PROBING ANHARMONIC PHONONS BY QUANTUM CORRELATORS FROM PATH INTEGRAL MOLECULAR DYNAMICS SIMULATIONS

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Introduction

- High-temperature high-pressure superconductivity in H_3S, LaH_{10} → fundamental role played by hydrogen.
- Key feature of hydrogen-rich materials → strong proton fluctuations. Need to go beyond the harmonic framework in *ab-initio* calcualtions.

This work → efficient scheme to determine vibrational properties from Path Integral Molecular Dynamics (PIMD) simulations (Mouhat et al., 2017). Method based on zero-time Kubo-transformed correlation functions → it captures the anharmonicity of the potential due to both temperature and quantum effects (Morresi et al., 2021).

Theory

Quantum mechanical Kubo-transformed time-correlation function:

$$\tilde{c}_{AB}(t) = \frac{1}{\beta Z}\int_0^{\beta} d\lambda\, \mathrm{tr}\left[e^{-(\beta-\lambda)\hat{H}}\hat{A}\, e^{-\lambda\hat{H}}e^{i\hat{H}t}\hat{B}\, e^{-i\hat{H}t}\right]. \qquad (1)$$

$\tilde{c}_{AB} \longrightarrow$ real and even with respect to t (property shared with classical MD correlation functions). Time dependence accessible over a short time-scale through PIMD simulations. Corresponding zero-time PIMD expression is:

$$\tilde{c}_{AB} = \int d^f\mathbf{p}\int d^f\mathbf{x}\, \frac{e^{-\beta_P H_P(\mathbf{x},\mathbf{p})}}{Z}\mathrm{A}(\mathbf{x})\mathrm{B}(\mathbf{x}), \qquad (2)$$

where $\mathrm{A}(\mathbf{x}) = \frac{1}{P}\sum_{j=1}^{P} A(\mathbf{x}^{(j)})$ is the bead-averaged operator. Shorthand notation for Eq. (2): $\tilde{c}_{AB} \equiv \langle\langle \mathrm{AB}\rangle\rangle$.

Force constant matrix (Dynamical matrix) ↔ Phonons

$$\bar{V}_{i_1 i_2} \equiv \left\langle \frac{\partial^2 V}{\partial x_{i_1}\partial x_{i_2}}\right\rangle. \qquad (3)$$

- Classical Molecular Dynamics → Canonical ensemble: two ways to get $\bar{V}_{i_1 i_2}$ (Martinez et al., 2006):
  i) force-force correlation matrix: $\langle F_{i_1}F_{i_2}\rangle = k_b T\bar{V}_{i_1 i_2}$;
  ii) displacement-displacement correlation matrix: $\langle \delta x_{i_1}\delta x_{i_2}\rangle \approx \left[\bar{V}^{-1}\right]_{i_1 i_2}/k_b T$.
- Path Integral Molecular Dynamics → Canonical ensemble:
  i) Quantum **force-force** eigen equation:

$$\langle\langle \mathrm{F}_{i_1}\mathrm{F}_{i_2}\rangle\rangle\, Y_{i_2,i_3} = \omega^2_{FF,i_3}\langle\langle \mathrm{p}_{i_1}\mathrm{p}_{i_2}\rangle\rangle\, Y_{i_2,i_3}, \qquad (4)$$

where both F and p observables are averaged over the whole ring polymers and $\langle\langle \mathrm{p}_{i_1}\mathrm{p}_{i_2}\rangle\rangle = m_{i_1}k_b T\delta_{i_1 i_2}$. Use of $\langle\langle \mathrm{p}_{i_1}\mathrm{p}_{i_2}\rangle\rangle$ on the right-hand side improves convergence by an order of magnitude. **Force-force quantum correlator gives access to the curvature of the potential energy averaged over the PIMD thermal quantum distribution; ω_{FF} is releated to the zero point energy**.

ii) Quantum **displacement-displacement** eigen equation:

$$\left[\langle\langle \delta\mathbf{x}\delta\mathbf{x}^T\rangle\rangle^{-1}\right]_{i_1,i_2} W_{i_2,i_3} = \omega^2_{\delta x\delta x,i_3}\left[\langle\langle \mathbf{v}\mathbf{v}^T\rangle\rangle^{-1}\right]_{i_1,i_2} W_{i_2,i_3}, \qquad (5)$$

where $\langle\langle \mathrm{v}_{i_1}\mathrm{v}_{i_2}\rangle\rangle = \delta_{i_1,i_2}k_b T/m_{i_1}$. **Eigenvalues $\omega_{\delta x\delta x,i}$ are directly related to the first energy excitation of the phonon modes. Also, Kubo-transformed displacement-displacement → direct access to the poles of the phonon Green's function G at zero frequency with static self energy.**

If V is harmonic, then $\omega_{FF} \equiv \omega_{\delta x\delta x}$

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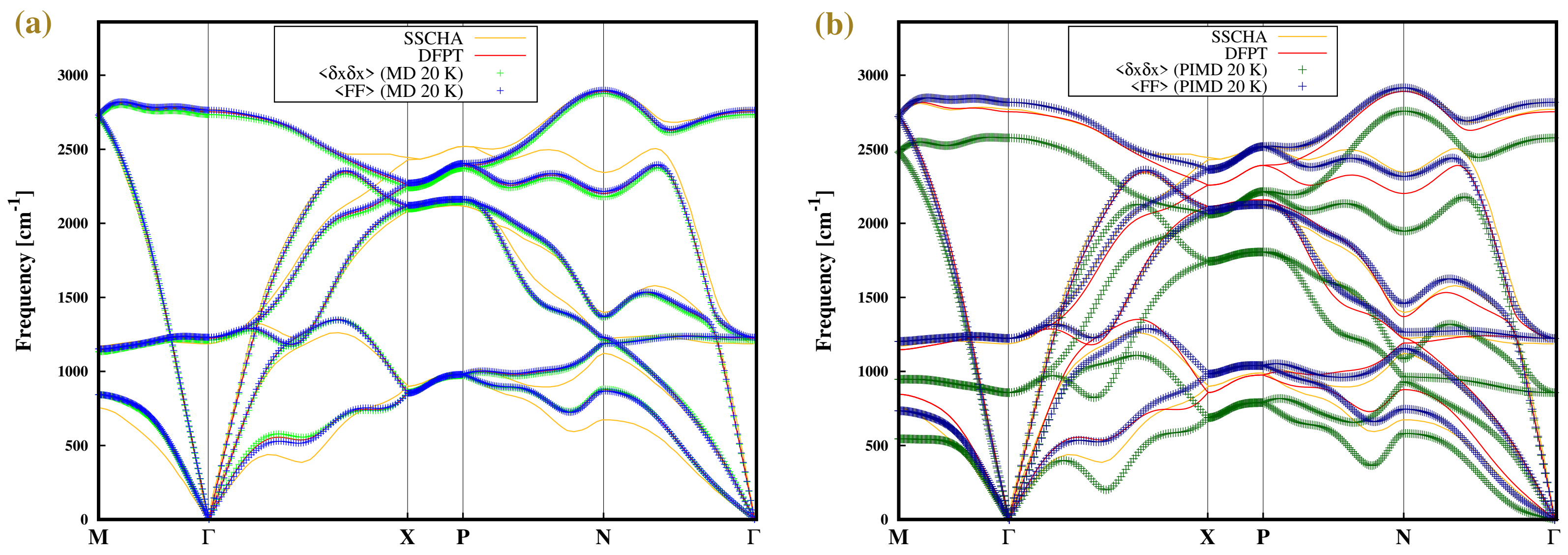
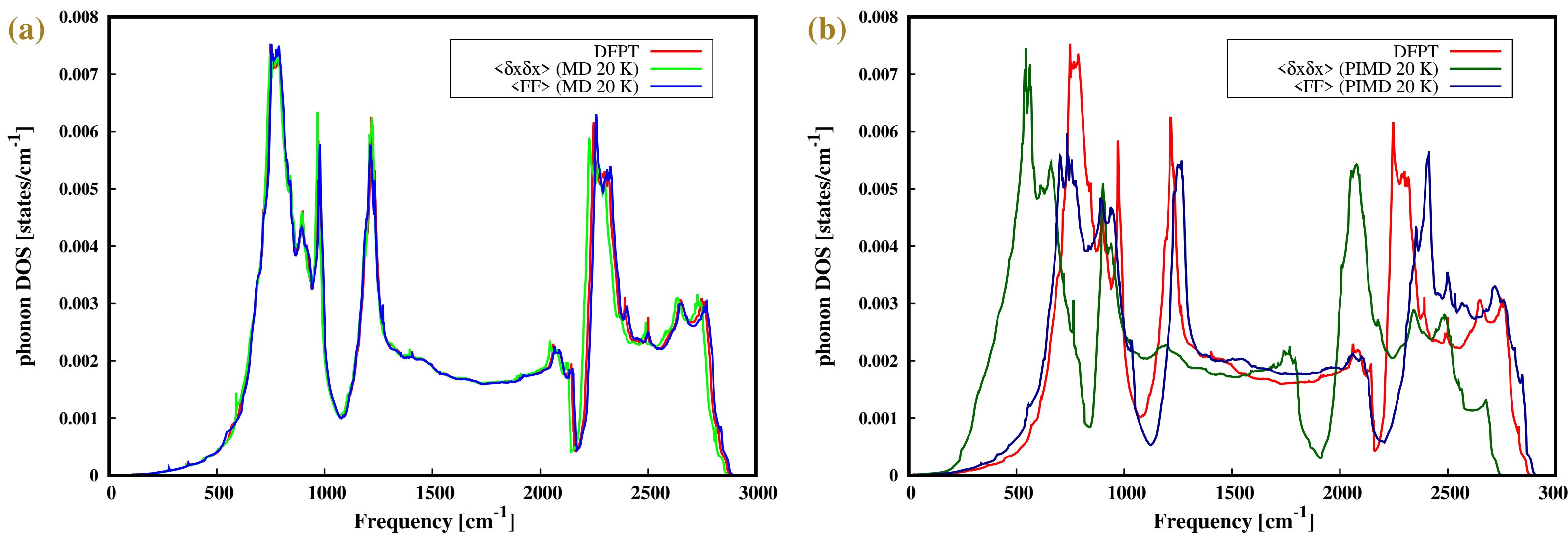
Results I: $I4_1$/amd atomic phase of solid hydrogen @500 GPa (Morresi et al., 2021)

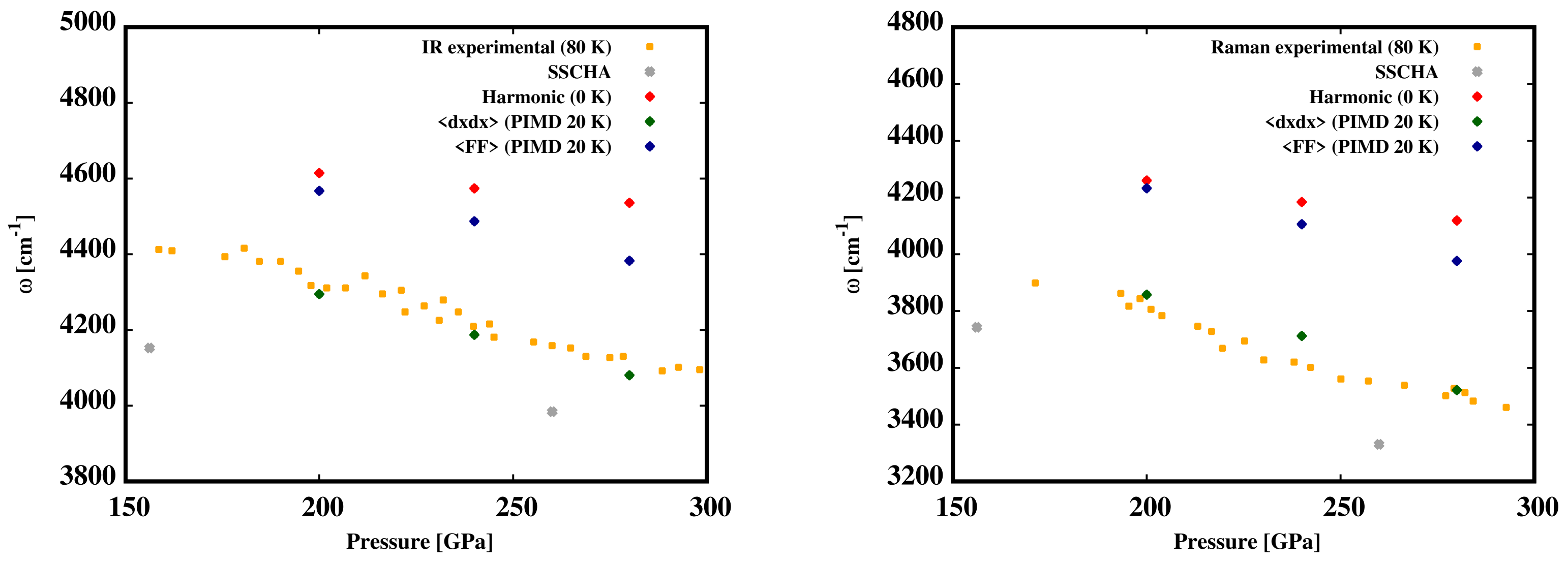


(a) Phonon dispersion from classical *ab-initio* MD simulations (PES evaluated at DFT level with PBE functional) at 20 K compared with DFPT calculation (red) and SSCHA (yellow). Red curve is perfectly covered by the force-force phonon estimator (blue). (b) Phonon dispersion from *ab-initio* PIMD (same PES as classical MD; 120 beads) simulations at 20 K.



(a) Total phonon DOS from classical MD simulations at 20 K compared with DFPT calculation (red); (b) Total phonon DOS from PIMD simulations at 20 K compared with DFPT calculation (red).

Results II: C2/c-24 molecular phase of solid hydrogen @[200-300] GPa (to be published soon)



Infrared (left) and Raman (right) vibron peaks of phase III of molecular hydrogen vs pressure. The experimental dots are reported in orange. Raman and infrared spectroscopies measure transitions from the ground state to (first) excited states: as expected, only the displacement-displacement estimator (green points) fits well with the experimental data. It is worth to note that, at variance with the atomic phase, the molecular phase should be evaluated with a coordinate transformation in order to decouple the rotational and vibrational states. *Ab-initio* PIMD simulations are performed with 120 beads and the PES is evaluated at DFT level with BLYP functional.

REFERENCES

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