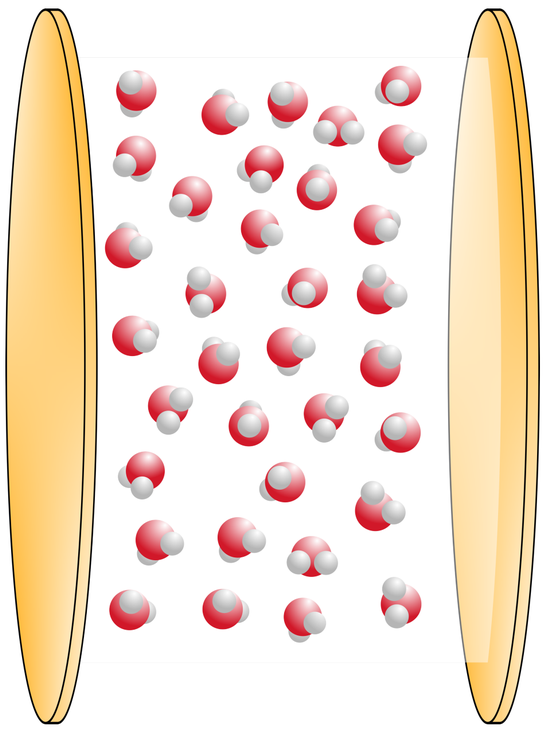
Demystifying polariton chemistry

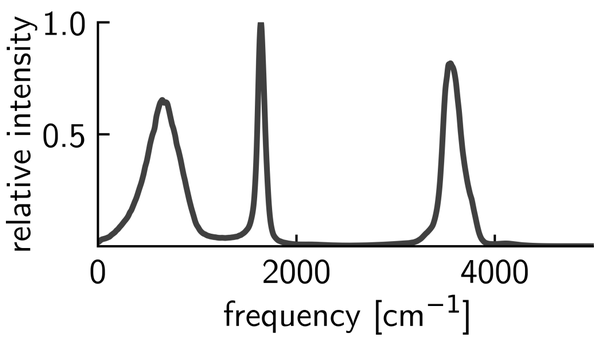
UNIVERSITY OF OXFORD

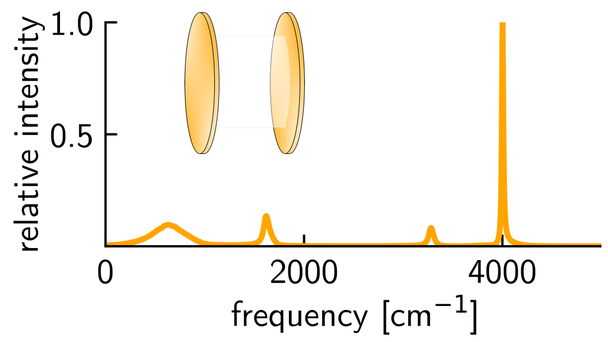


The origin of "cavity effects" is hotly debated.

Experiments have reported changes to molecules' behaviour when placed in a cavity

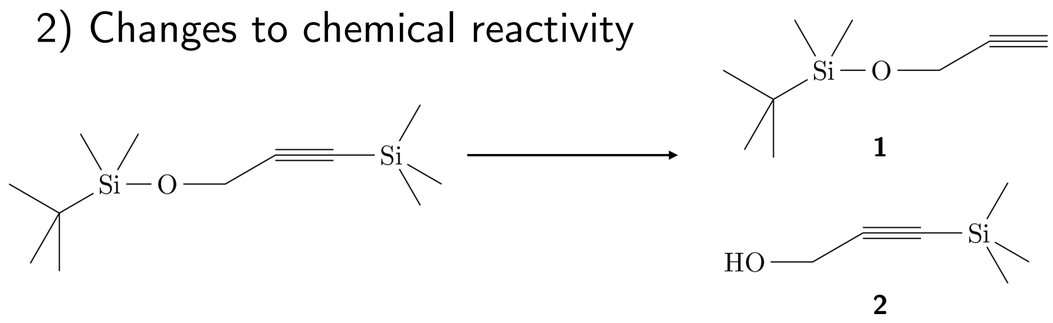
1) New **polariton** peaks in the IR spectrum





Previously, it was claimed that quantum effects can broaden the polariton peaks. Does this hint at a fundamental feature of cavity chemistry?

2) Changes to chemical reactivity

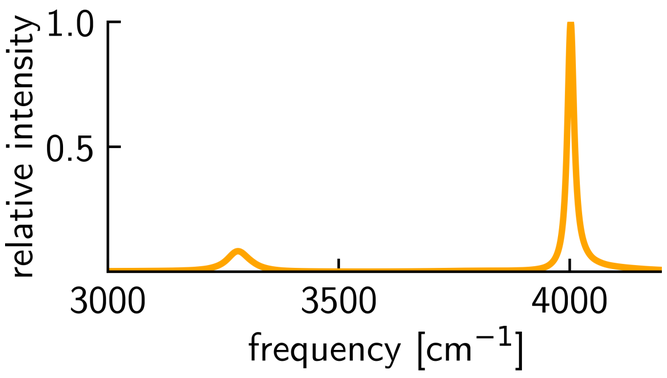


Functional group deprotection used in total synthesis

Outside cavity: **1** dominant
Inside cavity: **2** dominant

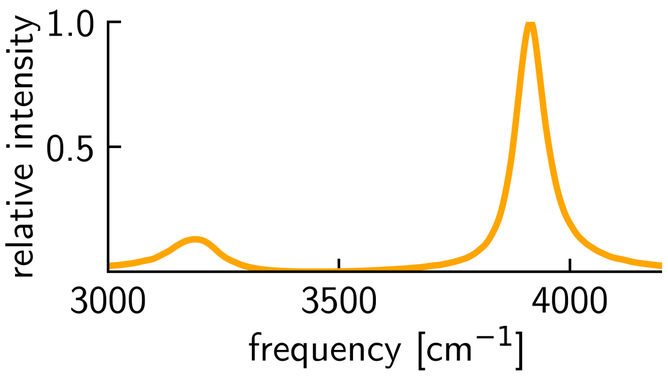
These effects have been reported in vacuum - without shining light on the cavity. But theory (so far) cannot explain them.

Classical spectrum



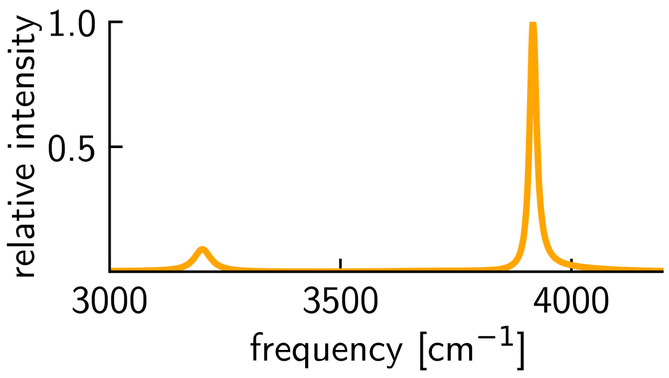
This simulation does not include any quantum effects and serves as a ground comparison.

Previous results



- This includes nuclear quantum effects.
- Peaks are shifted from those in the classical spectrum (which is expected).
- They are also noticeably broader.
- But the simulation method used is known to artificially broaden peaks.

Our work



- We recover the classical line widths. The broadening was hence a consequence of the previous method's known limitations.
- The shift in the peak positions persists. It is a real quantum effect.

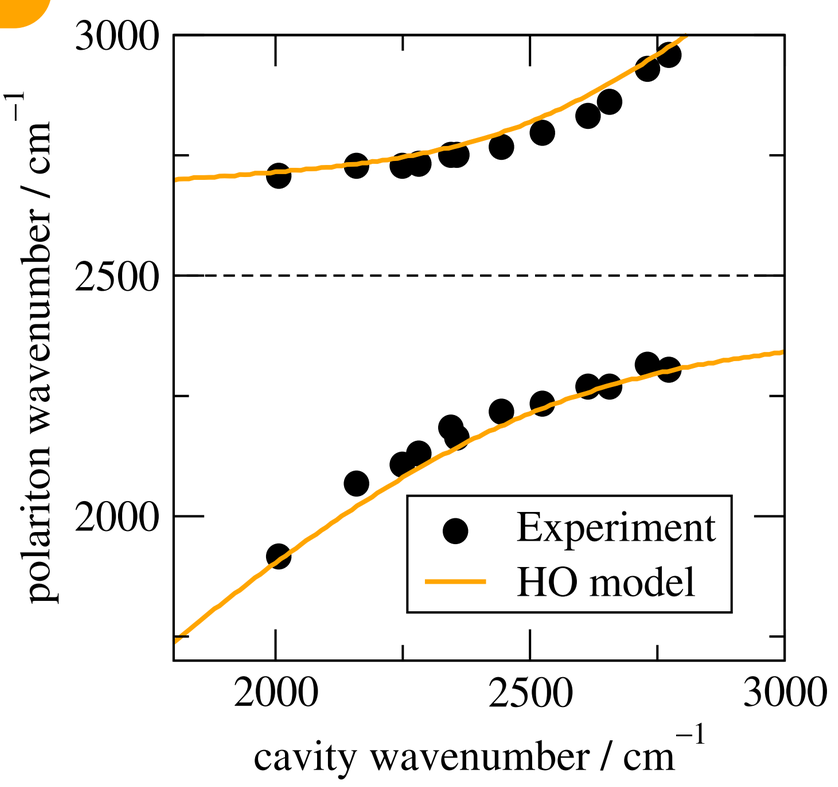
With new, state of the art simulations, we show that broadening in the IR spectrum is an artifact, and *not* a real quantum effect.

Moreover, we have derived a simple model that can predict the cavity IR spectra better than costly simulations. So, *is there anything special about cavity chemistry?*

Our model leverages our knowledge of harmonic oscillators.
Harmonic oscillators are a central model in physics. We understand them very well, which allows us to design an efficient algorithm to find the cavity spectrum.

- The HO model agrees well with experimental results
- The calculation takes less than 1 minute, whereas the other simulations can take days.
- The only required input is the cavity-free spectrum and the geometry of the cavity.

Within our model, the cavity does not change any physical properties of the system within it: It just allows one to "look at" the system in a different way. So where can any change in chemical reactivity possibly come from?



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[1] *J. Chem. Phys.* **158**, 234106 (2023)
[2] *J. Phys. Chem. B* **127**, 9172 (2023)
[3] *J. Phys. Chem. Lett.* **13**, 3890 (2022)
[4] *J. Chem. Phys.* **140**, 234116 (2014)
[5] *J. Am. Chem. Soc.* **144**, 12177 (2022)

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