Vibrational strong coupling in liquid water

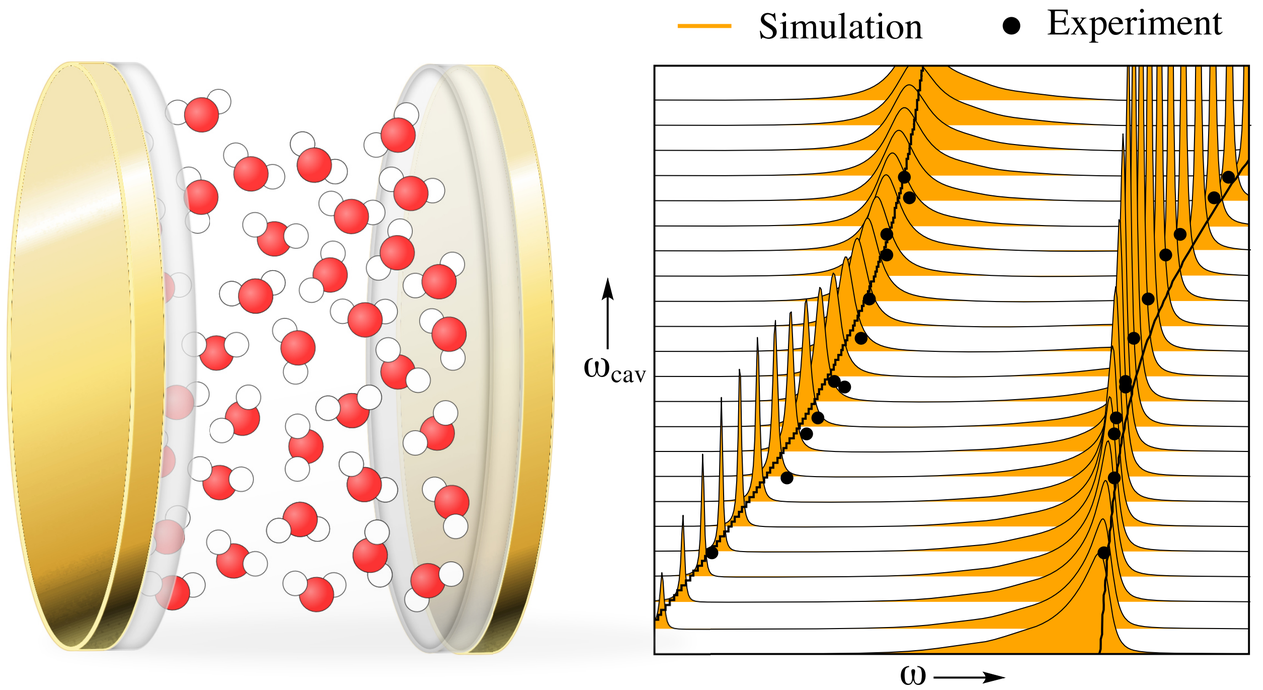

image: Seth Furniss

Annina Lieberherr, 01.05.2024

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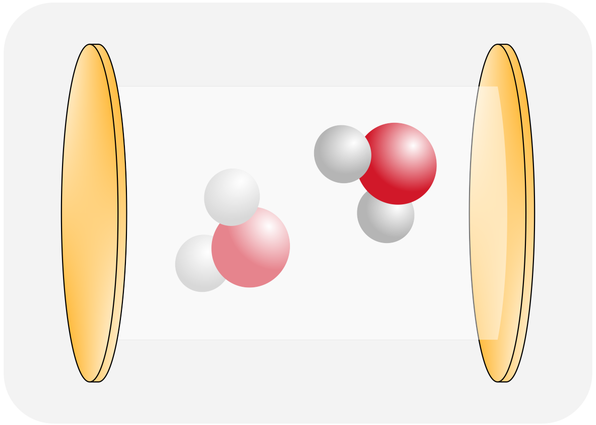
Department of Chemistry

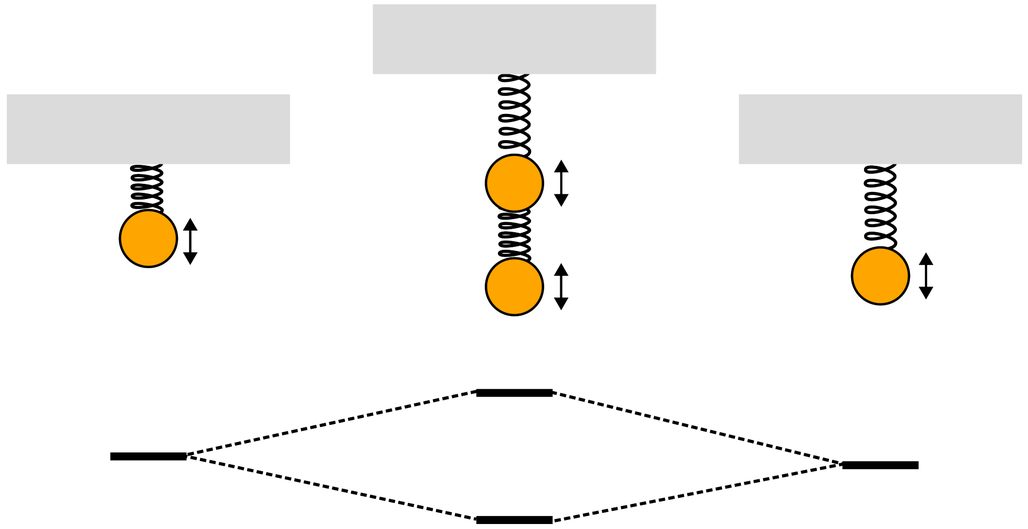
Molecules in a cavity



$$H = H_{\mathrm{sys}} + H_{\mathrm{cav}}$$

$$H_{\mathrm{sys}} = \sum_i \frac{\boldsymbol{p}_i^2}{2m_i} + V(\{\boldsymbol{q}_i\})$$

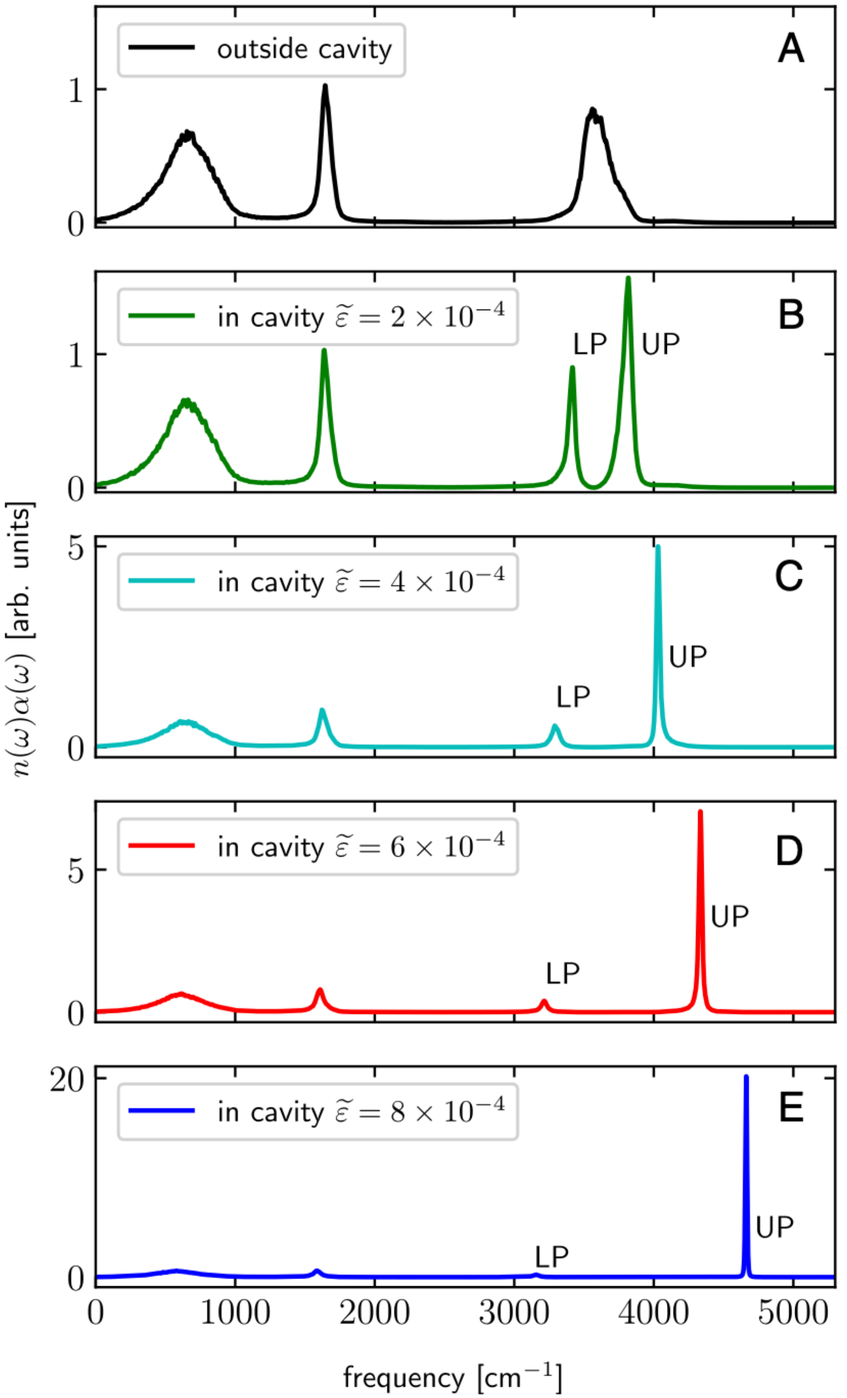
$$H_{\mathrm{cav}} = \sum_{cd} \left[\frac{1}{2} p_{cd}^2 + \frac{1}{2} \omega_c^2 \left(q_c + \frac{\mu_d(\{\boldsymbol{q}_i\}))}{\omega_c \sqrt{\varepsilon_0 V_{\mathrm{cav}}}} \right)^2 \right]$$



Previous work

Cavity molecular dynamics simulations of liquid water under vibrational ultrastrong coupling, T. E. Li, J. E. Subotnik, A. Nitzan, PNAS 117 (2020)

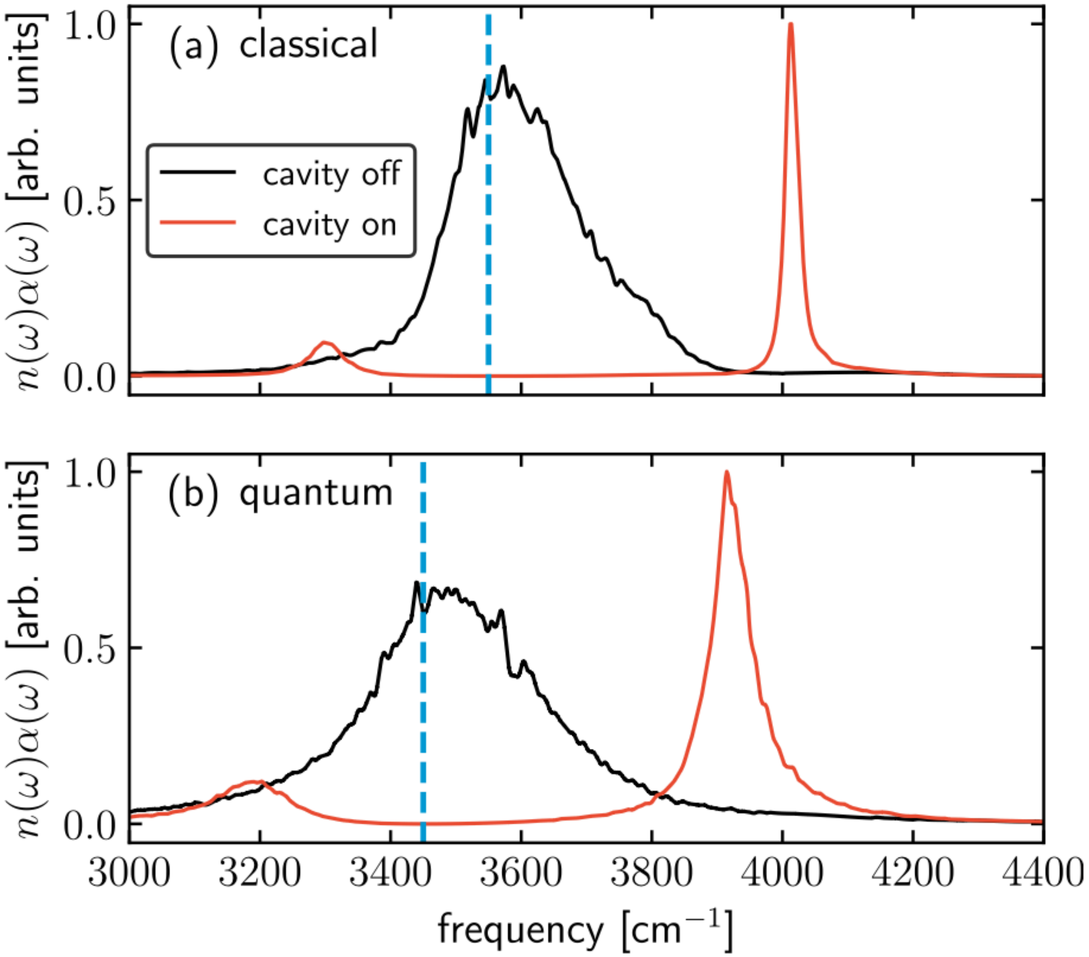
- Classical simulation of liquid water with the q-TIP4P/F force field
- Stretch band splits into two narrow **polariton bands**
- Rabi frequency increases with coupling strength



Previous work

Quantum simulations of vibrational strong coupling via path integrals, T. E. Li, A. Nitzan, S. Hammes-Schiffer, J. E. Subotnik, J. Phys. Chem. Lett. 13 (2022)

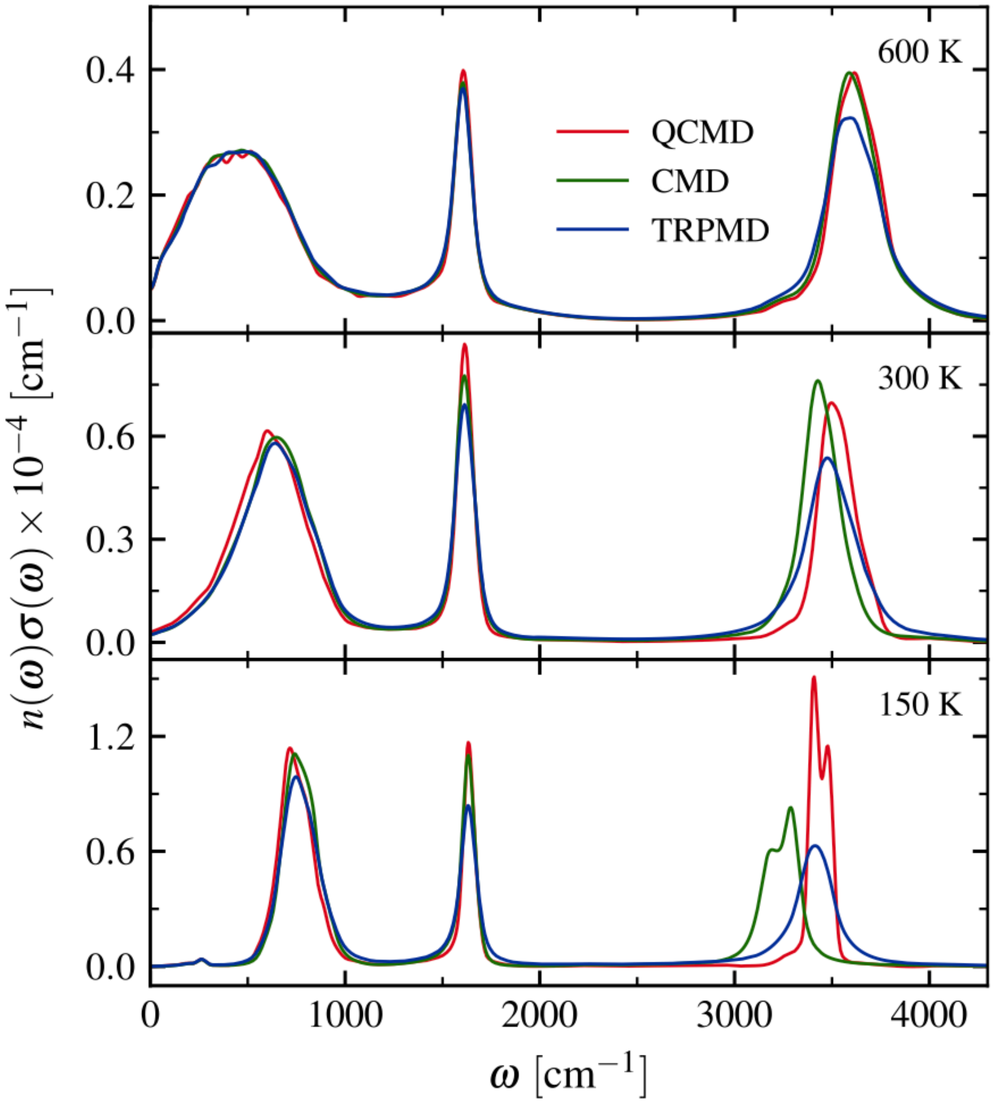
- Cavity resonant with stretch peak
- Quantum peaks are red-shifted and **broadened** compared to the classical peaks
- Unclear if this is a nuclear quantum effect, since simulations were done with TRPMD



Difficulties with simulated IR spectra

Path-integral dynamics of water using curvilinear centroids, G. Trenins, M. J. Willatt, S. C. Althorpe, J. Chem. Phys. 151 (2019)

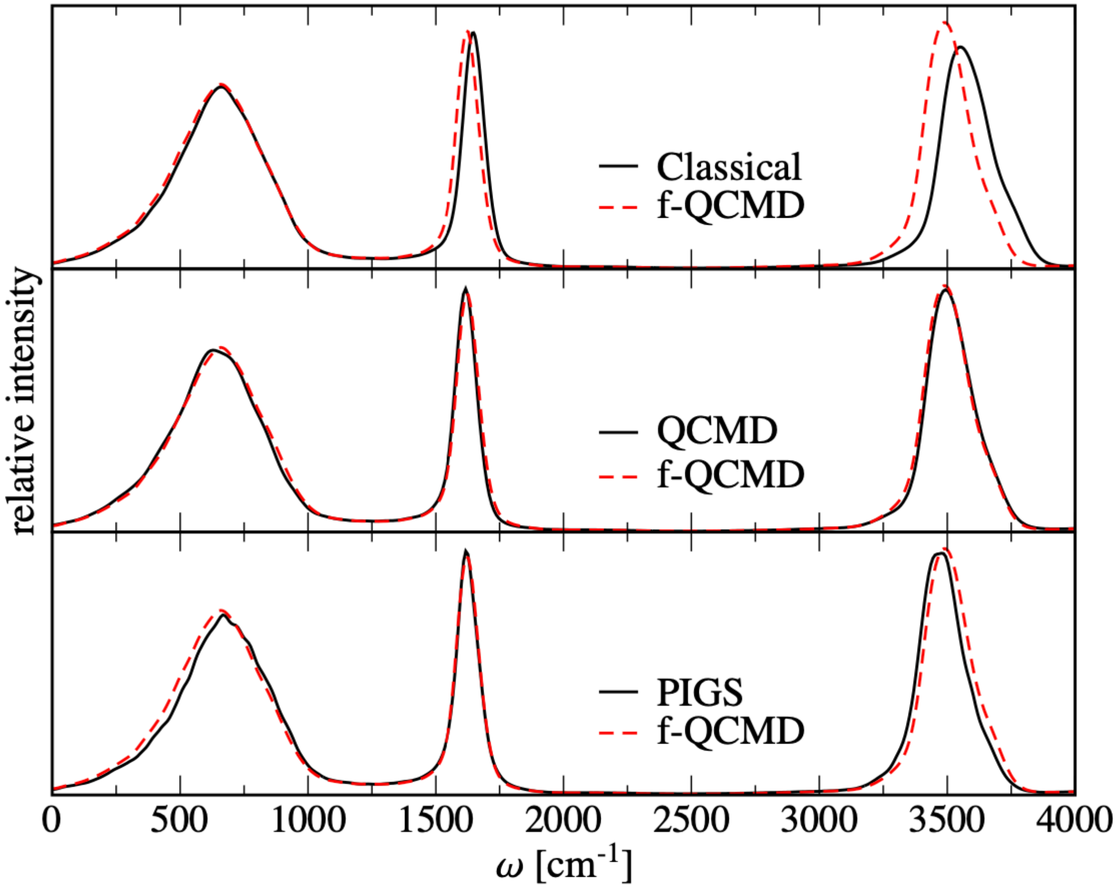
- TRPMD gives broadened peaks
- CMD peaks become red-shifted with lower temperatures
- QCMD is the most reliable method of the three



Modern simulation methods for IR spectra

Fast quasi-centroid molecular dynamics for water and ice, J. E. Lawrence, A. Z. Lieberherr, T. Fletcher, D. E. Manolopoulos, J. Phys. Chem. B 127 (2023)

- We use an approximate method, f-QCMD
- different simulation methods agree well with each other, so we have some confidence in our results



(PIGS: Musil, Zaporozhets, Noé, Clementi, Kapil, J. Chem. Phys. 157 (2022))

Cavity molecular dynamics

Cavity molecular dynamics simulations of liquid water under vibrational ultrastrong coupling, T. E. Li, J. E. Subotnik, A. Nitzan, PNAS 117 (2020)

$$H = H_{\mathrm{sys}} + H_{\mathrm{cav}}$$

$$H_{\mathrm{sys}} = \sum_i \frac{\boldsymbol{p}_i^2}{2m_i} + V(\{\boldsymbol{q}_i\})$$

$$H_{\mathrm{cav}} = \sum_{cd} \left[\frac{1}{2} p_{cd}^2 + \frac{1}{2}\omega_c^2 \left(q_c + \sqrt{R}\frac{\nu_d(\{\boldsymbol{q}_i\}))}{\omega_c} \right)^2 \right]$$

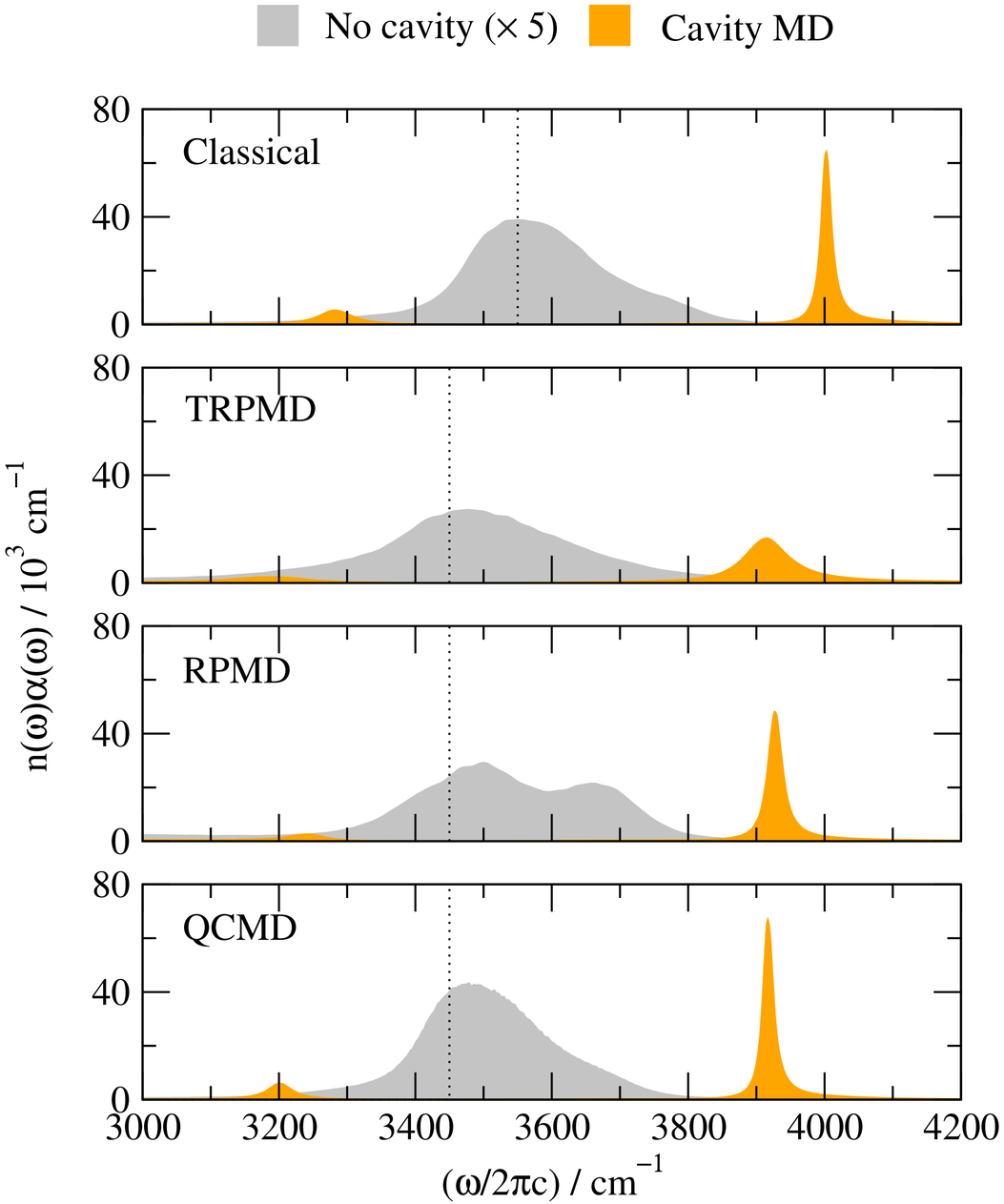
$$R = \frac{V_{\mathrm{sys}}}{V_{\mathrm{cav}}} \qquad \nu_d(\{\boldsymbol{q}_i\}) = \frac{\mu_d(\{\boldsymbol{q}_i\})}{\sqrt{\varepsilon_0 V_{\mathrm{sys}}}}$$

- Simulation includes system and photon positions and momenta
- Observable of interest: IR spectrum

$$I(\omega) = \frac{\beta}{2c\varepsilon_0 V_{\mathrm{sys}}} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \dot{\mu}_x(0)\dot{\mu}_x(t)\rangle \mathrm{d}t = \frac{\beta}{2c} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \dot{\nu}_x(0)\dot{\nu}_x(t)\rangle \mathrm{d}t$$

QCMD simulations

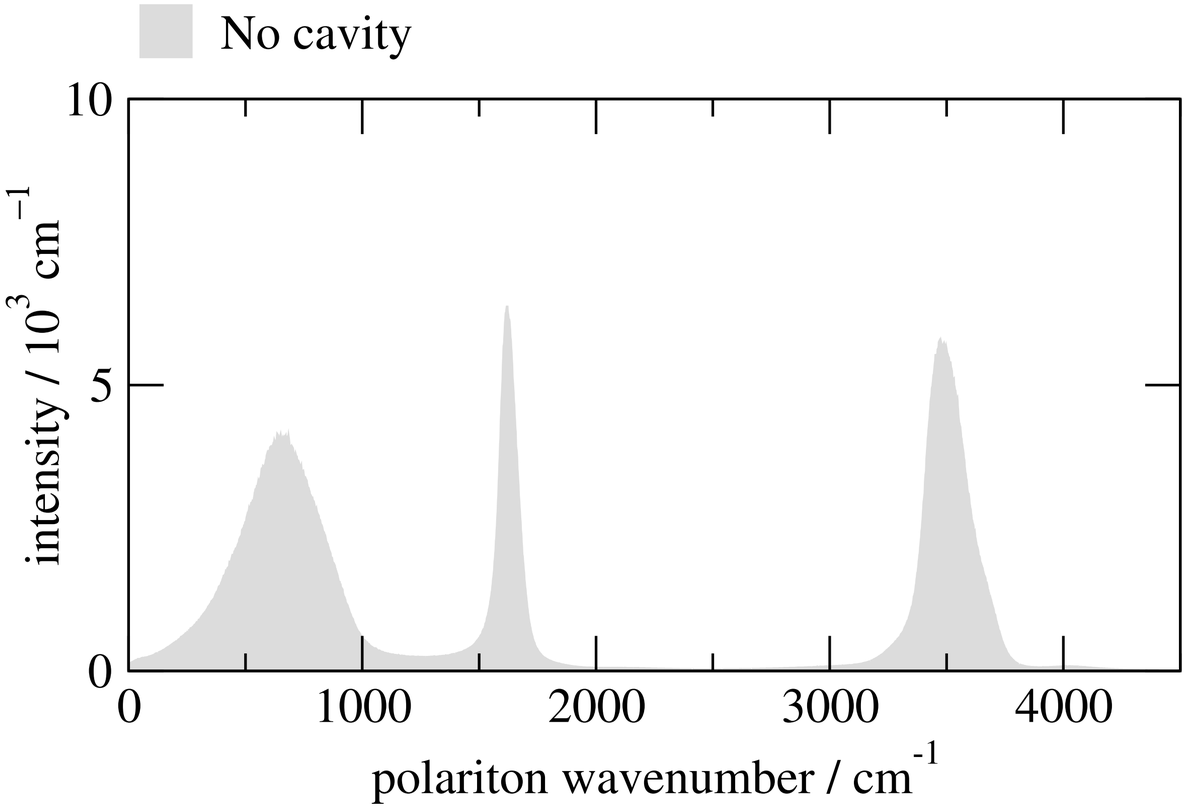
- We reproduce the broadening of the polariton bands in TRPMD
- But there is no broadening in the QCMD polariton bands
- So the broadening is an artifact of TRPMD, not caused by NQEs



A simple harmonic oscillator model

$$I(\omega) = \frac{\beta}{2c} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \dot{\nu}_x(0) \dot{\nu}_x(t) \rangle \mathrm{d}t$$

with $\nu_x = \dfrac{\mu_x}{\sqrt{\varepsilon_0 V_{\mathrm{sys}}}}$ system size-independent.



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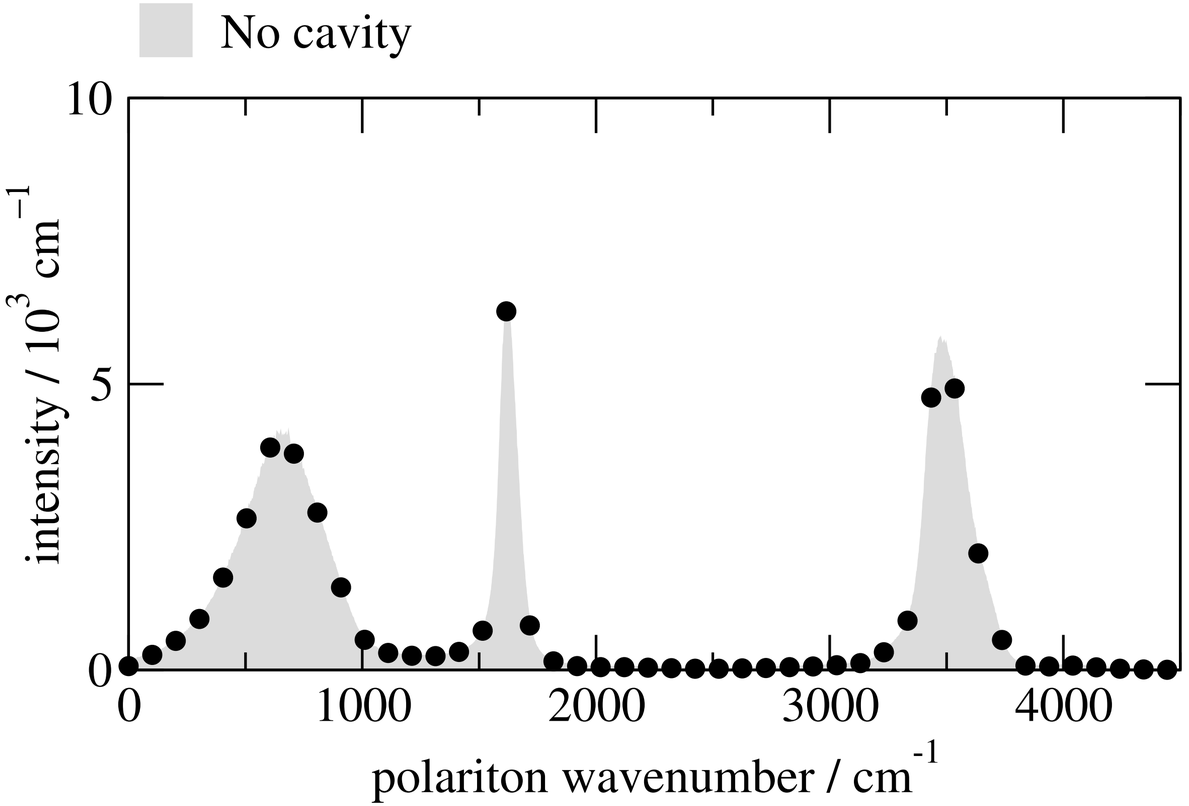
1. Decompose cavity-free spectrum into uncoupled harmonic oscillators

$$H_{\mathrm{sys}} = \sum_{i=1}^{N} \frac{1}{2} p_i^2 + \frac{1}{2} \omega_i^2 q_i^2 \qquad \nu_x = \sum_{i=1}^{N} \nu_i q_i$$



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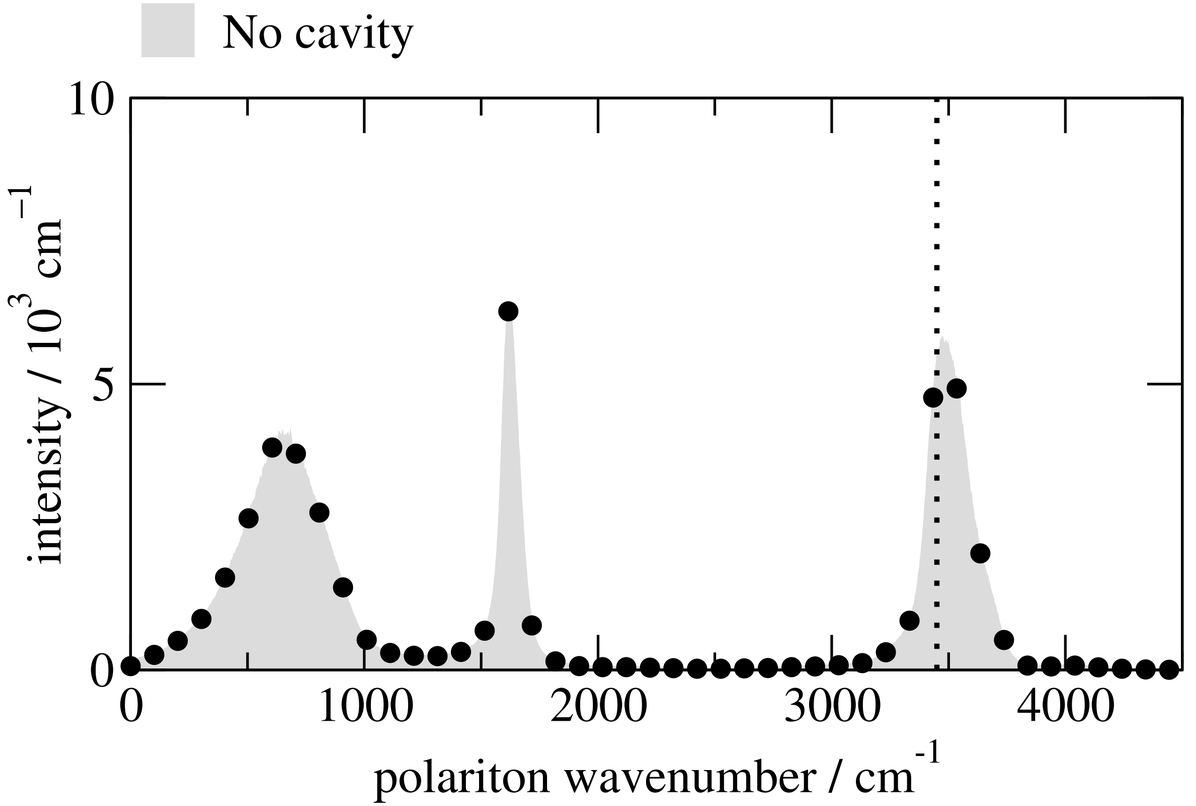
2. Introduce coupling to cavity mode



$$H = H_{\mathrm{sys}} + \sum_{c=1}^{M} \frac{1}{2} p_c^2 + \frac{1}{2} \omega_c^2 \left(q_c + \sqrt{R} \sum_{i=1}^{N} \frac{\nu_i q_i}{\omega_c} \right)^2$$

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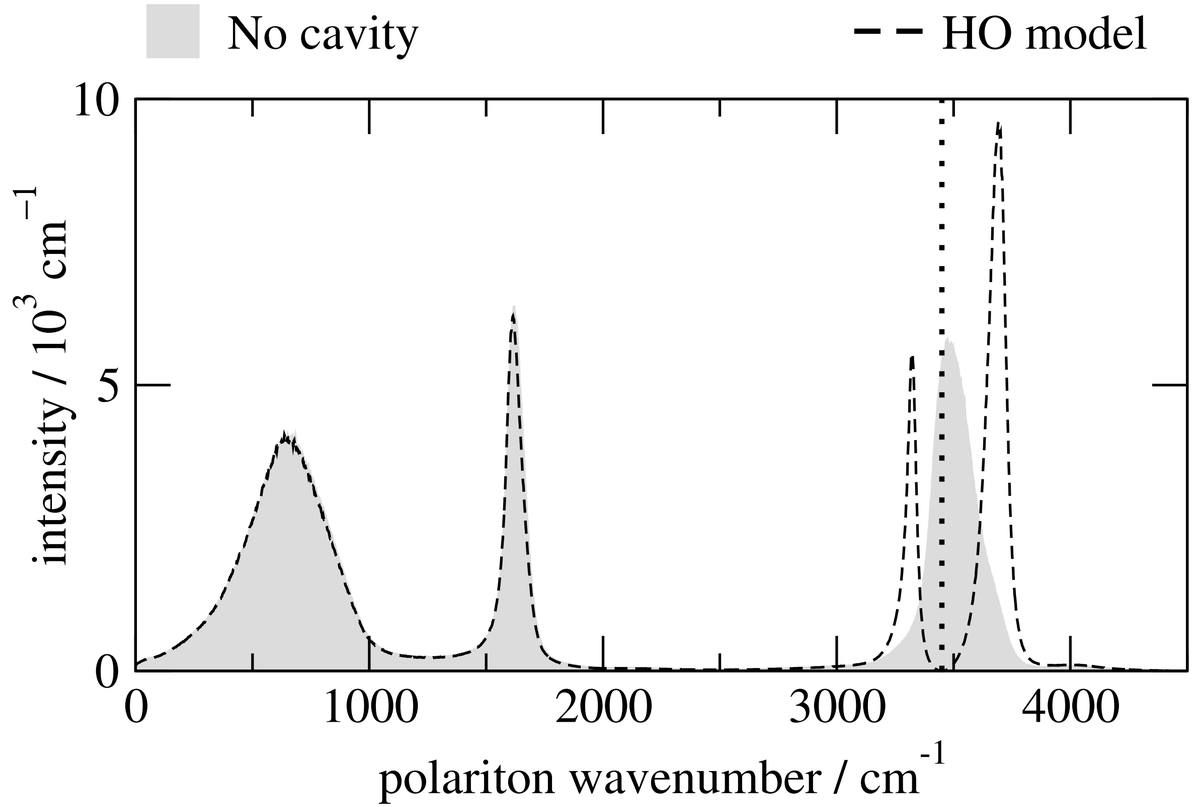
2. Introduce coupling to cavity mode

3. Find normal modes of the coupled system



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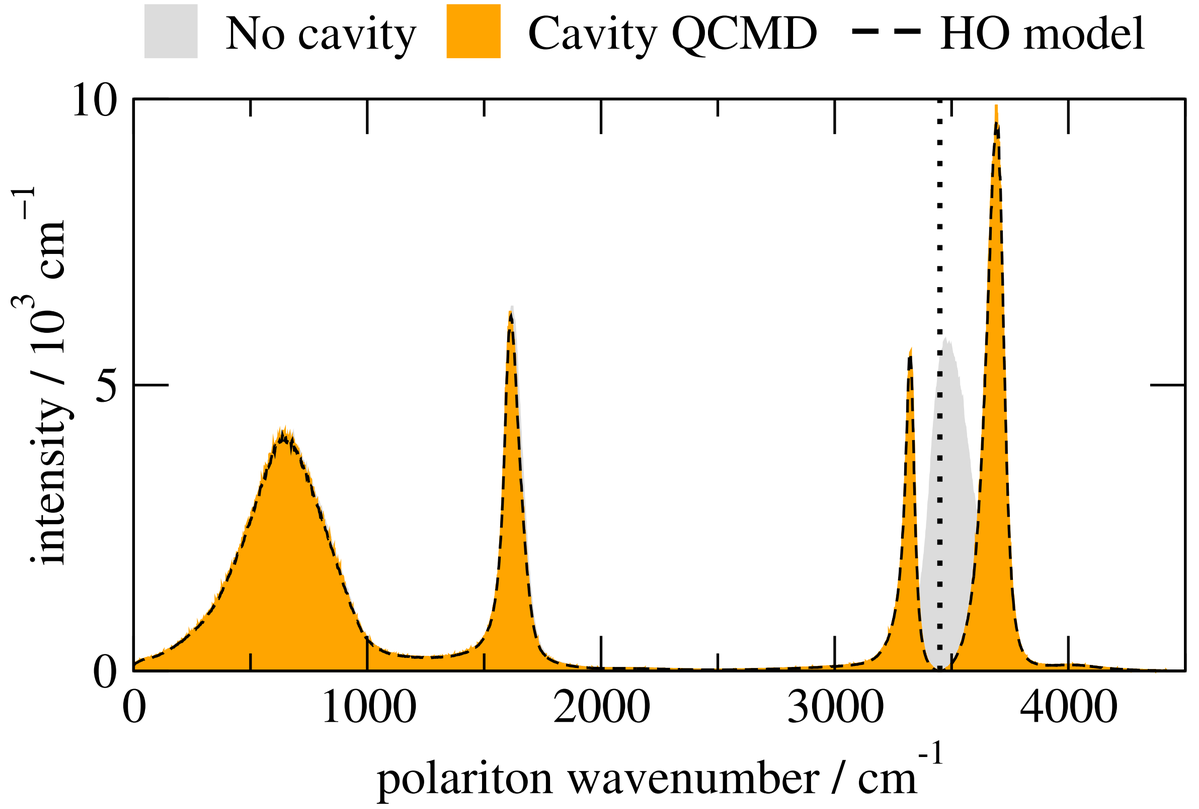

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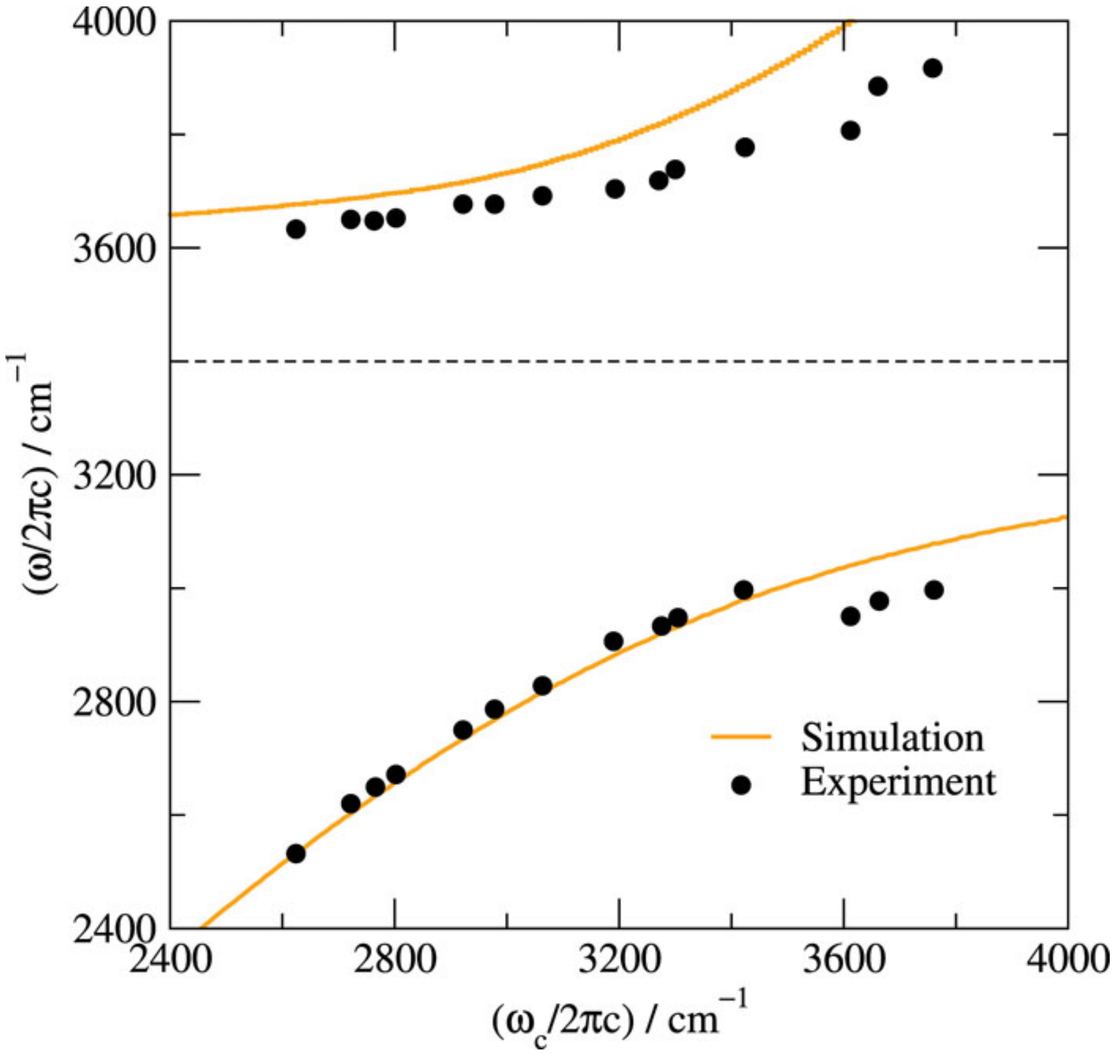
Comparison to experiment - H_2O

We can use the experimental H_2O spectrum as input!

Removes debate about simulation method, and experiments include nuclear quantum effects exactly.

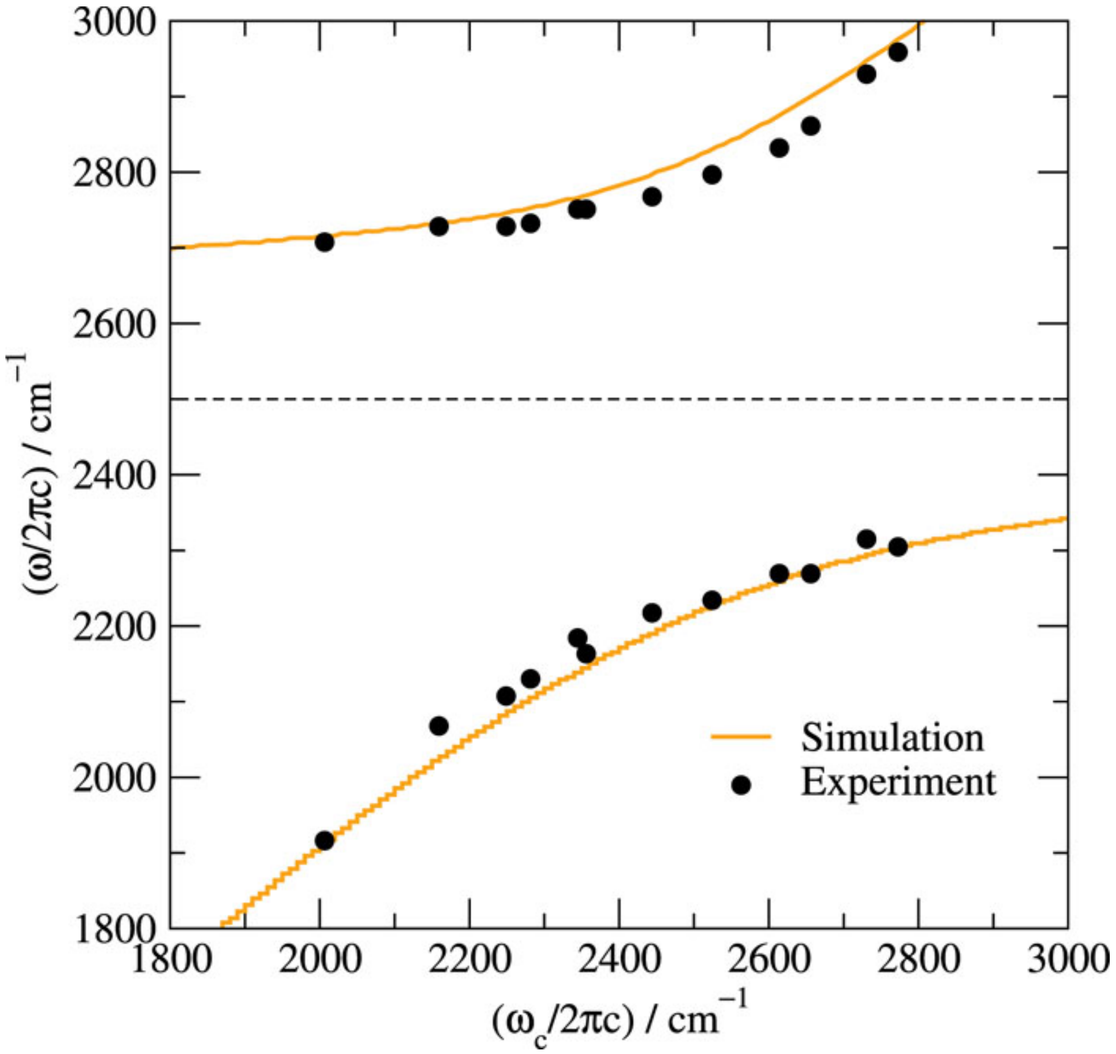
The upper polariton is not captured very well.



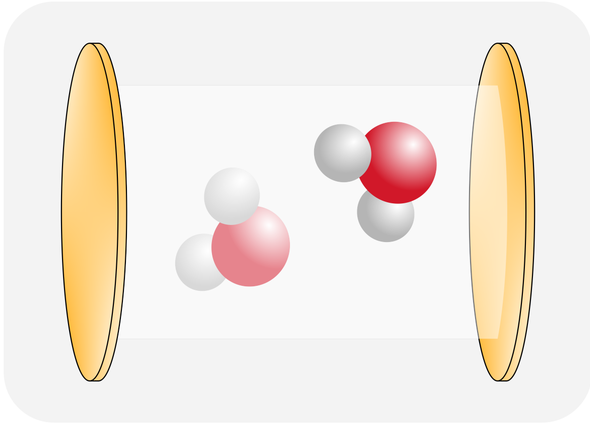
Comparison to experiment - D_2O

For D_2O, the agreement in the upper polariton is better.

So it may be that there were issues with the H_2O experiment.



Conclusions



- NQEs do not affect the polariton bands
- Cavity MD simulations can be reproduced exactly by a simple harmonic oscillator model
- The harmonic oscillator also agrees well with experimental measurements, and needs only the cavity geometry as input
- So IR spectra in a cavity are quite simple

- Other cavity phenomena like out-of-equilibrium dynamics and chemical rate modifications need more investigation

Acknowledgements

- Seth Furniss (now MIT)
- David Manolopoulos
- Joe Lawrence (now NYU)

- Manolopoulos group

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