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Title: Static High P/T Investigations of Organic Materials

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Buffalo Thunder Resort
Santa Fe, NM

Los Alamos
NATIONAL LABORATORY
EST. 1943

Static High P/T Investigations of Organic Materials

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Fran Rein and Dana Dattelbaum

Shock and Detonation Physics
Los Alamos National Laboratory

CHEMISTRY IN DYNAMIC EXTREMES WORKSHOP
Santa Fe, NM
January 18, 2012

CDAC

PETRA III
DESY
Deutsches Elektronen-Synchrotron
Hamburg, Germany

U2A *DEDICATED HIGH-PRESSURE AND MICROSPECTROSCOPY SYNCHROTRON INFRARED FACILITY*

nsls

Los Alamos
NATIONAL LABORATORY
EST. 1943

discover LDRD

HPCAT HIGH PRESSURE COLLABORATIVE ACCESS TEAM
at the Advanced Photon Source
GEOPHYSICAL LABORATORY, Carnegie Institution of Washington

NNSA

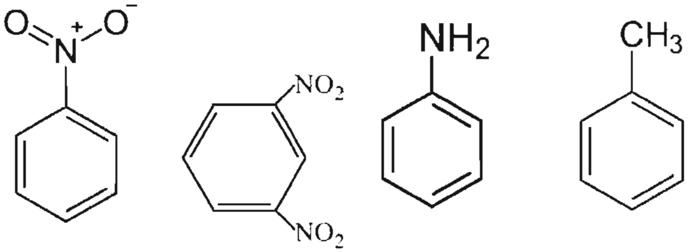
Abstract

A fundamental understanding of shock-induced chemical reactions in organics is still lacking and there are limited studies devoted to determining reaction mechanisms, evolution of bonding, and effect of functional group substitutions. The fast timescale of reactions occurring during shock compression create significant experimental challenges (diagnostics) to fully quantify the mechanisms involved. Static compression (using Diamond Anvil Cell: DAC) provides a complementary route to investigate the equilibrium phase space and metastable intermediates during high pressure chemistry, although at a much slower timescale. Here, we present results from our investigations to understand polymerization reactions in substituted acetylenes: tert-butyl acetylene [TBA: $(CH_3)_3$-C≡CH] and ethynyl trimethylsilane [ETMS: $(CH_3)_3$-SiC≡CH] and nitriles: Acrylonitrile ($CH_2CHC{\equiv}N$) and Benzonitrile ($C_6H_5C{\equiv}N$). The progress of the reactions were monitored *in situ* in a DAC using synchrotron x-ray diffraction and vibrational spectroscopy and the reaction products characterized using synchrotron Infrared spectroscopy measurements. For the acetylenes, we observed the reaction threshold pressure at room temperature was higher in static compression (TBA: 11 GPa and ETMS: 17 GPa) while at higher temperatures they were comparable to shock input pressures (TBA: 6.1 GPa and ETMS: 6.6 GPa). The products were polymeric in nature, recovered to ambient conditions with little degradation and fully characterized using spectroscopy. Acrylonitrile exhibited similar polymerization reactions at room temperature with a threshold pressure of ~12 GPa while Benzonitrile was stable up to ~30 GPa with little evidence for polymerization.

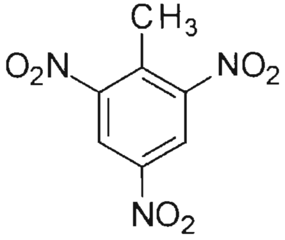
Static compression studies to explore phase stabilities and establish *P-T* phase diagrams

MOTIVATION

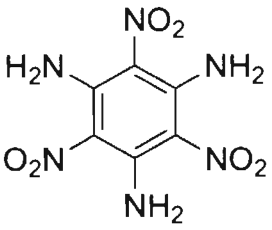
- Aid interpretation of shock-induced chemistry of simple molecules
  - Bond-breaking mechanisms (e.g. C≡C, C=C, C≡N, C=O) enroute to products; synchrotron IR, Raman, UV-Vis
- Input for theory
  - ***P-V-T*** Equation of State (EoS) data; synchrotron x-ray and neutron diffraction
  - Density of State (DOS); Inelastic Neutron Scattering, Far IR, and THz measurements
- Bridge the strain-rate gap with pressure jump DACs; in situ XRD
- Emphasis on "building block" organics that constitute advanced energetic materials



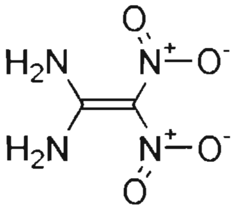
Building Blocks



TNT



TATB



FOX-7

Shock-induced chemistry is unique with reactions (and products) that can be different from thermal, and static *P-T* chemistry

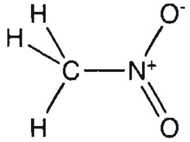
BACKGROUND

- There are two classes of possible reactions: DETONATION (DECOMPOSITION), POLYMERIZATION

- In some cases, there is correspondence between static high *P-T* and shock chemistry
  - Provide insights into bond-breaking steps in reactions, alternative pathways

DETONATION (DECOMPOSITION)

$\rho_{products} < \rho_{reactants}$



Nitromethane

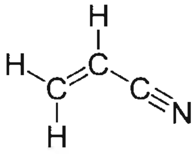
SHOCK: ~10 GPa → Gaseous Products

STATIC: 2-10 GPa → $[CH_2NO_2^-]$ Aci ion, Decomposition upon decompression from 10 GPa

Engelke et al. J. Phys. Chem. (1988)
Dick, J. Phys. Chem. (1993)
Citroni et al. J. Phys. Chem. B (2010)

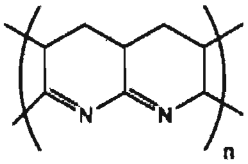
POLYMERIZATION

$\rho_{products} > \rho_{reactants}$



Acrylonitrile

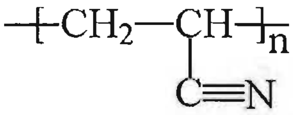
SHOCK: ~5 GPa → Polymerization solid-state transitions



STATIC: 0.5-10 GPa → Structural transitions, Polymerization (This work)

Dattelbaum et al. AIP Proc. (2011)
Yakushev et al. Fizika Goren. Vzry. (1974)

Nature of polymers from shock, static high *P-T*, ambient *P* synthesis can be very different



$$-\!\!\left[CH_2-\underset{\displaystyle C\equiv N}{CH}\right]_n\!\!-$$

PAN from ambient *P* synthesis

BACKGROUND

High *P-T* Polymerization Reactions: More Examples

ALIPHATIC

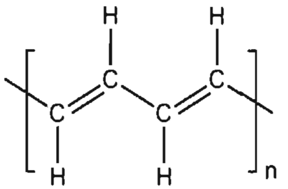
C≡C → C=C → C-C

C≡N → C=N → C-N

ACETYLENE POLYMERIZATION

Fluid $\xrightarrow{0.7\text{ GPa}}$ *Pa*3 (Cubic) $\xrightarrow{0.9\text{ GPa}}$ *Cmca* (Orthorh -ombic) $\xrightarrow{3.5\text{ GPa}}$

HC≡CH



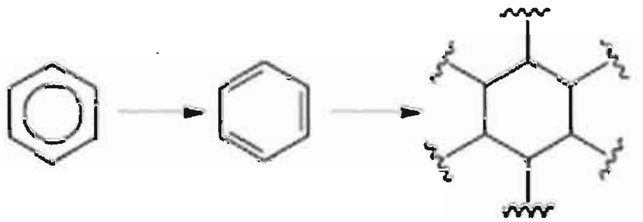
***trans*-(Polyacetylene) (Deep Red)**

POLYMERIZATION REACTION SIGNATURES

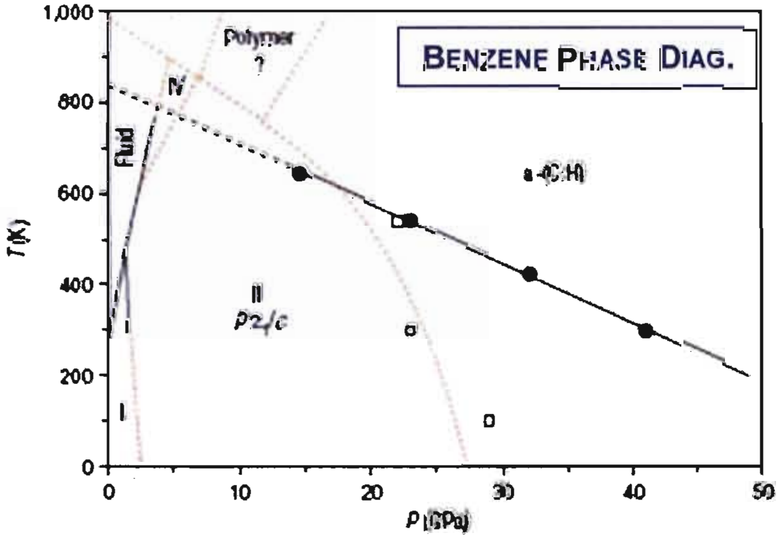
- Progressive saturation of bonds
- Dramatic color variations due to changes in electronic structure
- Mostly irreversible, occasionally irreversible when driven by H-bond formation (CO_2, HCOOH)
- Novel, functional polymeric products

AROMATIC

BENZENE POLYMERIZATION



- **Benzene (C_6H_6)** polymerizes > 20-25 GPa
- Full polymerization realized during decompression to form *amorphous*-(C:H)



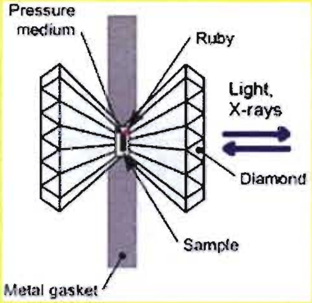
Ciabinni et al. *Nature Mater.* (2007)
Wen, Hoffmann, Ashcroft *JACS* (2011)

EXPERIMENTAL

Materials & Techniques

TECHNIQUES

STANDARD DIAMOND ANVIL CELL



Rub y or Gold as *P* calibrant

No *P* medium for liquid samples

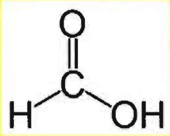
MEMBRANE DAC FOR MEDIUM STRAIN RATE

- HPCAT (Sector 16) Advanced Photon Source, Argonne National Laboratory
- U2A Beamline, National Synchrotron Light Source, Brookhaven National Laboratory
- In-house Raman (488, 514, 785) nm, UV-Vis
- Pressure jump experiments at PETRA III Beamline, DESY, Hamburg, Germany

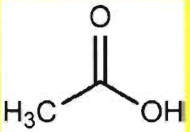
Increasing Complexity (Towards Explosive-like)

MATERIALS

High Oxygen

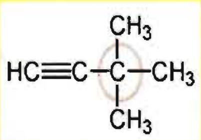


Formic Acid

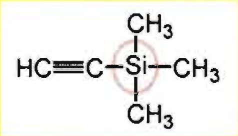


Acetic Acid

Substituted Acetylenes

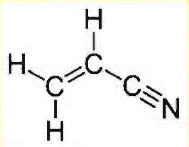

$HC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

t-Butyl Acetylene

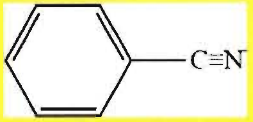

$HC\equiv C-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$

EthynylTriMethylSilane

Nitriles

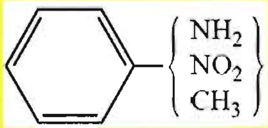


Acrylonitrile

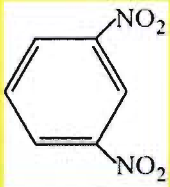


Benzonitrile

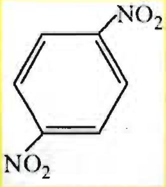
Substituted Aromatics



Aniline, Nitrobenzene, Toluene



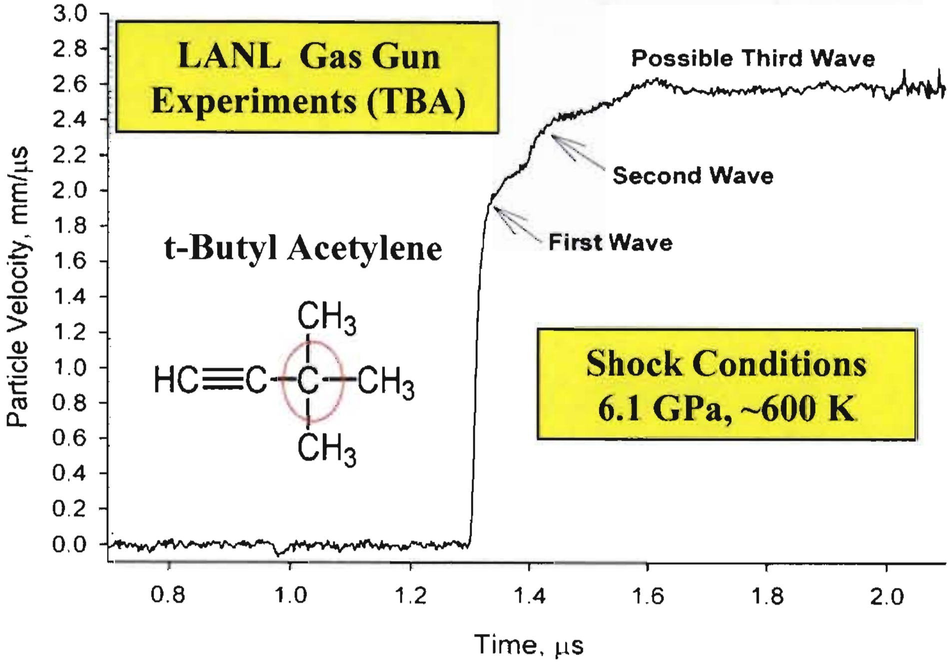
1,3-dinitrobenzene



1,4-dinitrobenzene

Static *P-T* experiments needed for insights into shock-induced chemistry in substituted acetylenes

RESULTS

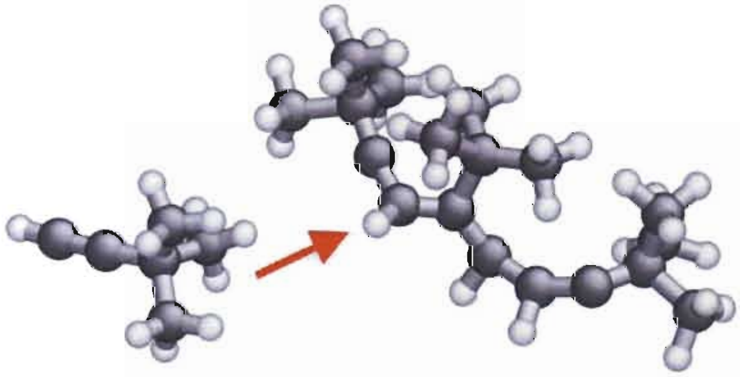


LANL Gas Gun Experiments (TBA)

t-Butyl Acetylene

Shock Conditions
6.1 GPa, ~600 K

- EoS for better prediction of shock temperature
- Characterization of reaction products (polymers), *P-T* phase boundaries
- Reactivity of C≡C bonds, bond-breaking mechanisms, kinetics
- Vibrational spectroscopy is critical



LATTE MD simulations point to an exothermic radical chain polymerization pathway

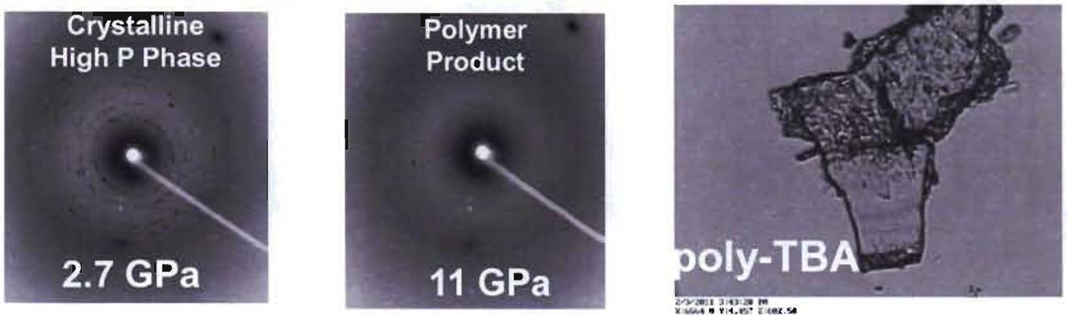
Dattelbaum et al. AIP Shock Proc. (2011)
Cawkwell et al. Detonation Symp. Proc. (2011)

Reactivity of -C≡CH moiety in t-butyl acetylene (TBA)

RESULTS

TBA reacts at high pressures at both room and high temperatures to form recoverable polymers

XRD Images at RT



TBA Fluid $\xrightarrow[\text{~2 GPa, RT}]{\textit{Solidifies}}$ High-*P* phase $\xrightarrow{\textit{polymerization}}$ TRANSPARENT GLASSY SOLID

Ortho. (*Pmmm*)

@11 GPa , 298K

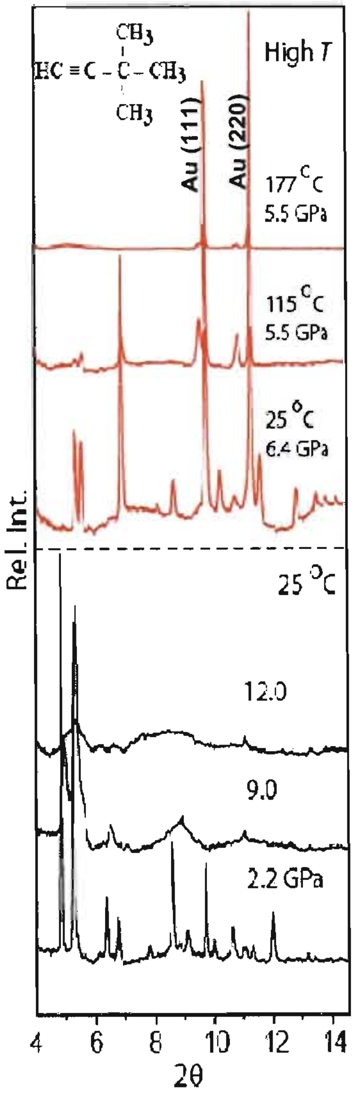
@ 5.5 GPa, 430-450K

0 GPa (Fluid) **1.9 GPa** **Recovered Polymer**

With increasing *T*, reaction threshold drops to be consistent with shock experiments.

XRD

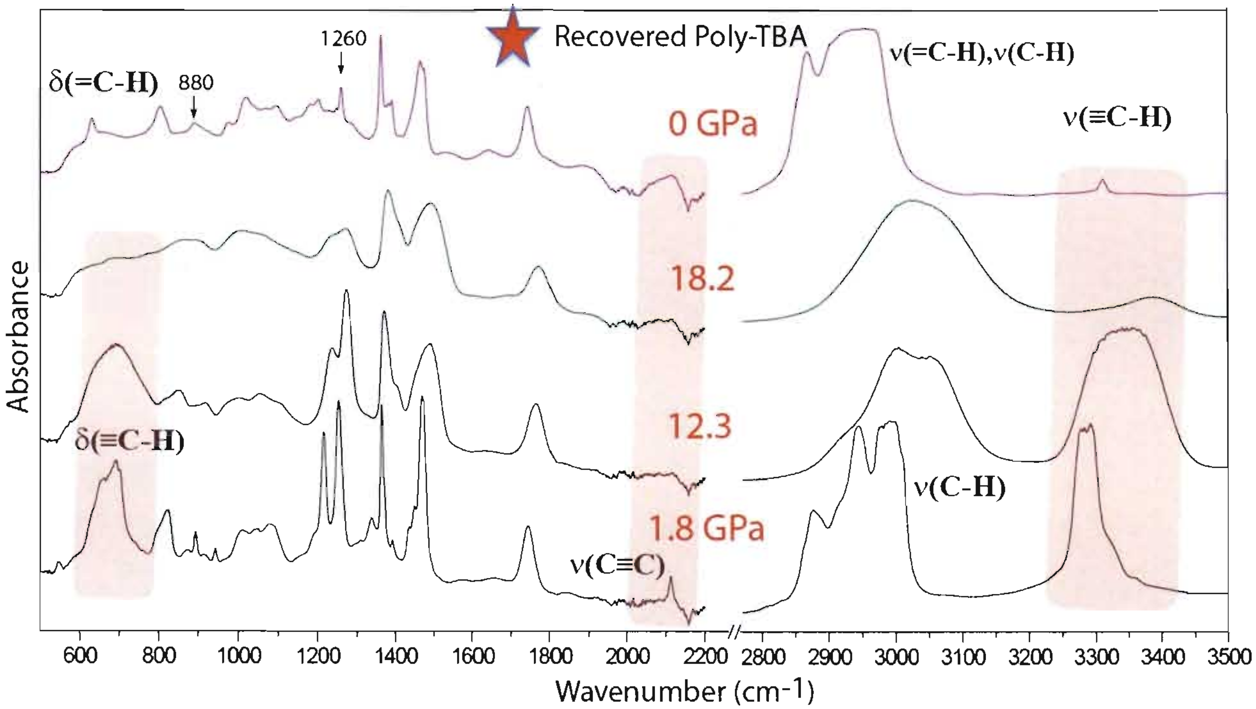
TertButylAcetylene (TBA)



Synchrotron IR for characterization of poly-TBA to identify polymer geometry and reaction yield

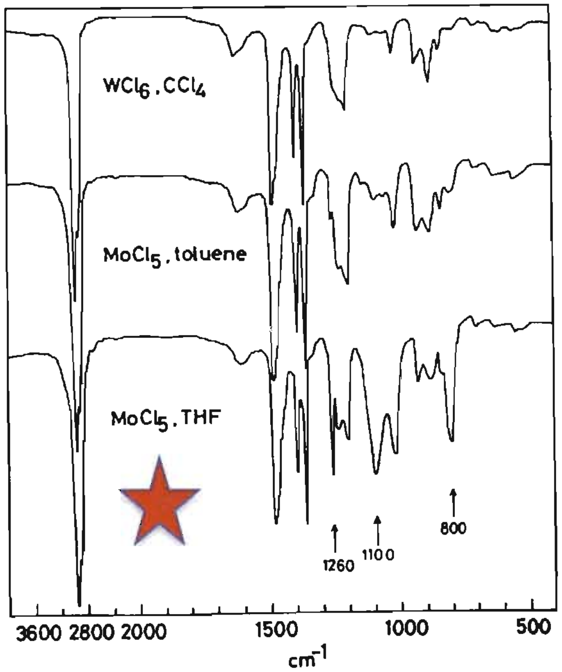
RESULTS

IR Spectra (RT) showing polymerization signatures



- **Beyond 15 GPa**, Loss / weak, broad ν (C≡C) mode; decrease in intensity of ν(≡C-H) modes; new modes of poly-TBA

Comparison with p-TBA from chemical synthesis



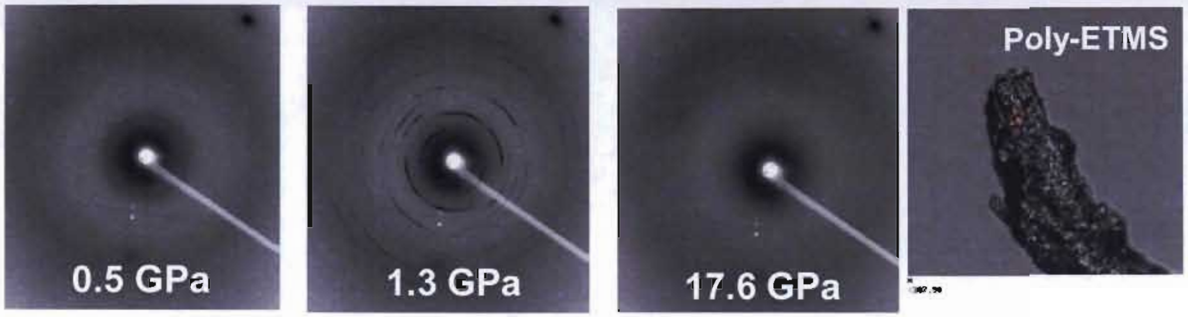
Poly-TBA synthesized via catalysis in various solvents; t ~ 24 hrs, 30 °C

Recovered polymer from high P is likely in *cis* geometry

Masuda et al. Polymer J. (1980)

RESULTS

Polymerization reaction thresholds in ETMS



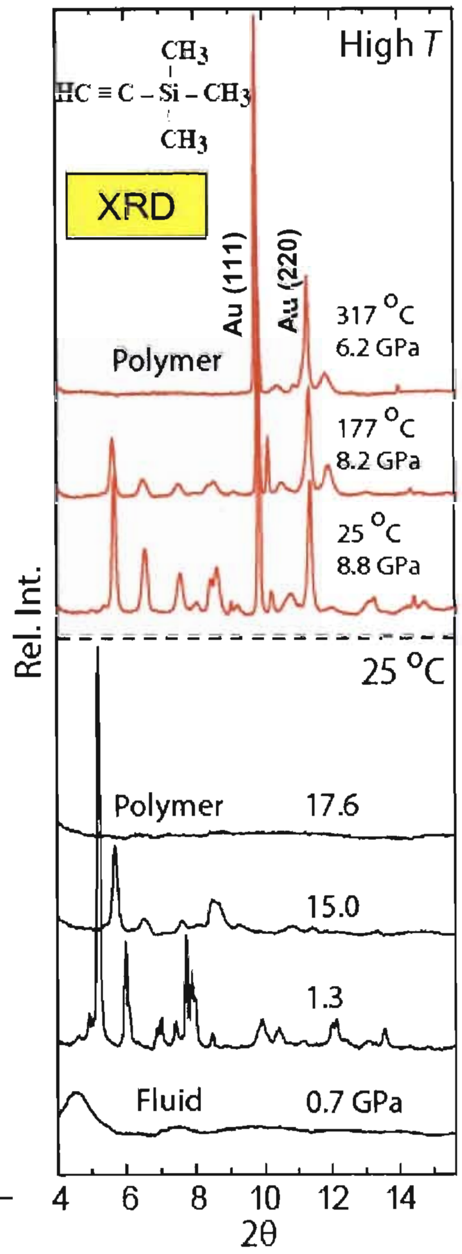
XRD Images at RT

ETMS Fluid $\xrightarrow[\text{~1 GPa, RT}]{\text{Solidifies}}$ High-P Phase $\xrightarrow{\text{polymerization}}$ OPAQUE SOLID

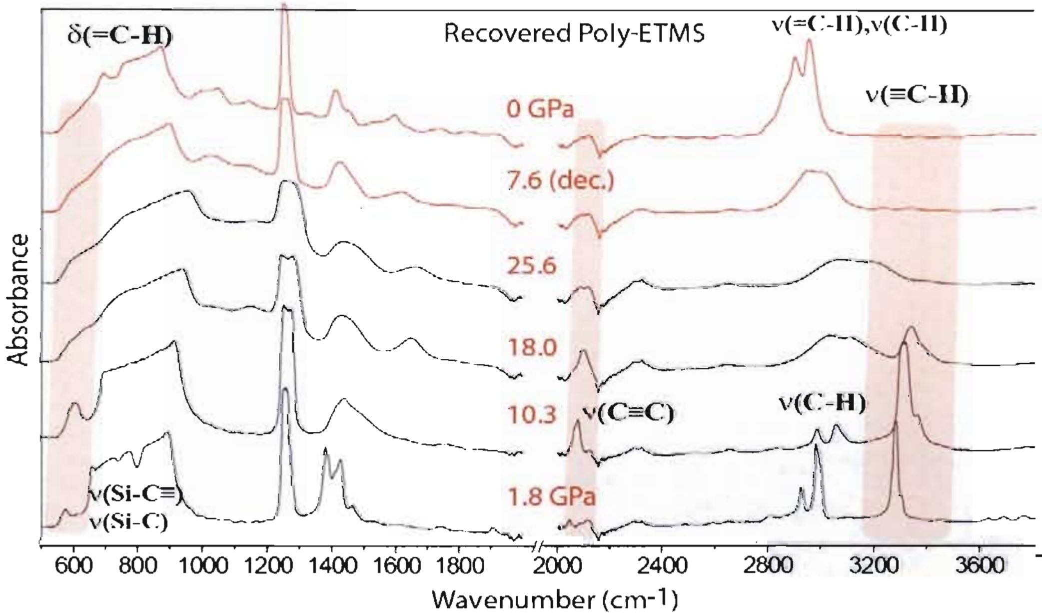
Ortho. (*Pmmm*)

@17 GPa , 298 K
@ 6 GPa, 590 K

EthynylTriMethylSilane (ETMS)



IR Spectra (RT) showing polymerization signatures

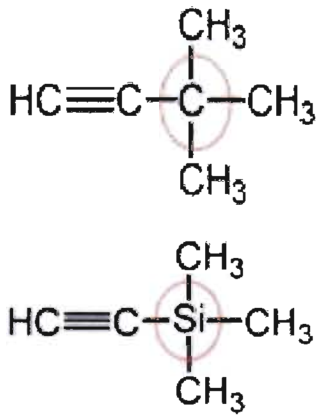


Beyond 25 GPa

- ☐ Loss of ν (C≡C)
- ☐ Decrease in int. of ≡CH str. Modes
- ☐ Loss of ν(Si-C) modes
- ☐ Poly-ETMS modes appear only weakly in the 1000-1300 cm^{-1} region

Reaction thresholds for C≡C ⟶C=C polymerization is dominated by by 'Si' substitution

RESULTS


$$HC\equiv C-C(CH_3)_3$$
$$HC\equiv C-Si(CH_3)_3$$

SUBSTITUTED ACETYLENES

	STATIC		SHOCK
TBA	***11 GPa*** ***298 K***	***5.5 GPa*** ***400-450 K***	***6.1 GPa*** ***~700 K***
ETMS	***17 GPa*** ***298 K***	***6 GPa*** ***590 K***	***6.6 GPa*** ***~700 K***

Approx. Bond Dissociation Energy (kJ/mol)

Si-C ~450
C-C ~600
C≡C ~800

- X-ray enhancement of kinetics
- Reaction yield less during IR study
- At higher *T*, shock & static thresholds are relatively close (as expected) due to thermal effects

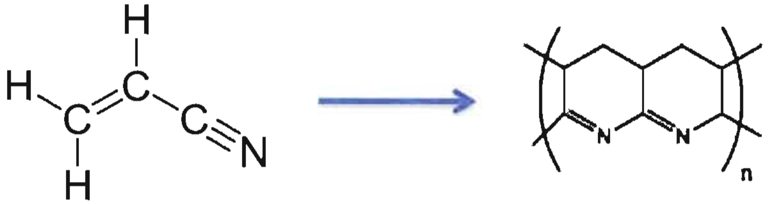
- Si-C bonds is weaker and polarized towards 'C'; higher ***P-T*** stability imparted by 'Si'

See Poster by Raja Chellappa

Acrylonitrile is a prototypical compound with the presence of both C=C and C≡N bonds

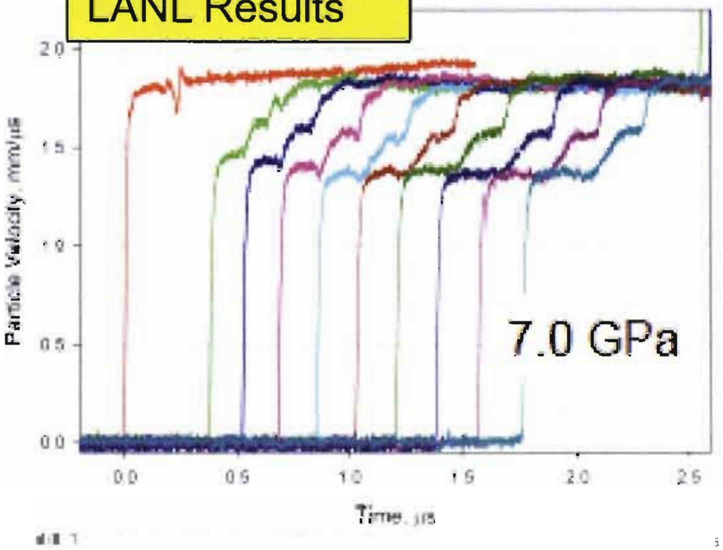
RESULTS

- Acrylonitrile exhibits 3-wave structure
- Wave evolution similar to solid-solid transitions
- At least 2 higher density species with reactive cusp at ~4.8-5.6 GPa
- Ladder polymers recovered by Dremin et al.



Dattelbaum et al. AIP Proc. (2011)
Yakushev et al. Fizika Goren. Vzry. (1974)

LANL Results



$$\text{Fluid} \xrightarrow{\text{1.1 GPa}} \text{Fluid + Phase I+ PAN} \xrightarrow{\text{1.3 GPa}} \text{Phase I+ PAN} \xrightarrow{\text{4 GPa}} \text{Phase II+ PAN}$$

Adams et al. Faraday Trans. (1981)

- Multiple phase transitions during decompression
- Polymerization reactions occur from liquid or solid phases

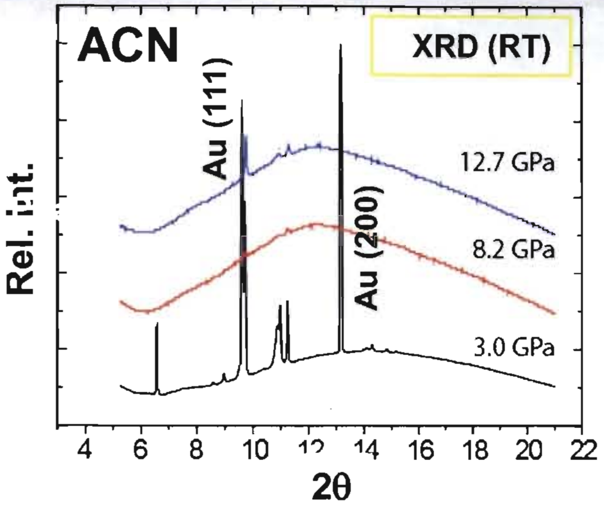
Zhulin et al. Science (1966)

Static high *P-T* studies are inconclusive

Need for static high ***P-T*** experiments to clarify phase transitions, reactivity thresholds & products

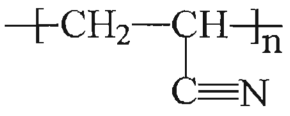
Polyacrylonitrile (PAN) recovered from static compression at RT is likely similar to PAN recovered from shock synthesis

RESULTS

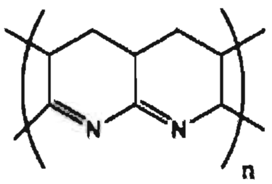


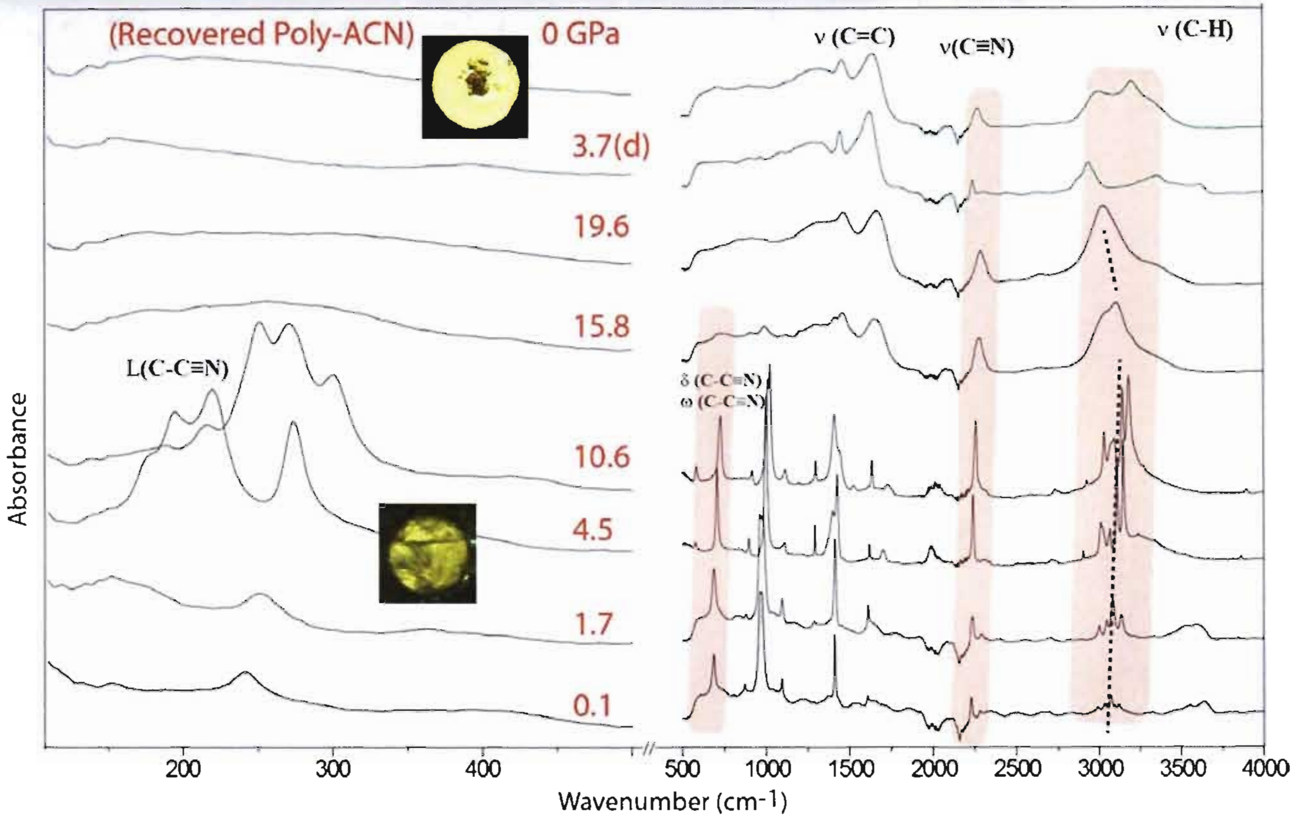
- Synchrotron x-rays induced some damage; accelerates polymerization

PAN from chemical synthesis


$$\left[CH_2 - \underset{C\equiv N}{\underset{|}{CH}} \right]_n$$

PAN recovered from High P



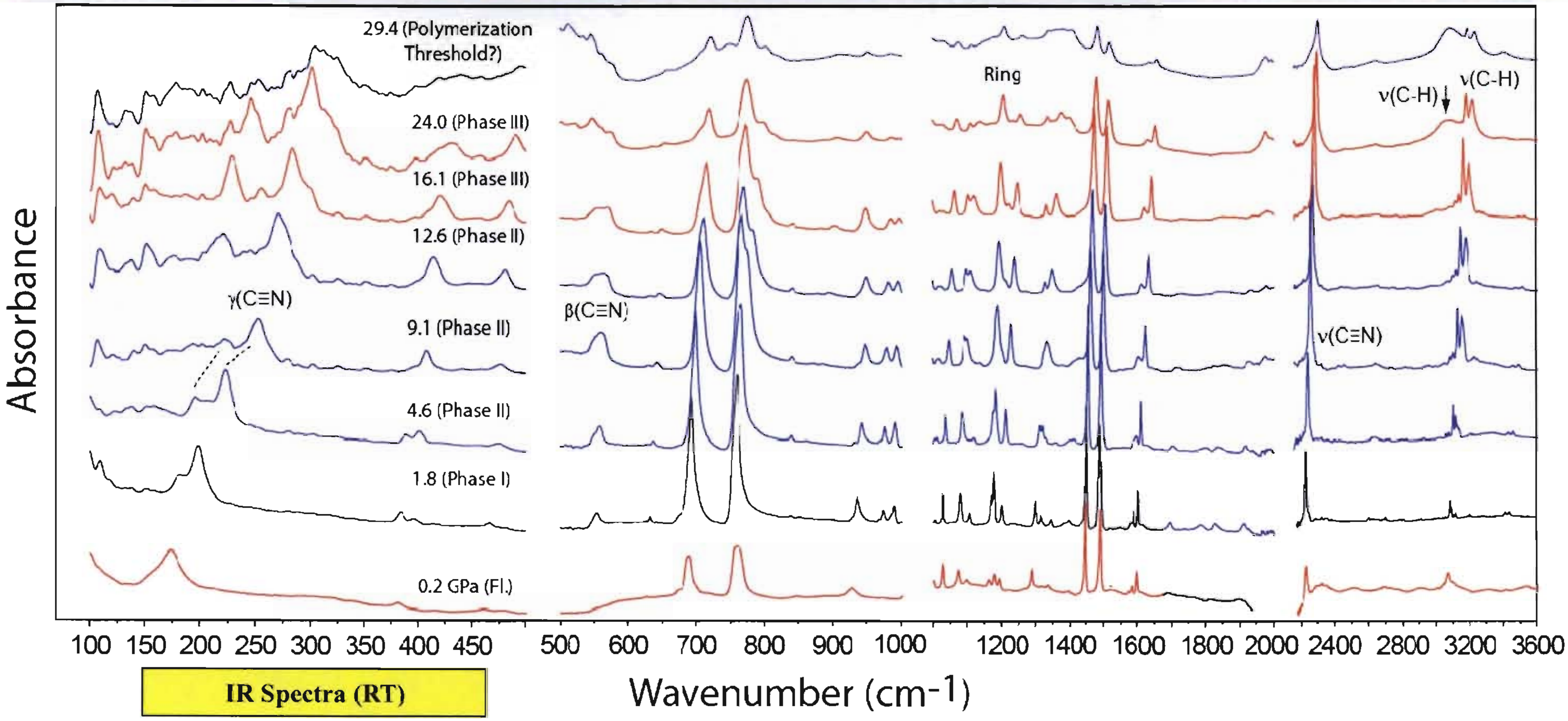


Fluid $\xrightarrow{\text{1 GPa}}$ Phase I $\xrightarrow{\text{~4 GPa}}$ Phase II $\xrightarrow{\text{~12 GPa}}$ PAN

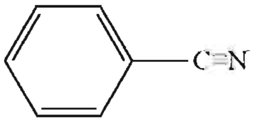
- ➢ IR spectra reveals that C=C and C≡N bonds are involved in the polymerization reaction (no decomposition); **note H-bonding**
- ➢ Hard, glassy PAN recovered from IR (Mushy from XRD)

RESULTS

Aromatic Benzonitrile reveals higher stability of C≡N bond



- BZN solidifies to Phase I at ~1.8 GPa and undergoes phase transitions at ~4.6 and ~13 GPa. (No
- Based on the IR spectra a threshold pressure of ~30 GPa is indicated; Zharov et al. (1984) report polymerization at 8 GPa under high pressure shear deformation.



Aliphatic vs Aromatic Nitriles: a brief summary

STATIC VS SHOCK THRESHOLDS FOR REACTION

	STATIC	*SHOCK*
AN	*8-10 GPa* *25 °C*	*4-5 GPa*
BZN	*> 30 GPa* *25 °C*	*?? GPa*

- Aromatic functional groups reduce the reactivity of the C≡N bonds and is observed here as well. The increase in stability is also reflected in lack of XRD damage to BZN.

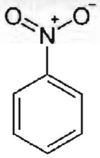
- Both AN and BZN exhibit multiple phase transitions < 5 GPa; multi-wave profiles expected corresponding to solid-solid phase transitions

- XRD studies are on-going

PREVIOUS WORK

Nitrobenzene: Shock & Static Literature

Nitrobenzene is the smallest building block of nitroaromatic explosives.



Shock Compression

- ☐ Yakushev et al. (1979) report a kink in the Hugoniot at 13 GPa with a density increase associated with decomposition to carbonaceous soot

$$C_6H_5NO_2 \longrightarrow 6H_2O+NH_3+N_2+18C$$

- ☐ The decomposition pressure of NB (13 GPa) coincides with the initiation of liquid TNT and pyrolysis of benzene
- ☐ Breakdown of benzene ring suggested as the first step in the chemical reactions of nitroaromatics (not the scisson of C-N bond)

LANL work in progress to resolve major discrepancies in available shock data (+ve or –ve volume change??)

Static Compression at RT

- ☐ Only one isothermal XRD study (Kozu et al. Jpn. J. Appl. Phys. (2000); no data beyond 13 GPa.
- ☐ Polymerization reported by Kozu et al. however suspected laser-induced

Static high *P-T* experiments to identify decompression induced decomposition and mechanisms, and polymerization reactions

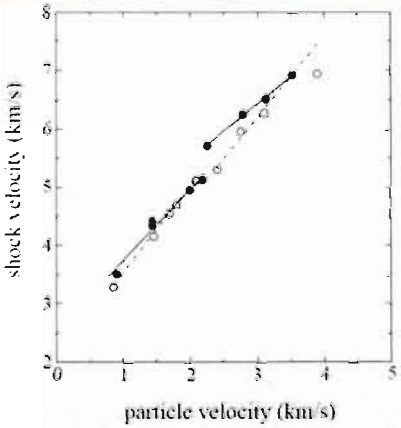
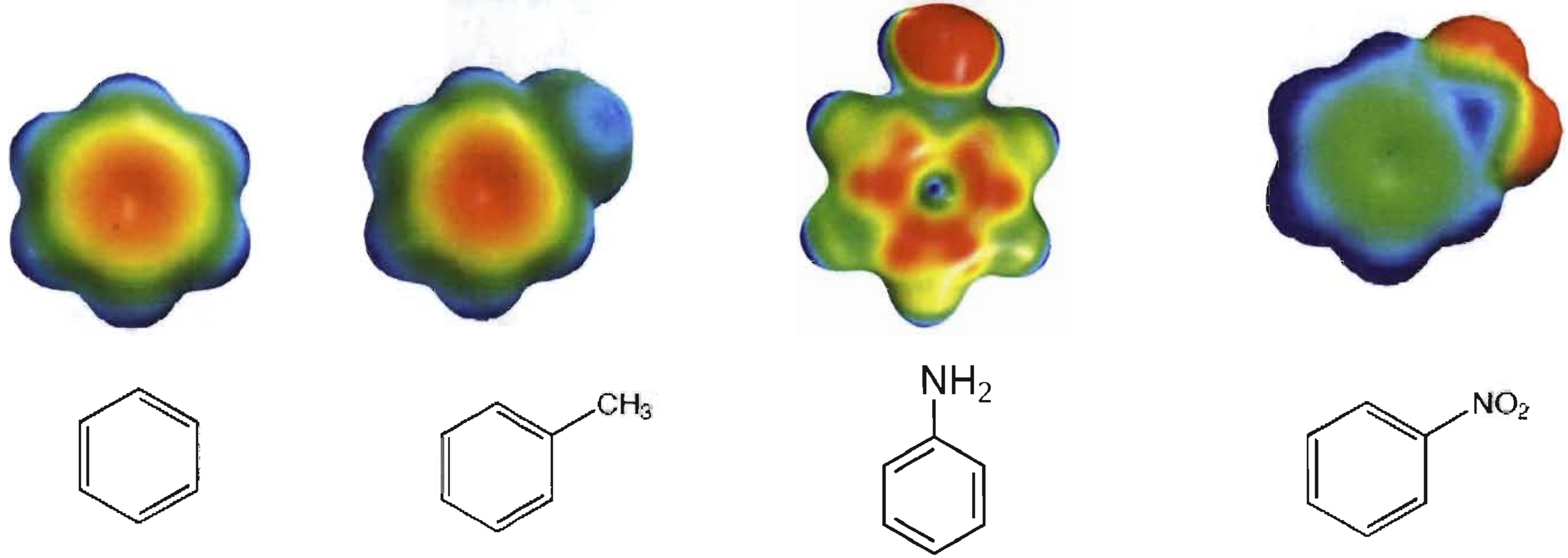


Fig. 3. Hugoniot of nitrobenzene on the U_s-u_p plane. The closed circles and the solid lines represent our experimental data and linear fits. The open circles and the dashed lines represent the data of Yakyshev *et al.*

RESULTS

The role of Nitro- & Amino- groups in ring stabilization at high *P-T*



Experimental data at high *P-T* is necessary to understand the shock & static high P-T reactivity of the aromatic ring

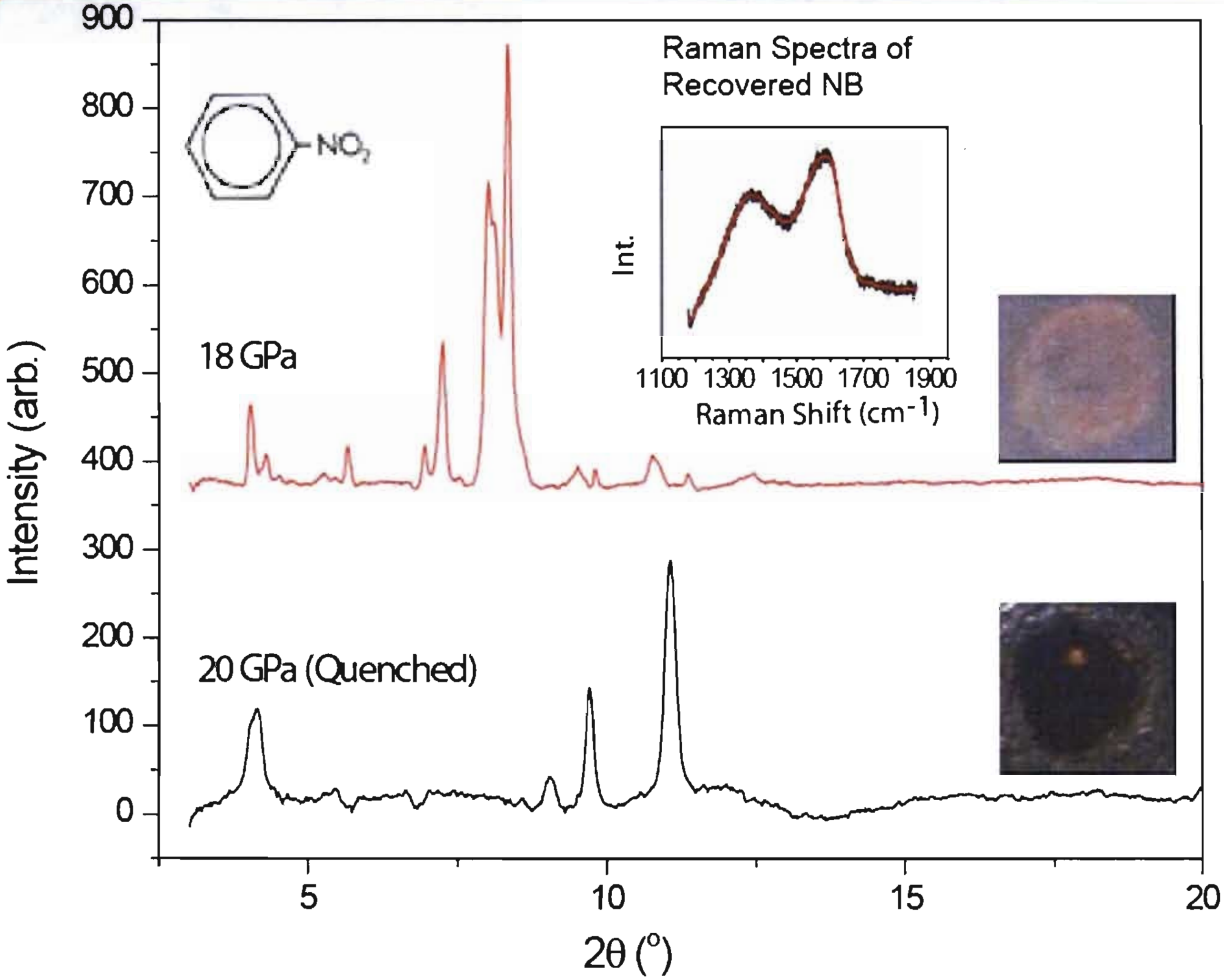
Static compression studies of Benzene are numerous but no studies on monosubstituted aromatics.

http://www.utdallas.edu/~biewerm/17.pdf

RESULTS

Decomposition reactions in Nitrobenzene

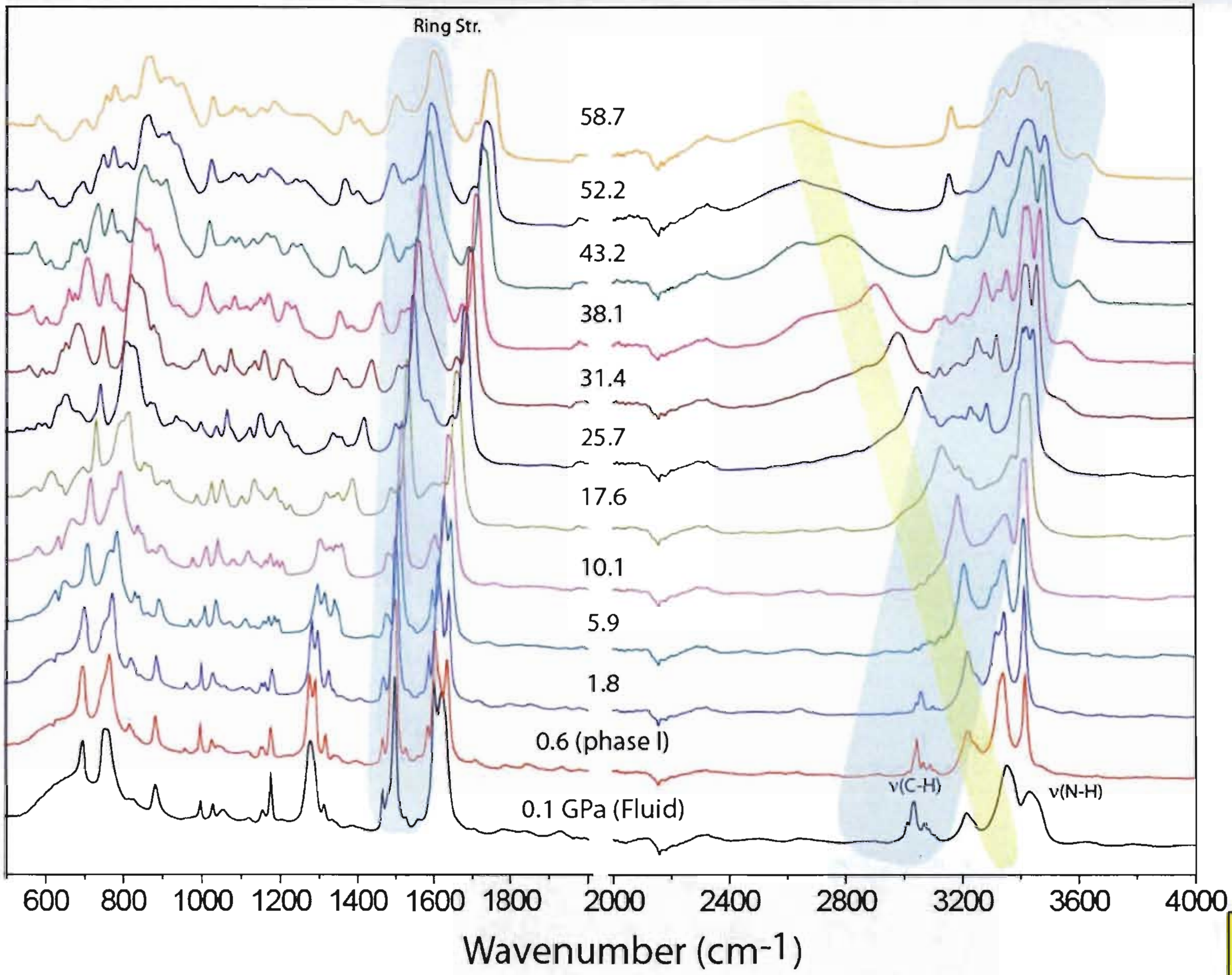
- ☐ NB freezes at ~0.5 GPa at RT to a crystalline, transparent *Phase I* which transforms orange colored *Phase II*
- ☐ The high pr. crystalline phase is stable upto ~40 GPa at RT and upto ~40 GPa (500 °C)
- ☐ Pressure quenching from ~40 GPa to 20 GPa decomposes NB with a carbonaceous phase recovered (which is crystalline)



Synchrotron XRD patterns of high pressure NB phase at 18 GPa and pressure quenched sample (from 40 GPa) NB at 20 GPa is shown along with photomicrographs of the sample in a DAC; Inset: Raman spectra of quenched sample at 1 bar, showing a doublet feature typical of C-rich soot.

Stability of Aniline up to 60 GPa: Strengthening of Aromatic Ring

RESULTS



The ν(N-H) modes are relatively stiff compared to the ν(C-H) modes with a crossover pressure of ~ 8 GPa

NH_2 functional group exhibits H-bonding

Aromatic ring is quite stable;' No evidence of polymerization

See Poster by Raja Chellappa

Bridging the strain-rate gap between shock & static experiments

RESULTS

Polymerization in TBA

Starting at 7.4 GPa, reaction complete by 14.4 GPa (***P*** increased by < 1 GPa /s)

Transparent polymer recovered

MEDIUM STRAIN-RATE EXPERIMENTS

- Bridge the strain-rate gap between shock & static conditions using pressure-jump experiments

Future Outlook

- Static high *P-T* experiments on Toluene have been planned to complete the series of mono-substituted aromatics

- Extend to di- and tri- substituted aromatics to gain insights on the effect of substitution of various functional groups
    - **Dinitrobenzenes** (1,3-DNB is an explosive while 1,4-DNB is not energetic)
    - Phenylenediamine and others

Related work in this symposia

☐ **Poster:** "Absorption studies in Nitrobenzene," Nathan Mack, Raja Chellappa, and Dana Dattelbaum

☐ **Poster:** "Simple Molecular Chemistry at High *P-T*: From Building Blocks to Energetic Materials," Raja Chellappa, Sourav Adak, Fran Rein, and Dana Dattelbaum

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