New high pressure phases of some typical molecular solids

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OUTLINE

- **Motivations**
  Why we are interested in molecular systems under high pressures

- **Our Researches in 2010**
  - Methods
  - Results and discussions
Motivations

- Rich types of interactions between atoms
  ——— Pressure-induced phase transition

- Functional materials
  ——— High-$T_c$ superconductors

- Energy storage materials
  ——— hydrogen and polymeric nitrogen

- Important problem in condensed matter physics
  ——— metallic hydrogen
Ab initio molecular dynamics studies of solid hydrogen sulfide under high pressure

Polar crystalline structure of CHBr₃ under high pressure by annealing method

Hydrogen bond symmetrization and superconducting phase of HBr and HCl under high pressure by softening mode of phonon

IVA Group hydrides under high pressure (SiH₄, Si₂H₆) by ab initio random structure searching

AsH₃ under extrahigh pressure by ab initio random structure searching

Hydrogen-dominant compounds KH₆ under high pressure by ab initio random structure searching

H$_2$S is similar to ice at molecule level, but is different with ice in condensed phases under high pressures, its structures are still unknown clearly.

The pressure-induce molecular dissociation in their solid states has been drawn great attentions. Ice is well studied, but H$_2$S is still unclear.

—— The structure of phase V, which is unknown, is the key to understand the dissociation of H$_2$S.
The Parrinello-Rahman scheme can describe the structural changes under pressure and/or temperature by introducing 9 variables of the cell $h$ to the system Hamiltonian.

Lagrangian: ($S$ is the atomic scale coordinates, $R=hS$, $\Omega$ is cell volume, $p$ is external pressure, $W$ is fictitious mass of the cell)

\[
L(R^N, \dot{R}^N) = \sum_{I=1}^{N} \frac{1}{2} M_I \dot{R}_I^2 - U(R^N)
\]

\[
L = \sum_{I=1}^{N} \frac{1}{2} M_I (\dot{S}_I^T h^T h \dot{S}_I) - U(h, S^N) + \frac{1}{2} W \star Tr(h^T h) - p\Omega
\]
Simulations are performed from an experimentally proposed structure of phase IV, the system was heated up to 400 K at 15 GPa in order to simulate the dissociation process of H$_2$S.

The hydrogen bonding network in the I4$_1$/acd (left) and Ibca (right) structures proposed for phase IV.

- The experimentally proposed I41/acd structure is unstable, we propose a stable structure with Ibca symmetry.
- I41/acd: the hydrogen bonds and molecule are coplanar; Ibca: they from a tetrahedron, which is more stable.
X-ray diffraction patterns of phase IV

(a) Experiment
(b) Calculations from snapshot of MD structures
(c) Calculations from averaged Ibca structure

Our structure is in good agreement with experimental X-ray diffraction patterns
Structural transformation induced by increasing temperature at 15 GPa

\[ O_1(R) = \left\langle \frac{\sum_{i<j} \cos \theta \delta(R_{ij} - R)}{\sum_{i<j} \delta(R_{ij} - R)} \right\rangle \]
\[ O_2(R) = \left\langle \frac{\sum_{i<j} (2\cos^2 \theta - 1) \delta(R_{ij} - R)}{\sum_{i<j} \delta(R_{ij} - R)} \right\rangle \]

- **S-S RDF**: Shoulder at ~3.1 Å disappears at 350 K; Coordination number of S changes from 4 to 12 above 350 K
- **S-H RDF**: Zero area between the first and second peaks disappears above 350 K, indicating that protons can move between molecules occasionally
- **ACF**: at 300 K, molecular ordered state, above 350 K, molecular disordered state
Sulfur lattice has a space symmetry of $P6_3/mmc$, and hydrogen density maxima locate around the $S$ symmetry sites.

Phase $V$ of $H_2S$ is proton disordered.

XRD of phase $V$

Spectra evidence

The splitting of molecular bending peak at $\sim 1000 \text{ cm}^{-1}$ indicates the dissociation of hydrogen sulfide; the splitting gap at 42 GPa and 300 K is 62 cm$^{-1}$, which is in close agreement with experimental value of 80 cm$^{-1}$.
The dissociation mechanism:
hydrogen dynamics in phases IV and V

- **IV**: protons are localized
- **V**: protons are delocalized. Protons can jump into another molecule during dynamically
- **V**: dissociation dynamically

Sub-summary

- The structures of phase IV and V of H₂S are obtained via variable cell MD

- The strongly delocalized behavior of hydrogen in phase V leads to the dissociation of H₂S molecules in its solid state
Haloforms are ideal systems for studying the nature of hydrogen bond and halogen bond, especially under high pressures. These weak interactions play an important role in the formation of crystal structures.

Polar crystals can be widely applied in nonlinear optics, optoelectronic transducers, ferro-, piezo-, and pyroelectric areas.
Known structures of bromoform

- **α-CHBr₃**: at ambient pressure from 281 to 268 K, dynamically orientational disordered, P₆₃/m

- **β-CHBr₃**: Slowly cooling from α phase, observed between 268 K and 14 K. Centro-symmetric triclinic, P-1

- **γ-CHBr₃**: Rapidly cooling its liquid or α phase to liquid nitrogen temperature. Centro-symmetric trigonal, P-3

- **δ-CHBr₃**: at 0.20~0.35GPa, 295K, P6₃, polar crystal

How about the high pressure phases of bromoform?
Theories and Methods

◆ Theory: density functional theory
   Classical molecular dynamics

◆ Software: CASTEP and FOCITE package in MS

◆ Methods: Pseudopotential Plane-Wave
   Classical simulated annealing

◆ The generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Eruzerhof was used to describe the exchange and correlation potential.

◆ We chose the COMPASS force field and used the Ewald summation method to calculate the electrostatic interactions and van der Waals interactions.
Annealing method

- One of the effective optimizing methods
- Originated from annealing of solid, the total energy of system minimize with decreasing temperature
- In 1982, Kirkpatrick et al firstly recognized the similarity between the annealing and optimization
- Introducing the Metropolis principle into the optimization, obtained a optimization arithmetic in the sense of analogous with annealing procedure of solids
From $\beta$ and $\gamma$ phases, four new structures with lower energies are obtained

- CC ($\varepsilon$-CHBr$_3$ phase)
- $P2_1$ ($\lambda$-CHBr$_3$ phase)
- $Pm$ ($\zeta$-CHBr$_3$ phase)
- $C2/m$ ($\eta$-CHBr$_3$ phase)
Thermodynamics of bromoform under high pressure

\begin{equation*}
\beta^{-}\text{CHBr}_3 \rightarrow 1 \text{ GPa}, \ \gamma^{-}\text{CHBr}_3 \rightarrow 90 \text{ GPa}, \ \varepsilon^{-}\text{CHBr}_3
\end{equation*}
Dynamical stability of ε-\text{CHBr}_3

Phonon dispersion with pressure
### Mechanical stability of $\varepsilon$-CHBr$_3$

<table>
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<th>P (GPa)</th>
<th>$C_{11}$</th>
<th>$C_{22}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{55}$</th>
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<th>$C_{15}$</th>
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</table>
At ambient pressure, the $\beta$ phase has indirect band gap of 3.55 eV,

$\gamma$-CHBr$_3$ exists as an insulator in the pressure range from 1 to 90 GPa

$\varepsilon$-CHBr$_3$ begins to metalize at 130 GPa

Sub- summery

Suggest a novel monoclinic structure of bromoform at high pressure (ε phase), which exhibits a polar symmetry with space group \( CC \)

The \( \text{Br} \cdots \text{Br} \) and \( \text{C} - \text{H} \cdots \text{Br} \) interactions in the \( \varepsilon \) phase are important for the polar aggregation at high pressure

The phase transition sequence of bromoform at zero temperature: from \( \beta \) phase to \( \gamma \) phase at 1 GPa, then to \( \varepsilon \) phase at 90 GPa, which is stable at least up to 300 GPa

The pressure-induced metallization in \( \varepsilon \) phase happens at 130 GPa, which mainly caused by the hybridization of C-s, \( p \) and Br-s, \( p \)
(3) Hydrogen-rich materials ($\text{Si}_2\text{H}_6$) under high pressure by *ab initio* random structure searching

- High pressure

**Metallic Hydrogen**

- High energy density (>400 kJ/mole)
- Room temperature superconductor (>300 K)?

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E. Wigner, et al. JCP(1935)
N.W. Ashcroft, PRL(1968)
D.A. Papacon et al. PRB(1977)
......
Phase III of solid hydrogen is Cmca symmetry.

Cmca phase is metallic above 400GPa.

$T_c$ up to 242 K at 450 GPa.

$T_c$ as a function of pressure.

Metallization of hydrogen is not observed at 342 GPa experimentally!

Metallization of hydrogen is not observed at 342 GPa experimentally!


One of important topics is how to reduce the metallic pressure of hydrogen system!
Group IV hydrides under high pressure

“Chemically precompressed”

Most interesting hydrides:

\[ \text{CH}_4, \text{SiH}_4, \text{GeH}_4, \text{SnH}_4 \]

Becoming a high-\( T_c \) superconductors at lower pressures

- Structures under high pressures
- Metallization conditions
- Superconductivity

Can other hydrogen-rich compounds are expected to be better candidates for high-$T_c$ superconductivity, especially for disilane?

Method used in this part

Computational details

Searching a structure
- Random Strategy
- Evolutionary algorithm
Geometry Optimization
- BFGS optimizer
- Damped MD
Enthalpy calculations
Lattice dynamics
EPC calculations

Density Functional Theory
CASTEP & VASP
Quantum-ESPRESSO package
Ab initio random structure searching (AIRSS)

Positions of the atoms are chosen randomly.

Cell angles are chosen randomly and uniformly in the suitable range.

Volume are scaled randomly in the range of desired value.

Random structure

Continue generating configurations until the lowest enthalpies with optimized structures are convergent.

Stable structure with global minimum energy.
The structures of disilane under high pressure. The $P-1$ phase at 175 GPa (a), the $Pm-3m$ phase at 275 GPa (b), and $C2/c$ phase at 300 GPa (c)
Thermodynamic stability

- A wide decomposition pressure range up to 135 GPa
- The P-1 disilane from 135 GPa to 275 GPa
- Near 275 GPa, Pm-3m disilane has the lowest enthalpy
- Above 300 GPa, the C2/c disilane exists

Main figure: Calculated enthalpies of various disilane structures as functions of pressure with respect to the decomposition enthalpies. Inset: Enthalpies in the enlargement range of pressure between 250 GPa and 400 GPa.

## Mechanical stability

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<td>634.43</td>
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<td>143.60</td>
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The phonon band structure and projected phonon DOS charts of $P$-1 phase at 175 GPa (a), $Fm-3m$ phase at 275 GPa (b) and $C2/c$ phase at 300 GPa (c).
Three kinds of disilanes are all metallic

High DOS values near Fermi level might favor the superconducting behavior
The Eliashberg phonon spectral function $\alpha^2 F(\omega)$ and the electron-phonon integral $\lambda(\omega)$ for phases of $P-1$, $Fm-3m$ and $C2/c$ calculated at 175, 275 and 300 GPa, respectively.
Superconductive mechanisms

\[ P-1: \quad \zeta = 0.75, \]
\[ \langle I^2 \rangle = 0.295 \text{(Ry/Bohr)}^2 \]
\[ \omega_{\log} = 1121.42 \text{ K} \]

\[ Pm-3m: \quad \zeta = 0.46, \]
\[ \langle I^2 \rangle = 0.651 \text{(Ry/Bohr)}^2 \]
\[ \omega_{\log} = 1443.60 \text{ K} \]

\[ C2/c: \quad \zeta = 0.60, \]
\[ \langle I^2 \rangle = 0.278 \text{(Ry/Bohr)}^2 \]
\[ \omega_{\log} = 866.13 \text{ K} \]

The large EPC parameter \( \lambda \) of \( P-1 \) and \( Pm-3m \) phases mainly profit form the high values of \( \xi(Q) \) and \( \langle I^2 \rangle \), respectively.

Fermi surface nesting function \( \xi(Q) \) of \( P-1 \) phase at 175 GPa (top), \( Fm-3m \) phase at 275 GPa (middle) and \( C2/c \) phase at 300 GPa (bottom) along high-symmetry directions at selected pressures. The 3D Fermi surface as insets calculated for the corresponding phases at high pressure.

XL Jin, T Cui*, et al, PNAS 107, 9969(2010)
Three metallic structures, i.e. $P-1$, $Pm-3m$ and $C2/c$, are suggested under high pressure.

A remarkably wide decomposition pressure range of 50~135 GPa is uncovered.

High-$T_c$ superconductivity of $Pm-3m$ and $P-1$ phases are found.
Summary

- High-pressure behavior of the typical molecular systems are investigated extensively by means of first-principles density functional theory and structure-searching methods.

- New structures, phases transition have been observed theoretically.

- Novel superconductivity in disilane has been suggested under high pressure.
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