

Molecular Dynamics and Properties Determined by Nuclear Characters

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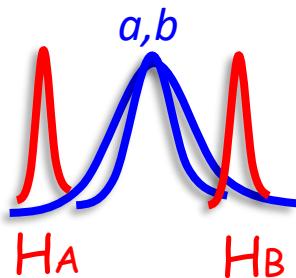
- [1] J. Phys. Chem. Lett. **11**, 4186 (2020)
- [2] J. Phys. Chem. B, **122**, 8233 (2018)
- [3] J. Phys. Chem. Lett. **8**, 3595 (2017)
- [4] Phys. Chem. Chem. Phys. (Communication) **18**, 2314 (2016)
- [5] J. Chem. Phys. (Communication) **143**, 171102 (2015)
- [6] Phys. Rev. B, **90** 165132 (2014)
- [7] J. Chem. Phys. (Communication) **140**, 171101 (2014)
- [8] Chem. Phys. Lett., **532** 124 (2012)
- [9] 日本物理学会誌, Vol.72 No.8, 563 (2017)

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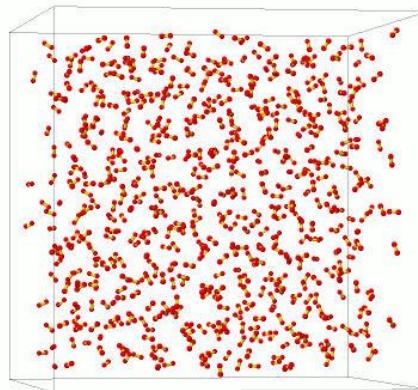
1. Nuclear Quantum Effects
2. Theoretical Framework
3. Results
 - Liquid
 - Solid
 - Supercooled Solid
 - Nonequilibrium
 - Isotope Effects
 - Isotope Mixtures

Nuclear and Electron Wave Packet Molecular Dynamics (NEWPMD)

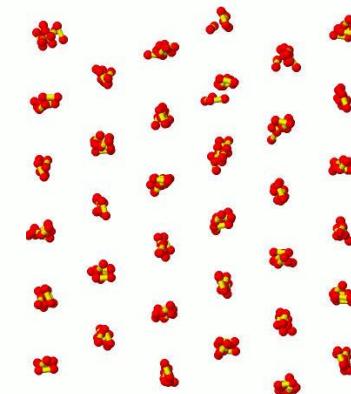
Gas@50K



Liquid@25K



Solid@2.5 K



Jmol

- ✓ No Empirical Parameter/No Model Potential
- ✓ Nuclear Quantumness
- ✓ Long-Range Dispersion Force
- ✓ Gas–Liquid–Solid–Metastable–Nonequilibrium
- ✓ Real-Time Dynamics
- ✓ Orientation & H-H Vibration
- ✓ Low Computational Cost

Nuclear and Electron Wave Packet Molecular Dynamics (NEWPMD)

Time-Dependent Wave Function

$$\psi(t) = \mathcal{A}[\underbrace{\phi_a(\mathbf{q}_1)\phi_b(\mathbf{q}_2)}_{(a,b)}\underbrace{\phi_c(\mathbf{q}_3)\phi_d(\mathbf{q}_4)}_{(c,d)}\Theta(1, 2, 3, 4)]\underbrace{\Phi_A(\mathbf{Q}_1)\Phi_B(\mathbf{Q}_2)}_{H_A - H_B}\underbrace{\Phi_C(\mathbf{Q}_3)\Phi_D(\mathbf{Q}_4)}_{H_C - H_D}$$

\mathcal{A} : Antisymmetrizer

Perfect-Pairing Valence Bond Theory : (a,b) (c,d) in Singlet

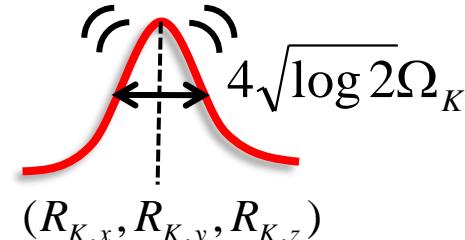


$$\Theta(1, 2, 3, 4) = \frac{(\alpha(1)\beta(2) - \beta(1)\alpha(2))}{\sqrt{2}} \frac{(\alpha(3)\beta(4) - \beta(3)\alpha(4))}{\sqrt{2}}$$

Thawed Gaussian NWP

$$\Phi_K(\mathbf{Q}_i) \equiv \left(\frac{1}{2\pi\Omega_K^2(t)} \right)^{\frac{3}{4}} \exp \left[-\frac{(\mathbf{Q}_i - \mathbf{R}_K(t))^2}{4\Omega_K(t)^2} + \frac{i\Pi_K(t)}{2\Omega_K(t)}(\mathbf{Q}_i - \mathbf{R}_K(t))^2 + i\mathbf{P}_K(t) \cdot (\mathbf{Q}_i - \mathbf{R}_K(t)) \right]$$

$\hbar=1$
electron charge = 1
electron-mass scaled



Nuclear Quantum Effects

Zero Point Energy
Nuclear Delocalization

Time-Dependent Variational Principle

Action Integral

$$\Gamma \equiv \int L dt = \int dt \langle \psi, t | i \frac{\partial}{\partial t} - \hat{H} | \psi, t \rangle$$

Hamiltonian

$$\hat{H} = \sum_{i=1}^4 -\frac{1}{2M_{\text{nuc}}} \frac{\partial^2}{\partial \mathbf{Q}_i^2} + V(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4; \mathbf{Q}_1, \mathbf{Q}_2, \mathbf{Q}_3, \mathbf{Q}_4)$$

Equations of Motion

$$\begin{aligned}\dot{\mathbf{R}}_K &= \frac{\partial H_{\text{ext}}}{\partial \mathbf{P}_K}, & \dot{\mathbf{P}}_K &= -\frac{\partial H_{\text{ext}}}{\partial \mathbf{R}_K}, \\ \dot{\boldsymbol{\Omega}}_K &= \frac{1}{3} \frac{\partial H_{\text{ext}}}{\partial \boldsymbol{\Pi}_K}, & \dot{\boldsymbol{\Pi}}_K &= -\frac{1}{3} \frac{\partial H_{\text{ext}}}{\partial \boldsymbol{\Omega}_K}\end{aligned}$$

$$H_{\text{ext}} \equiv \sum_K^{\text{A,B,C,D}} \left[\frac{\mathbf{P}_K^2}{2M_{\text{nuc}}} + \frac{3\Pi_K^2}{2M_{\text{nuc}}} + \frac{3\hbar^2}{8M_{\text{nuc}}\Omega_K^2} \right] + \boxed{\langle V_{\text{ke,elec}} \rangle} + \boxed{\langle V_{\text{ee}} \rangle} + \boxed{\langle V_{\text{nn}} \rangle} + \boxed{\langle V_{\text{ne}} \rangle}$$

Kinetic energy of electrons

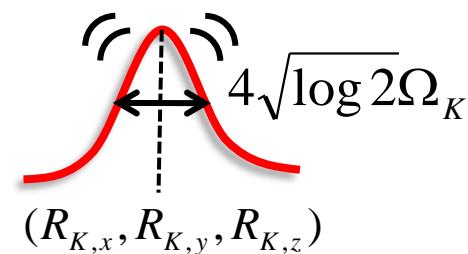
Electrostatic energies

electron-electron
nucleus-nucleus
nucleus-electron

- Kinetic energy of elec.
- Coulomb energies
 - electron-electron
 - nucleus-nucleus
 - nucleus-electron

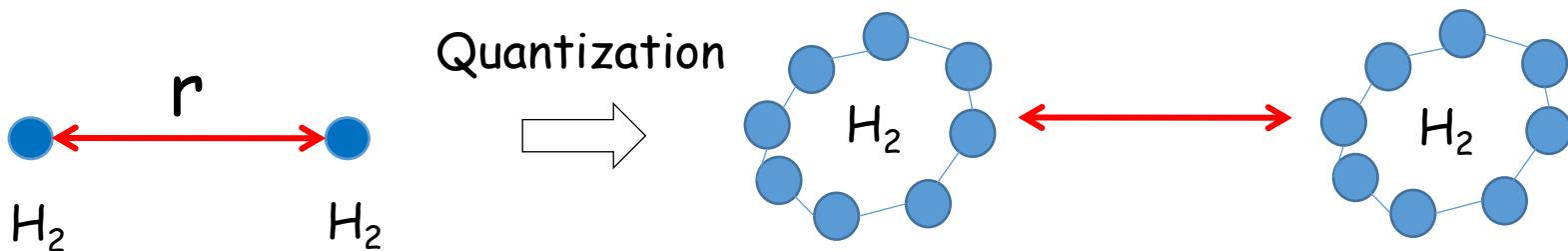
$\delta\Gamma/\delta\mathbf{R}_K = 0$, etc.

NWP



Semiquantum Path Integral Method

Centroid Molecular Dynamics
Ring Polymer Molecular Dynamics



Silvera-Goldman Model

$$V(r) = e^{\alpha - \beta r - \gamma r^2} - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} - \frac{C_9}{r^9} + \frac{C_{10}}{r^{10}} \right) f_c(r)$$

$$f_c(r) = \begin{cases} e^{-(r_c/r - 1)^2}, & \text{if } r \leq r_c \\ 1, & \text{otherwise} \end{cases}$$

Ring Polymer

$$\begin{aligned} Z_n = & \frac{1}{(2\pi\hbar)^{9Nn}} \int \int \prod_{j=1}^{3N} \prod_{k=1}^n d\mathbf{p}_j^{(k)} d\mathbf{r}_j^{(k)} e^{-\beta_n H_n(\{\mathbf{p}_j^{(k)}\}, \{\mathbf{r}_j^{(k)}\})} \\ H_n(\{\mathbf{p}_j^{(k)}\}, \{\mathbf{r}_j^{(k)}\}) = & \sum_{j=1}^{3N} \sum_{k=1}^n \left[\frac{(\mathbf{p}_j^{(k)})^2}{2m_j} + \frac{1}{2} m_j \omega_n^2 (\mathbf{r}_j^{(k)} - \mathbf{r}_j^{(k-1)})^2 \right] \\ & + \sum_{k=1}^n V(\mathbf{r}_1^{(k)}, \dots, \mathbf{r}_{3N}^{(k)}) \end{aligned}$$

Silvera-Goldman Model

Many Empirical Parameters
No Intramolecular Degree of Freedom
Limited Thermodynamic States

+

Path Integral

Equilibrium State
High Computational Cost
No Real-Time Trajectory

Simulation Details

1200 H₂ Molecules

Cubic Box with a Periodic Boundary

Initial Structure: Hexagonal Close-Packed Lattice with Random Orientation

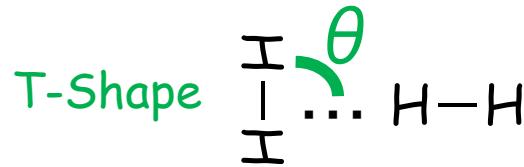
Equilibration: Velocity Scaling & Berendsen Methods

Time integration: Velocity-Verlet Method with Time Step 0.5 fs

NVE microcanonical simulation up to nanoseconds

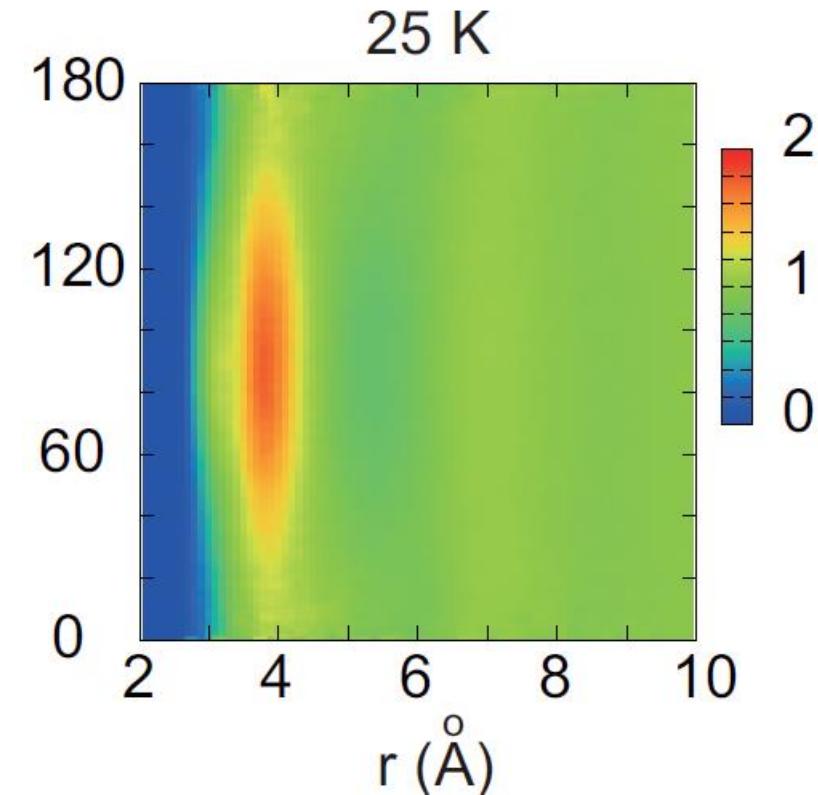
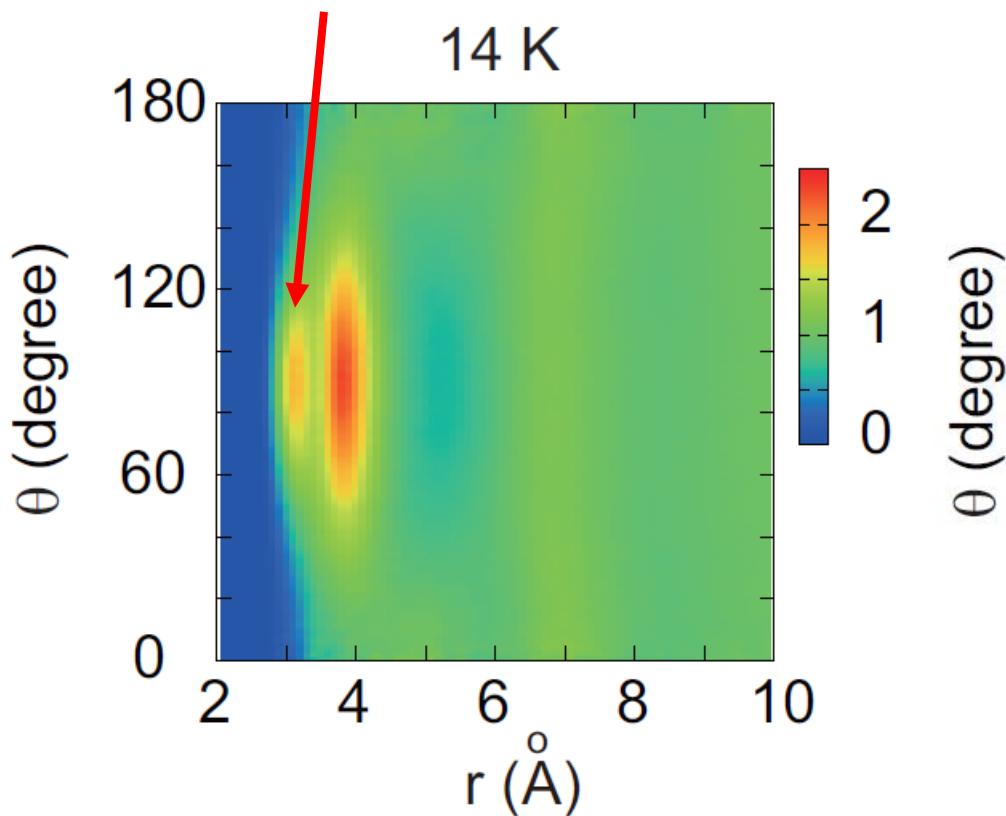
CPU time: 9 min. for 1 ps dynamics of 1200 molecules with 16 cores

2D Radial Distribution Function



$$g(r, \theta) = \frac{\langle n(r, \theta) \rangle}{2\pi n_0 r^2 dr \sin \theta d\theta}$$

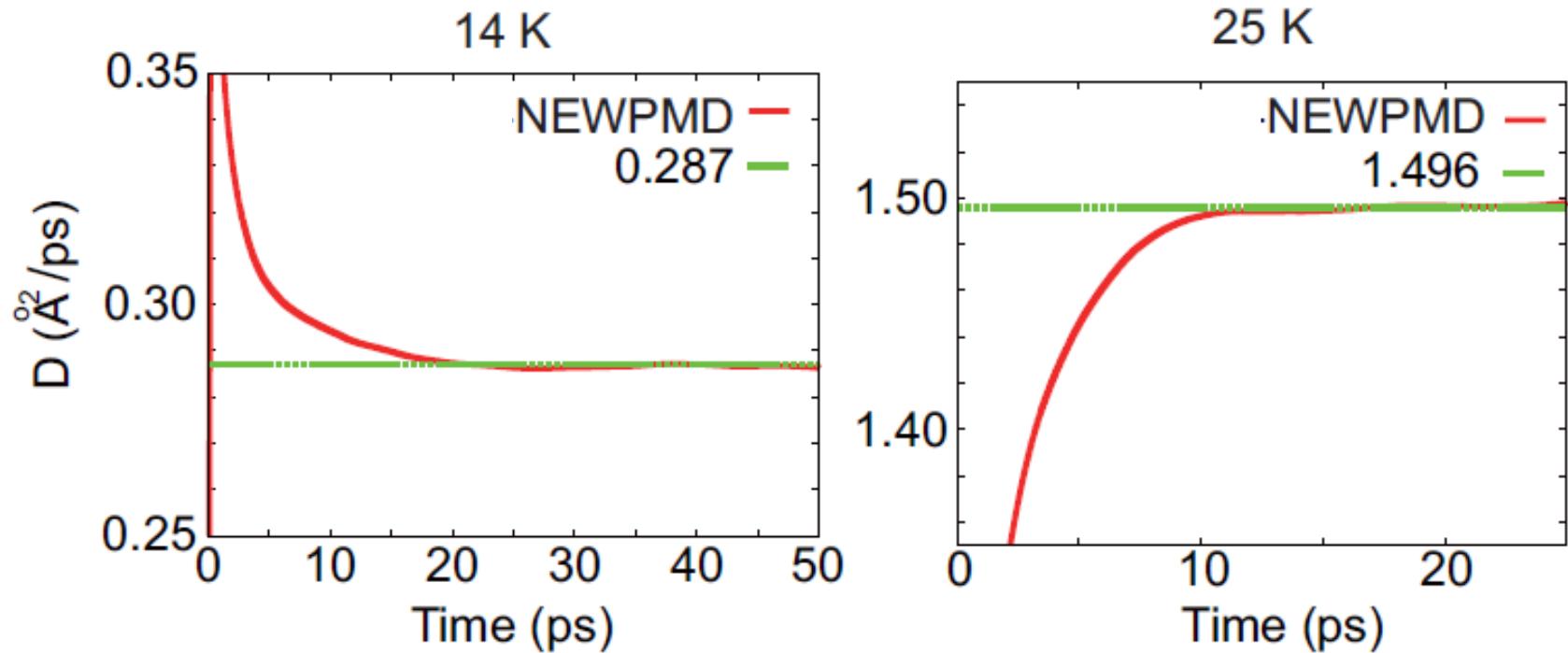
Diatomic Shoulder



Diffusion Coefficient

$$D(t) = \frac{\langle |\mathbf{R}(t) - \mathbf{R}(0)|^2 \rangle_{\text{avg}}}{6t}$$

$\mathbf{R}(t)$: Position Vector of H-H Center



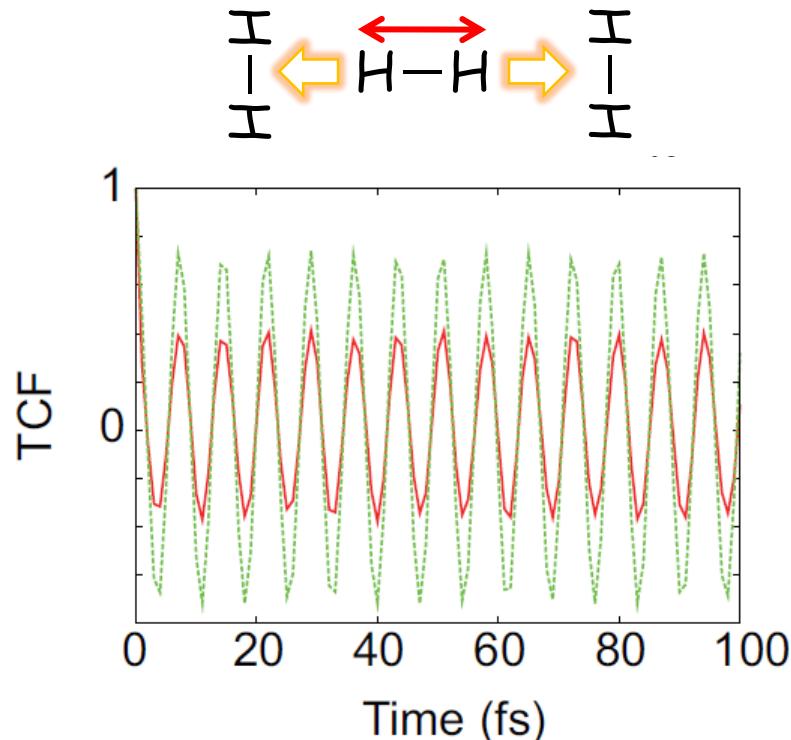
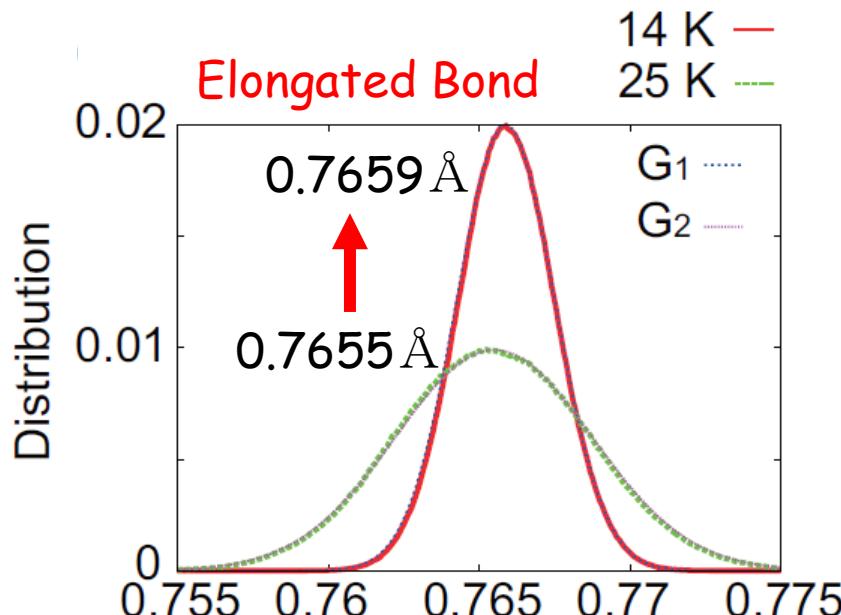
$$\frac{25}{14} = 1.79$$

Temperature

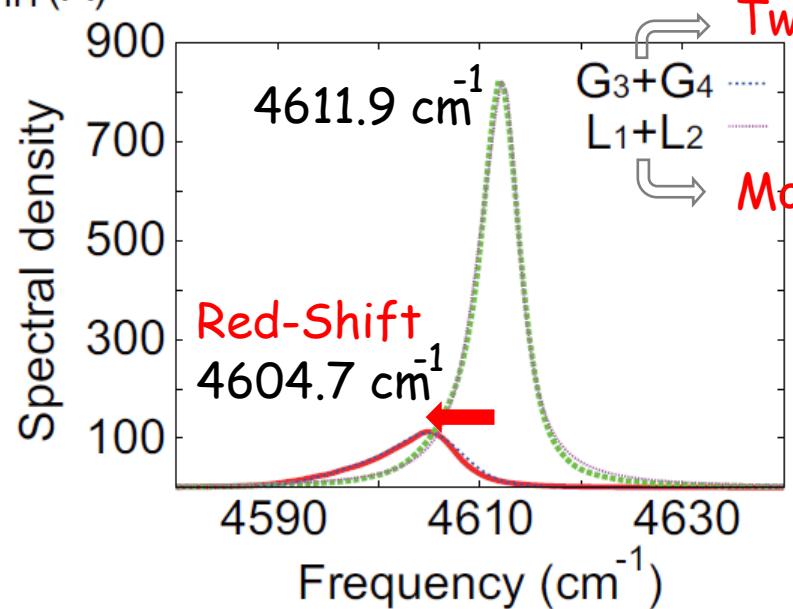
$$\frac{1.496}{0.287} = 5.21$$

Diffusion

H-H Bond



Isolated $\sim 0.7643 \text{ \AA}$ $r_{\text{HH}} (\text{\AA})$



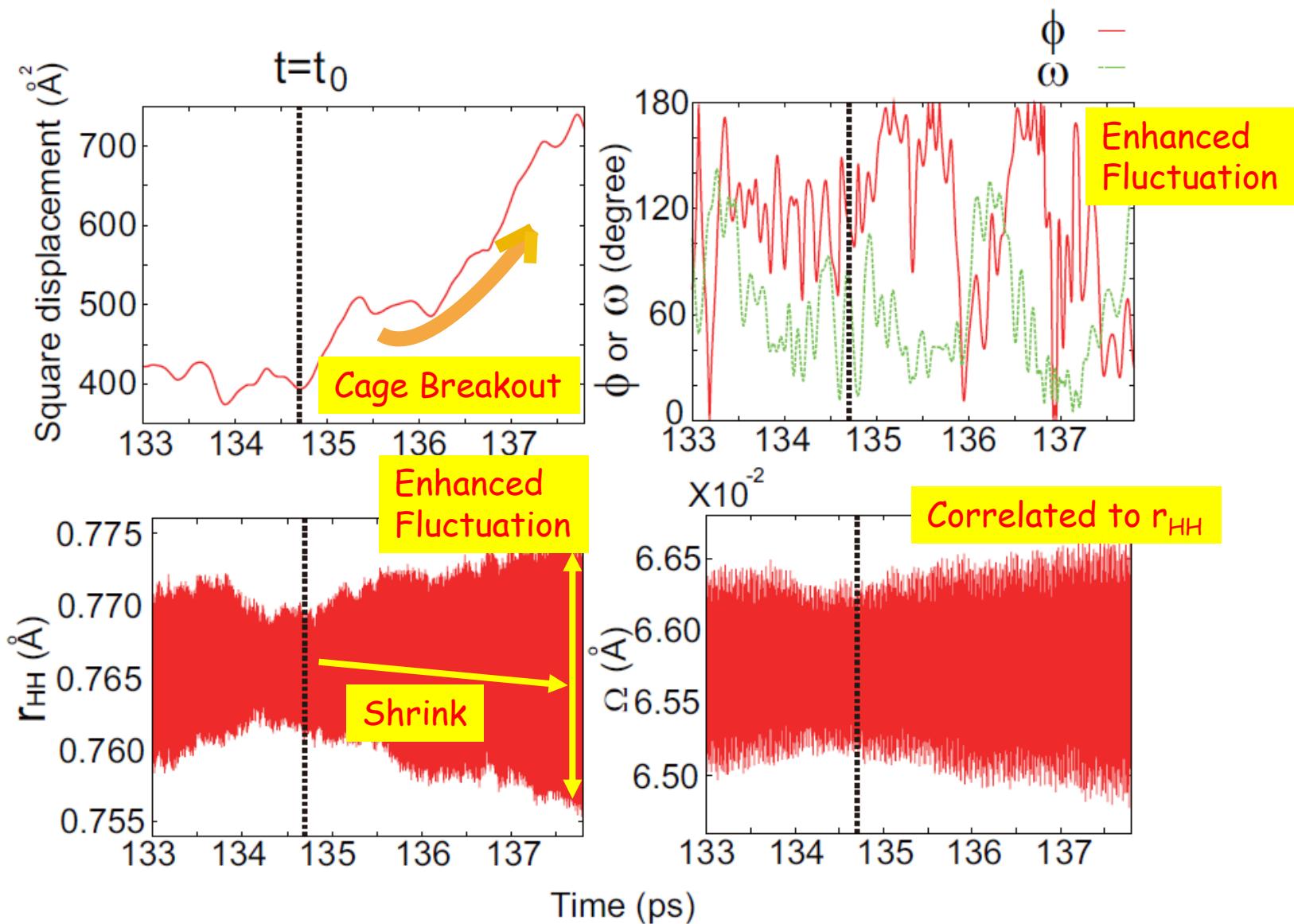
Two Structures

Motional Narrowing

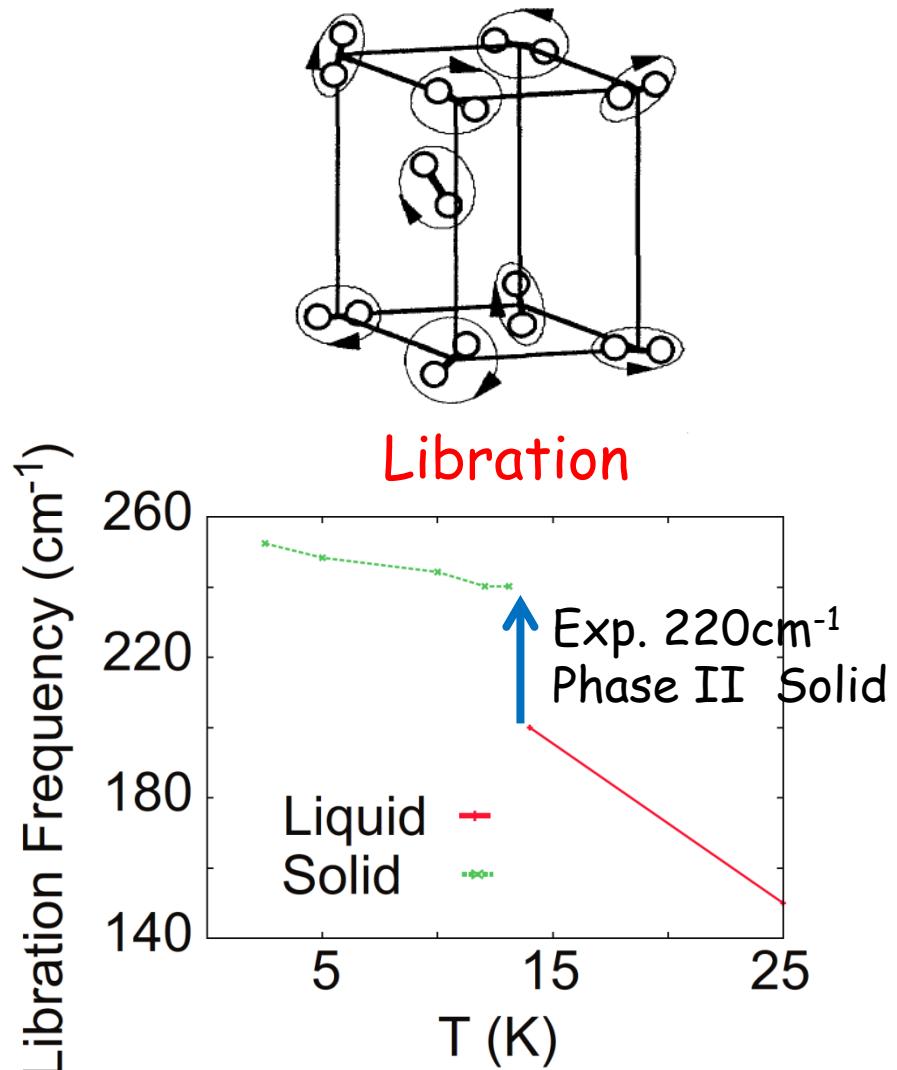
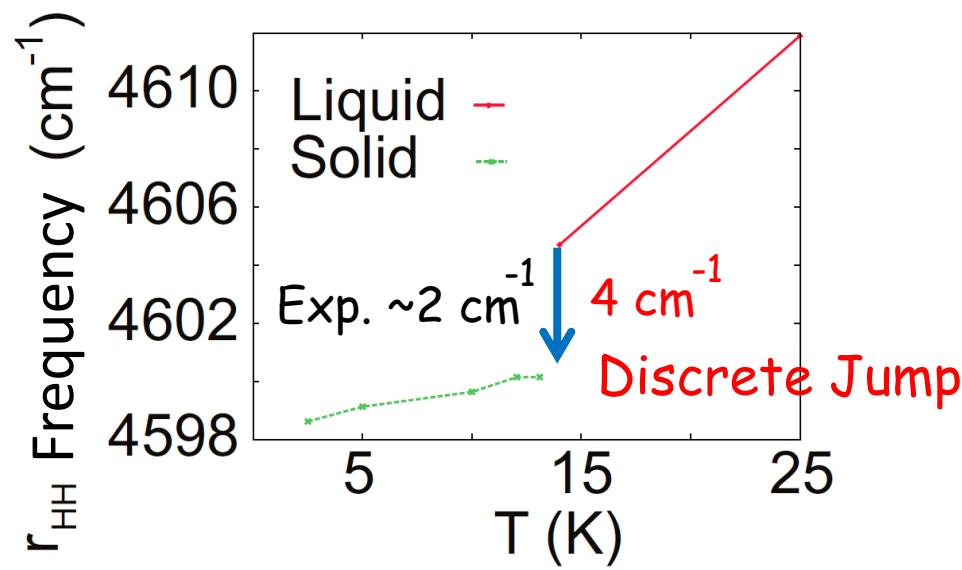
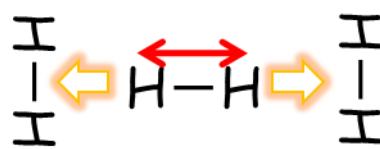
Isolated $\sim 4629.2 \text{ cm}^{-1}$
Exp. $\sim 4151.5 \text{ cm}^{-1}$

Real-Time Dynamics of H₂ Molecule

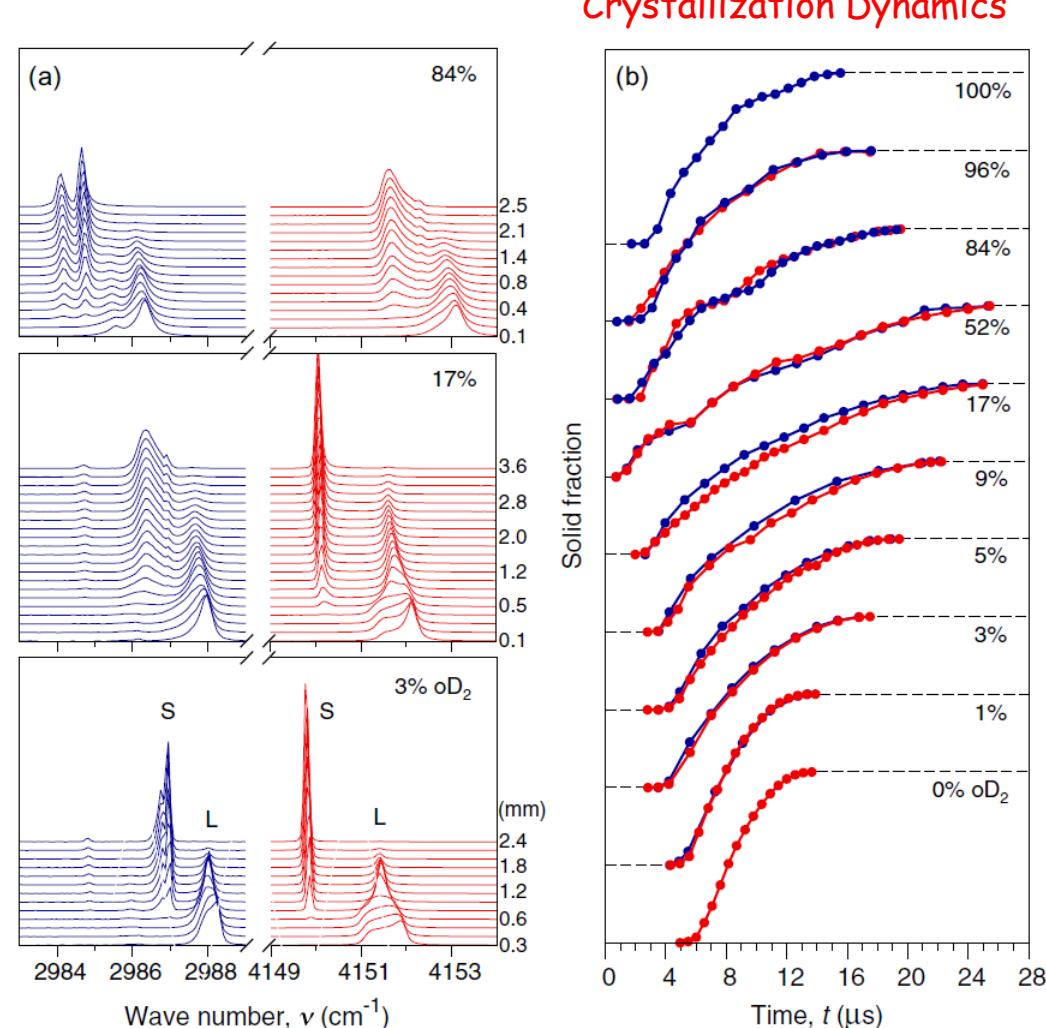
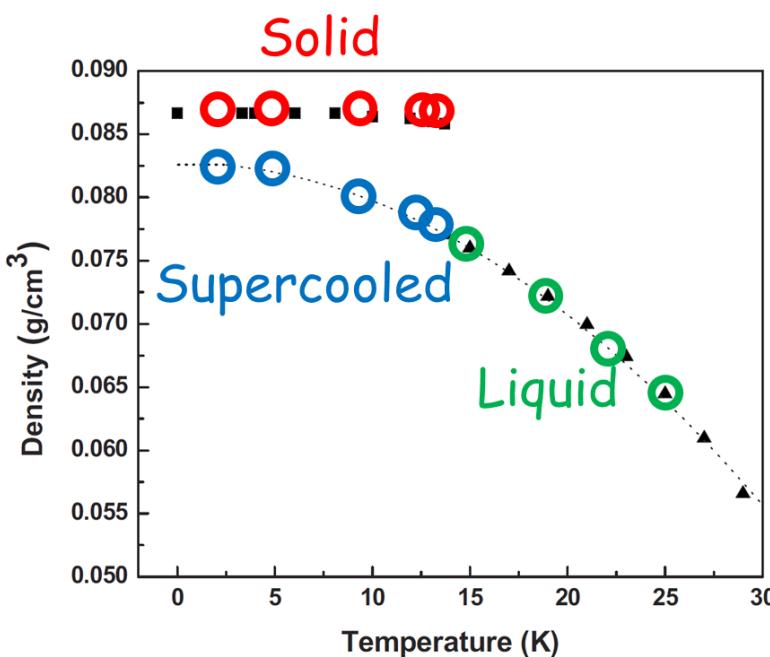
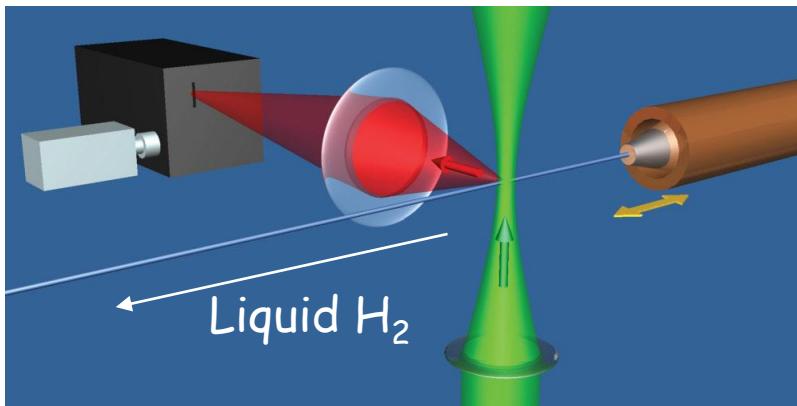
25 K



Microscopic Molecular Dynamics around Phase Transition

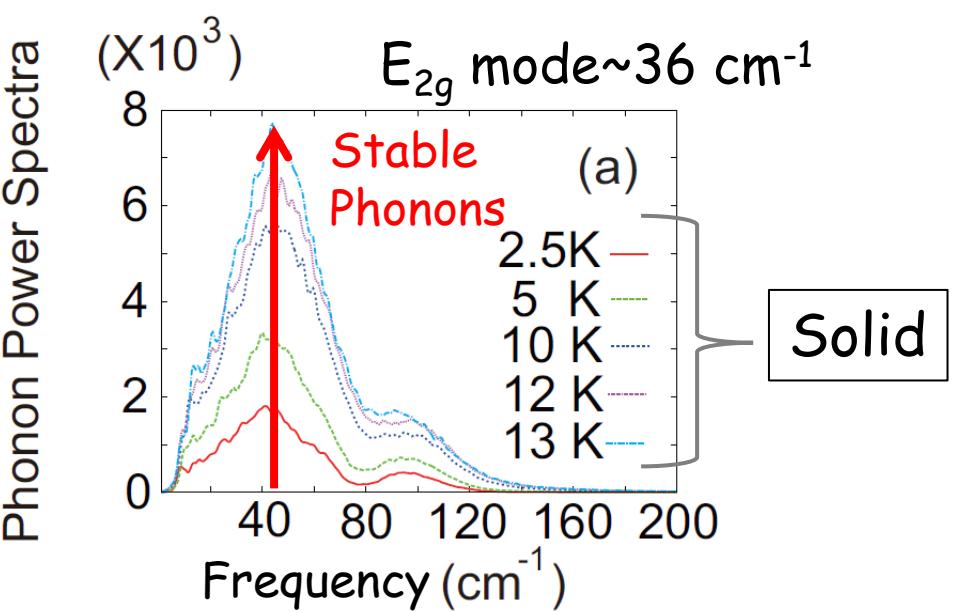
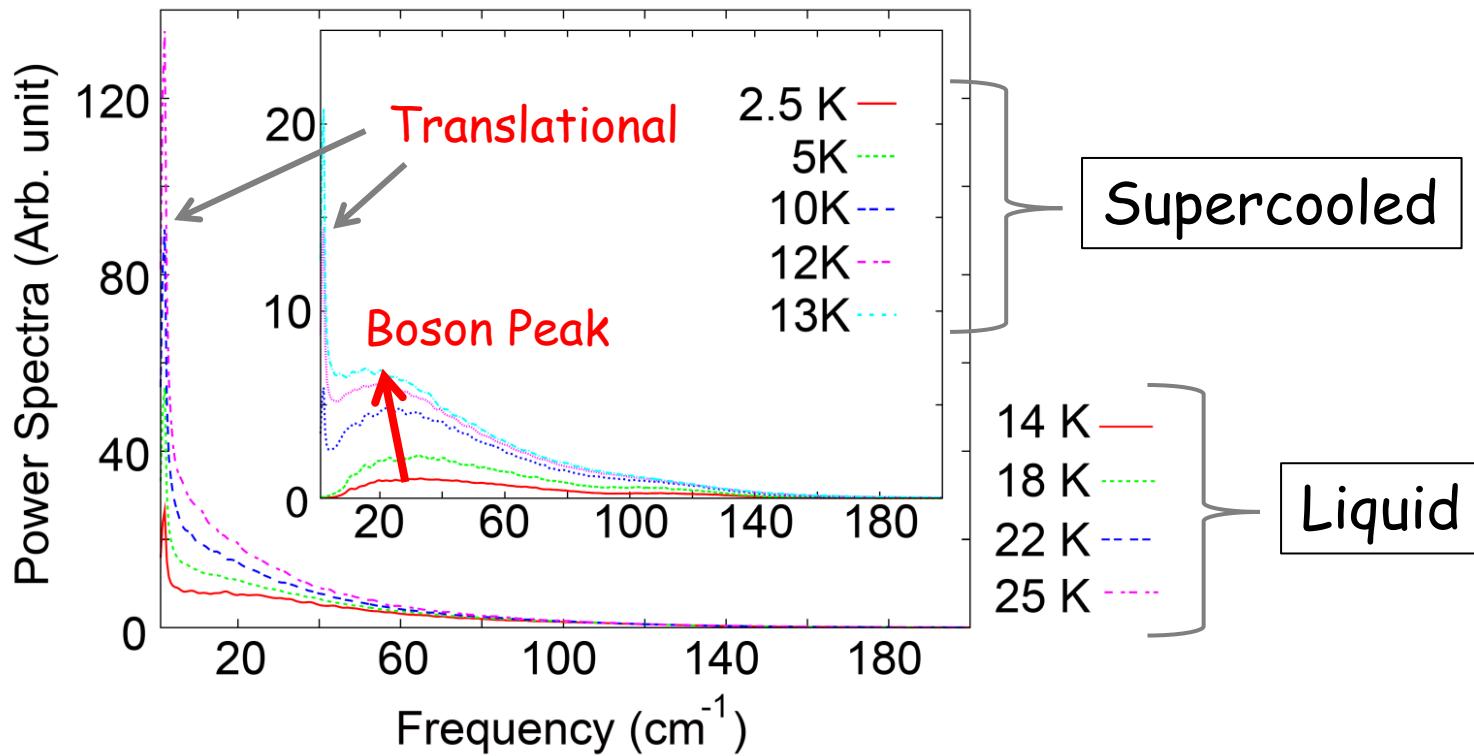


Crystallization Dynamics



Boson Peak

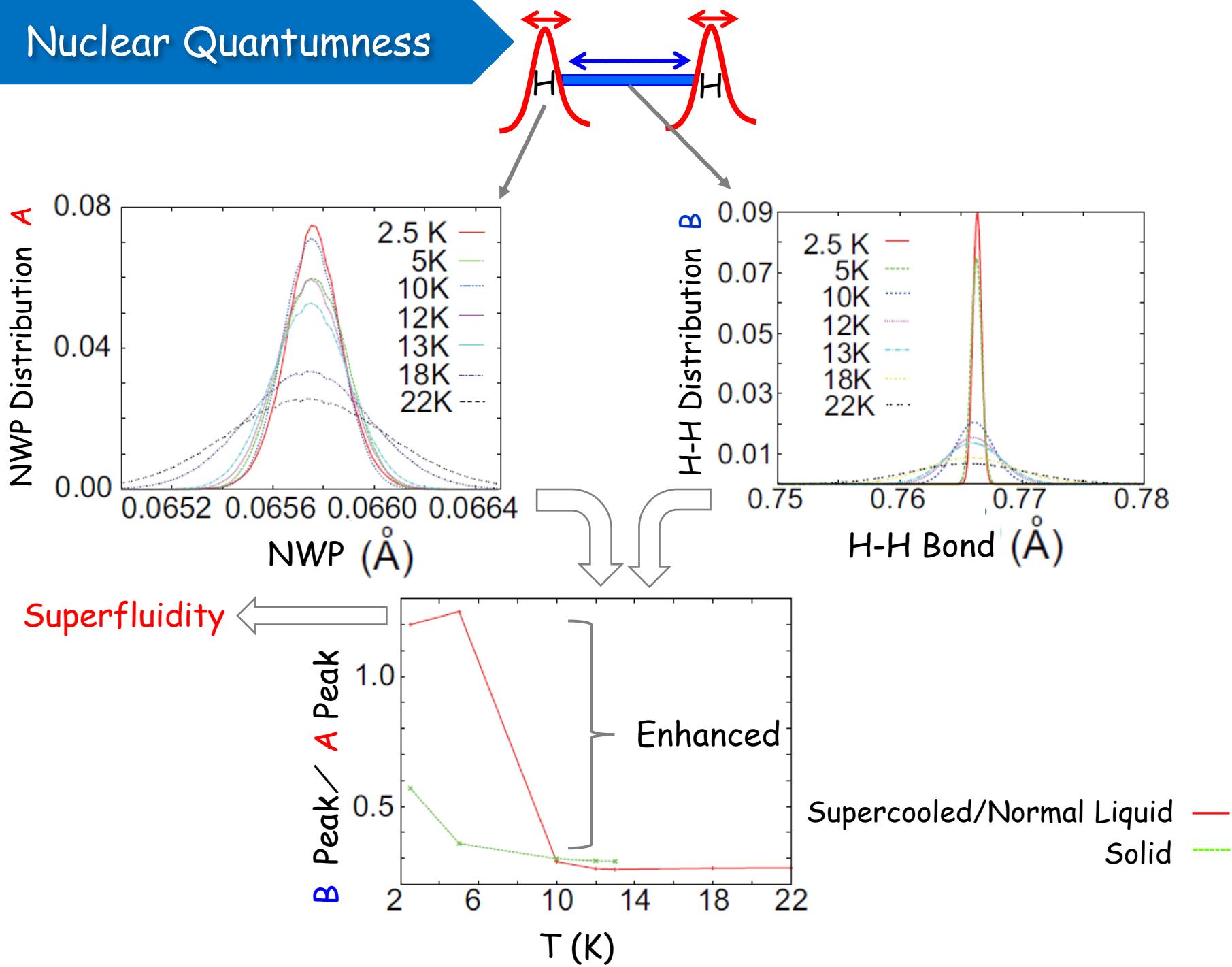
Partially Broken Phonons
in Mesoscale Clusters



Supercooled

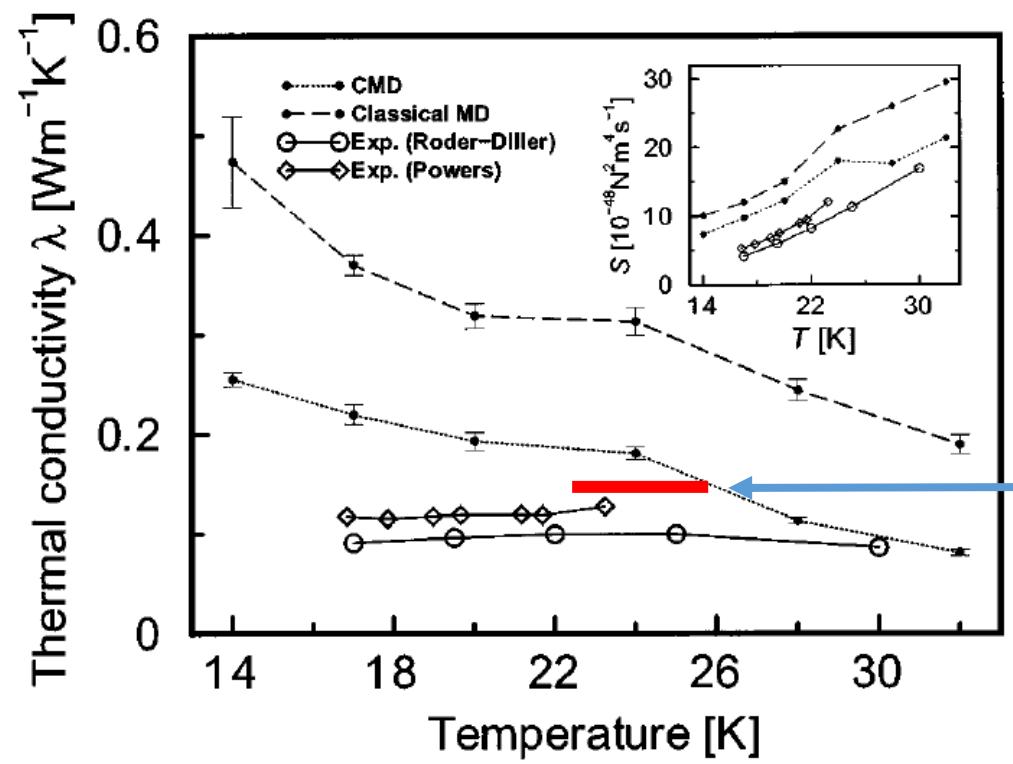
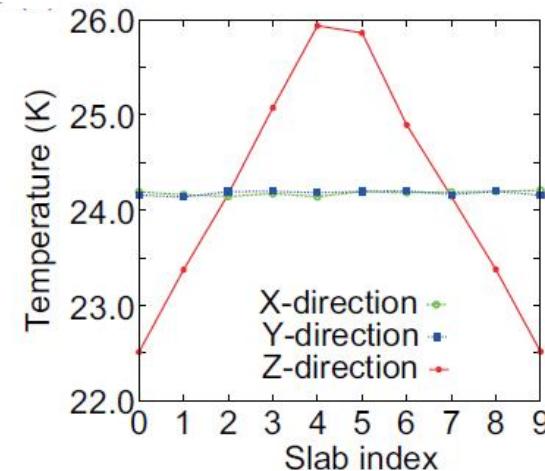
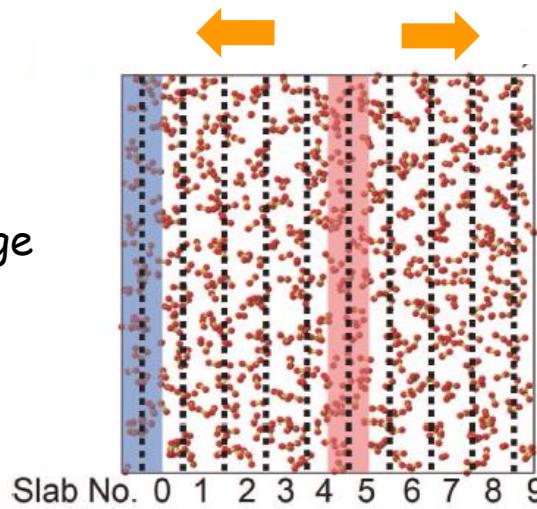
Liquid

Nuclear Quantumness



Non-Equilibrium State – Heat Conduction –

Velocity-Exchange
576 mol.
13 ns+3 ns



Heat Flux

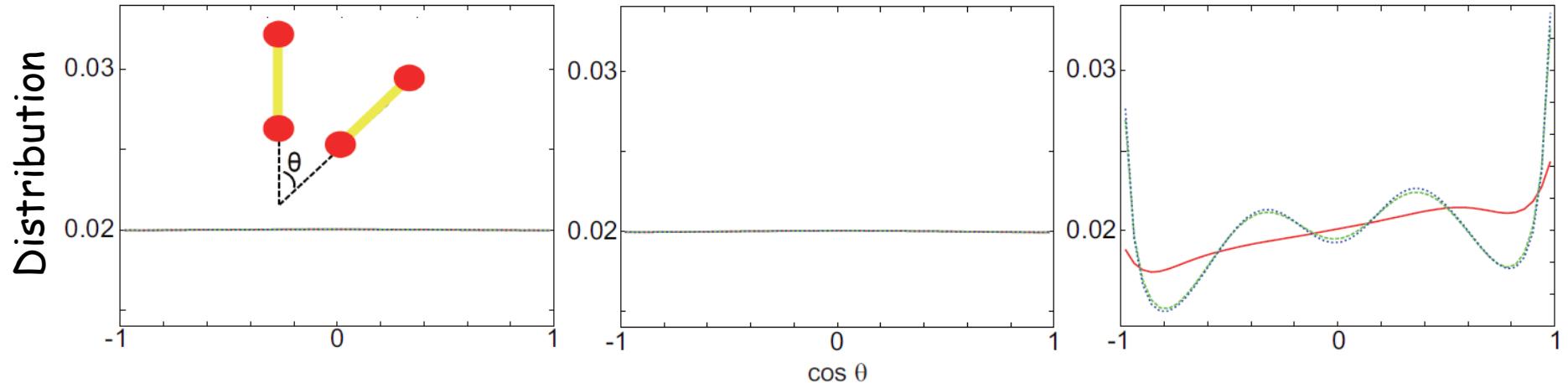
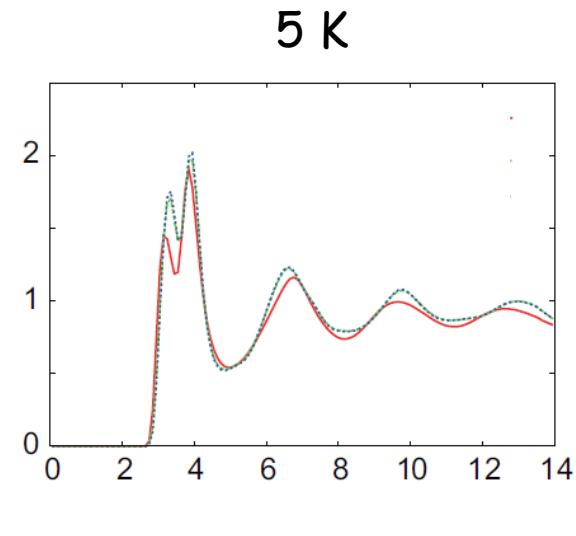
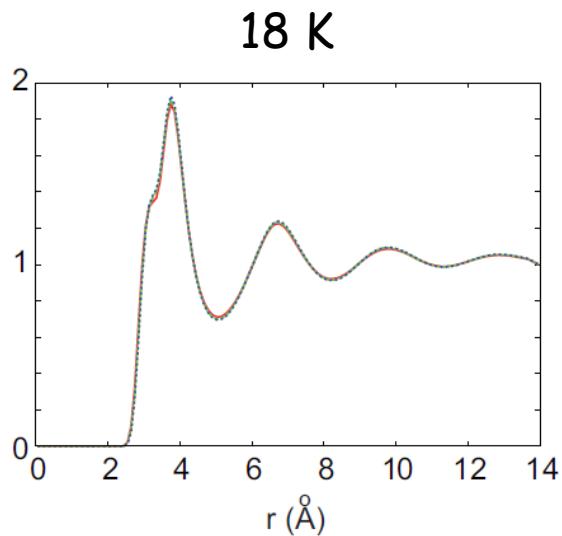
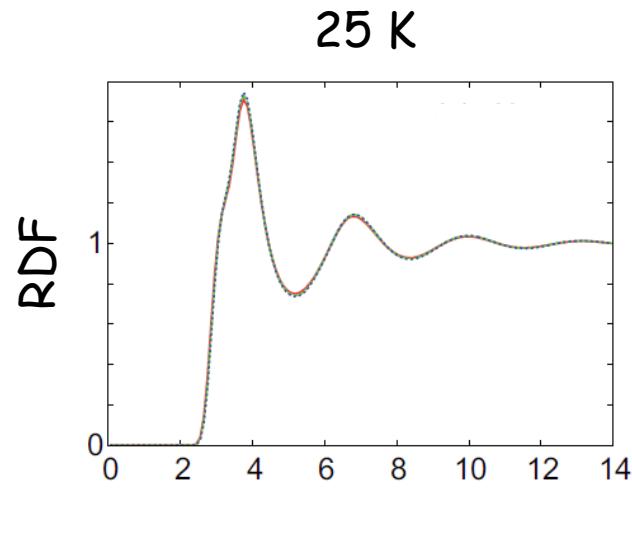
$$J = -\lambda \nabla T$$

Current Result
 $\sim 0.16 \text{ Wm}^{-1}\text{K}^{-1}$

Isotope Effects -Liquid Structure-

@ D_2 Vapor-Pressure Density

H_2 v.s. D_2 v.s. T_2



More Structured

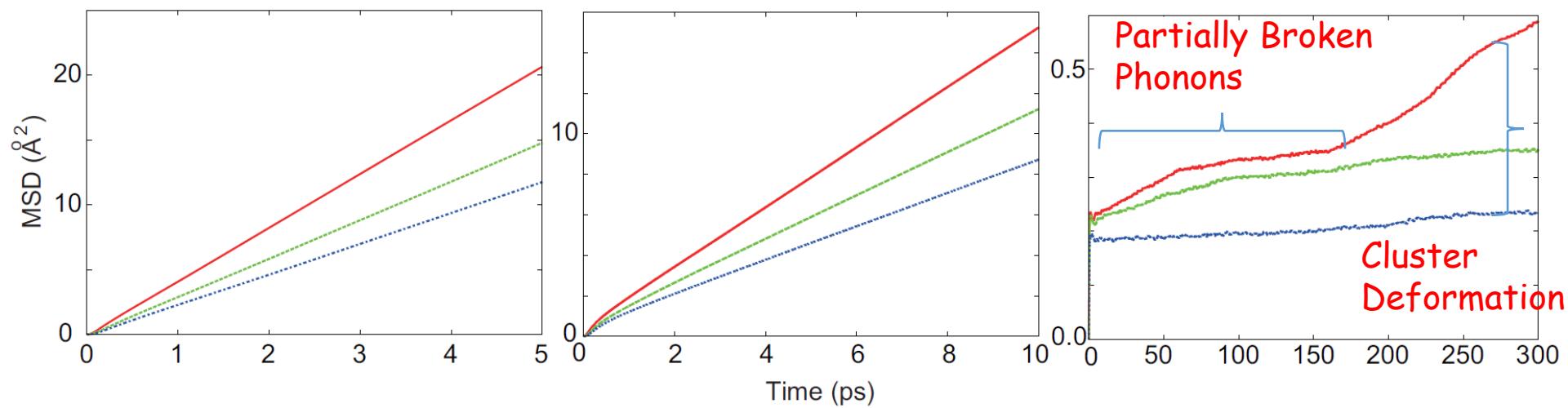
Isotopic Effects -Diffusion-

H_2 v.s. D_2 v.s. T_2

25 K

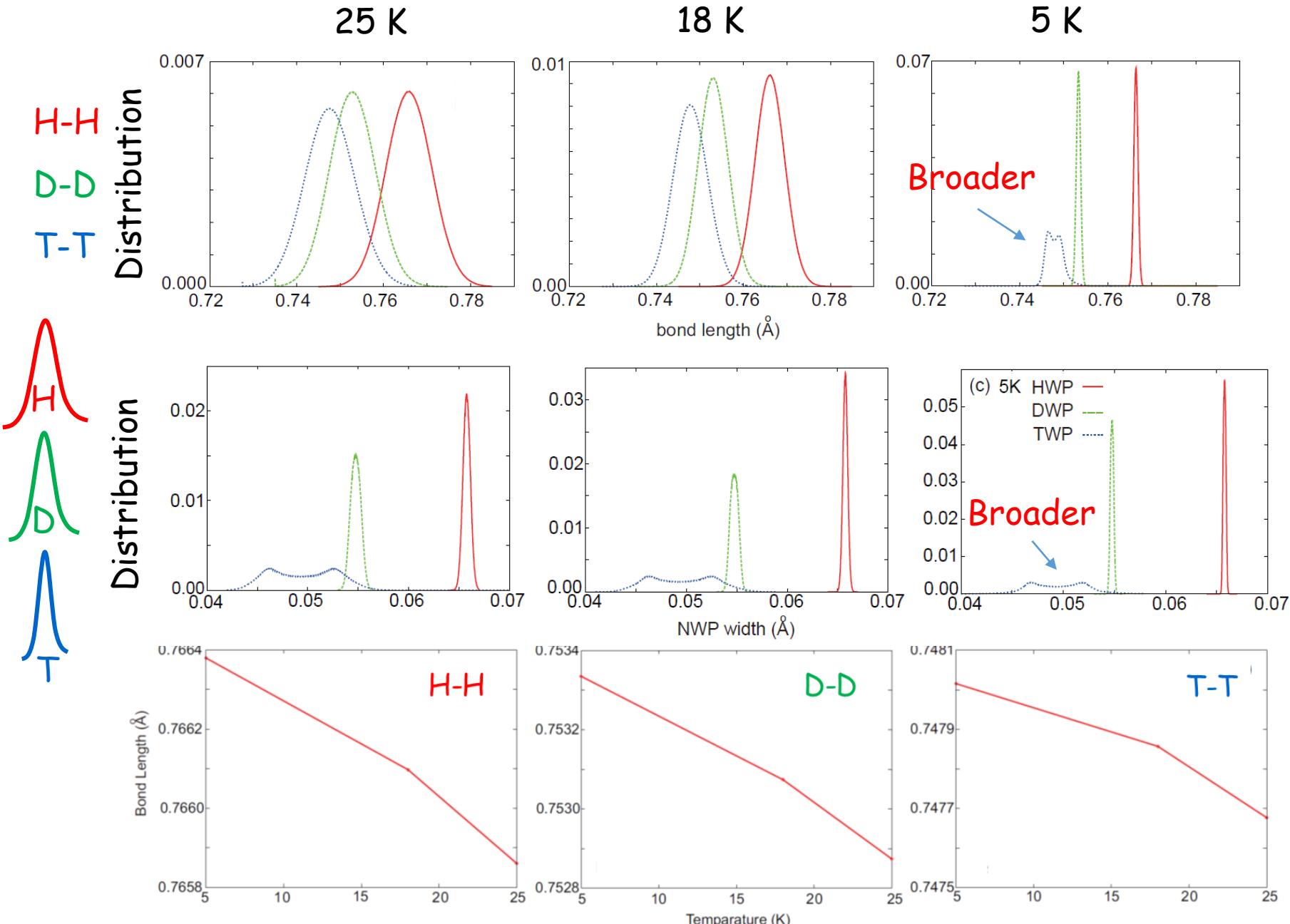
18 K

5 K



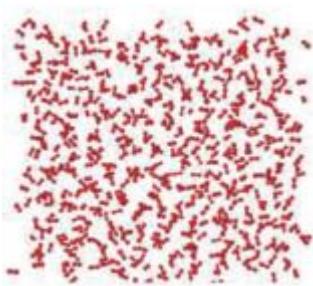
Isotope	25 K	18 K	Ratio
H_2	$0.680(1.10 \times 10^{-4})^a$	$0.243(4.21 \times 10^{-5})$	2.80
D_2	$0.505(2.58 \times 10^{-5})$	$0.179(1.88 \times 10^{-5})$	2.82
T_2	$0.395(1.21 \times 10^{-4})$	$0.131(2.40 \times 10^{-5})$	3.02

Isotope Effects- Intramolecular Structure-

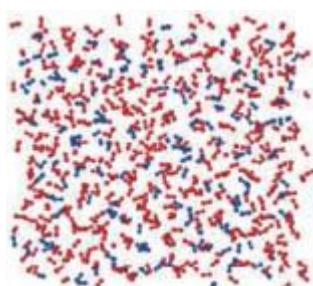


H₂:D₂ Mixtures

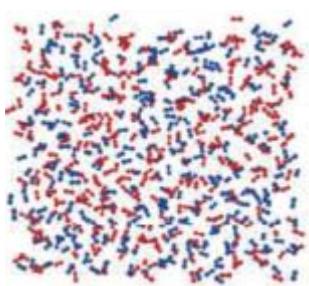
1:0



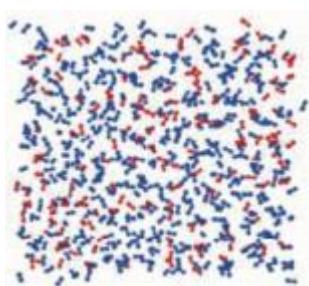
3:1



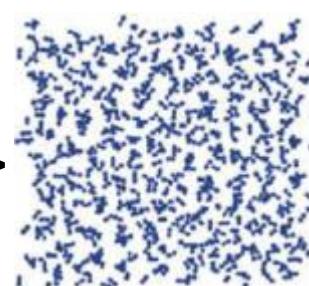
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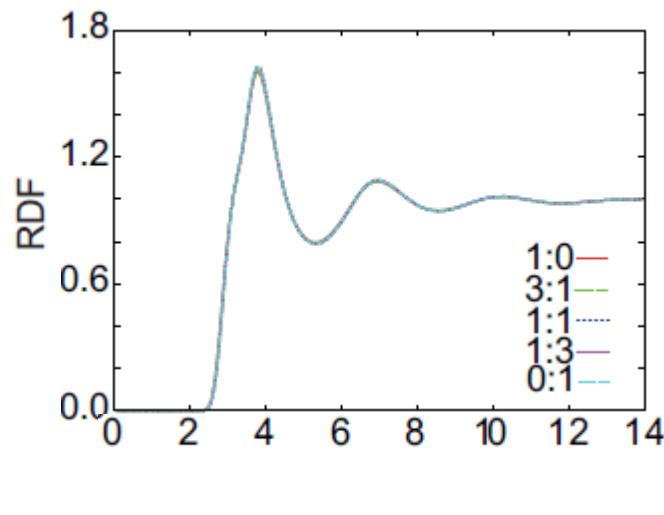
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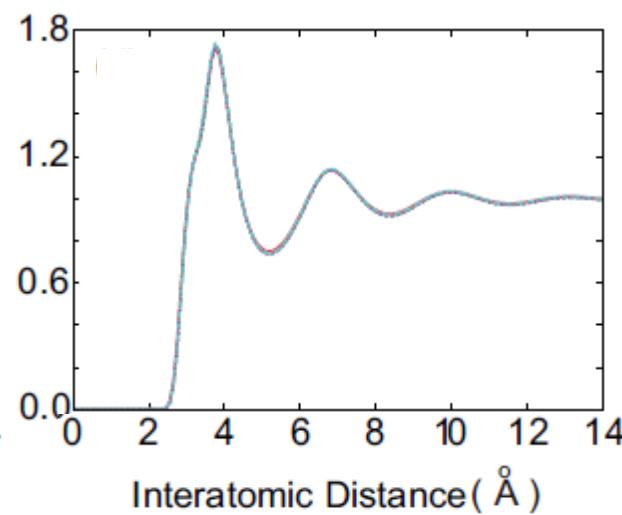
0:1



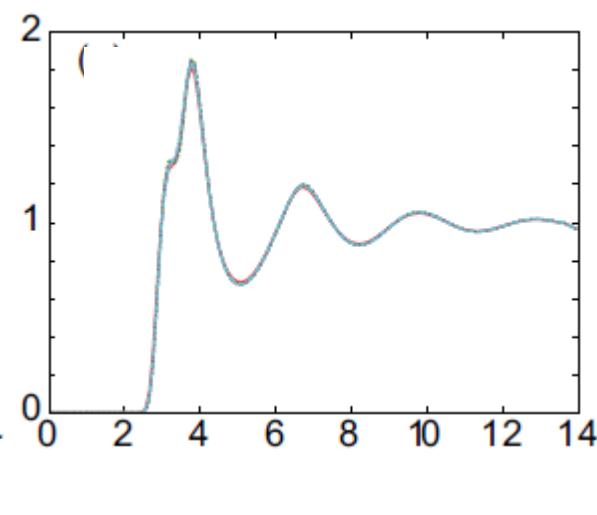
30 K



25 K



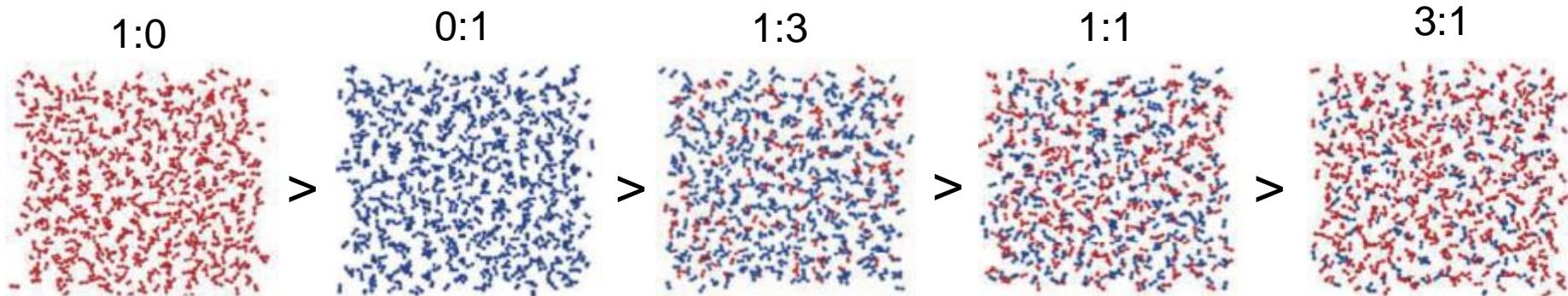
18 K



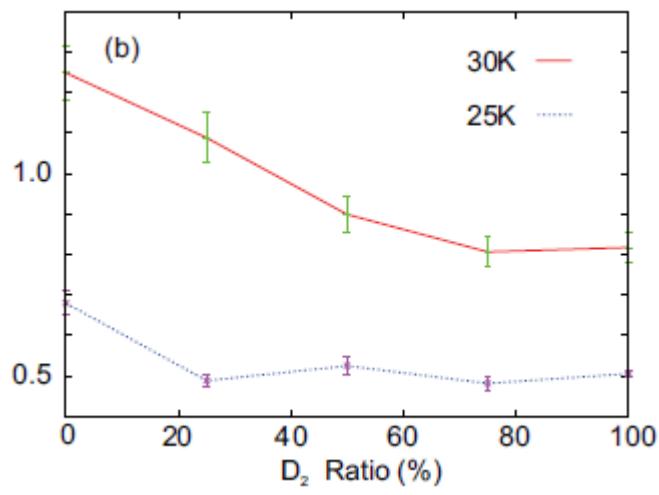
Diffusion of Isotope Mixtures

@ D_2 Vapor-Pressure Density

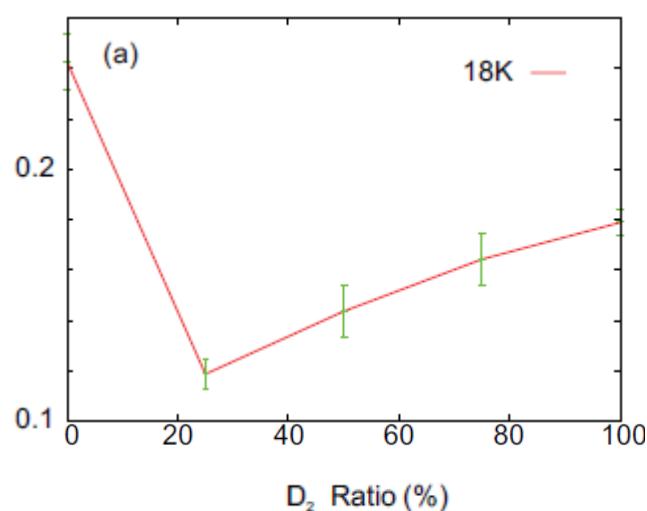
$H_2:D_2$ Mixtures



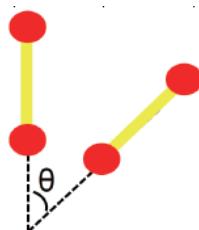
Mass



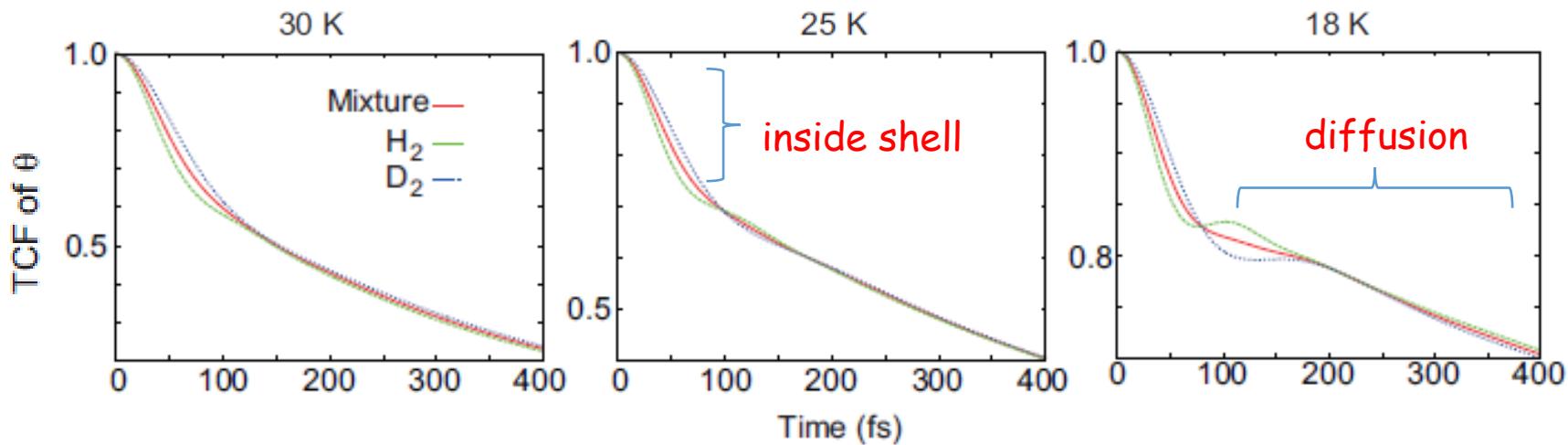
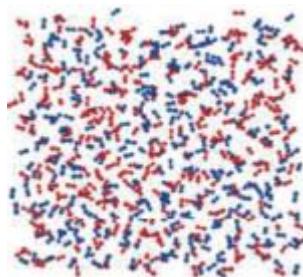
Supercooling \leftrightarrow Mass



Energy Exchange between Isotopes



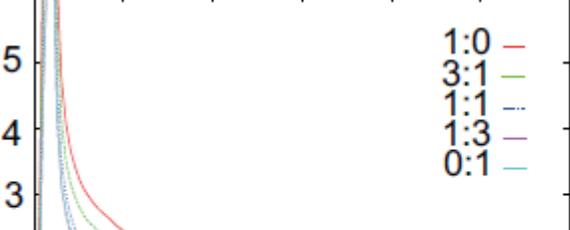
1:1



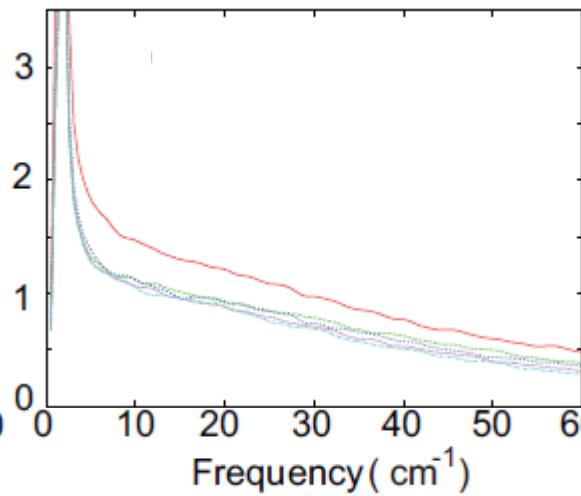
Supercooled Isotopes

Power Spectra of Atomic Displacement

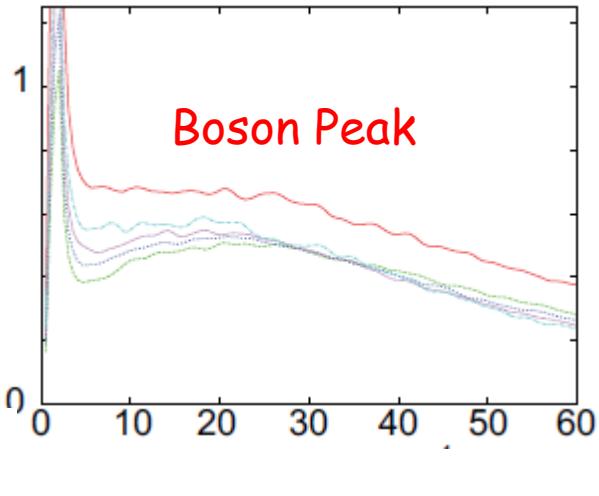
30 K



25 K



18 K



Boson Peak