HIGH-PRESSURE SYNCHROTRON INFRARED SPECTROSCOPY:

New Light on Materials under Extreme Conditions

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# ACKNOWLEDGEMENTS

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I. Introduction

STATIC HIGH-PRESSURE SCIENCE
UNIQUE ADVANTAGES OF SYNCHROTRON INFRARED

II. Highlights: A Decade of New Findings

SELECTED APPLICATIONS:
Physics, Chemistry, Materials Science,

III. New Opportunities and Challenges

SELECTED GRAND CHALLENGES
A NEW OF HIGH-PRESSURE DEVICES
POSSIBILITIES FOR NSLS-II

THEMES
Synchrotron infrared and high pressure
- an extraordinary match
Synchrotron IR/x-ray probes
- unique capabilities of the NSLS
Full integration of techniques
- future facilities
RANGE OF PRESSURE IN THE UNIVERSE

- Hydrogen gas in intergalactic space
- Interplanetary space
- Atmosphere at 300 miles
- Center of Jupiter
- Center of Sun
- Center of white dwarf
- Center of neutron star
- Deepest ocean
- Best mechanical pump vacuum
- Water vapor at triple point
- Atmospheric pressure (sea level)
- Center of the Earth
ADVANCES IN STATIC HIGH PRESSURE

PRESSURE UNITS

- $10^3$ atm $\approx$ kbar
- $10^6$ atm $\approx$ Mbar
- 10 kbar = 1 GPa
- 1 Mbar = 100 GPa

- 1 Gigapascal = $10^9$ N/m²
Free Energy Changes and Chemical Bonding

- $P-V$ work can exceed binding energies
- Dramatic changes in bonding and electronic states
- Stored energy in metastable phases

[Hemley and Ashcroft, *Physics Today* 51, 26 (1998)]
HIGH-PRESSURE TECHNOLOGY
Plethora of New Instruments
Synchrotron Infrared Spectroscopy and High Pressure

U4IR: 1990-1992
- First megabar synchrotron IR measurements

- PRT with NSLS, Northrup Grumman
- Nicolet 750; custom built microscopes

U2A: 1998-
- PRT with NSLS
- Integrated optical/IR spectroscopy facility

U2A: 2004-
- Improved beam delivery
- Far-IR enhancement

High-Pressure Beam lines

Infrared Brightness

Photons/sec/0.1%bw/mm²/°sr
Wavelength (microns)

- 10000 1000 100 10 1
- 10⁻¹⁵ 10⁻¹⁴ 10⁻¹³ 10⁻¹² 10⁻¹¹ 10⁻¹⁰ 10⁻⁹ 10⁻⁸ 10⁻⁷ 10⁻⁶

- U4IR
- NSLS U2B Mk.2
- 40 mrad hor
- 40 mrad vert.
- 2000K Black Body
- NSLS U2B
- 12 mrad hor
- 8 mrad vert.

N

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U2A Beamline Upgrade: IMPROVED FAR-IR AND BEAM DELIVERY

- Near IR through far IR spectral range
- Reflectivity and absorption measurements
- Low-temperature measurements
- Mapping of the samples
- In situ Raman and fluorescence measurements
- Diamond lens
- Small diamonds

Bruker IFS66v/s FTIR Spectrometer

- N₂ purged Low-T Far/Mid-IR MICROSCOPE

Visible spectrograph

- MCT 1
- Bolometer

- MCT 2

- Laser
- Diamond lens in the cryostat
- Notch filters
- Diamond cell

Microscope 1
- N₂ purged
- Bruker IRscope II

Microscope 2
- MCT Detector
- Bolometer

Microscope 3
- Visible Microscope
- Vacuum microscope
- Microscope
- N₂ purged
- Laser
- Diamond lens
- CCD detector
- Eyepiece

Diamond lens
- N₂ purged
- Diamond window
- Vacuum box
- Vacuum pipe
- M2
- M1

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A WEALTH OF FINDINGS:
1. Condensed Matter Physics

- HYDROGEN AT MEGABAR PRESSURES

ANOMALOUS CHARGE TRANSFER STATE
[Hemley et al., Nature 369, 384 (1994)]

UNEXPECTED PHASE DIAGRAM
[Mazin et al., Phys. Rev. Lett. 78, 1066 (1997);
Goncharov et al., ibid. 75, 2514 (1996);
Lorenzana et al., ibid., 63, 2080 (1989)]

NO “MOLECULAR” METALLIZATION (to 230 GPa)
Multimegabar Vibrational Spectroscopy

- Molecules stable to 300 GPa in solid
- Constraints on the crystal structure


A WEALTH OF FINDINGS:
1. Condensed Matter Physics

- INFRARED EXCITATIONS IN HIGH-Tc SUPERCONDUCTORS


- NOVEL TRANSFORMATIONS

Pressure-induced amorphization of HfW$_2$O$_8$

- MAGNON EXCITATIONS

Sr$_2$CuCl$_2$O$_2$ magnon excitations

IR, NaCl medium


[Chen et al. Phys. Rev. B 64, 20040 (2002)]
A WEALTH OF FINDINGS:

2. Chemistry

HIGH PRESSURE SPECTRA
Synchrotron Infrared Reflectivity

Compression of H₂O
(300 K)

- bcc-like oxygen for ice VII and X
- No other major phase transitions to at least 210 GPa

[Goncharov et al., Science 273, 218 (1996)]

- Non-molecular ice identified by IR reflectivity above 60 GPa
- X-ray Confirms spectroscopic data: bcc-based structure
A WEALTH OF FINDINGS:
2. Chemistry

- ANOMALOUS TRANSITIONS IN ICE VIII

Pressure dependence of IR translational and rotational mode frequencies in D$_2$O → No transition

A WEALTH OF FINDINGS:

2. Chemistry

- VAN DER WAALS COMPOUNDS

[Loubeyre et al. (1994); Datchi et al. (1997); Hemley (2000); Ulivi et al. (2001)]

- NOVEL MOLECULAR PHASES

- Quenchable to 300 K
- Polynitrogen: e.g., \( N_5^+ \) \( N_5^- \)
A WEALTH OF FINDINGS:

2. Chemistry

- NOVEL MOLECULAR PHASES

• NO⁺-NO₃⁻: an unusual ionic phase probed by far-IR and x-ray

[Somayazulu et al., Phys. Rev. Lett. 87, 135504 (2001); Song et al. 119, 2232 (2003)]
A WEALTH OF FINDINGS:
3. Earth and Planetary Science

- VIBRATIONAL PROPERTIES
  (Transition mechanisms and thermodynamic properties)
- INSULATOR-METAL TRANSITIONS
- MICROSCOPIC SPECROSCOPY OF INCLUSIONS
- DENSE SILICATES IN THE MANTLE

HYDROUS PHASES IN THE DEEP MANTLE:
Hydrogen Incorporation in Dense Silicates

Phase A
Lawsonite
Phase D
Phase B
Superhydrous B
Phase E

Displacive transformation in cummingtonite

[Yang et al., Am. Mineral. 83, 288 (1998)]
A WEALTH OF FINDINGS:
3. Earth and Planetary Science

High-Pressure Behavior of K$_{1.54}$Mg$_{1.93}$Si$_{1.89}$O$_7$H$_{1.04}$

- H disordering above ~15 GPa
- Crystalline-crystalline transformation

A WEALTH OF FINDINGS:
3. Earth and Planetary Science

- PLANETARY GASES AND ICES

- Hydrocarbon stability to megabar pressure
  300 K compression
- Consistent with powder and single-crystal diffraction
- New physics (H-rich alloy)?

[Badro et al., to be published]
A WEALTH OF FINDINGS:
4. Biology and Soft Matter

- BIOCHEMICAL REACTIONS
  IN HYDROTHERMA FLUIDS
- LIFE IN EXTREME ENVIRONMENTS
  (>1600 MPa)

HEME DOMING-MODE

- BIOMOLECULE VIBRATIONAL DYNAMICS

[Sharma et al., Science 295, 1514 (2002)]

- Doming mode found at 57 cm\(^{-1}\)
- Far-IR at high pressure

A WEALTH OF FINDINGS:
5. Materials Science and Technology

- SUPERHARD MATERIALS
  [Zhao et al., J. Mat. Sci., in press]

- HYDROGEN STORAGE MATERIALS
  Novel H₂-H₂O structure II clathrate
  Stable at ambient pressure to 145 K
  5.3 % hydrogen (4.5 % DOE 2005 target)

- HIGH ENERGY DENSITY MATERIALS

NITROGEN DISSOCIATION SEMICONDUCTING BEHAVIOR

[W. Mao et al. Science 297, 2247 (2002)]
OPPORTUNITIES AND CHALLENGES

• Higher pressures and temperatures
  - *physics/chemistry/astrophysics/planetary science*
• Higher precision/accuracy/sensitivity
  - *all pressure ranges*
• Broader wavelength range
  - far-IR, THz
• Time resolution
  - *transition kinetics to chemical dynamics*
• Integration of techniques
  - *diffraction, inelastic scattering, imaging*
• New generation of instrumentation
  - *large volume, smart anvil cell designs*
**OPPORTUNITIES AND CHALLENGES:**

*Grand Challenge of Hydrogen at Extreme P-T*

- Liquid ground state?
- High-$T_c$ superconductor?
- Higher $P-T$ needed
- Infrared combined with x-ray inelastic scattering phonons/electrons

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OPPORTUNITIES AND CHALLENGES:
Electronic Structure, Bonding, Synthesis of Novel Materials

- **NOVEL SUPERCONDUCTORS**
  (e.g., 23 elements; O, S, B, Fe, Li)

- **HIGHEST TEMPERATURE SUPERCONDUCTIVITY**
  \( T_c = 164 \text{ K at 30 GPa} \) [Gao et al. (1994)]

- **EXCITONIC INSULATOR STATES?**

- Integrated studies to >300 GPa and to millikelvin temperatures
- Far-IR to optical range
- Combined with x-ray inelastic scattering phonons/electrons
- Recovery to ambient

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OPPORTUNITIES AND CHALLENGES:
Spectroscopy of Earth Materials at Extreme P-T

- NATURE OF THE CORE FROM IN SITU OPTICAL STUDIES
- CHEMICAL REACTIONS IN THE DEEP EARTH
- HYDROCARBON STABILITY AND ENERGY RESOURCES
- IN SITU HIGH P-T STUDIES OF PLANETARY GASES AND ICES
OPPORTUNITIES AND CHALLENGES:
Life in Extreme Environments and Origin of Life

- BIOCHEMICAL REACTIONS
- HIGH-PRESSURE MICROBIOLOGY

- IR/optical/x-ray imaging with \( P-T-\dot{t} \)
- Single cells under stress
- “Test-tube” study of microbial evolution and adaptation
- Combined with other probes in new instrumentation

[Sharma et al., Science 295, 1514 (2002)]
OPPORTUNITIES AND CHALLENGES:
Towards TPa Pressures with Large Volume Anvil Cells

GOALS:

- Higher pressures (1 TPa or 10 Mbar) and temperatures (>1 eV)
- Larger sample volumes needed (e.g., diffraction limited far-IR)
- Accuracy/precision compromised
- Applications of several simultaneous probes limited

Growth of Diamond Anvils by Homoepitaxial Chemical Vapor Deposition

**[Yan et al. PNAS 99, 12523 (2002)]**

- 2.45 mm high
- 0.28 carats
- 0.45 mm seed
- Grown in 1 day


CVD homoepitaxial growth

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Carat</th>
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<tr>
<td>1.7mm</td>
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<tr>
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<tr>
<td>7.5mm</td>
<td>2.5 ct</td>
</tr>
<tr>
<td></td>
<td>25 ct</td>
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</tbody>
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OPPORTUNITIES AND CHALLENGES:
Towards TPa Pressures with Large Volume Anvil Cells

CVD single crystals are utratough and/or ultrahard


Single-crystal CVD anvils can generate multimegabar pressures

OPPORTUNITIES AND CHALLENGES:
Towards TPa Pressures with Large Volume Anvil Cells

Characterization of CVD diamond single crystals by synchrotron IR

- Unusual hydrogen impurity structure
- Largely homogeneous based on IR mapping
- Enhanced far-IR transparency on annealing
- X-ray topography (X19) in progress
CONCLUSIONS

1. High pressure: a superb application of synchrotron IR techniques, complementing hard x-rays and other methods.
2. An essential tool for uncovering new physics and chemistry of materials under extreme conditions.
3. Numerous problems in Earth and planetary science can now be addressed.
4. Particularly important are the new far-IR developments and integrated multi-probe approaches.
5. Numerous new high-pressure technique developments are coming on line to complement the new generation of synchrotron facilities: NSLS-II.
6. The pressure parameter should be an integral part of sample environments at beamlines throughout NSLS-II.