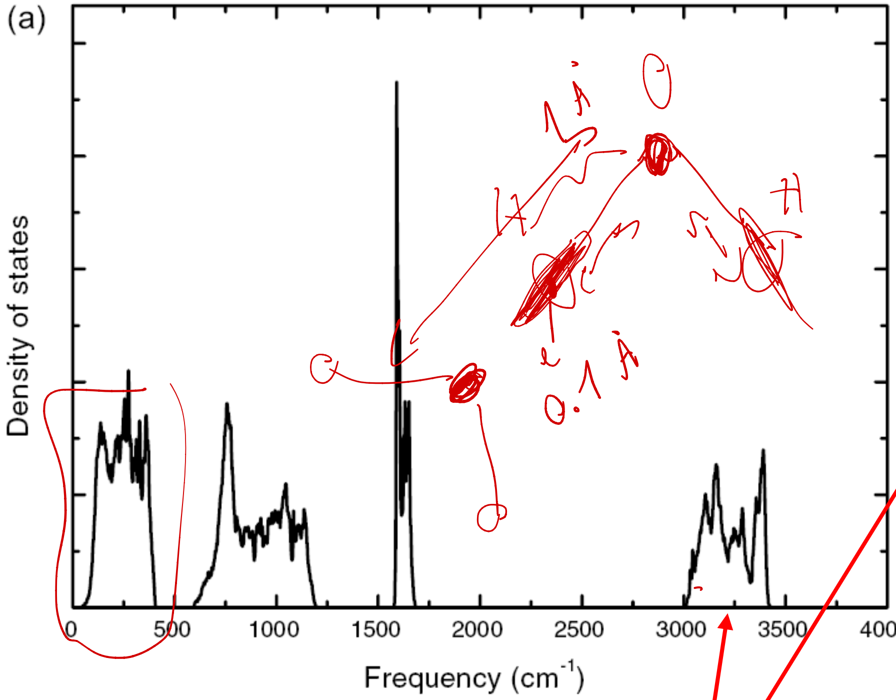
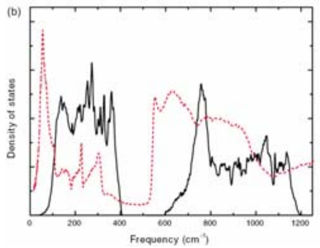
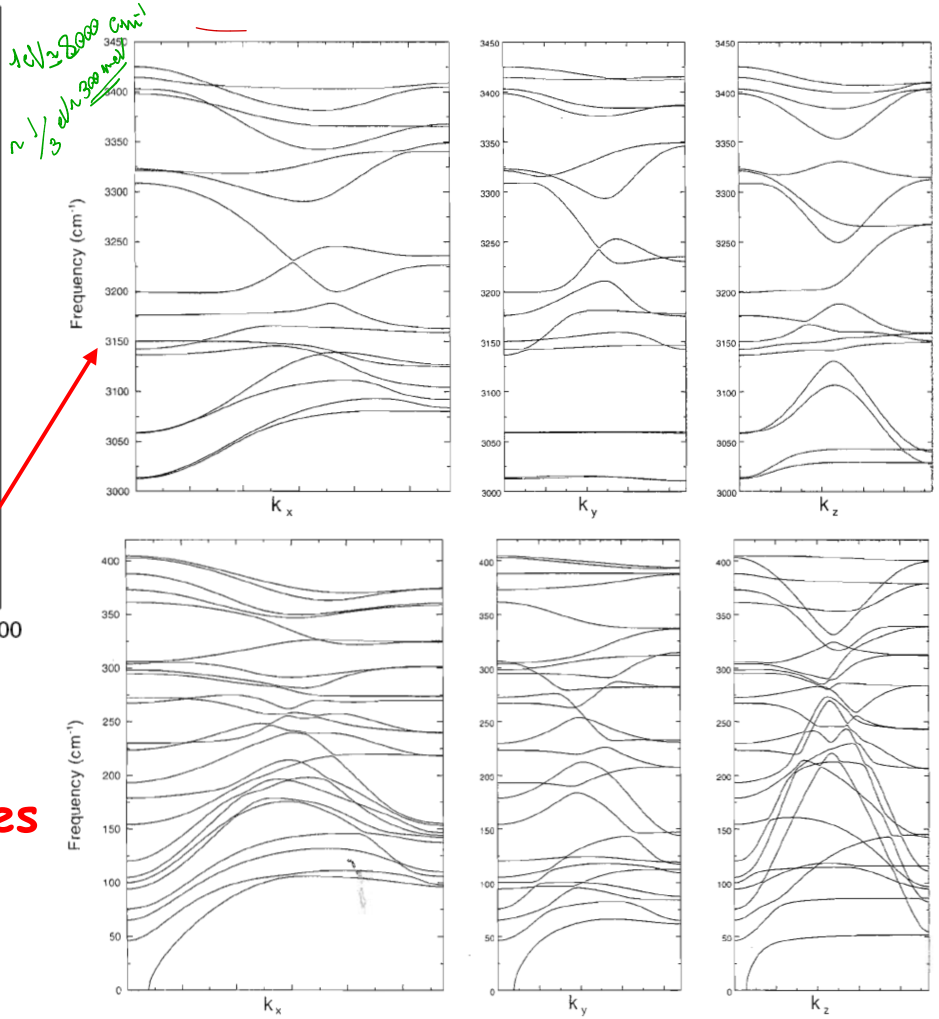
A. S. Cote, I. Morrison, X. Cui X, S. Jenkins, and D. K. Ross,
*Ab-initio density-functional lattice-dynamics studies of ice*
CAN. J. PHY. 81, 115 (2003).

8 molecules/cell ➔ 72 branches





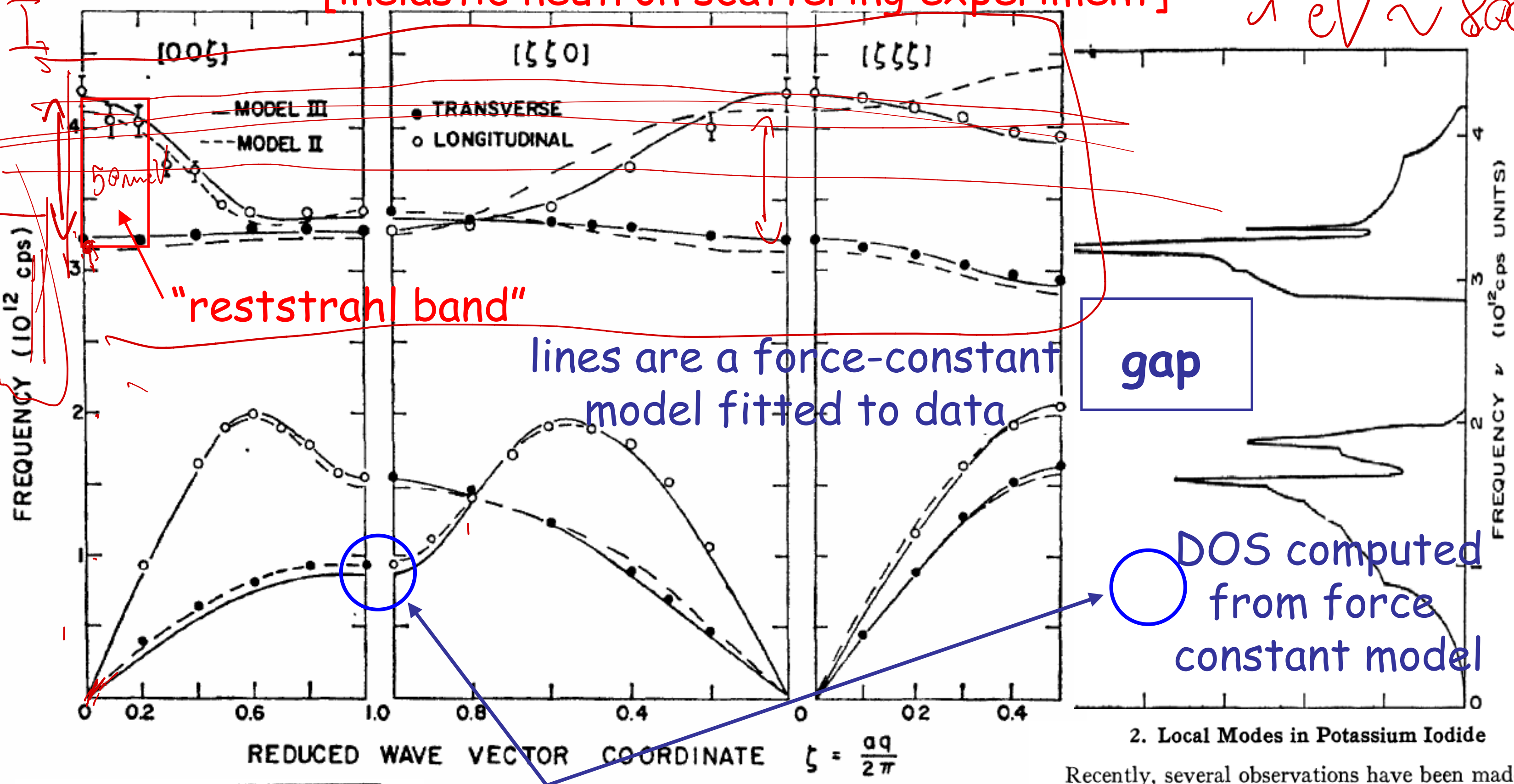
"OH stretch" modes



G. Dolling, R. A. Cowley, C. Schittenhelm, and I. M. Thorson,
*Normal Vibrations of Potassium Iodide*, Phys. Rev. **147**, 577 (1966)

[inelastic neutron scattering experiment]

$1 \text{ eV} \sim 8000 \text{ cm}^{-1}$



"reststrahl band"

lines are a force-constant model fitted to data

**gap**

DOS computed from force constant model

A nice 3-d saddle point van Hove singularity

### 2. Local Modes in Potassium Iodide

Recently, several observations have been made[7–9] of localized modes of vibration in KI containing small amounts of $KNO_2$. A calculation of the vibration frequency of the $NO_2^-$ ion in the KI lattice, on the basis of simple mass-defect theories,[10] indicated that it would probably fall in the gap in the frequency distribution function of the host. In practice, a complex spectrum of localized modes is observed, which is believed[8,11] to be associated with various rotational degrees of freedom of the $NO_2^-$ ion. The present experiments and calculations give the location of the energy gap in pure KI with a precision of 2 or 3%, and confirm that the local modes of the KI:$KNO_2$ system do in fact fall within that gap.

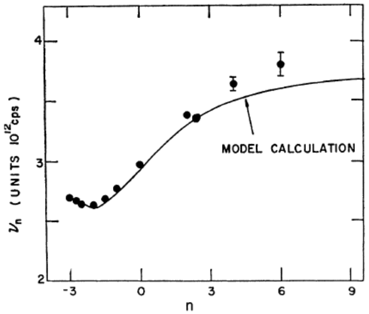


FIG. 4. Equivalent "Debye" frequencies computed from the moments of the distribution function (Fig. 2) and compared with values (filled circles) derived from heat-capacity data.[24]

Fcc (Rock salt),

$1 \text{ GeV} \sim 0.4 \text{ fm}^{-1}$

# Measurement of phonons

· We already saw that the determination of the structure of crystals is done with elastic x-ray scattering methods.

→ high energy x Rays (keV) scattered by electrons.

$\vec{k} = \vec{p}/\hbar$

⟹ Momentum is conserved, energy is conserved. $\hbar\omega_{\vec{q}} \to 0$

$\sum_{q_j}$ $q_j$ $\boxed{3N}$

$\boxed{\vec{K}'} = \vec{K} + \vec{G}$ ; $\vec{K}$ ⟹ incident momentum ; $\vec{K}'$ → diffracted momentum

$|\vec{G}| = 2|\vec{K}|\sin\theta$ → Ewald conditions $|K| = |K'|$

x-Ray elastic scattering ⟹ map of the reciprocal lattice.

$\lambda = \frac{h}{mv}$

· We can use x-Rays (photons) to measure phonon dispersion relations, but the technique is much harder due to the very small change in momentum.

$\lambda = \frac{h}{\sqrt{2\pi M k T}}$

The De Broglie wave length of neutrons with energy ~ 0.1eV is ~ lattice spacing. The shift due to phonon energy ($\sim k_B\Theta_D \sim$ 0.01eV) can be measured. For electrons, λ ~ lattice spacing E ~ keV

→ very hard to detect.

$\omega \sim (M)^{-1/2}$

# Conservation of crystal momentum

→ Lattice : Quantum harmonic hamiltonian

$$|\phi_i^L\rangle = |\{n_{q\boxed{j}}\}\rangle$$ → There are $n_{qj}$ phonons of q,j type

→ The normal mode q,j is in its $n_{q,j}$ excited state.

→ a neutron comes, and it's scattered by the lattice. The energy and momentum of the neutron changes, leaving the lattice in state $|\phi_f^L\rangle$

$$\longrightarrow |\phi_f^L\rangle = |\{n'_{qj}\}\rangle$$

$$E' - E = -\sum_{qj} \hbar\omega_{q,j}\,\Delta n_{qj} \qquad \Delta n_{q,j} = n'_{q,j} - n_{qj}$$

The change in energy of the neutron = energy of the phonons it has absorbed or emited along it's passage.

To be able to get info on the phonon frequencies from experiment we need another conservation rule:

Conservation of crystal momentum.

$$H_{n-i} = \sum_{R_\alpha} w(r - \vec{R} - \vec{u}_\alpha(\vec{R}))$$ w → neutron-ion (nucleus) interaction potential

$\boxed{H_{ni}}$, unaffected by translations by DLV $\begin{cases} r \to r + R_0 & (1) \\ U(\vec R) \to U(R + \vec R_0) & (2) \end{cases}$

(1) Shift of the neutron coordinate by a lattice vector

(2) shift of the ion displacement.

$$H_{ni} = \sum_R w(\vec r + \vec R_0 - \vec R - U(\bar R - \vec R_0)) = \sum_R w(\vec r - \underbrace{(\bar R - \vec R_0)}_{\vec R'} - U(\underbrace{\vec R - \vec R_0}_{\vec R'}))$$

$$\vec p\,' - \vec p = -\sum_{qj} \hbar \vec q \, \Delta n_{qj} + \underset{RLV}{\vec G} \cdot \hbar$$

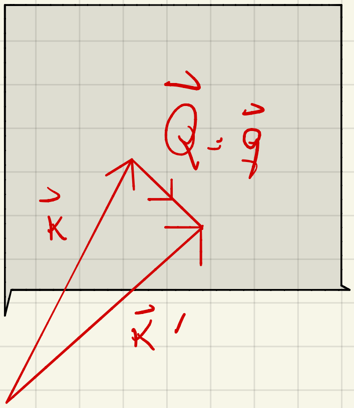
$\vec p$ = wave vector of neutron

$$\psi_N^i = \frac{1}{\sqrt V} e^{i \vec p \vec r / \hbar}$$

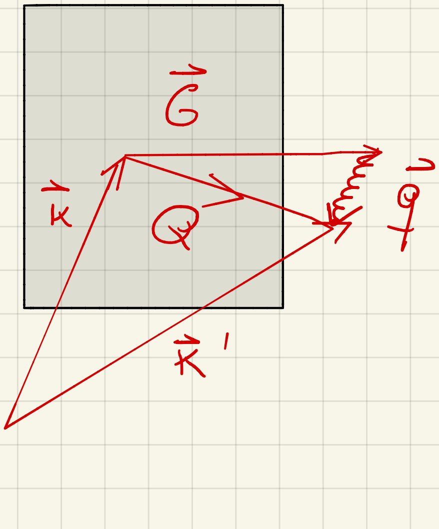
crystal momentum of phonon $\vec q \Rightarrow \boxed{\hbar \vec q}$

change in neutron momentum = - change in total phonon crystal momentum to within an additive RLV

NORMAL



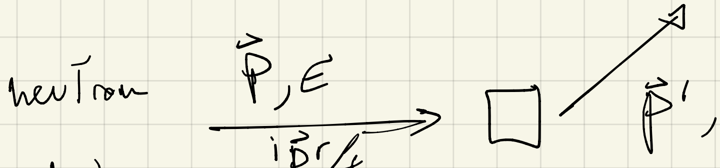
UMKLAPP



$\vec q = \vec Q - \vec G$

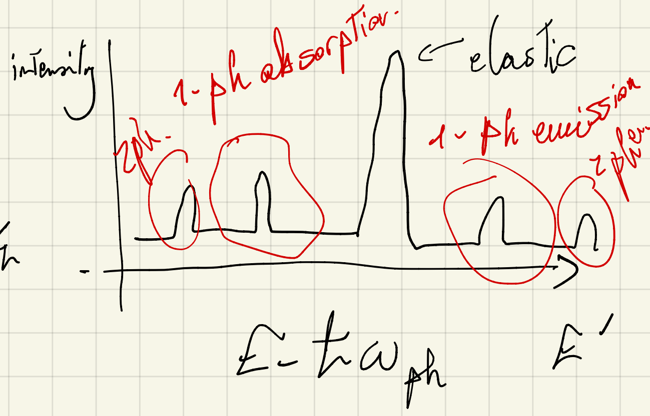
# Neutron scattering by a crystal

- Neutron interacts only with nuclei (or with $e^-$ through their magnetic moment).



$$\psi_p = \frac{1}{\sqrt V} e^{i\vec p r/\hbar}$$

$$\psi_{p'} = \frac{1}{\sqrt V} e^{i\vec p\,'/\hbar}$$



Neutron $M_n \simeq 1838\, m_e$

$$E_n = \frac{p^2}{2M_n}$$

$$\hbar\omega = \frac{p'}{2M_n} - \frac{p^2}{2M_n}$$

$$\hbar\vec q = \vec p - \vec p\,'$$

Neutron interacts with lattice potential

$$V(\vec r) = \sum_R \underbrace{v(\underset{\text{neutron}}{\vec r} - \underset{\text{ion}}{\vec r(\vec R)})}$$

neutron-ion interaction potential

$$r(\vec R) = \vec R + \underset{\text{displacement}}{u(\vec R)}$$

↓ Fourier transform

$$V(r) \propto \sum_R \frac{1}{V} \sum_q v_q\, e^{iq(r-R(R))}$$

neutron $\sim 10^{-13}$ cm $\rightarrow$ fourier components $q \sim 10^{13}$ cm$^{-1}$

$V_q \sim$ constant for ranges $\sim 10^{8}$ cm$^{-1}$ (the experimental energy range)

$$V(r) = \frac{2\pi\hbar^2 a}{M_n V} \sum_{q,R} e^{iq[r-R(t)]}$$

Scattering probability $\Rightarrow$ Fermi Golden Rule (lowest order time dependent perturbation th.)

$\swarrow$ $p \rightarrow p'$

$\sim$ cross section

Initial energy : $\mathcal{E}_i = E_i + \frac{p^2}{2M}$

$\swarrow$ Eigenstate of the lattice Hamiltonian.

Final energy : $\mathcal{E}_f = E_f + \frac{p'^2}{2M}$

probability

$$\rightarrow P = \frac{2\pi}{\hbar} \sum_j \delta(E_j - E_i + \hbar\omega)\, |\text{Matrix Element}|^2$$

· Initial state : $\frac{1}{\sqrt{V}} e^{i\vec{p}\vec{r}/\hbar}$ , $|\phi_i^{lattice}\rangle = |\{n_{qj}\}\rangle$

· Final state : $\frac{1}{\sqrt{V}} e^{i\vec{p}\vec{r}/\hbar}$ , $|\phi_j^{L}\rangle = |\{n'_{qj}\}\rangle$

Matrix element $\propto \langle e^{i\vec{p}'\vec{r}/\hbar}\phi_f | \sum_R \delta(\vec{r}-\vec{r}(R)) | e^{i\vec{p}\vec{r}/\hbar}\phi_i \rangle$

$$\propto \sum_R \langle \phi_f | e^{i(\vec{p}-\vec{p}')\cdot\vec{r}(\vec{R})/\hbar} | \phi_i \rangle$$

$$= \sum_R \langle \phi_f | e^{-iQr(\vec{R})} | \phi_i \rangle$$

$\vec{Q} = \frac{(\vec{p}'-\vec{p})}{\hbar}$ = scattering wave vector $\quad ME \propto \sum_R \langle \phi_f | e^{-iQ(\vec{R}+u(R))} | \phi_i \rangle$

→ static, ideal lattice

$$ME \propto \sum_R e^{-i\vec{Q}\vec{R}} \langle \phi_f | \phi_i \rangle = N\, \delta_{\vec{Q},\underset{\nwarrow \text{RLV}}{\vec{G}}}\, \delta_{i,f}$$

$$E_i + \frac{\vec{p}^2}{2M} = E_f + \frac{\vec{p}'^2}{2M}$$

$\delta_{i,f} \Rightarrow E_i = E_f \longrightarrow$ Elastic scattering

$\delta_{Q,G} \Rightarrow p - p' = \hbar G$ Laue Condition.

Bragg difraction of neutrons

# Real crystals (3D system, only 1 atom in basis)

$$ME \propto \sum_R e^{-iQR} \langle \phi_f | e^{-iQ\underset{\downarrow}{U(R)}} | \phi_i \rangle$$

displacement about eq.

$$= \sum_R e^{-iQR} \langle \phi_f | \left( \boxed{1} - \underline{iQU(R)} - \frac{1}{2}(Q\cdot U(R))^2 + \dots \right) | \phi_i \rangle$$

$$\boxed{U(R) = \frac{1}{\sqrt{N}} \sum_{q,j} e^{iqR} \underset{\downarrow}{A(q_j)}\, \vec{\epsilon}_r(\vec{q}_j)} \qquad \boxed{\epsilon(q) = \epsilon(-\vec{q})}$$

amplitude of the normal mode $\propto (a + a^+)$

$$\text{So: } ME = \sum_R e^{-\vec{Q}\vec{R}} \langle \phi_f | \Big\{ 1 - \frac{i}{\sqrt{N}} \sum_{q_j} e^{iq_j\vec{R}} A(q_j)\, \vec{\epsilon}(q_j)\cdot\vec{Q}$$

$$- \frac{1}{2N} \sum_{q_j} \underbrace{A(q_j) A(-q_j) \left(\vec{Q}\cdot\vec{\epsilon}(q_j)\right)^2}_{A} + \underbrace{O(q^2, q^3, q^4 \dots)}_{B} \Big) |\phi_i\rangle$$

1st Term (1) → elastic diffraction by real crystal.

$$\underline{\text{2nd Term}} = -\frac{i}{\sqrt{N}} \sum_{q_j} \Big( \underbrace{\sum_R e^{i(\vec{q}-\vec{Q})\vec{R}}}_{(C)} \underbrace{(\vec{Q}\cdot\vec{\epsilon}(q_j))}_{(D)} \Big) \underbrace{\boxed{\langle \phi_f | A(q_j) | \phi_i \rangle}}_{(E)}$$

(E) $A_1(q_j) = \sqrt{\dfrac{\hbar}{2M\omega(q_j)}}\left(a_{q_j} + a^{+}_{-q_j}\right) \Rightarrow$ One phonon operator

$$|\phi_i\rangle = |\dots n_{-q_j} \dots n_{q_j} \dots\rangle$$

$$|\phi_f\rangle = \underset{(2)}{|\dots n_{-q_j} \dots n_{q_j}-1 \dots\rangle} \text{ or } \underset{(1)}{|\dots n_{-q_j}+1 \dots n_{q_j} \dots\rangle}$$

$\left.\begin{array}{l}(1)\ + \rightarrow \text{phonon emission process}\\ (2)\ - \rightarrow \text{'' absorption}\end{array}\right\}$ one phonon processes

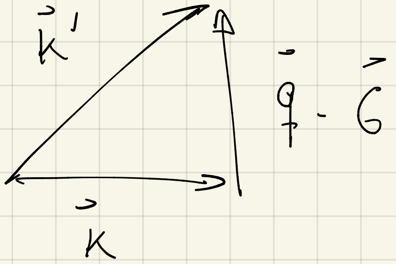
(D) $\underline{\vec{Q}\cdot\vec{\epsilon}(q_j)} = 0$ if $\vec{Q} \perp \vec{\epsilon}(q_j)$

Polarization selection rule, useful for determining phonon polarization

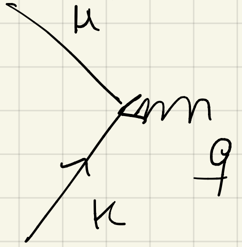
(C) $\sum_R e^{i(q-\vec{Q})R} = N\,\delta_{q-\vec{Q},\vec{G}}$ $\quad \vec{G}$ = RLV

$\boxed{\hbar\vec{Q} = \vec{p}' - \vec{p} = \hbar(q-G)}$ Conservation of crystal momentum $\begin{cases} G=0 & \text{Normal} \\ \vec{G}\neq 0 & \text{Umklapp} \end{cases}$

Note: The extra momentum $\hbar\vec G$ is transferred to the crystal as a whole, this is a translation of the center of mass of the crystal, which has no effect on the # of normal modes.

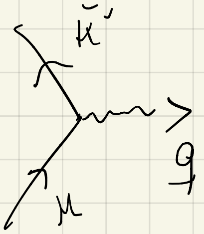


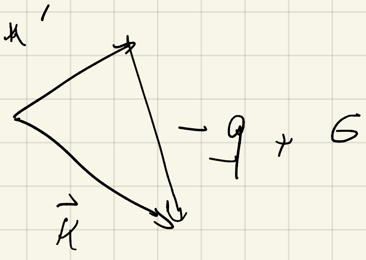
· phonon absorption:



Energy conserved $$\frac{(\hbar k')^2}{2M_n} = \frac{(\hbar k)^2}{2M_n} + \hbar\omega(\vec q_j)$$

· Phonon Emission; phonon momentum $= \hbar(-\vec q)$





$$\vec k = \vec k' + \vec q - \vec G$$

Energy conserved $$\frac{(\hbar\vec k)^2}{2M_n} = \frac{(\hbar\vec k')^2}{2M_n} + \underset{\hbar\omega_{q_j}}{\hbar\omega(-q_j)}$$

$A(q_j) = a_{q_j} + a^{+}_{q_j}$ $\qquad a|n\rangle = \sqrt{n}\,|n-1\rangle$

$a^{+}|n\rangle = \sqrt{n+1}\,|n+1\rangle$

$T=0,\ n=0$

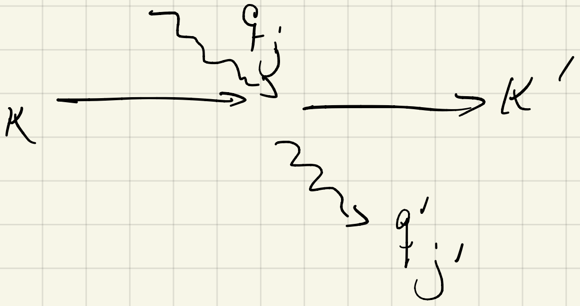
$a|0\rangle =$ no phonon absorbtion

$a^{+}|0\rangle = |1\rangle$, phononon emission allowed.

(B) $O(q^2, q^3, q^4)$ → smooth background in the scattering data.

$q^n$ → n phonon operator.

eg $n=2$



$$ME = \sum_{R} e^{-i\vec{Q}\vec{R}^{0}} \langle \Phi_f | 1 + \text{one phonon terms} - \overbrace{\frac{1}{2N}\sum_{q_j} \underbrace{q_j(q)\, q_j(-q)}_{A(q_j)\ A(-q_j)}}^{(A)}$$

$$\underbrace{(Q\cdot\vec{\epsilon}(q_j))^2} + O(q^2, q^3 \ldots) |\Phi_f\rangle\rangle$$

(A) special kind of 1 phonon processes

Consider elastic scattering $|\phi_i\rangle \to |\phi_f\rangle$

$$ME = \sum_A e^{-i\vec{Q}\hat{A}} \left\{ \langle \phi_i | \phi_i \rangle + 0 - \frac{1}{2N} \sum_{q_j} \left( \vec{Q}\vec{\epsilon}_j(q_j) \right)^2 \right.$$

$$\langle \phi_i | A(q_j) A(-q_j) | \phi_i \rangle + \underline{\langle \phi_i | A(q_j) A(-q'_j) | \phi_i \rangle}$$

$$\langle \phi_i | A(q_j) A(-q'_{j'}) | \phi_i \rangle = \text{const} \langle \phi_i | (a_{q_j} + a^+_{q_j})(a_{q'_{j'}} + a^+_{q'_{j'}}) | \phi_i \rangle$$

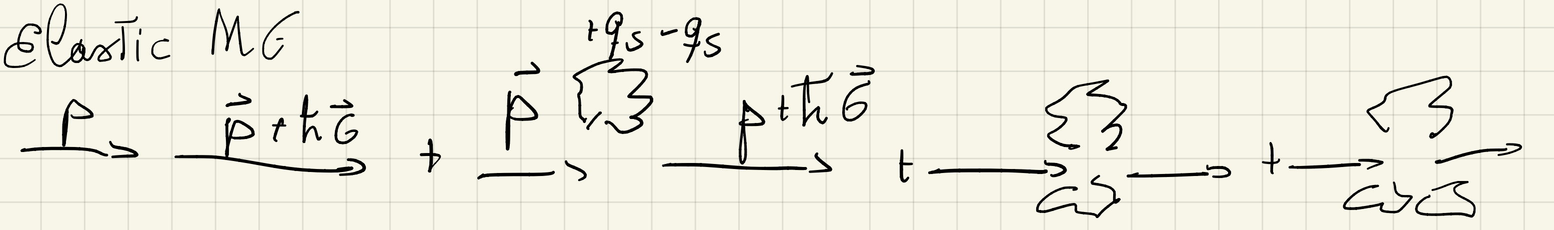
$$\propto \langle \phi_i | \cancel{a_{q_j} a_{-q'_{j'}}} + \underbrace{a^+_{-q_j} a_{-q'_{j'}} + a_{q_j} a^+_{q'_{j'}}} + \cancel{a^+_{q_j} a^+_{-q'_{j'}}} | \phi_i \rangle$$

$$\propto \delta_{qq'} \delta_{jj'}$$

$$\text{Elastic ME}: N \delta_{\vec{Q},\vec{G}} \left\{ 1 - \frac{1}{2N} \sum_{jq} \left( \vec{Q}\epsilon(q_j) \right)^2 \underline{\langle \phi_i | A(q_j) A(-q_j) | \phi_i \rangle} \right.$$

$+ 4$ phonon Terms $+ 6$ phonon Terms $\ldots \}$

Elastic MG

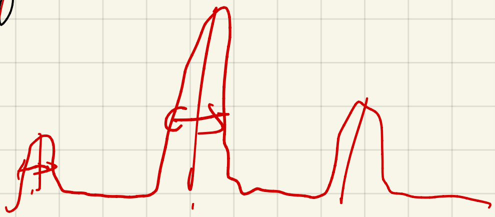


Can be shown :

$$ME = N \int_{\vec{Q}\,\vec{G}} \underbrace{\prod_{q_j} \left(1 - \frac{1}{2N} \left(\vec{Q} \cdot \epsilon(q_j)\right)^2 \langle \Phi_i | A(q_j) A(-q_j) | \Phi_i \rangle\right)}_{\boxed{e^{-W}}}$$

Elastic ME = ME for ideal crystal × $e^{-W}$ ← Debye Waller factor

$$\boxed{\lim_{N\to\infty} \prod_{n=1}^{\infty}\left(1 - \frac{a_n}{N}\right) = e^{-\frac{1}{N}\sum_{n=1}^{N} a_n}}$$



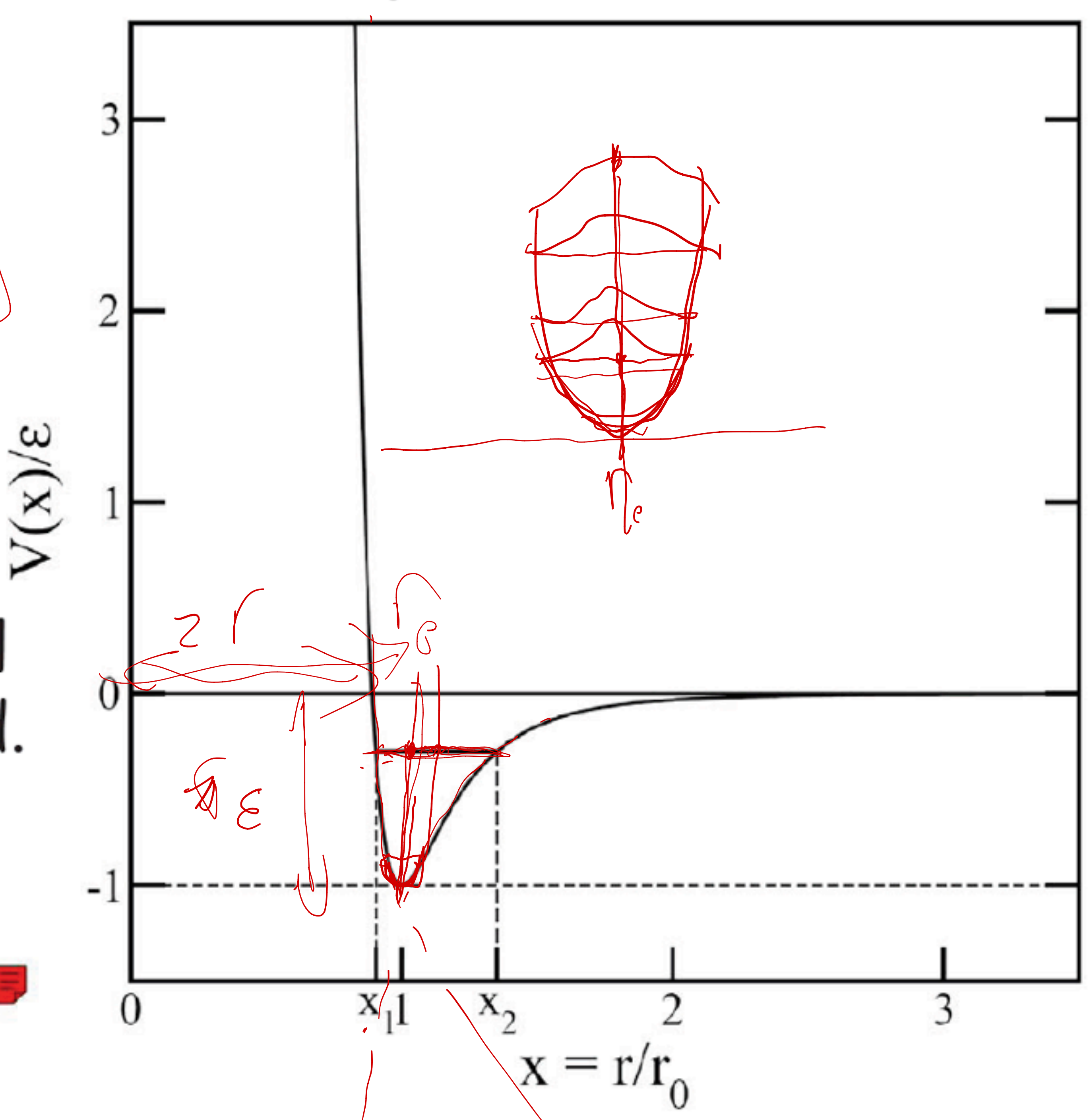
$$\boxed{W = \frac{1}{2N} \sum_{q_j} \frac{\hbar}{2M\omega(q_j)} \left(2n_{q_j} + 1\right)\left(\vec{Q}\,\vec{\epsilon}(q_j)\right)^2}$$

# Lennard-Jones interatomic potential $V_{LJ}(r)$

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The minimum is at $r_0 = 2^{1/6}\sigma$

$$V(r) = \epsilon\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right]$$



If a particle in this potential has energy E>0, it is unbound. If the energy obeys -ε<E<0, then it oscillates between $x_1$ and $x_2$.

# Harmonic approximation is not enough

- High T Cv does not approach the classical Dulong&Petit Law.
- No Thermal Expansion
- No Infinite thermal conductivity
- $C_v$ and $C_p$ are the same
- Adiabatic and isothermal compressibilities are the same

Energy is conserved.

$$E = \frac{M}{2}\left(\frac{dr}{dt}\right)^2 + V(r)$$

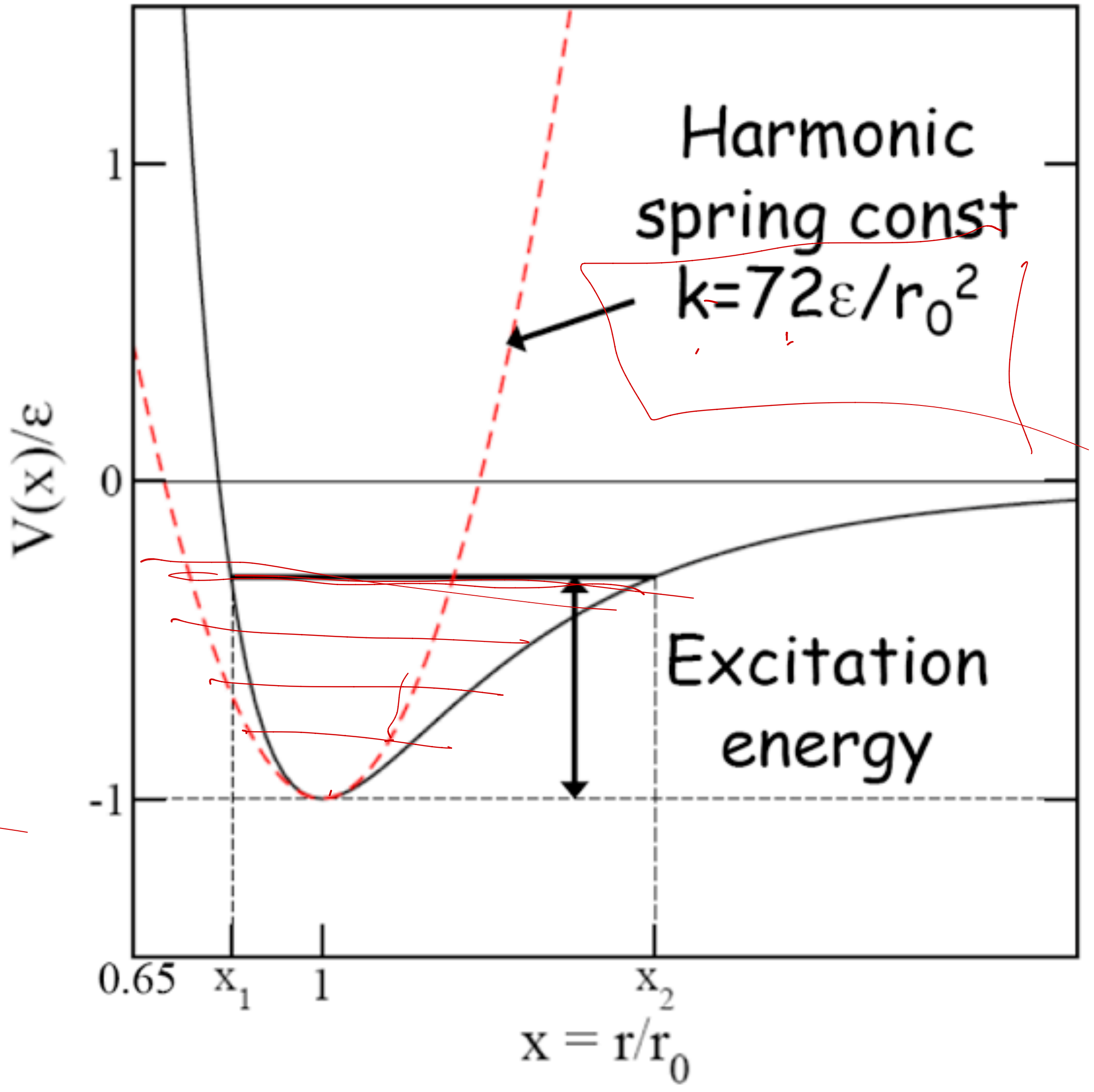
Solve for $dt$ and integrate.

$$t - t_0 = \int_{t_0}^{t} dt = \int_{r(t_0)}^{r(t)} \frac{dr}{\sqrt{2(E - V(r))/M}}$$

$$\boxed{\text{If } V(r) = V_0 + kr^2/2 \text{ then}}$$

$$r - r_0 = A\cos(\omega t + \phi)$$

where $\omega = \sqrt{k/M}$.



Harmonic spring const $k=72\varepsilon/r_0^2$

Excitation energy

Classical harmonic oscillator

has a natural scale of time ($\omega^{-1}$)

but **no natural scale of distance.**

A is arbitrary. Excitation energy $E - V_0 = kA^2/2$ is also.

# Quantum Harmonic Oscillator

$$\mathcal{H} = p^2/2M + kx^2/2$$

Add quantum mechanics. Operators p,x:

$$[p,x] \equiv px - xp = \hbar/i \quad \text{implies} \quad p = (\hbar/i)\partial/\partial x$$

Time-dependent Schrödinger Eqn.

$$i\hbar\frac{\partial\psi}{\partial t} = \mathcal{H}\psi$$

Stationary solutions.

If $\mathcal{H}\psi_n = E_n\psi_n$ then $\psi_n(t) = \psi_n e^{-iE_nt/\hbar}$

The new constant $\hbar$, together with $k$ and $M$, define scales of length, time, and energy.

$$x \sim \sqrt{2\hbar/M\omega} \equiv a_0$$

$$p \sim \sqrt{2\hbar M\omega} = M\omega a_0$$

$$E \sim kx^2/2 \sim p^2/2M \sim \hbar\omega$$

Factorize the Hamiltonian.

$$\frac{\mathcal{H}}{\hbar\omega} = \left(\frac{p}{M\omega a_0}\right)^2 + \left(\frac{x}{a_0}\right)^2 = \frac{1}{2}(aa^\dagger + a^\dagger a)$$

$$a = \frac{x}{a_0} + i\frac{p}{M\omega a_0} \qquad a^\dagger = \frac{x}{a_0} - i\frac{p}{M\omega a_0}$$

$$[a, a^\dagger] = \frac{2i}{M\omega a_0^2}[p,x] = 1$$

$$\frac{1}{2}(aa^\dagger + a^\dagger a) = a^\dagger a + \frac{1}{2} \qquad \mathcal{H} = \hbar\omega(a^\dagger a + \frac{1}{2})$$

Ground State

$$\psi_0 \equiv |0\rangle \sim e^{-\frac{1}{2}(x/a_0)^2}$$

Excited States

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \qquad a|n\rangle = \sqrt{n}|n-1\rangle$$

$$\mathcal{H}|n\rangle = \hbar\omega(n+\frac{1}{2})|n\rangle$$

**Level spacing $E_{n+1} - E_n = \hbar\omega$**

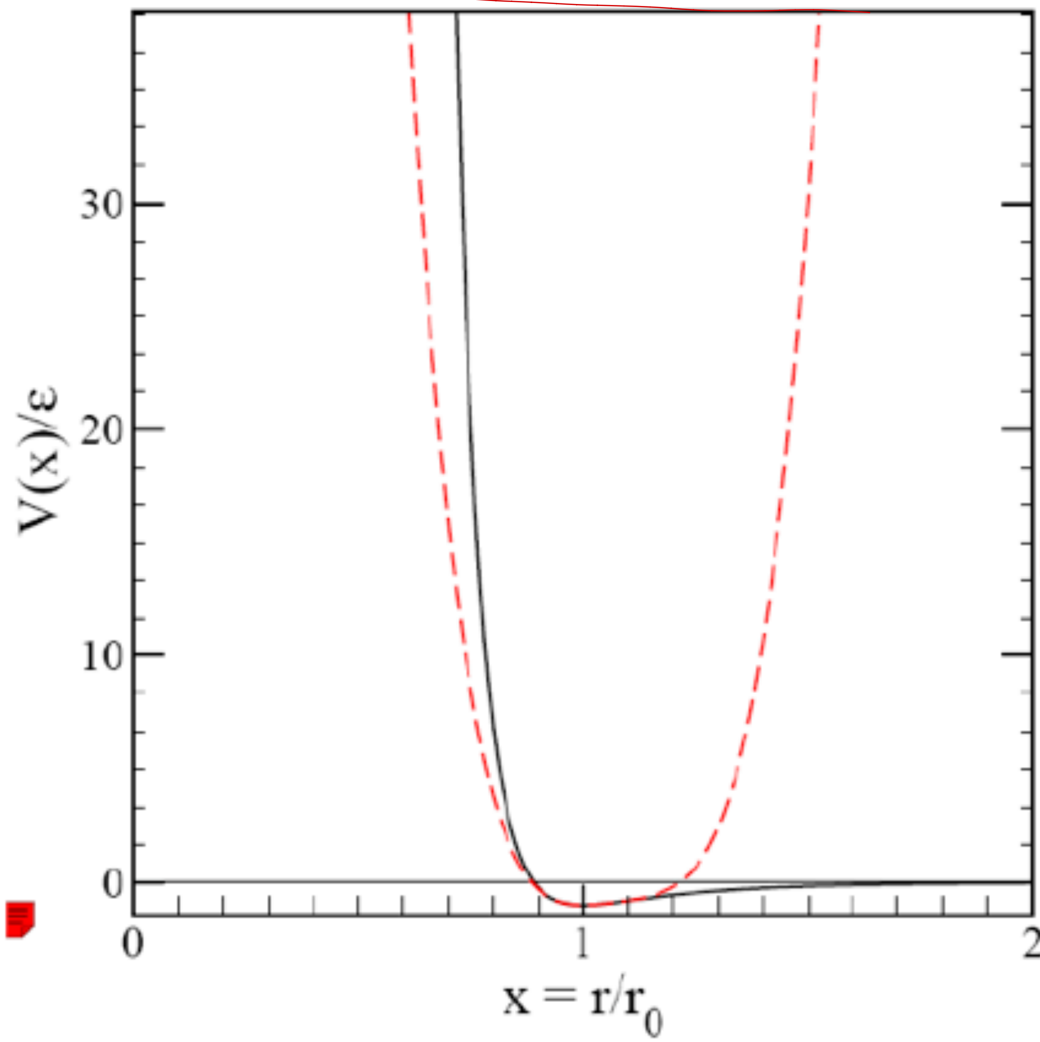
# Lennard-Jones Potential

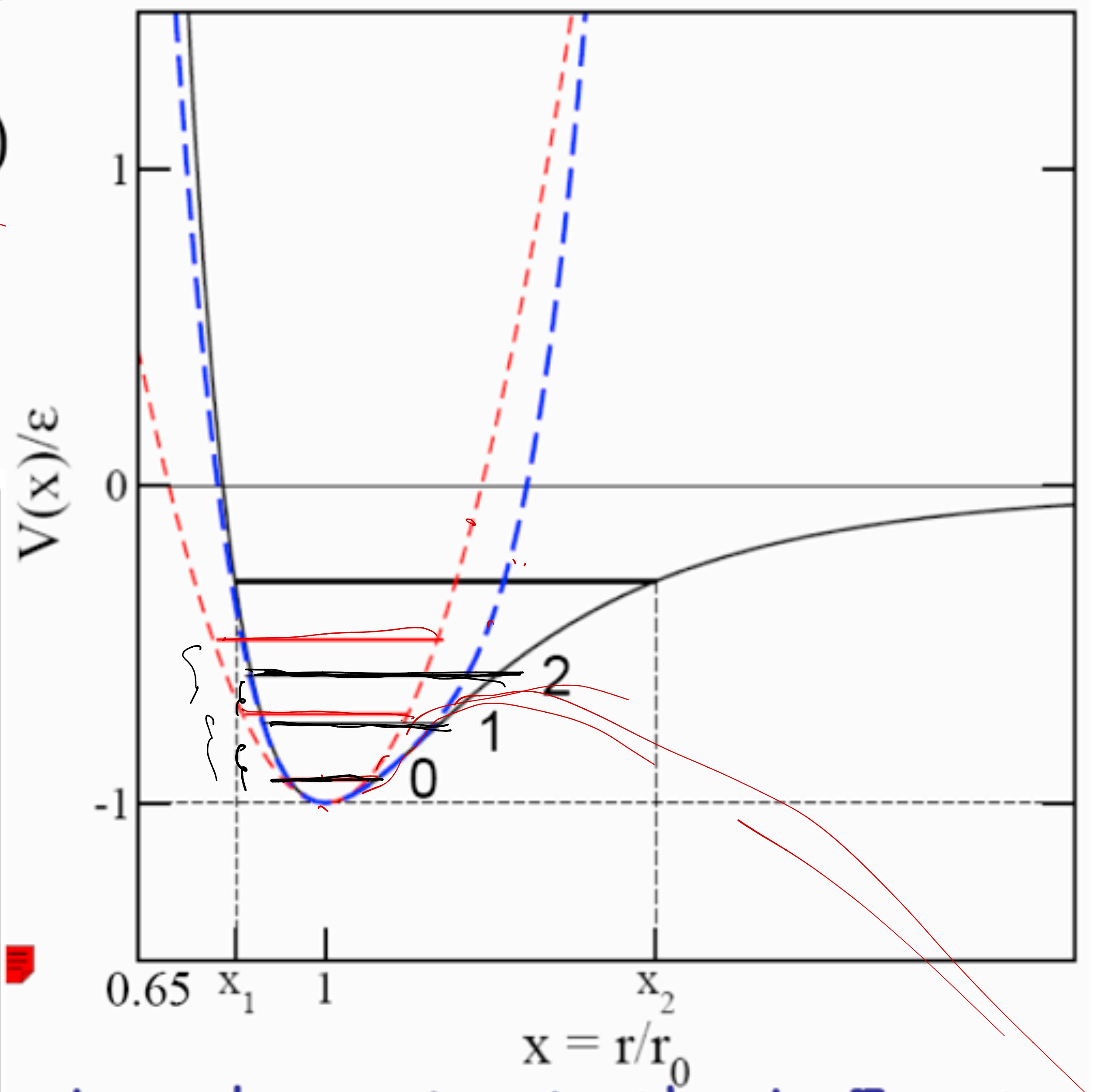
$V(x)/\varepsilon = 1/x^{12} - 2/x^{6}$

**Taylor series** (around $x=1$)

First 5 terms

$$V(x)/\varepsilon \approx -1 + 0 + 72(x-1)^2/2! \\ -1512(x-1)^3/3! \\ +20664(x-1)^4/4!$$





Level spacing in the L-J potential will diminish as n increases. Compute this by perturbation theory. Small parameter: $\hbar\omega/\varepsilon$ or $k_BT/\varepsilon$

Landau & Lifshitz, *Quantum Mechanics*, sec 38, problem 3

$$E_n - E_{n0} = \Delta E_n = \left(\frac{V_4}{4!}\right)\left(\frac{\hbar}{2M\omega}\right)^2 3(2n^2+2n+1) - \left(\frac{V_3}{3!}\right)^2 \frac{1}{\hbar\omega}\left(\frac{\hbar}{2M\omega}\right)^3 (30n^2+30n+11)$$

Use Lennard-Jones values for $V_3$, $V_4$, and $M\omega^2 = V_2$.

$$\Delta E_n = \frac{7}{384}\frac{(\hbar\omega)^2}{\epsilon}\left[\frac{41}{3}\left(n^2+n+\frac{1}{2}\right) - 35\left(n^2+n+\frac{11}{30}\right)\right]$$

Shift of ground state level $\Delta E_0 = -\frac{7}{64}\frac{(\hbar\omega)^2}{\epsilon}$.

$$\boxed{\frac{\Delta E_0}{\hbar\omega} = -\frac{7}{64}\left(\frac{\hbar\omega}{\varepsilon}\right)}$$

Shift of spacing of $n^{\text{th}}$ level $= \frac{\Delta E_{n+1} - \Delta E_{n-1}}{2} = -\frac{7}{9}\frac{(\hbar\omega)^2}{\epsilon}\left(n+\frac{1}{2}\right)$

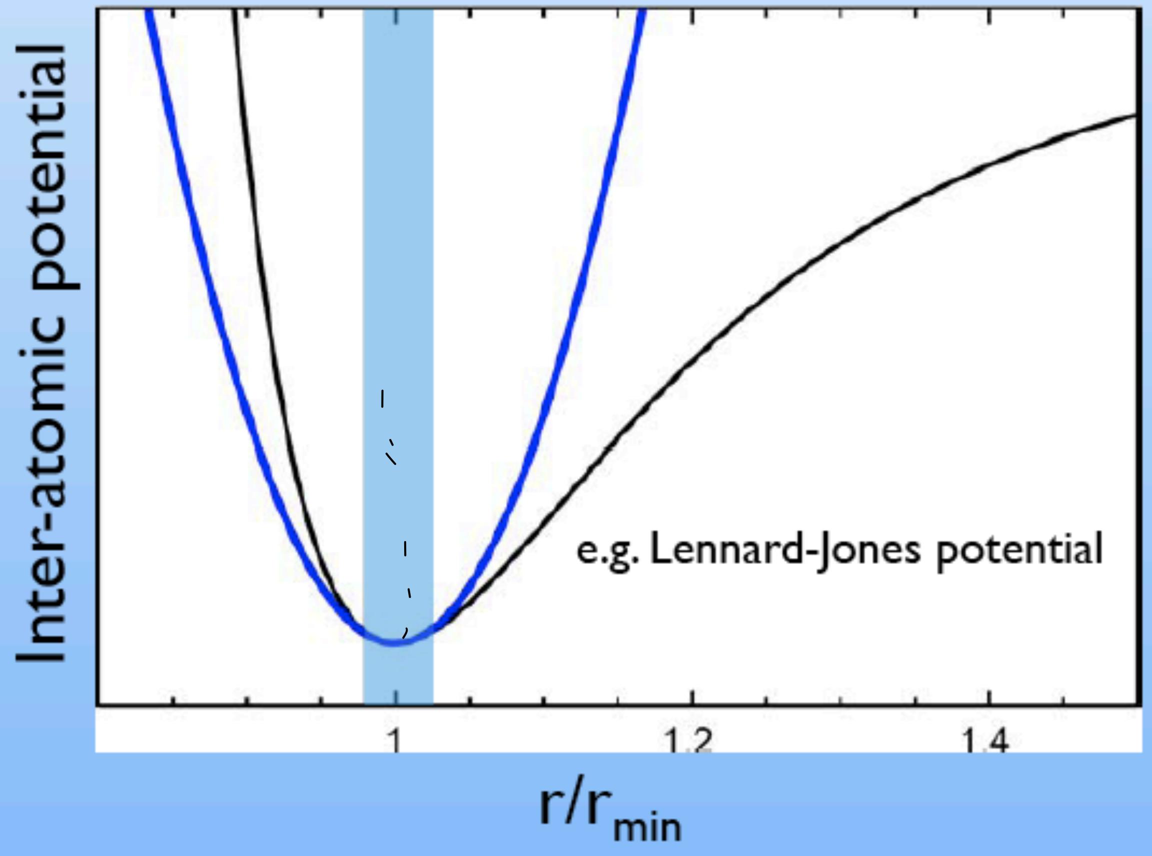
Relative shift of level spacing, for thermal average level $\bar{n}$:

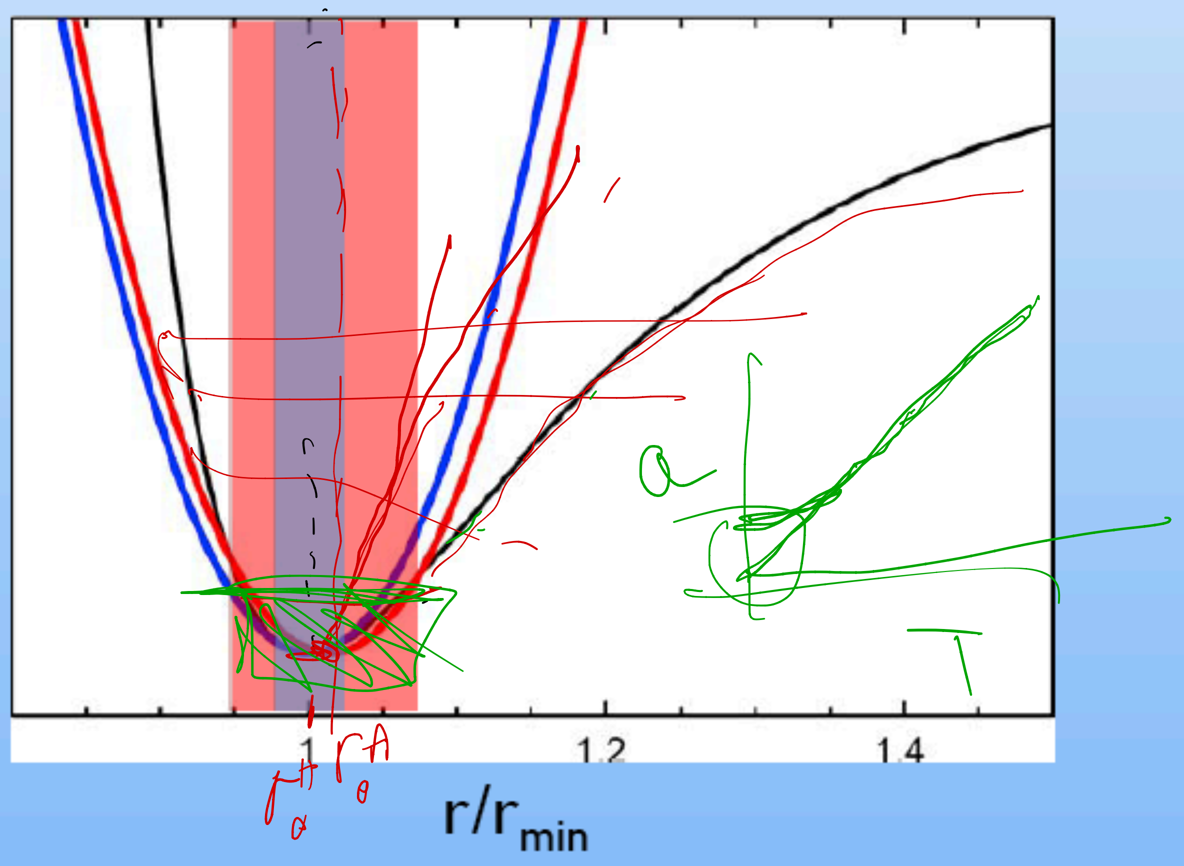
$$\boxed{\frac{\delta\omega_{\bar{n}}}{\omega} = -\frac{7}{9}\frac{k_BT}{\epsilon}}$$

Predicted oscillator frequency shift

This harmonic approx will not change the bond length

In reality, temperature increases the phonon amplitude, and at high temperature the bond length changes (blue → red)





# Thermal expansion

$$F = U - k_B T \sum_{q,s} lnZ; \qquad Z = \sum_{n=0}^{\infty} e^{[-\beta(n+\frac{1}{2})\hbar\omega]} = \frac{e^{(-\frac{1}{2}\beta\hbar\omega)}}{1 - e^{(\beta\hbar\omega)}}$$

$$F = U_{eq} + \sum_{q,s}(\frac{1}{2}\hbar\omega_s(q) + k_B T ln[1 - e^{-\beta\hbar\omega_s(q)}])$$

$$P = -(\frac{\partial F}{\partial V})_T = -(\frac{\partial U_{eq}}{\partial V})_T - \sum_{q,s}\hbar(\frac{\partial \omega_s(q)}{\partial V})_T[\frac{1}{2} + \frac{e^{(-\frac{1}{2}\beta\hbar\omega)}}{1 - e^{(\beta\hbar\omega)}} = -\frac{\partial U_{eq}}{\partial V} - \sum_{q,s}\hbar\frac{\partial \omega_s(q)}{\partial V}(\frac{1}{2} + n(\beta\omega_s(q)))$$

T independent

Zero for a perfectly harmonic crystal

In a perfect harmonic crystal the pressure required to maintain a given volume does not depend on T

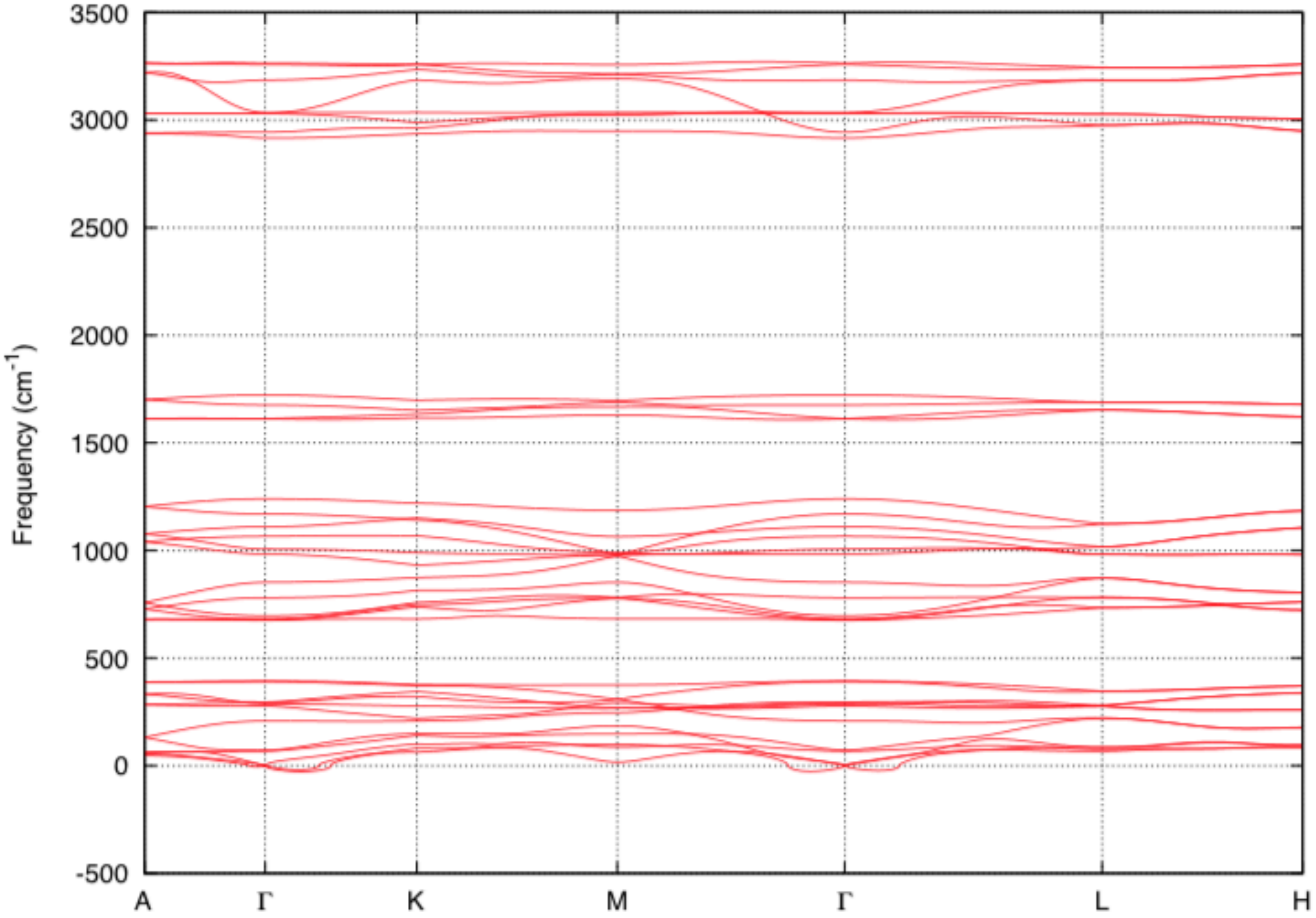


Figure 7: Phonon bands of proton ordered ice XI.

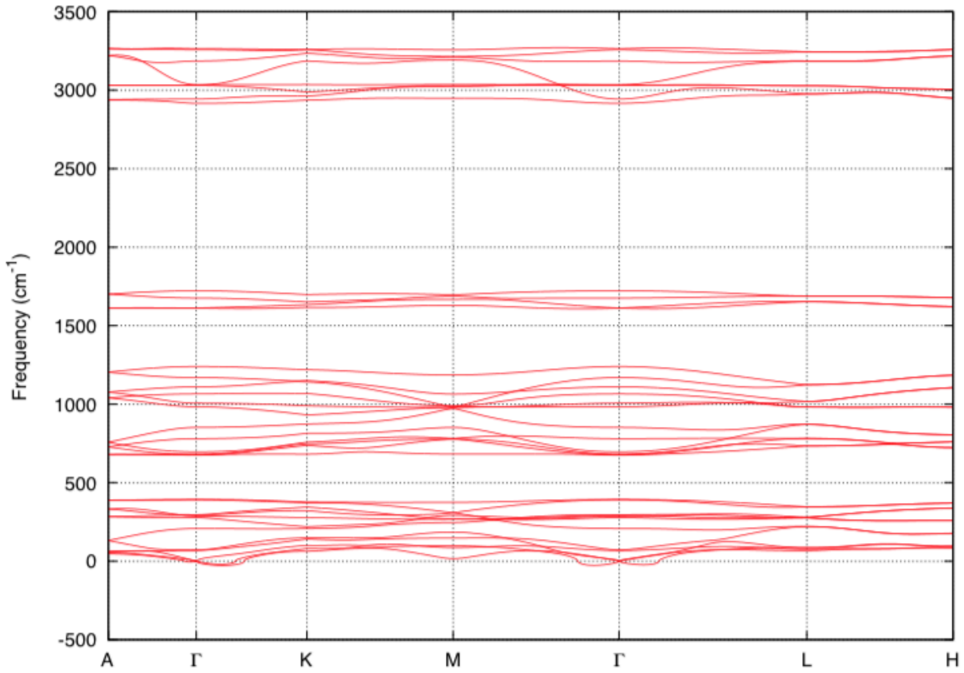


Figure 7: Phonon bands of proton ordered ice XI.

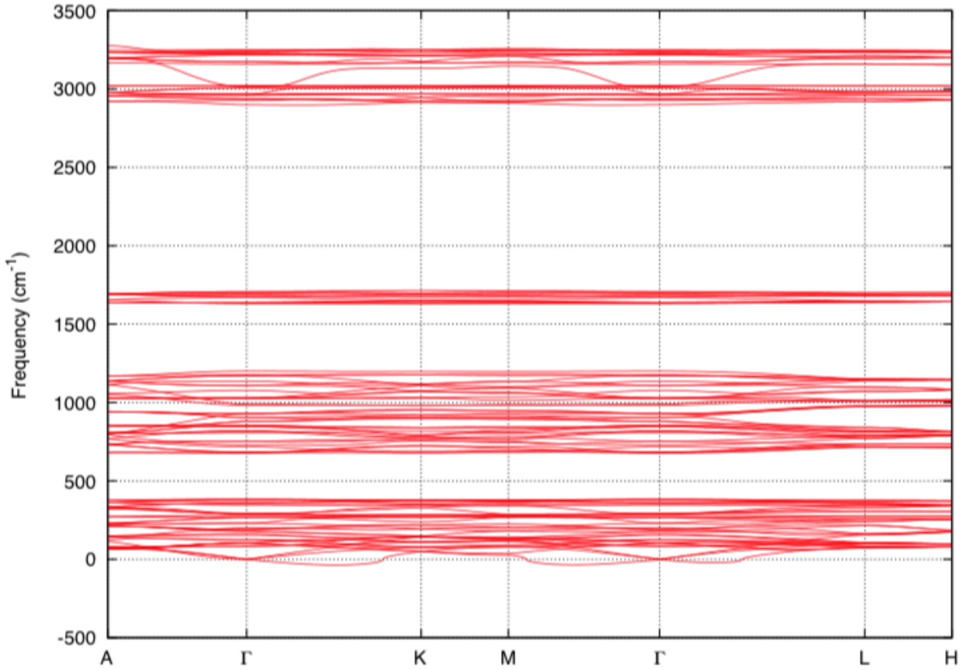


Figure 8: Phonon bands of proton ordered BF-ice.

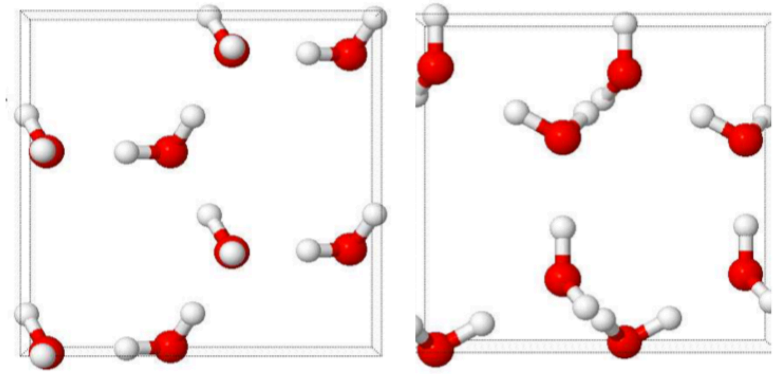


Figure 3: Proton ordered ice XI structure. The image on the left is the top view of the x-y plane; the image on the right is the side view of the x-z plane.

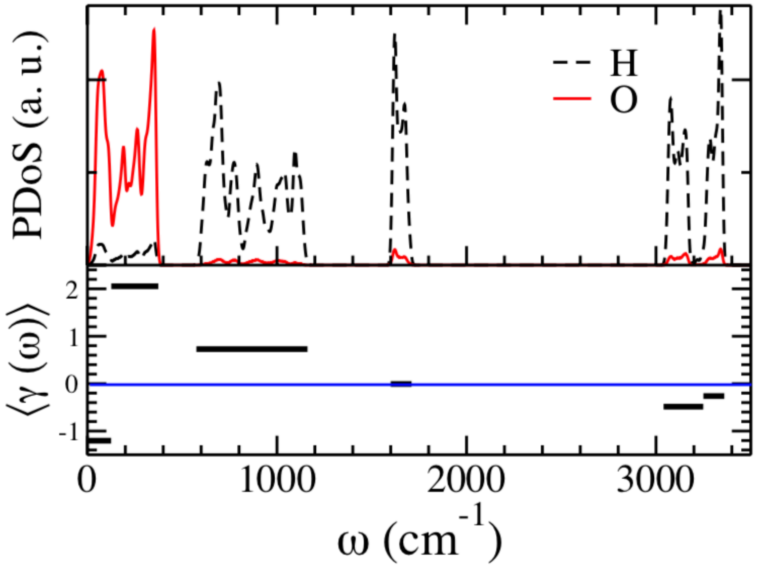
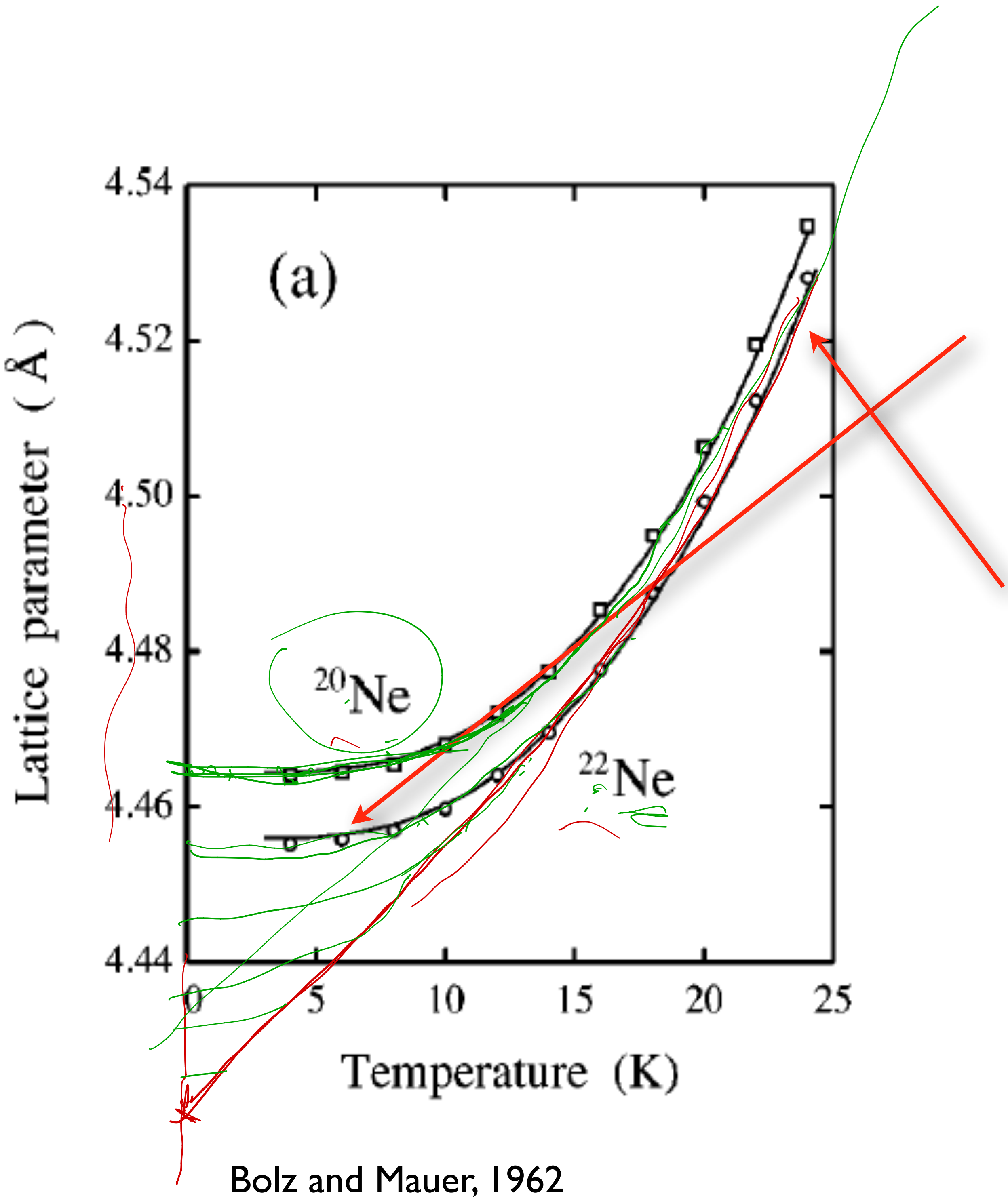


Figure 9: Phonon density of states projected on hydrogen and oxygen for $H_2O$ of proton ordered ice XI.

# Isotope shift of lattice constant



Bolz and Mauer, 1962
Batchelder, Losee, and Simmons 1968

Heavy neon ($^{22}$Ne) occupies 0.19% less space than light neon ($^{20}$Ne) at T=0.

Fraction diminishes at high T.

Isotope shift vanishes at high T.

$$\omega = \sqrt{\frac{K}{M}} \quad M \to \infty$$

# Outline

1. Theory of zero point and thermal lattice expansion: Frozen lattice constant.
2. Isotope effects in Ne: Theory and experiments.
3. Isotope effects in ice: Experiments
4. Isotope Effects in ice: Empirical Force Field
5. Isotope Effects in ice: DFT
    1. Frozen Volume
    2. T=0
    3. T>0
6. Hbond and quantum anomalies
7. Other H-bonded systems. How anomalous is this effect?
8. Can we say anything about water?
9. Conclusions.

# Theory of zero point and thermal lattice expansion (I)

- To find V at T=0, we minimize:

$$E_{gs} = E_{el,0} + \sum_q \frac{\hbar\omega_q}{2} \longleftarrow E_{zp}$$

- At T>0 the equilibrium V minimizes the Helmholtz free energy:

$$F(V,T) = E_0(V) + \sum_q \left[ \frac{\hbar\omega_q}{2} + k_B T \ln\left(1 - e^{\frac{-\hbar\omega_q}{k_B T}}\right)\right]$$

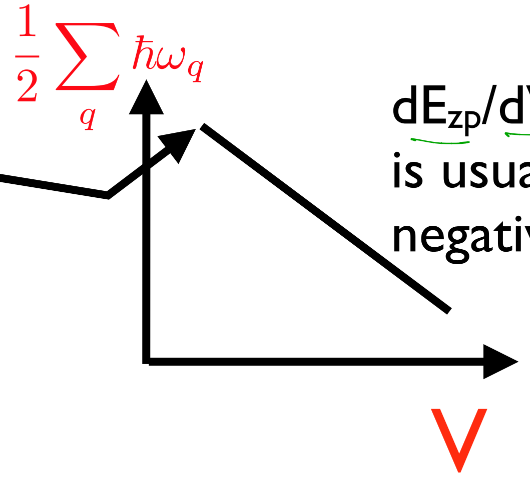
- Volume dependent Quasiharmonic approximation: Frequencies depend only on V(T).

$$\omega_q(V) = \omega_q(V_0)\left[1 - \frac{(V-V_0)}{V_0}\gamma_q\right]$$

$\omega_q(V,T)$

- Grüneisen parameter

$$\gamma_q \equiv -\left(\frac{V_0}{\omega_q}\right)\left(\frac{\partial\omega_q}{\partial \mathrm{V}}\right)_{V_0}$$



$dE_{zp}/dV$ is usually negative

# Theory of zero point and thermal lattice expansion (II)

quasi-harmonic
volume shift

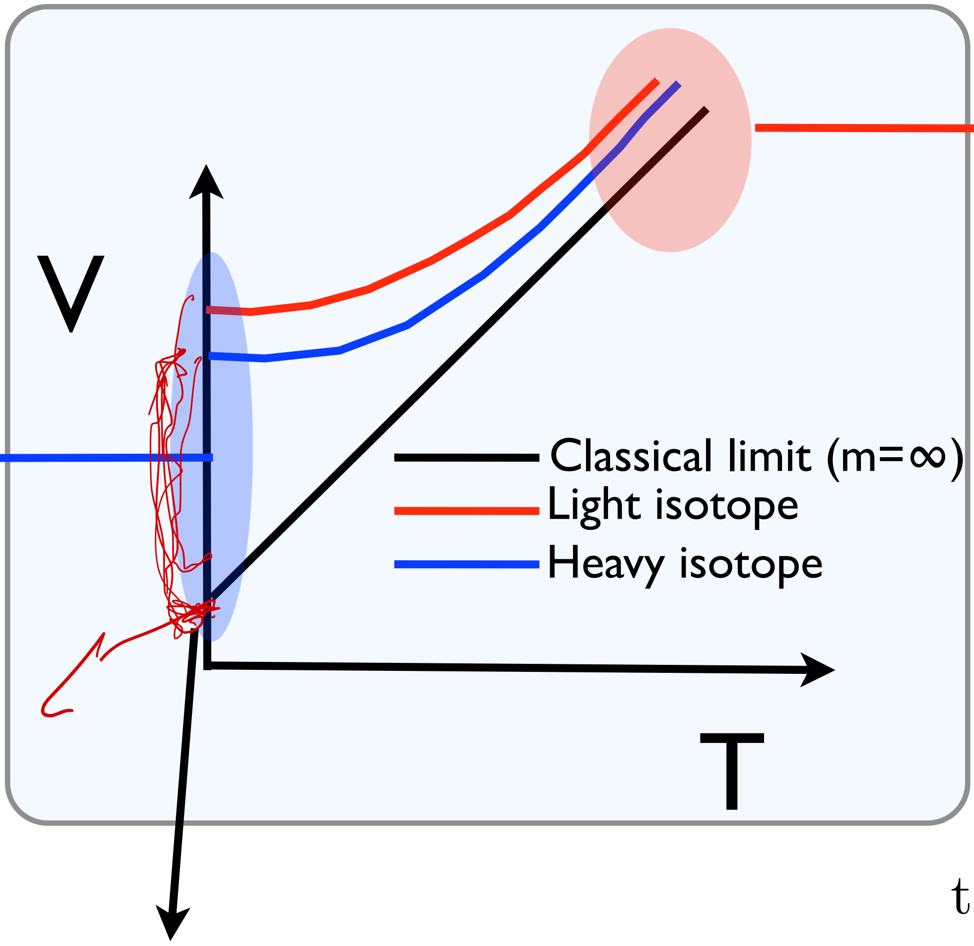
$$\frac{V - V_0}{V_0} = \frac{1}{V_0 B_0} \sum_k \gamma_k \hbar\omega_k \left( n_k + \frac{1}{2} \right)$$

$\omega = \sqrt{\frac{K}{M}}$

At T=0

$$\Delta V \propto \langle \gamma_q \omega_q \rangle$$

Isotope
dependent



Frozen
Volume.

High T limit:

$$\Delta V \propto T \langle \gamma_q \rangle$$

Isotope independent

$$\sum_q \gamma_q = -\frac{V}{2} \sum_q \frac{1}{\omega_q^2} \frac{\partial \omega_q^2}{\partial V} = -\frac{V}{2} \mathrm{tr} \left[ \hat{D}^{-1} \frac{\partial \hat{D}}{\partial V} \right]$$

$$\mathrm{tr} \left[ \hat{D}^{-1} \frac{\partial \hat{D}}{\partial V} \right] = \mathrm{tr} \left[ \hat{K}^{-1} \frac{\partial \hat{K}}{\partial V} \right]$$

$$K_{ij} = \frac{\partial^2 E}{\partial u_i \partial u_j}$$

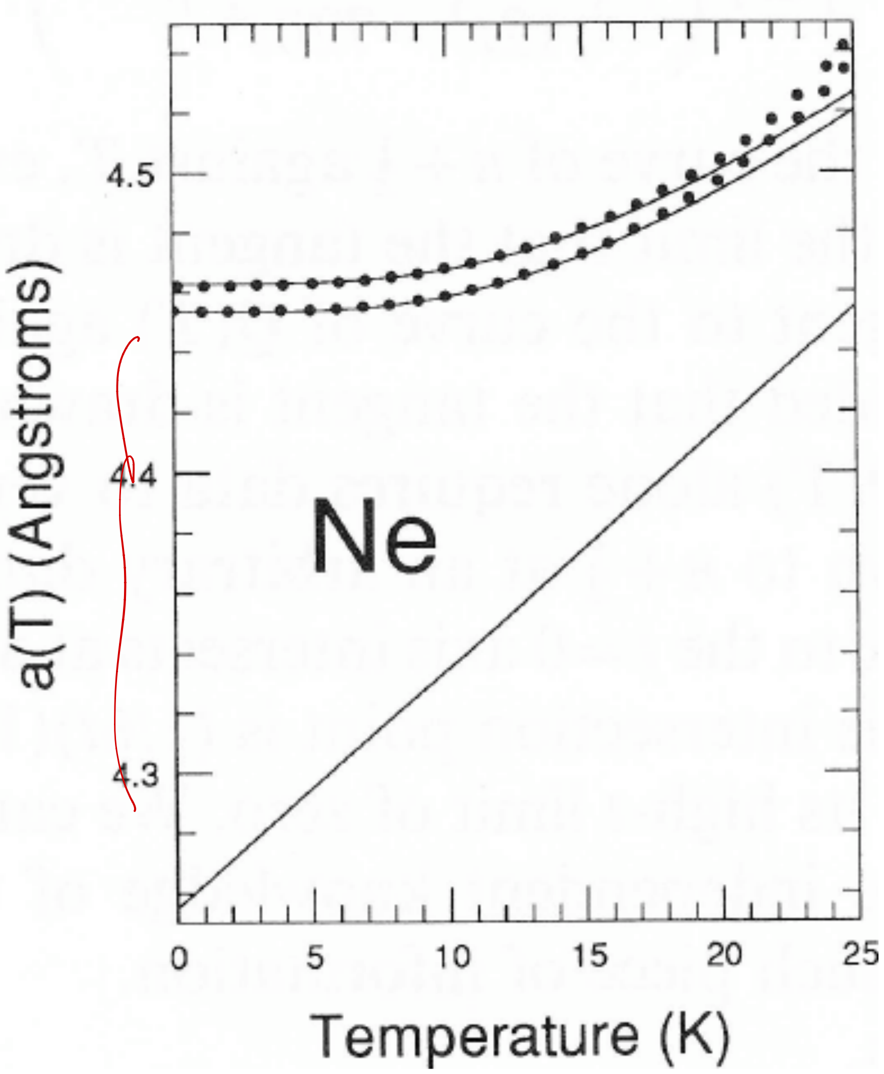
T=0 classical limit:
Frozen volume. This is
what DFT provides.

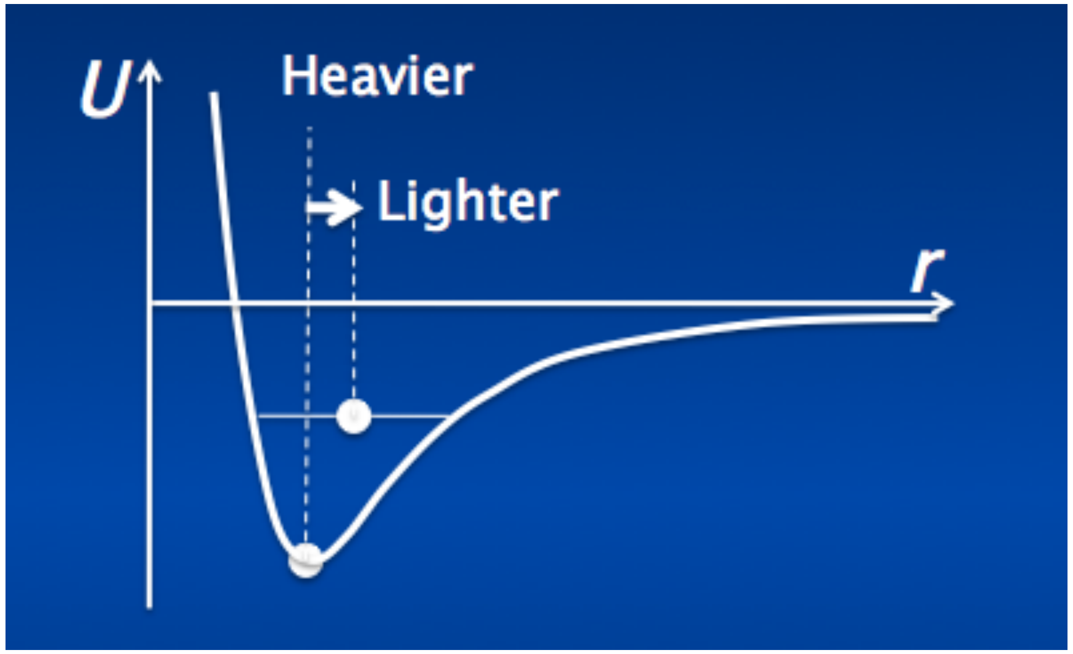
# Theory of zero point and thermal lattice expansion applied to Ne

$a(M) < a(m)$

- Normal Isotope Effect
- Large zero point lattice expansion.

P.B. Allen, Phil. Mag. B 70, 527 (1994)





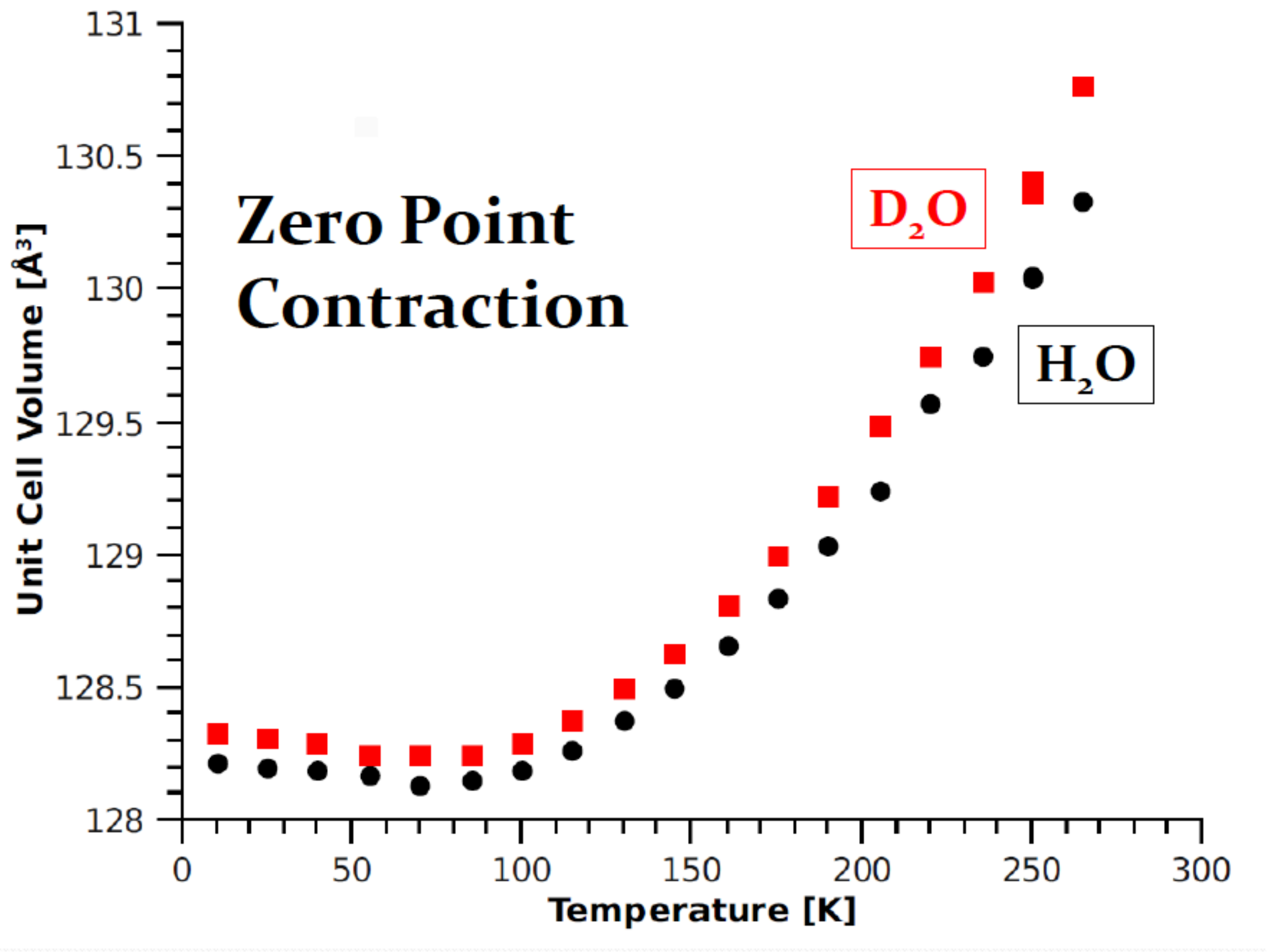
Extrapolated bare lattice constant a=4.255A

~15% zero point volume expansion

# Isotope effects in ice: experiments

K. Röttger, A. Endriss, J. Ihringer, S. Doyle and W. F. Kuhs

Lattice constants and thermal expansion of $H_2O$ and $D_2O$
ice Ih between 10 and 265K
Acta Cryst. (1994). B50, 644-648



- Inverse isotope effect!
- $V(H_2O)<V(D_2O)$ by 0.09%
- Deviation is increasing rather than decreasing as T increases

Should $V_0$ be
> exps. or < exps?

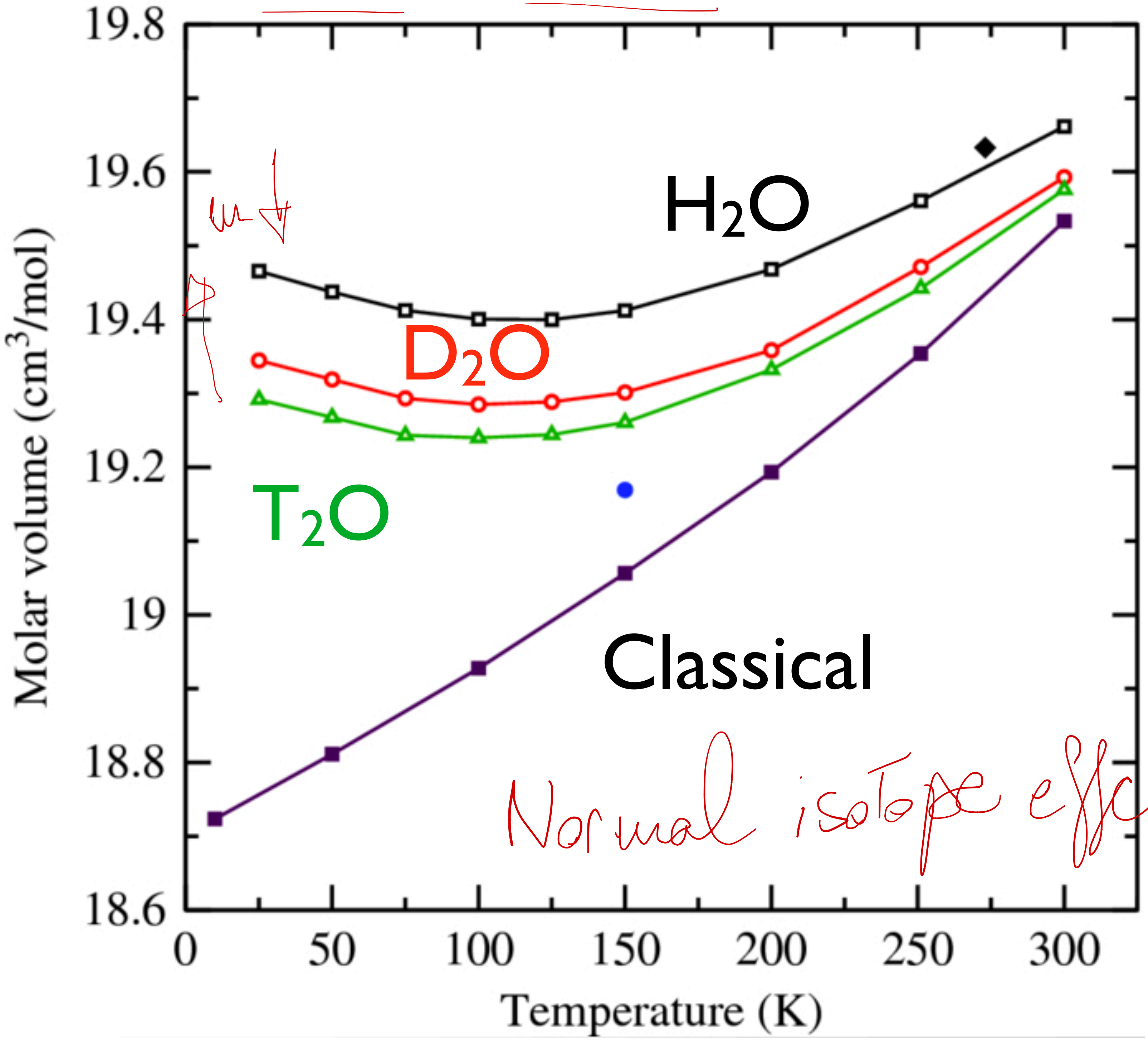
# 1.Can Some Theory Reproduce experiments?

- Path Integral Molecular Dynamics & Empirical force Field

NO

Isotope effects in ice Ih: A path-integral simulation

Carlos P. Herrero and Rafael Ramírez, JCP 134, 9, 2011

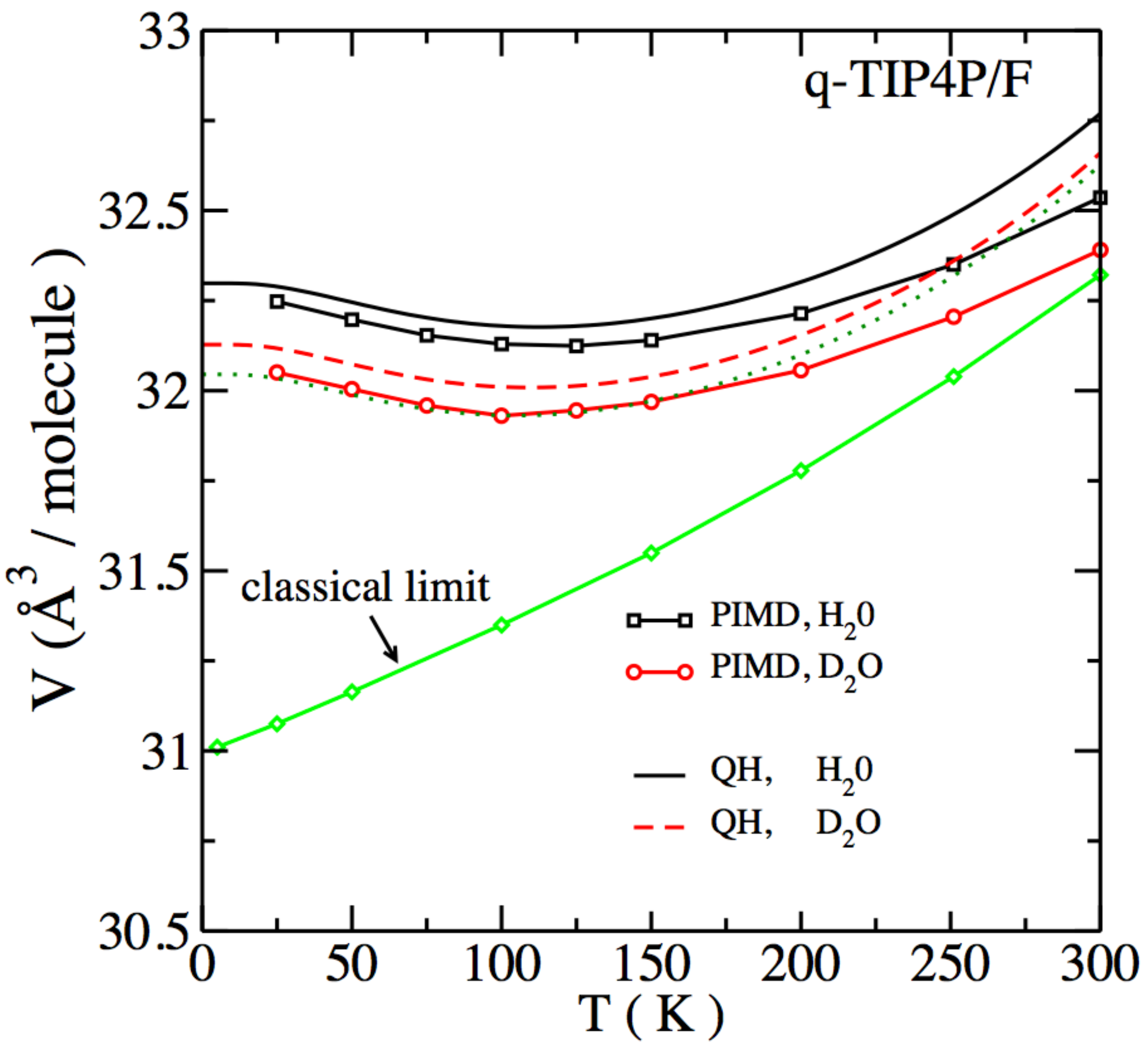


Normal isotope effect.

- QTip4P-F (S. Habershon, T. E. Markland, and D. E. Manolopoulos, J. Chem. Phys. 131, 024501 (2009).)
- Ring polymer, 32 beads,
- NPT ensemble
- All anharmonicities taken into account.
- System: 96 $H_2O$, proton disordered ice.

# 2.Is the QHA sufficient?
# Compare PIMD to QHA using q-TIP4PF

YES



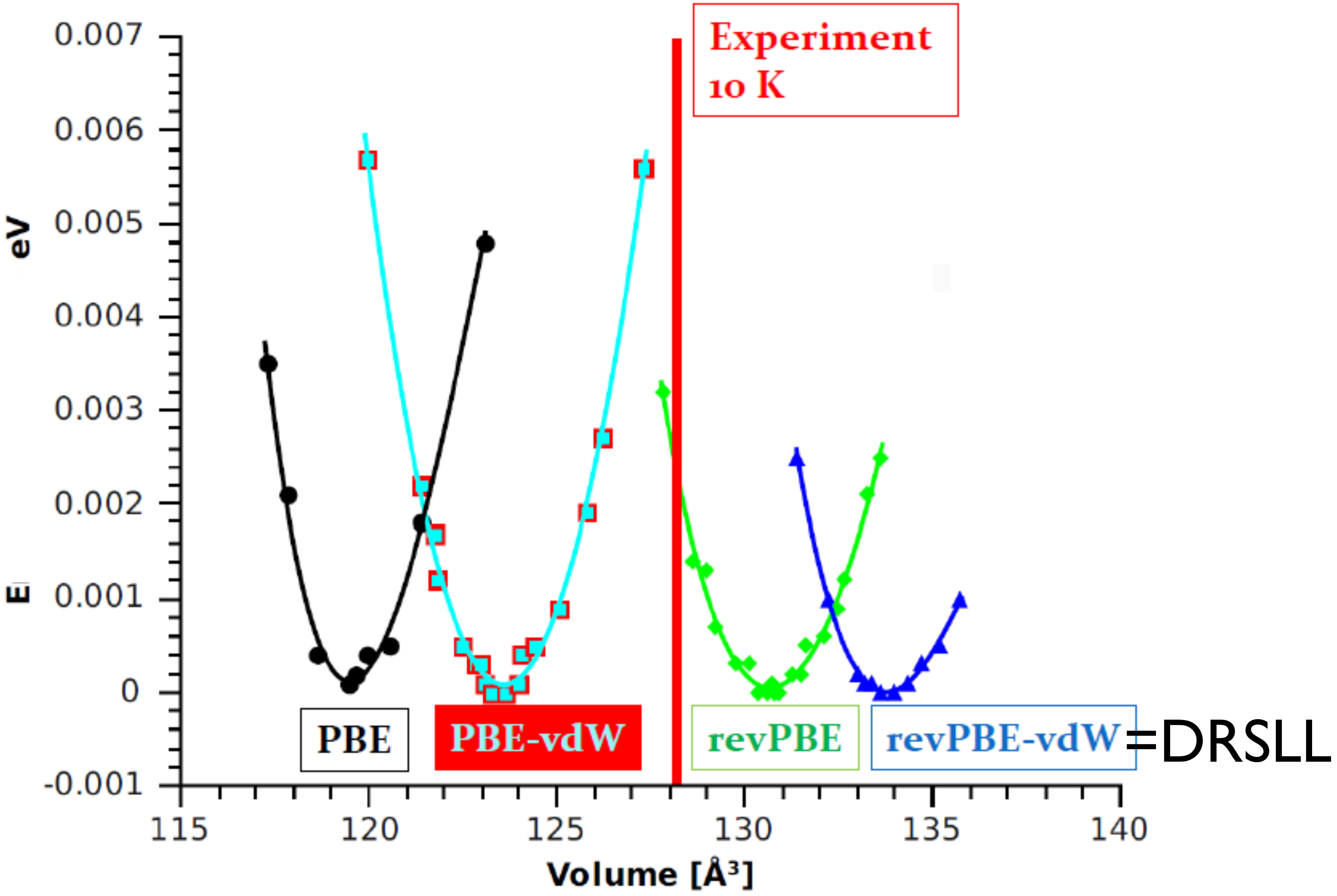
QH2⇒

$$\omega_k(V) = \omega(V_0)\left(1 - \gamma_k \frac{V - V_0}{V_0}\right)$$

Although temperature dependent anharmonicities are not negligible, the overall results and behavior are very well reproduced by the QHA

# 3.Can DFT Reproduce experiments?

- Performance of different XC potentials on the Frozen Lattice parameter



# 3.Can DFT Reproduce experiments?

- T=0

Different Ice Structures

ice Ih (BF structure, proton ordered)

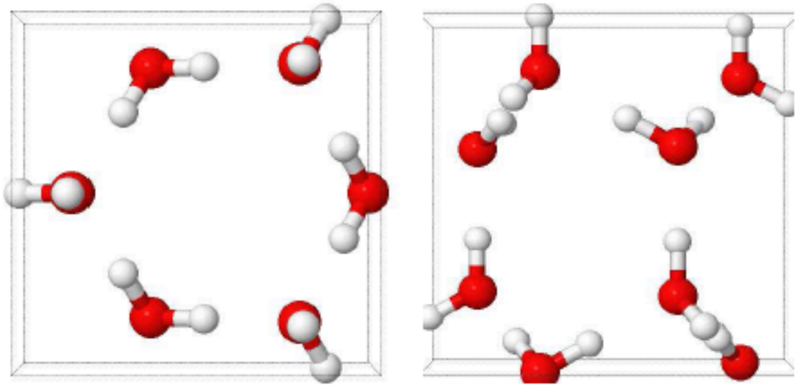


FIG. 2. Bernal-Fowler ice Ih structure. The image on the right is the top view of the x-y plane; the image on the left is the side view of the x-z plane.

ice XI

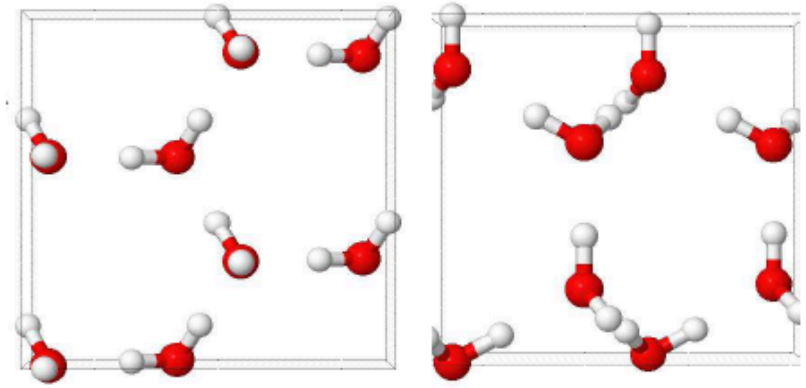


FIG. 1. Unit cell of the H-ordered ice XI structure. The image on the right is the top view of the x-y plane; the image on the left is the side view of the x-z plane.

ice Ih, 96 H2O, proton disordered

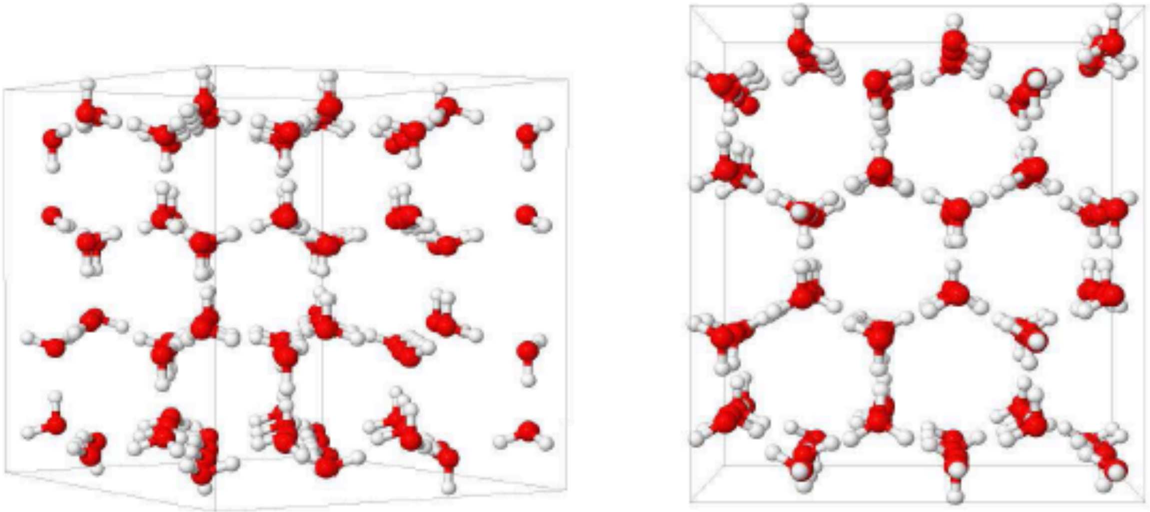
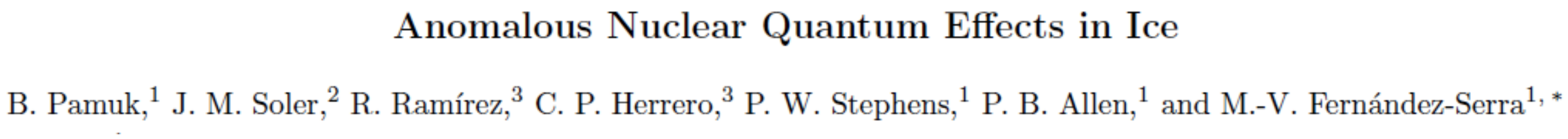


FIG. 3. H-disordered ice Ih structure. The image on the right is the top view of the x-y plane; the image on the left is the side view of the x-z plane.

# 3.Can DFT Reproduce experiments?

## •Calculation details

- SIESTA code, TZP basis.
- 5(3) volumes, relaxations with F<0.001 ev/A
- Phonon calculations: Frozen Phonon approximation + q sampling (gamma only in disordered proton system).
- Several finite phonon displacements.
- Grüneisen parameters: Numerical evaluation of frequency derivative (3 or 5 data points).
- PIMD simulation (32 beads) for ice XI (100K).



Anomalous Nuclear Quantum Effects in Ice

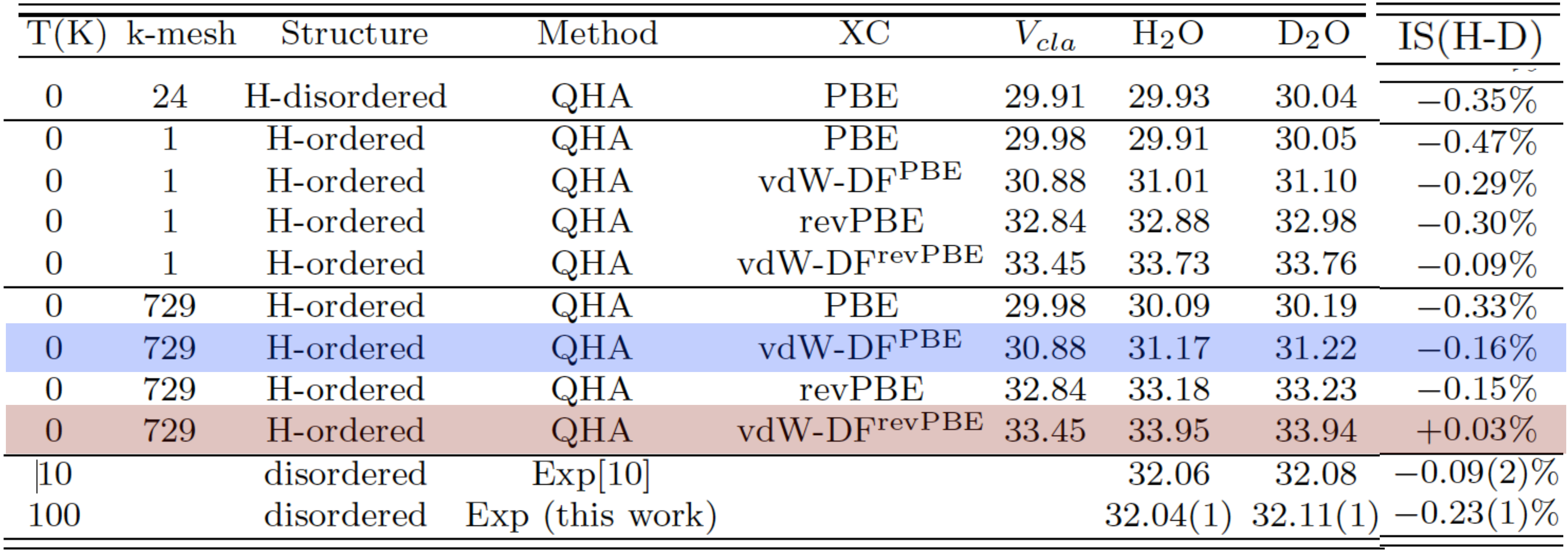
B. Pamuk,[1] J. M. Soler,[2] R. Ramírez,[3] C. P. Herrero,[3] P. W. Stephens,[1] P. B. Allen,[1] and M.-V. Fernández-Serra[1,*]

ArXiv, submitted

# 3.Can DFT Reproduce experiments?

- T=0

## Isotope Substitution: Proton site



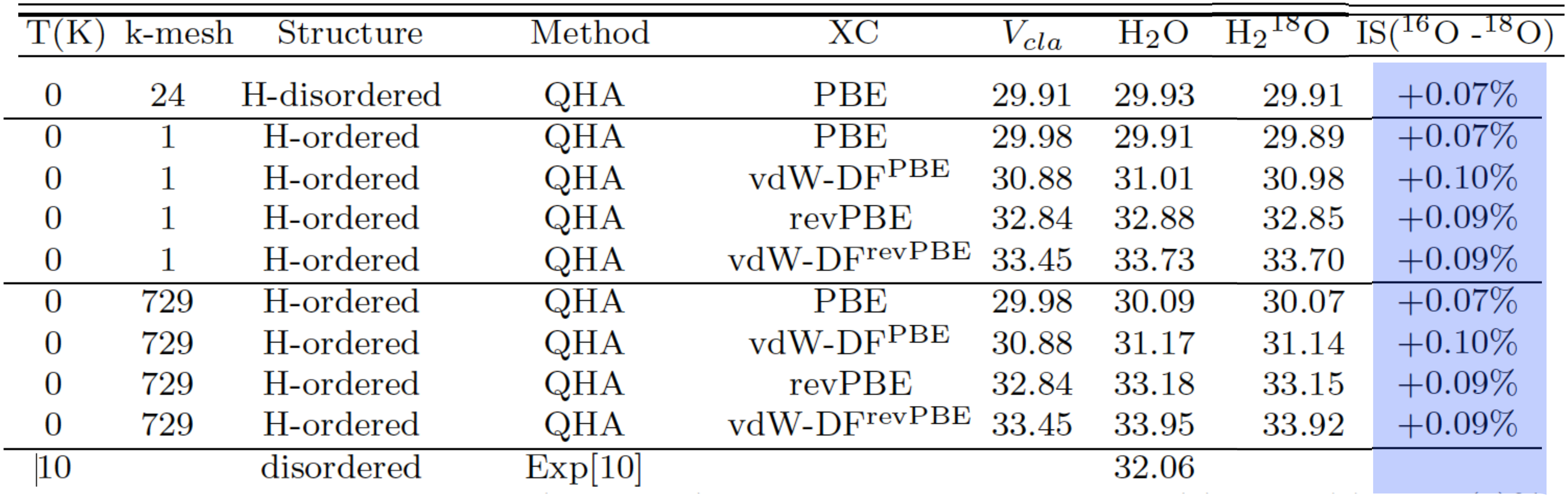
| T(K) | k-mesh | Structure | Method | XC | $V_{cla}$ | $H_2O$ | $D_2O$ | IS(H-D) |
|---|---|---|---|---|---|---|---|---|
| 0 | 24 | H-disordered | QHA | PBE | 29.91 | 29.93 | 30.04 | −0.35% |
| 0 | 1 | H-ordered | QHA | PBE | 29.98 | 29.91 | 30.05 | −0.47% |
| 0 | 1 | H-ordered | QHA | vdW-DF$^{PBE}$ | 30.88 | 31.01 | 31.10 | −0.29% |
| 0 | 1 | H-ordered | QHA | revPBE | 32.84 | 32.88 | 32.98 | −0.30% |
| 0 | 1 | H-ordered | QHA | vdW-DF$^{revPBE}$ | 33.45 | 33.73 | 33.76 | −0.09% |
| 0 | 729 | H-ordered | QHA | PBE | 29.98 | 30.09 | 30.19 | −0.33% |
| 0 | 729 | H-ordered | QHA | vdW-DF$^{PBE}$ | 30.88 | 31.17 | 31.22 | −0.16% |
| 0 | 729 | H-ordered | QHA | revPBE | 32.84 | 33.18 | 33.23 | −0.15% |
| 0 | 729 | H-ordered | QHA | vdW-DF$^{revPBE}$ | 33.45 | 33.95 | 33.94 | +0.03% |
| 10 | | disordered | Exp[10] | | | 32.06 | 32.08 | −0.09(2)% |
| 100 | | disordered | Exp (this work) | | | 32.04(1) | 32.11(1) | −0.23(1)% |

- Except for one case, anomalous effect is reproduced
- The frozen lattice constant should be < experimental value.

# 3.Can DFT Reproduce experiments?

- T=0

## Isotope substitution: O site



| T(K) | k-mesh | Structure | Method | XC | $V_{cla}$ | $H_2O$ | $H_2{}^{18}O$ | IS($^{16}O$ -$^{18}O$) |
|---|---|---|---|---|---|---|---|---|
| 0 | 24 | H-disordered | QHA | PBE | 29.91 | 29.93 | 29.91 | +0.07% |
| 0 | 1 | H-ordered | QHA | PBE | 29.98 | 29.91 | 29.89 | +0.07% |
| 0 | 1 | H-ordered | QHA | vdW-DF$^{PBE}$ | 30.88 | 31.01 | 30.98 | +0.10% |
| 0 | 1 | H-ordered | QHA | revPBE | 32.84 | 32.88 | 32.85 | +0.09% |
| 0 | 1 | H-ordered | QHA | vdW-DF$^{revPBE}$ | 33.45 | 33.73 | 33.70 | +0.09% |
| 0 | 729 | H-ordered | QHA | PBE | 29.98 | 30.09 | 30.07 | +0.07% |
| 0 | 729 | H-ordered | QHA | vdW-DF$^{PBE}$ | 30.88 | 31.17 | 31.14 | +0.10% |
| 0 | 729 | H-ordered | QHA | revPBE | 32.84 | 33.18 | 33.15 | +0.09% |
| 0 | 729 | H-ordered | QHA | vdW-DF$^{revPBE}$ | 33.45 | 33.95 | 33.92 | +0.09% |
| 10 |  | disordered | Exp[10] |  |  | 32.06 |  |  |

- Isotope effect on O is normal
- All functionals predict very similar isotope effect on O.

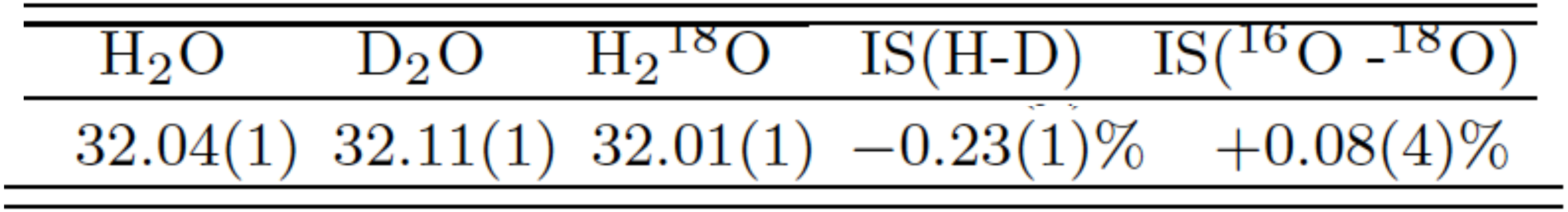
# 3.Can DFT Reproduce experiments?

- T>0 New experiments

## Isotope effect on O site predicted by Experiments

Peter Stephens, Stony Brook University
NSLS, BNL

T=100 K



| $H_2O$ | $D_2O$ | $H_2{}^{18}O$ | IS(H-D) | IS($^{16}O$ - $^{18}O$) |
|---|---|---|---|---|
| 32.04(1) | 32.11(1) | 32.01(1) | −0.23(1)% | +0.08(4)% |

# 3.Can DFT Reproduce experiments?

- T>0

## Temperature dependence.

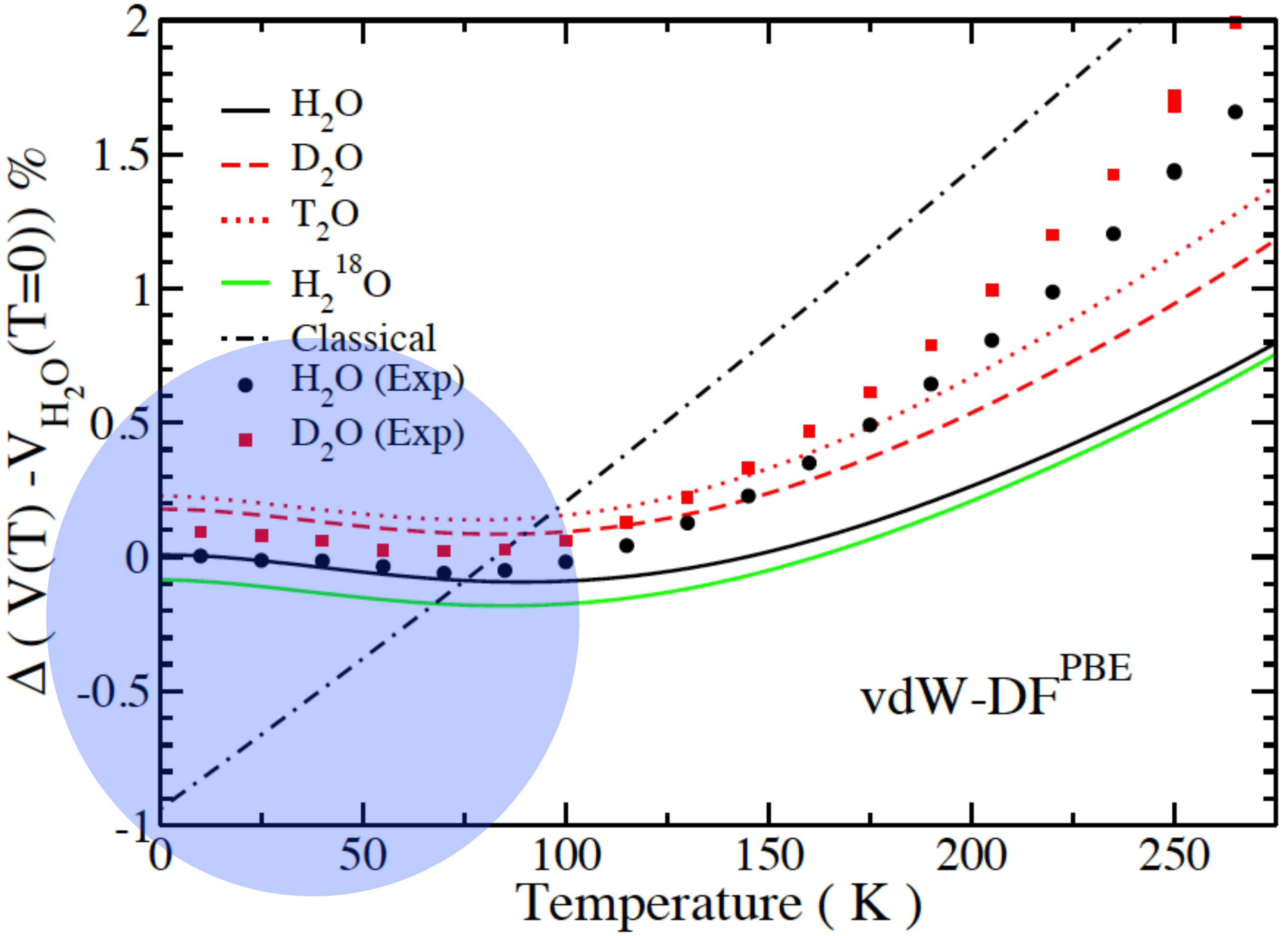


FIG. 2. (Color Online). Volume change $V(T)/V_{H_2O}(0) - 1$, relative to that of $H_2O$ at $T = 0$, for different isotopes calculated using the QHA with the vdW-DF$^{PBE}$ functional. Also shown are the experimental results from Ref. 10.

# 3.Can DFT Reproduce experiments?

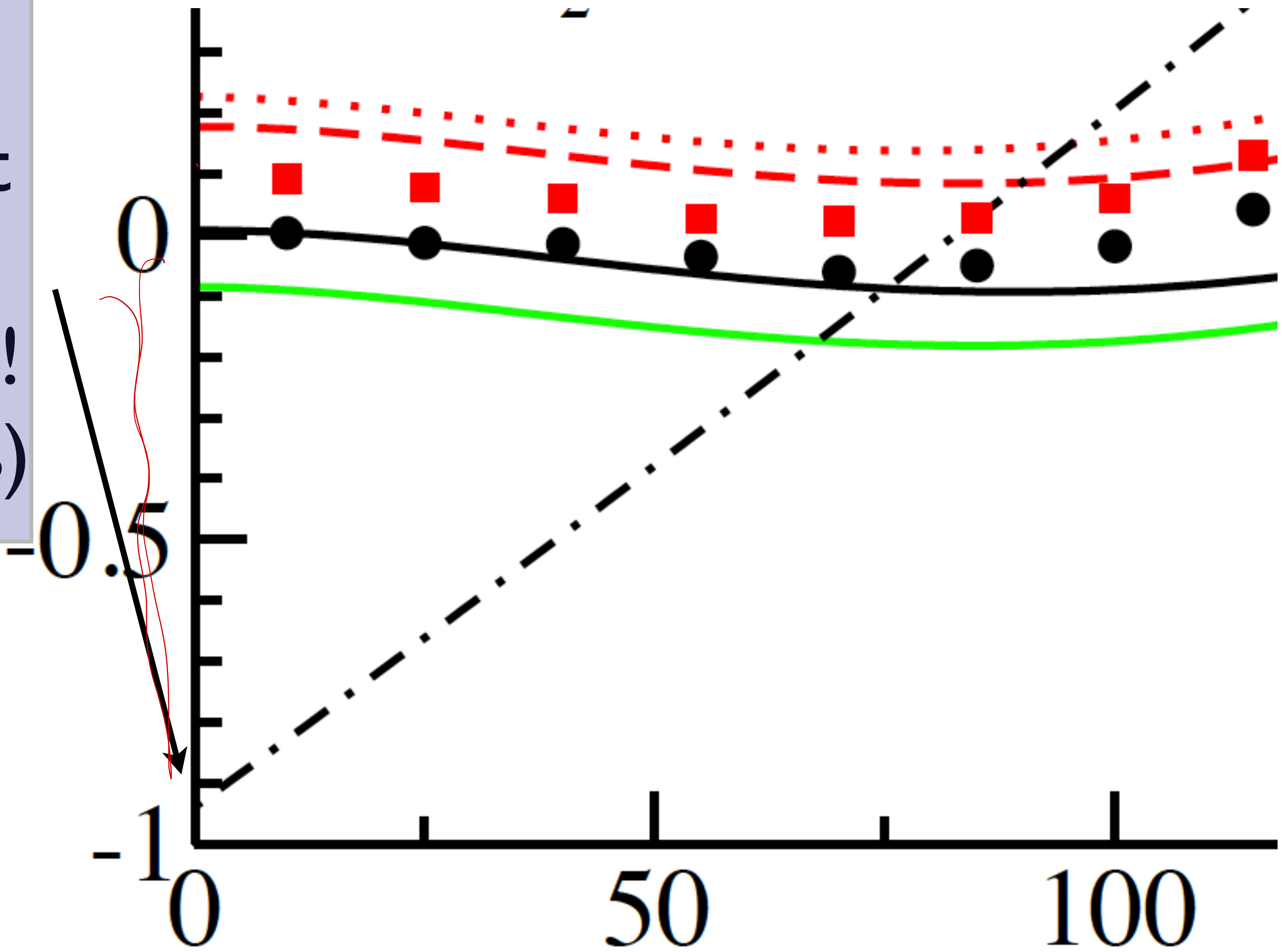
- T>0

$m(Ne) = 20$

$m(H_2O) = 18$

T< 100 K

Only 1% zero point volume expansion! (Ne ~15%)



Overall normal isotope effect, O dominated

# 3.Can DFT Reproduce experiments?

- T>0

## Temperature dependence.

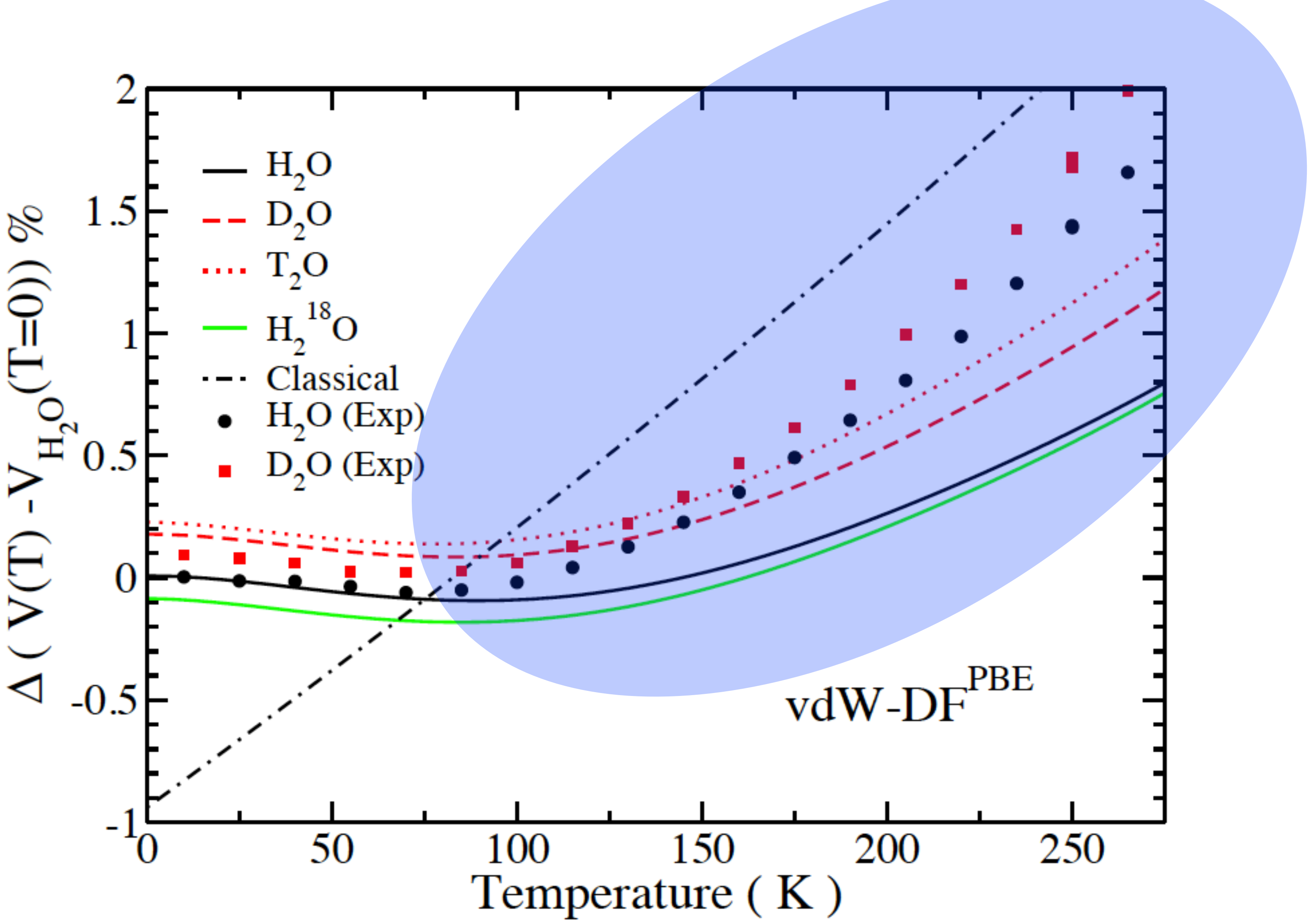
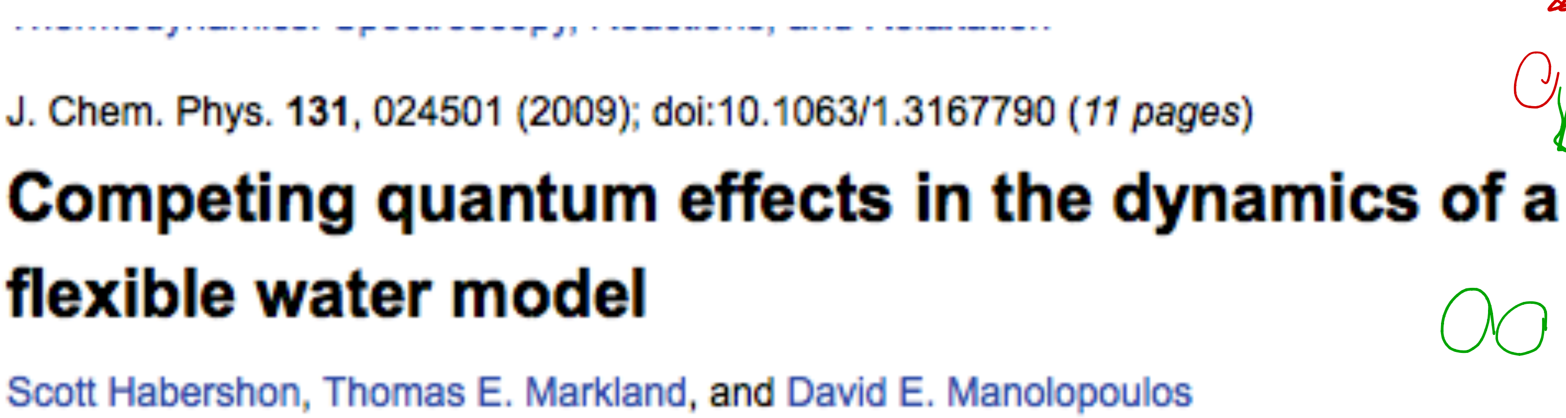


FIG. 2. (Color Online). Volume change $V(T)/V_{H_2O}(0) - 1$, relative to that of $H_2O$ at $T = 0$, for different isotopes calculated using the QHA with the vdW-DF$^{PBE}$ functional. Also shown are the experimental results from Ref. 10.

Overall anomalous isotope effect, H dominated

# What does the anomalous effect tell us about hydrogen bonding?



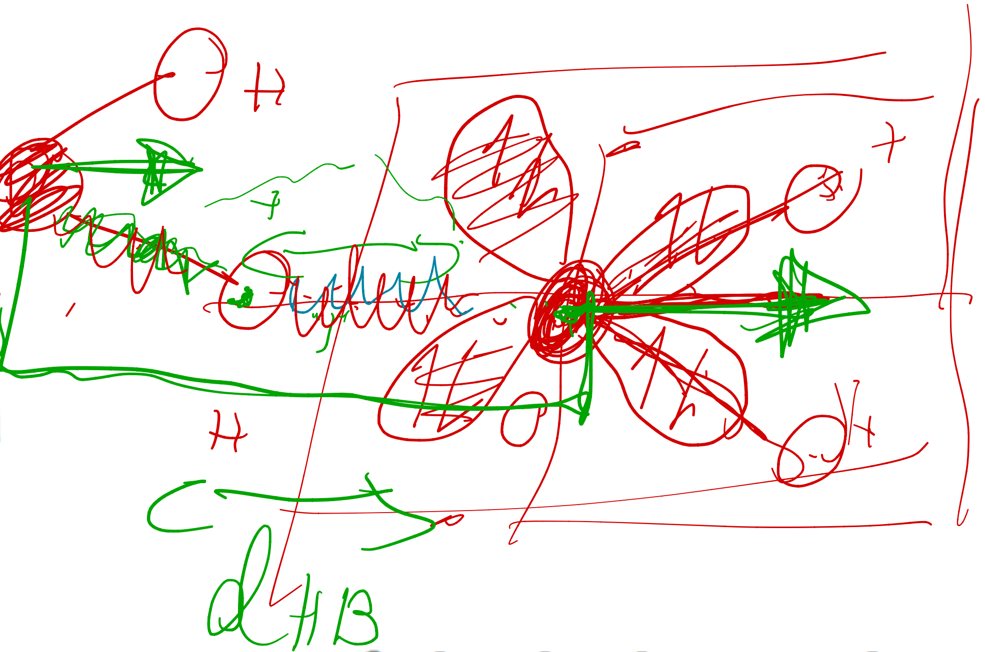
J. Chem. Phys. **131**, 024501 (2009); doi:10.1063/1.3167790 (*11 pages*)

**Competing quantum effects in the dynamics of a flexible water model**

Scott Habershon, Thomas E. Markland, and David E. Manolopoulos

"Intramolecular zero point fluctuations increase the average O–H bond length and the average molecular dipole moment, leading to stronger intermolecular interactions and slower diffusion, while intermolecular quantum fluctuations disrupt the hydrogen-bonding network leading to more rapid diffusion. In our q-TIP4P/F model, these two effects nearly cancel one another, leading to a comparatively small net quantum effect on the diffusion coefficient."

PIMD, 32 beads



**Quantum nature of the hydrogen bond**

Xin-Zheng Li, Brent Walker, and Angelos Michaelides[1]

PNAS, 108, 2011

Quantum effects weaken "weak" H-bonds and strengthen "Strong" Hbonds.

DFT (PBE)PIMD, only 16 beads!

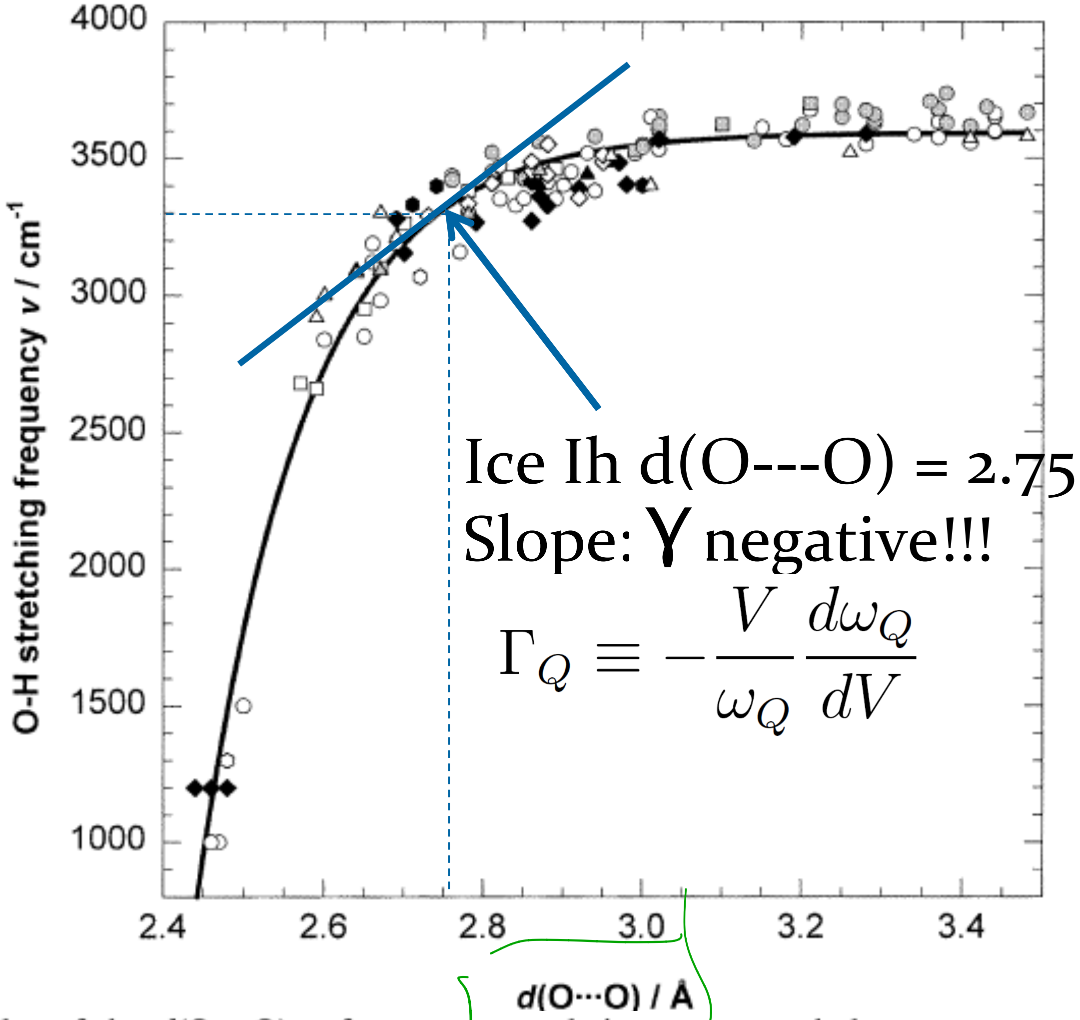
$H_2O \Rightarrow Ne$

# What does the anomalous effect tell us about hydrogen bonding?

## OH--O Anti-correlation Effect

- Well know effect in water and ice
- Common in Hbonded systems.

C. J. Burnham, G. F. Reiter, J. Mayers, T. Abdul-Redah, H. Reichert and H. Dosch, **On the origin of the redshift of the OH stretch in Ice Ih: evidence from the momentum distribution of the protons and the infrared spectral density**, Phys. Chem. Chem. Phys., 2006, 8, 3966



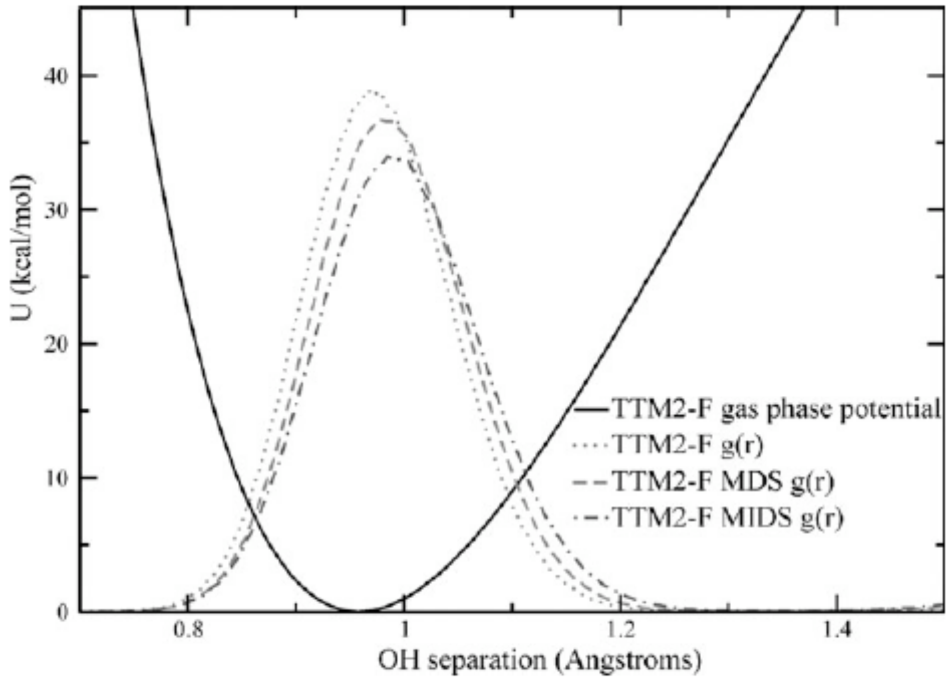
Ice Ih d(O---O) = 2.75 Å

Slope: γ negative!!!

$$\Gamma_Q \equiv -\frac{V}{\omega_Q}\frac{d\omega_Q}{dV}$$

**Fig. 1.** Plot of the $d(\mathrm{O}\cdots\mathrm{O})$ – frequency correlation; open symbols represent straight H bonds, shaded symbols mark bent H bonds, and filled ones denote copper compounds; circles – silicates, squares - (oxy)hydroxides, hexagons – carbonates, diamonds – sulfates, triangles – phosphates and arsenates; the regression curve was calculated for distances $<3.5$ Å ($n = 124$) in the form $\nu = 3592 - 304 \cdot 10^9 \cdot \exp(-d/0.1321)$, $R^2 = 0.96$

E. Libowitzky, 1999



# What does the anomalous effect tell us about hydrogen bonding?

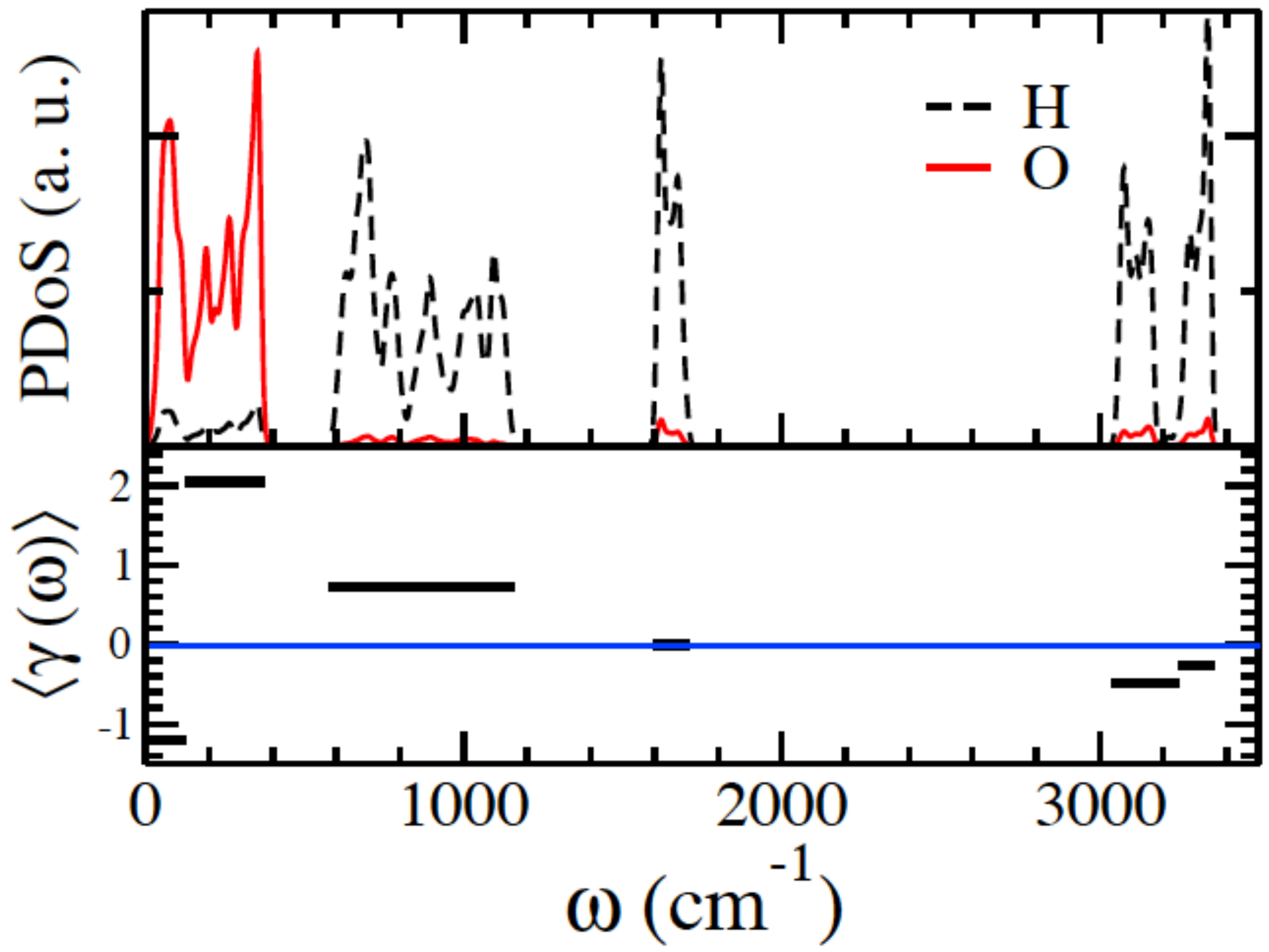


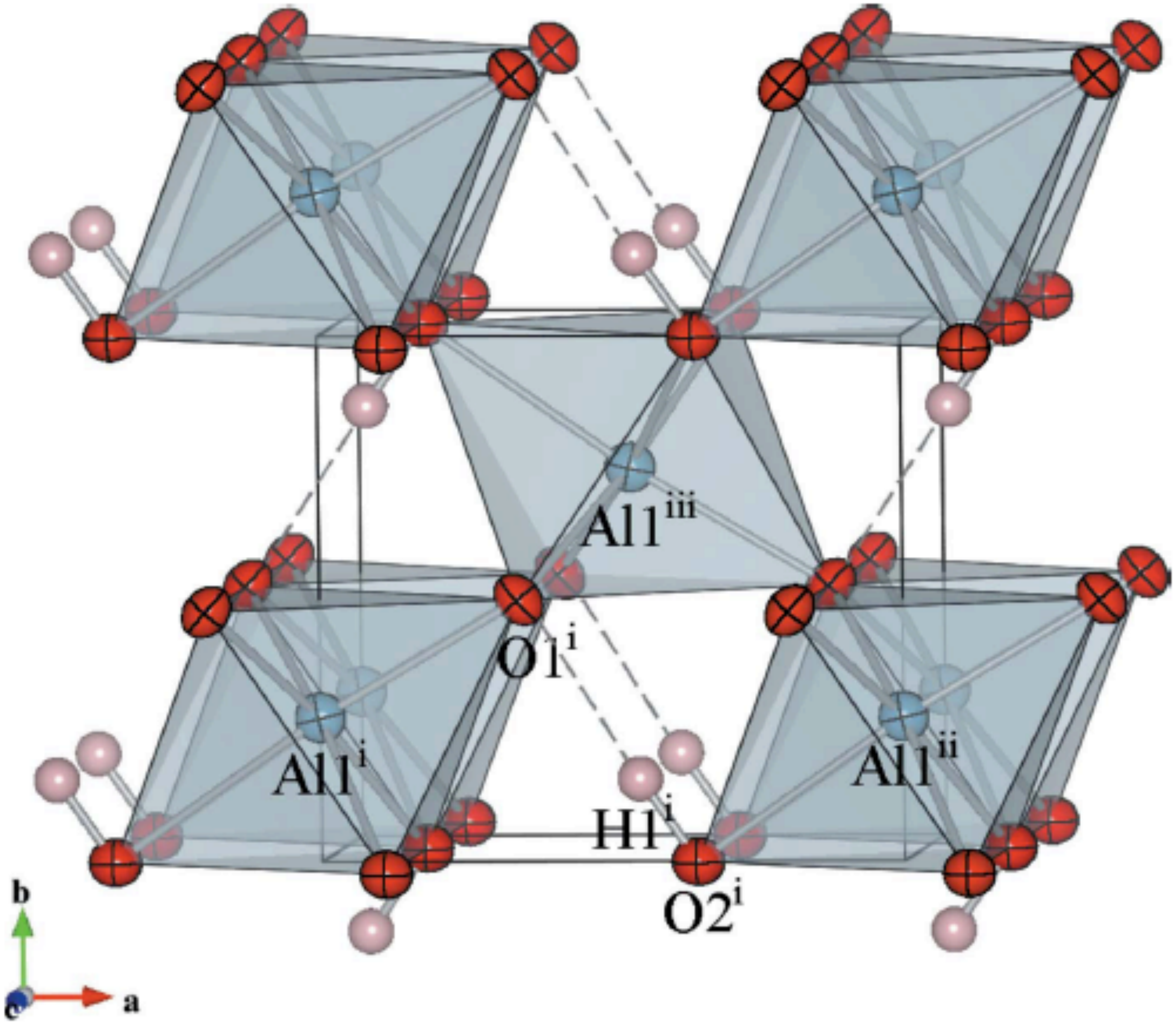
FIG. 3. (Color online). Top: Density of vibrational states for $H_2O$, projected onto H and O atoms, for the ordered ice Ih structure, as obtained with vdW-DF$^{PBE}$ functional. Bottom: average Grüneisen constants of the different modes.

# Is this anomaly exclusive to ice?

K. Komatsu, T. Kuribayashi, A. Sano, E. Ohtani and Y. Kudoh, Redetermination of the high-pressure modification of AlOOH from single-crystal synchrotron data, Acta Cryst. E, 62, i216 (2006).

Metastable at atmospheric pressure; an important deep earth water sink?
$(Al_2O_3)\cdot H_2O$

Each O atom binds to 3 Al, and shares 1 H with another O. A different kind of H-bond?



A. Sano-Furukawa, H. Kagi, T. Nagai, S. Nakano, S. Fukura, D. Ushijima, R. Iizuka, E. Ohtani, and T. Yagi, Change in compressibility of δ-AlOOH and δ-AlOOD at high pressure: A study of isotope effect and hydrogen-bond symmetrization, Am. Mineral. 76, 1769 (2009).

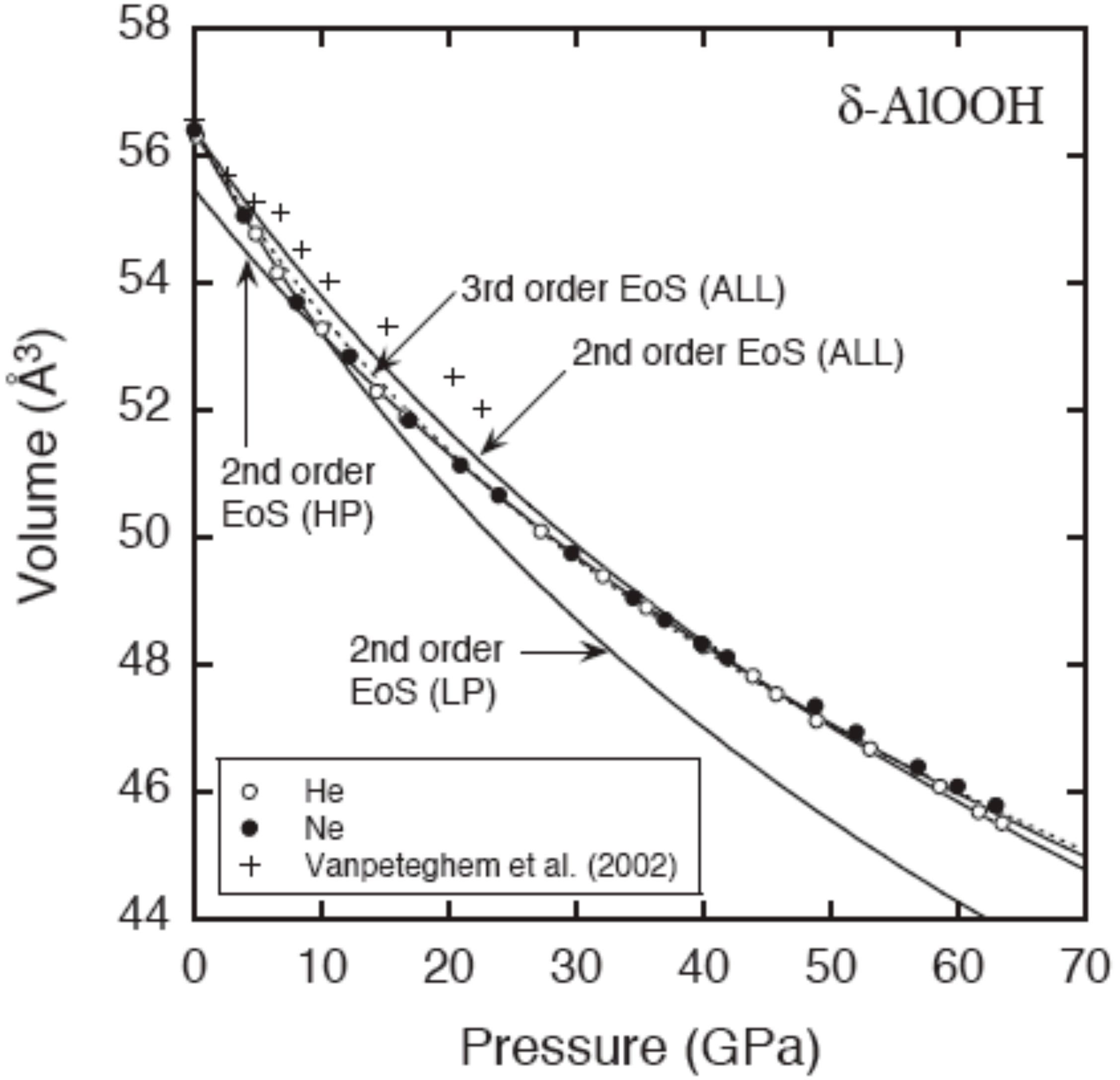


**FIGURE 5.** Pressure evolution of the unit-cell volume of δ-AlOOH. The solid lines represent the fit using a second-order Birch-Murnaghan equation of state for the data from ambient pressure to 63.5 GPa (ALL), to 10 GPa (LP = low pressure) and from 10 to 63.5 GPa (HP = high pressure). The dashed line represents the fit to a third-order Birch-Murnaghan equation of state for the data to 63.5 GPa. Error bars are smaller than the symbol size.

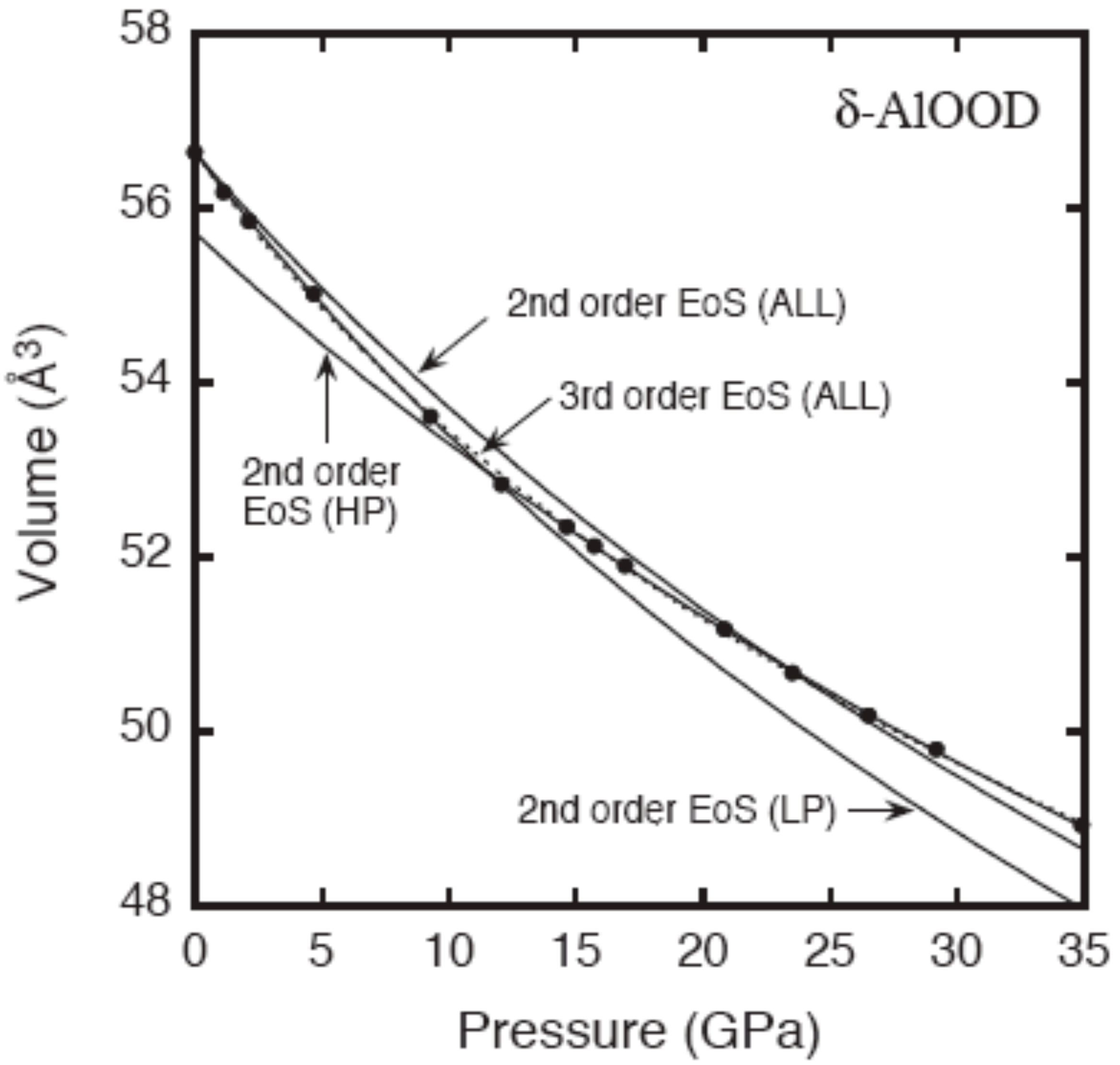
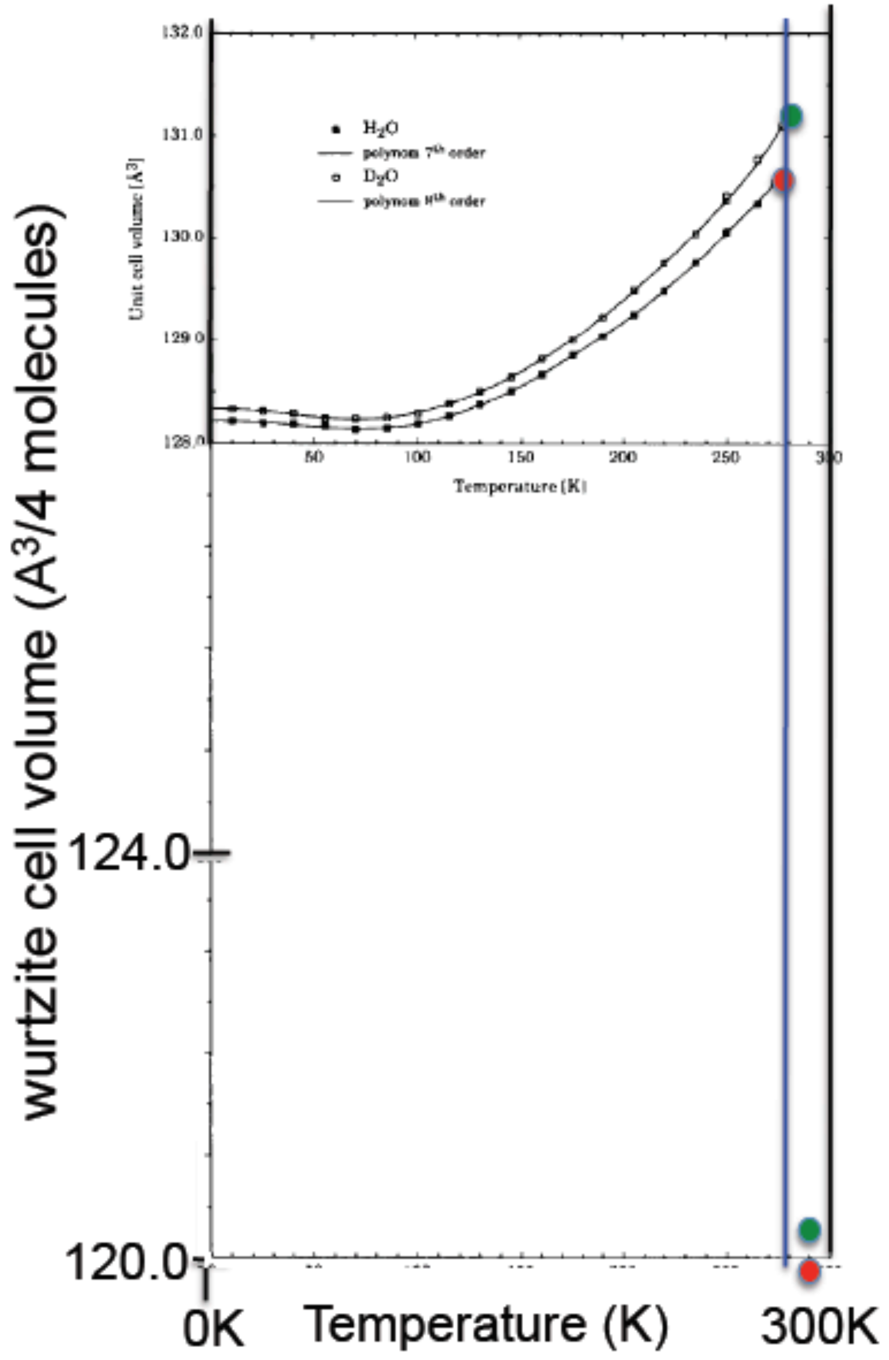


**FIGURE 6.** Pressure evolution of the unit-cell volume of δ-AlOOD. The solid lines represent the fit using second-order Birch-Murnaghan equation of state for the data from ambient pressure to 34.9 GPa (ALL), to 12.1 GPa (LP) and from 12.1 to 34.9 GPa (HP). The dashed line represents the fit to a third-order Birch-Murnaghan equation of state for the data to 34.9 GPa. Error bars are smaller than the symbol size.

0.4% inverse isotope volume shift at 300K

# Is this anomaly exclusive to ice?



Heavy water (at 290K) has 0.37%
more volume per molecule than light water.

•Heavy ice melts at 3.82°C
and (at 265K) has 0.24% more
volume per molecule than light water.

•Deviation is increasing rather
than decreasing as T increases

Questions:

1\. Can good force fields reproduce experiments?

2.Is quasi-harmonic theory? sufficient?

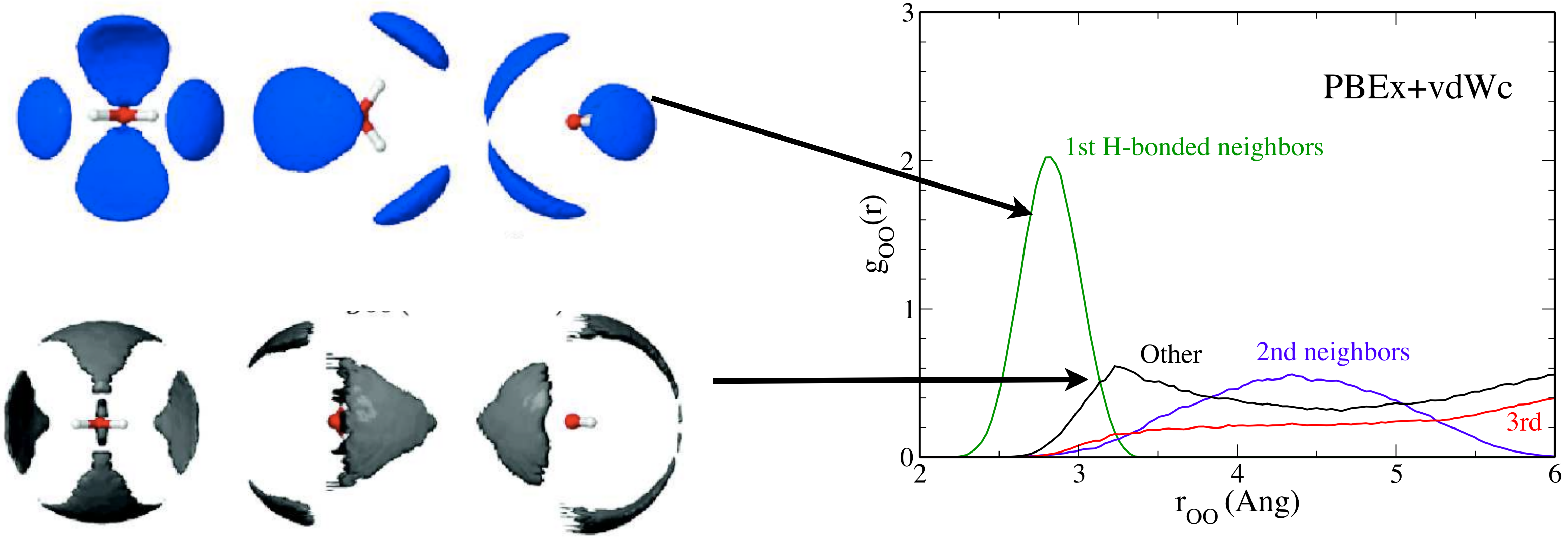
3\. Can DFT reproduce experiments?

- Are van der Waals correlations important
- How sensitive are Grüneisen parameters to the XC?

3.What does it tell us about hydrogen bonding?

# Can we predict what will nuclear quantum effects will do in water?

- The structure of water is very different. There are interstitial vdW-type bonds that change the potential energy surface.
- Both stretching and libration frequencies are red-shifted in water, therefore an argument cannot be made in favor of an overall strengthening or weakening effect without detailed analysis.
- The QHA works very well for ice. It might also give useful information in the analysis of inherent structures in water.



3.15 H-bonds/molecule

# Conclusions

- Quasi-harmonic approximation works very well in ice.
- “New” water anomaly: inverse (proton) and normal (O) isotopes effect in the volume of ice.
- At low T the normal effect dominates, but for T>~100K the inverse isotope effect governs the behavior.
- The effects are large at the melting temperature, might also be important in liquid water.
- Flexible force fields should aim to reproduce frequencies and their derivatives in order to capture the effect.