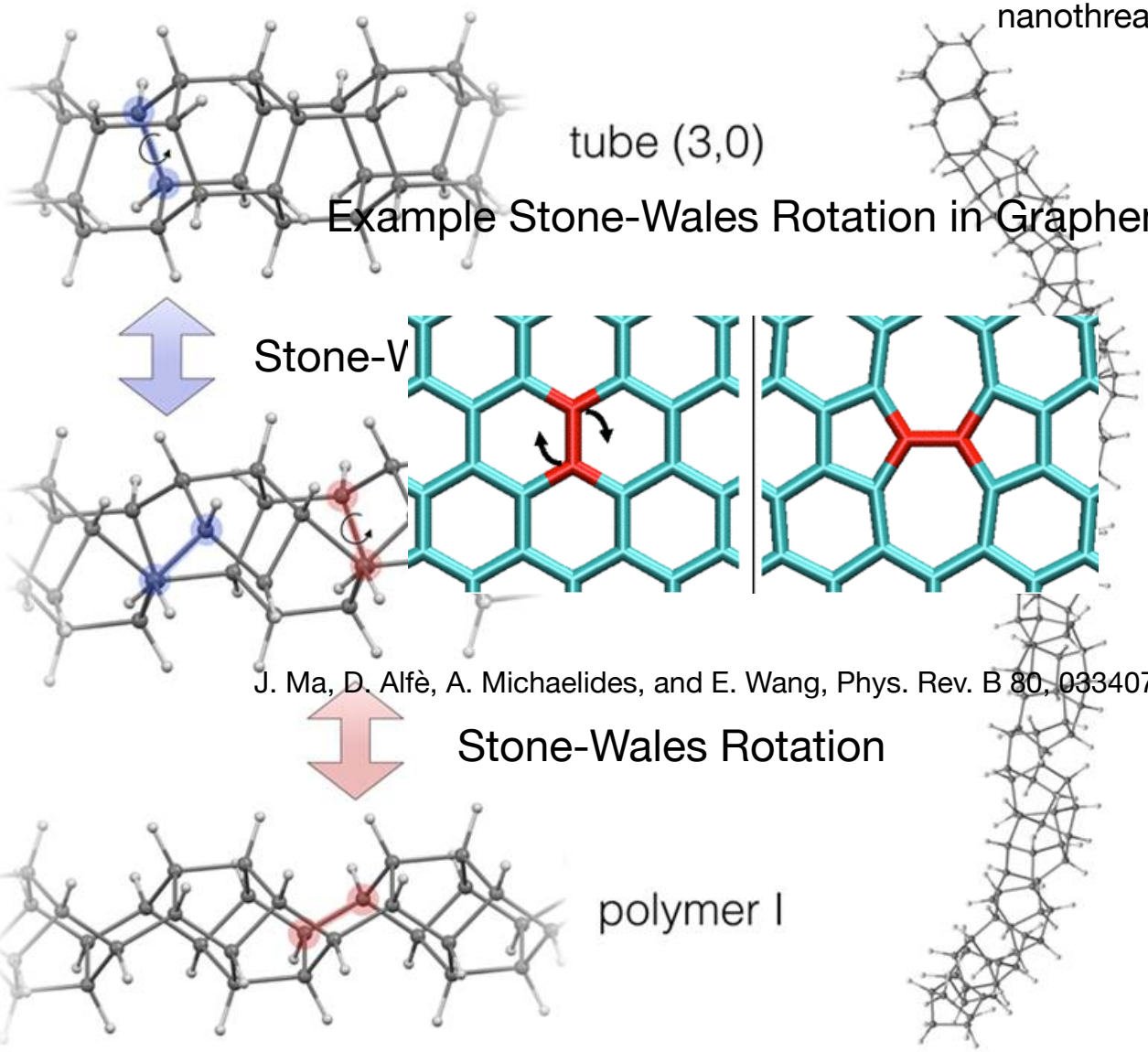
Diffraction to High Q Indicates Disorder in 1-D



Bragg peaks at low Q with diffuse scattering at high Q

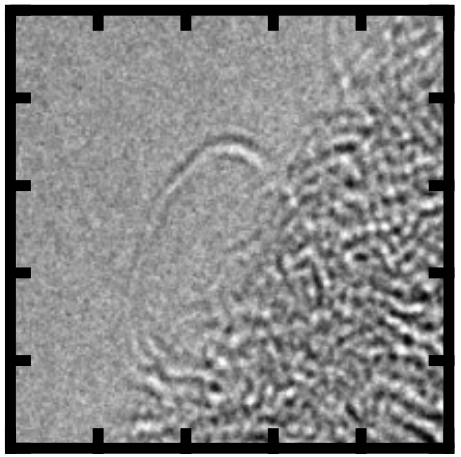
Theory Helps Predict Disorder

Fitzgibbons et.al., Benzene-derived carbon nanothreads. *Nat. Mater.* **14**, 43-47 (2015)



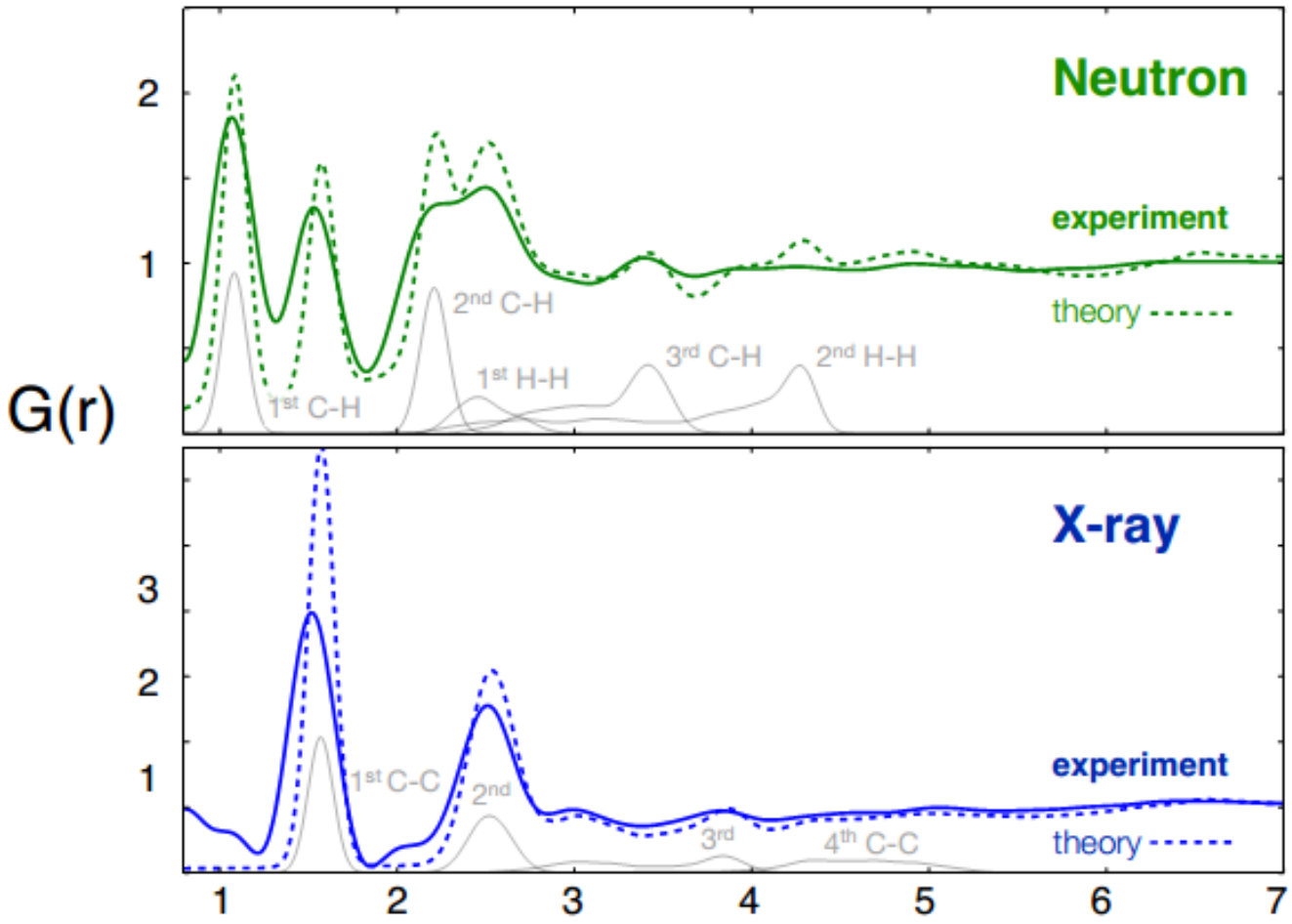
Monte Carlo simulation allowing only Stone-Wales rotation defects.

Defects induce curvature observed in TEM



PDF Analysis Supports Nanothread Interpretation

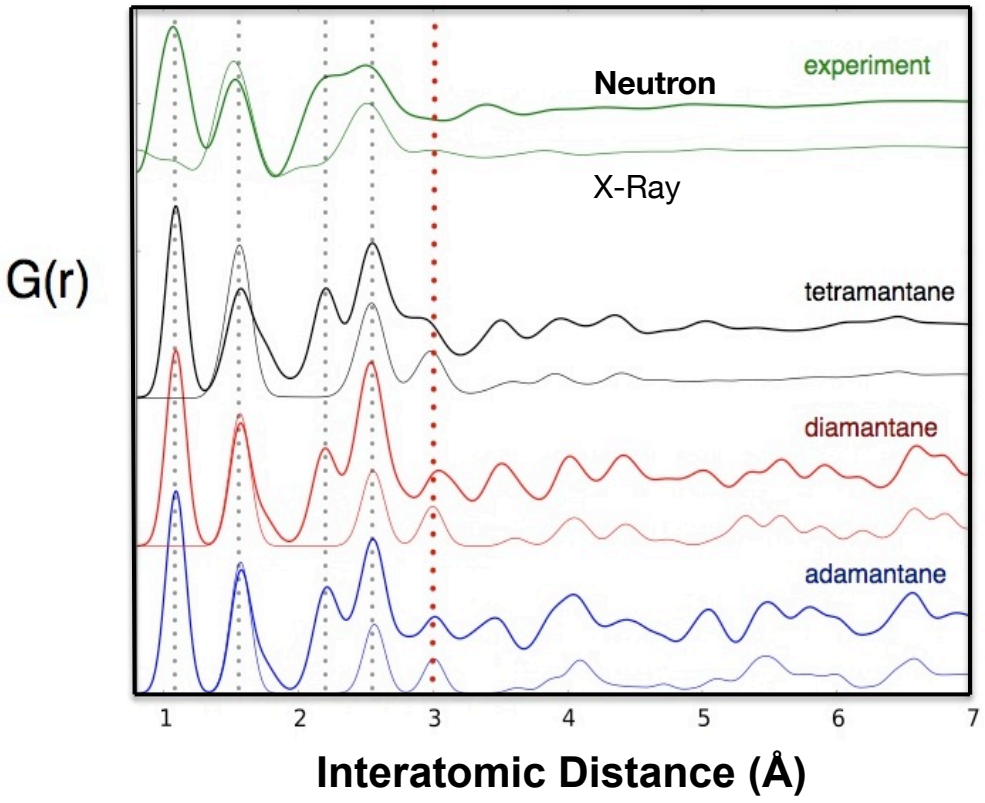
Pair distribution function



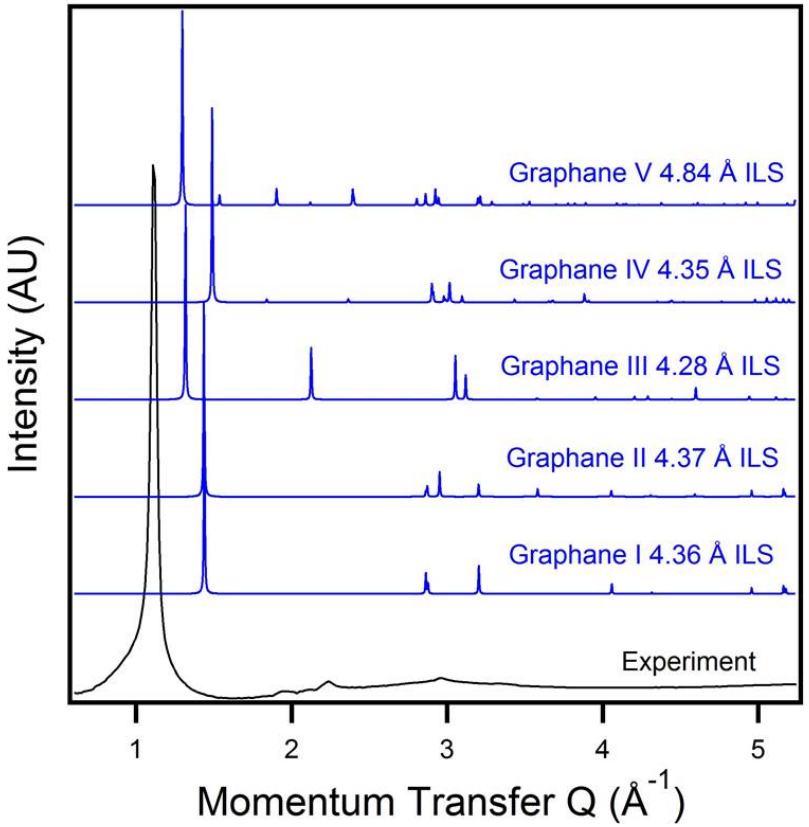
Good agreement out to 3rd nearest neighbors!

Other Carbon Nanomaterials Excluded

Diamondoids have peaks not present in experiment.

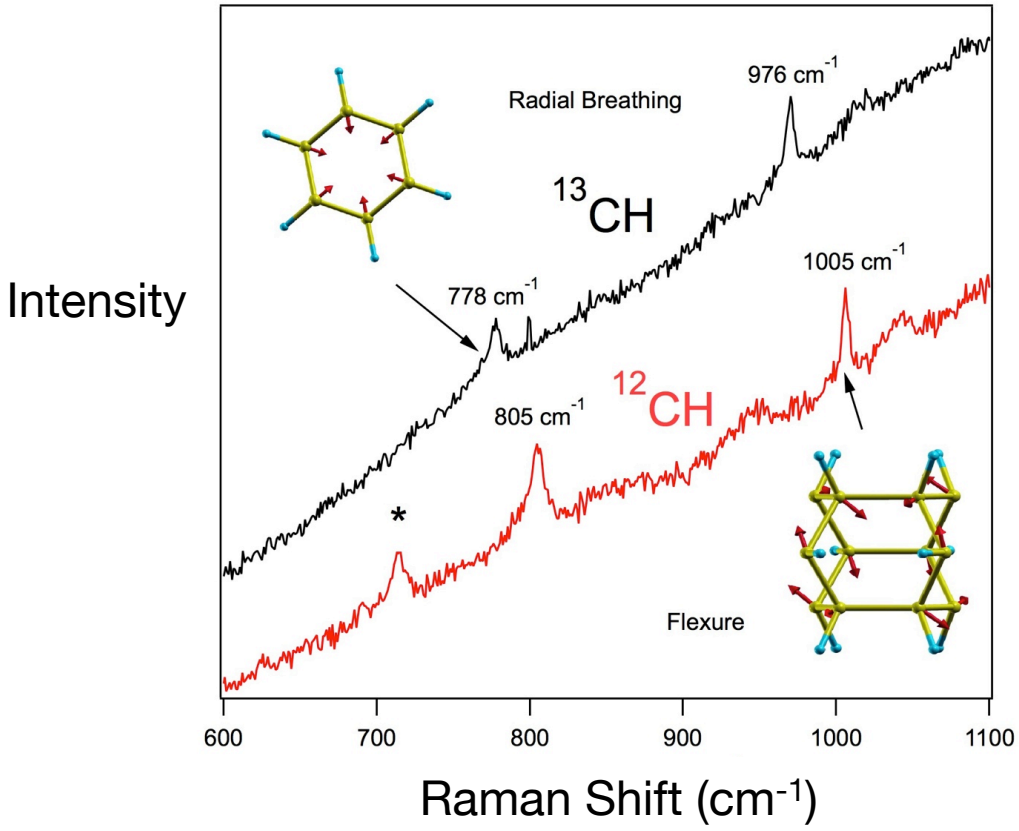


Graphane interlayer spacings do not match large d spacings present in experiment

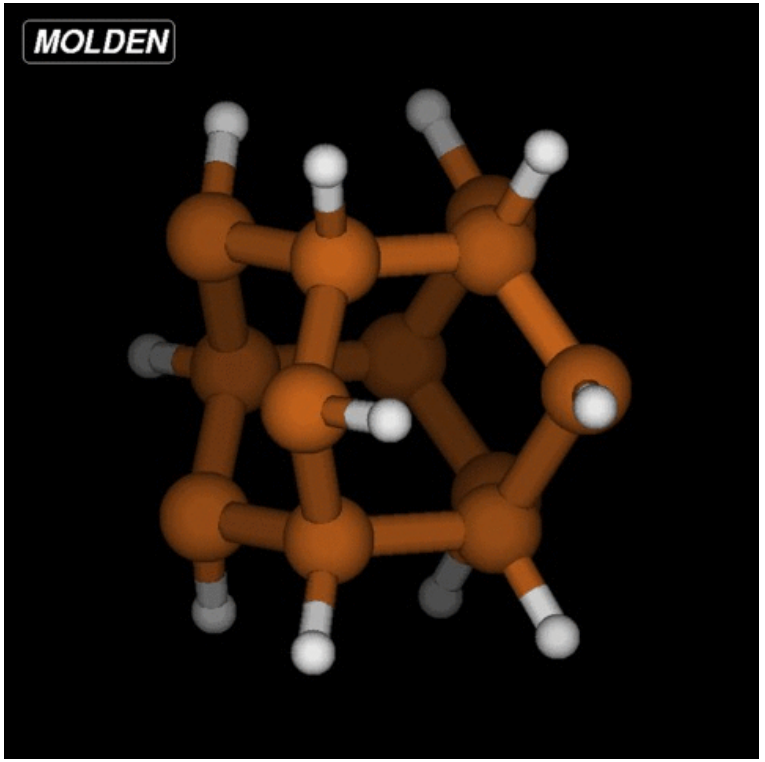


Vibrational Spectra Support Nanothread Interpretation

C-C Raman mode isotope shifts match predictions



Flexure Mode

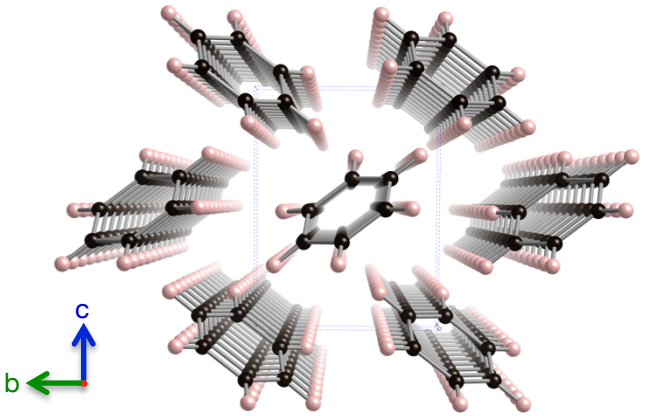


Further experiment shows totally symmetric radial breathing mode is polarized and non-totally symmetric flexure is not: strong constraints on structure

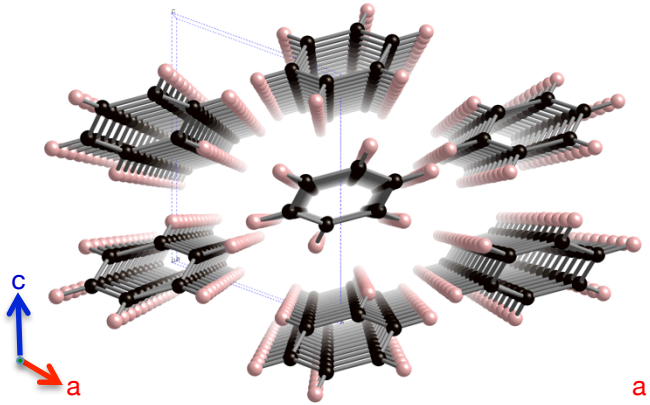
“Crystal Directed” Chemical Reaction?

Benzene II Molecular Crystal at 2.5 GPa

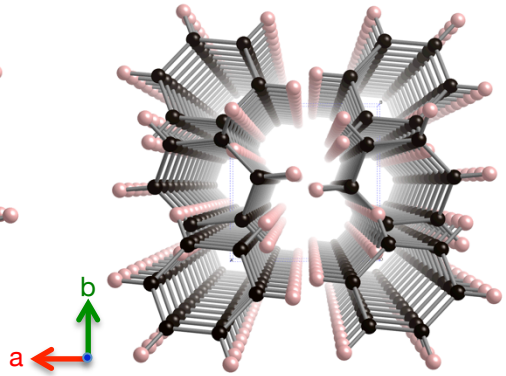
a axis



b axis

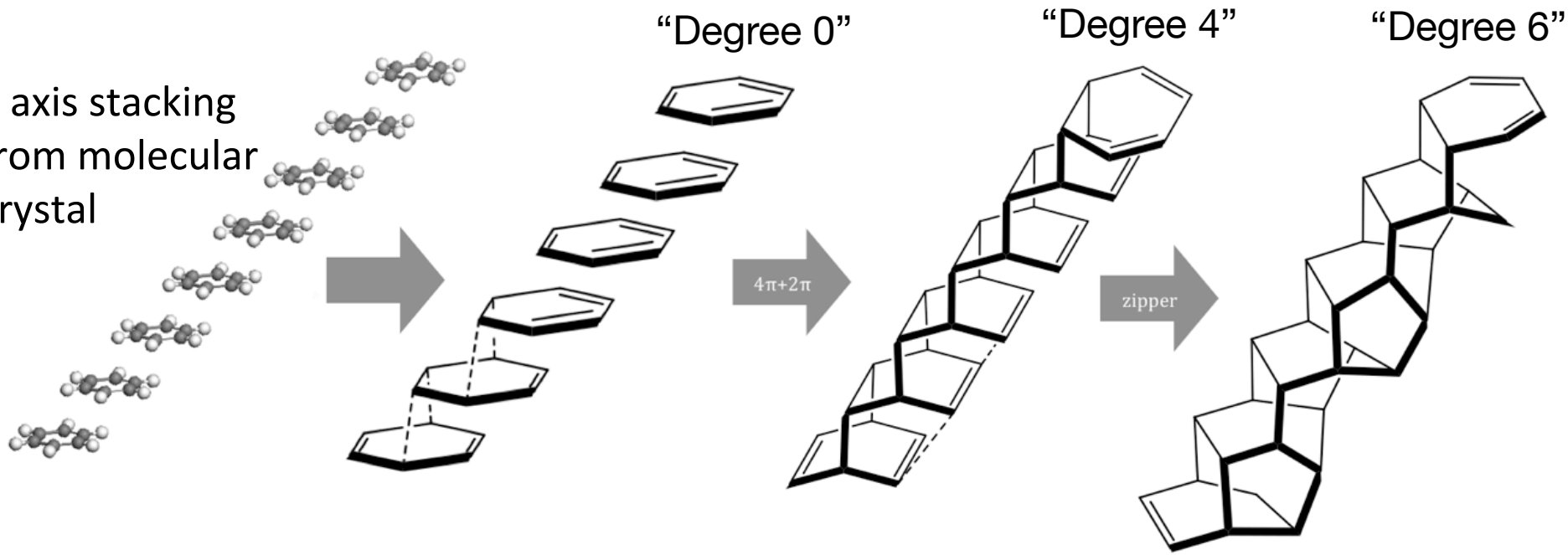


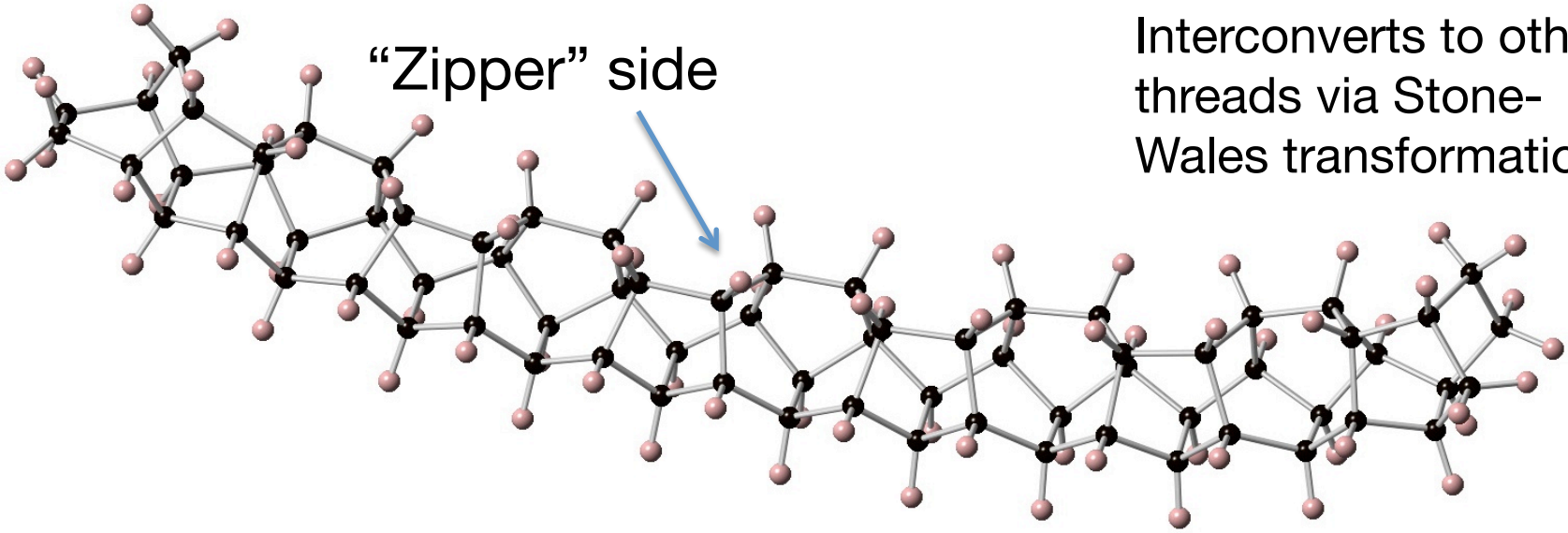
c axis



Block, S., Weir, C. E. & Piermari, G. *Science* **169**, 586 (1970)

Possible Cycloaddition + “Zipper” Reaction Mechanism





Interconverts to other threads via Stone-Wales transformations

Evidence for Axial Order

TEM of second sample

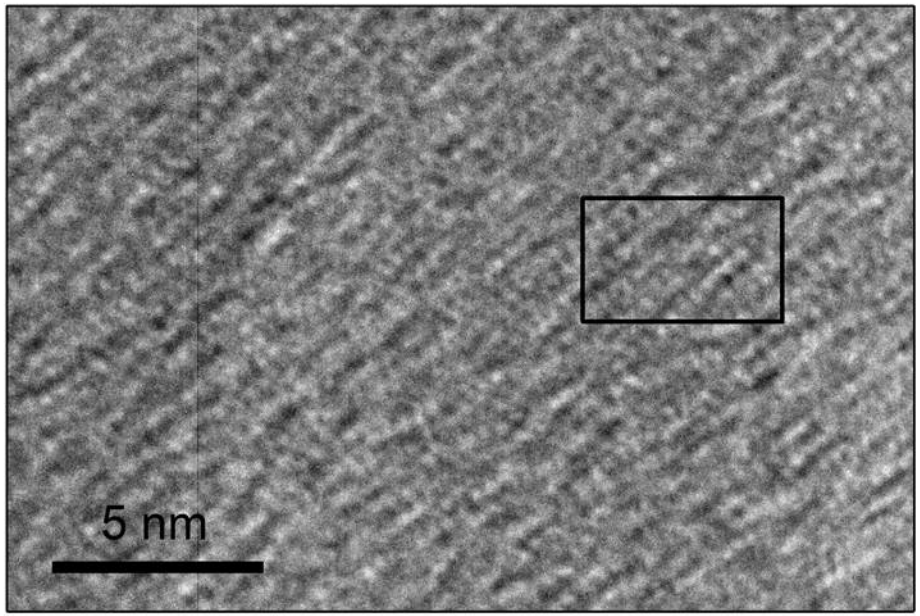
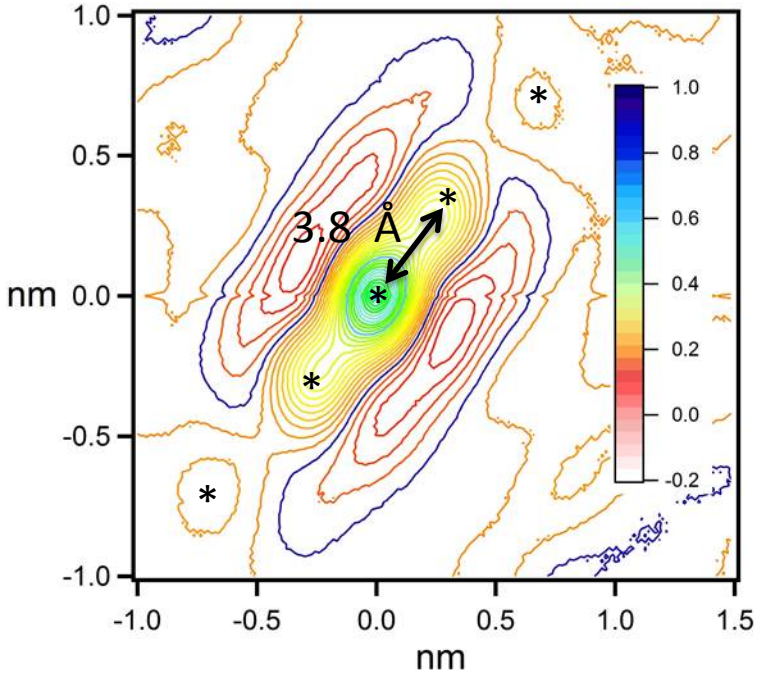


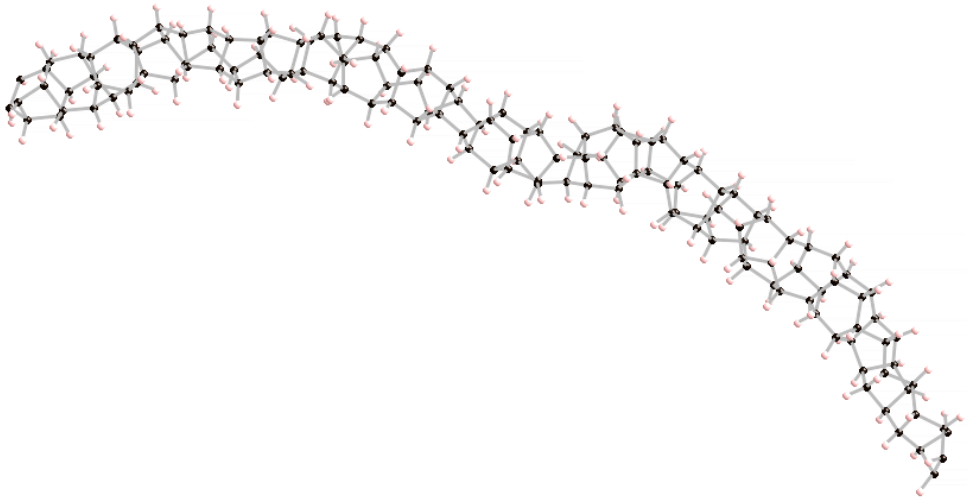
Image Autocorrelation



* Axial beading at ≈ 3.8 Å

Future

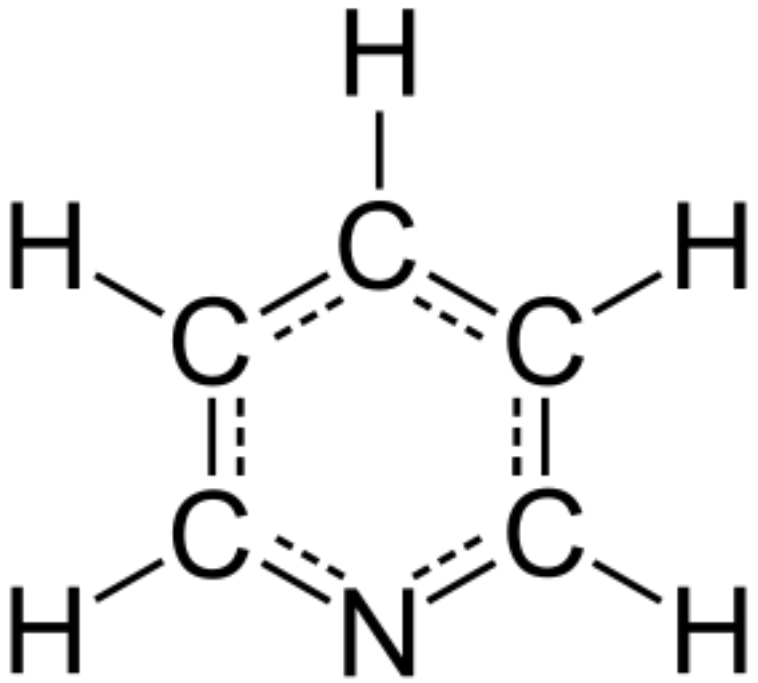
Increased axial order possible?



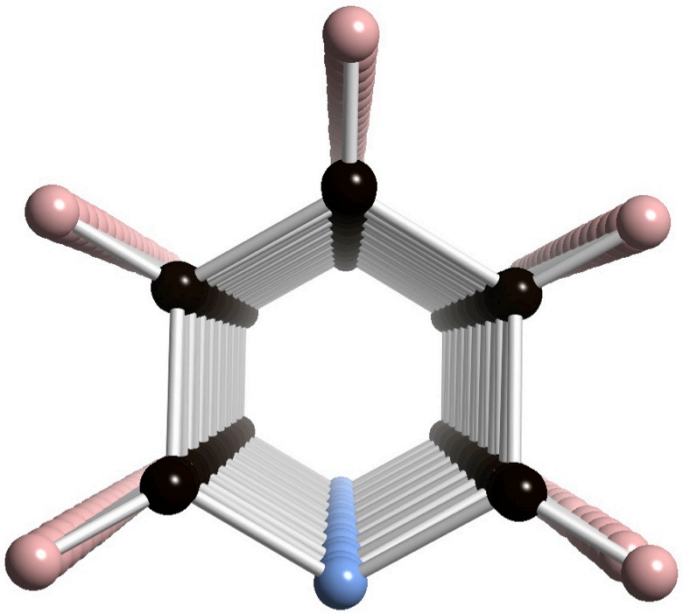
- Higher tensile moduli(1.5 TPa) than nanotubes?
- Intercalation of metals and molecules?
- Chemical functionalization?
- Conducting sp^2/sp^3 threads?
- Cross linked high strength composites?
- Low pressure synthesis?

Kinetic Control of Carbon Nanomaterials Synthesis?

Heteroatoms? Substitutions? Multiple Aromatic Rings?



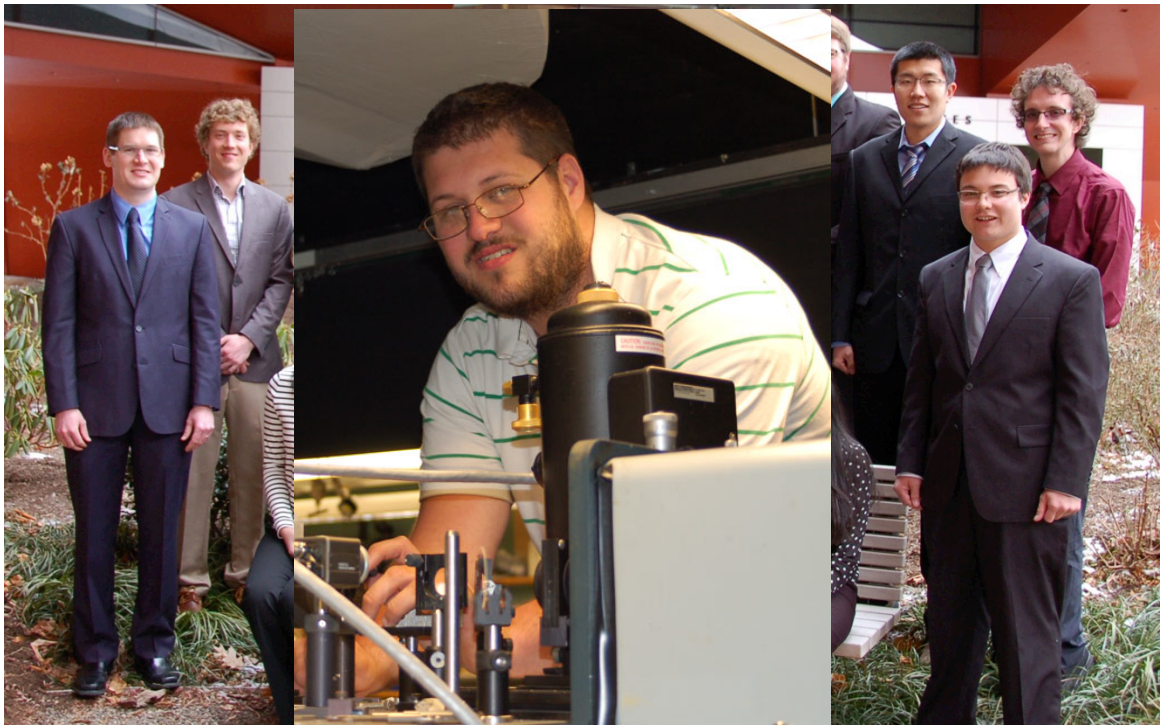
?



Methods of organic chemistry are more versatile than conventional carbon nanomaterials thermolytic synthesis from individual atoms

Acknowledgements

Tom Fitzgibbons and Badding Group



Synthesis: Stephen Aro, Kuo Li, and Jamie Molaison

TEM: Ke Wang and Trevor Clark

Neutron Diffraction: Joerg Neuefeind

X-ray Diffraction: Chris Benmore

NMR: Jeffery Yarger, Gregory Holland

Funding: EFRee DOE Energy Frontier Research Center

Spallation Neutrons at Pressure (SNAP) beamline Oak Ridge National Lab

HPCAT Beamline, Advanced Photon Source, Argonne National Lab