TREX Symposium
Luxembourg, February 5-9 2024

Structural properties and phase transitions of hydrogen and hydrogen-rich compounds by Quantum Monte Carlo

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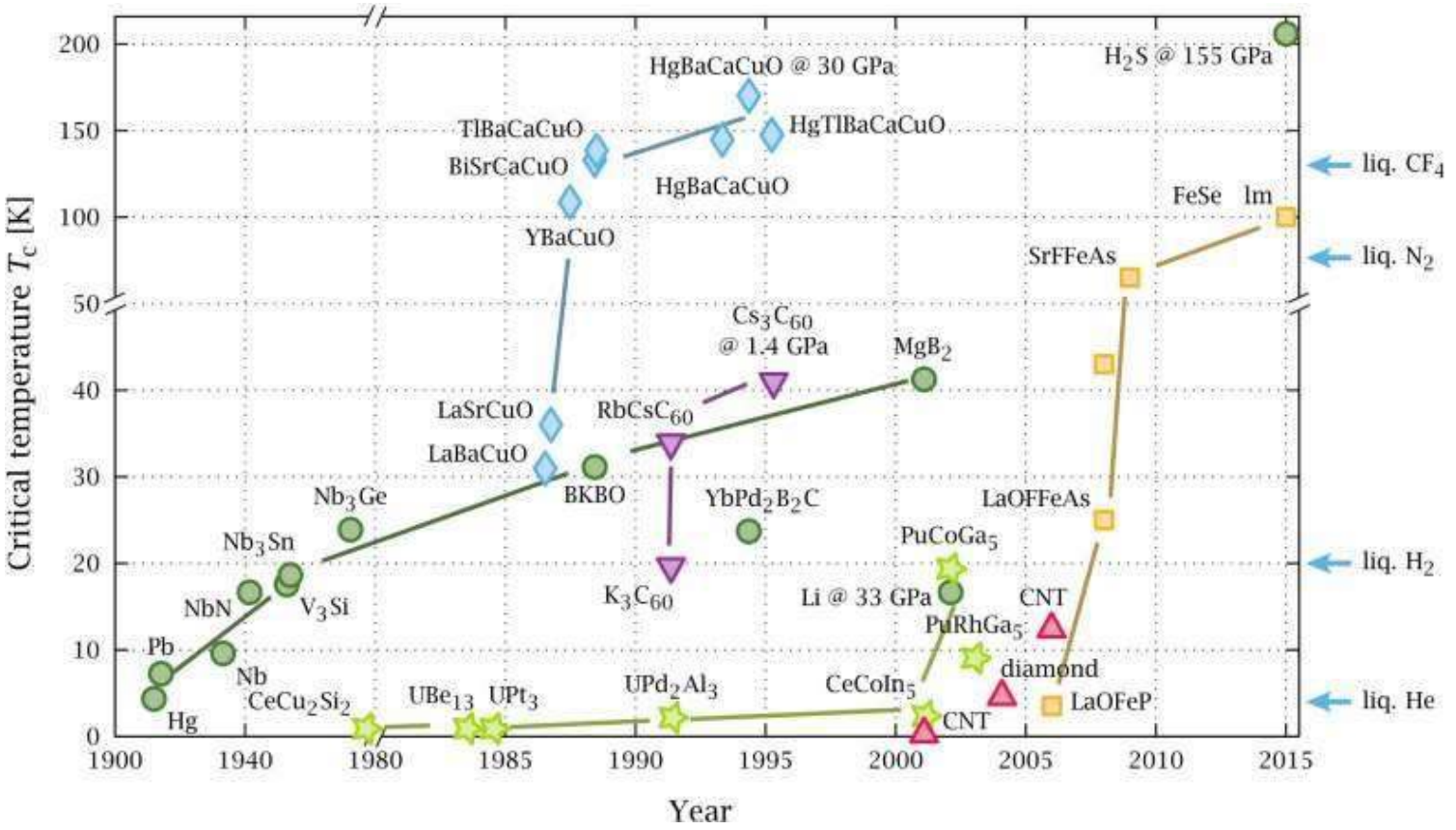
Outline

1. Theoretical/Computational challenges
2. High-pressure hydrogen phase diagram
3. Proton transfer in water clusters
4. Perspectives

Quantum Materials

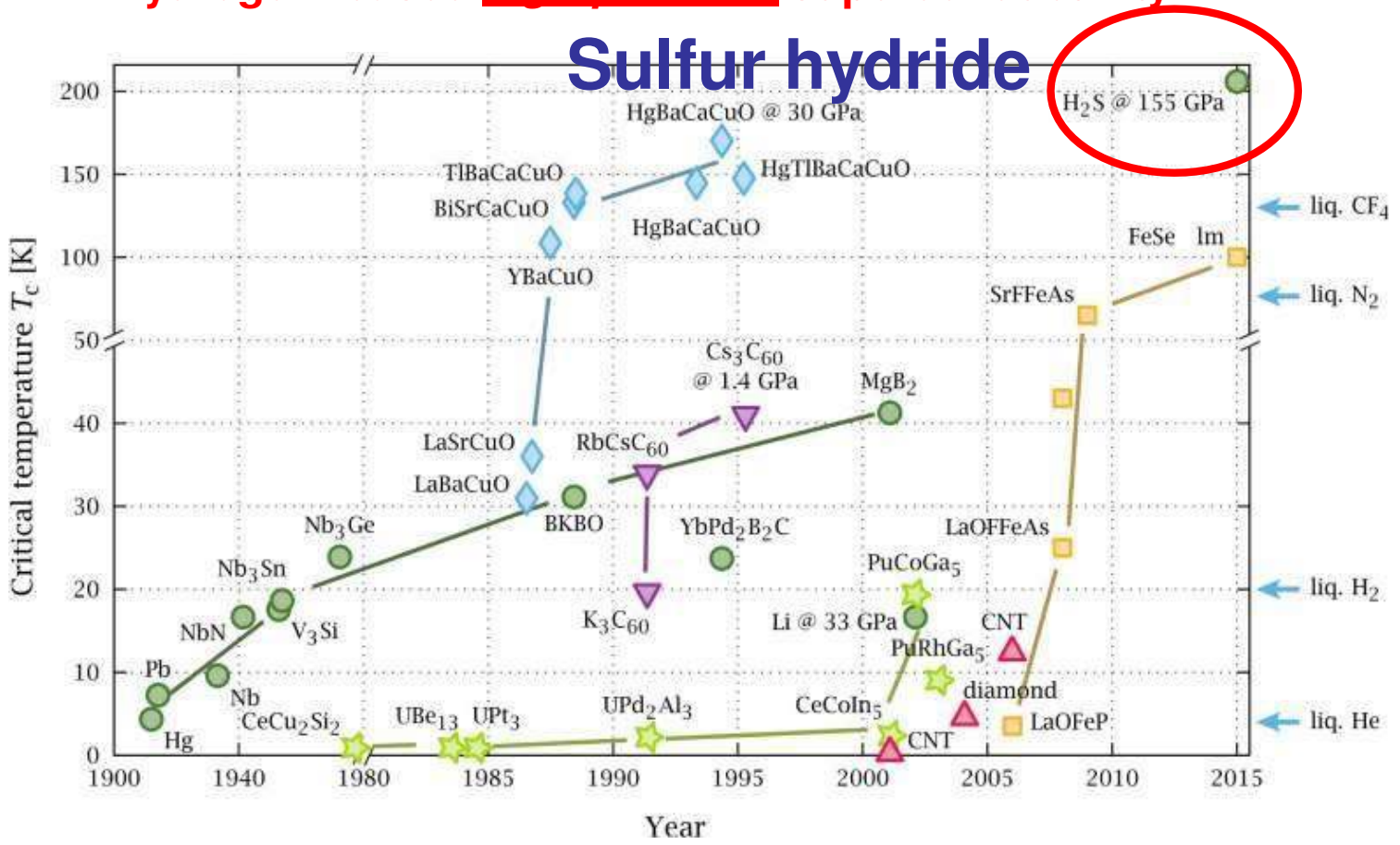
- **Hydrogen and hydrogen-rich materials** belong to the family of *quantum* materials / *quantum* crystals:
  - Both electrons and nuclei are **quantum particles**
  - **Nuclei with light mass → quantum nuclear delocalization**
  - **Nuclear quantum effects (NQE) lead to remarkable properties**

Towards room temperature superconductivity



Towards room temperature superconductivity

Hydrogen–based *high-pressure* superconductivity



Hydrogen as **conventional** high-temperature superconductor

Three Bardeen-Cooper-Schrieffer (BCS) golden rules to maximize

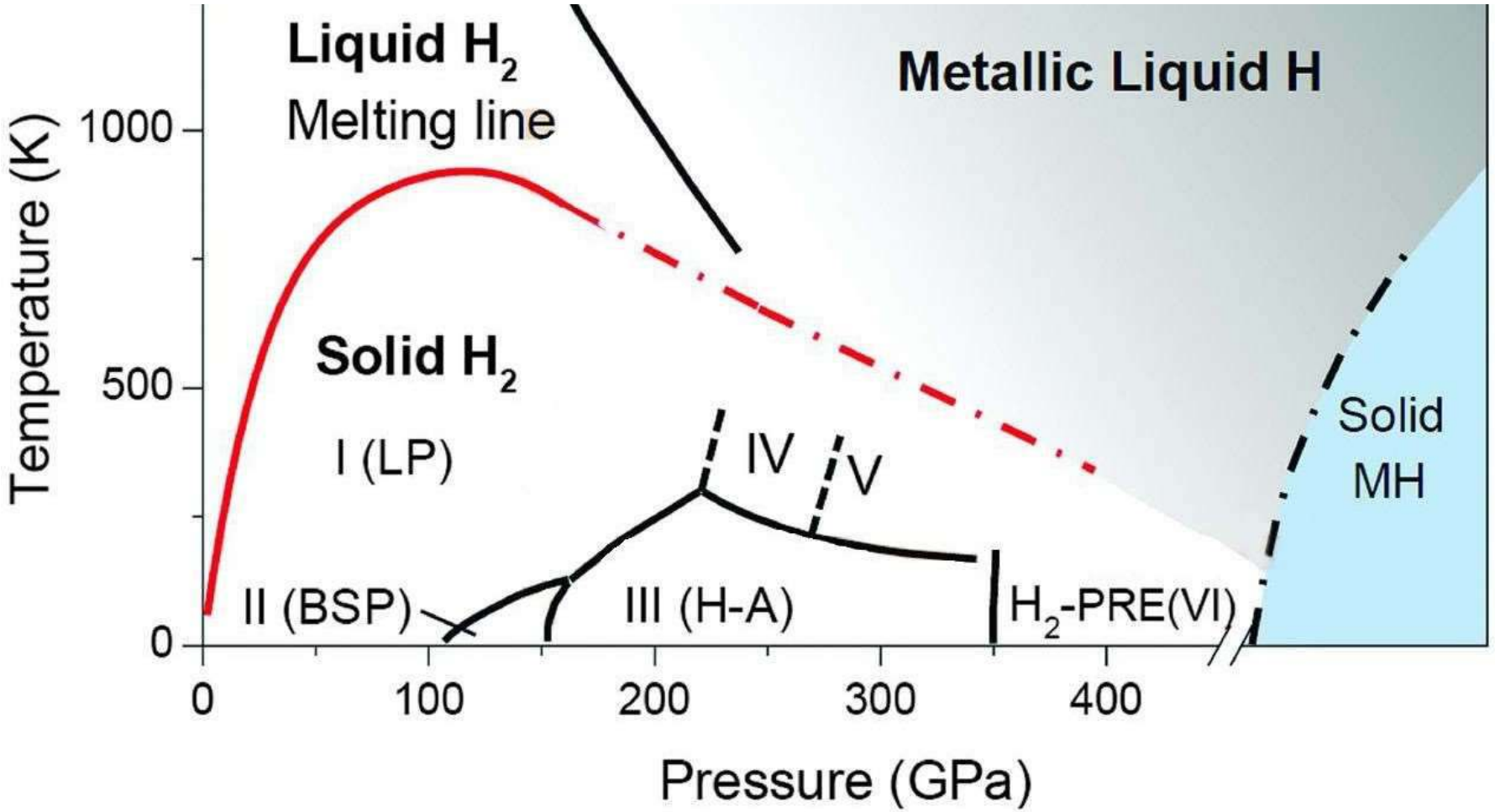
$$\Delta = 2\sim\omega_{cut}\, e^{-1/N(\varepsilon_F)V}$$

1. **large nuclear vibrations**
2. **high electronic density of states at the Fermi level**
3. **strong coupling between phonons and electrons**

Hydrogen will meet the above requirements thanks to its light mass

But first it needs to become a metal!

Hydrogen phase diagram



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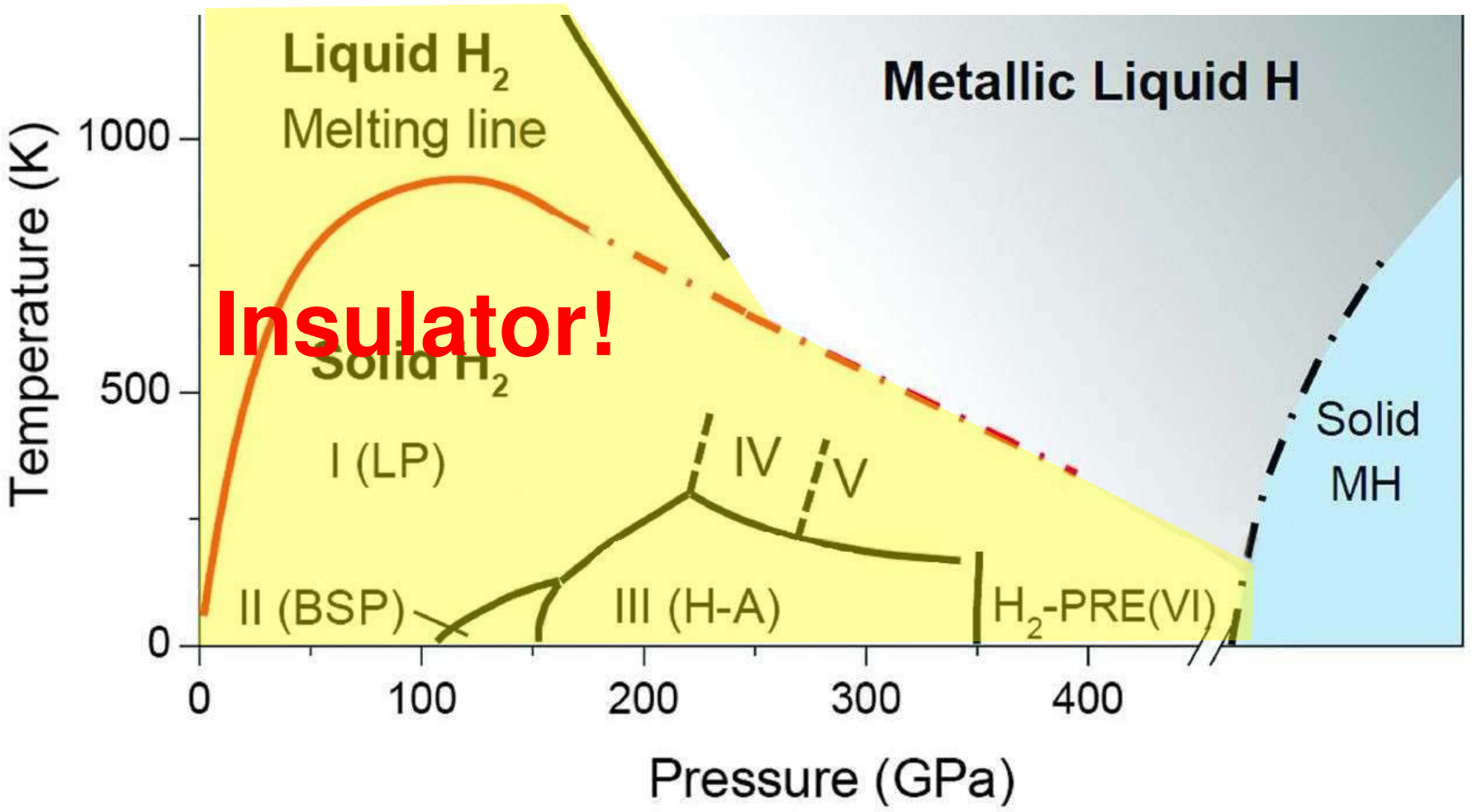
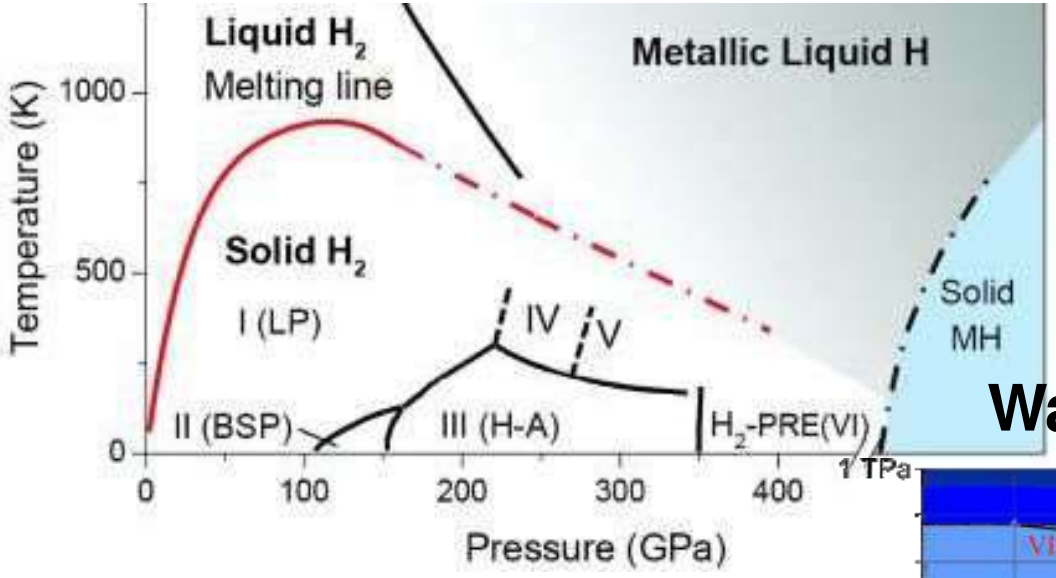
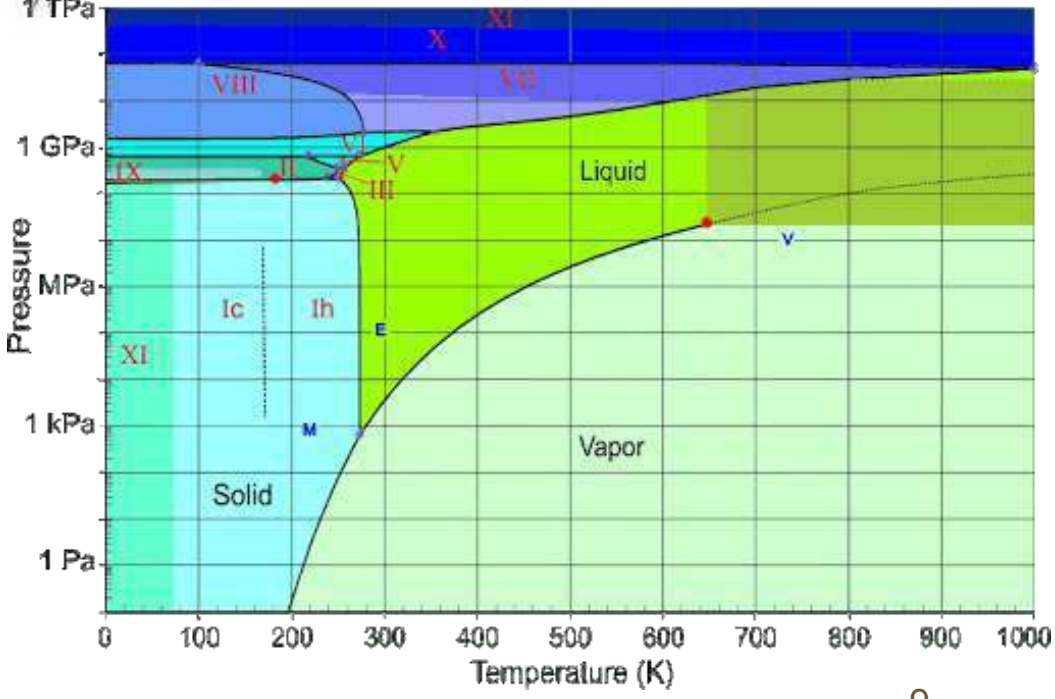


Hydrogen/Water phase diagrams



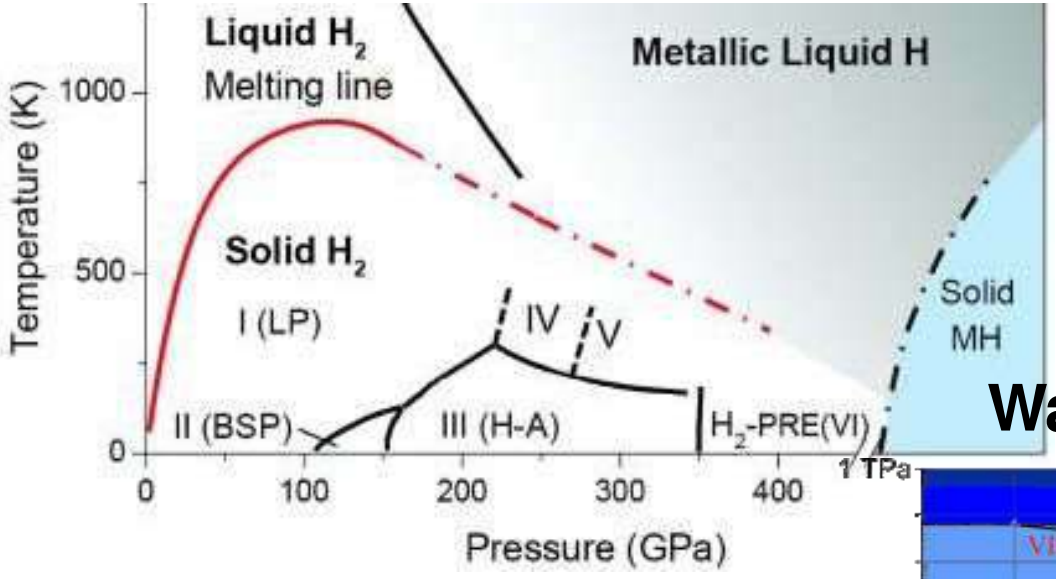
Hydrogen

Water (H-bonded network)



<u>Quantum materials</u>:
Very complex and rich phase diagrams

Hydrogen/Water phase diagrams



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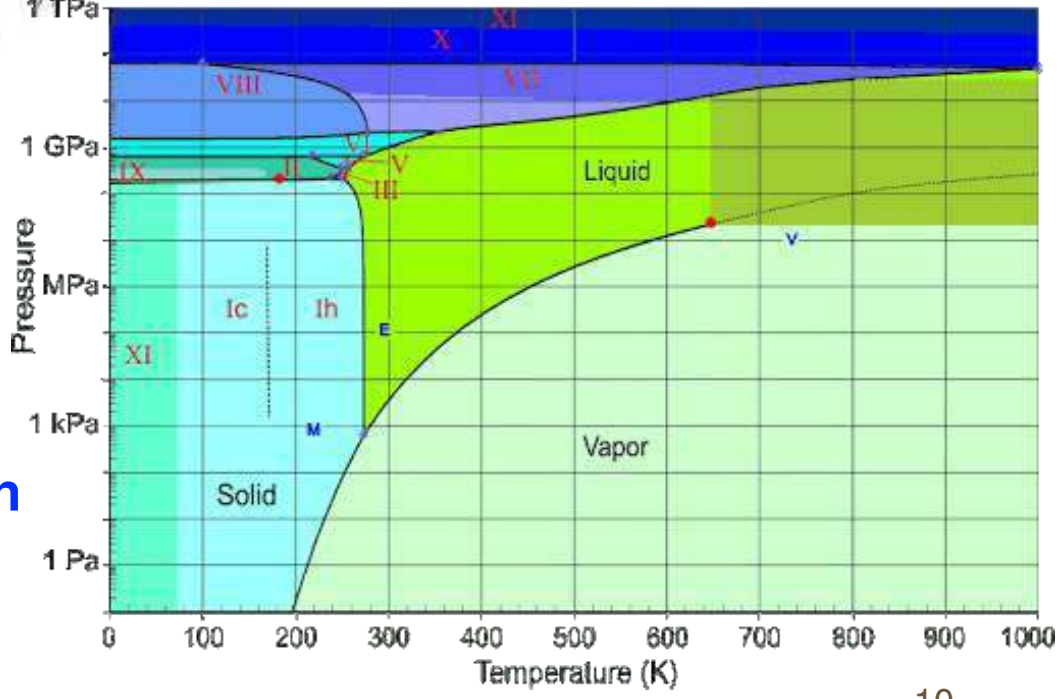

<u>Quantum materials</u>:
Very complex and rich phase diagrams

Competition/interplay between *internal (electronic)* and *vibrational (nuclear)* energies

Theoretical/computational challenges

- Accurate evaluation of **electronic internal energies** (i.e. full account of *electronic correlation*)
- Accurate treatment of **the nuclear degrees of freedom by a quantum description** (i.e. full account of *nuclear quantum effects*)
- Non-trivial **interplay** between the two

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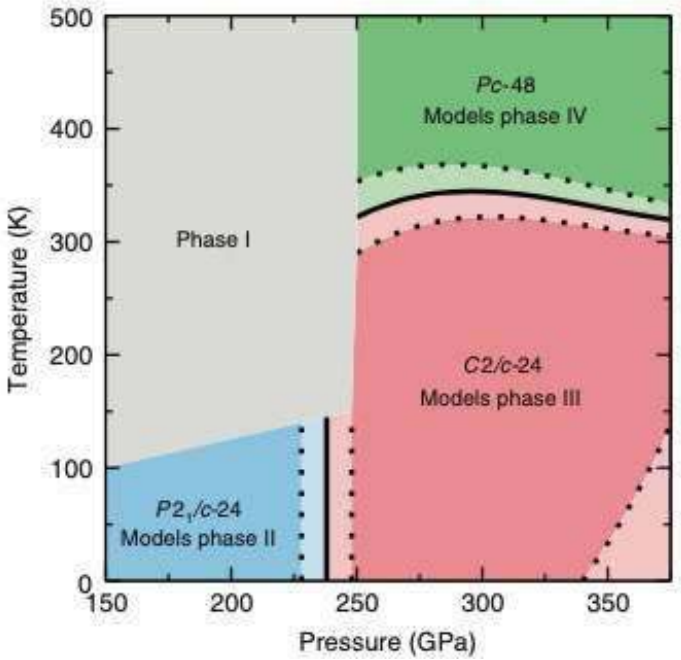
- Non-trivial **interplay** between the two

Large variety of structures (in competition) spanning a wide pressure-range

→ ***Quantum Monte Carlo (QMC) most valuable method***

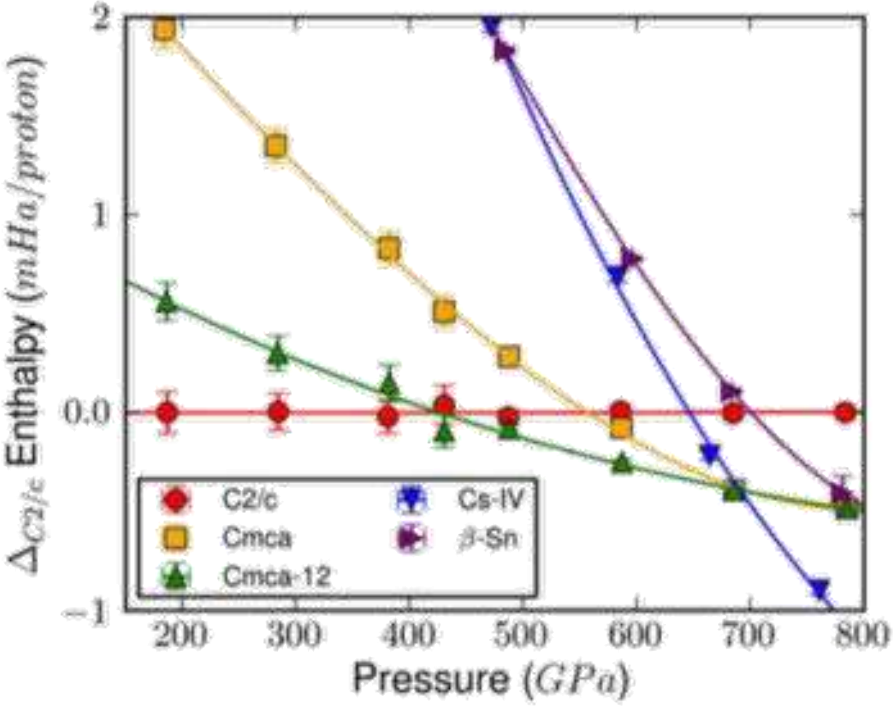
Hydrogen phase diagram from DMC

Several works!

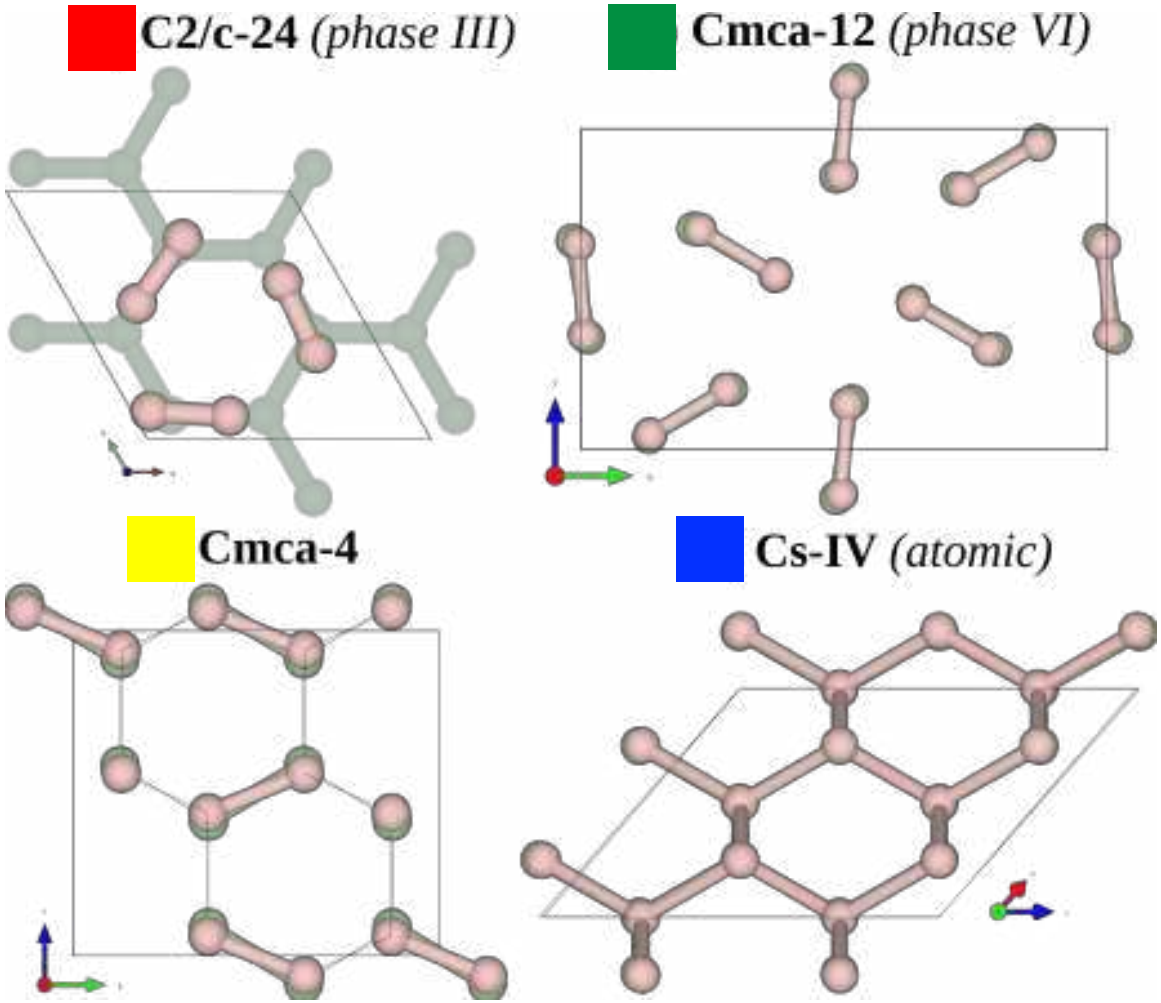


Nat Comm **6**, 8794 (2015)
N.D. Drummond *et al.*

PRL **114**, 105305 (2015)
McMinis, Clay III, Lee, Morales



Competing symmetries



Hydrogen phase diagram from DMC

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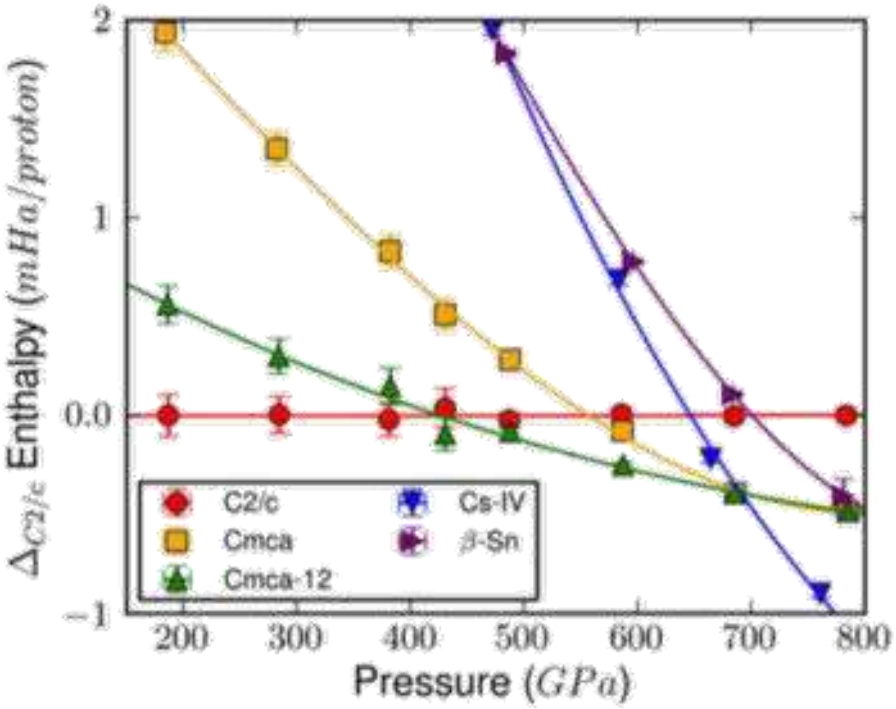
Internal energies from QMC
Static *lattice*
(DFT-DF equilibrium geometry)



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Internal energies from QMC
Harmonic *zero point energies*
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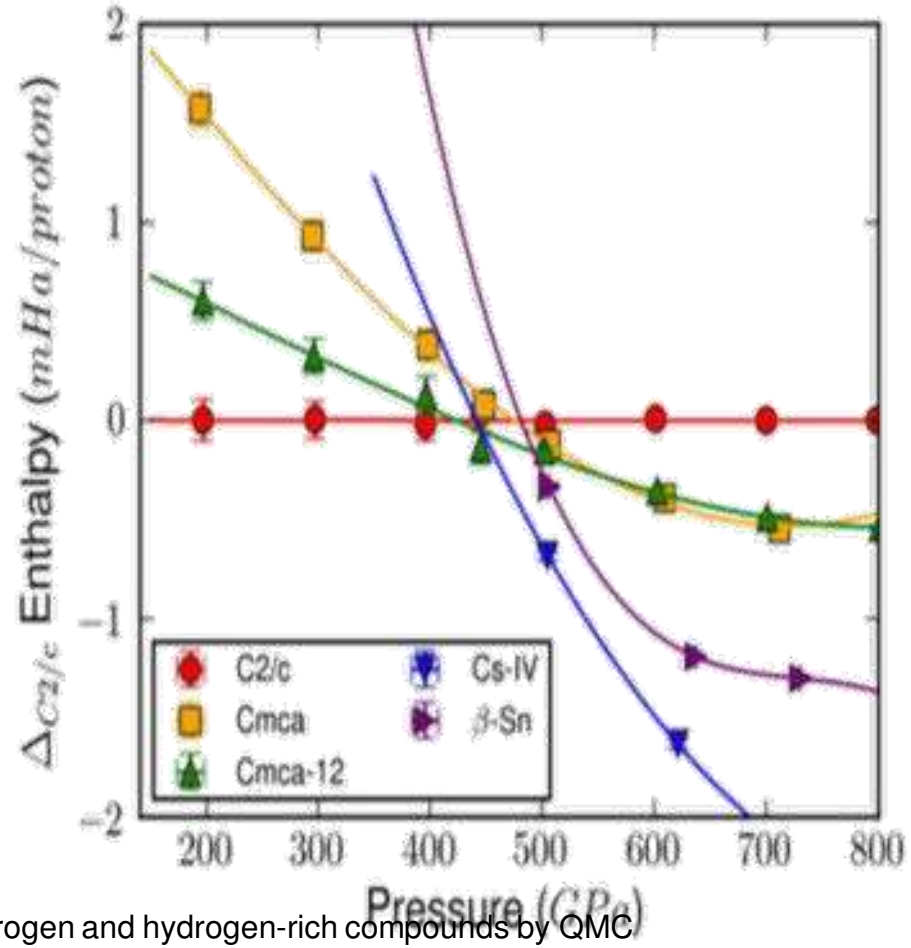

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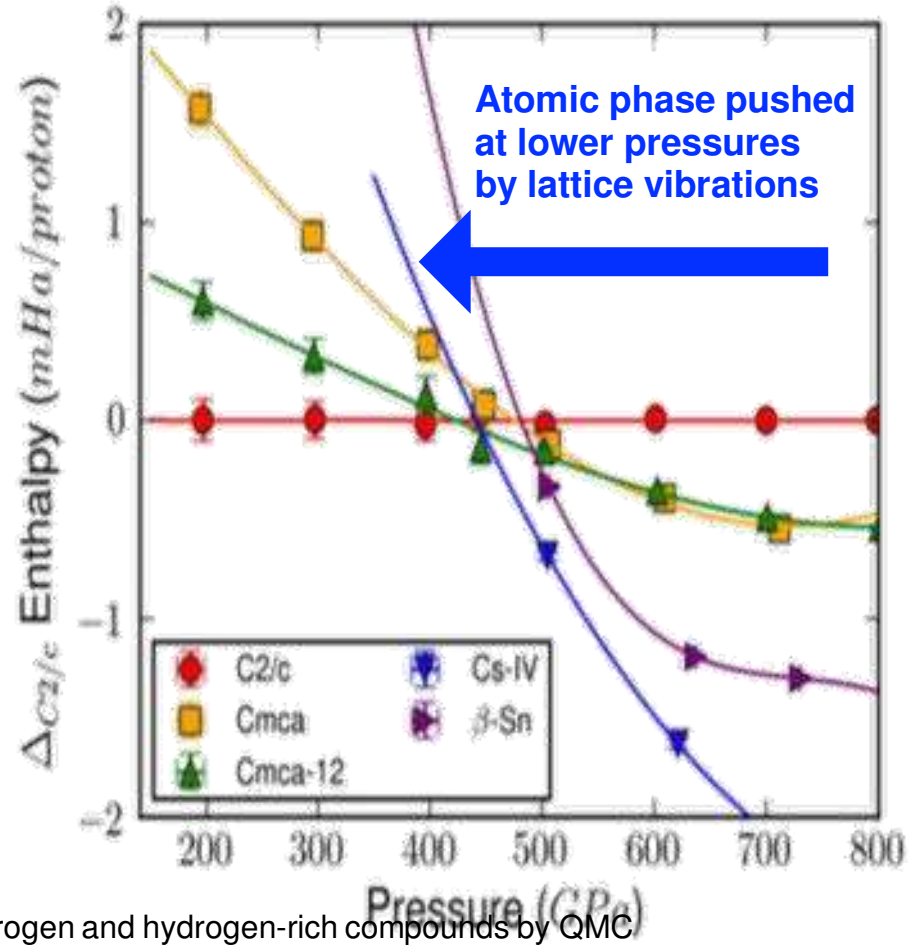

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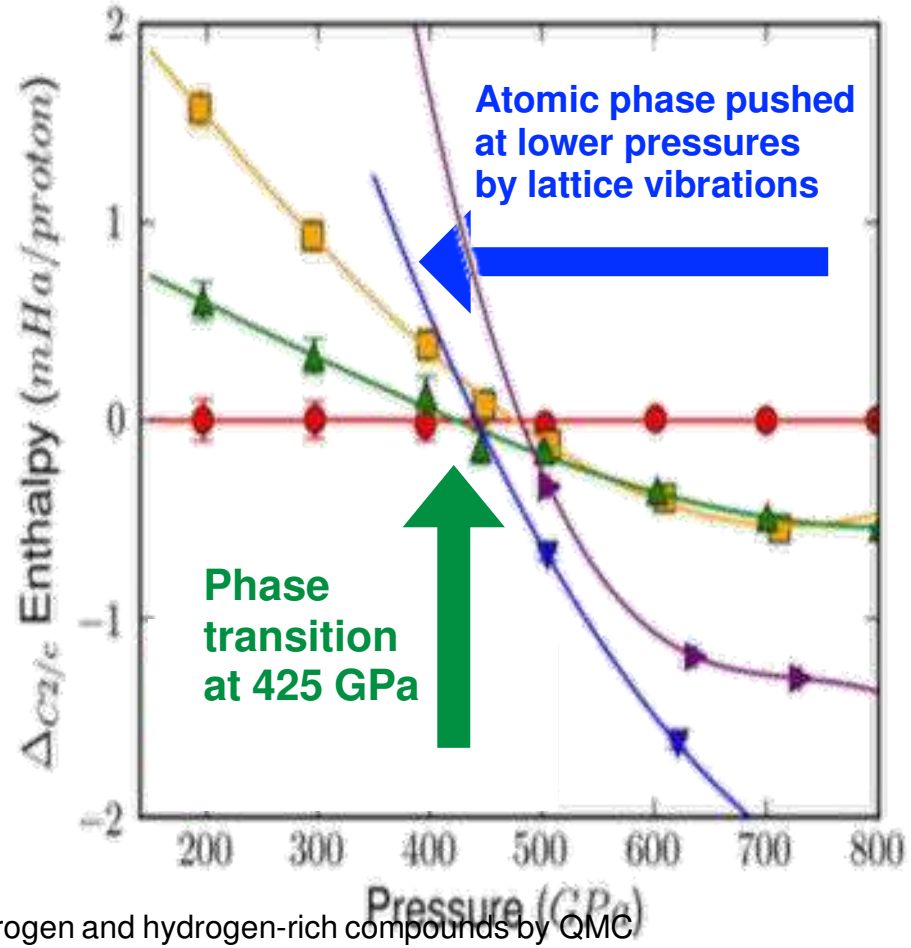
Predicted transition
from C2/c to Cmca-12
However atomic phase very close!



Phase transition @ 425 GPa observed!

Synchrotron infrared spectroscopic evidence of the probable transition to metal hydrogen

https://doi.org/10.1038/s41586-019-1927-3
Received: 12 April 2019
Accepted: 26 November 2019
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Paul Loubeyre[1]*, Florent Occelli[1] & Paul Dumas[1,2]

Hydrogen has been an essential element in the development of atomic, molecular and condensed matter physics[1]. It is predicted that hydrogen should have a metal state[2];

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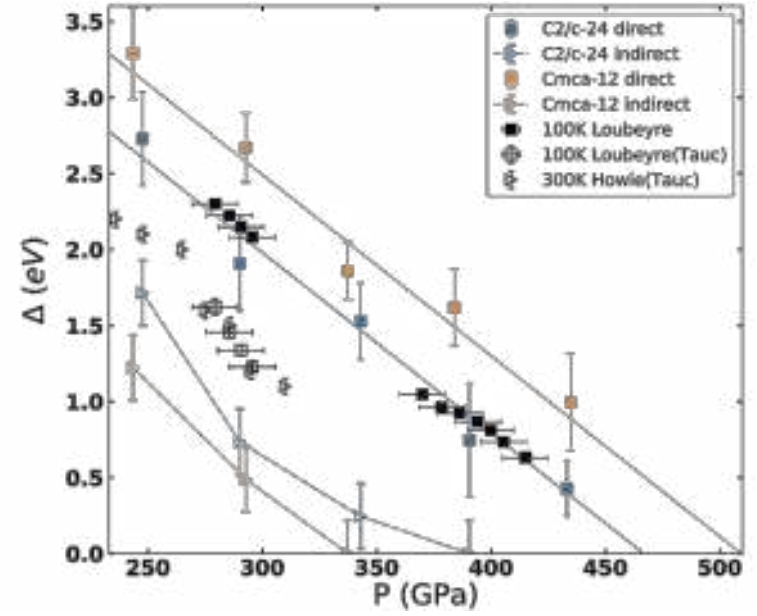
PRL **124**, 1 6401 (2020),
Gorelov, Holzmann, Ceperely, Pierleoni

Direct gap computed by reptation QMC on coupled electron-ion Monte Carlo lattice configurations

C2/c gap closure in agreement with infrared spectroscopy
Strong renormalization by NQE!!!
(as also suggested by Azadi, Drummond, Foulkes in PRB **95**, 035142 (2017))



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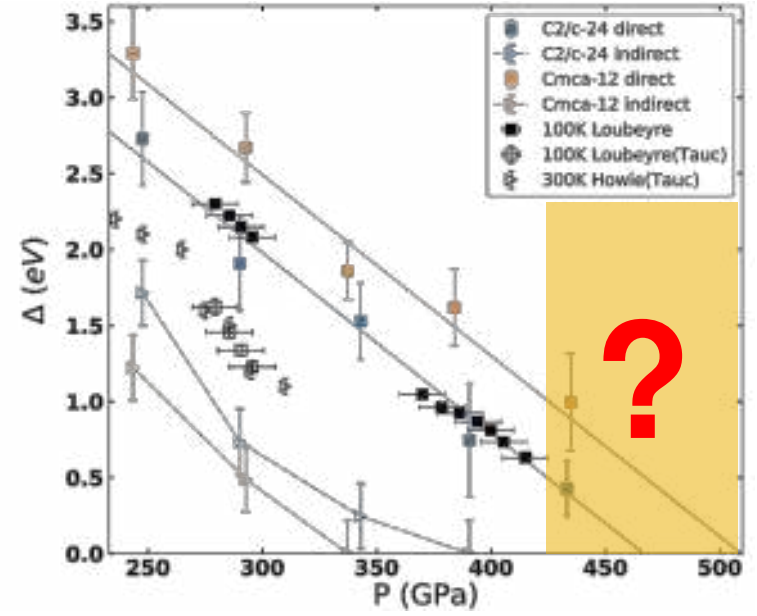
Which metallic phase above 425 GPa?

Where is the atomic phase located?



Including quantum anharmonicity

Strategy:

1. Compute **anharmonic vibrational energies** using the self consistent harmonic approximation (**SCHA**) within DFT (BLYP)

2. Compute **internal electronic energies** by **diffusion Monte Carlo** on the SCHA centroids (which include structural deformation due to NQE)

3. Add the **SCHA vibrational zero point energy** to the DMC internal energy for the **final phase diagram**

Self consistent harmonic approximation

By construction, the “best harmonic approximation” for the nuclear degrees of freedom at a given potential energy surface.

It minimizes the vibrational free energy functional of the system.

$$\mathcal{F}[\tilde{\rho}] = E[\tilde{\rho}] - TS[\tilde{\rho}] \geq F$$

Gaussian density matrix solution of auxiliary harmonic Hamiltonian

$$\mathcal{H}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}} = K + \frac{1}{2}\sum_{ab}(R_a - \mathcal{R}_a)\Phi_{ab}(R_b - \mathcal{R}_b).$$

The stochastic SCHA implementation minimizes:

$$\mathrm{F} = \min_{\mathrm{R},\Phi} \mathrm{F}[\mathrm{R},\Phi] = \mathrm{F}[\mathrm{q},\Phi_{\mathrm{eq}}]$$

q are the centroid positions, Φ_{eq} is the force constant matrix

QMC wave function

$$\Psi^k_{\mathbf{q}}(\mathbf{x}_1,\ldots,\mathbf{x}_{N_{\rm el}}) = J_{\mathbf{q}}(\mathbf{r}_1,\ldots,\mathbf{r}_{N_{\rm el}})\Psi^k_{SD,q}(x_1,\ldots,x_{N_{el}})$$

q is the ion position, the wave function depends explicitly on the ion coordinates through the ion-centered periodized Gaussian basis set
The Jastrow is optimized at the variational VMC level

$$J_q = \exp\left[\sum_{i}^{N_{el}}\sum_{j}^{N_{atoms}} J_q^{1body}(|r_i - q_j|) + \sum_{i<j}^{N_{el}} \Phi_{J_q}(r_i, r_j)\right]$$

1-body Jastrow $$J_q^{1body}(r-q) = Z_q \frac{1-e^{-aP(|r-q|)}}{a}$$

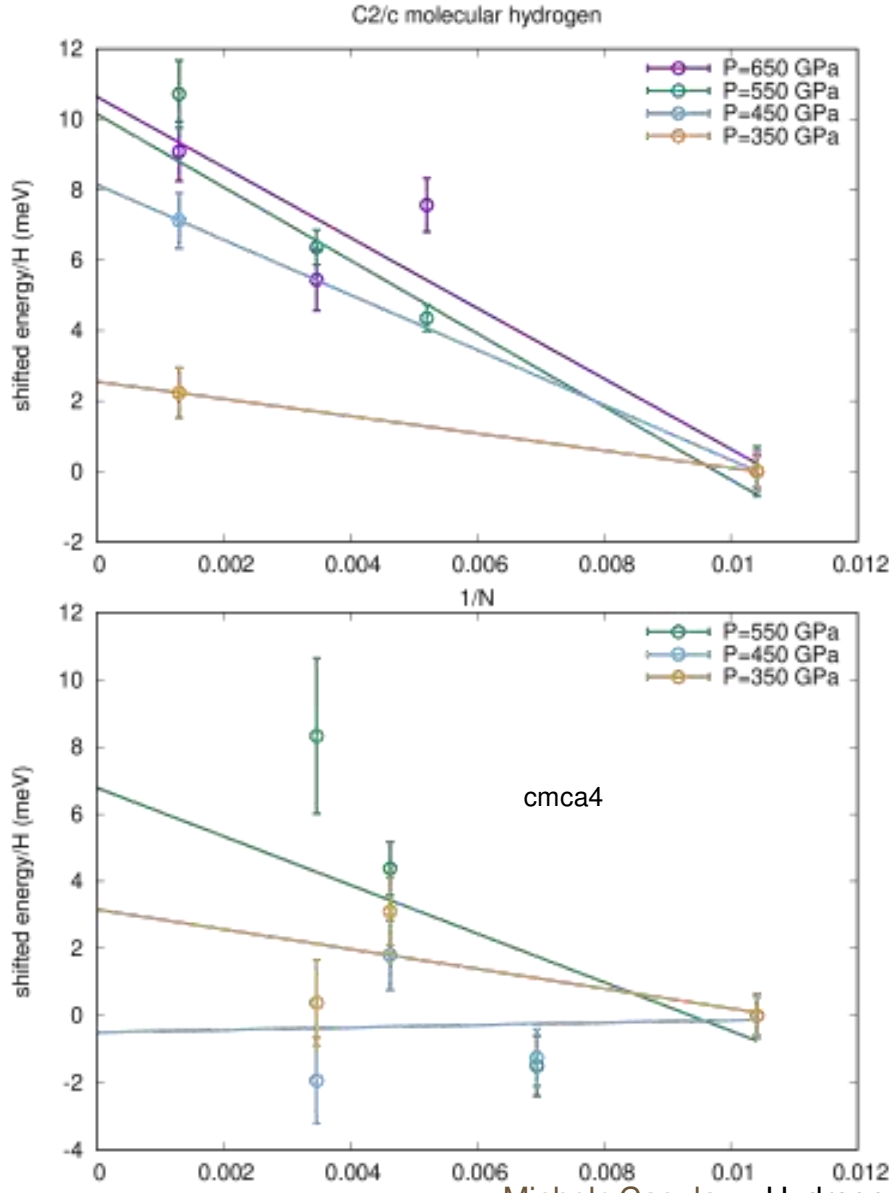
many-body Jastrow $$\Phi_{J_q}(r_i, r_j) = \frac{1}{2}\frac{P(|r_i - r_j|)}{1+bP(|r_i - r_j|)} + \sum_{a,b}^{N}\sum_{\mu,\nu}^{N_{basis}} g^{a,b}_{\mu,\nu}\psi^J_{a,\mu}(r_i - q_a)\psi^J_{b,\nu}(r_j - q_b)$$

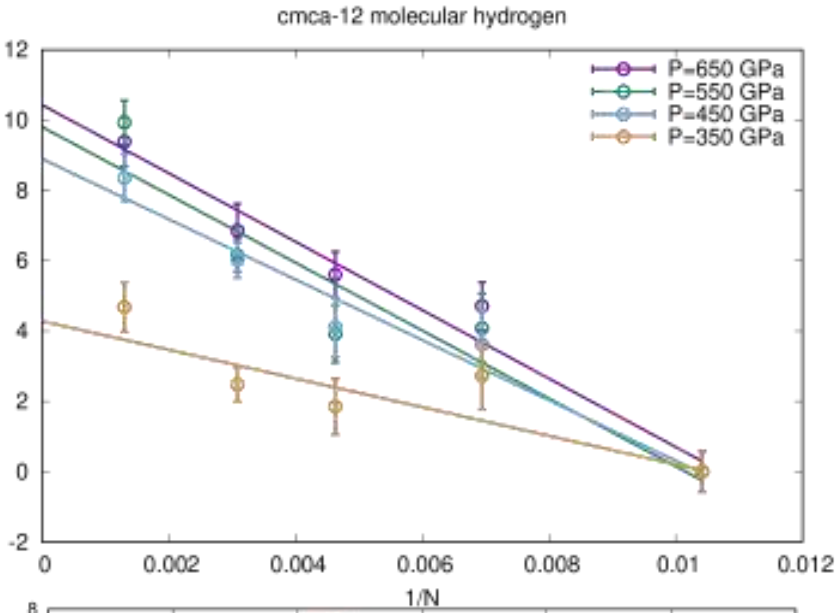
mapping function $$P(x) = \begin{cases} x & (-\frac{1}{6} < x < \frac{1}{6}) \\ -\frac{1}{54(1/2+x)^2} & (-\frac{1}{2} \leqslant x \leqslant -\frac{1}{6}) \\ \frac{1}{54(1/2-x)^2} & (\frac{1}{6} \leqslant x \leqslant \frac{1}{2}). \end{cases}$$ in crystal units

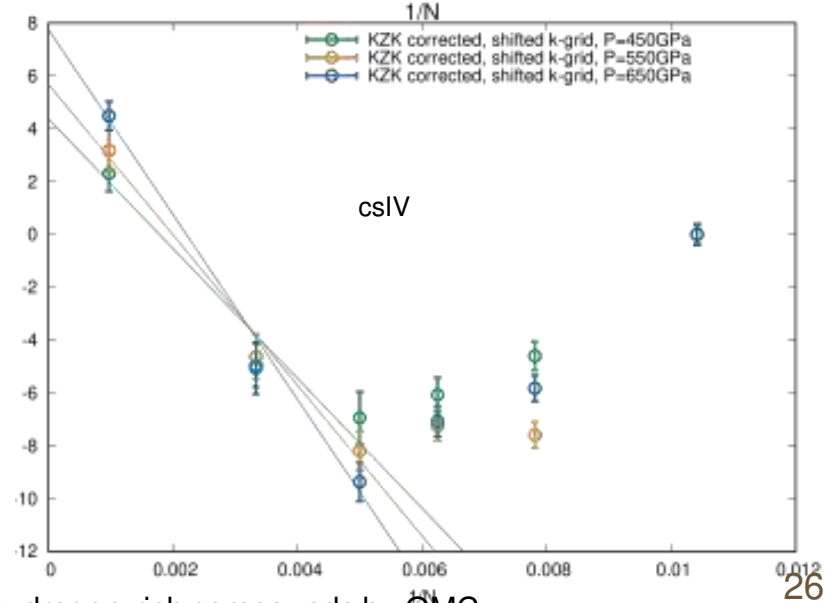
QMC technicalities

- TurboRVB QMC package
- SD orbitals taken from density functional theory (DFT) within the local density approximation (LDA) built in TurboRVB
- Dense k-point sampling (twist average over 18x18x18 in most phases)
- Kwee-Zhang-Krakauer (KZK) functional for finite size corrections
- Explicit finite-size extrapolation up to N_{el}=1024 for the atomic phase and N_{el}=768 for the main molecular phases
- Jastrow optimization
- Nodal relaxation through orbital optimization for N_{el}=96 at some pressure/phase
- Variational and Lattice regularized diffusion Monte Carlo simulations

Finite size-extrapolation







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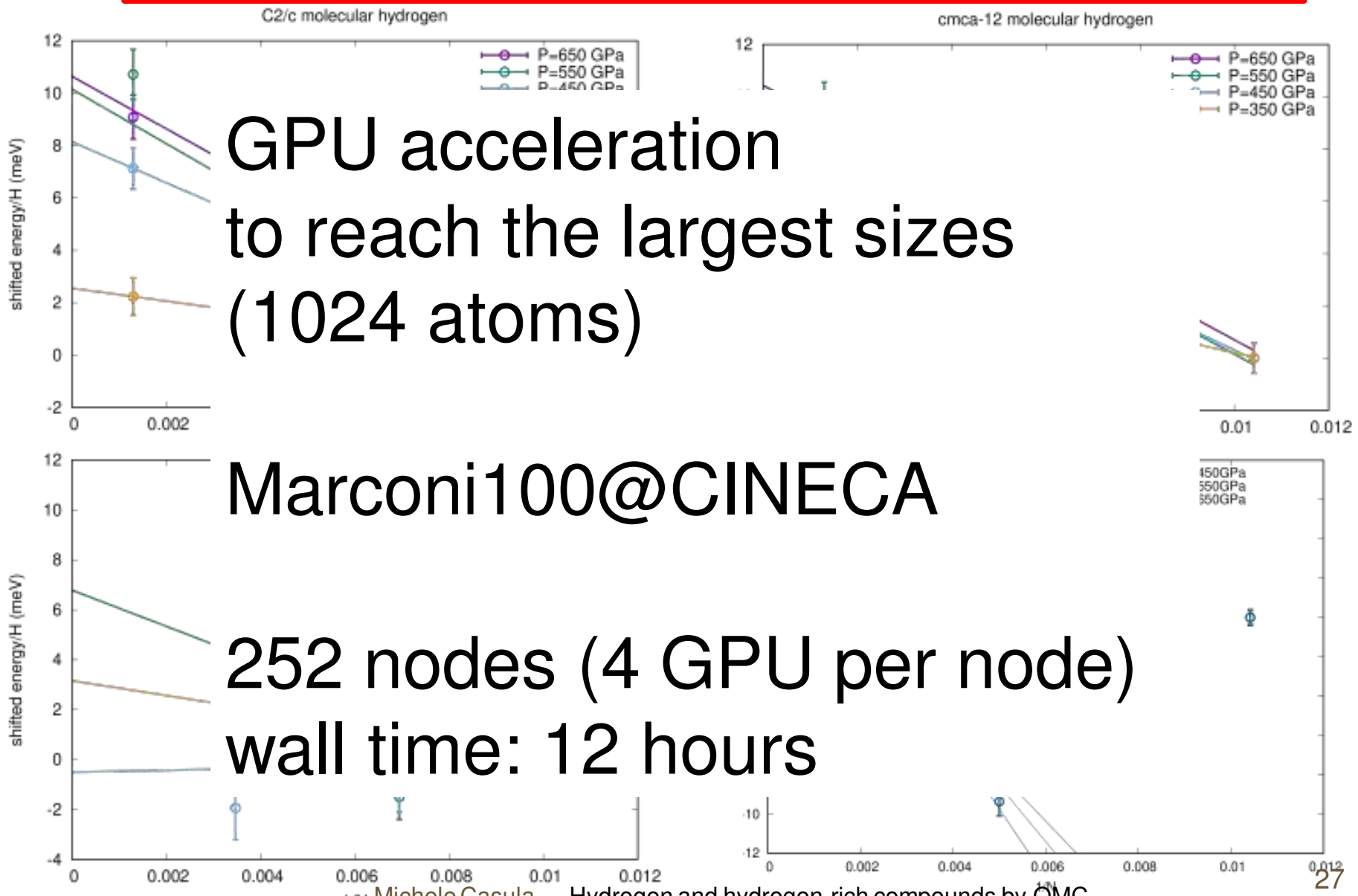
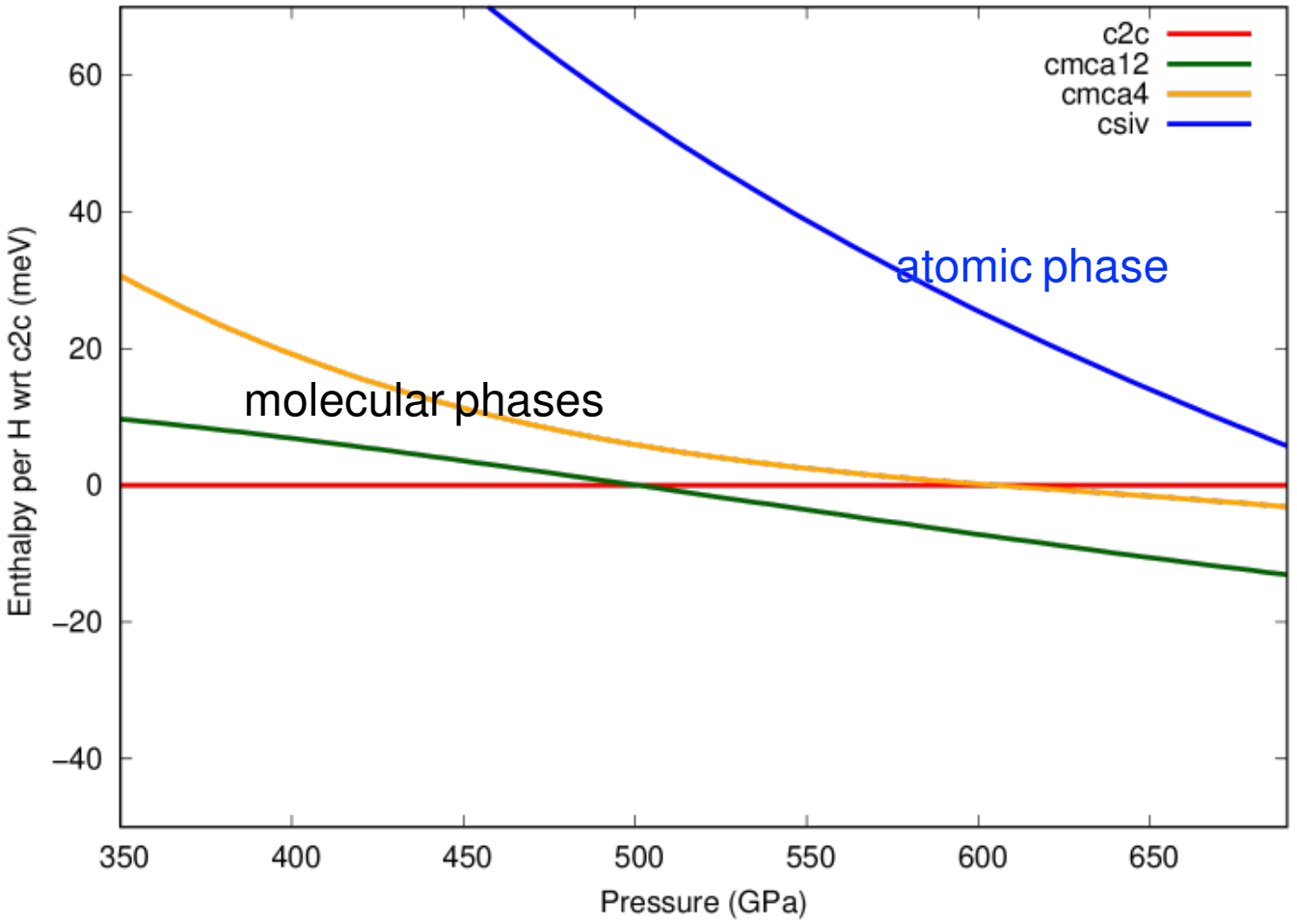


GPU acceleration
to reach the largest sizes
(1024 atoms)

Marconi100@CINECA

252 nodes (4 GPU per node)
wall time: 12 hours

Static lattice (SCHA centroid)



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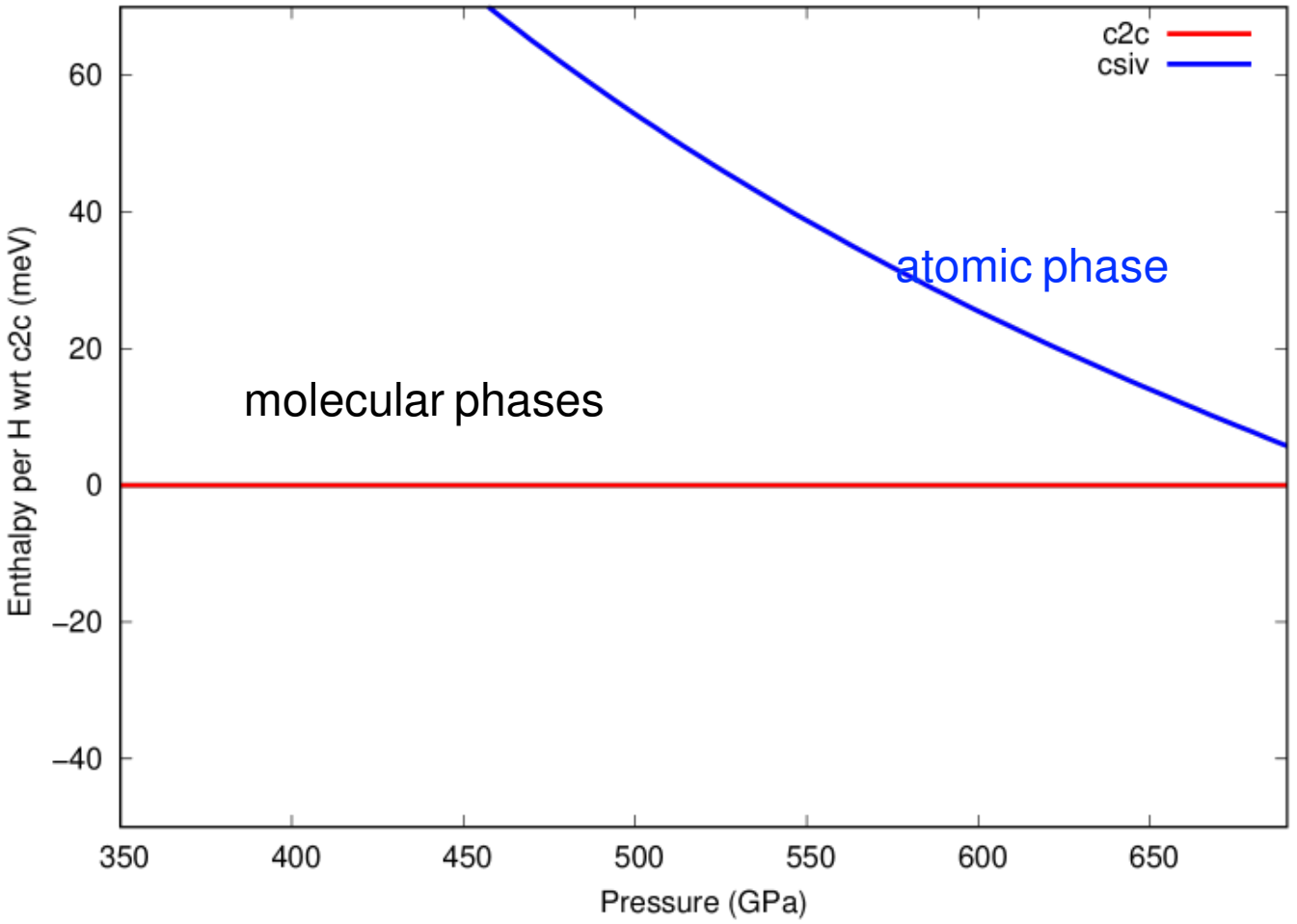
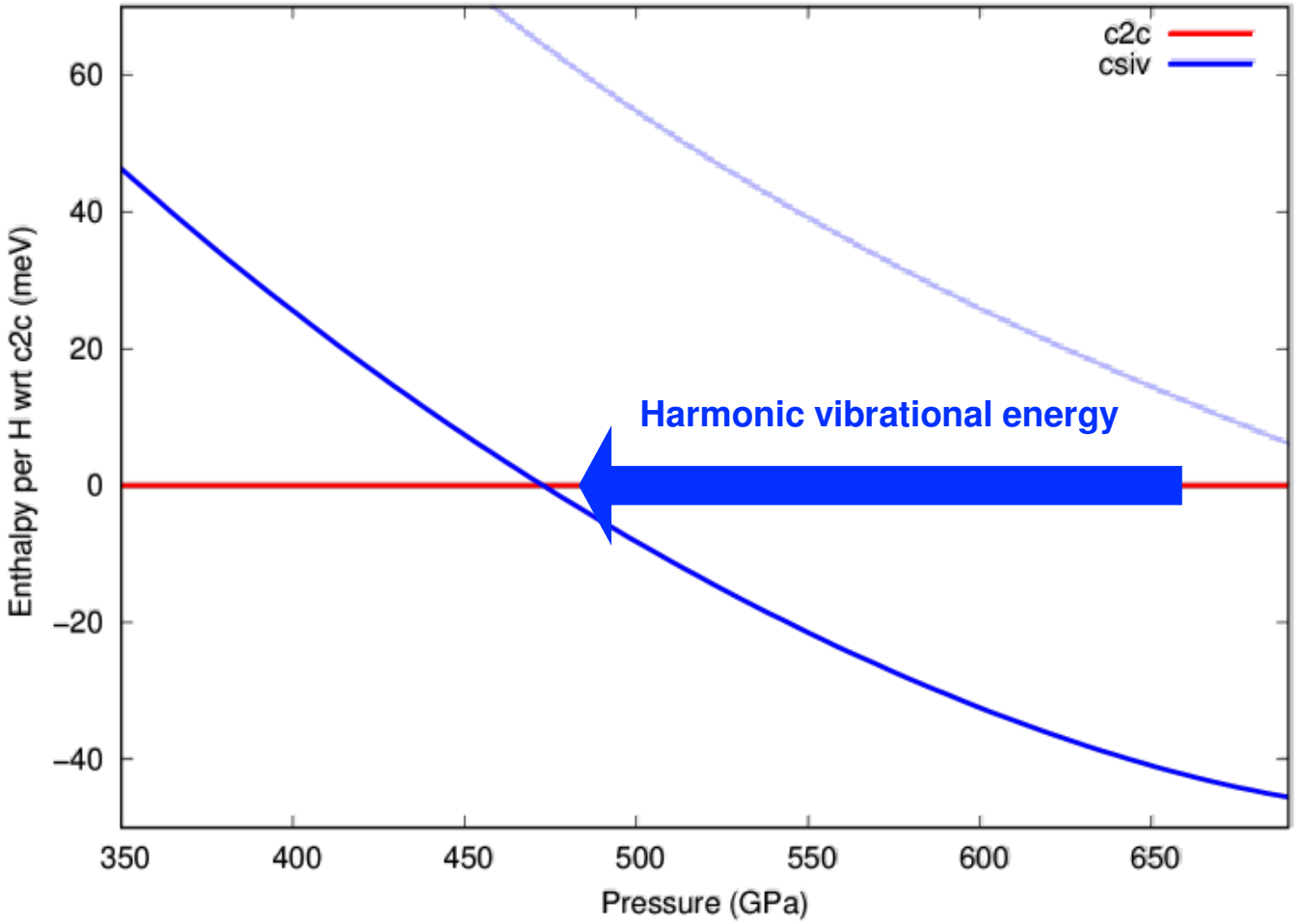
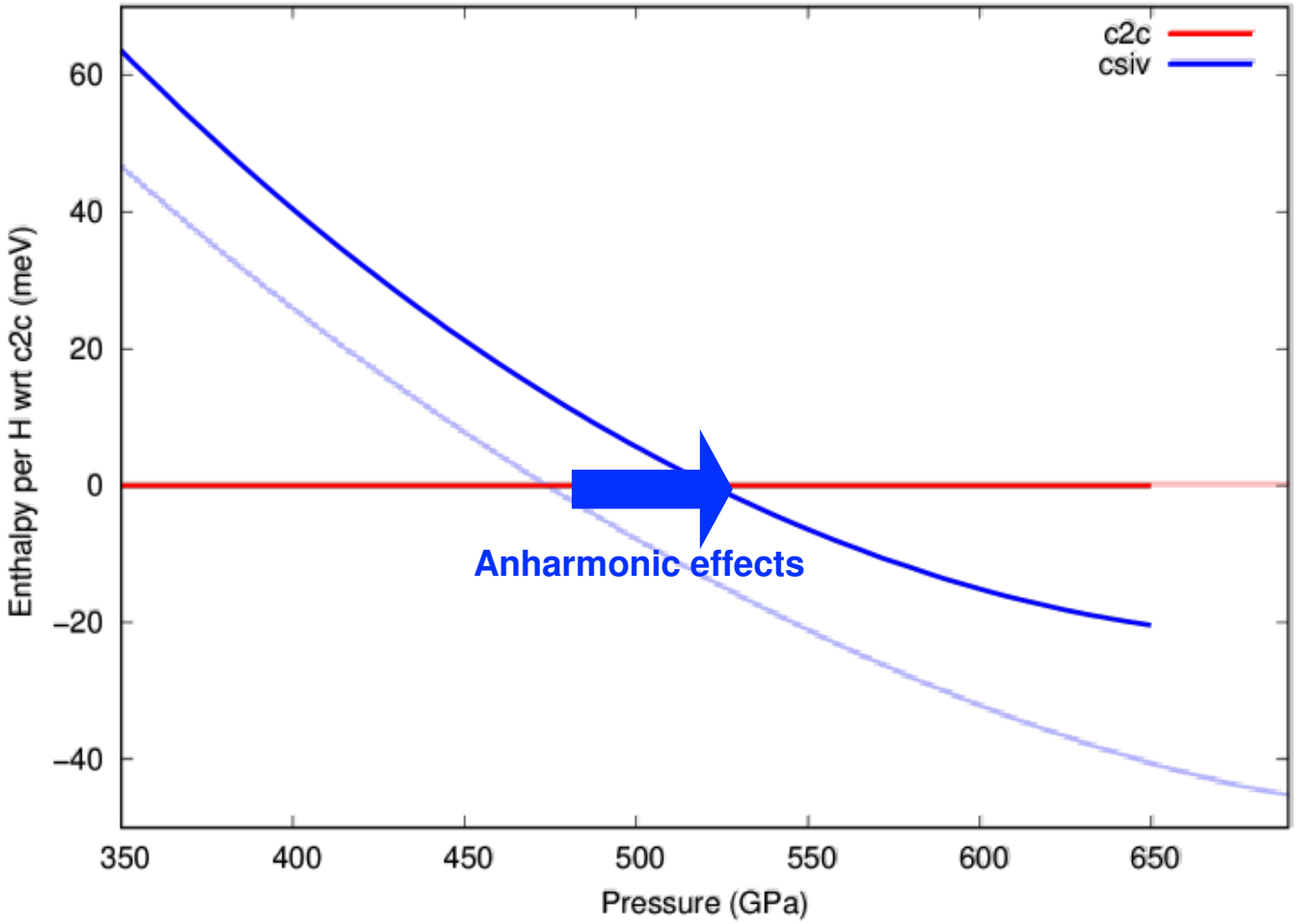


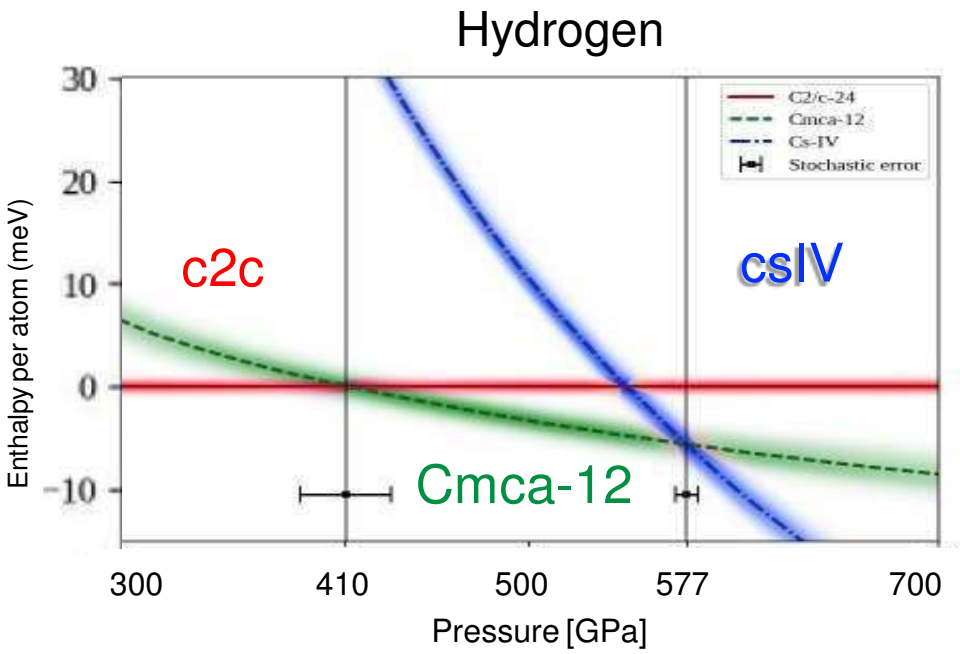
Harmonic lattice (BLYP phonons)



Anharmonic lattice (SCHA phonons)

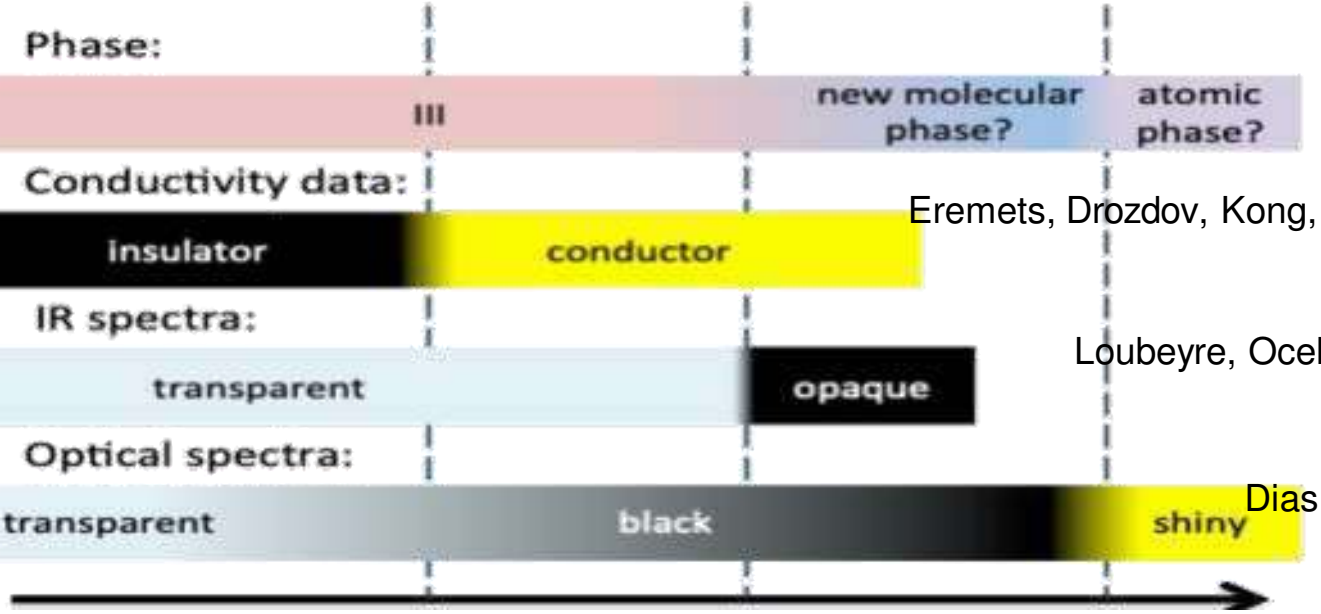


High-pressure phase diagram



- Molecular c2c → Cmca-12 transition pressure **slightly reduced** by anharmonicity
- Atomic phase transiton **pushed up** by anharmonic effects

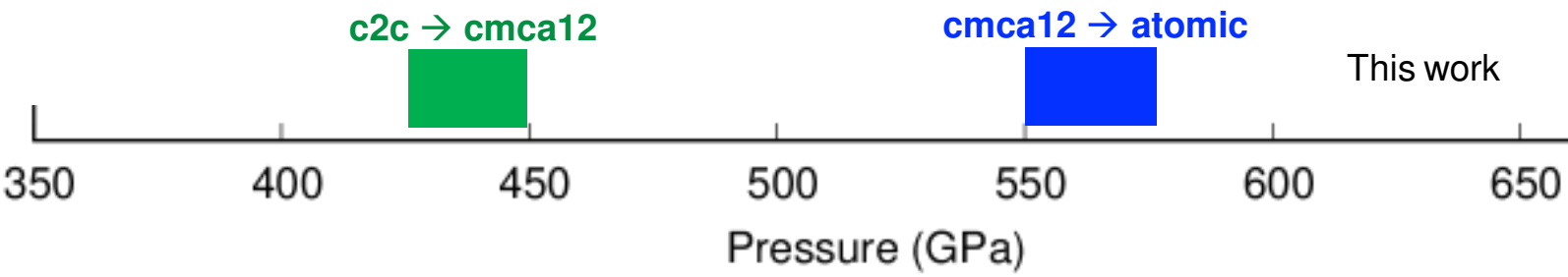
Transition pressures



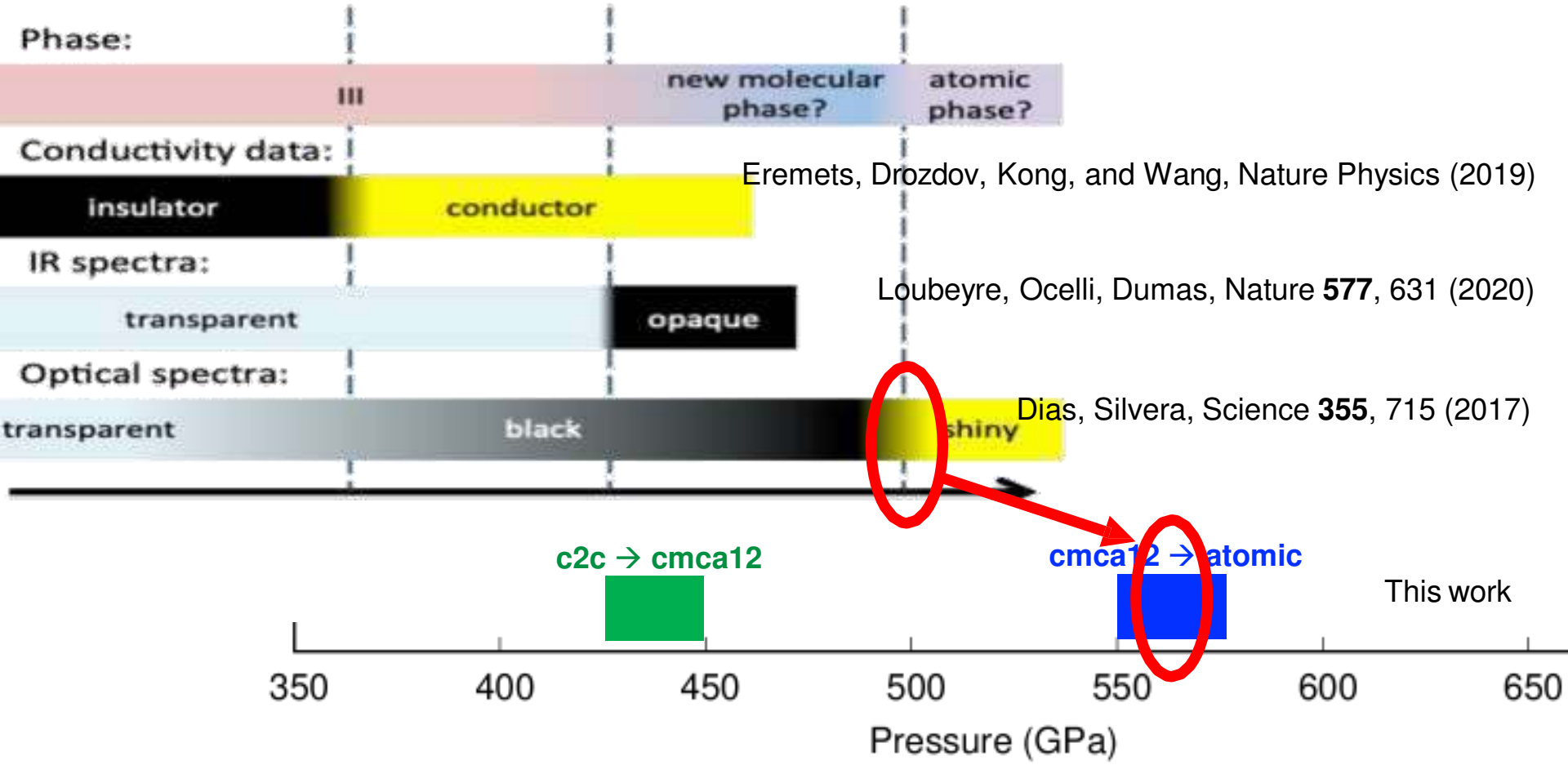
Eremets, Drozdov, Kong, and Wang, Nature Physics (2019)

Loubeyre, Ocelli, Dumas, Nature **577**, 631 (2020)

Dias, Silvera, Science **355**, 715 (2017)



Transition pressures



Eremets, Drozdov, Kong, and Wang, Nature Physics (2019)

Loubeyre, Ocelli, Dumas, Nature **577**, 631 (2020)

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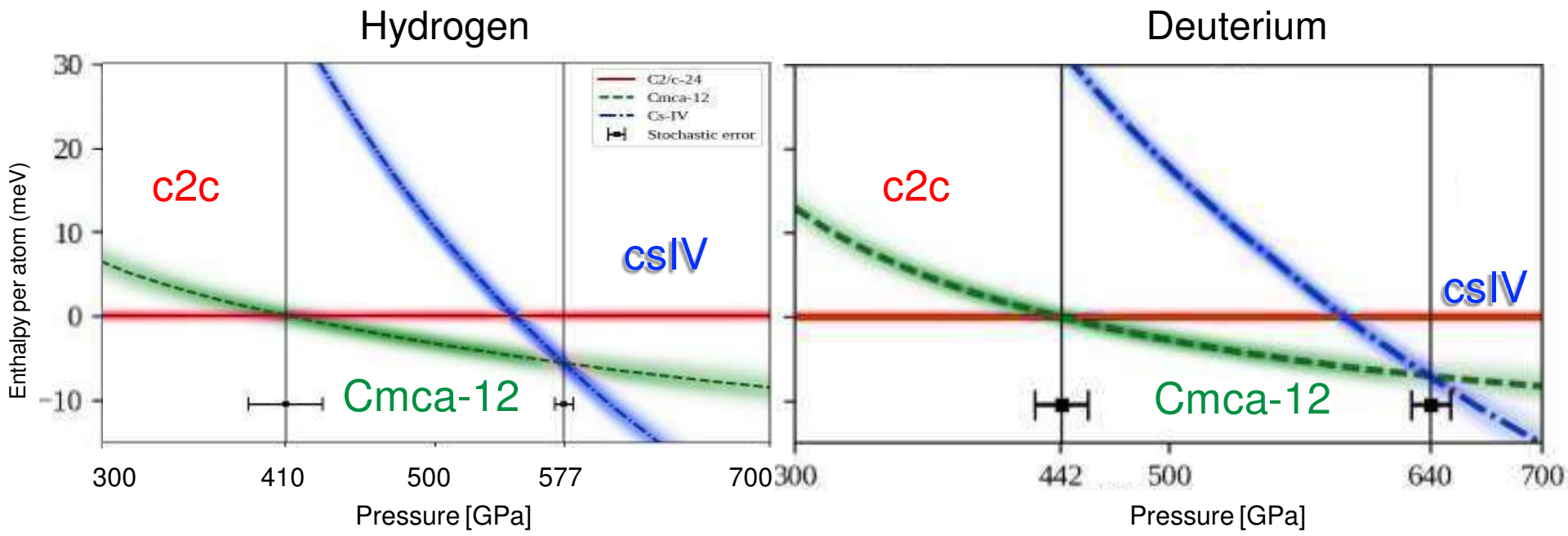
This work

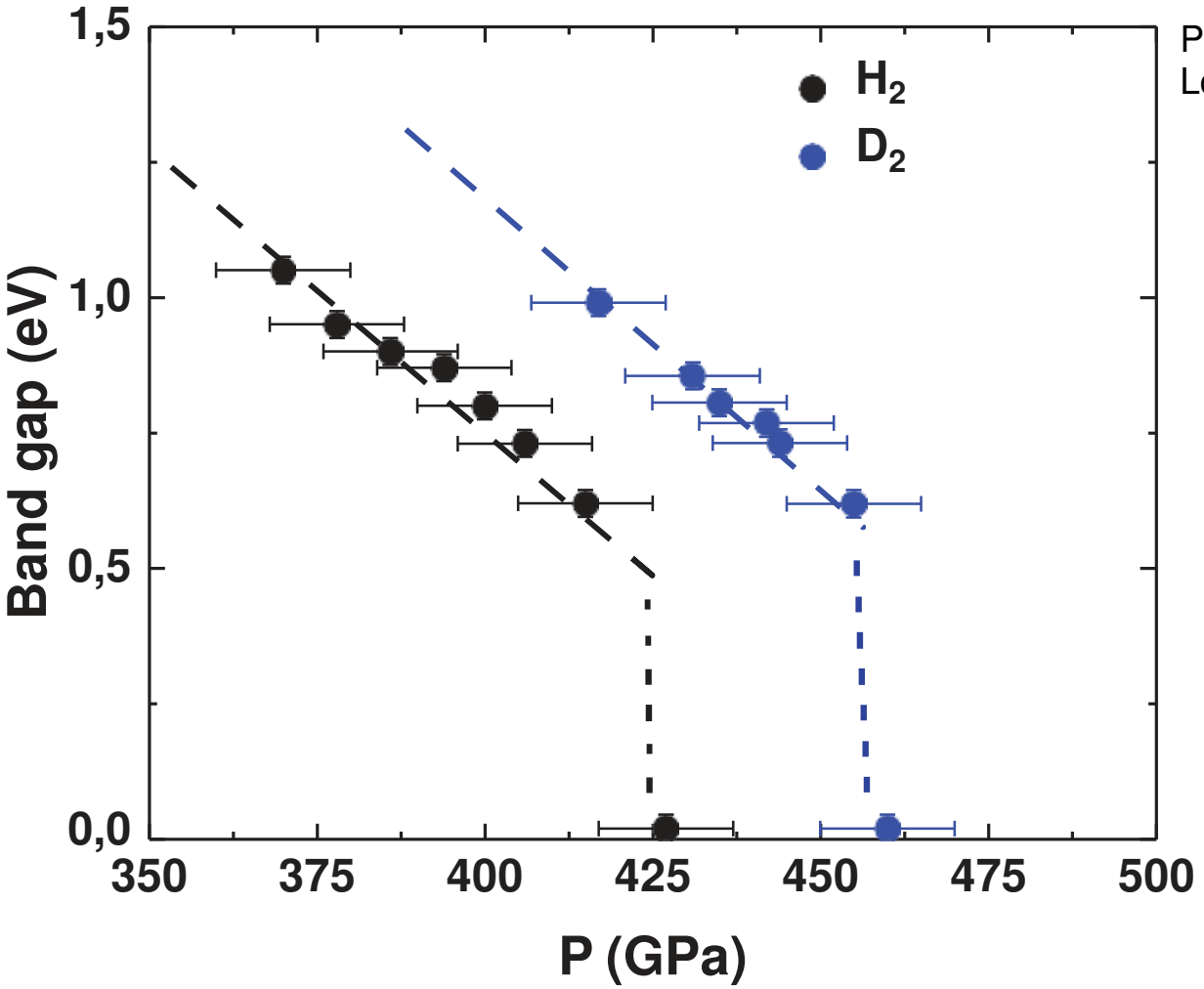
Isotope effect



- **Isotope effect affecting both c2c → Cmca-12 and Cmca-12 → csIV phase transitions:**

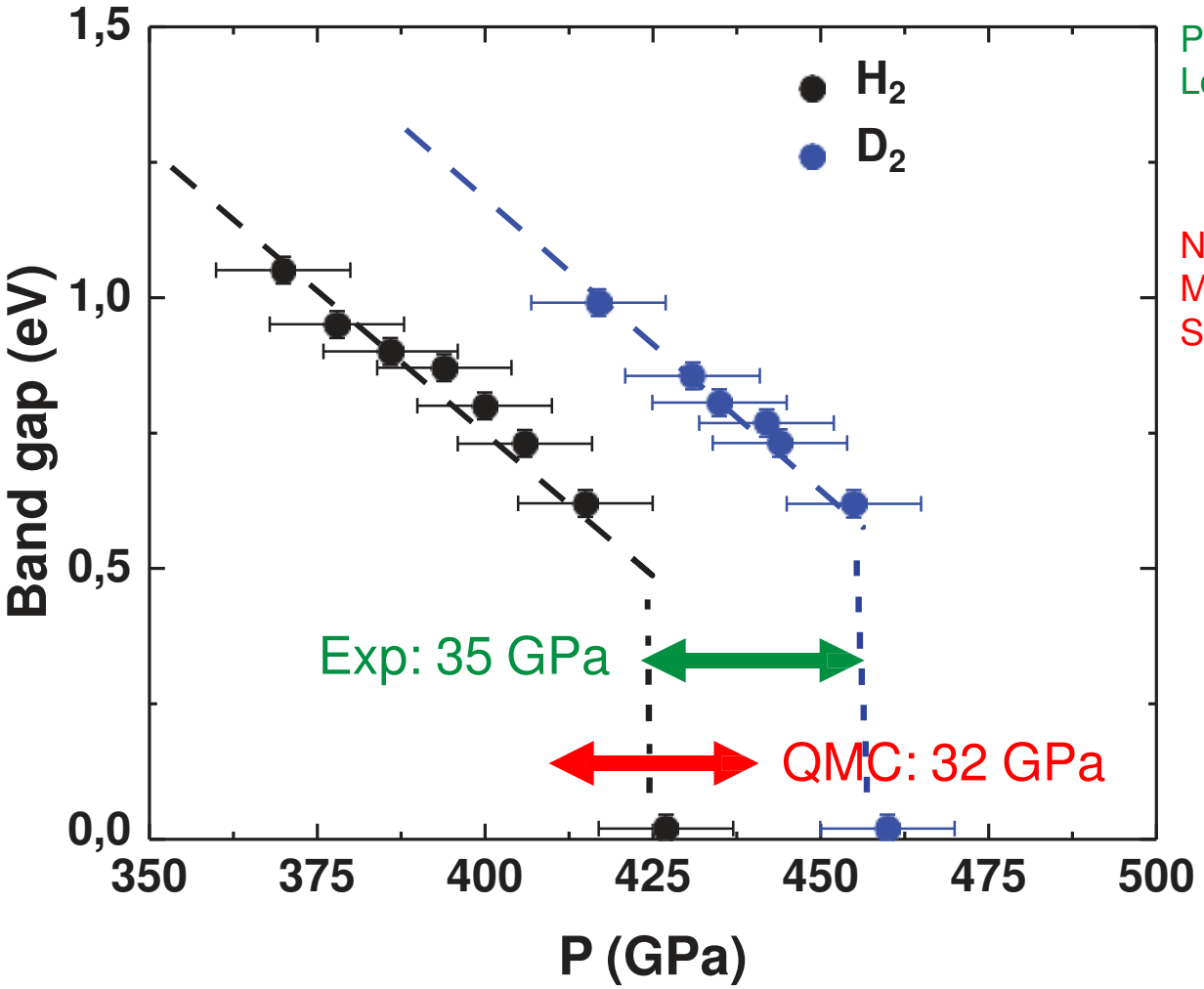
  - ✓ **c2c → Cmca-12 : ~ 32 GPa**
  - ✓ **Cmca-12 → csIV : ~ 63 GPa**

Isotope effect



PRL **129**, 035501 (2022),
Loubeyre, Occelli, Dumas

Isotope effect



PRL **129**, 035501 (2022), Loubeyre, Occelli, Dumas

Nature Physics **19**, 845 (2023), Monacelli, Casula, Nakano, Sorella, Mauri

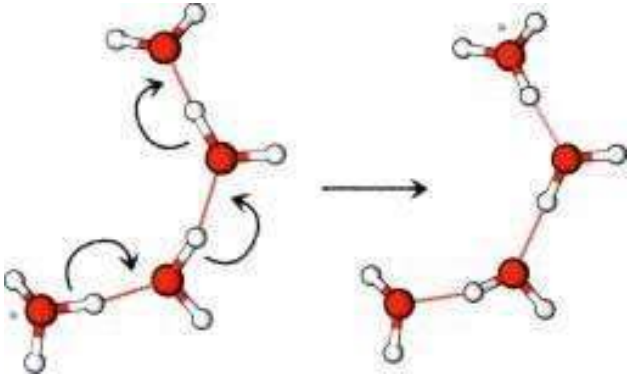
Hydrogen wrap-up

- Combining QMC with SCHA
- Importance of anharmonic contributions enhanced by NQE to determine the phase diagram of hydrogen
- In solid hydrogen, anharmonicity strongly affects the molecular-to-atomic phase transition (molecular crystals more anharmonic than atomic crystals)
- First-order phase transition (associated with direct gap closure) numerically found around 410 GPa between molecular phases
- Large isotope effect in the transitions
- Atomic phases (superconductivity?) pushed well above 500 Gpa

Reference: Nature Physics **19**, 845 (2023), Monacelli, Casula, Nakano, Sorella, Mauri

Hydrated proton

Exploring properties of **hydrogen bond** in protonated water clusters

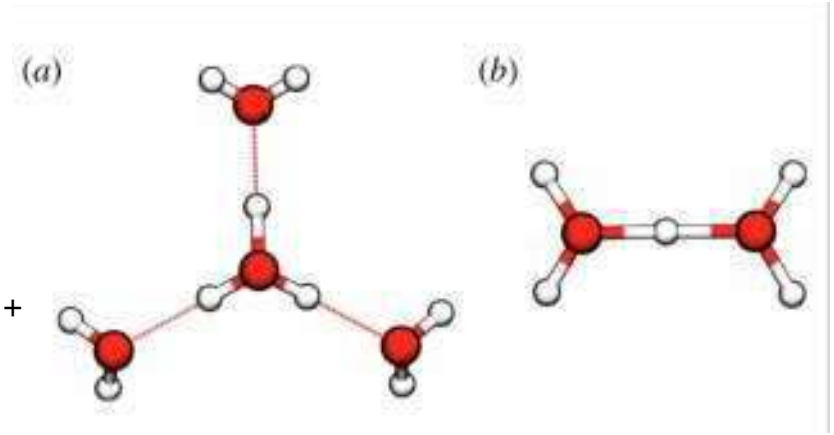


Hydrogen bond network defect (by excess proton) to study **proton hopping**

Two limiting species exist

(a) Eigen $H_9O_4^+$: localized H^+

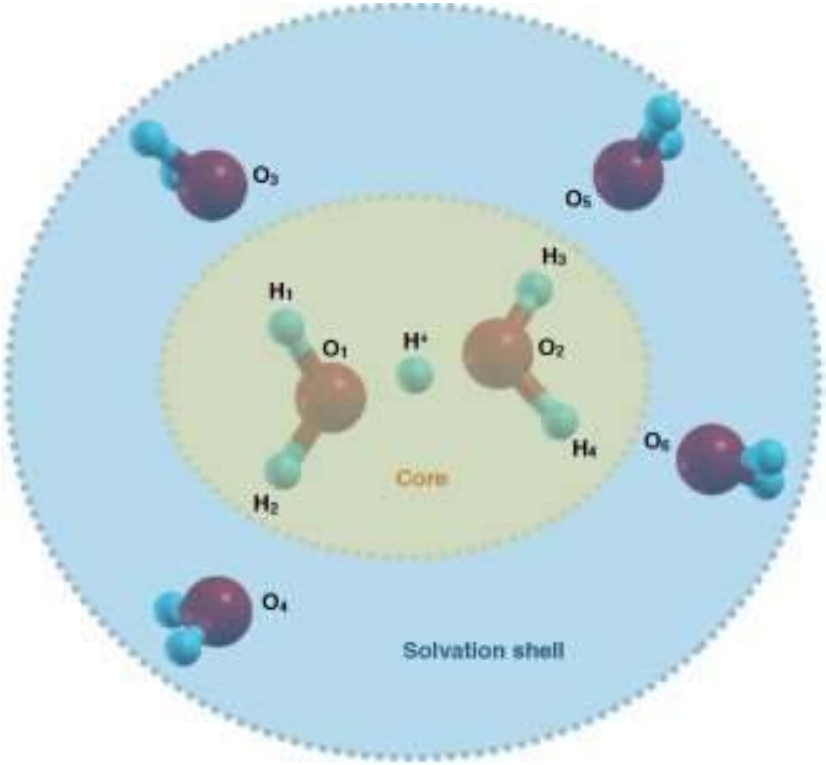
(b) Zundel $H_5O_2^+$: delocalized / shared H^+

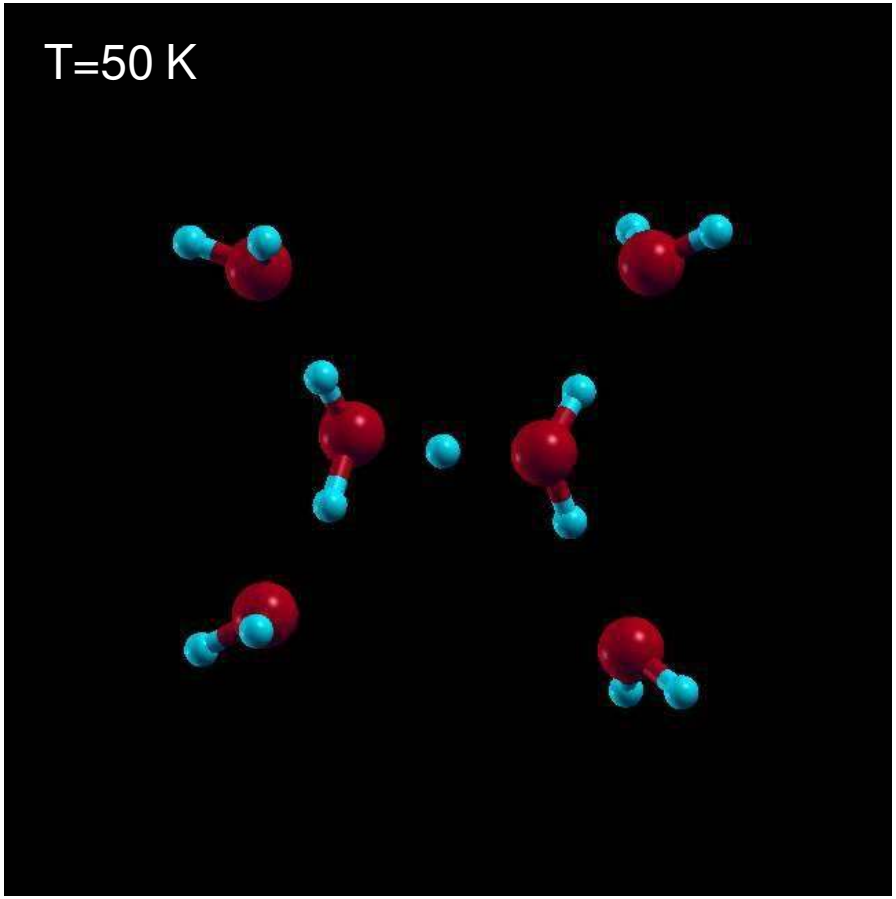


What is their role in proton diffusion?
Broader definition necessary to explain IR experiments?

(Nature Chemistry **10**, 932 (2018))

Taking solvation into account





"realistic" cluster to simulate proton defect in water:
protonated water hexamer $H_{13}O_6^+$

Lapid, Agmon, Petersen, Voth, J. Chem. Phys. **122**, 014506 (2005)

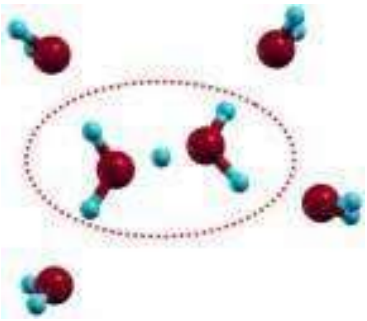
Protonated water hexamer

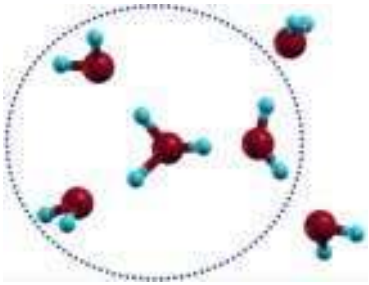
Smallest system to include both Zundel and Eigen structures.

Zundel-like

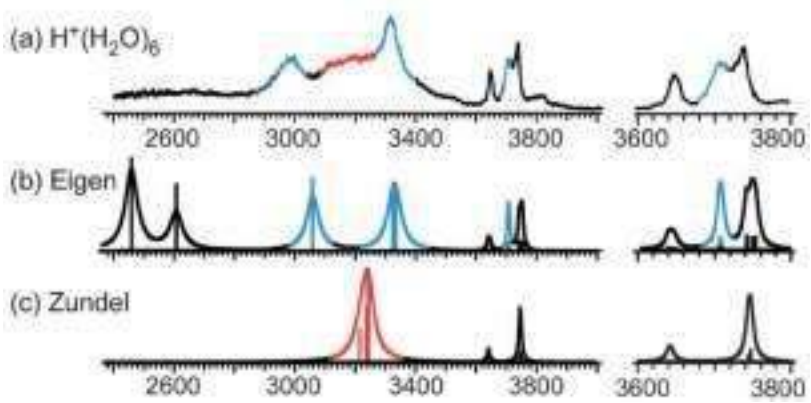
Eigen-like

symmetric





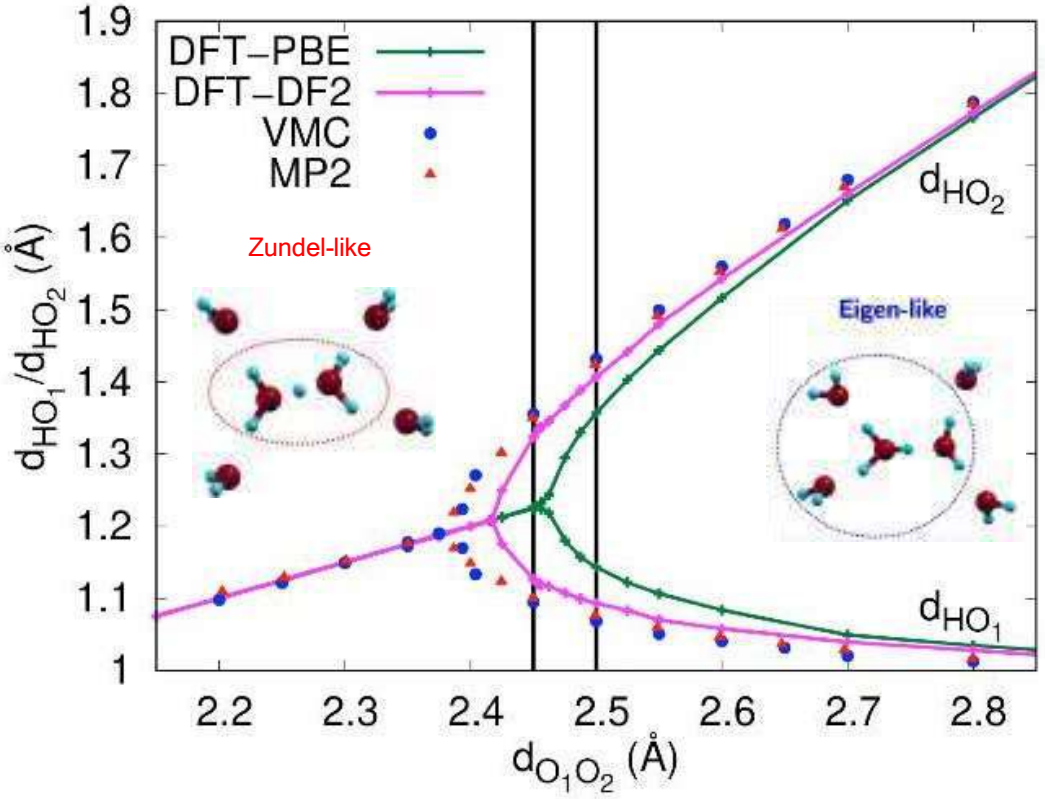
asymmetric (localized)



Infrared photodissociation spectroscopy: K. Mizuse *et. al*, PCCP **13**, 7129 (2011)

Broadband 2D IR spectroscopy: Fournier, Carpenter, Lewis, Tokmakoff, Nat. Chem. **10**, 932 (2018).

Proton potential and barriers at 0K in the protonated water hexamer

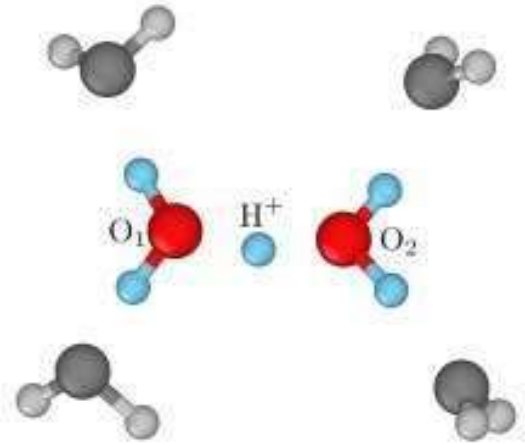


energies are in K

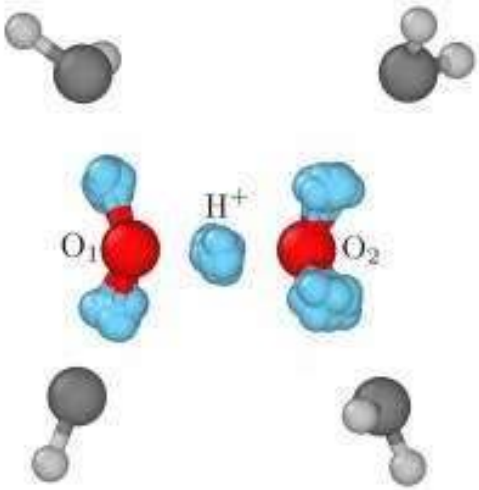
dO_1O_2	2.45 Å	2.50 Å
DFT-PBE	0	96
DFT-DF2	39	483
VMC	195 +/- 25	562 +/- 27
DMC	222 +/- 56	389 +/- 64
MP2	85	327
CCSD(T)	141	431

At the most relevant OO distances, *barriers are of the order of room temperature!*
Short OO distance, H symmetrized; large OO distance, H localized

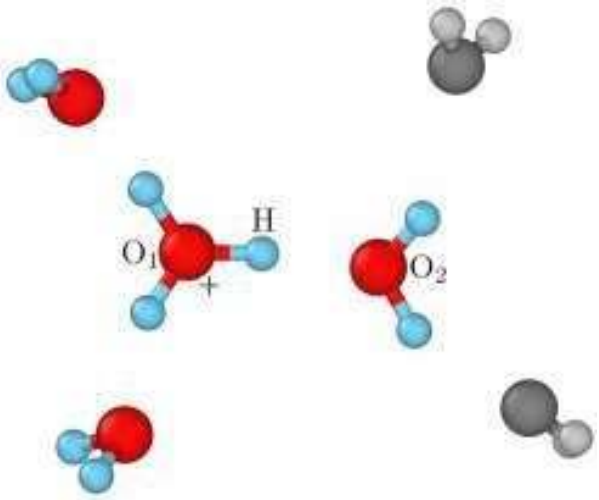
Three “species”



short Zundel



elongated Zundel



distorted Eigen

$d_{O_1O_2} \leq d_{symm} \approx 2.38\text{Å}$

No barrier
Proton equally shared

Dereka *et al.*,
Science **371**, 160 (2021)

Around equilibrium volume

Small barrier (< 500 K)
Proton equally shared
due to *zero-point energy*

$d_{O_1O_2} > 2.5\text{Å}$

Larger barrier (> 500 K)
Proton localized
more classical behavior

What is the effect of temperature?

Scheme followed:

1. **very accurate treatment of the electronic part**
   → Quantum Monte Carlo at the variational level

2. **include thermal effects**
   → Langevin Dynamics at finite temperature

3. **propagate equations of motion for quantum nuclei**
   → Path Integral + Langevin Dynamics (PILD)

Algorithm to combine QMC with PILD →
Path Integral Ornstein-Uhlenbeck Dynamics (PIOUD)

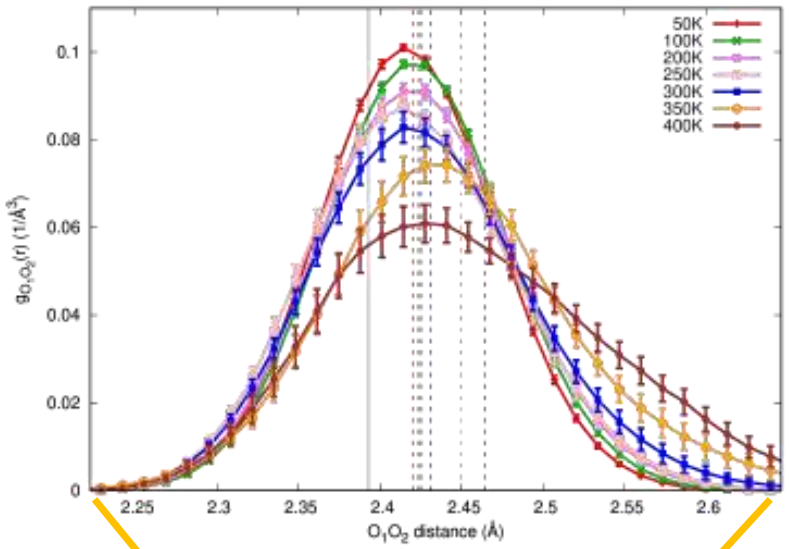
Mouhat *et al.*, J. Chem. Theory Comput. **13**, 2400 (2017)

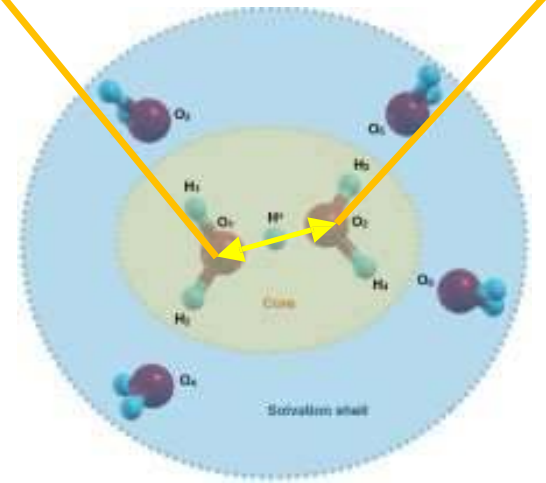
HPC simulations

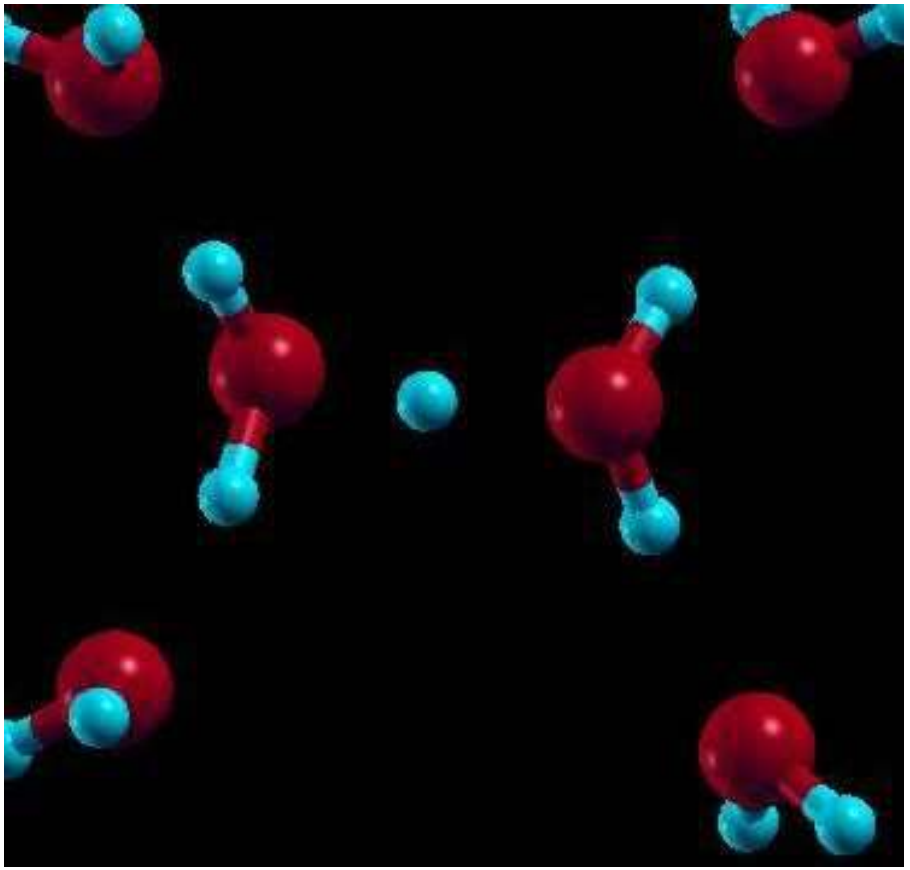
	quantum simulations			classical simulations	
T(K)	N_{beads}	$N_{iterations}$	$t_{iteration}$(h)	$N_{iterations}$	$t_{iteration}$(h)
50	128	35282	119.4[1]	-	-
100	128	52184	24.4[2]	21454	42.0[2]
150	64	11218	-	-	-
200	64	32553	95.7[1]	20478	103.6[1]
250	32	23912	92.2[1]	24154	123.5[1]
300	32	31929	106.3[1]	22656	109.9[1]
350	32	18489	102.4[1]	26481	130.5[1]
400	32	23026	120.9[1]	27517	134.0[1]

1: 68-core Intel Xeon Phi 7250 CPU (Knights Landing) nodes at 1.40 GHz
2: dual-processor (2x64 cores) AMD Rome (Epyc) compute nodes at 2.6 GHz

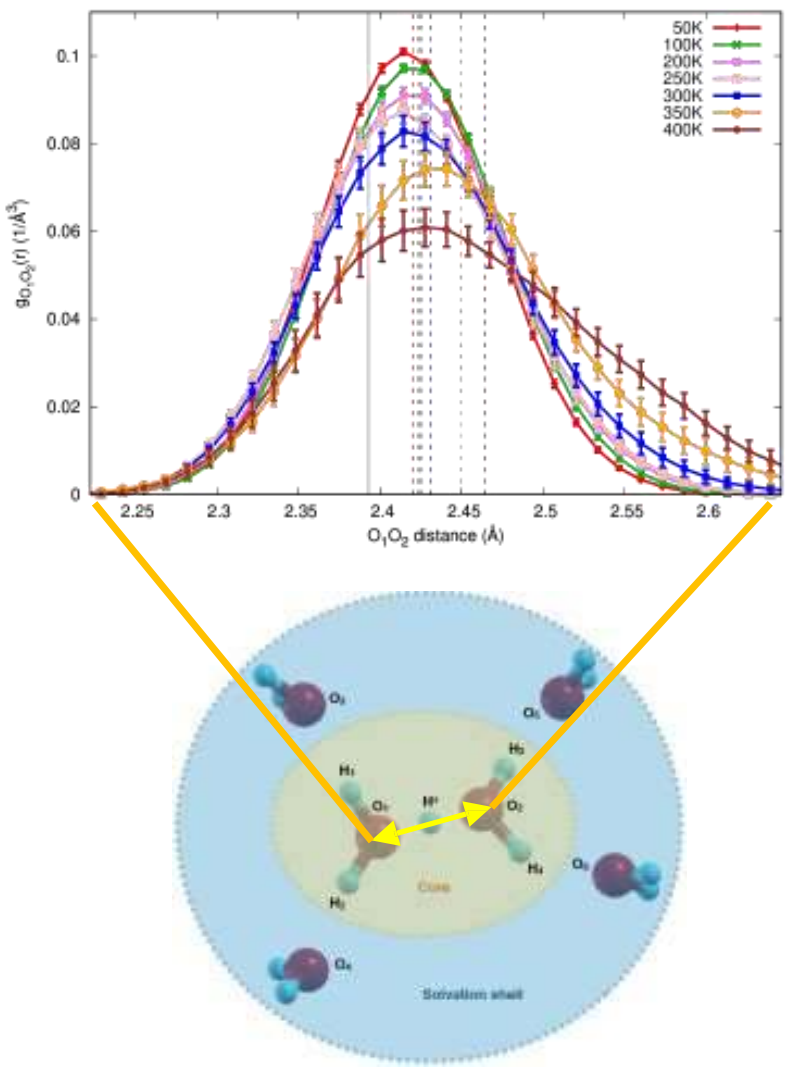
Core size of protonated water hexamer

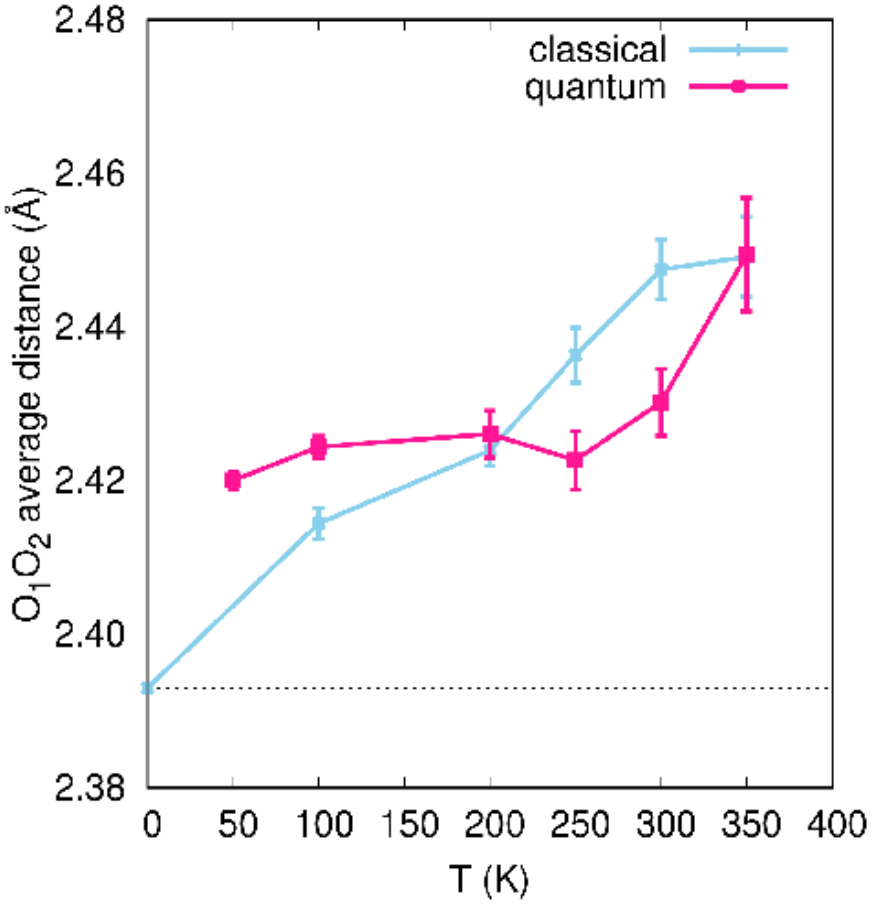




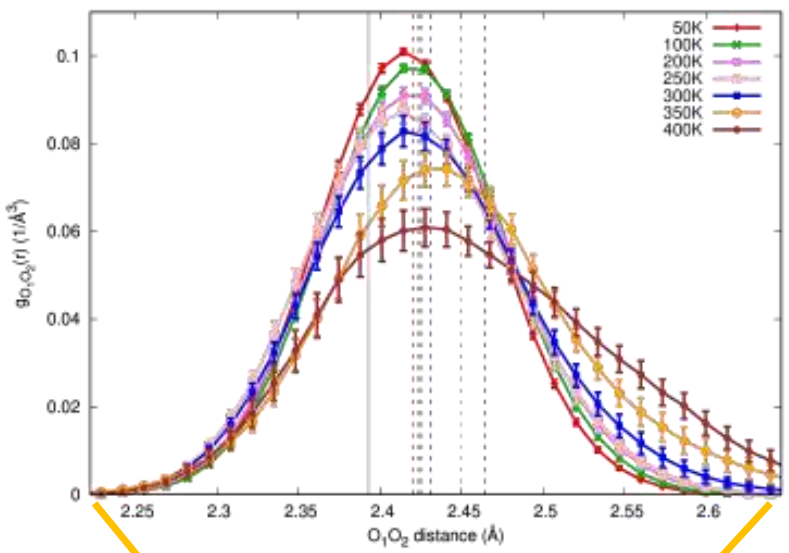


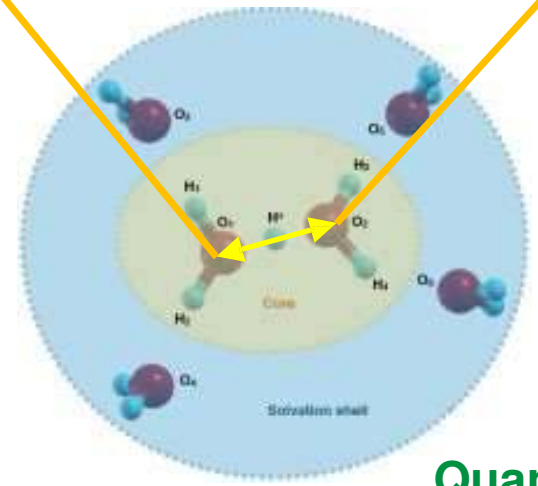
Core size of protonated water hexamer

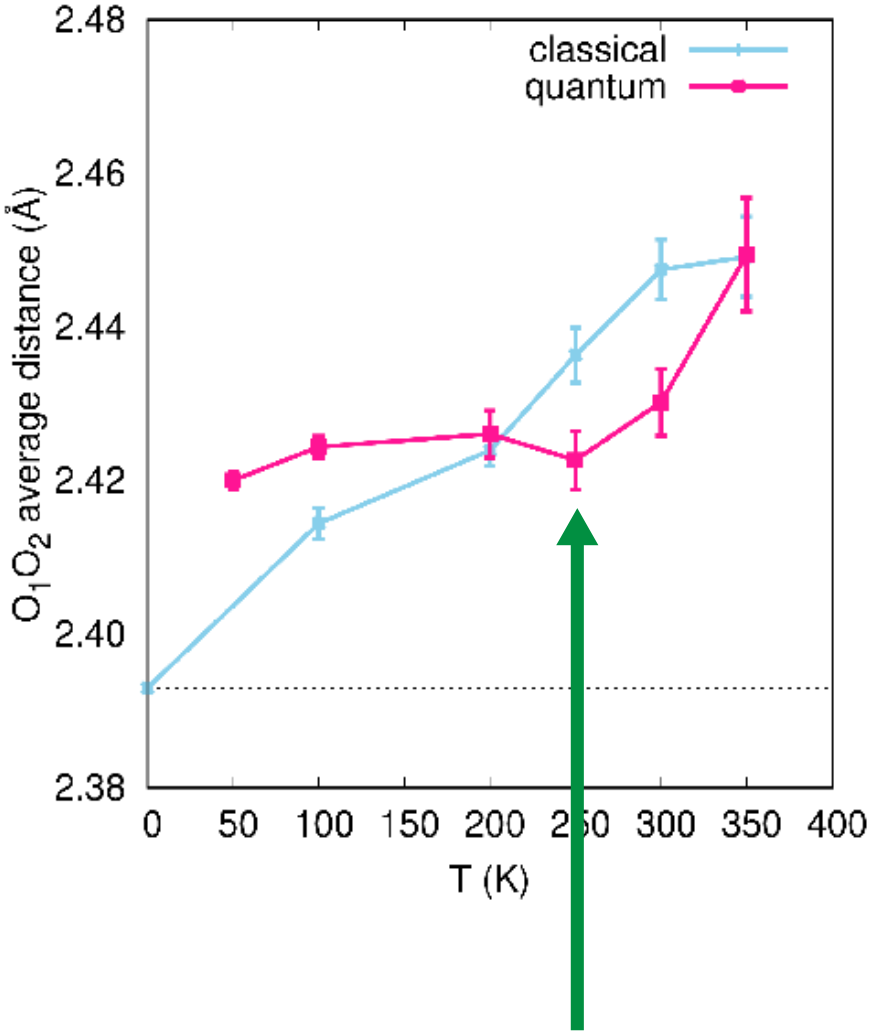




Core size of protonated water hexamer



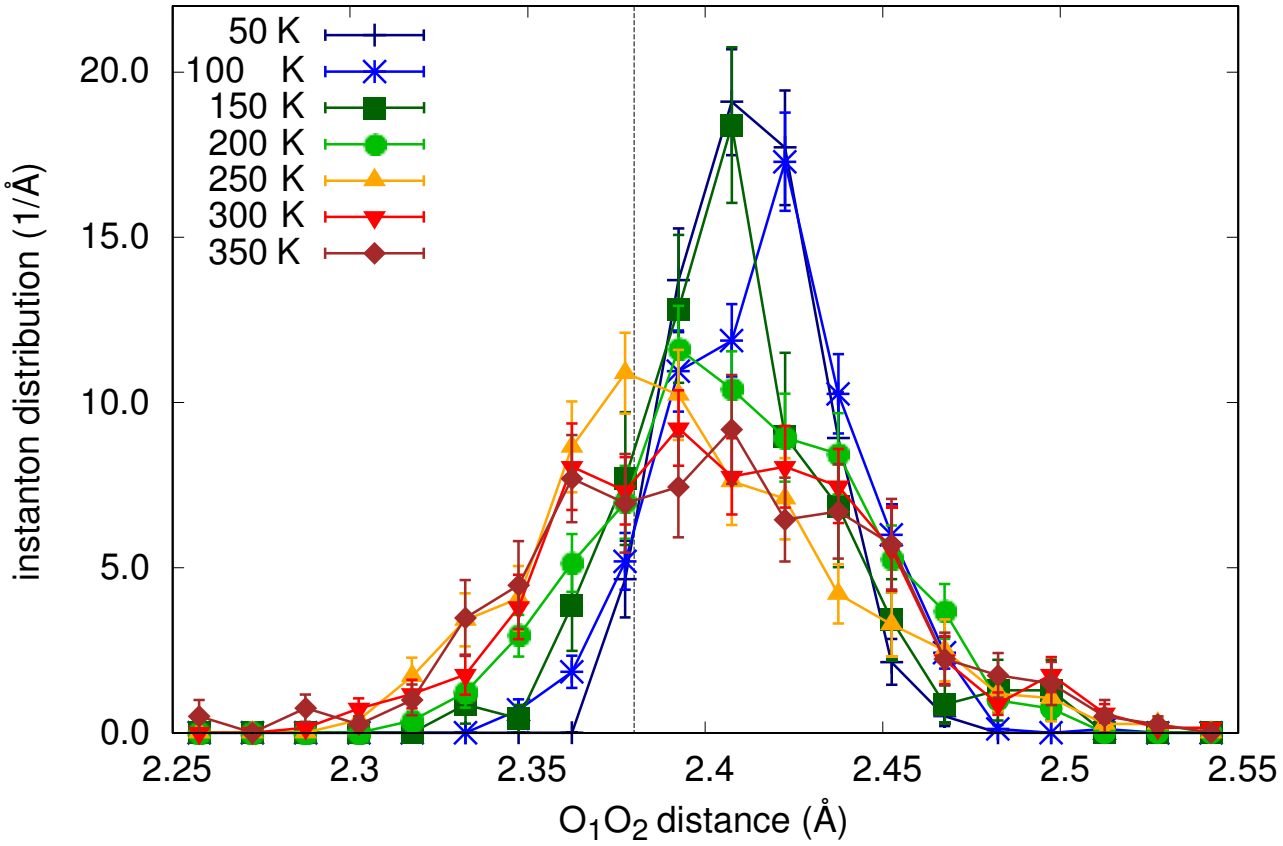




Quantum effects make H-bond robust in temperature

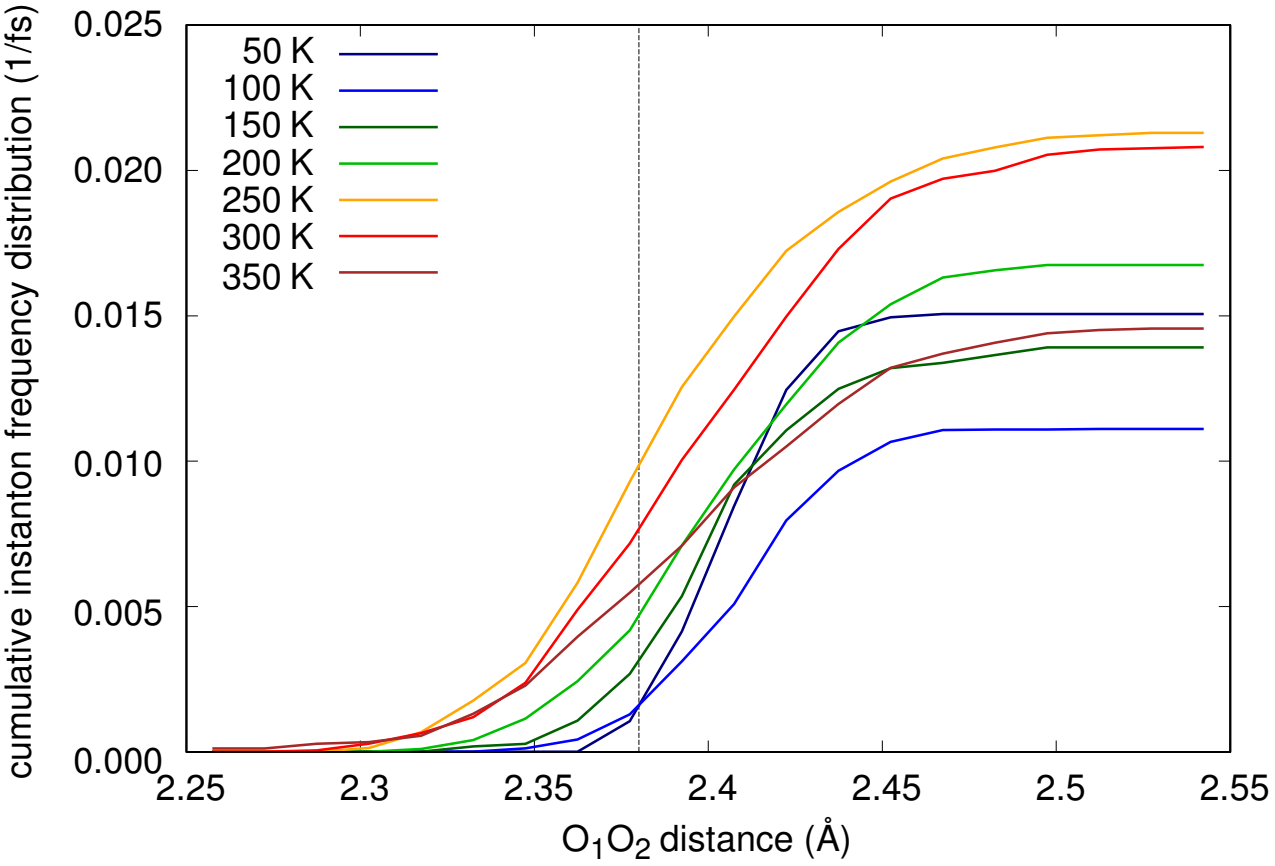
Proton hopping frequency

Instanton statistics: **instanton distribution**



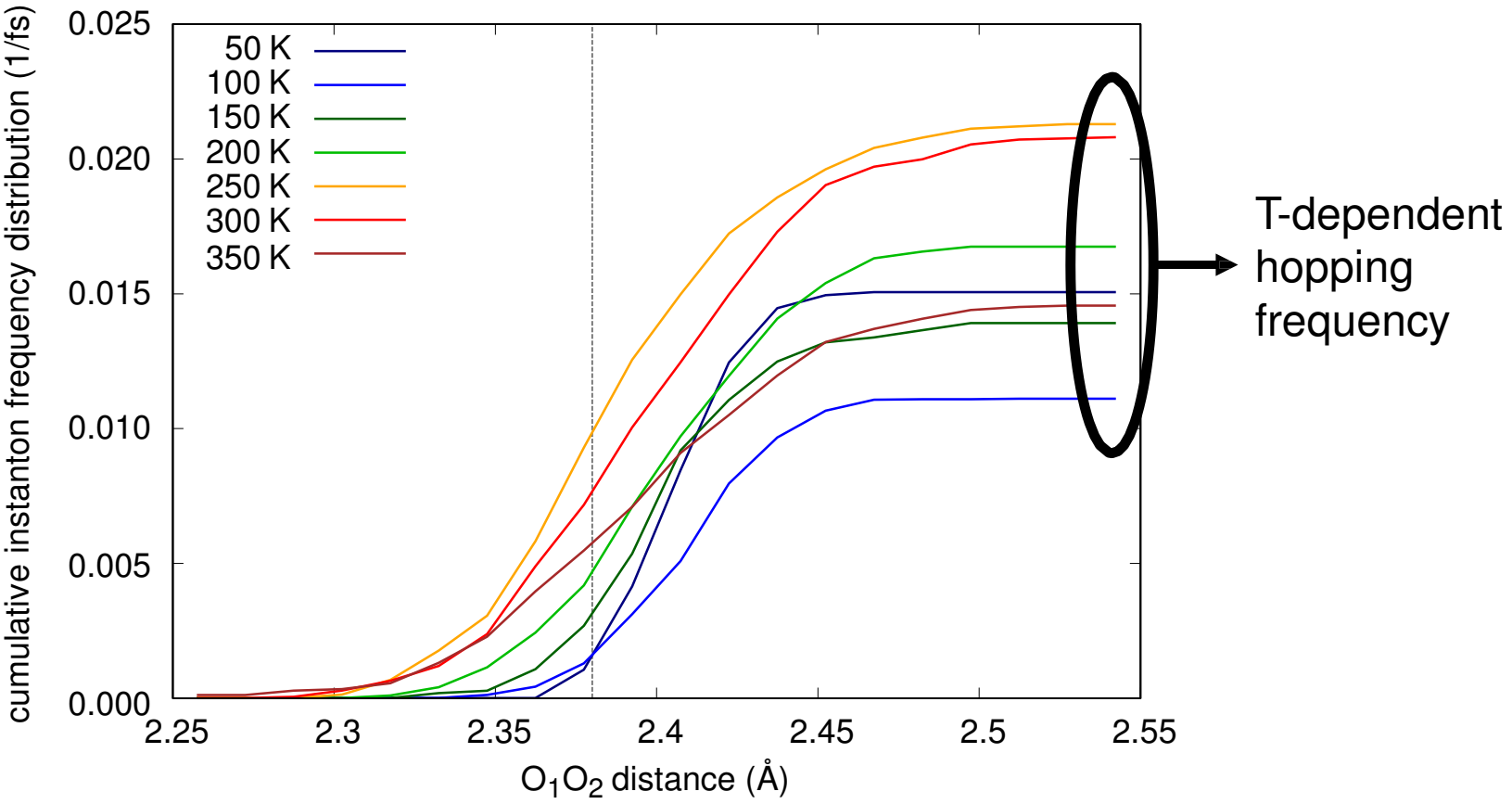
Proton hopping frequency

Instanton statistics: **cumulative frequency distribution**



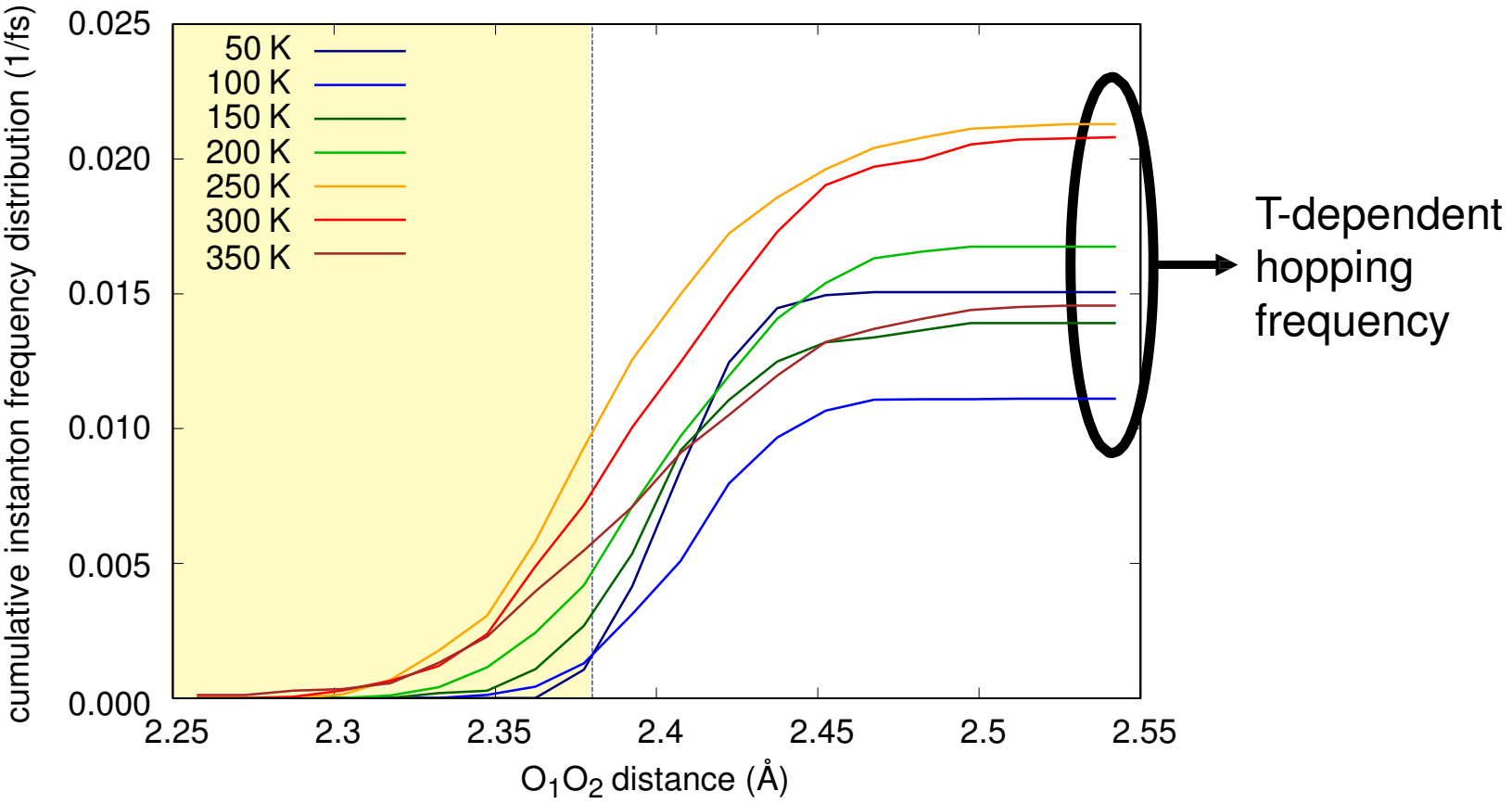
Proton hopping frequency

Instanton statistics: **cumulative frequency distribution**



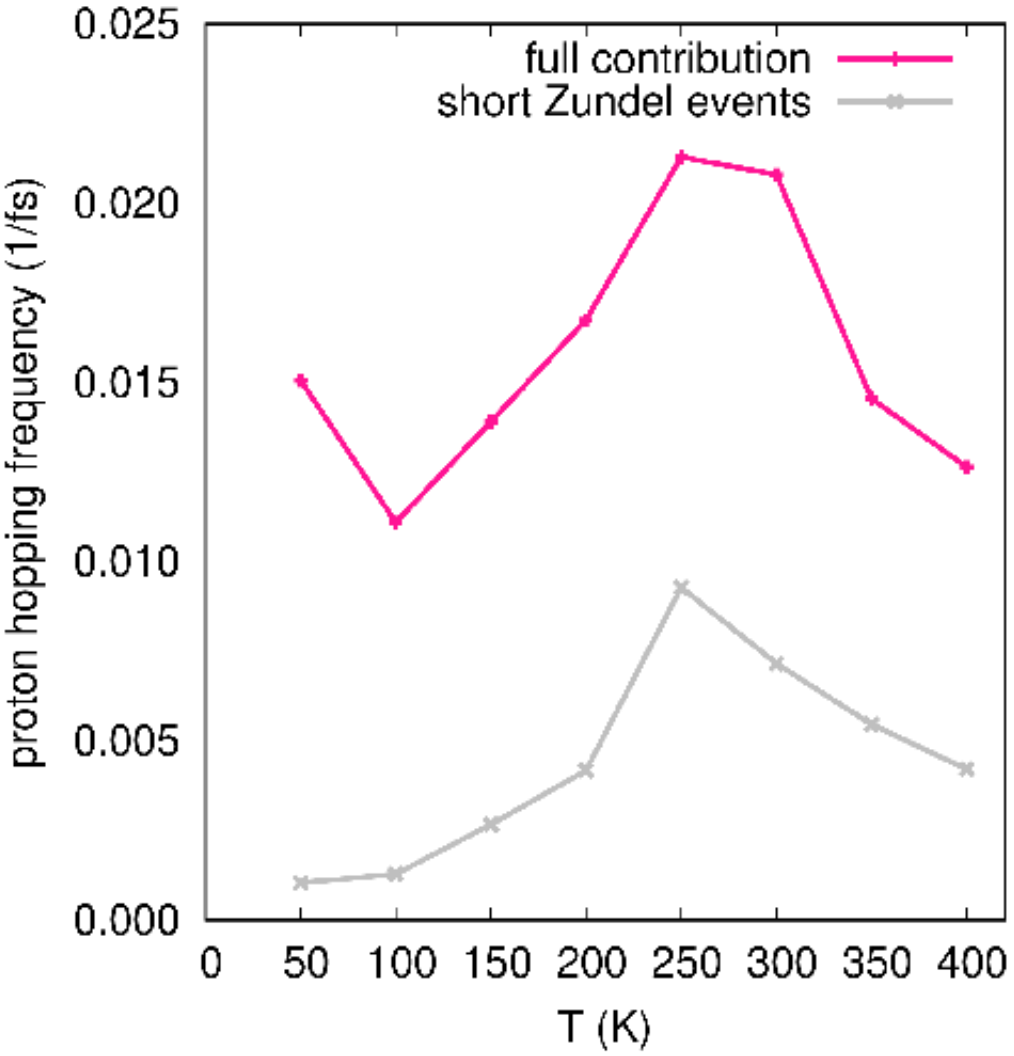
Proton hopping frequency

Instanton statistics: **cumulative frequency distribution**

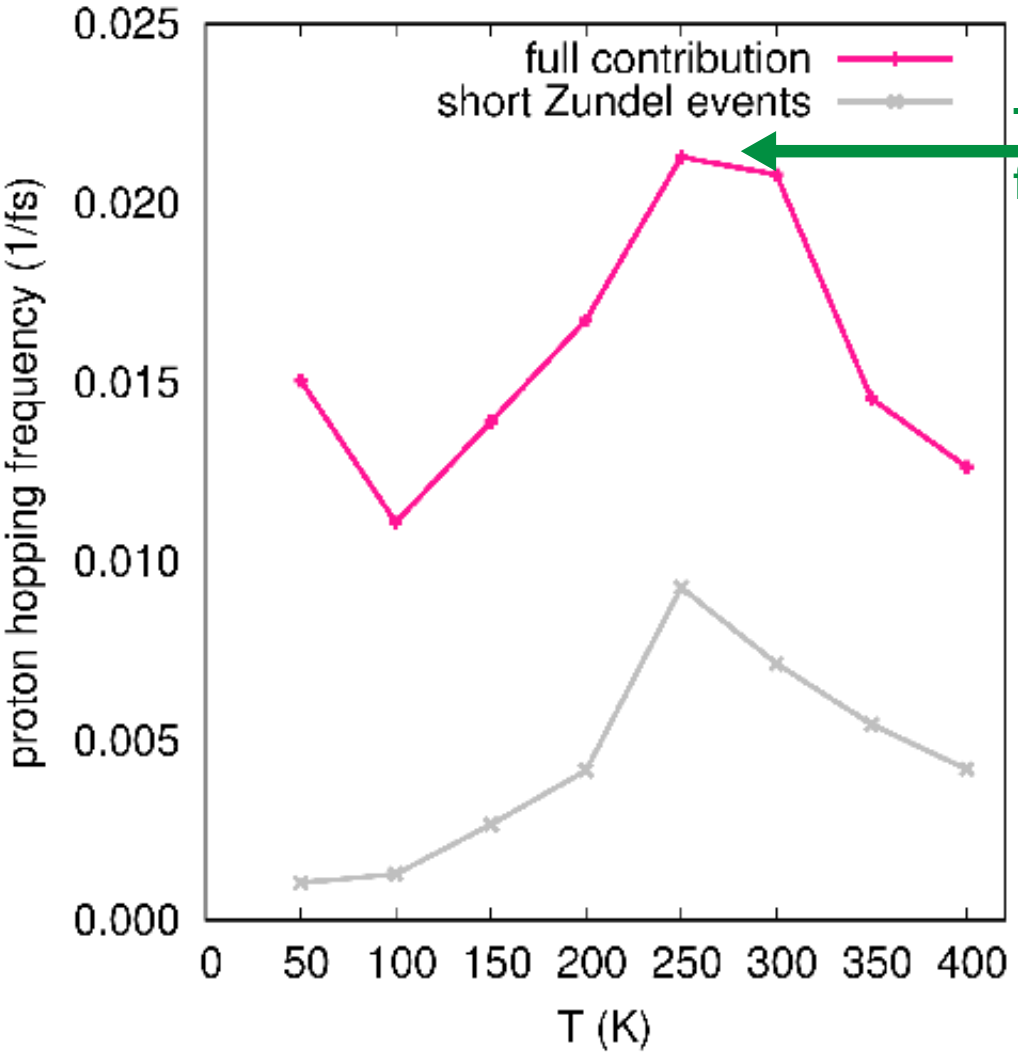


Contribution of the short Zundel (symmetric H) configurations to proton transfer

Proton hopping frequency

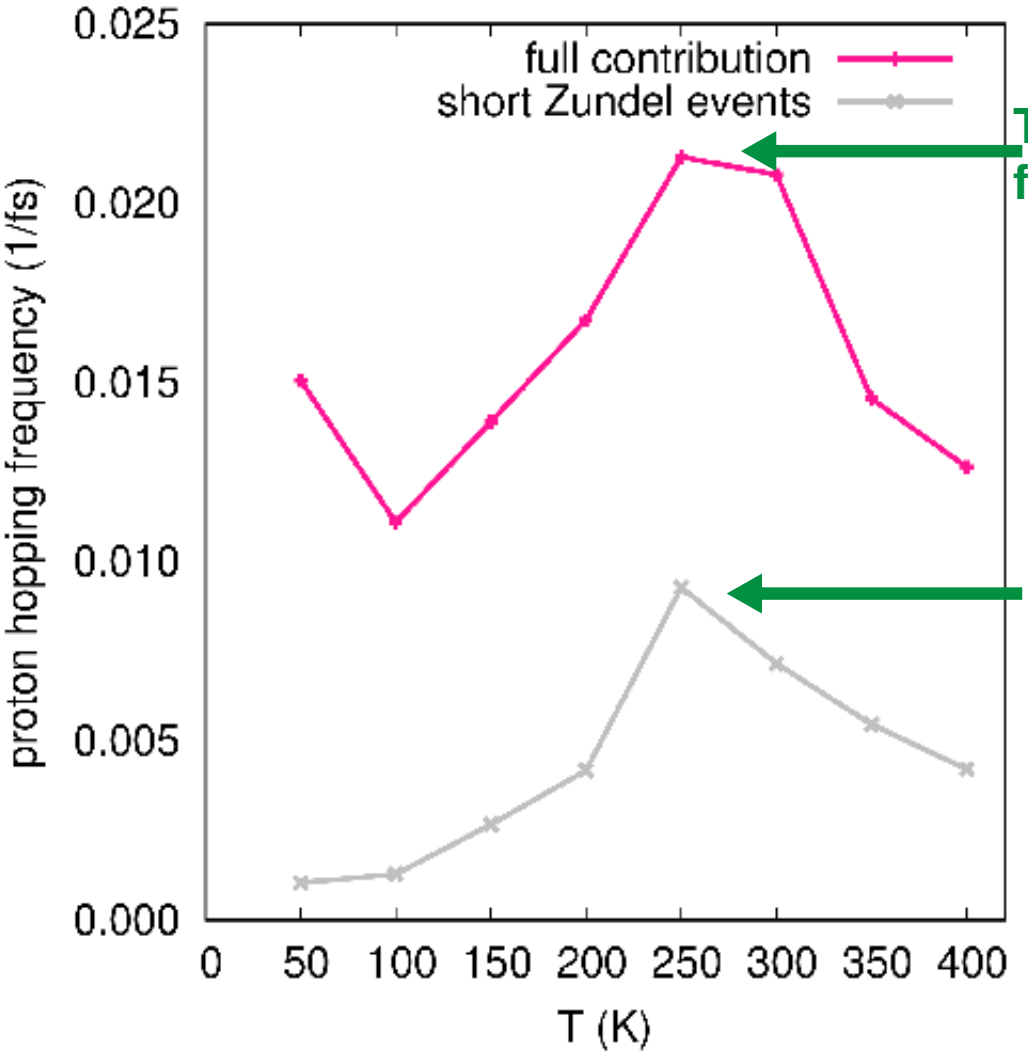


Proton hopping frequency



Temperature sweet spot for proton transfer

Proton hopping frequency

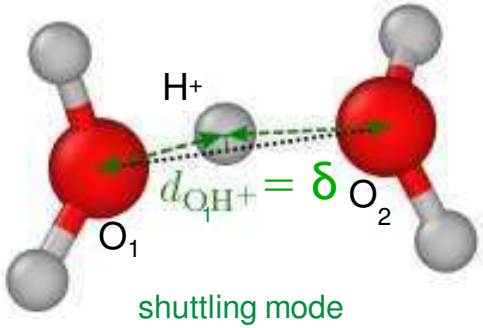


Temperature sweet spot for proton transfer

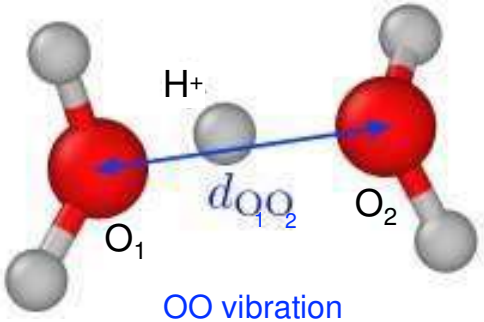
Sweet spot correlated with occurrence of short-Zundel events

Potential energy reconstruction from QMC-driven MD

Two relevant degrees of freedom:

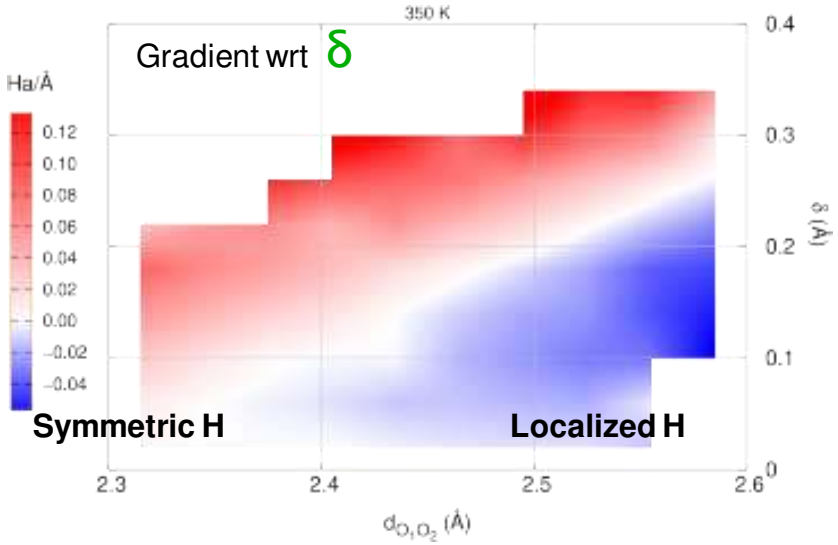


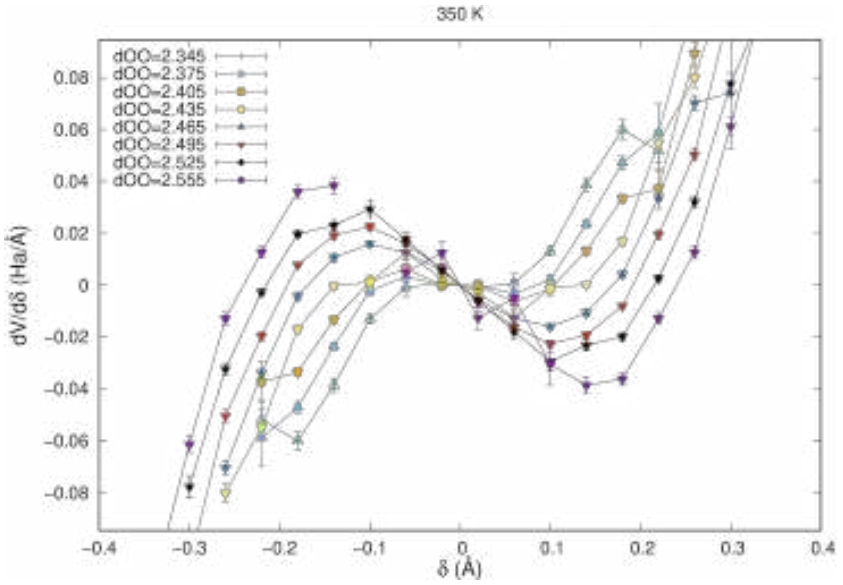
shuttling mode



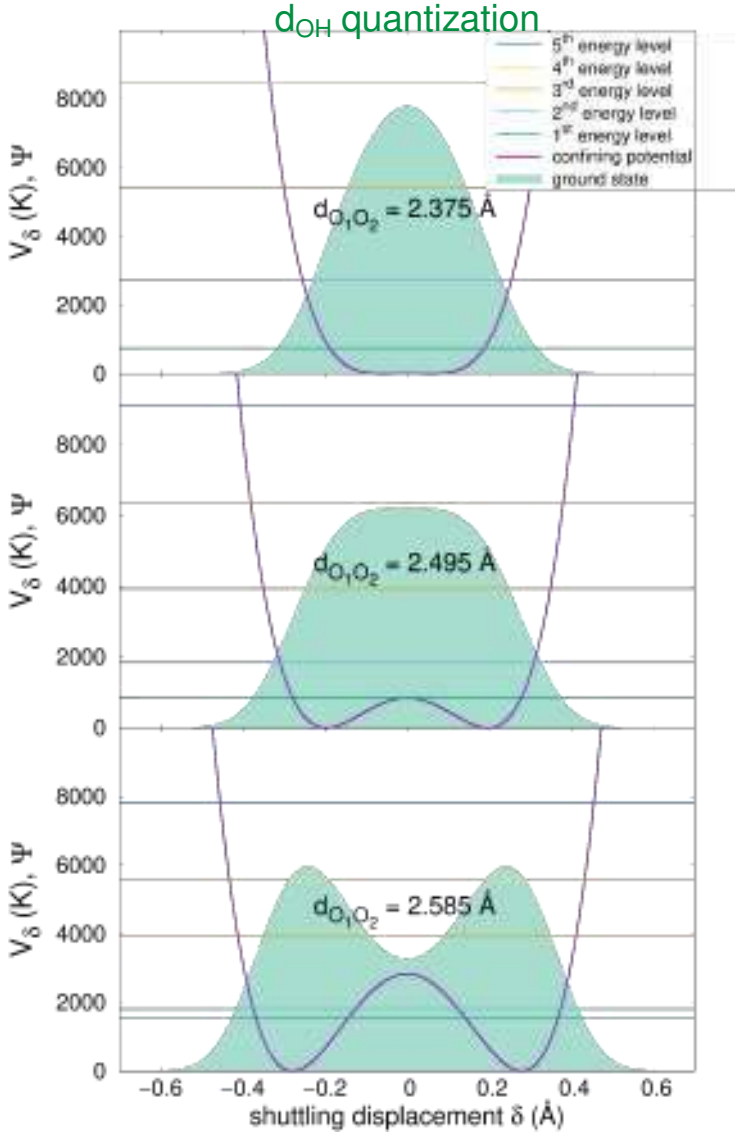
OO vibration

$V_{2D}(d_{OO}, \delta)$ potential reconstructed from VMC-driven classical MD data





Zero point energy (ZPE) variation

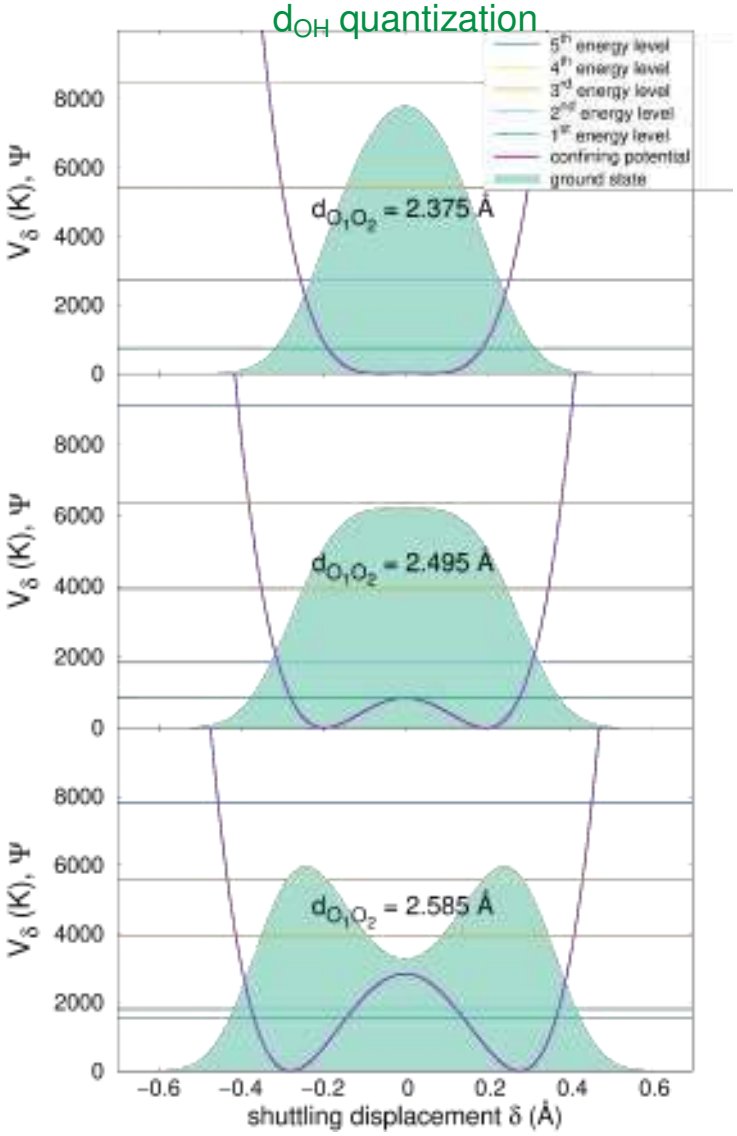


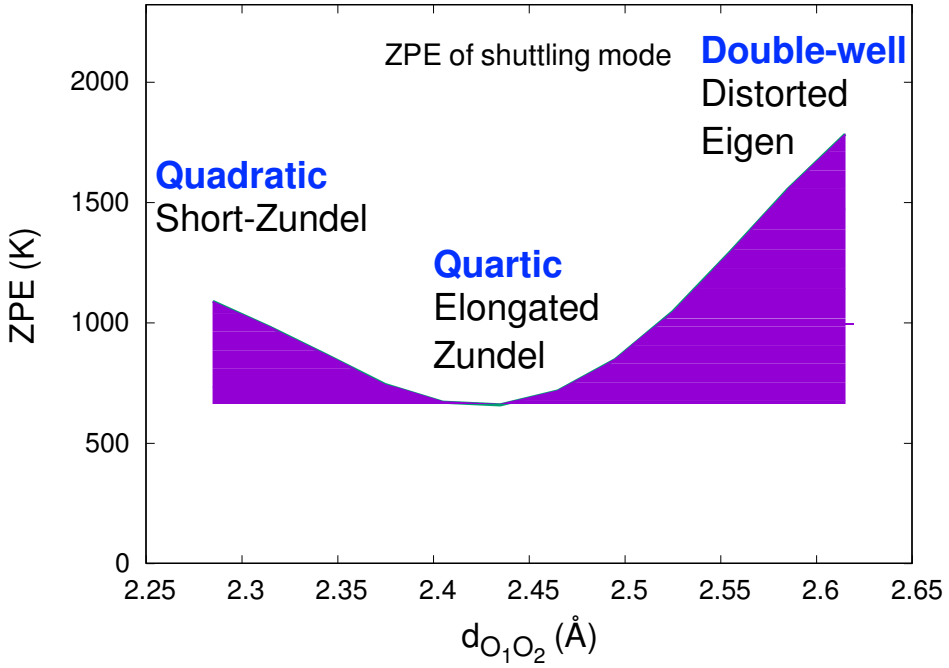
Short-Zundel

Elongated-Zundel

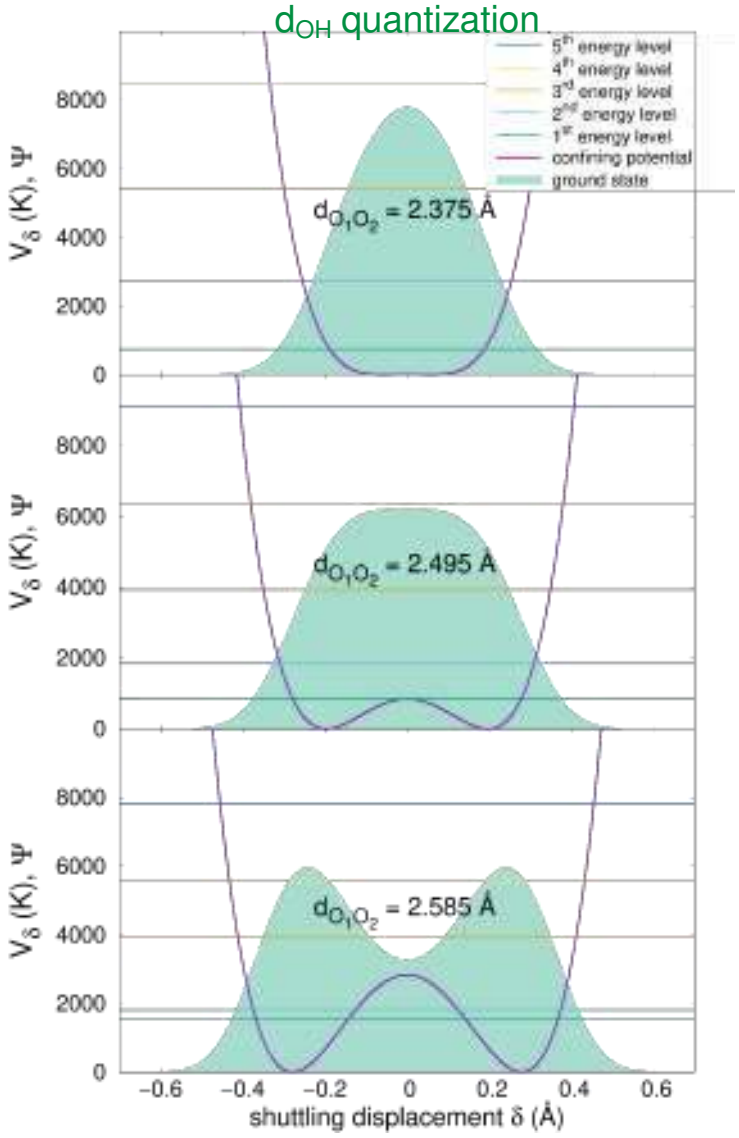
Distorted-Eigen

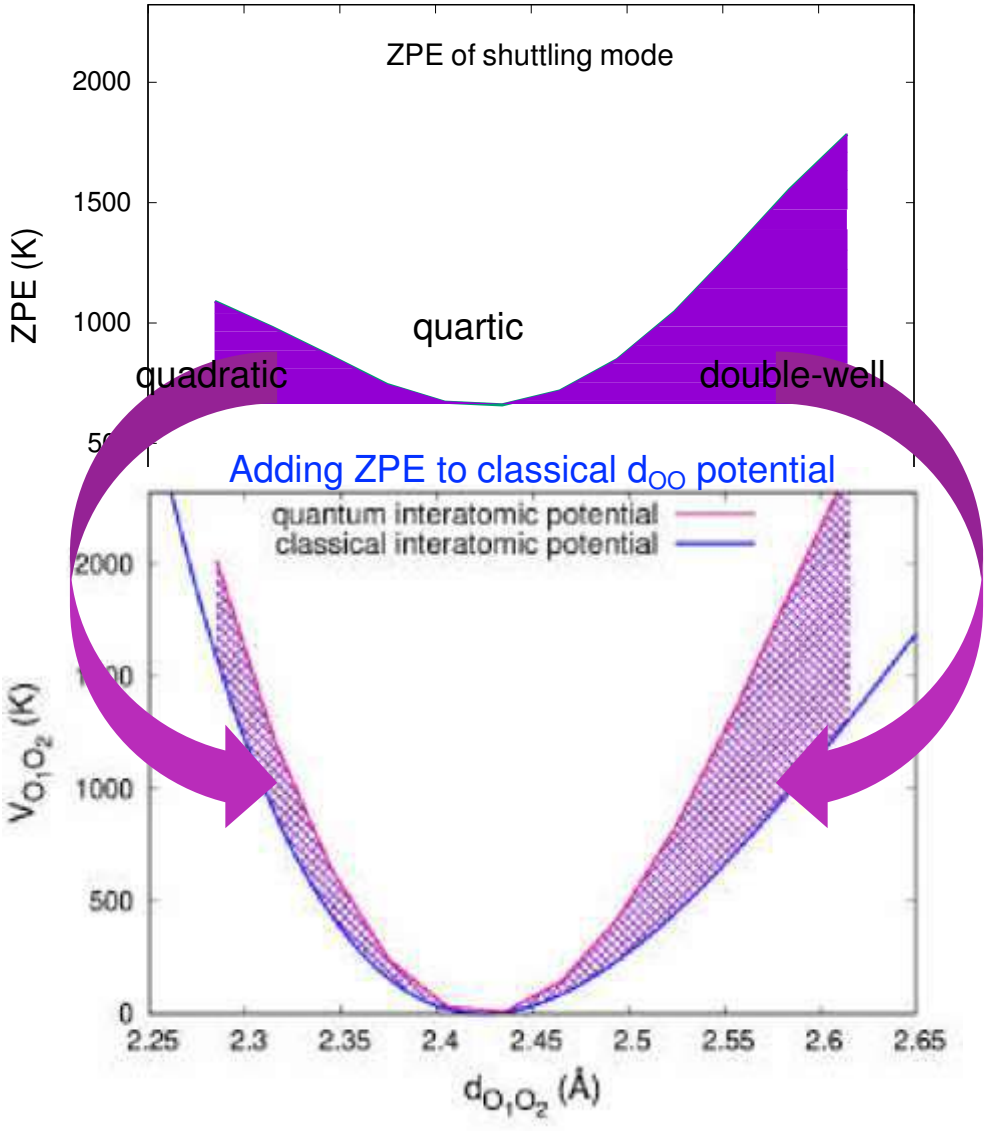
Zero point energy (ZPE) variation



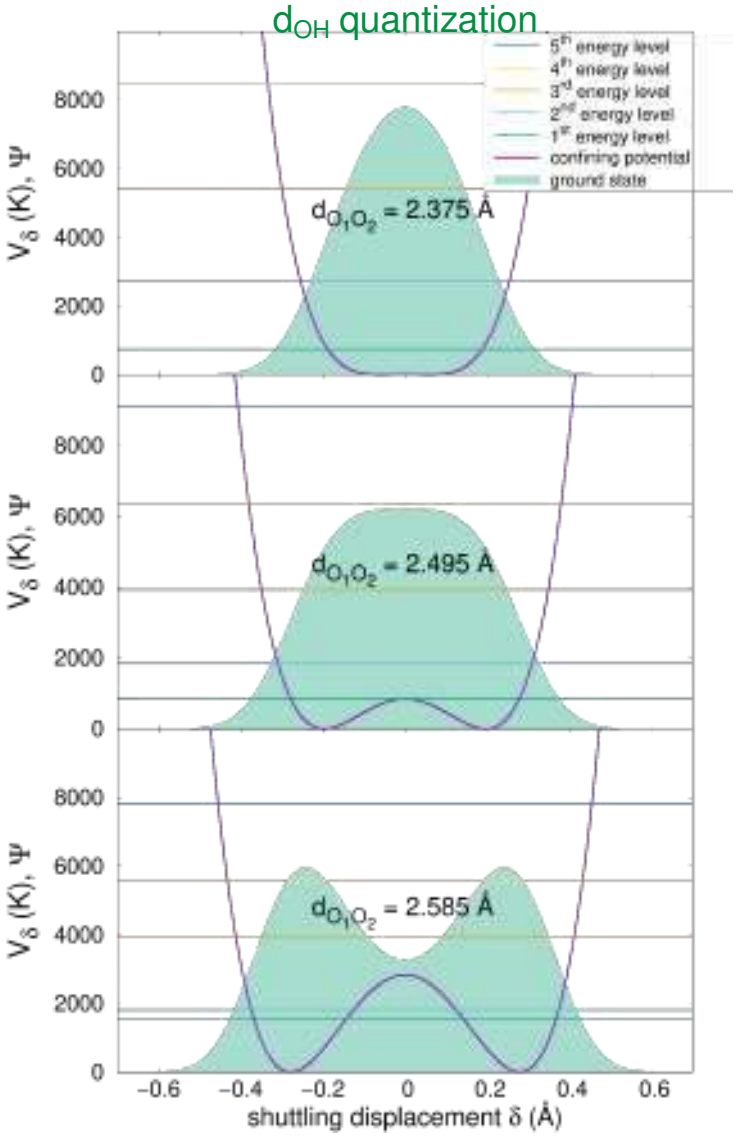


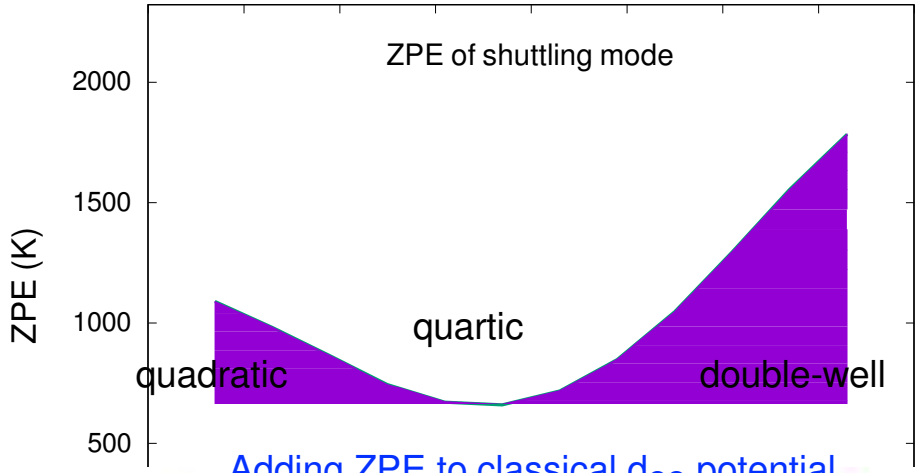
Zero point energy (ZPE) variation



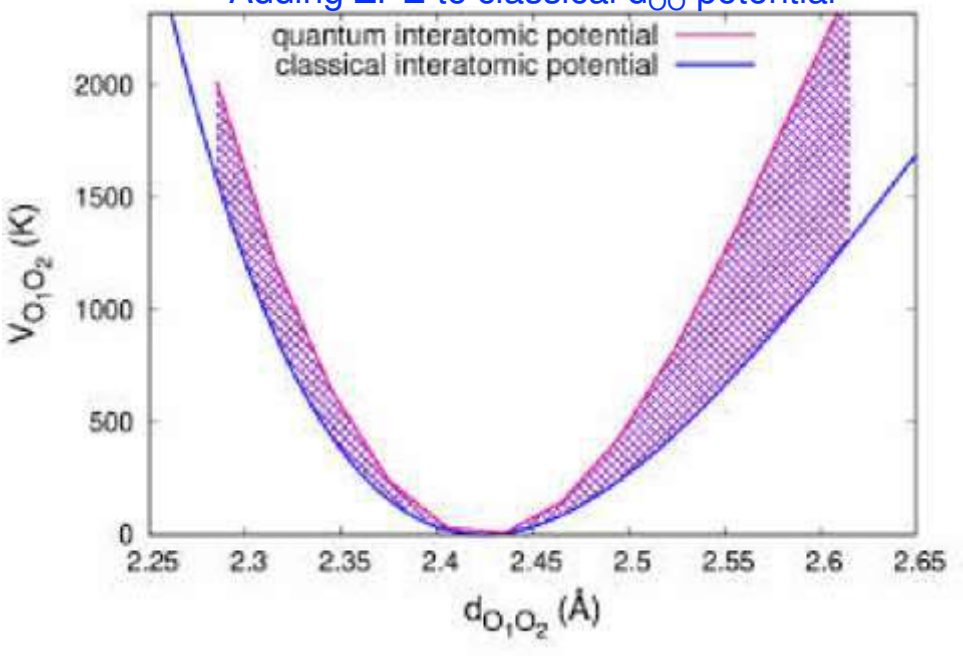


Zero point energy (ZPE) variation

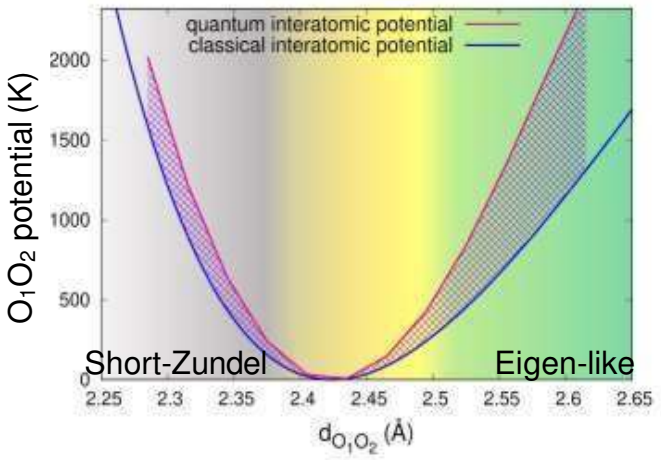


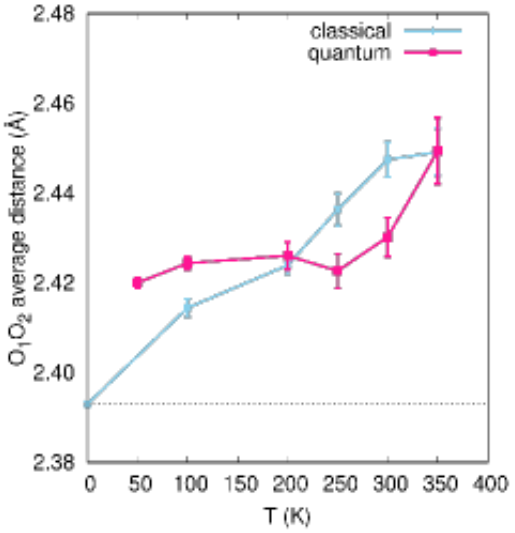


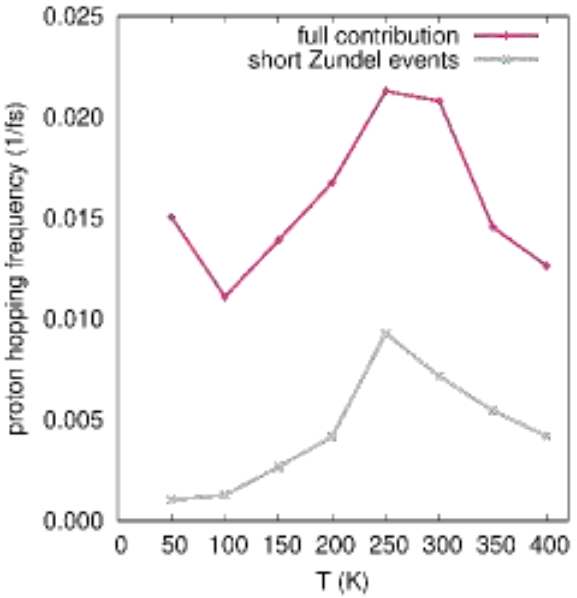
Adding ZPE to classical d_{OO} potential



Conclusions...







- Eigen-like configurations penalized by ZPE in favor of Short-Zundel

(importance of short-H bond highlighted by Dereka *et al.*, Science **371**, 160 (2021))

- Resulting potential explains low thermal expansion of the Zundel-core
- Synergistic interplay between T and ZPE leads to sweet spot in proton transfer

Reference: F. Mouhat, M. Peria, T. Morresi, R. Vuilleumier, A. M. Saitta, M. Casula, Nature Communications **14**, 6930 (2023)

Conclusions and perspectives

- Different combinations of QMC with methods treating quantum nuclei (QMC+SCHA, QMC+PIMD) to predict phase diagram and structural properties of hydrogen-rich compounds

- ML techniques combined with QMC forces very promising to provide reliable force fields, which can then be used in SCHA or molecular dynamics for anharmonic phonon analysis

QMC and ML for PES determination: very recent works!

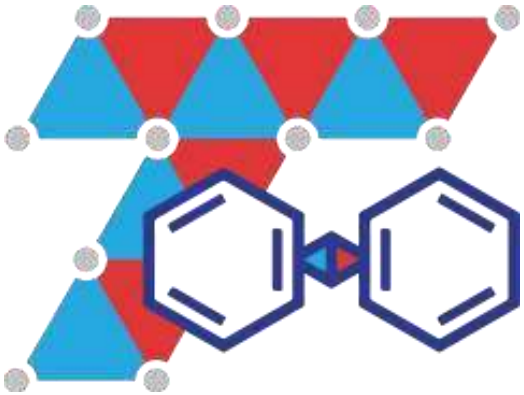
Ryczko, Krogel, Tamblyn, *Machine Learning Diffusion Monte Carlo Energy Densities*, arXiv preprint arXiv:2205.04547 (2022)

Niu, Yang, Jensen, Holzmann, Pierleoni, and Ceperley, *Stable solid molecular hydrogen above 900K from a machine-learned potential trained with diffusion Quantum Monte Carlo*, arXiv preprint arXiv:2209.00658 (2022)

Tirelli, Tenti, Nakano, and Sorella, *High-pressure hydrogen by machine learning and quantum Monte Carlo*, Physical Review B **106**, L041 05 (2022)

Tenti, Tirelli, Nakano, Casula and Sorella, *Principal deuterium Hugoniot via Quantum Monte Carlo and Δ-learning*, arXiv:2301.03570

TurboRVB code



Github repository:
https://github.com/sissaschool/turborvb
Open source under GPL-3.0

Manual: https://sissaschool.github.io/turborvb_website/

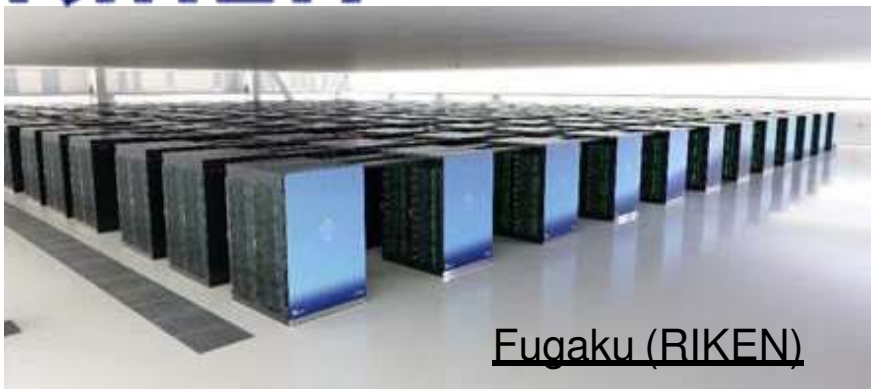
Sandro Sorella

Kosuke Nakano

Acknowledgments

Computing support and grants:
•IDRIS, CCRT (France)
•CINECA (Italy)
•RIKEN, Fugaku (Japan)
•TREX center of excellence

Joliot Curie (TGCC)


Fugaku (RIKEN)

Targeting Real chemical accuracy at the EXascale

Students and Collaborators

Lorenzo Monacelli

Sandro Sorella

Kosuke Nakano

Francesco Mauri

Matteo Peria

Félix Mouhat

Rodolphe Vuilleumier

A. Marco Saitta