HIGH PRESSURE WATER, QUANTUM COMPUTERS, AND MORE

Bryan Clark

Two (unrelated) short stories

1. What happens in water at high pressure and high temperature?

with Jiming Sun and Roberto Car

2. Will we all be using quantum computers to do quantum chemistry soon?

with Dave Wecker, Bela Bauer, Matt Hastings, Matthias Troyer

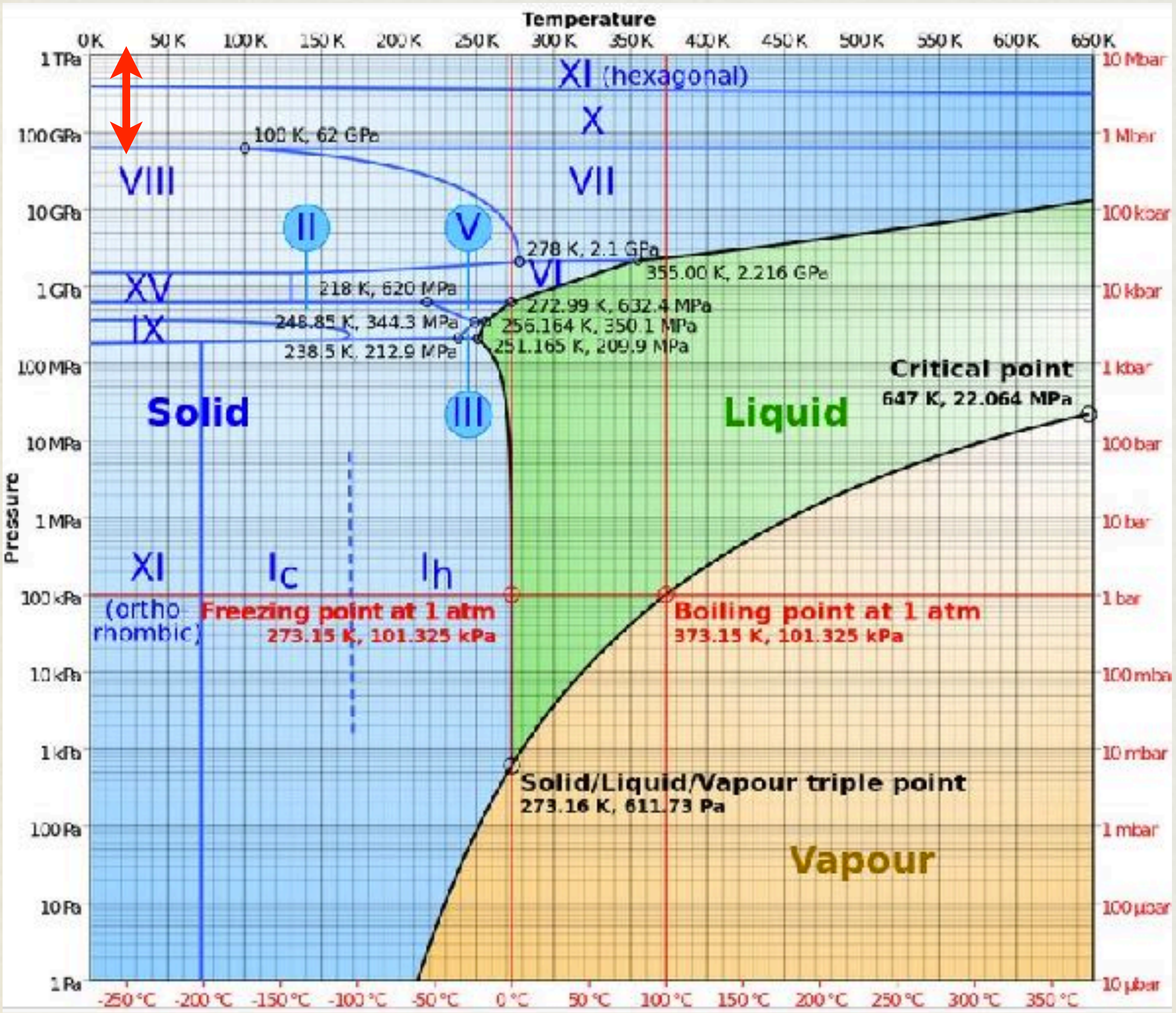
Two (unrelated) short stories

1. What happens in water at high pressure and high temperature?

2. Will we all be using quantum computers to do quantum chemistry soon?

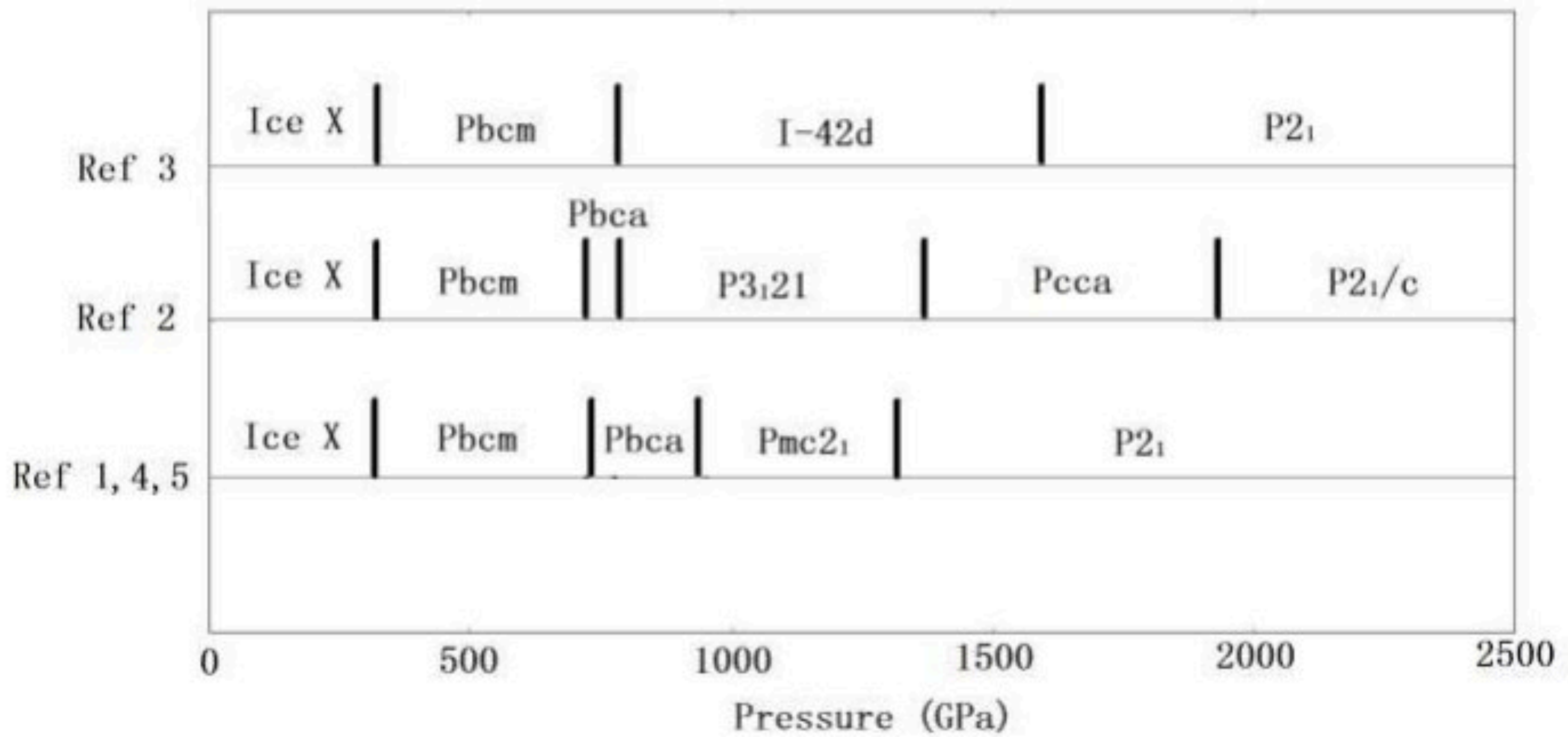
Water is complicated...

What happens at high pressure?



What happens at high pressure?

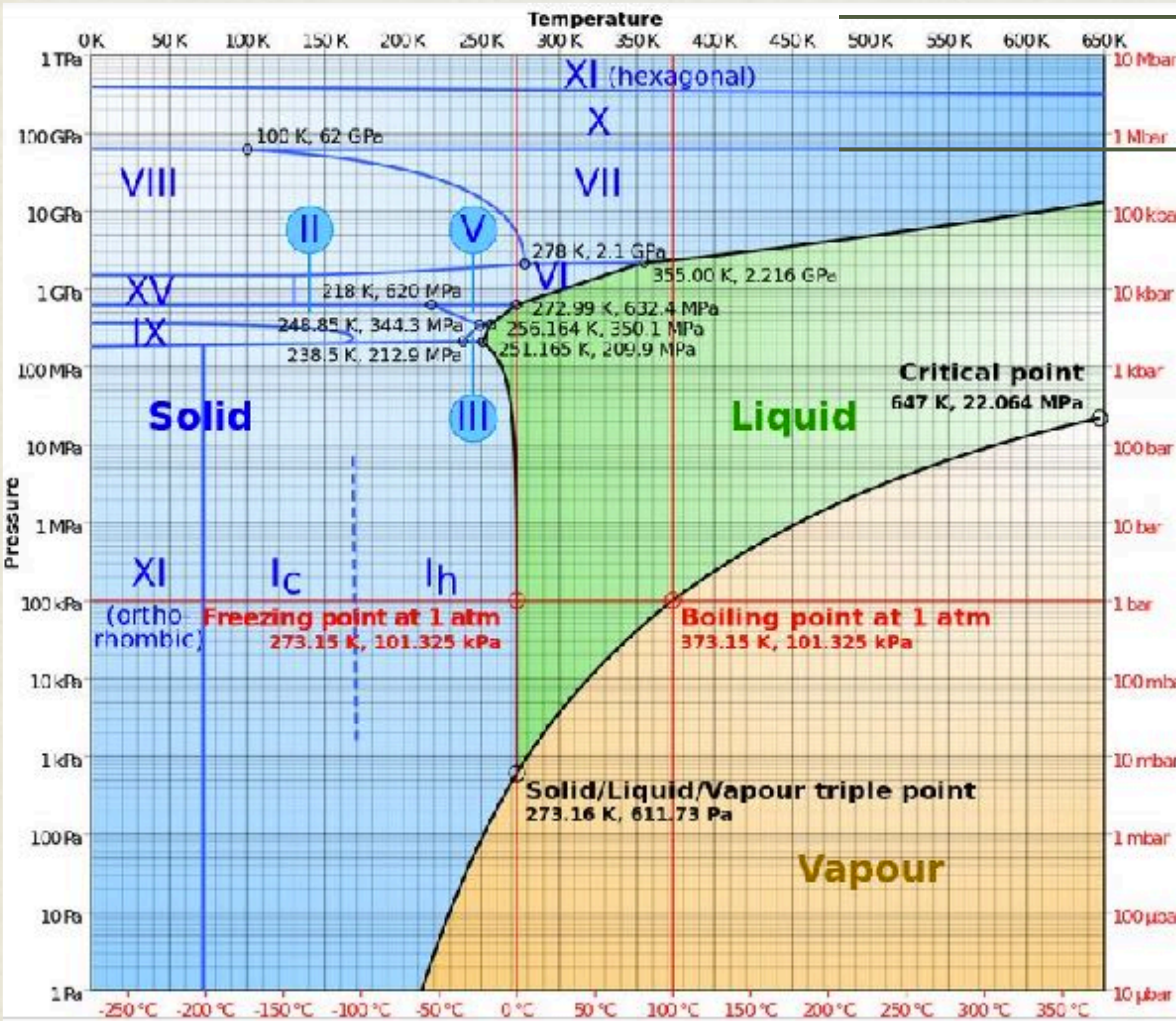
It's a mess. Many groups…many results.



Phase diagram of high pressure ice at 0K

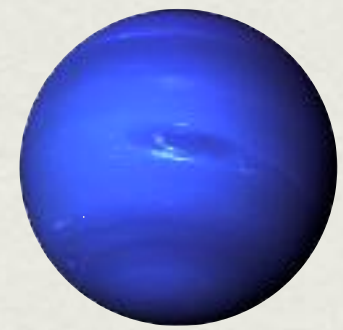
Ref 1. A. Hermann et al., PNAS, 109, 745(2012)
Ref 2. Chris J. Pickard et al., PRL, 110, 245701 (2013)
Ref 3. Yanchao Wang et al., Nature Comm, 2, 563 (2011)
Ref 4. Jeffrey M. McMahon, PRB, 84, 220104(2011)
Ref 5. Min Ji et al., PRB, 84, 220105(2011)

High Pressure + High Temperature



2000 K

What happens out here?



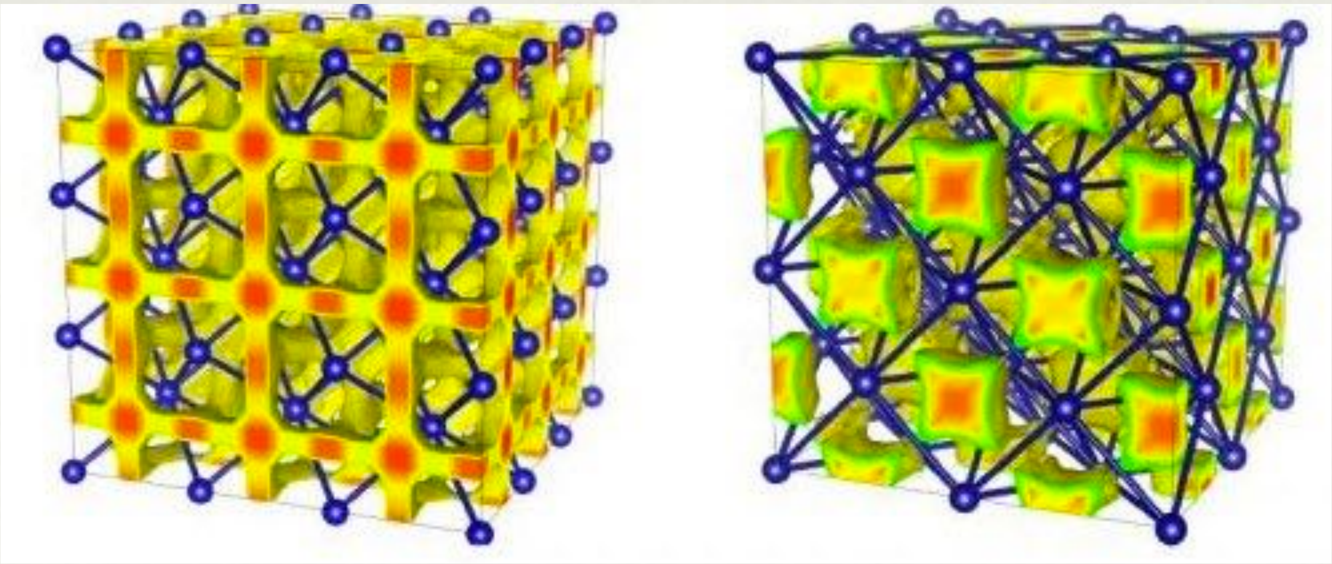
700 GPa - 5400 Kelvin

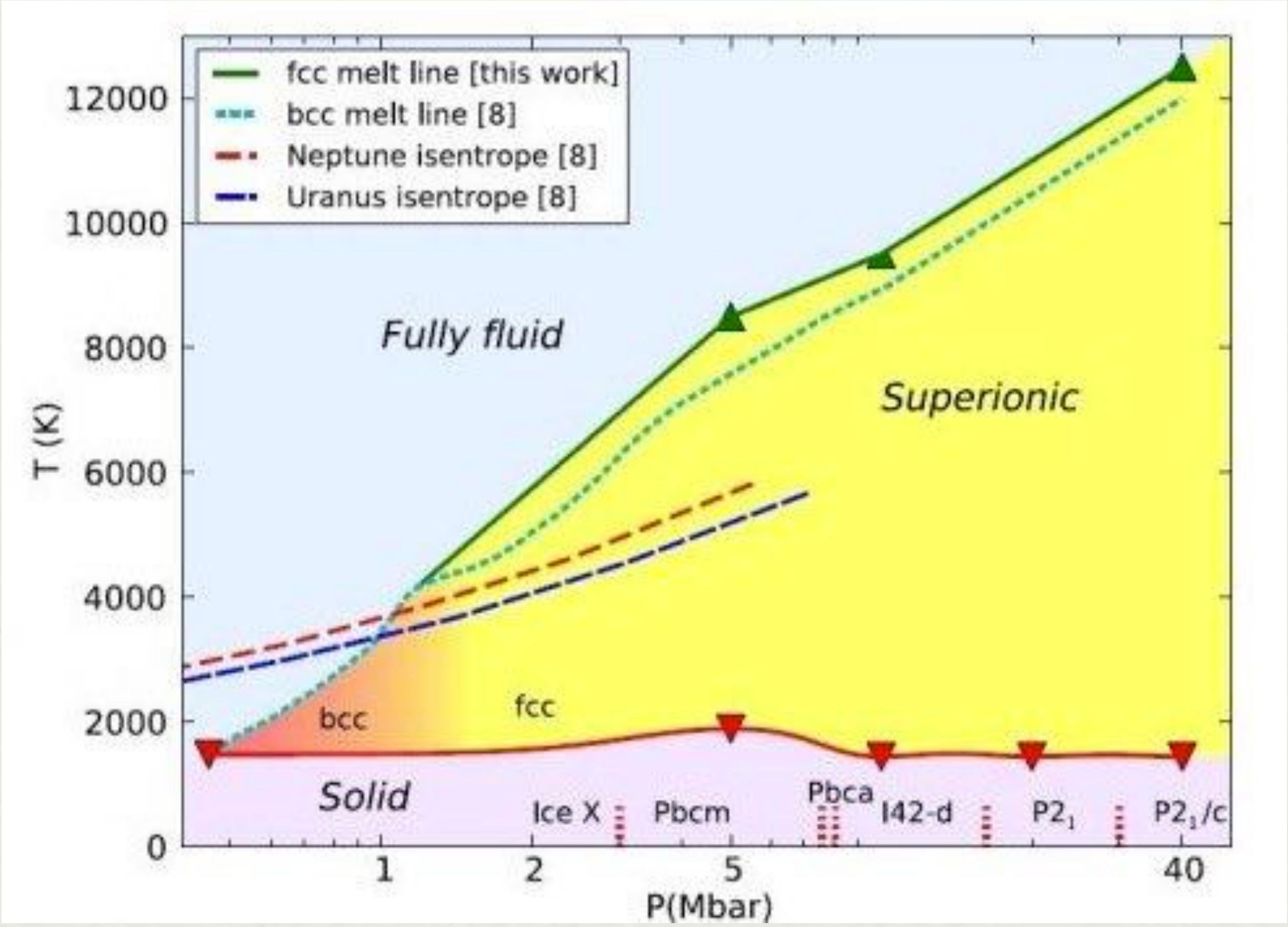
800 GPa - 5000 Kelvin

1500 GPa - 6000 Kelvin

3400 GPa - 3600 Kelvin

Superionic ice





Hugh F. Wilson, Michael L. Wong, and Burkhard Militzer. Superionic to superionic phase change in water: Consequences for the interiors of uranus and neptune. Phys. Rev. Lett.,110:151102, Apr 2013.

Lots of approaches:

random structure searching

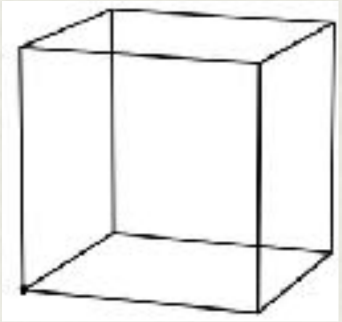
genetic algorithms

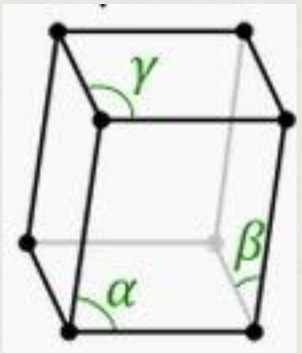
Variable cell Car-Parinello molecule dynamics

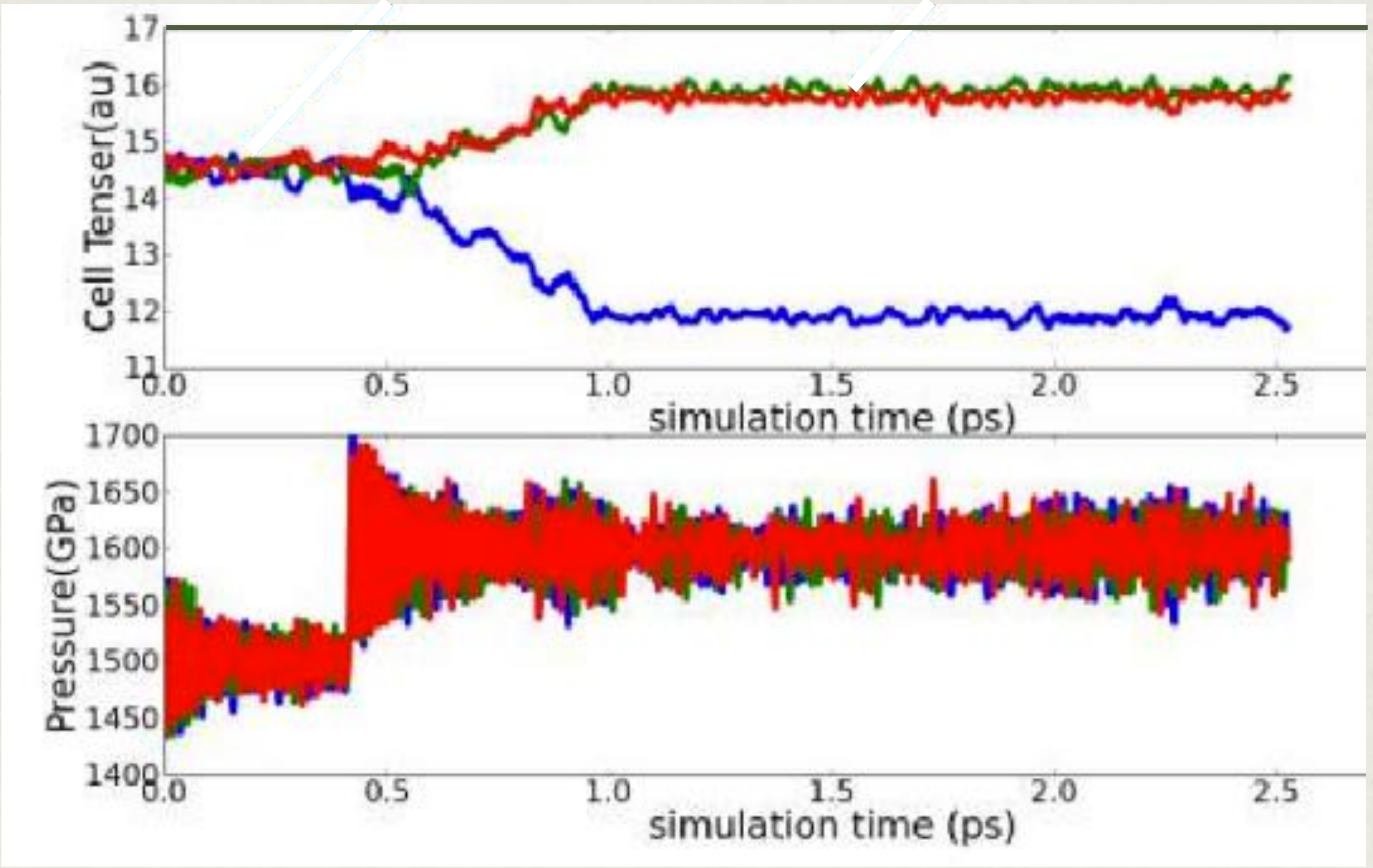
- Γ point
- More than 108 particles
- PBE Functional
- 1500 eV cutoff
- 'trick' to keep energy cutoff same as cell changes

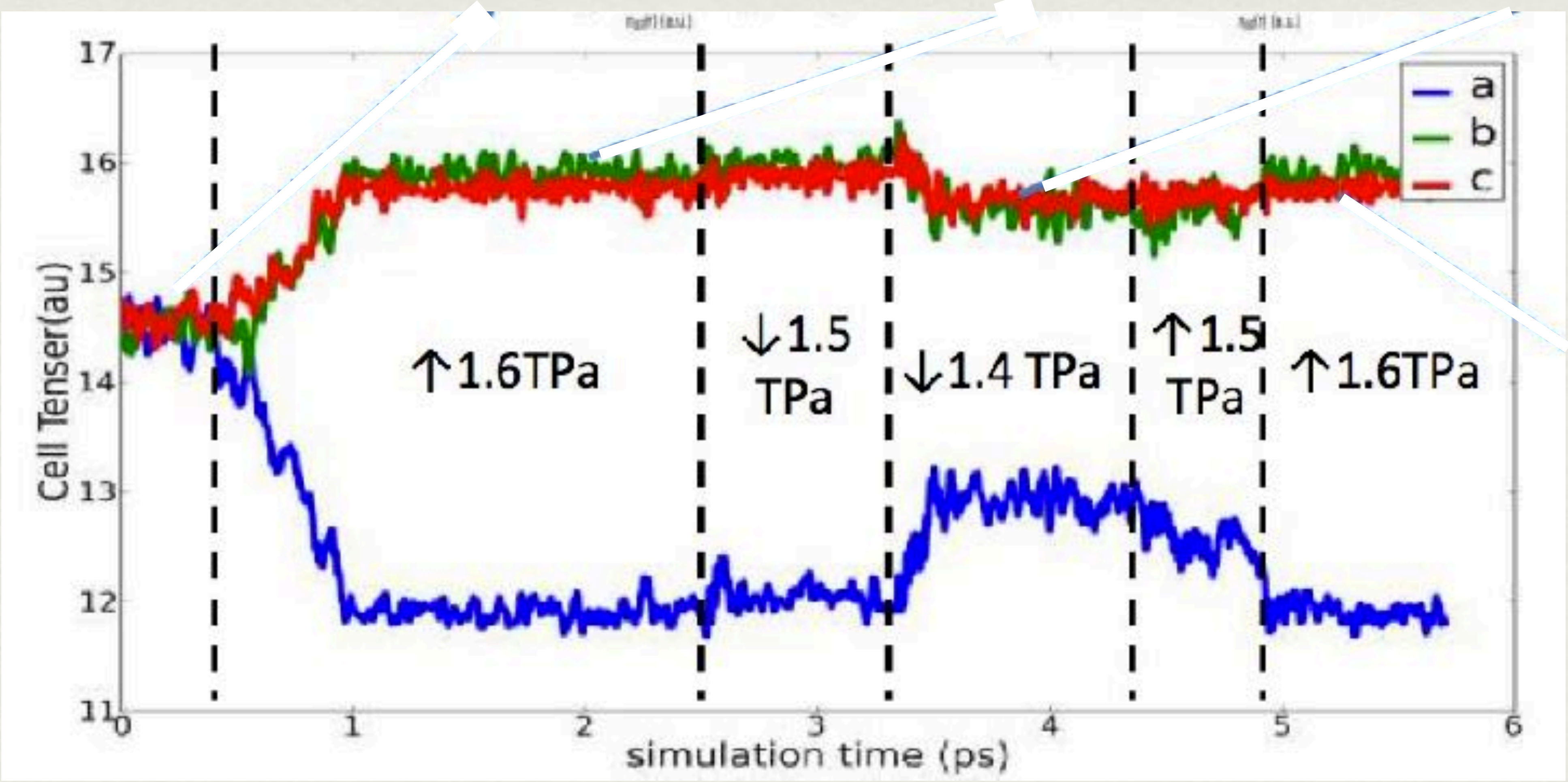
FCC

P21/c

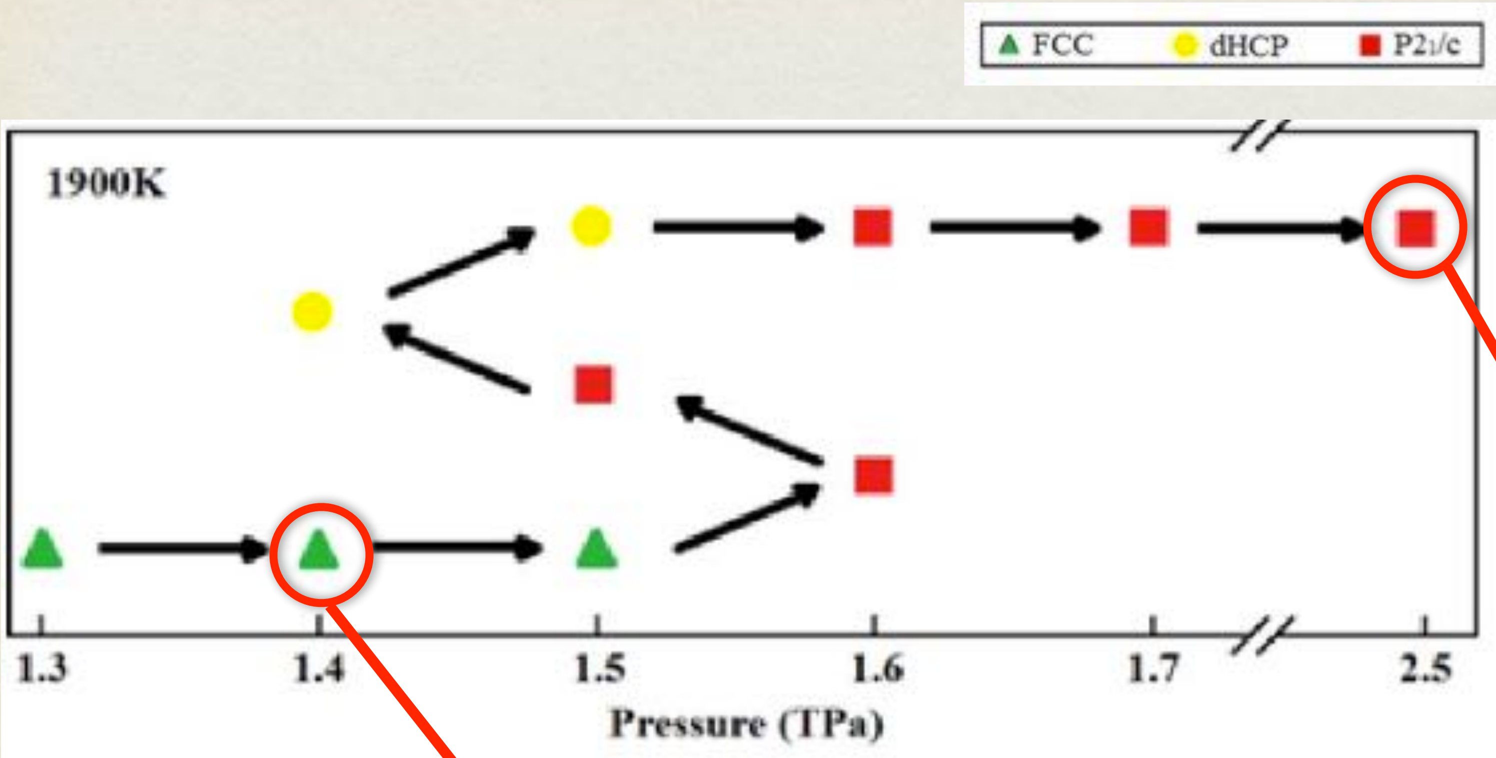


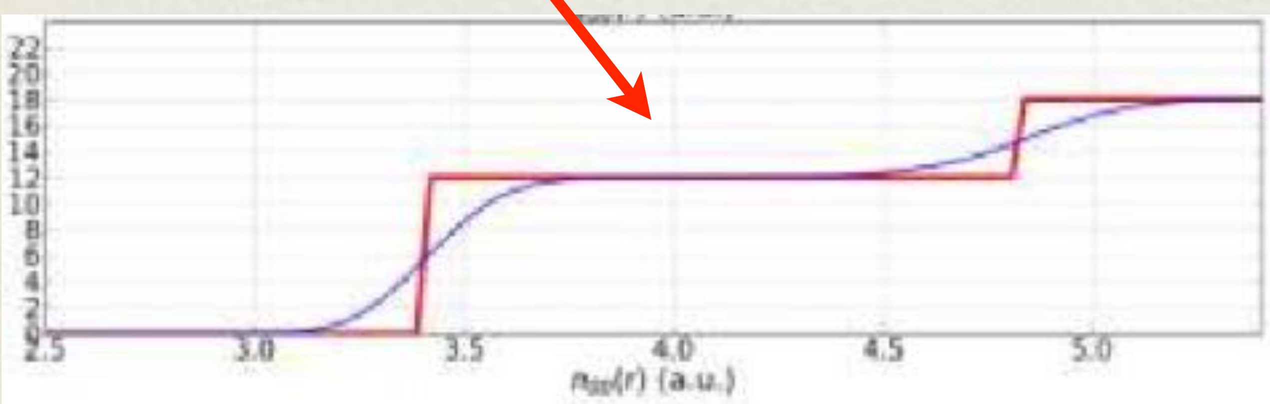

γ
β
α

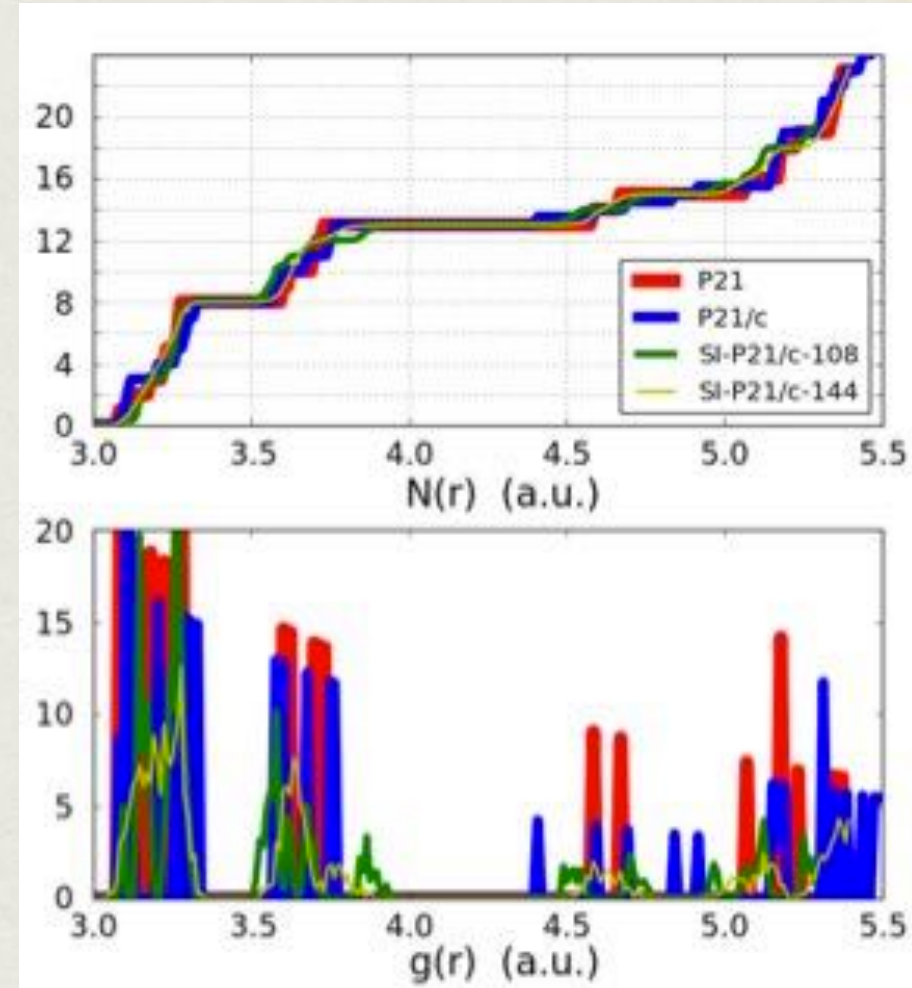

Cell Tenser(au)
17
16
15
14
13
12
11
0.0
0.5
1.0
1.5
2.0
2.5
simulation time (ps)
Pressure(GPa)
1700
1650
1600
1550
1500
1450
1400
0.0
0.5
1.0
1.5
2.0
2.5
simulation time (ps)



Cell Tenser(au)
simulation time (ps)
a
b
c
↑1.6TPa
↓1.5 TPa
↓1.4 TPa
↑1.5 TPa
↑1.6TPa

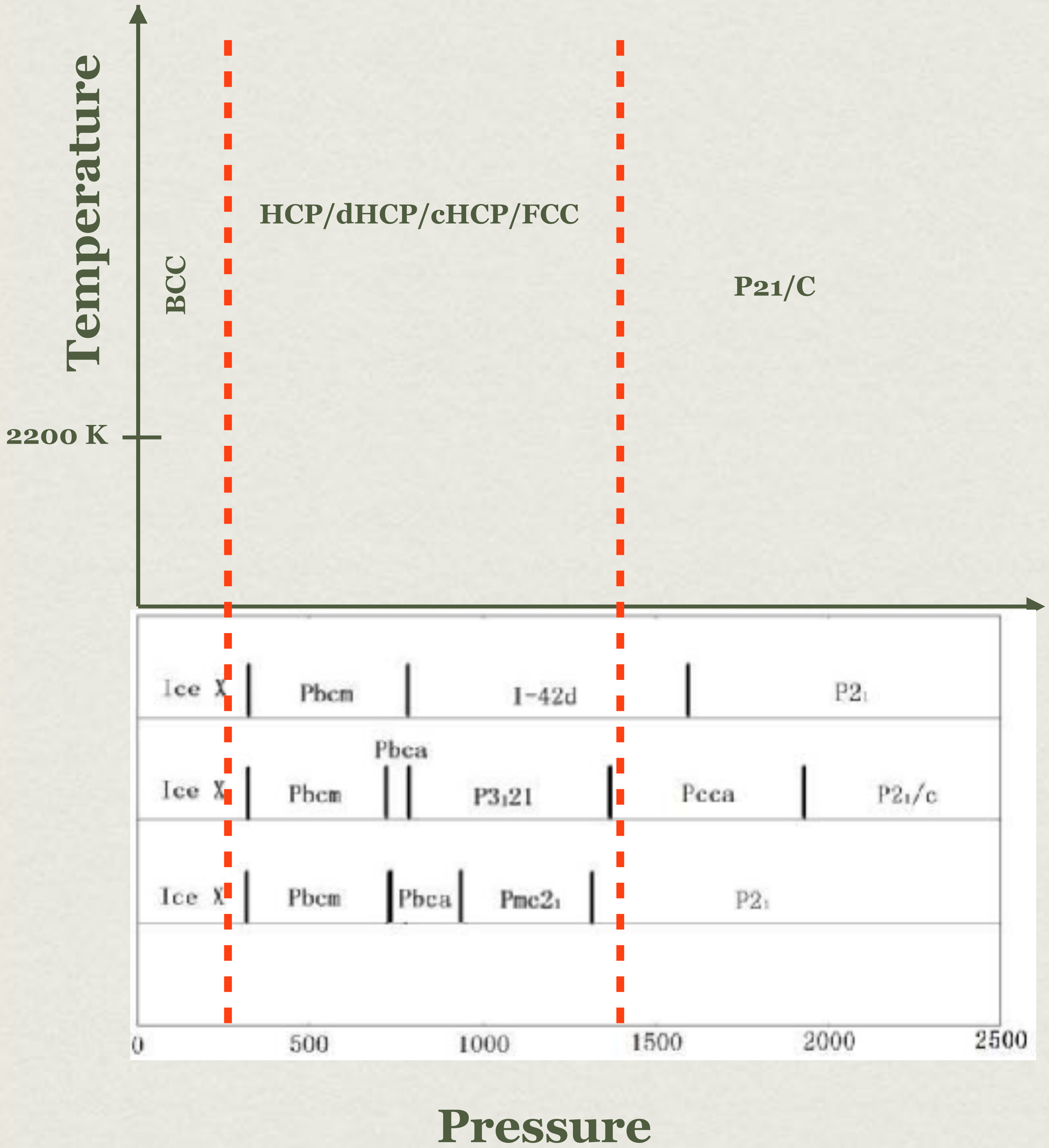






- Like ground state P21
- Like ground state P21/c
- Symmetry of P21/c
- 4 atom per unit

cell


Temperature
2200 K
BCC
HCP/dHCP/cHCP/FCC
P21/C
Ice X
Pbcm
I-42d
P2₁
Pbca
P3₁21
Pcca
P2₁/c
Pmc2₁
0
500
1000
1500
2000
2500
Pressure

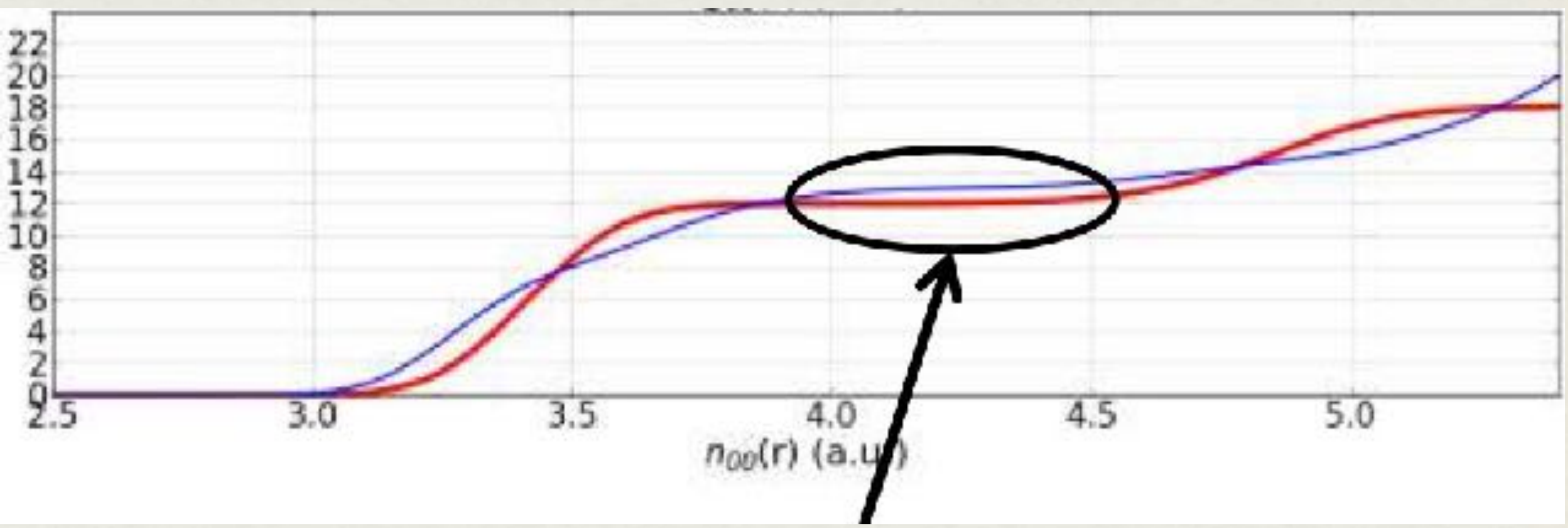
Why P21/c?

$$\Delta H = \Delta U + P\Delta V$$

Higher Packing fraction

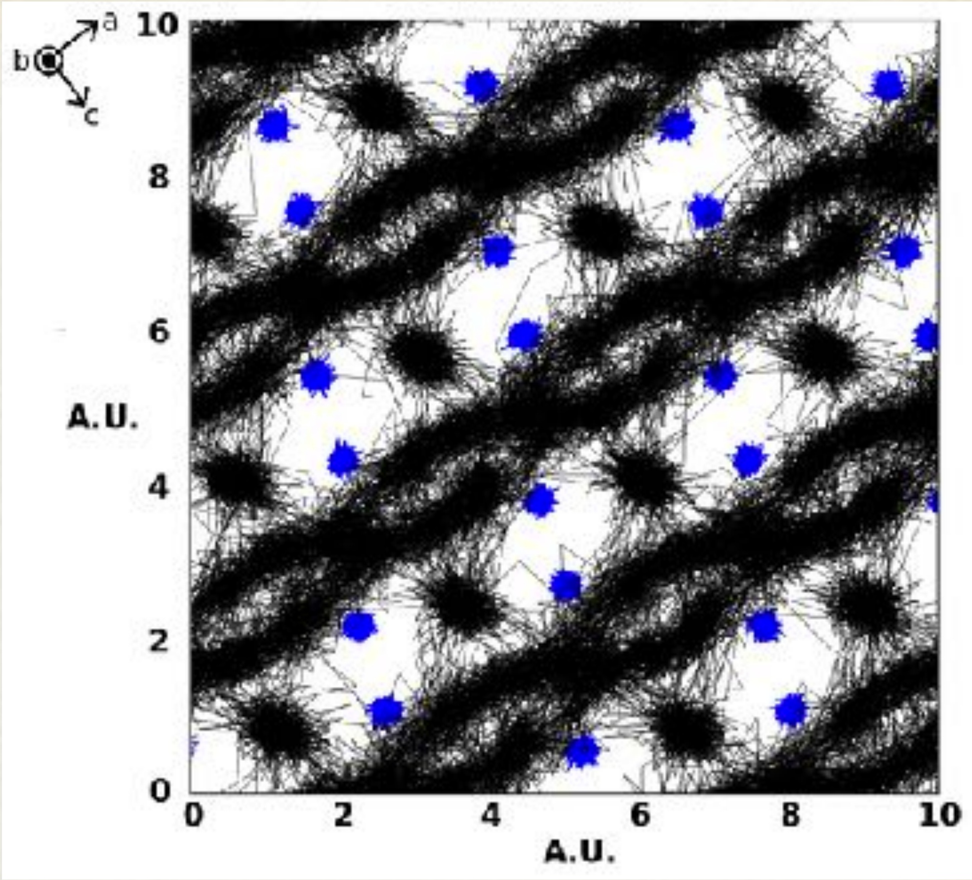
Change (FCC->"P21")	
ΔH	-0.23eV/mol
ΔV	-0.19au³/mol
PΔV	-0.28eV/mol
ΔU	+0.05eV/mol

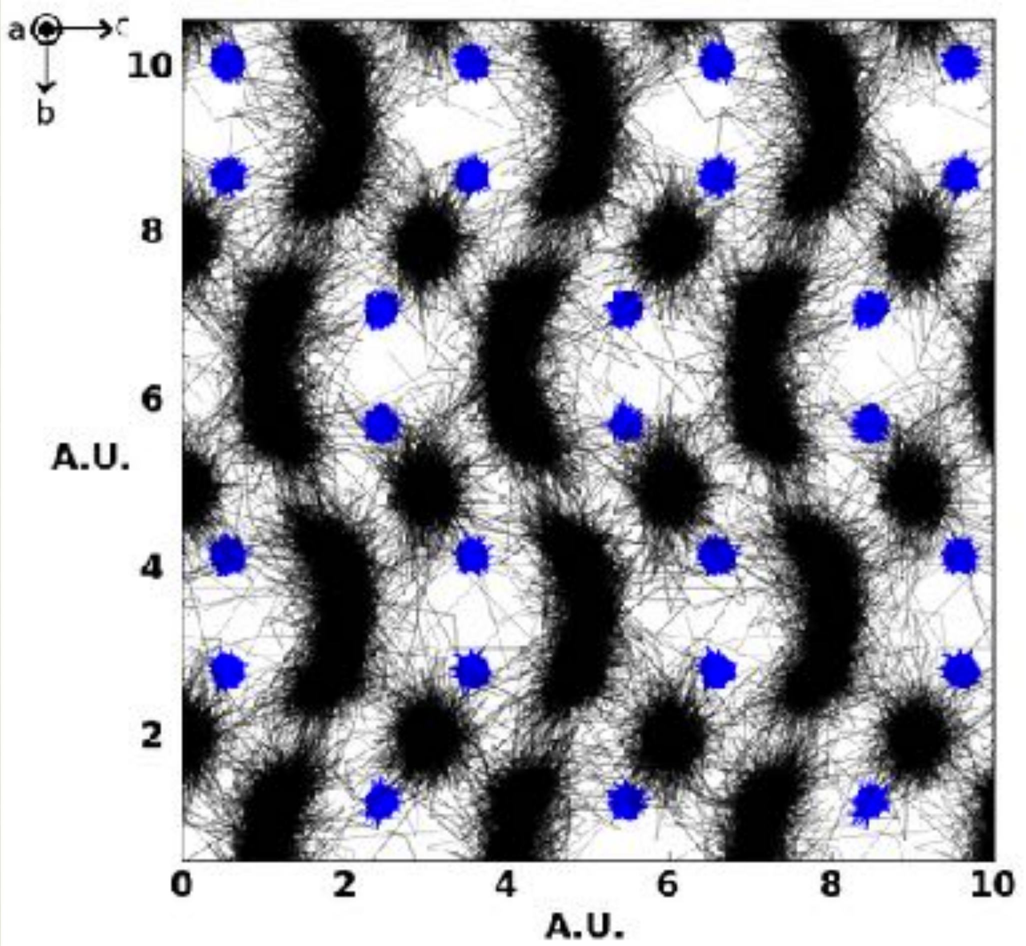
Coordination #

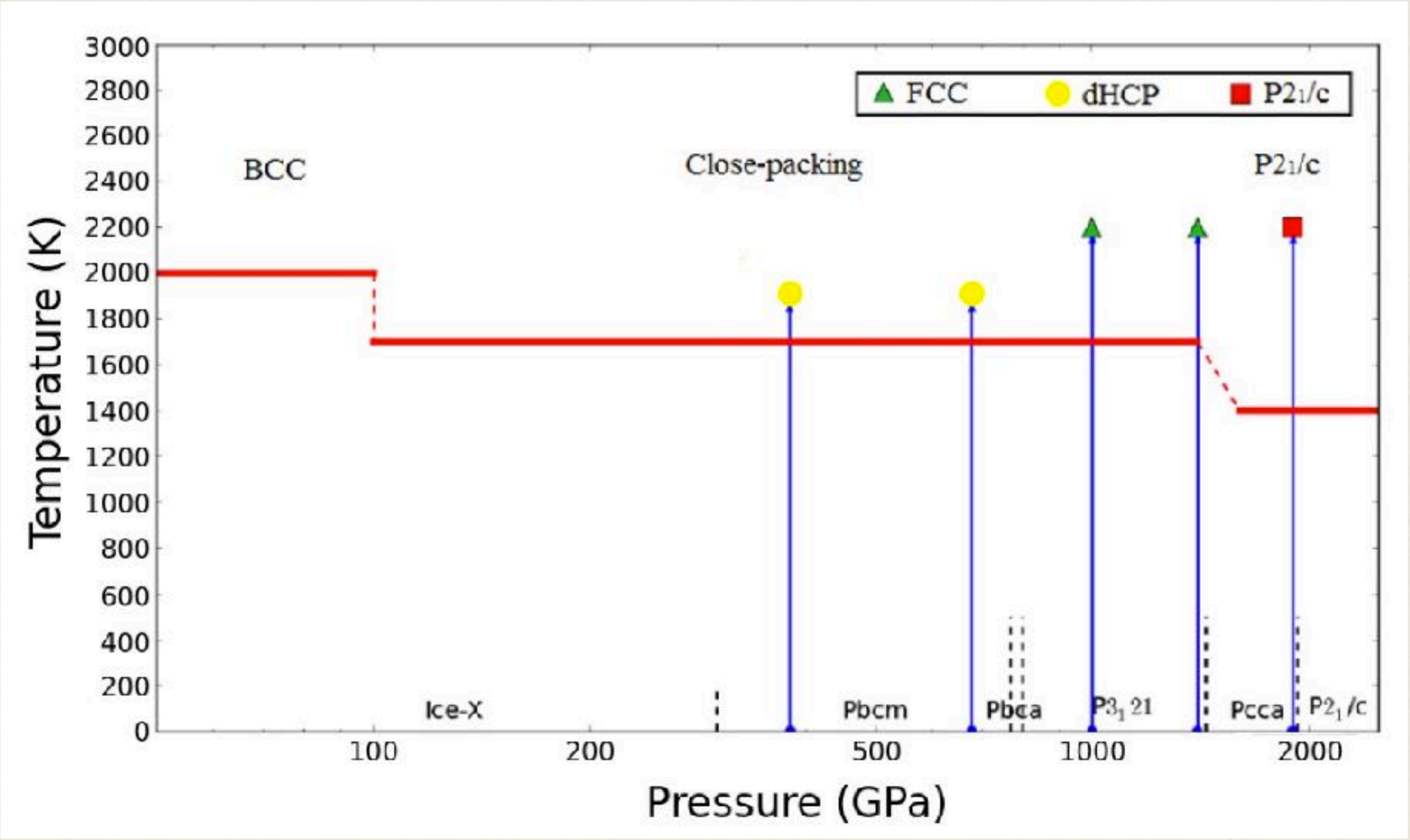


One more oxygen

- Diffusion: 4:3:1
- 2d liquid planes
- slow diffusion
- 8 out of 10 sites





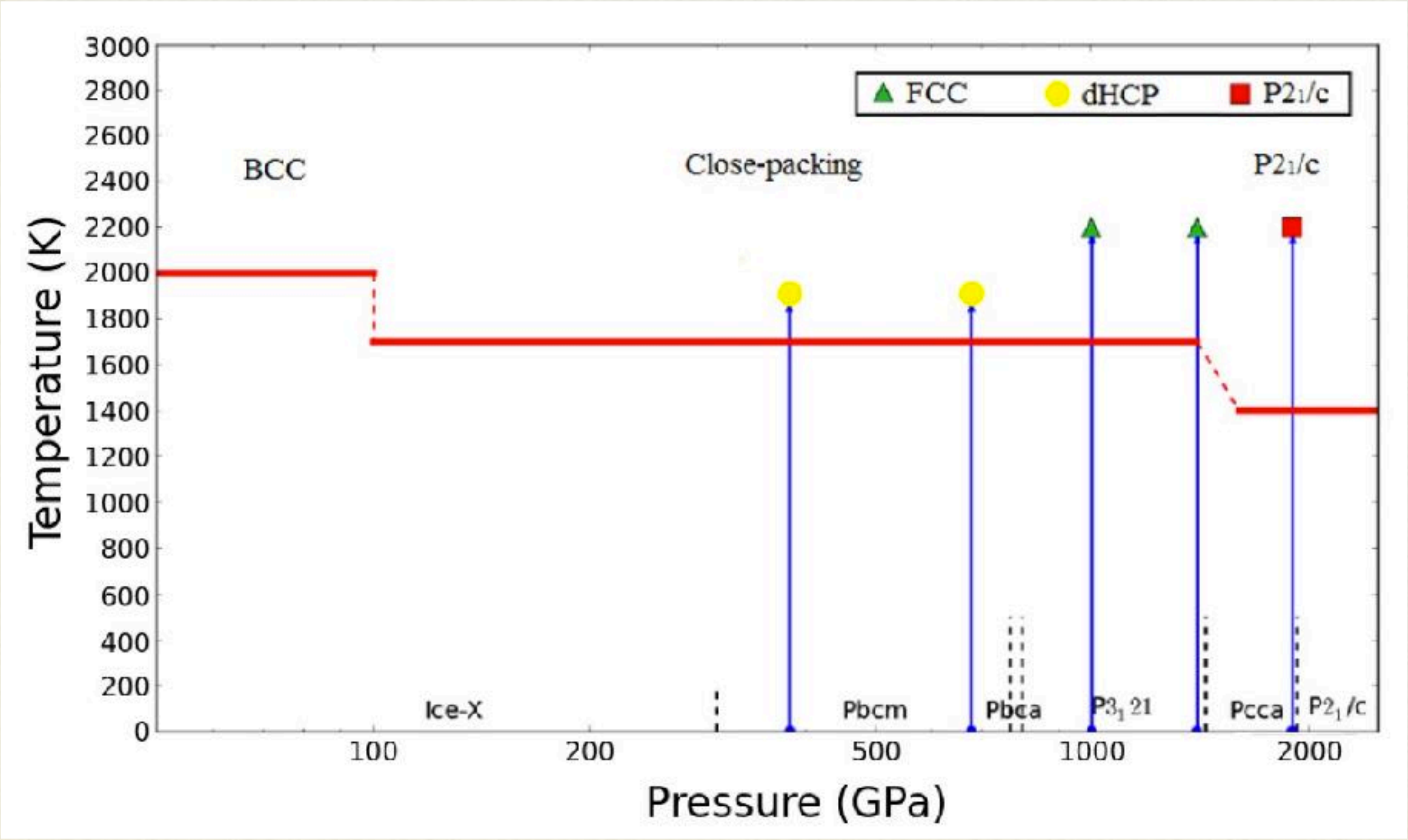


FCC
dHCP
P2₁/c
BCC
Close-packing
P2₁/c
Temperature (K)
Pressure (GPa)
Ice-X
Pbcm
Pbca
P3₁21
Pcca
P2₁/c

Melting...

Hydrogen: 600 - 1000K
Deuterium: 300-500K
Oxygen: 200K

$$T_{eff} = T + \frac{\hbar^2}{12T^2 m_i} \overline{(\frac{\partial U}{\partial q_{i\alpha}})^2},$$



Conclusion: Story I

At high temperature and high pressure, there is an additional superionic “P21/c” phase and it might melt around 500K

Two (unrelated) short stories

1. What happens in water at high pressure and high temperature?

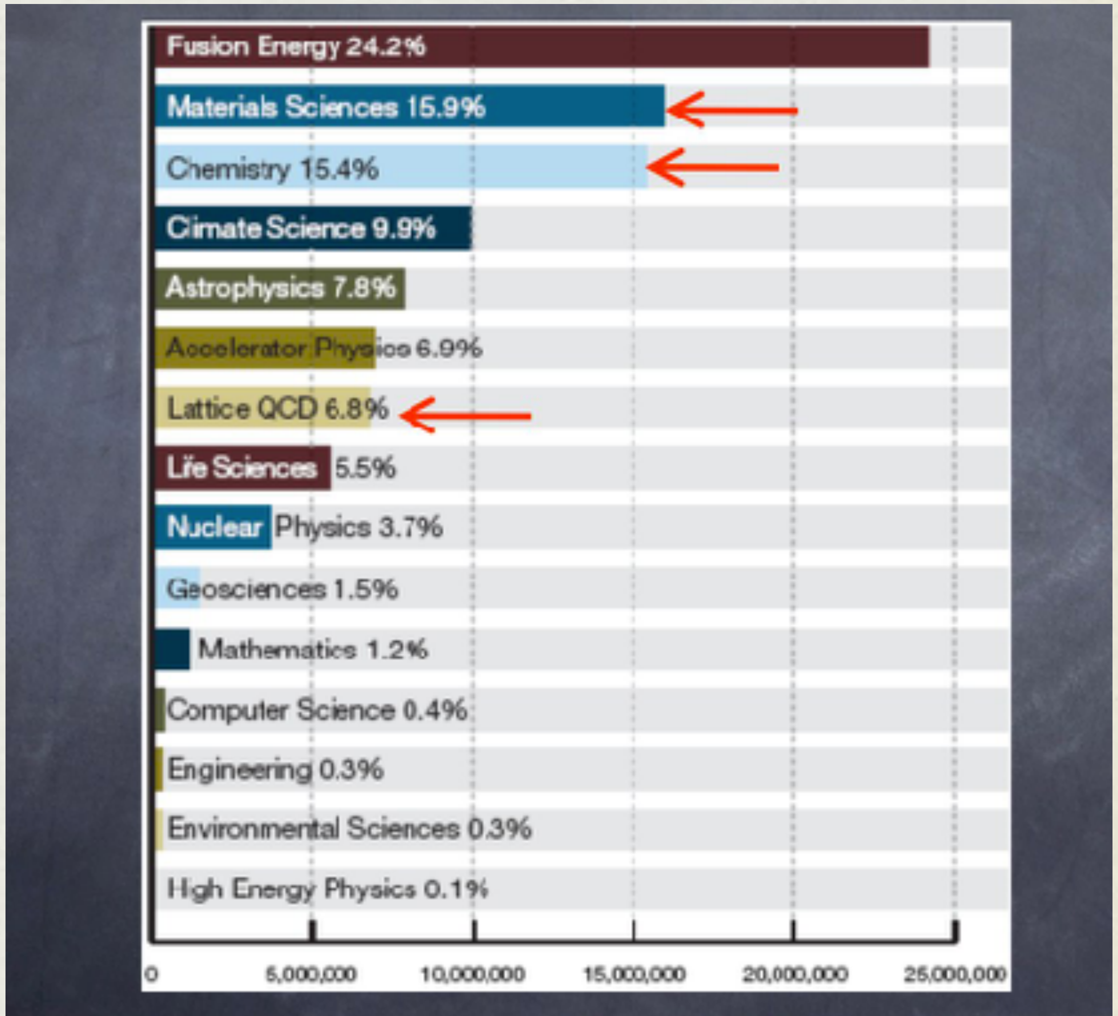
2. Will we all be using quantum computers to do quantum chemistry soon?

Quantum Simulation is hard...

Will quantum computers make it easier?

1. Are quantum computers faster than classical computers?

2. Are they fast enough to compute anything in a graduate student lifetime?



From a talk by S. Aaronson from a talk by A. Aspuru-Guzik.

The quantum chemistry Hamiltonian:

$$H = \sum_{pq} t_{pq} c_p^\dagger c_q + \frac{1}{2} \sum_{pqrs} \underline{V_{pqrs}} c_p^\dagger c_q^\dagger c_r c_s$$

Calculated once per molecule
N^4 numbers

Only N^4 non-zeros per row

Sparse and structure-full....

Want: Ground state energies, forces....

Naively this looks like it might be hard for a quantum computer.
Quantum computers do unitary things and this is dissipative.

Even for sign-problem highly-entangled problems there are often classical algorithms which achieve a ‘good enough’ approximation.

Metric of ‘good enough’: chemical accuracy

1 milliHartree (out of 100 Hartree)

To chemical accuracy:

- N=50 spin orbitals - Lancoz
- N=70 spin orbitals - Tensor Networks
- N>>100 spin orbitals - CCSD(T) on weakly correlated
- Electrons ~ 30 - QMC Variants

- ED: 1 site per year
- Tensor Networks: ~10 site per year

Aside: Any QC algorithm ~30-50 qubits simulatable

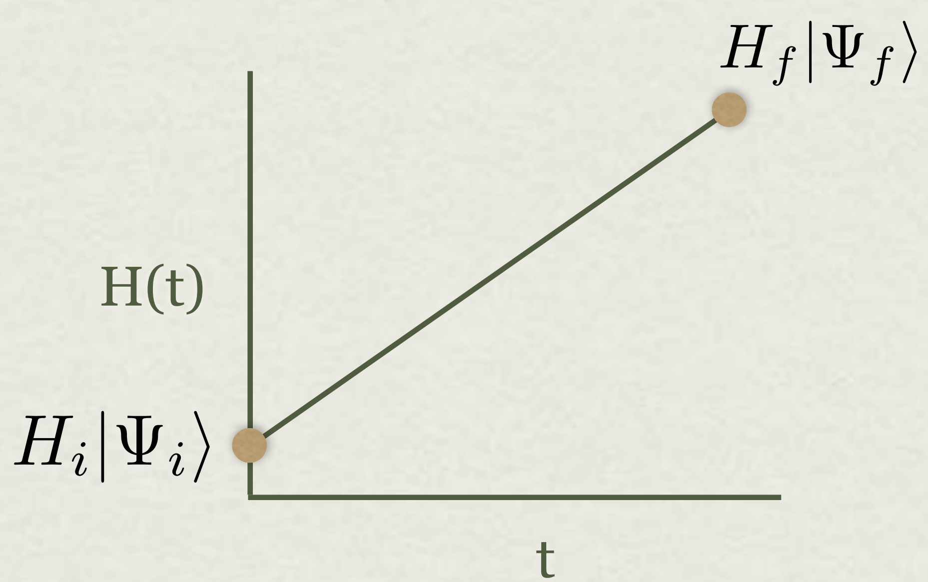
38 qbits -> 10 minutes per step

The quantum algorithm for getting ground state (energies)?

Two generic approaches

Adiabatic

- ☐ Start in Ψ_i as ground state of H_i
  $\exp[-itH(t)]$
- ☐



Phase Estimation

- ☐ Start close to ground state: $|\Psi_T\rangle = \sum_i \alpha_i |0\rangle|\Psi_i\rangle$
- ☐ Apply Phase Estimation: $\sum_i \alpha_i |E_i\rangle|\Psi_i\rangle$
- ☐ Measure E_i with probability α_i^2 getting Ψ_i

1. Are quantum computers faster than classical computers?
   Yes
2. Are they fast enough to compute anything in a graduate student lifetime?

The quantum algorithm for getting ground state (energies)?

Two generic approaches

Adiabatic

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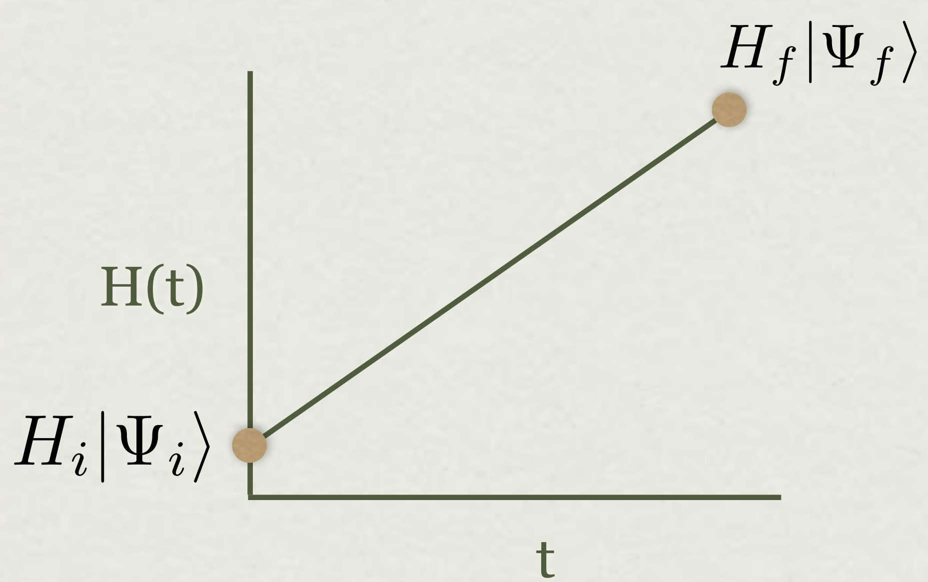

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- Measure E_i with probability α_i^2 getting Ψ_i

Let's just worry about this for the moment...

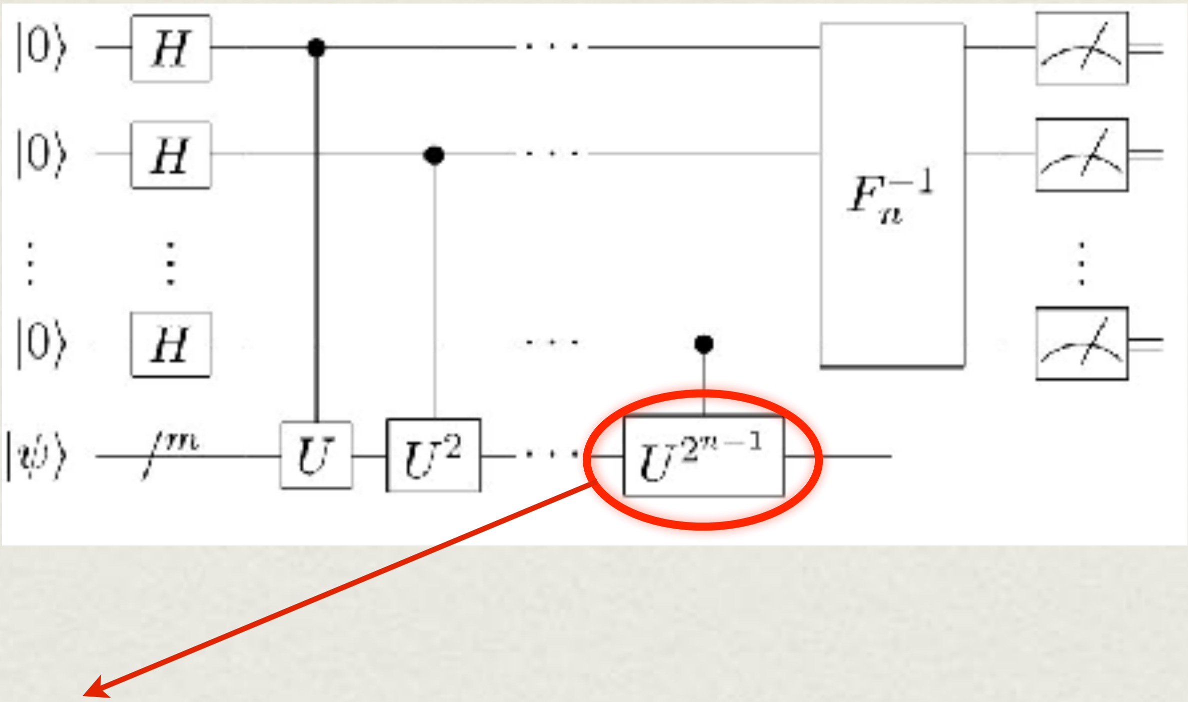
1. Are quantum computers faster than classical computers?

   Yes

2. Are they fast enough to compute anything in a graduate student lifetime?

Quantum Phase Estimation

How quickly can this be done?



Algorithms

- Trotter Decomposition
- Sparse Hamiltonian Problem
  - Quantum Walks
  - Trotter

e^{-iTH} This is your computational bottleneck.

What T do we need?

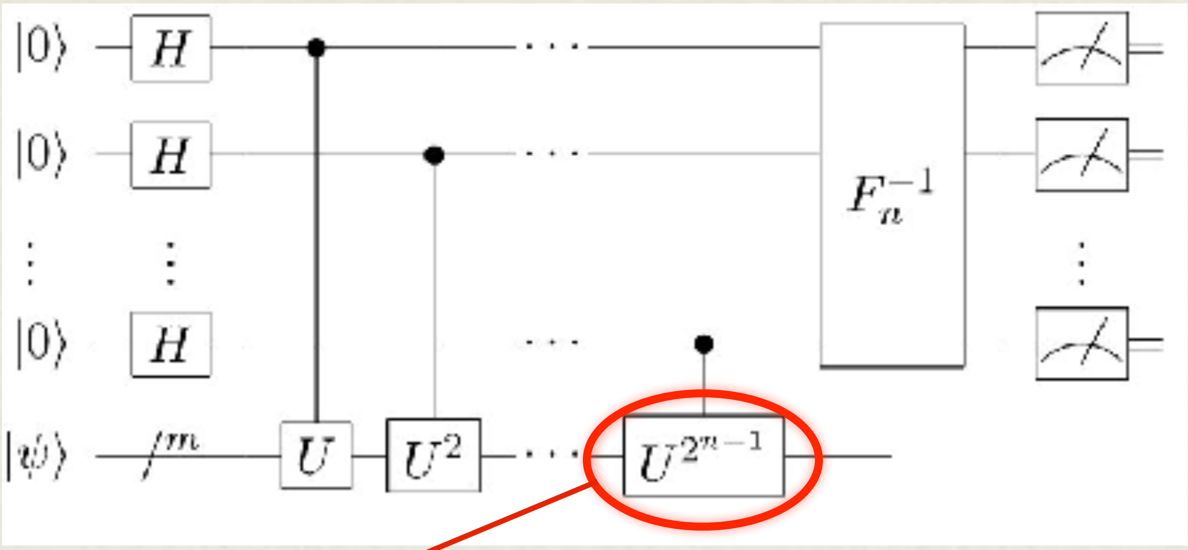
Set by required accuracy: $T \approx 6000 E_h^{-1}$

Interesting note: What matters is absolute accuracy not relative accuracy.

$1/\tau$

Quantum Phase Estimation

How quickly can this be done?



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- ❑ Trotter Decomposition
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  - ❑ Quantum Walks
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What T do we need?

Set by required accuracy: $T \approx 6000 E_h^{-1}$

Interesting note: What matters is absolute accuracy not relative accuracy.

We also need to evaluate $1/\tau$ and number of gates.

Trotter

$$\exp[-itH]^{T/t}$$

$$\exp\left[-it\sum_{pqrs} V_{pqrs}c_p^\dagger c_q^\dagger c_r c_s\right]^{T/t}$$

$$\approx$$

$$\left(\prod_{pqrs}\exp\left[-itV_{pqrs}c_p^\dagger c_q^\dagger c_r c_s\right]\right)^{T/t}$$

# of trotter steps

Cost per term

How many terms?

Parallel Circuit	Global $\mathbf{R}_z$	$\mathbf{H}$, $\mathbf{Y}$, $\mathbf{Y}^\dagger$	CNOT	$\mathbf{CR}_z$	BSM	Total
H_{pp}				1		1
H_{pq}		8	2	4	4	18
H_{pqqp}	1		2	3		1+5
H_{pqqr}		4	8	4	4	24
H_{pqrs}		$8 \cdot 2$	$8 \cdot 2$	$8 \cdot 1$	$8 \cdot 2$	$8 \cdot 7$

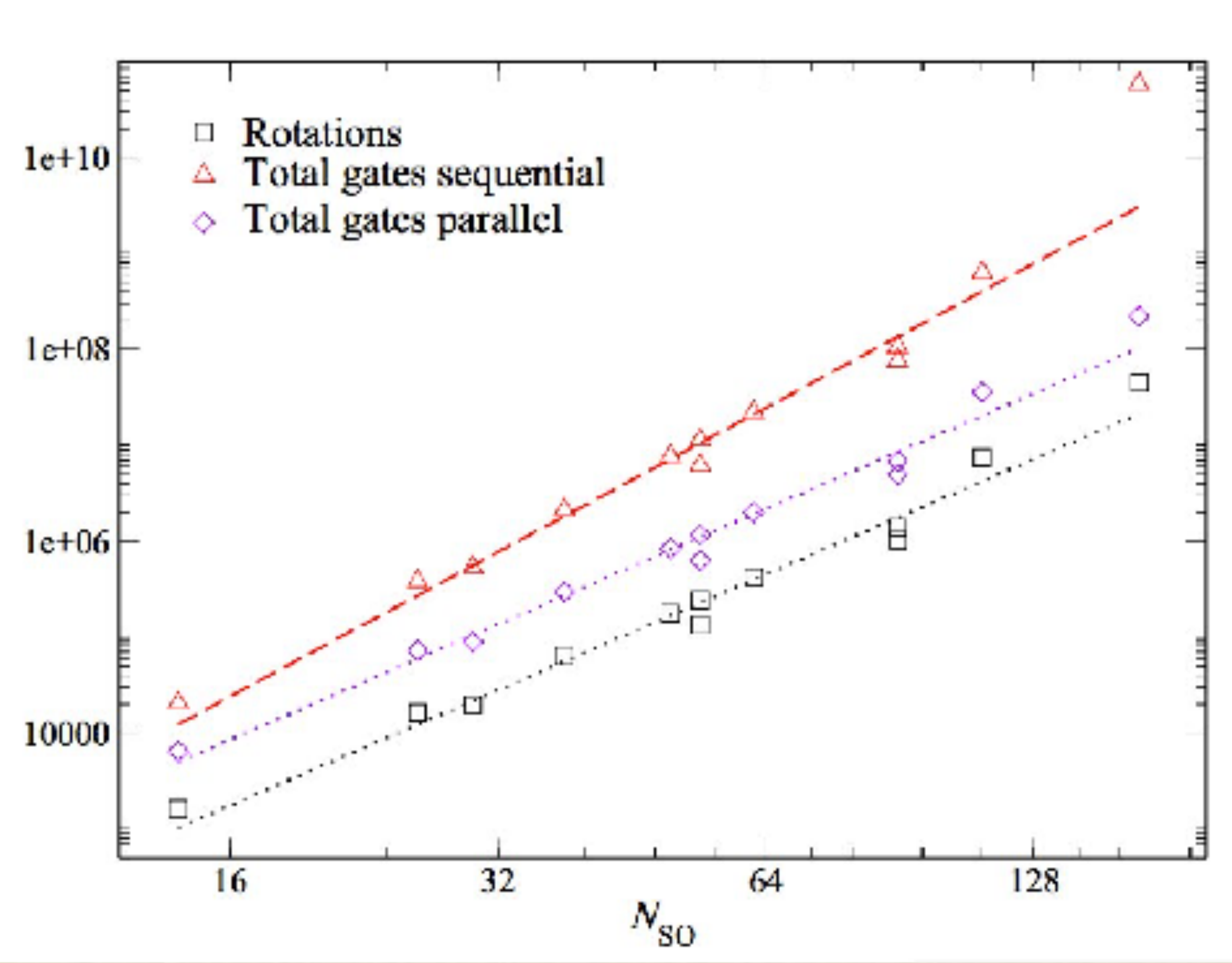
Computing number of gates: $O(\underline{N^4} \times \underline{N}) = O(N^5)$

terms in Hamiltonian

Jordan-Wigner strings for sign

Some of this back from parallelization

Matches empirically



Computing $1/\tau$

Theory: # trotter steps for fixed time (for fixed trace norm distance)

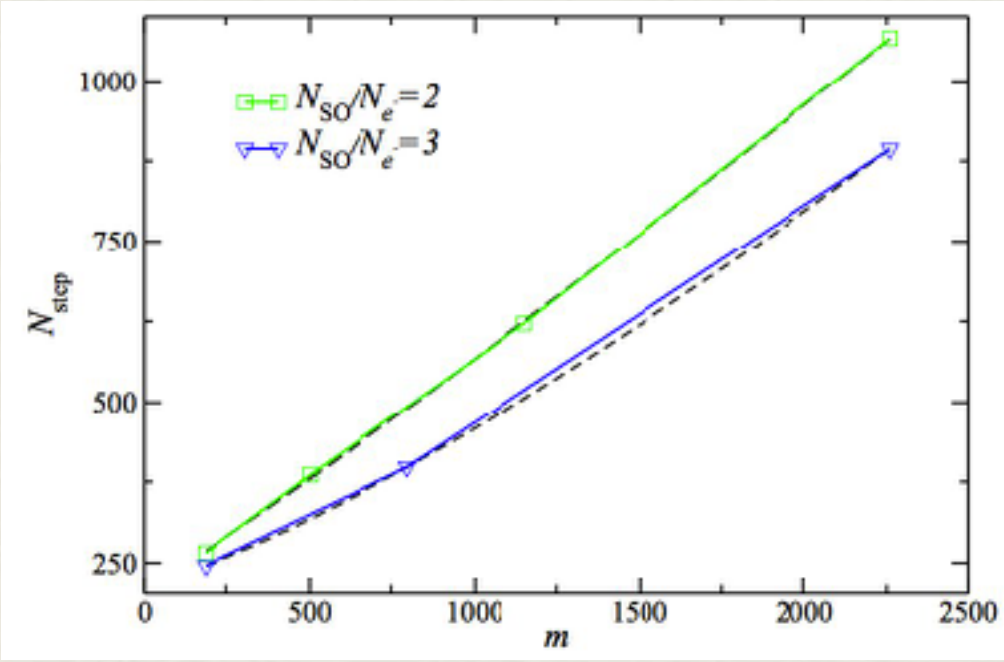
$O(m^{1+1/2k})$ m: terms in Hamiltonian | For k=1: $m^{3/2}$

k: trotter order

O(n) terms mutually commute. New theoretical bound:

For k=1: $Km^{1/2} \sim m^{3/4}m^{1/2} \sim m^{1.25}$

Empirically: # trotter steps for fixed time (for fixed energy error)



- Computed with imaginary molecules
- For k=1, $m^{1.08}$ - $m^{1.27}$

terms in trotter series $m \sim N^4$

Scaling: N^4- N^5

Putting it together ...

(Gates per trotter step) x (Steps per fixed time) x (time)

N_g	$1/\tau$	T
N^5	N^4	$6000E_h^{-1}$

$$6000N^9$$

Water (STO-3G): 10^{10} serial gates (441 x 441 matrix - 14 s.o.)
(by counting)

Fe_2S_2 (STO-3G): 10^{18} serial gates (112 s.o.)
(by extrapolation)

75 years of quantum Moore's law

Parallelization saves factor of 20

With 100 qubits, can never save more then factor of 100

What's the runtime?

	Logical Qubit time	Computation time
'Fast'	1 micro-second	3000 years
'Fantasy'	1 ns	3 years

Plus…no checkpointing!

This is (no matter how good hardware gets) unrealistic.

1. Are quantum computers faster than classical computers?

Yes

2. Are they fast enough to compute anything in a graduate student lifetime?

No

What's the runtime?

	Logical Qubit time	Computation time
'Fast'	1 micro-second	3000 years
'Fantasy'	1 ns	3 years

Plus...no checkpointing!

This is (no matter how good hardware gets) unrealistic.

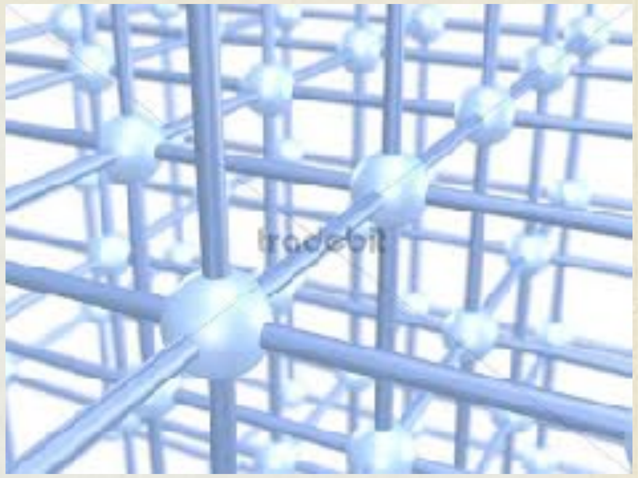
- ❑ Can we do better?
- ❑ Is their anything better already in the literature?

Localized orbitals

	(Gates per trotter step) x	(Steps per fixed time) =	Total
	N_g	$1/\tau$	
quartic:	N^5	N^4	N^9
quadratic:	N^3	$N^{3/2}$	$N^{4.5}$

10,000 localized orbitals <---> 100 delocalized orbitals

Real Space



$$e^{-H} = e^{-K} e^{-V}$$

	(Gates per trotter step) x	(Steps per fixed time) =	Total
	N_g	$1/\tau$	
quartic:	N^5	N^4	N^9
	N^2	2	N^2

1 million grid points <---> 100 delocalized orbitals

100 points per dimension

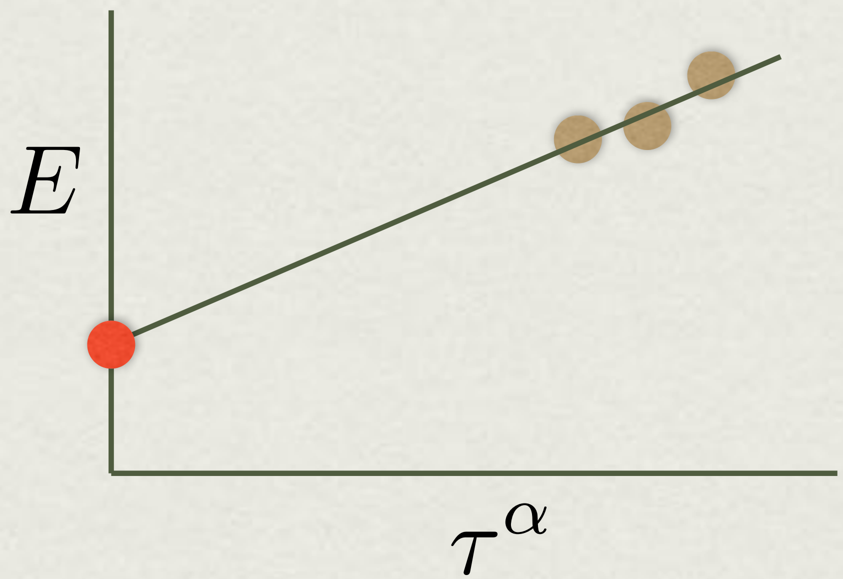
Other problems: Antisymmetrization, etc.

Other Approaches

Different breakup

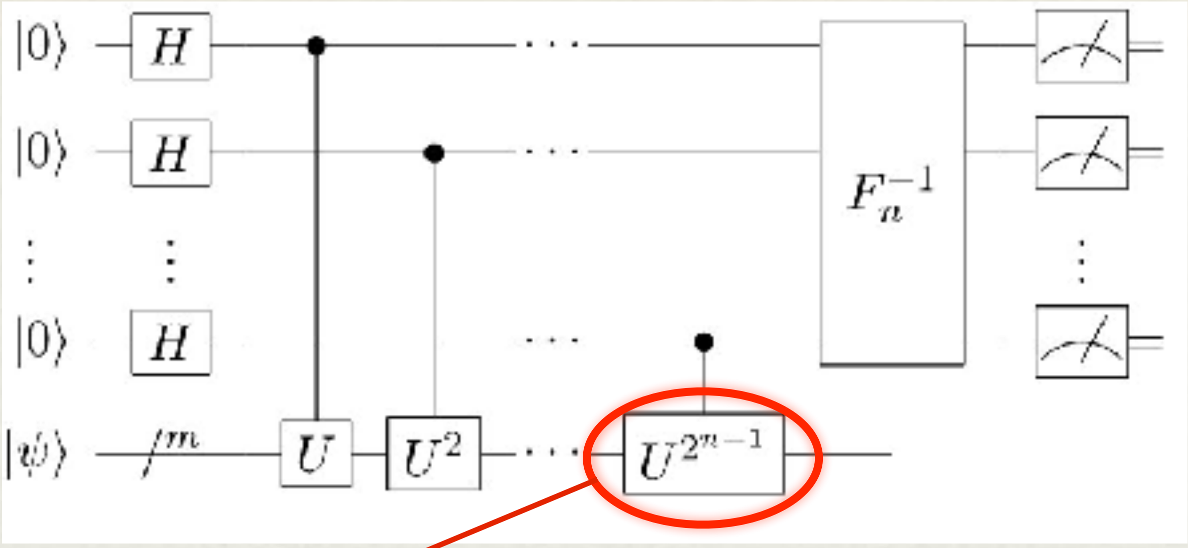
$$e^{-H} = e^{-h_1} e^{-h_2} e^{-h_3} \cdots e^{-h_n}$$

Time step extrapolation:



Quantum Phase Estimation

How quickly can this be done?



e^{-iTH} This is your computational bottleneck.

Algorithms

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  - Quantum Walks

What T do we need?

Set by required accuracy: $T \approx 6000 E_h^{-1}$

Interesting note: What matters is absolute accuracy not relative accuracy.

We also need to evaluate $1/\tau$ and number of gates.

Sparse Hamiltonian Problem

Given an oracle to elements of $H = \sum_{j=1}^{m} H_j$, compute $\exp[-iTH]$

d non-zeros per row

Oracle: $U_f|x, i\rangle|0\rangle = |\phi_{x,i}\rangle|y_i, H_{x,y_i}\rangle$

Quantum chemistry Hamiltonian: $d = N^4$

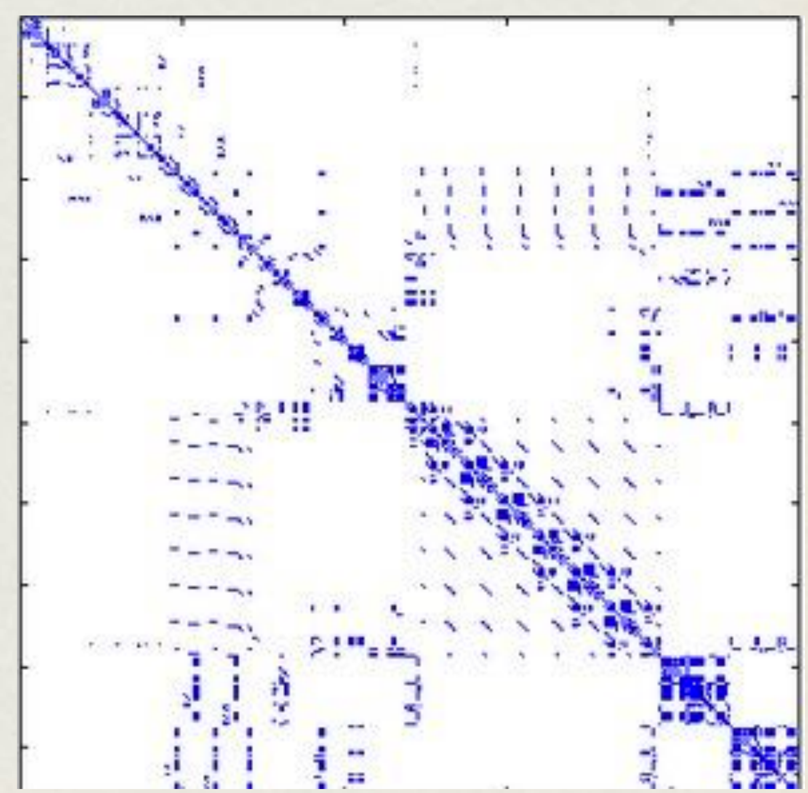
Two ‘current’ winners:

D. W. Berry, R. Cleve, and R. D. Somma, Preprint (2013), arXiv:1308.5424.

‘Trotter Approach’

D. W. Berry and A. M. Childs, Quantum Information & Computation **12**, 29 (2012).

‘Quantum Walks’



Trotter Steps*

$$O(d^2 T \log^3(Td))$$

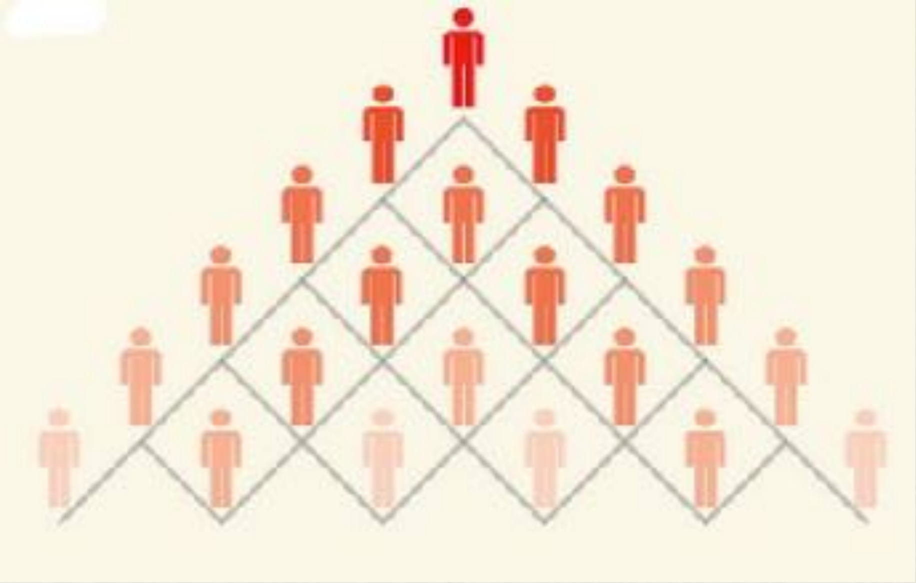
$$O(N^8 T \log^3(TN^4))$$ oracle queries.

Not much better then our current results.

Crossover $N \lesssim 100$

* D. W. Berry, R. Cleve, and R. D. Somma, Preprint (2013), arXiv:1308.5424.

Quantum Walks*



$$O(d^{2/3}((\log\log d)t||H||)^{4/3})$$

$$O(N^{8/3}((\log\log N^4)||H||)^{4/3})$$

$$||H|| \to O(N)$$ (operator norm)

$$O(N^{8/3}N^{4/3}((\log\log N^4))^{4/3}) = O(N^4)$$ oracle queries

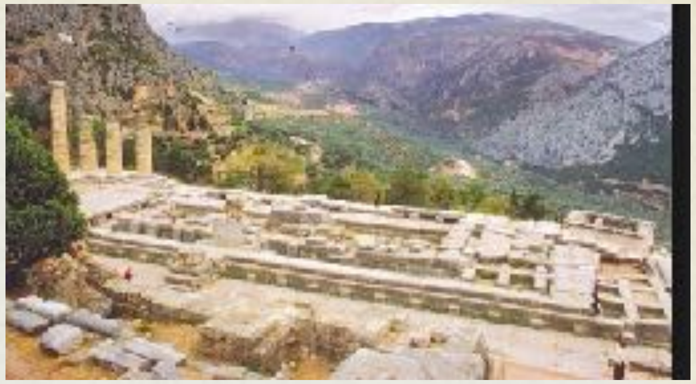
$$O(d\Lambda_{max}t)$$

$$O(N^4)$$ oracle queries

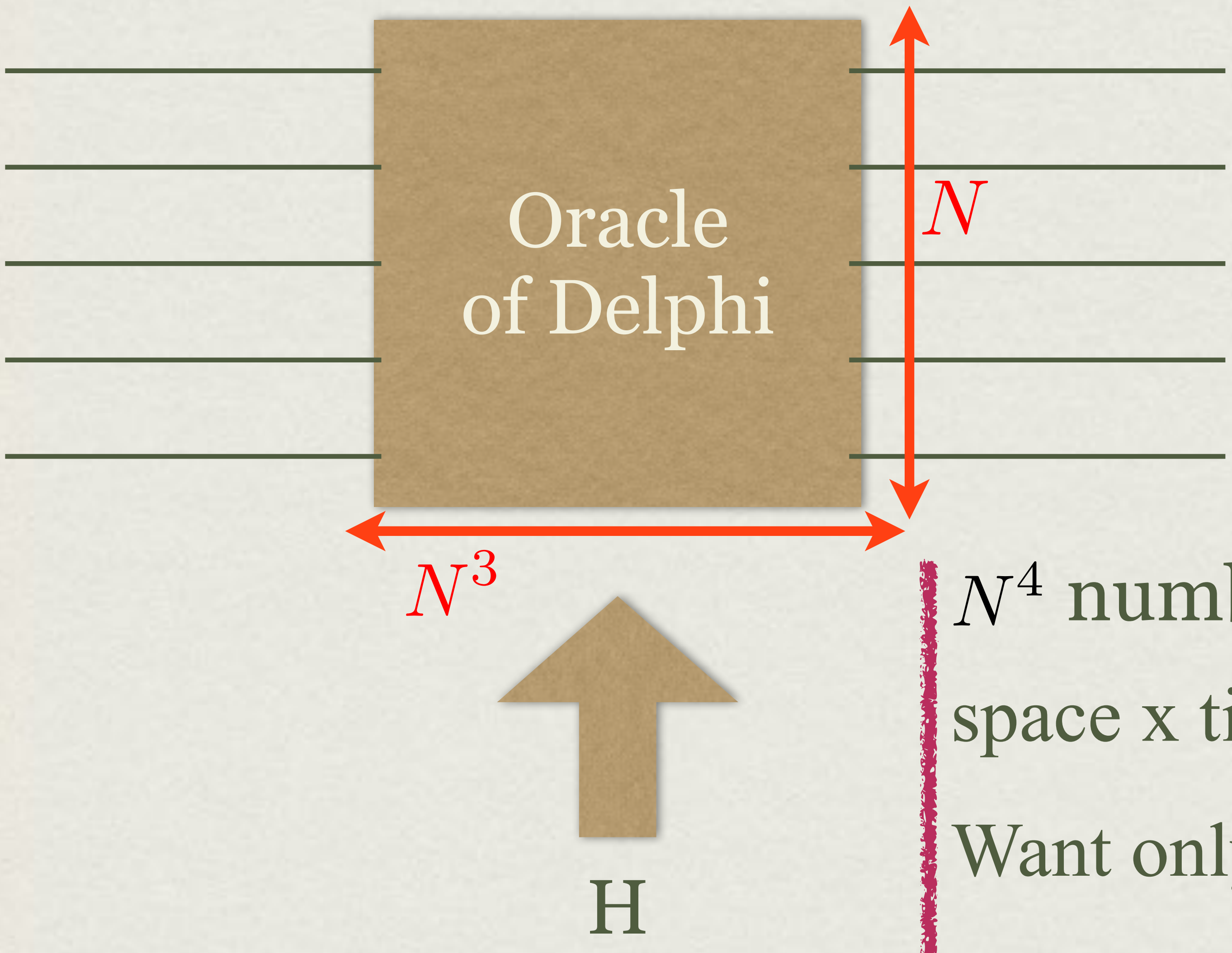
This looks quite promising.....

*Berry and Childs

until you think about the 'oracle'...



Oracle: $U_f|x,i\rangle|0\rangle = |\phi_{x,i}\rangle|y_i, H_{x,y_i}\rangle$



N^4 numbers in the box

space x time = N^4

Want only N qubits

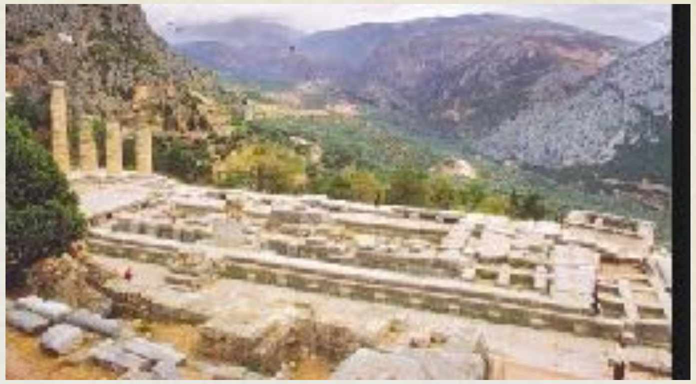
time: N^3 x N (Jordan-Wigner) = N^4

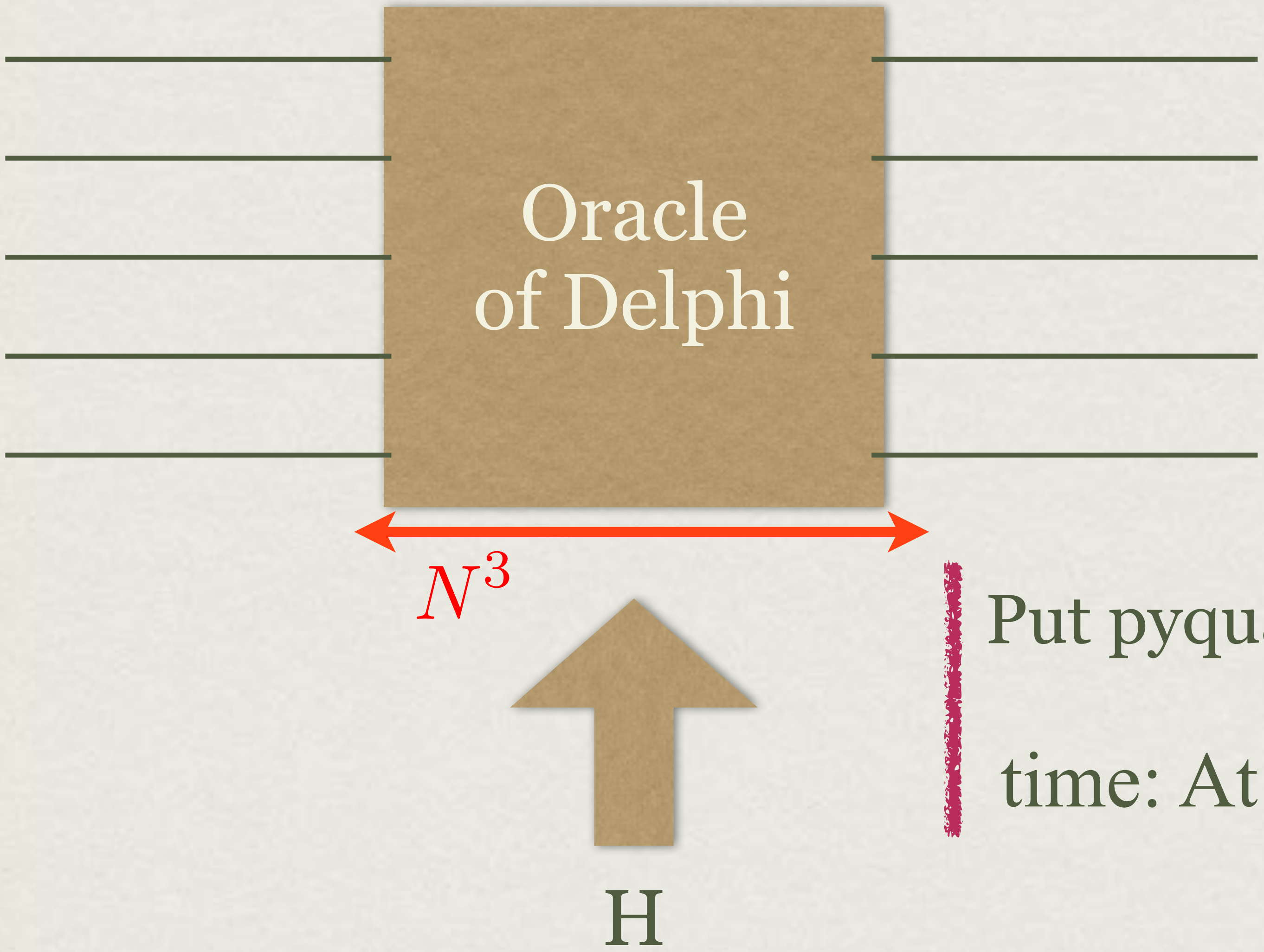
With quantum walks: N^8 time.

You can trade-off time for space here.

until you think about the 'oracle'...

Oracle: $U_f|x,i\rangle|0\rangle = |\phi_{x,i}\rangle|y_i, H_{x,y_i}\rangle$

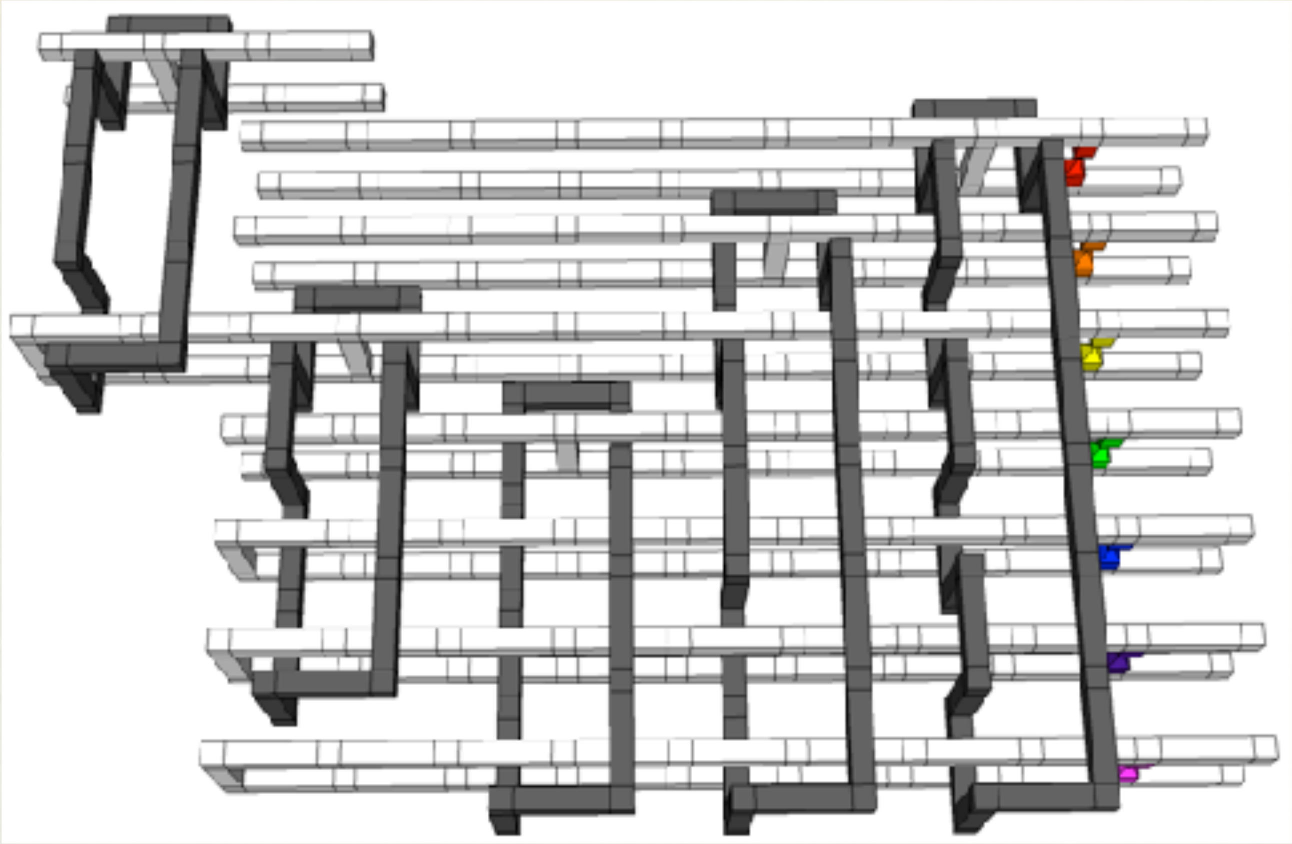




- Put pyquante in the box
- time: At least N^3 but probably more

- With quantum walks: At least N^7 time.

What we've ignored....



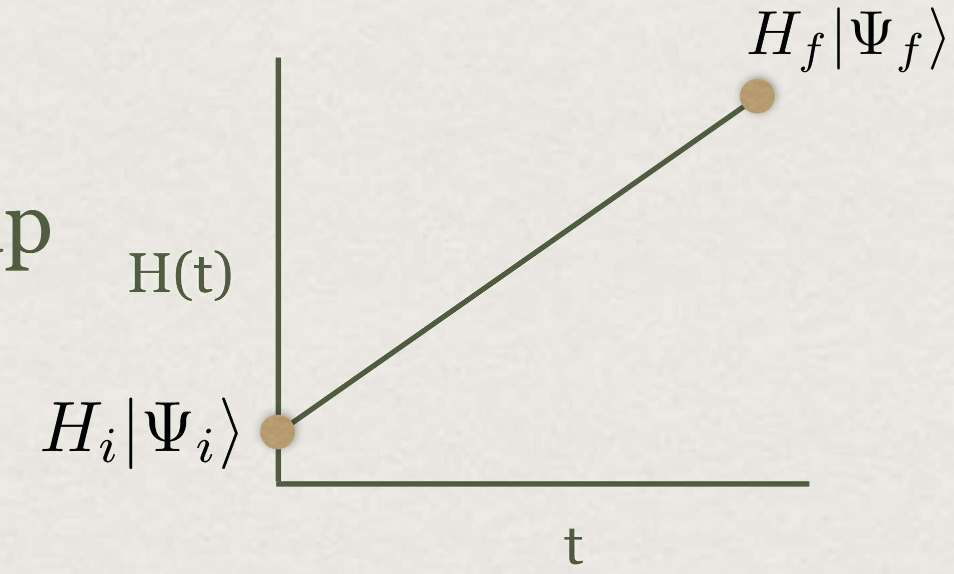
- Error correction

  ~ factor of 100

- Adiabatically evolving, measurements, ...

  Similar difficulties

  Speed depends on gap



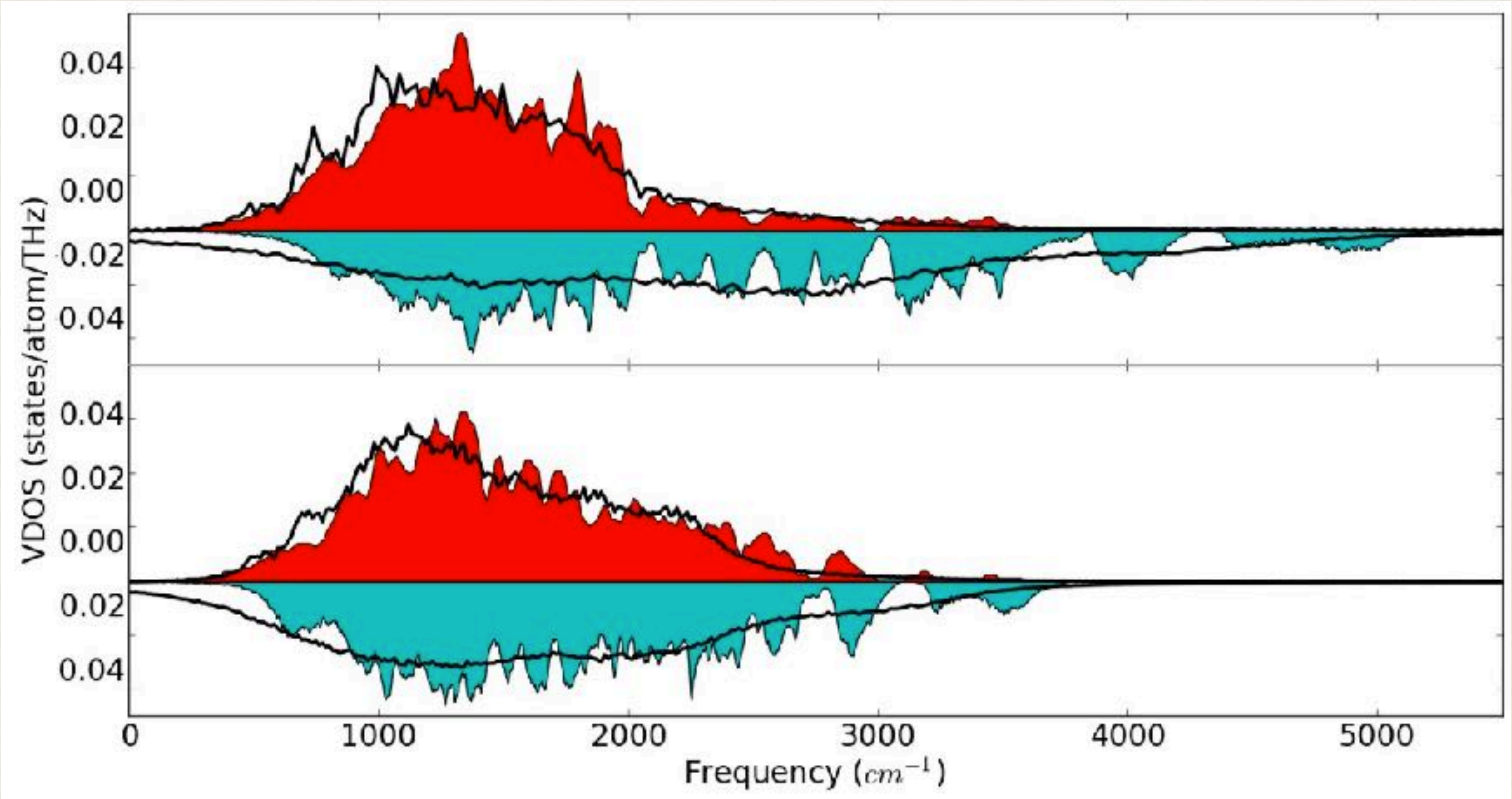
Conclusion (part 2): Quantum Chemistry on a Quantum Computer

The 'standard' approach

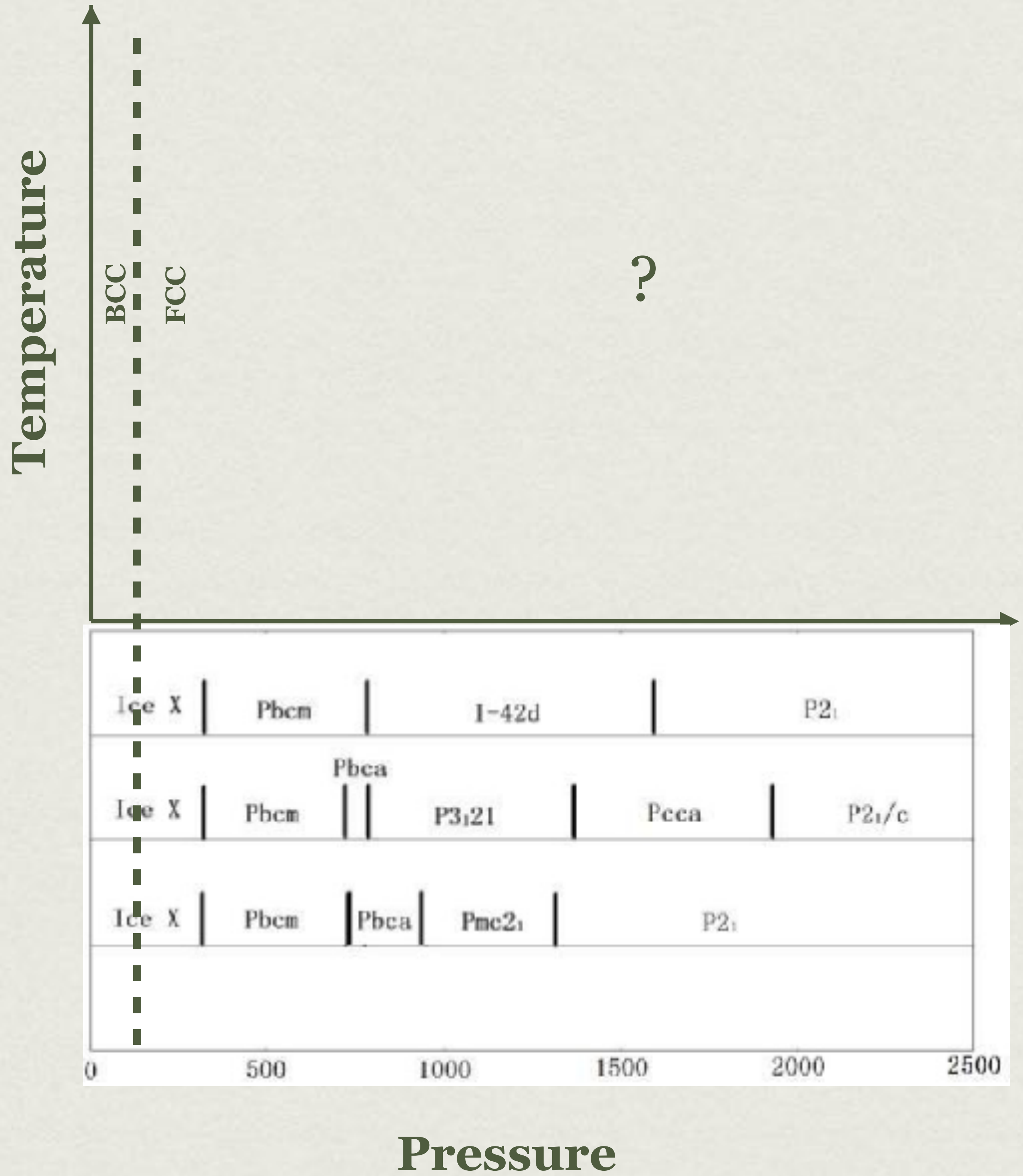
- (Number gates) x (Trotter per fixed time)
- N^5 x N^4 = N^9
- 100 spin orbitals => 10^{17} parallel depth

Other approaches

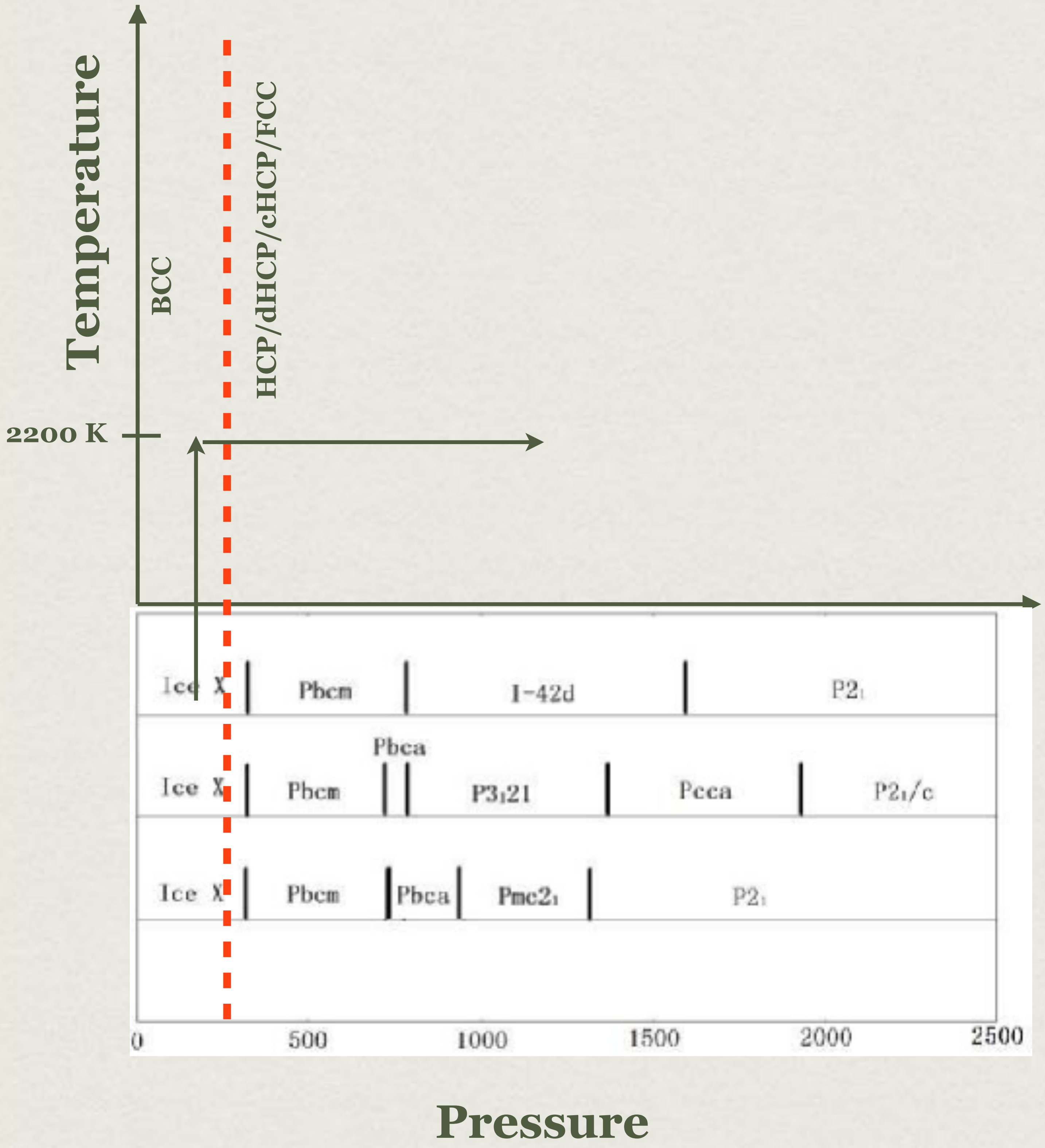
- Quantum walks => N^8 but can trade space/time
- Real Space => N^2



0.04
0.02
0.00
0.02
0.04
0.04
0.02
0.00
0.02
0.04
VDOS (states/atom/THz)
0
1000
2000
3000
4000
5000
Frequency (cm^{-1})



Temperature
BCC
FCC
?
Ice X
Pbcm
I-42d
$P2_1$
Pbca
Ice X
Pbcm
$P3_121$
Pcca
$P2_1/c$
Ice X
Pbcm
Pbca
$Pmc2_1$
$P2_1$
0
500
1000
1500
2000
2500
Pressure



Temperature
BCC
HCP/dHCP/cHCP/FCC
2200 K
Ice X
Pbcm
I-42d
P2₁
Pbca
P3₁21
Pcca
P2₁/c
Pmc2₁
0
500
1000
1500
2000
2500
Pressure

Like P21

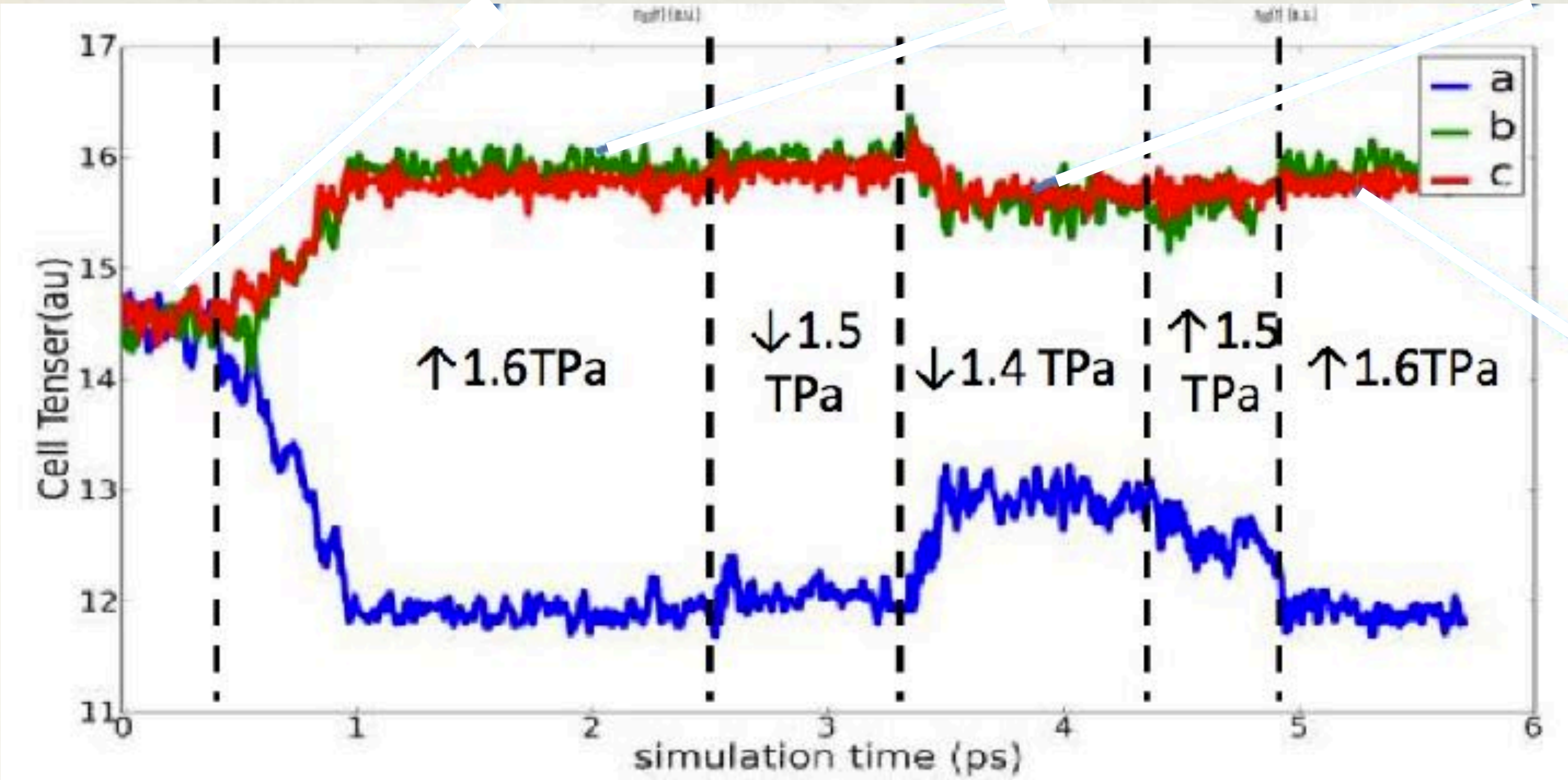
Like P21/c

Higher symmetry

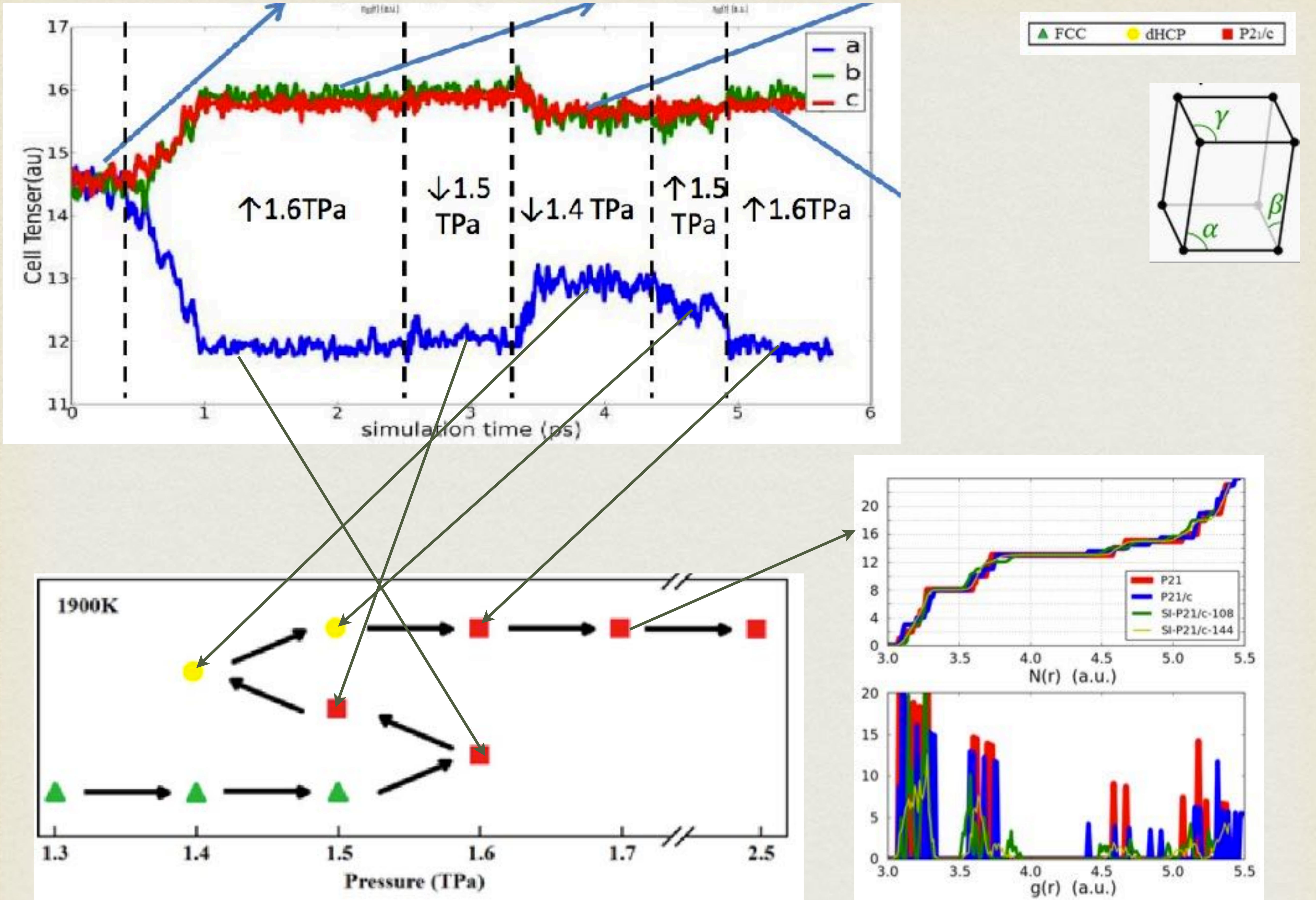
8 atoms per unit cell

What structure is it?

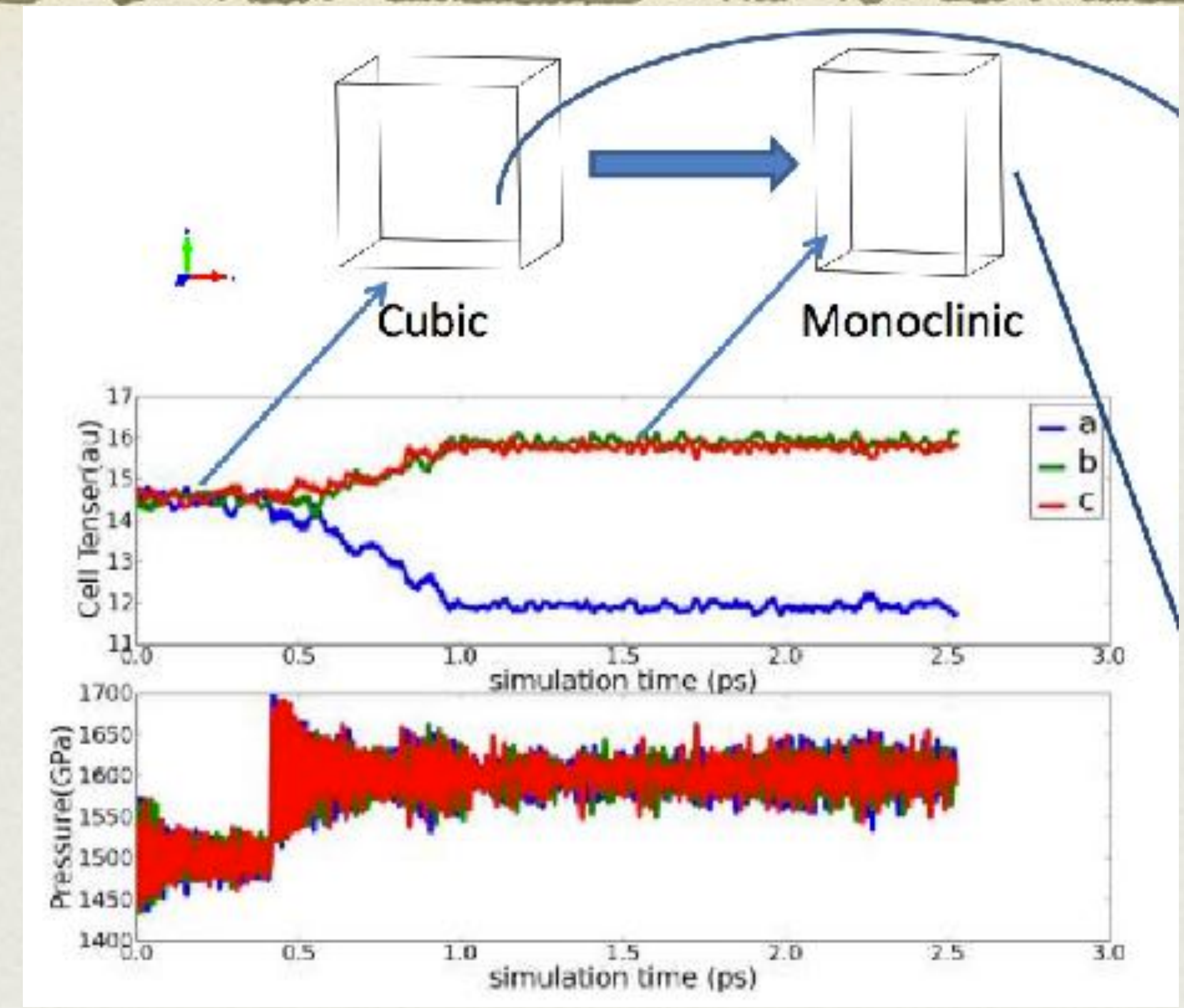
Instead, we estimated the position of each oxygen in the superionic phase by taking the centroid of the simulated trajectory. Although the oxygen sublattice of the new superionic phase we found is very close to the oxygen sublattice of 0K P21 or P21/c structure, we found the centroid of oxygen atoms has a higher symmetry. The oxygen sublattice of the new superionic phase has P21/c space group with 4 oxygen atoms in the unit cell, which is more symmetric than the 0K P21/c structure, who has 8 oxygen atoms per unit cell. It is also has a higher symmetry than the P 21 structure at 0K. Table 1 summarizes the structural parameters of oxygen sublattice. Based on the space group of the oxygen sublattice, we name the new superionic phase as P 21/c phase.



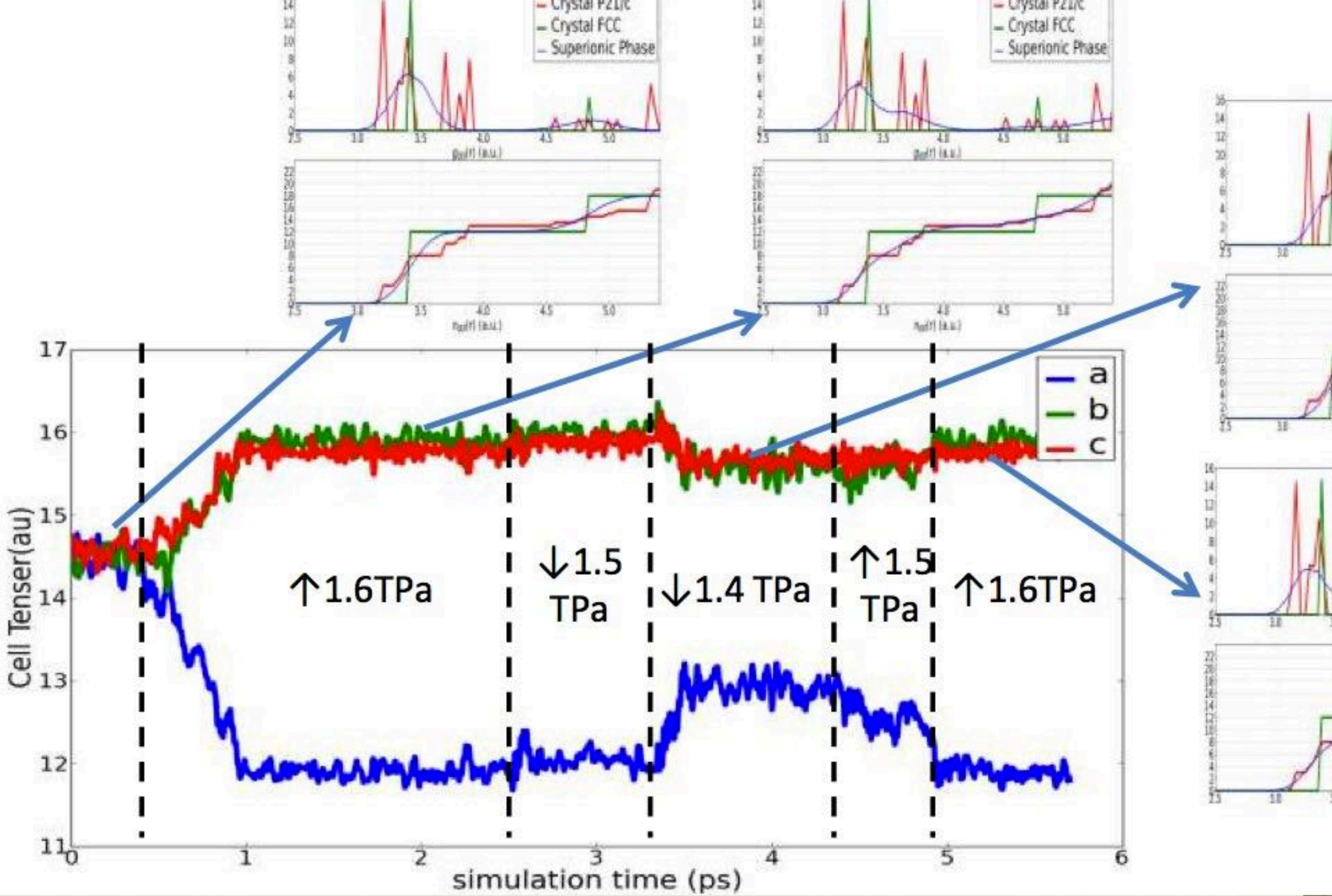
Cell Tenser(au)
simulation time (ps)
a
b
c
↑1.6TPa
↓1.5 TPa
↓1.4 TPa
↑1.5 TPa
↑1.6TPa



Cell Tenser(au)
simulation time (ps)
a
b
c
↑1.6TPa
↓1.5 TPa
↓1.4 TPa
↑1.5 TPa
↑1.6TPa
FCC
dHCP
P21/c
γ
β
α
1900K
Pressure (TPa)
1.3
1.4
1.5
1.6
1.7
2.5
N(r) (a.u.)
g(r) (a.u.)
P21
P21/c
SI-P21/c-108
SI-P21/c-144

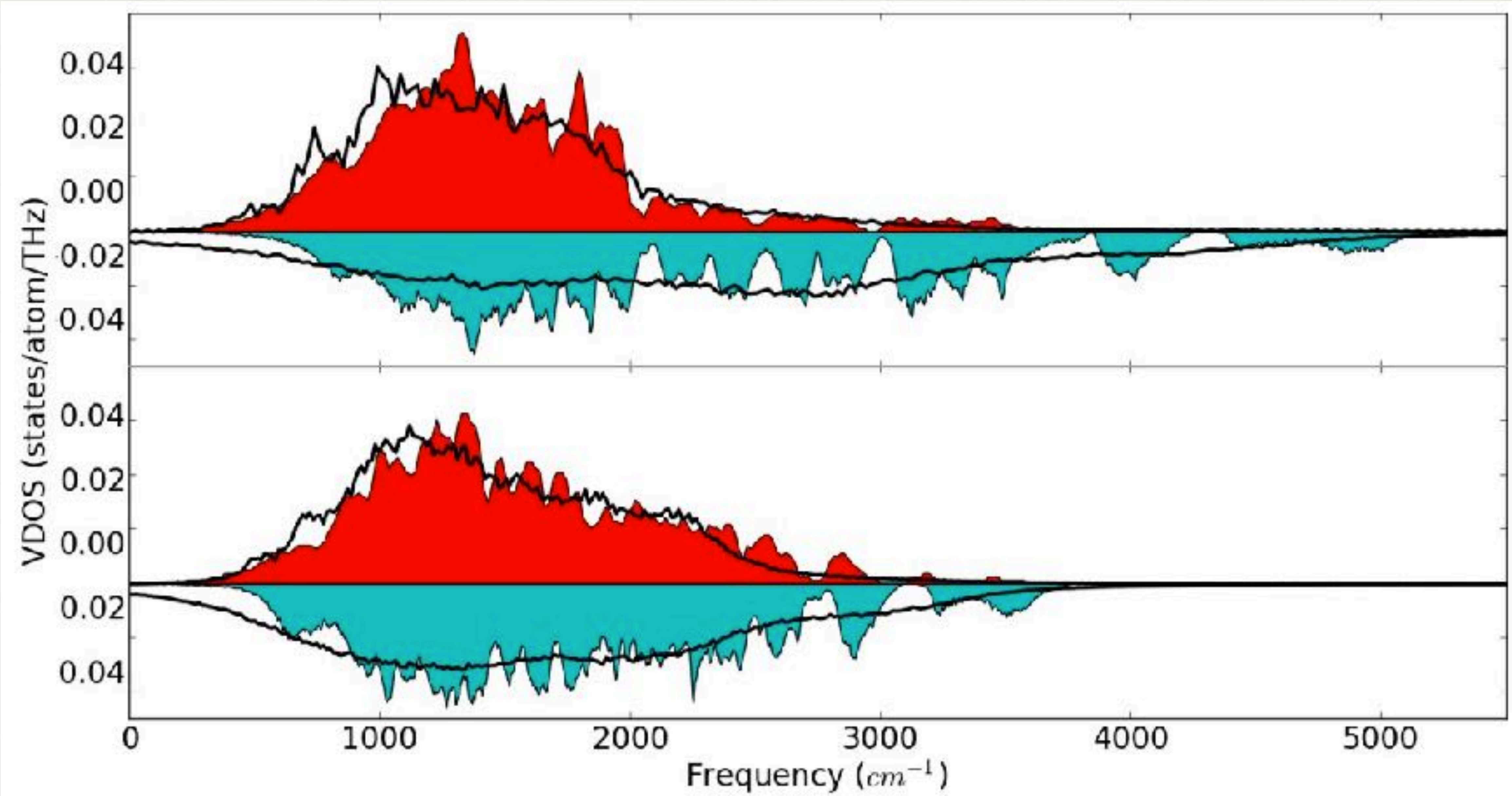


Cubic
Monoclinic
Cell Tenser(au)
simulation time (ps)
a
b
c
Pressure(GPa)
simulation time (ps)


Crystal P21/c
Crystal FCC
Superionic Phase
Crystal P21/c
Crystal FCC
Superionic Phase
a
b
c
Cell Tenser(au)
simulation time (ps)
↑1.6TPa
↓1.5 TPa
↓1.4 TPa
↑1.5 TPa
↑1.6TPa

What structure is it?

Instead, we estimated the position of each oxygen in the superionic phase by taking the centroid of the simulated trajectory. Although the oxygen sublattice of the new superionic phase we found is very close to the oxygen sublattice of 0K P21 or P21/c structure, we found the centroid of oxygen atoms has a higher symmetry. The oxygen sublattice of the new superionic phase has P21/c space group with 4 oxygen atoms in the unit cell, which is more symmetric than the 0K P21/c structure, who has 8 oxygen atoms per unit cell. It is also has a higher symmetry than the P 21 structure at 0K. Table 1 summarizes the structural parameters of oxygen sublattice. Based on the space group of the oxygen sublattice, we name the new superionic phase as P 21/c phase.



0.04
0.02
0.00
0.02
0.04
0.04
0.02
0.00
0.02
0.04
VDOS (states/atom/THz)
0
1000
2000
3000
4000
5000
Frequency (cm^{-1})