Understanding Cavity-Mediated Dynamics in Vibrational Polaritonic Chemistry

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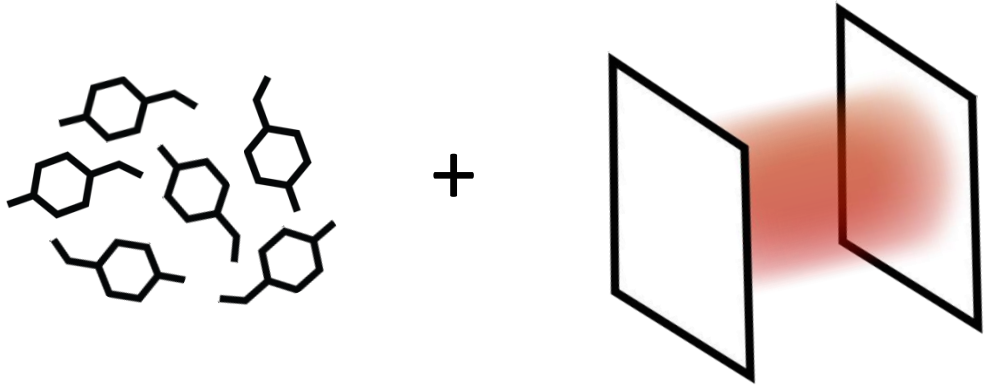
03/12/2024

Introduction to Polaritonic Chemistry - Overview

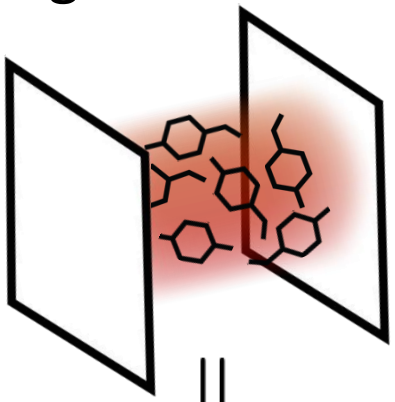


Matter + Light

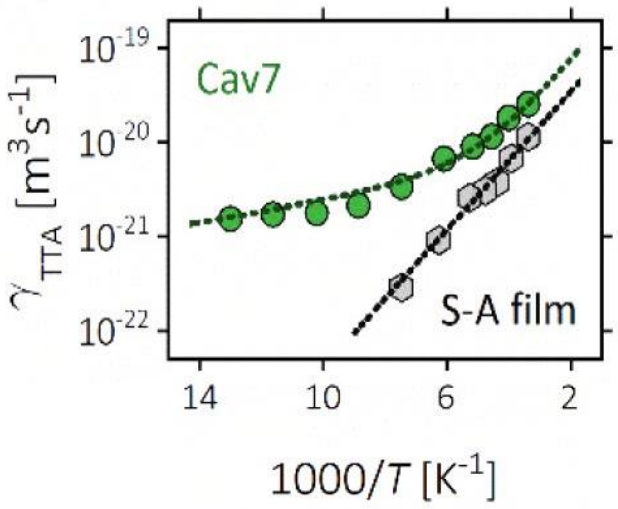
Controlling chemical kinetics through confined electromagnetic fields

Introduction to Polaritonic Chemistry - Overview

Light-Matter

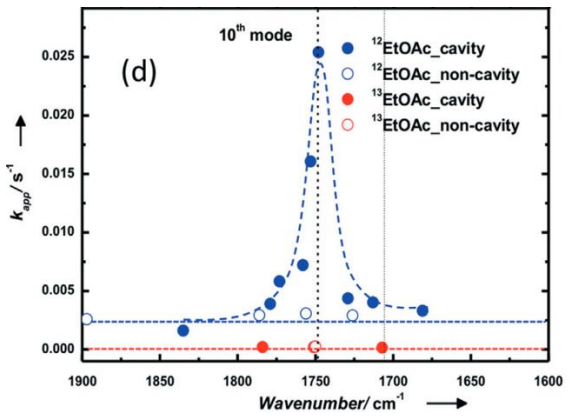


Photochemistry



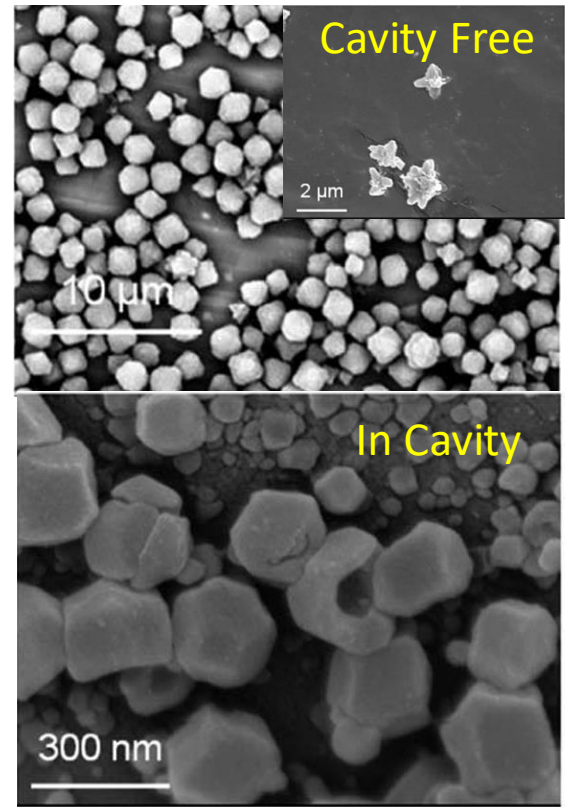
Ye, et al. *J. Am. Chem. Soc.* (2021)

Hydrolysis



Lather, et al. *Angew. Chem., Int. Ed* (2019)

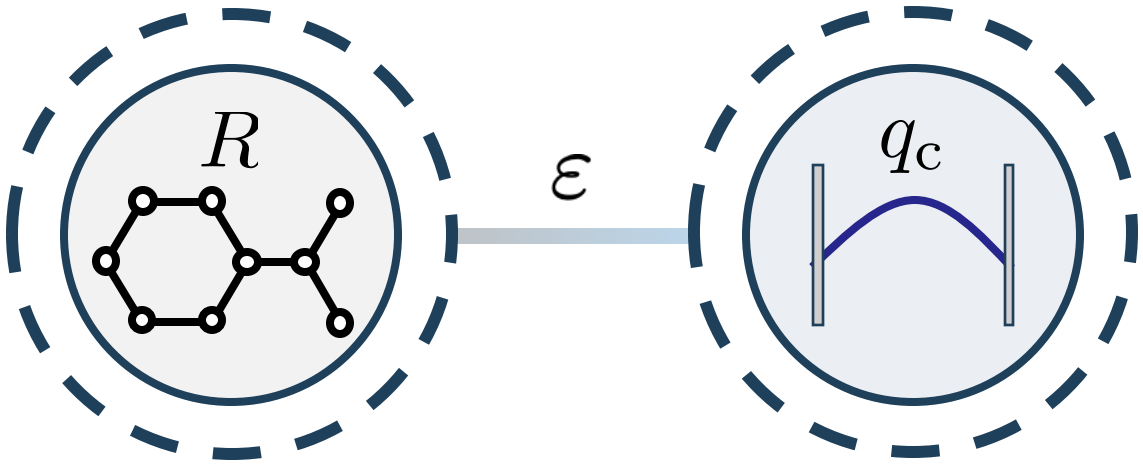
Crystallization



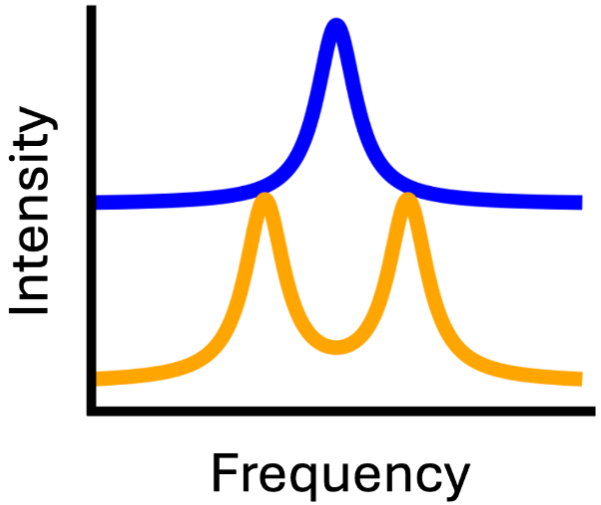
Hirai, et al. *Chem. Sci.* (2021)

Controlling chemical kinetics through confined electromagnetic fields

Introduction to Polaritonic Chemistry - Polaritons



$$\hat{H}_{\mathrm{M}} + \hat{H}_{F} + \hat{H}_{\mathrm{int}}$$



Formation of hybrid light-matter states called **polaritons**

Introduction to Polaritonic Chemistry - Polaritons

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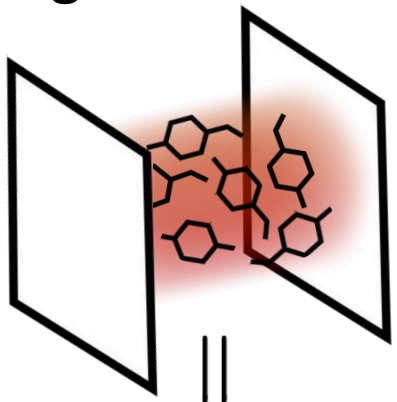

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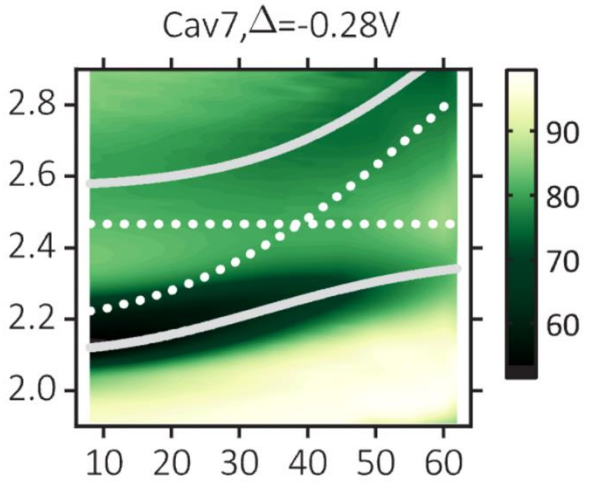

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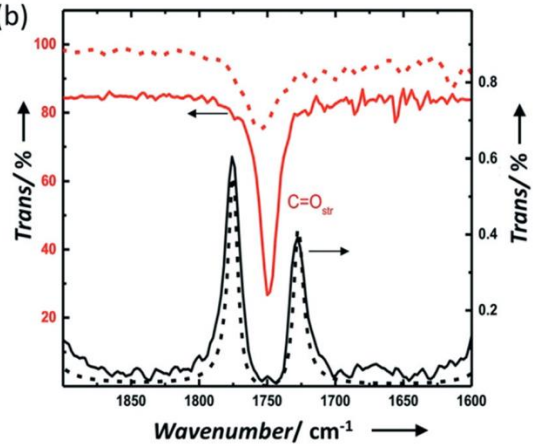

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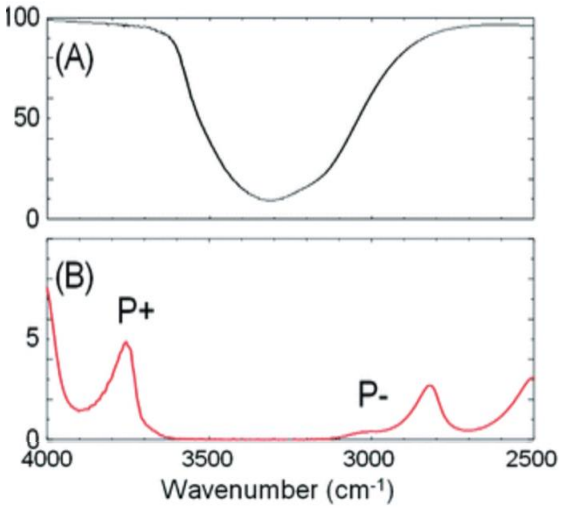

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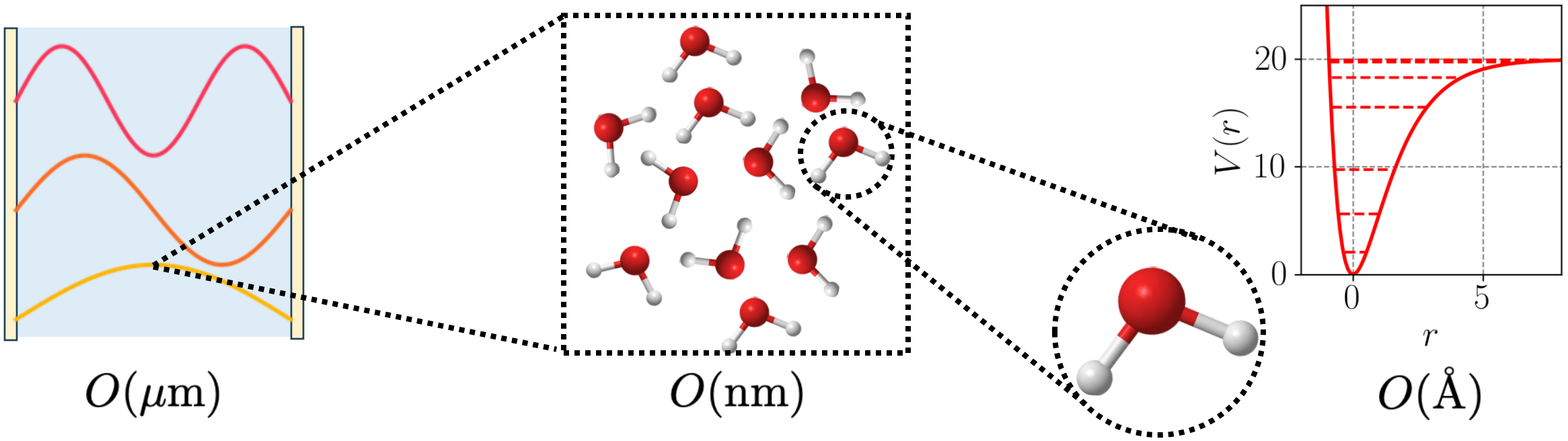
Formation of hybrid light-matter states called **polaritons**

Polaritonic Chemistry as a Multiscale Problem



A unique multiscale problem!

1. Amplitude of light modes span microns in length-scale (affect coupling!)
2. A single mode couples to interacting molecules (collective)
3. Single-molecule vibrations must be treated accurately (quantum)

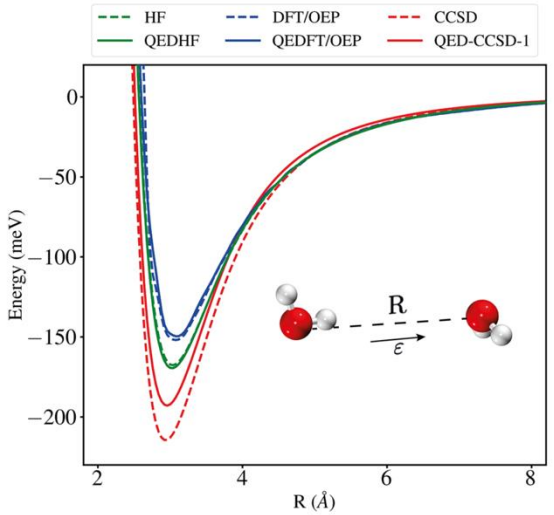
Polaritonic Chemistry as a Multiscale Problem

$O(\text{Å})$ $O(\text{nm})$ $O(\mu\text{m})$

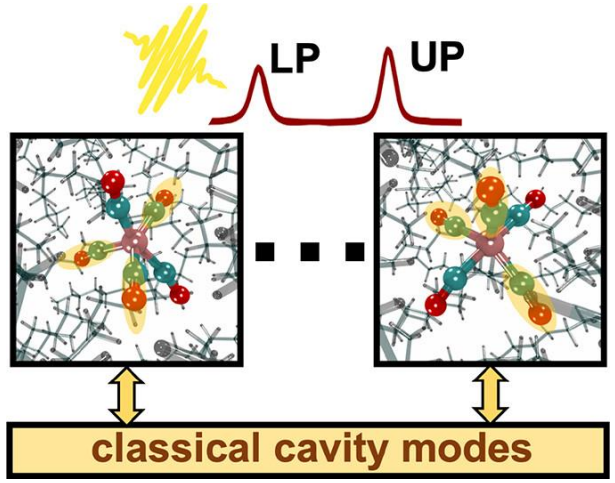
$N \sim 1\text{–}100$
Fully quantum

$N \sim 10\text{–}1000$
Quantum and classical approach

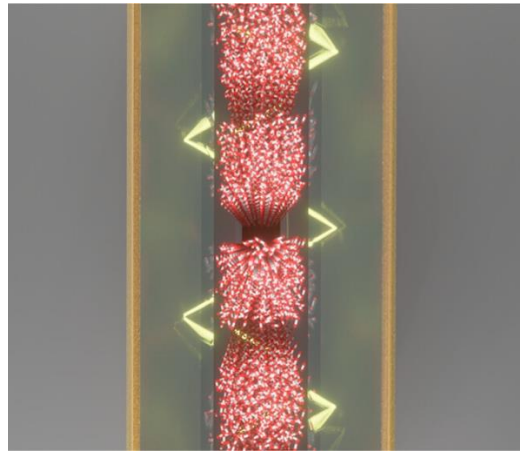
$N \gg 1000$
All-classical



Haugland, et al. *JCP* (2021).



Li and Hammes-Schiffer
JACS (2022)



Li *JCTC* (2024)

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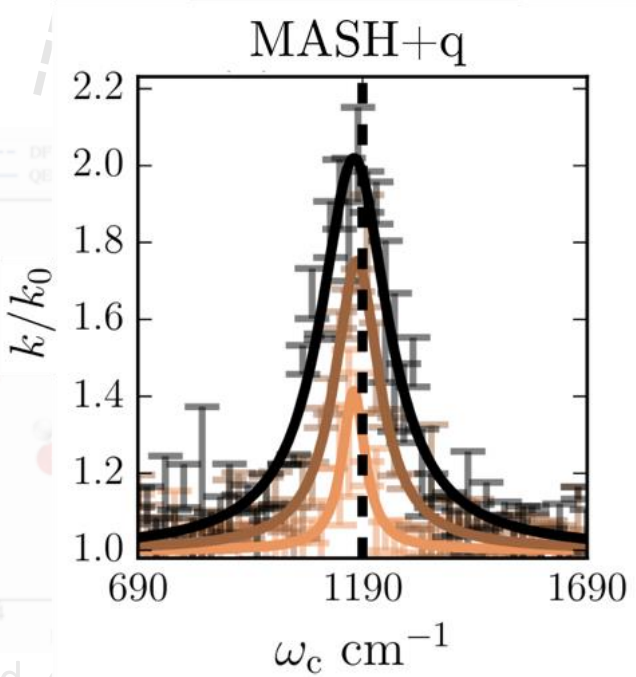
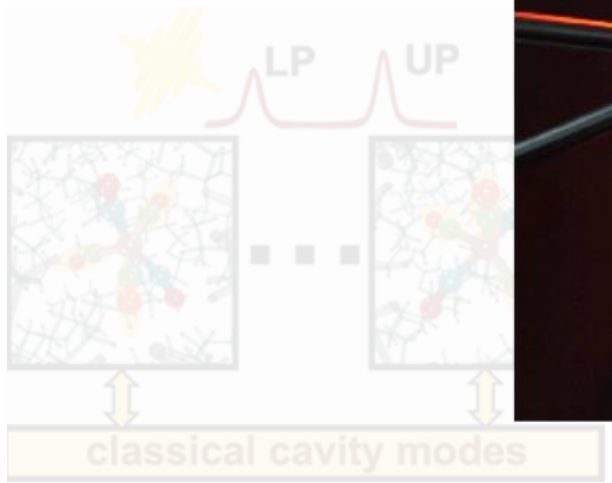


Hasyim, Mandal, and Reichman
arXiv:2502.04570 (2025)



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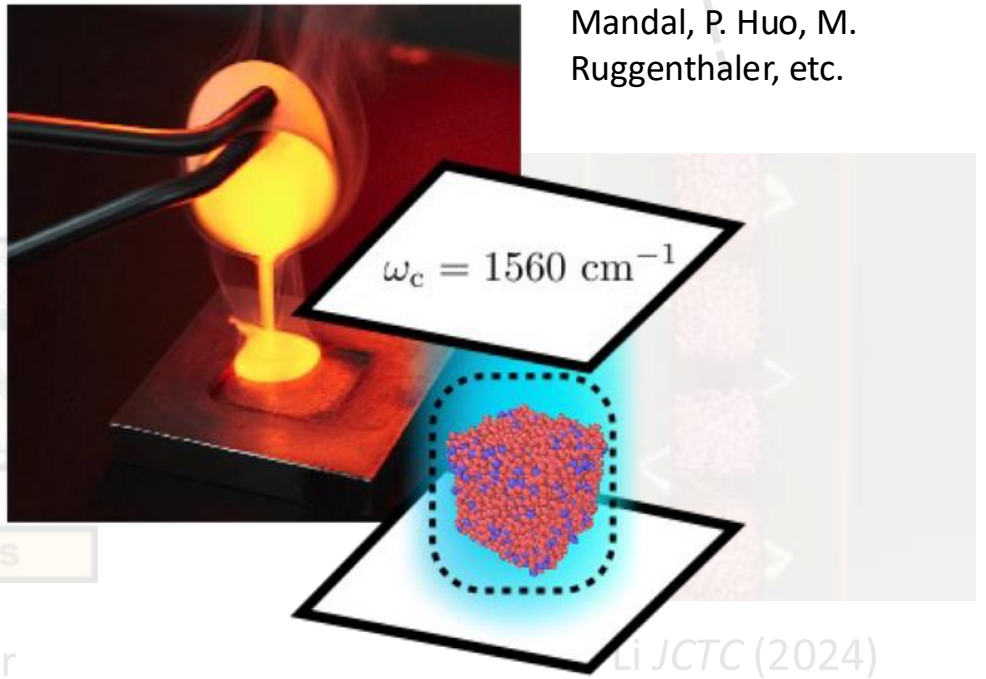
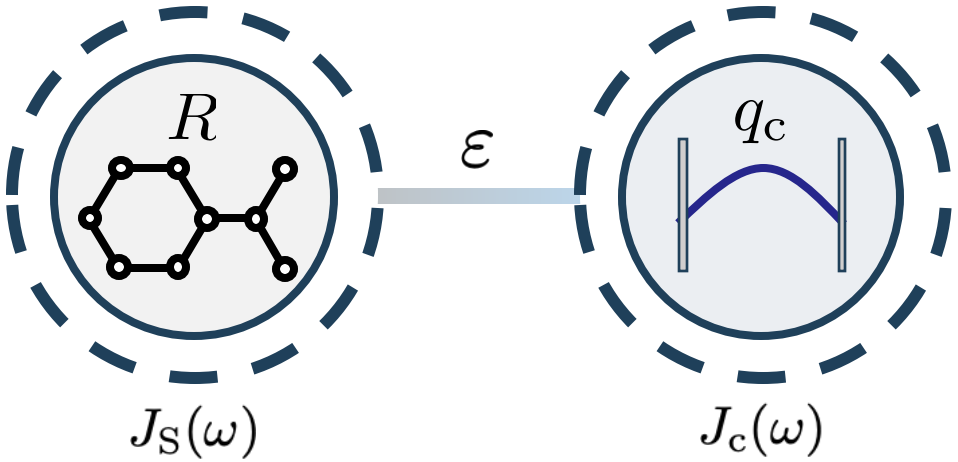
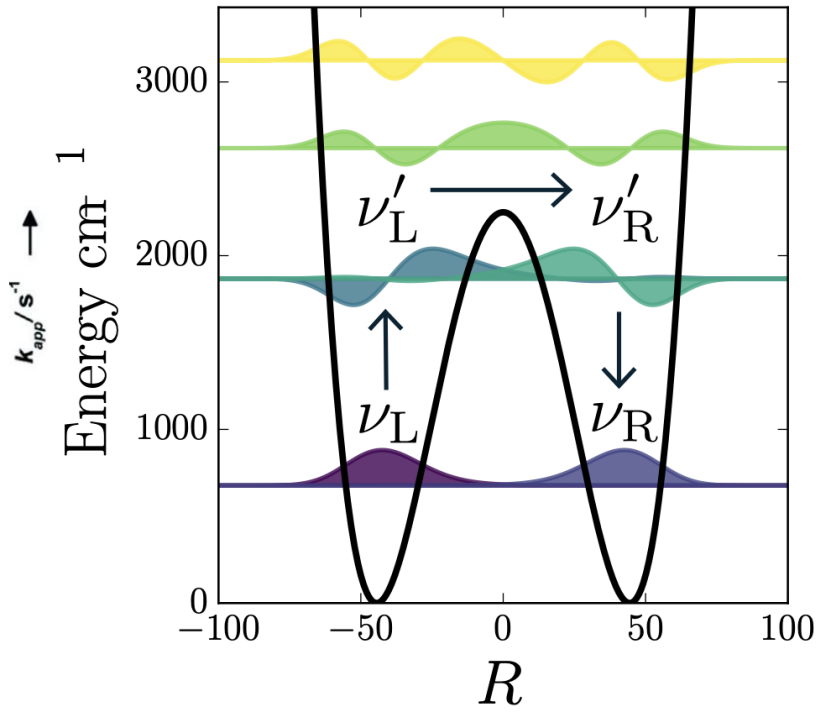


Hasyim, Damiani, and Hoffmann *in preparation* (2025)

And many others! J. Flick, J. Feist, N. Hoffmann, A. Mandal, P. Huo, M. Ruggenthaler, etc.

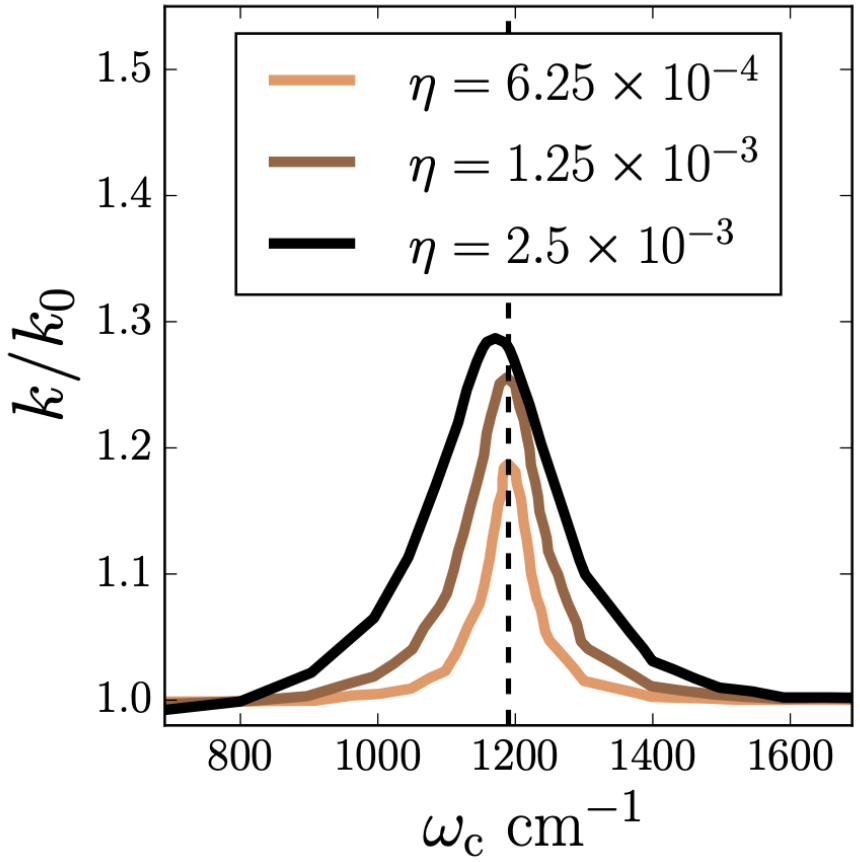
Motivation: Understanding Reaction Modification





- Experiments document suppression and enhancement of rates. Why?

Motivation: Understanding Reaction Modification



HEOM calculations reveal modest enhancement (Hu, Ying, Huo, *J. Phys. Chem. Lett.* (2023))

- Experiments document suppression and enhancement of rates. Why?
- Scale up to atomistic, many-molecule limit?
- Use mixed quantum classical (MQC) simulations

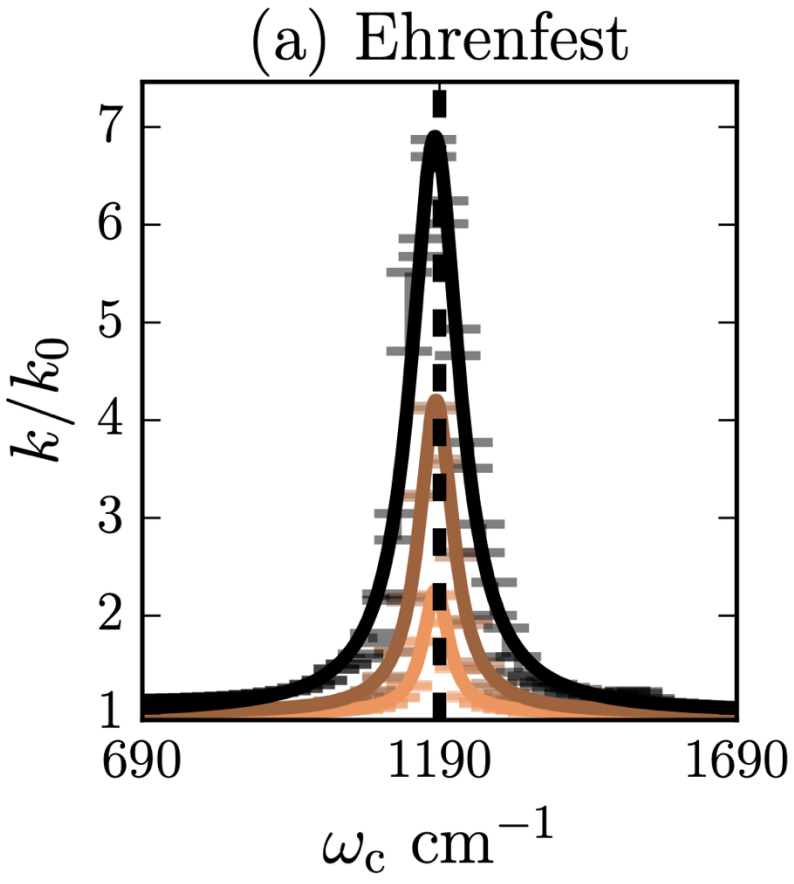
$$\hat{H} = \hat{H}_M + \hat{H}_F + \hat{H}_b$$

$$\hat{H}_M = \frac{\omega_b^4}{16E_b} \cdot \hat{R}^4 - \frac{1}{2}\omega_b^2 \cdot \hat{R}^2$$

$$\hat{H}_F = \frac{1}{2}\hat{p}^2 + \frac{1}{2}\omega_c^2 \left(\hat{q} + \sqrt{\frac{2}{\omega_c}}\eta_c \hat{R} \right)^2$$

$$\hat{H}_b = \frac{1}{2}\sum_i \left[\hat{p}_i^2 + \omega_i^2 \left(\hat{x}_i - \frac{c_i}{\omega_i^2}\hat{R} \right)^2 \right] + \frac{1}{2}\sum_j \left[\hat{\tilde{p}}_j^2 + \tilde{\omega}_j^2 \left(\hat{\tilde{x}}_j - \frac{\tilde{c}_j}{\tilde{\omega}_j^2}\hat{q}_c \right)^2 \right]$$

Motivation: Understanding Reaction Modification



MQC methods overpredict the rate enhancement! (Hu, Ying, Huo, *J. Phys. Chem. Lett.* (2023))

- Experiments document suppression and enhancement of rates. Why?
- Scale up to atomistic, many-molecule limit?
- Use mixed quantum classical (MQC) simulations

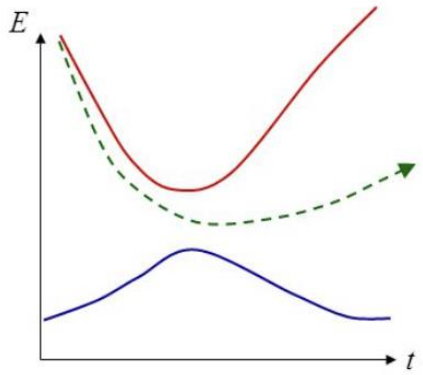
Main Problem

How to reach quantitative accuracy (towards HEOM's modest predictions)?

First Strategy: Which Dynamics Method to Use?

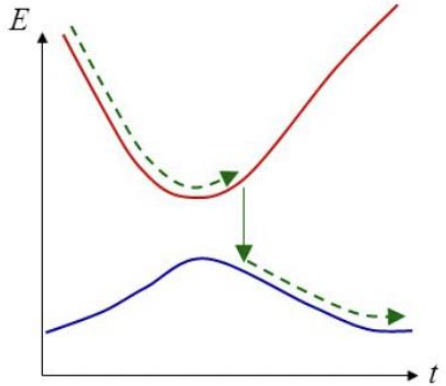
Quantum: $\dot{c}_\mu = -\mathrm{i}\sum_\nu E_{\mu\nu}(\mathbf{q})c_\nu\,,$ or $\dot{c}_m = -\mathrm{i}E_m(\mathbf{q})c_m - \sum_j \frac{p_j}{m_j}\sum_n d^j_{mn}(\mathbf{q})c_n$

Classical: $\dot{q}_j = p_j/m_j\,,\quad \dot{p}_j = F_j(\mathbf{q})$



Mean-field
Classical DOFs evolve in an averaged PES

$$F_j = -\langle\psi|\nabla_j\hat{E}(\mathbf{q})|\psi\rangle$$



Surface Hopping
Classical DOFs hop through different PESs

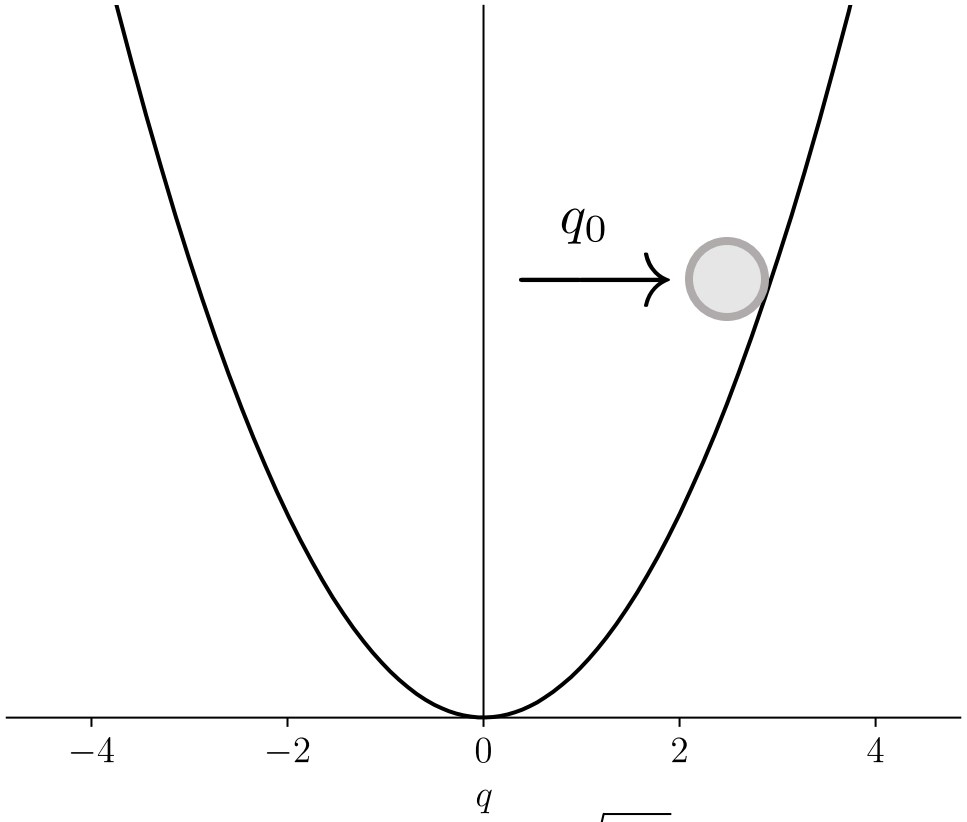
$$F_j = -\nabla_j E_a(\mathbf{q})$$

Mapping Approach to Surface Hopping (MASH)

$$F_j = -\nabla_j E_a(\mathbf{q}) - \sum_n \Delta E_{na}(\mathbf{q})\delta\left(\mathbf{q}-\mathbf{q}_{na}\right)\delta^j_{na}$$
$$a = \arg\max_n\{\rho_n\}$$

Mannouch and Richardson JCP (2023); Runeson and Manolopoulos JCP (2023)

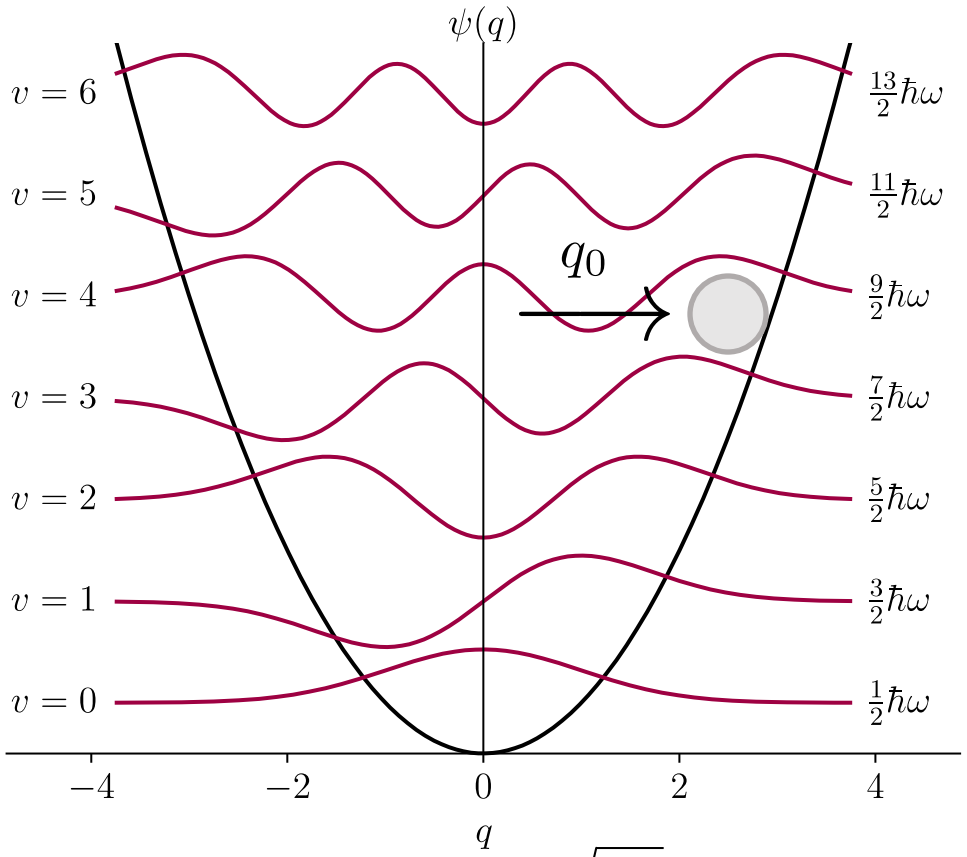
Second Strategy: Quantum or Classical Photon?



where $q_0 = -\sqrt{\frac{2}{\omega_c}}\eta_c R$

- So far, we treated the photon classically.
- But the cavity mode is quantum mechanical in nature!

Second Strategy: Quantum or Classical Photon?

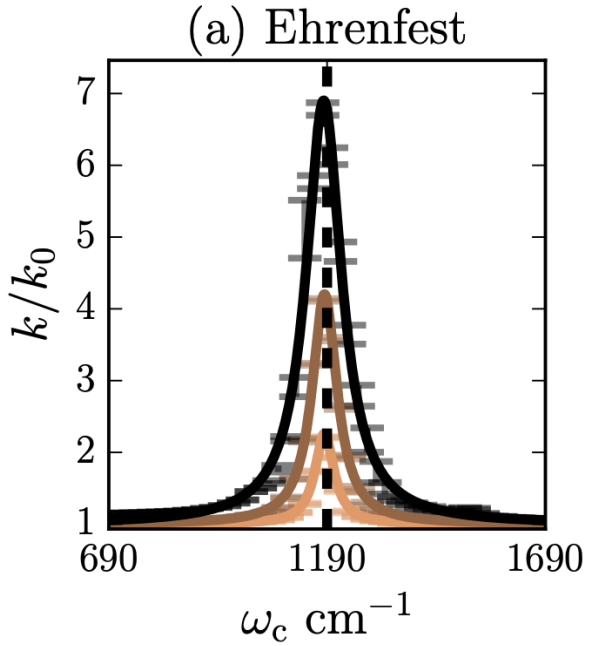


where $q_0 = -\sqrt{\frac{2}{\omega_c}}\eta_c R$

- So far, we treated the photon classically.
- But the cavity mode is quantum mechanical in nature!
- **Challenge:** At very strong coupling, high number of Fock states is needed!
- **Solution:** Polaron transform

$$\hat{H}' = \hat{U}_{\mathrm{PL}}^{\dagger}\hat{H}\hat{U}_{\mathrm{PL}} \text{ where } \hat{U}_{\mathrm{PL}} = e^{\mathrm{i}\hat{q}_0\hat{p}_c}$$

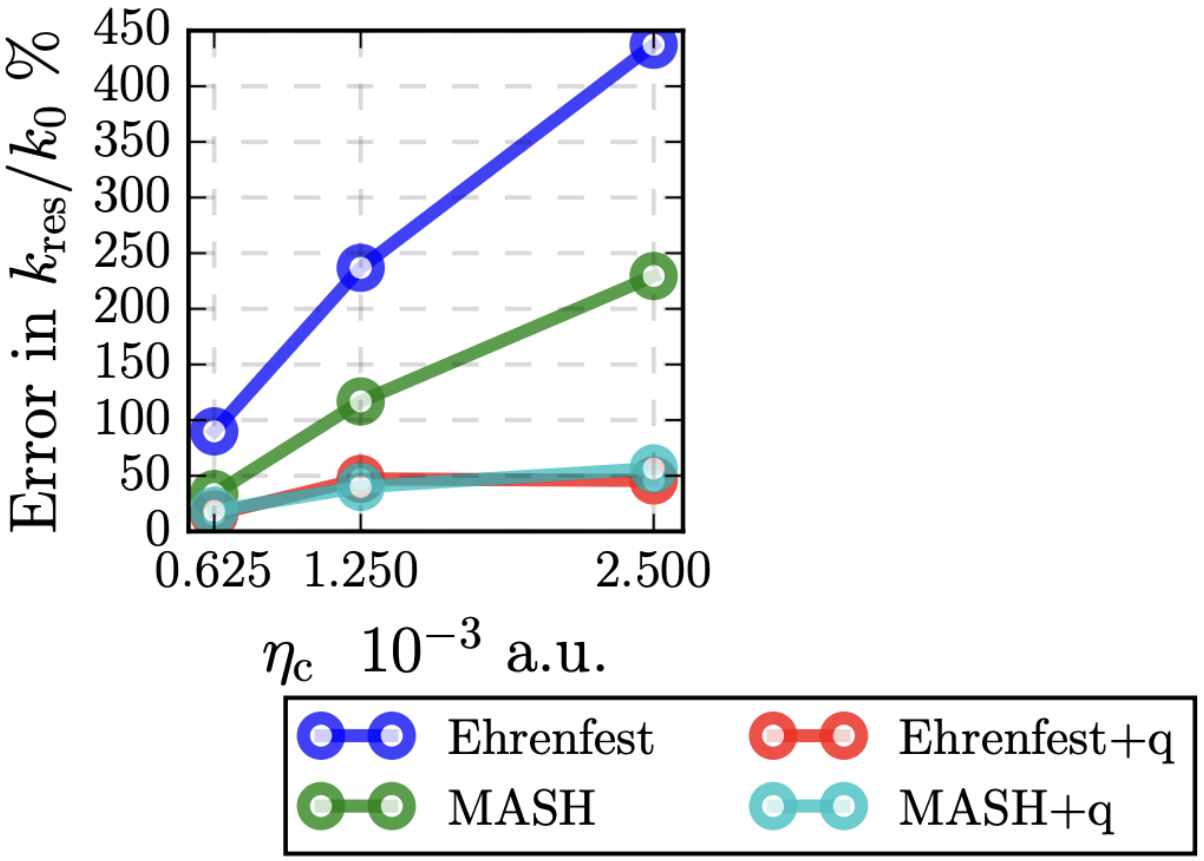
Results



$\eta_c = 6.25 \times 10^{-4}$ $\eta_c = 1.25 \times 10^{-3}$ $\eta_c = 2.5 \times 10^{-3}$

- MASH with classical cavity mode leads to immediate improvement, but not enough
- Quantum cavity mode improves both Ehrenfest and MASH calculation
- Modest rate enhancements (less than two times)

Problem 2: Quantum or Classical Photon?



- So does MASH offer no further improvement than Ehrenfest?
- MASH predicts the **absolute rate** better than Ehrenfest!

Key Point

Use MASH and quantum cavity mode to reach more quantitative accuracy

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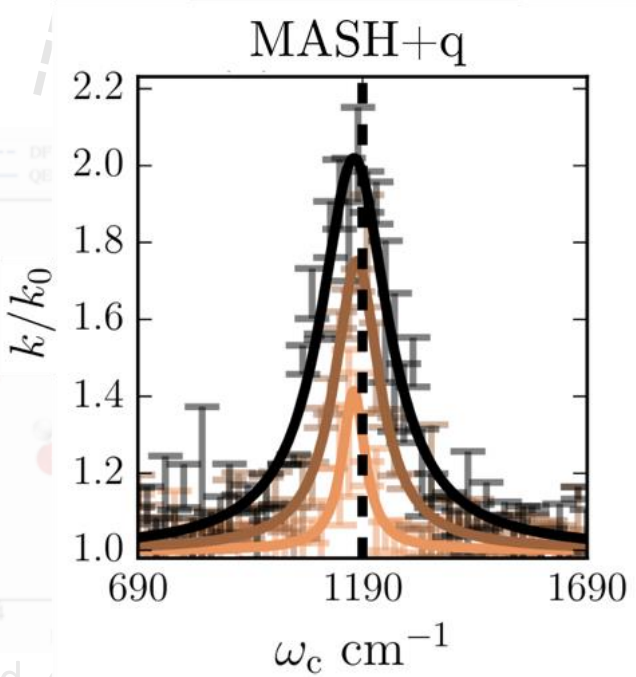

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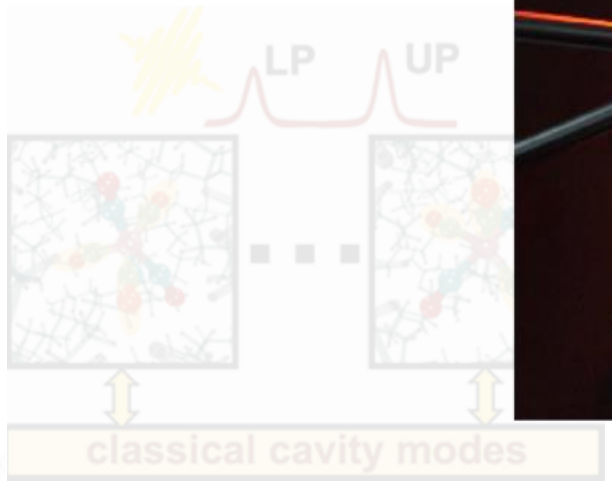

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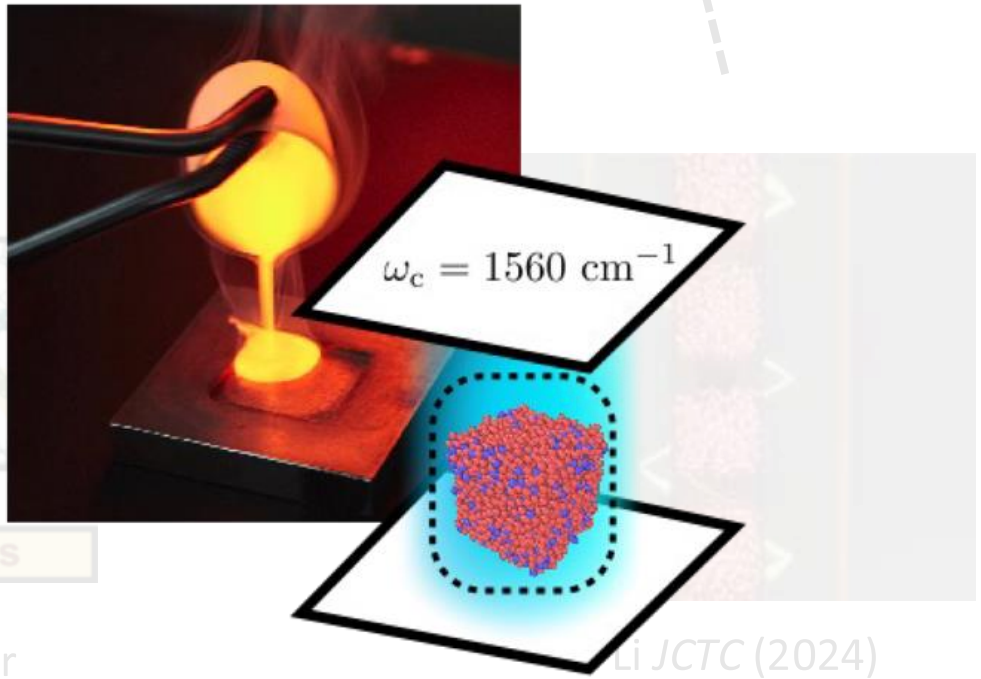
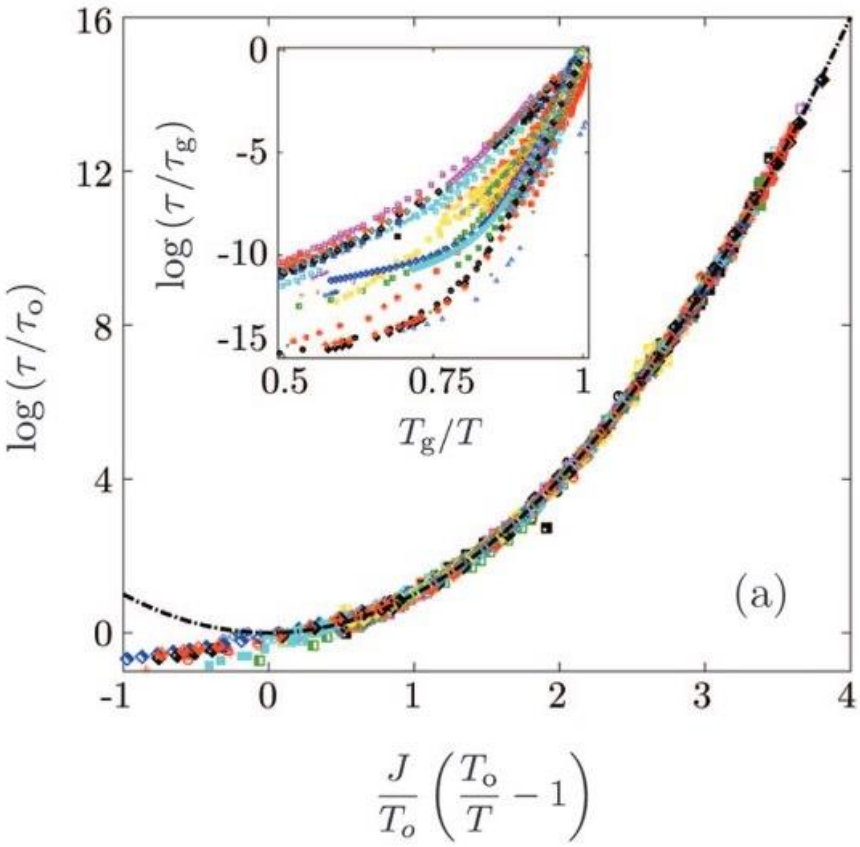


Hasyim, Damiani, and Hoffmann *in preparation* (2025)

Motivation: Beyond Reactivities in Polaritonic Chemistry

We see evidence of reaction rate modifications, but what about **diffusivity, viscosity**, **thermal conductivity**?



Transport properties of organic and inorganic systems collapsible to one master curve. Elmatad, et al. *J. Phys. Chem.* (2009)

Study supercooled liquids because . . .

1. Unique yet ubiquitous

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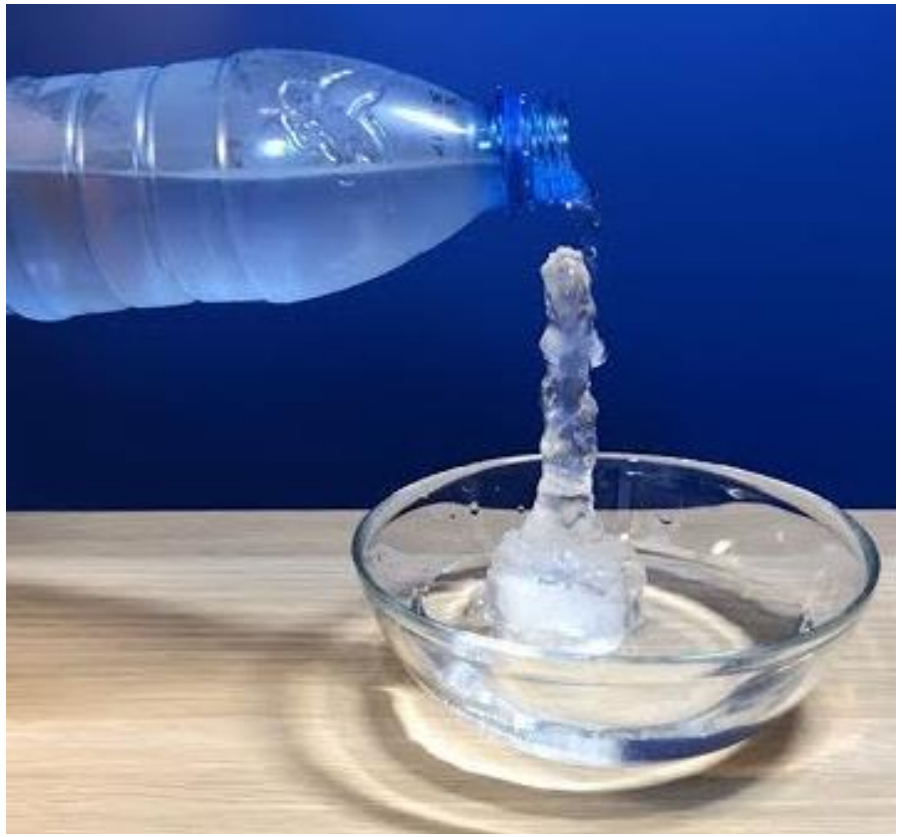
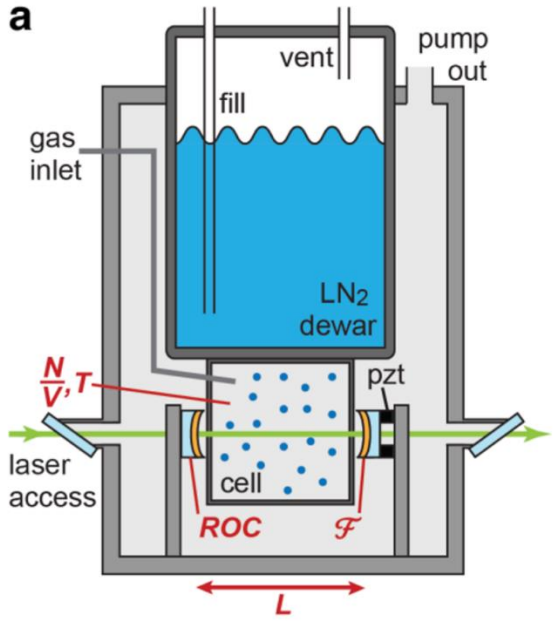


Spontaneous crystallization of supercooled water. Source: youtu.be/OCRnmBGl-BE

Study supercooled liquids because . . .

1. Unique yet ubiquitous
2. Supercooled state precedes crystallization



Experiments are already exploring cold temperatures!
Nelson and Weichman *JCP* (2024)

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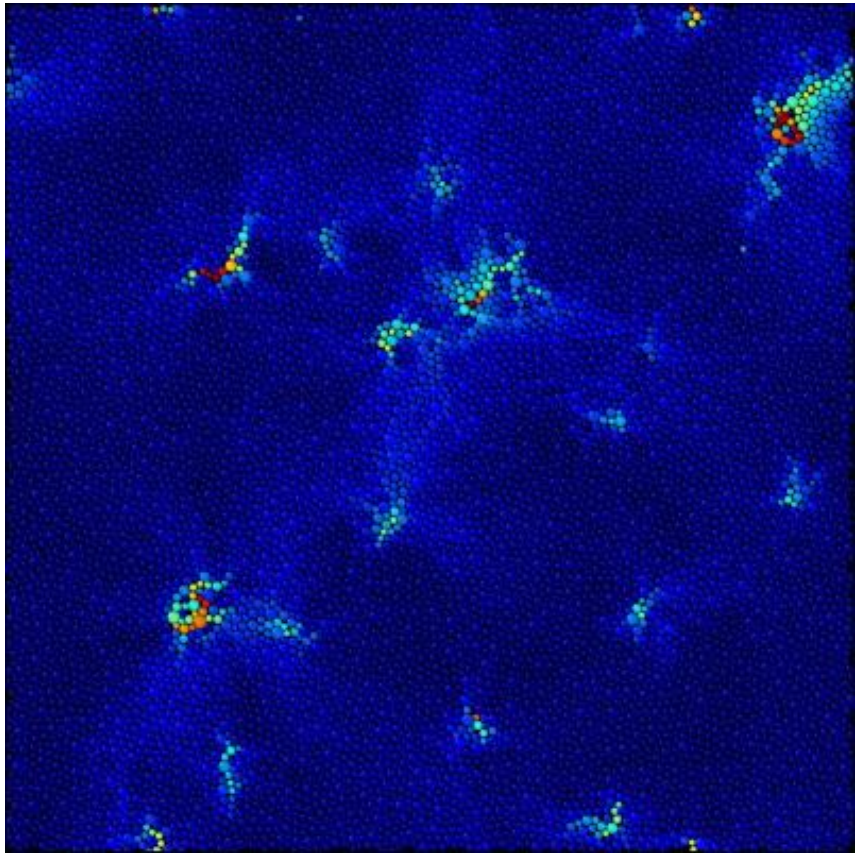


Supercooled Lennard-Jones fluid in two-dimensions. Color is displacement magnitude.

Study supercooled liquids because . . .

1. Unique yet ubiquitous
2. Supercooled state precedes crystallization
3. A playground of collective dynamics

Main Question

Is transport or relaxation in supercooled liquids slower/faster in microcavities?

Choosing a Model Supercooled Liquid System

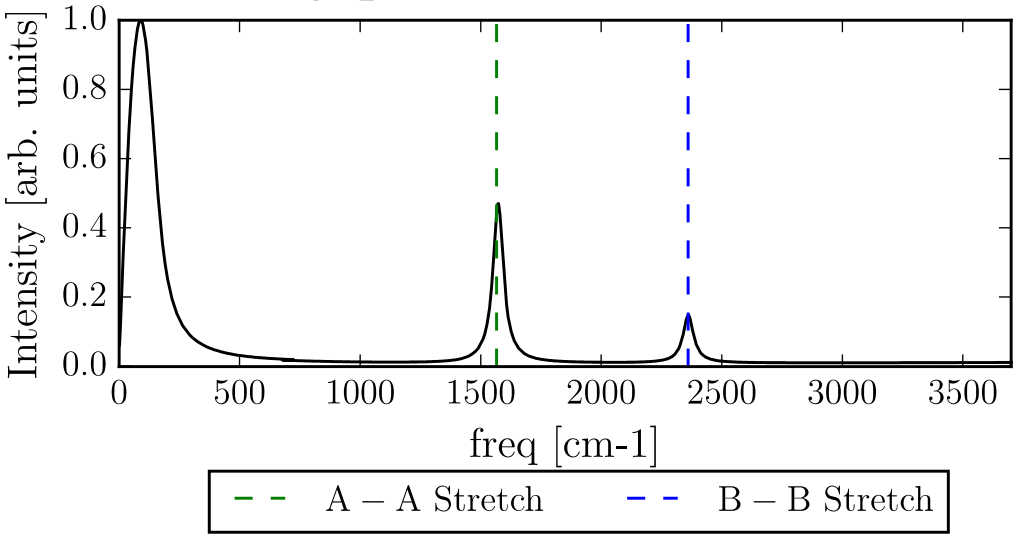
$$H = H_M + H_F$$

$$H_M = \sum_j^N \frac{\mathbf{P}_j^2}{2M_j} + V(\{\mathbf{R}_j\})$$

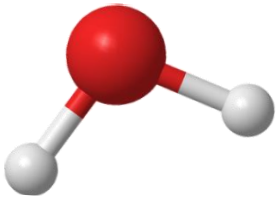
$$H_F = \sum_{\lambda=1,2} \frac{1}{2}p_\lambda^2 + \frac{1}{2}\omega_c^2 \left(q_\lambda + \frac{\varepsilon}{\omega_c^2}\mu_\lambda\right)^2$$

Li, Subotnik, Nitzan PNAS (2020)

where $\boldsymbol{\mu} = \sum_{i=1}^N q_i \mathbf{R}_i$ is the dipole moment



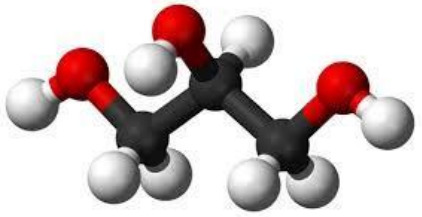
Candidate Systems to Study



Water

✓ "Simple" vibrational spectrum

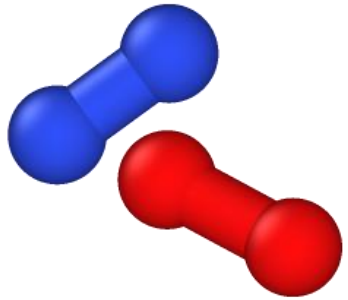
✗ Easy to crystallize



Glycerol

✓ Resist crystallization

✗ Complicated vibrational spectrum



Solution:

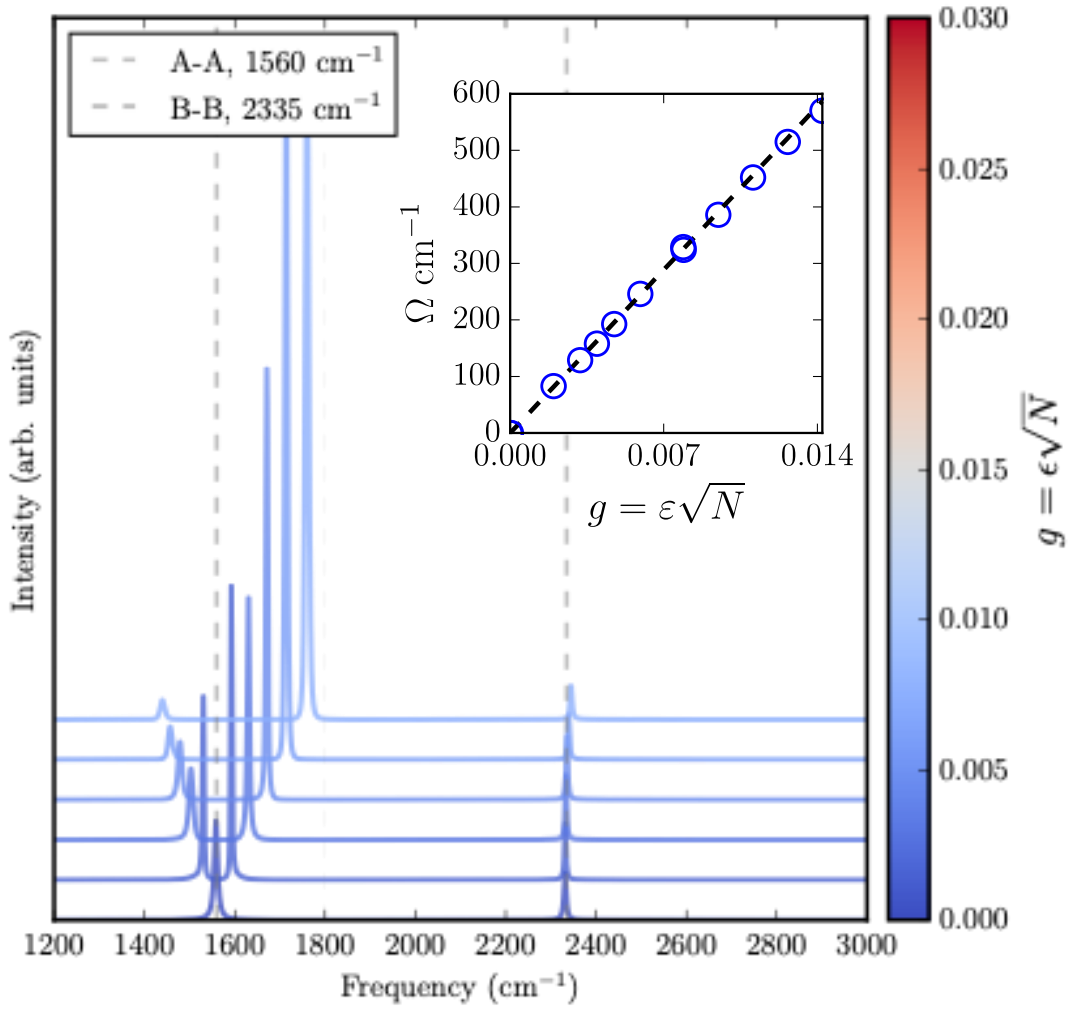
Create a model system!

✓ Resist crystallization

✓ Simple vibrational spectrum

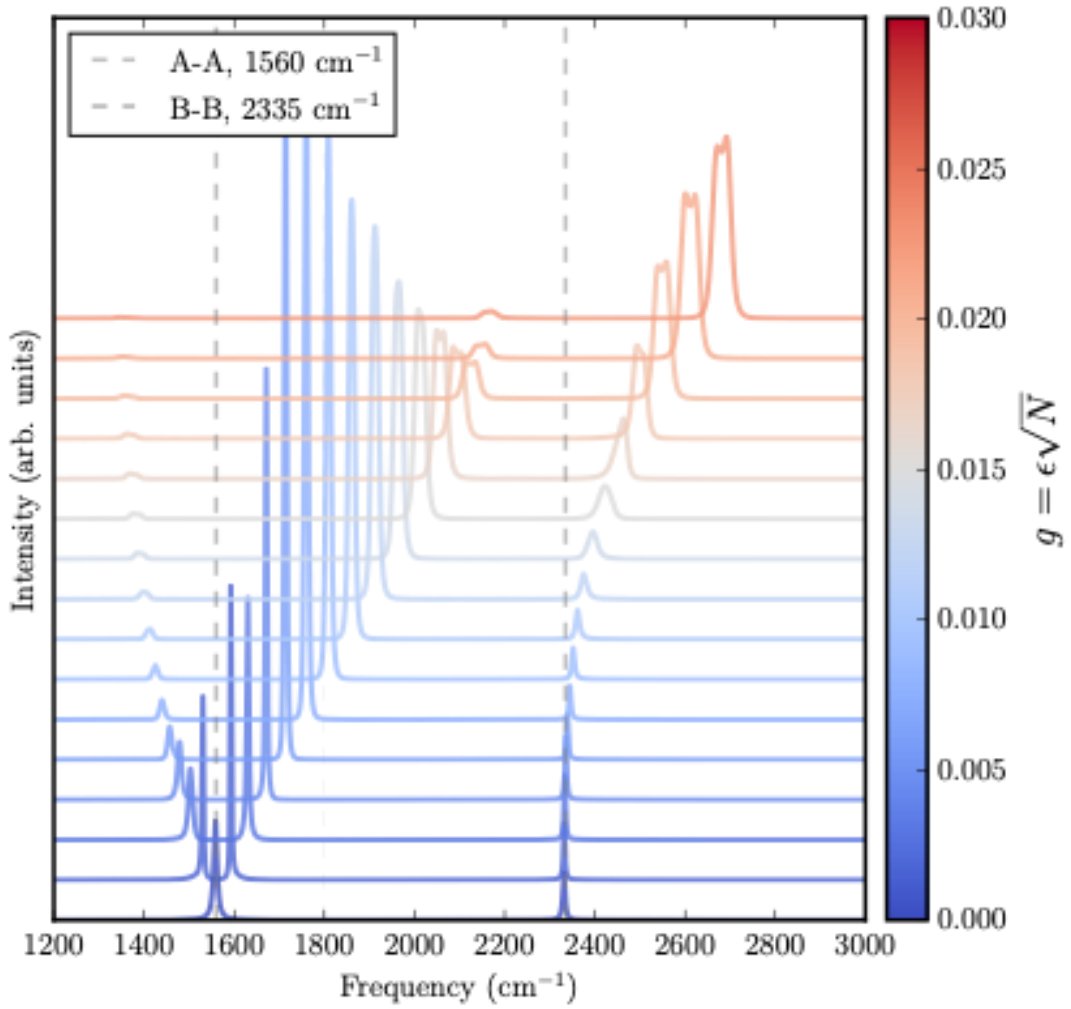
✗ Extreme conditions

Results: IR Spectra and Polariton Formation

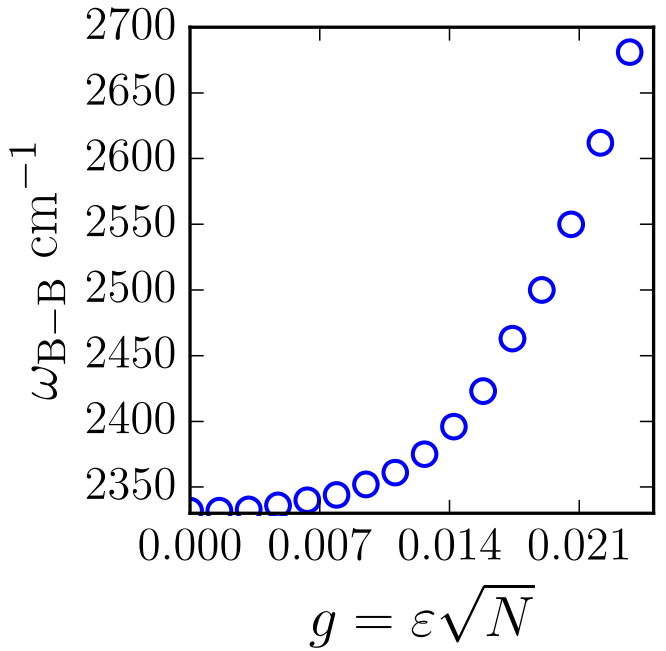


- Formation of vibrational polaritons with increasing coupling strength ε

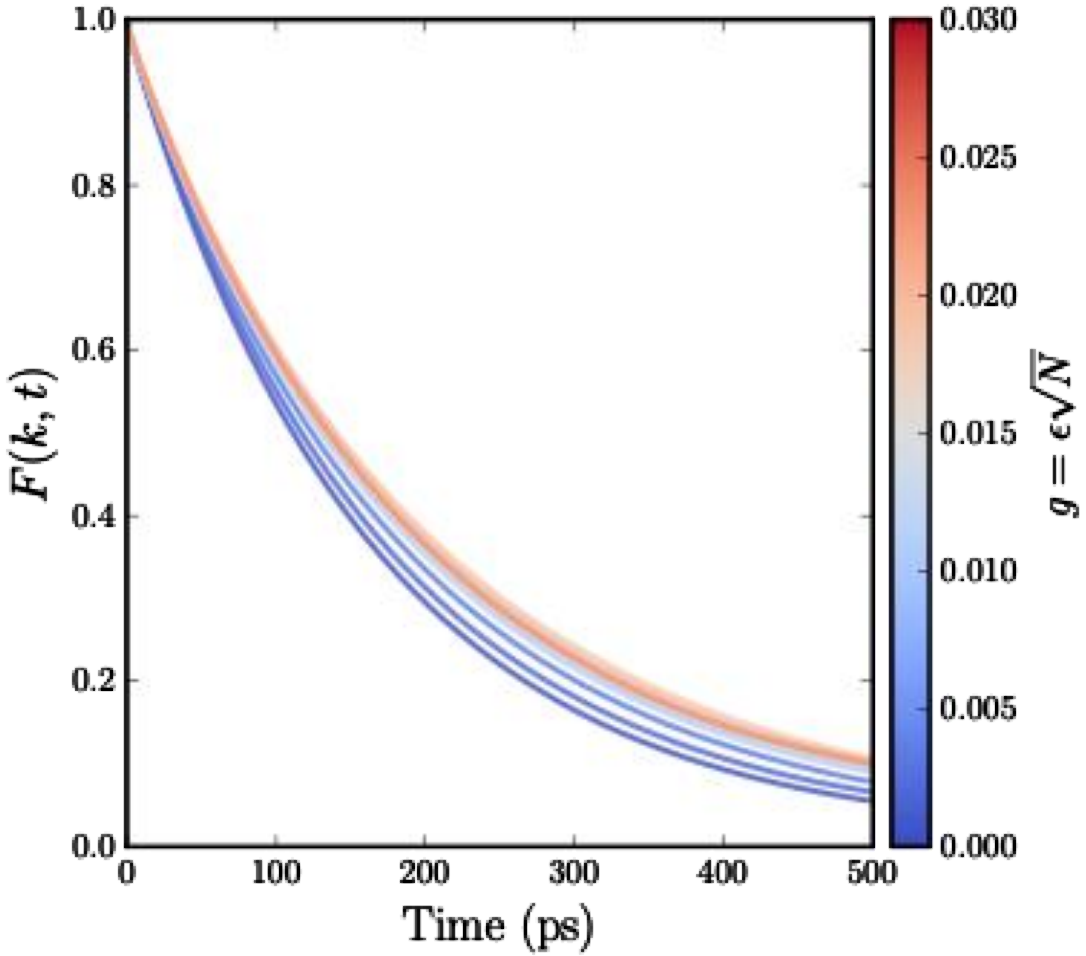
Results: IR Spectra and Polariton Formation



- Formation of vibrational polaritons with increasing coupling strength ε
- Blue-shifting and intensity increase of second peak.



Measuring Relaxation from Supercooled Liquids



- See how fast density field fluctuations relax:

$$F(\mathbf{k},t) = \frac{1}{N}\left\langle \rho_{\mathbf{k}}(t)\rho_{-\mathbf{k}}(0)\right\rangle$$

- Slowdown in dynamics as we increase coupling strength!

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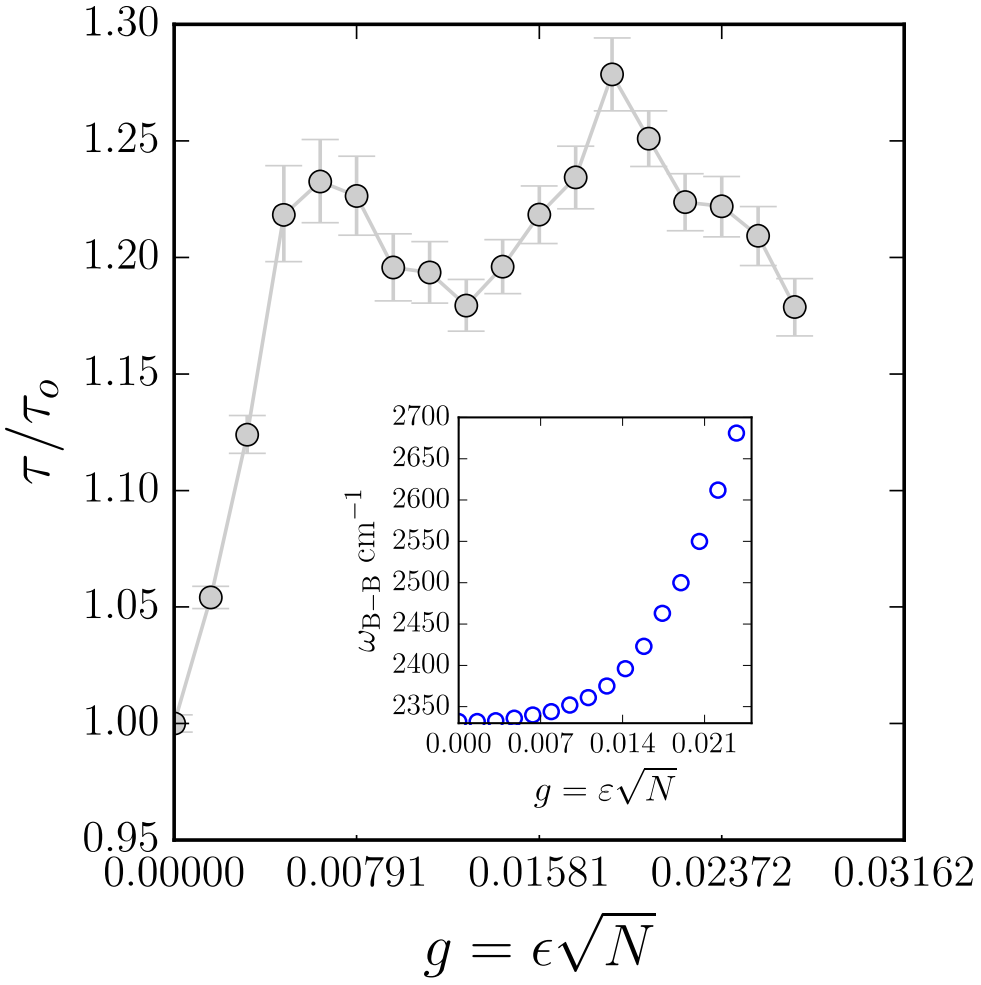


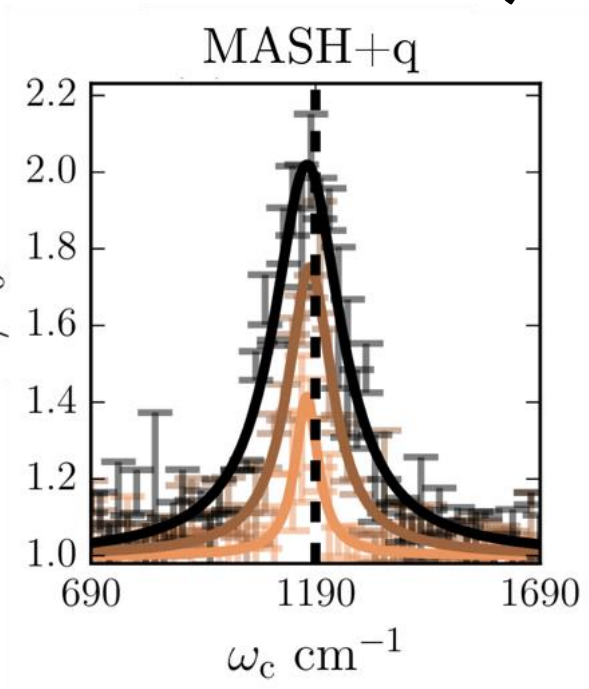
- See how fast density field fluctuations relax:

$$F(\mathbf{k}, t) = \frac{1}{N} \langle \rho_{\mathbf{k}}(t) \rho_{-\mathbf{k}}(0) \rangle$$

- Slowdown in dynamics as we increase coupling strength!
- **Bumps** in relaxation time
- Coincide with the ultra-strong coupling regime

Future Direction: Understanding Collective Effects

$O(\text{Å})$ $O(\text{nm})$ $O(\mu\text{m})$



Hasyim, Mandal, and Reichman
arXiv:2502.04570 (2025)

Collective

$N \sim 2-10$ reacting molecules

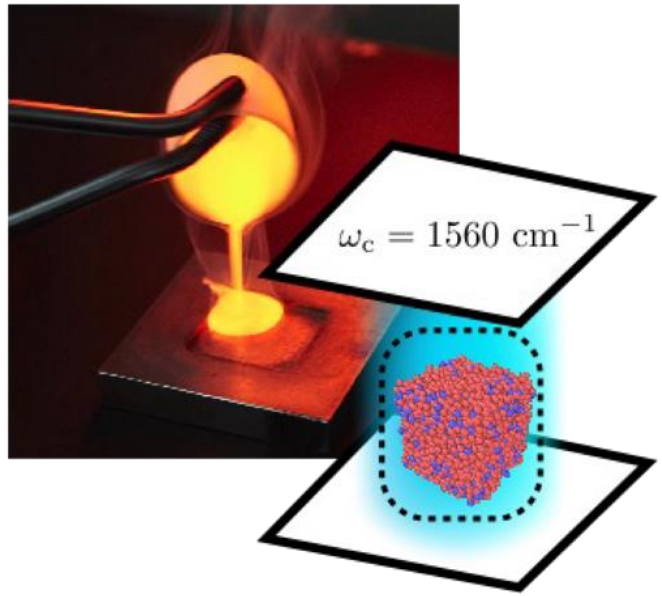
$N \gg 250$ explicit solvent

MQC

Quantum: Reactive Molecules
Classical: Explicit Solvents

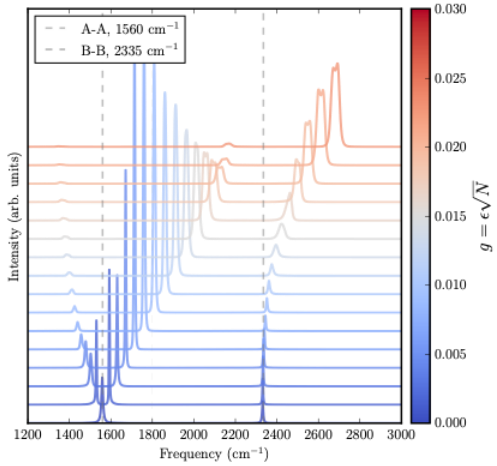
Scalable

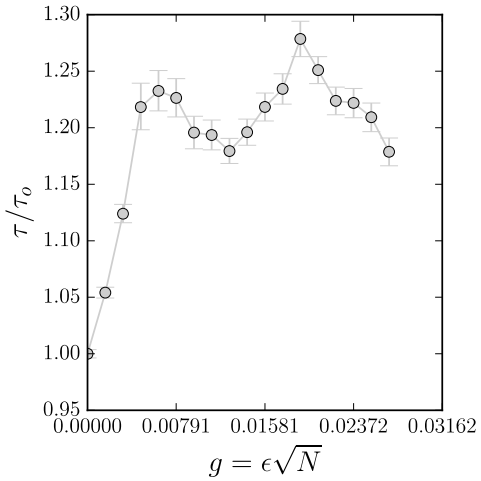
Classical MD + TDSE (GPU)



Hasyim, Damiani, and Hoffmann *in preparation* (2025)

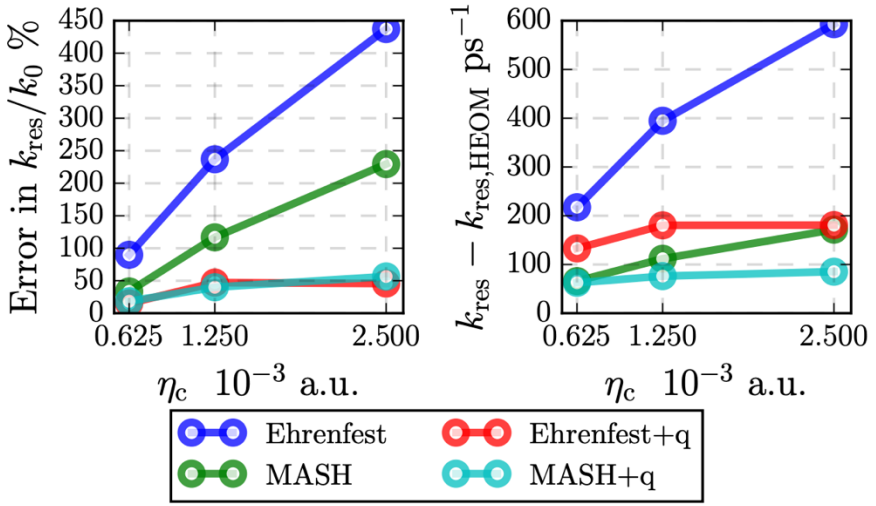
Acknowledgements





What causes the bumps in relaxation time? Is it a collective effect?

Acknowledgements: Arianna N. Damiani and Norah M Hoffmann (NYU)



Other surface hopping methods? Can we improve MASH+q even further?

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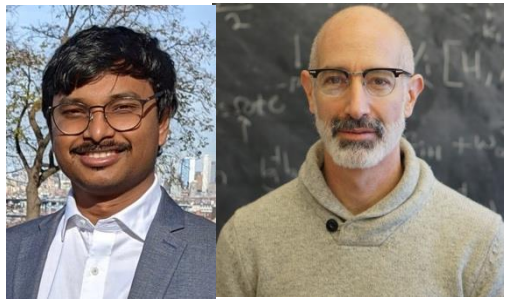

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Acknowledgements

CCQ NYU
LIGHT-MATTER SEMINAR

More at CCQ NYU Light Matter Seminar **(tomorrow, 03/13 11 AM EST)** Contact me for Zoom access and details (**mh7373@nyu.edu**)

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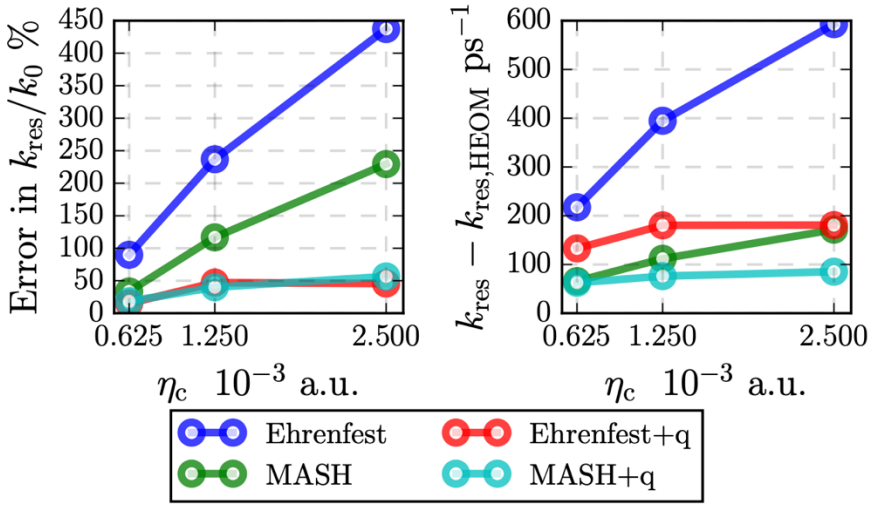

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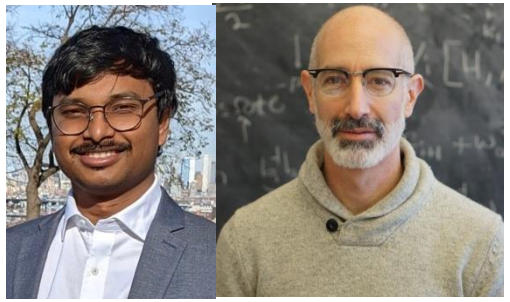

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