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GAS PHASE CHEMICAL PHYSICS

Time-Resolved Optical Diagnostics

Today's Topic: New Fundamental Discoveries in Gas-Surface Adsorption and Energy Transfer from Nonlinear Optics

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BES Gas Phase Chemical Physics Contractor's Meeting

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Sandia National Laboratories

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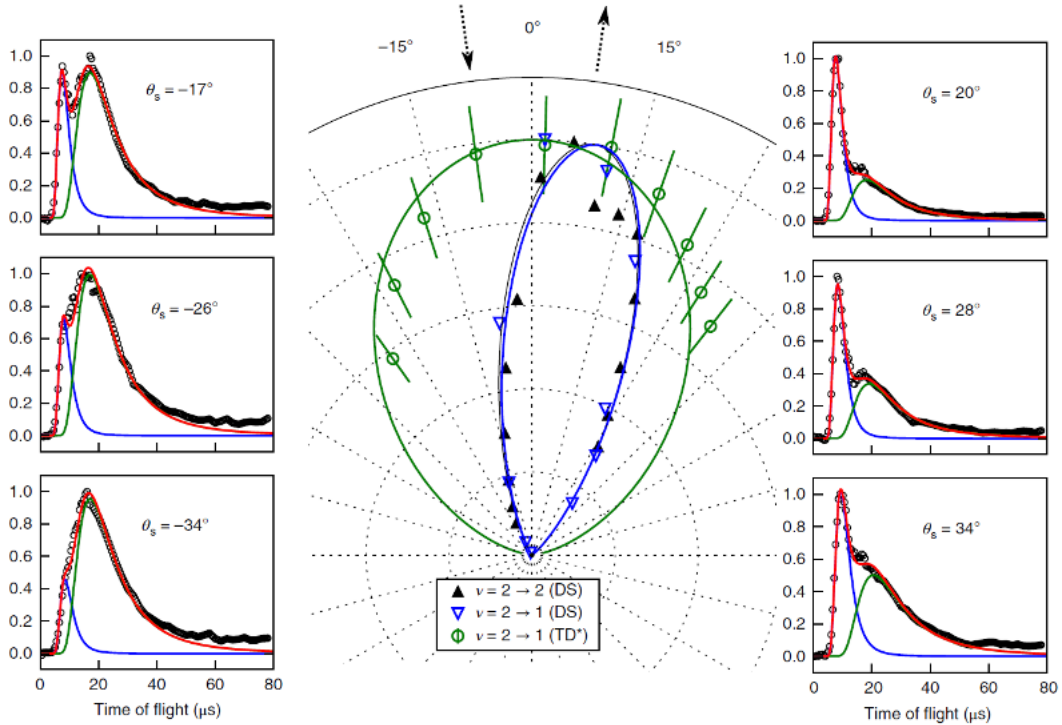
First evidence for nonthermalized trapping desorption on a metal: possibly major implications for LH surface mechanisms



- CO prepared into v=2 is observed after scattering from the surface via REMPI.
- CO with a delayed arrival time is thought to originate from adsorbed molecules, and was ovserved with some fraction in excited vibrational levels.
- Delayed CO emitted at wide angles is further evidence for trapping desorption with nonthermalized CO
- Predicted excited vibrational lifetimes of ~100 ps or more. Whereas the longest previous lifetime measurements for molecules on metals was ~2 ps.

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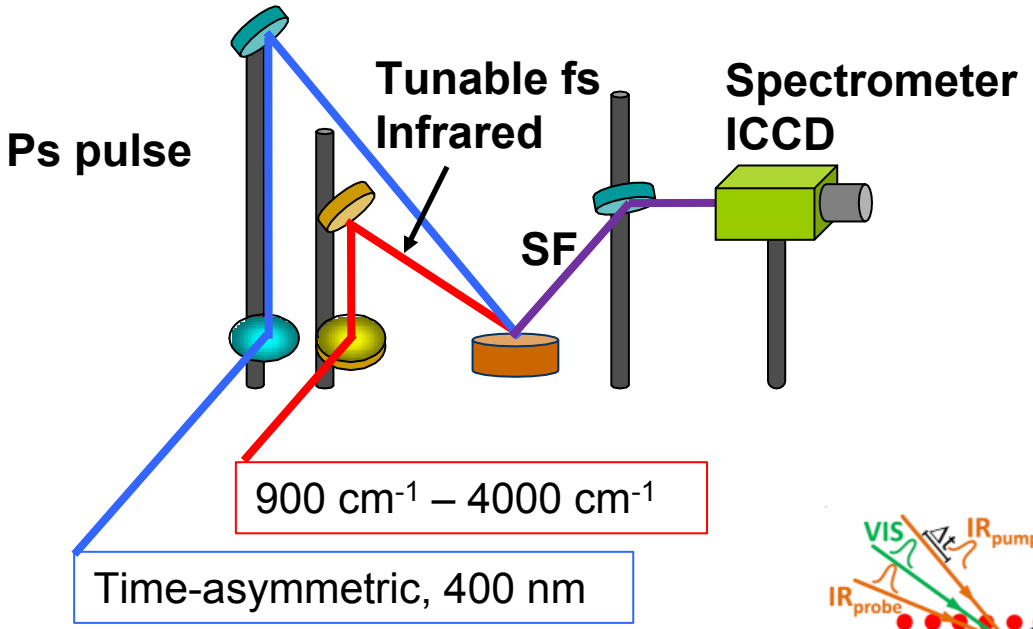
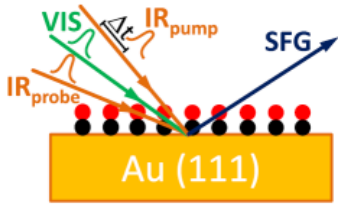
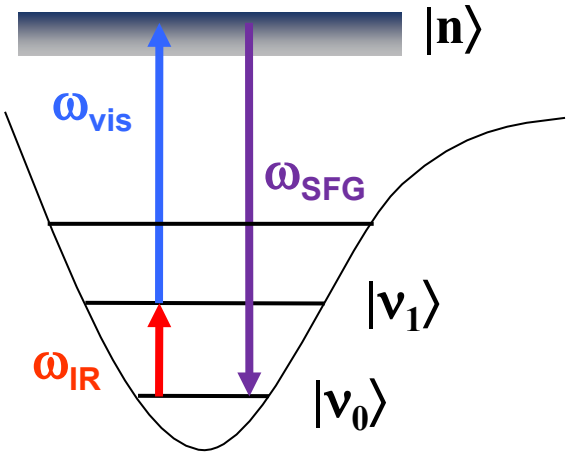
Sum-frequency generation vibrational spectroscopy can be used to monitor surface adsorbed molecules







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Sum-frequency generation vibrational spectroscopy can be used to monitor surface adsorbed molecules

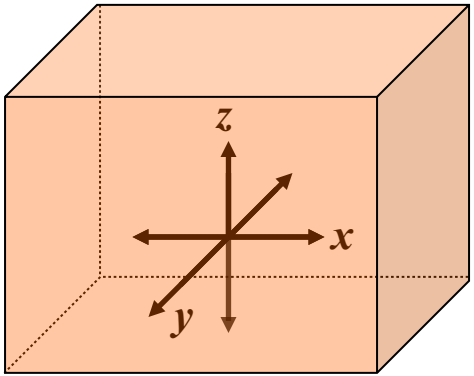
- **SFG intensity from a centrosymmetric medium is parity-forbidden.**

  x = -x
  y = -y ⟶ $\chi_{xyz} = \chi_{(-x)(-y)(-z)} = -\chi_{xyz} = 0$
  z = -z

- **$z \neq -z$ at an interface (usually):**

  $\chi_{xyz} = \chi_{(-x)(-y)(z)} = \chi_{xyz}$

$\chi^{(2)}$ is nonzero → *surface-specific signal*



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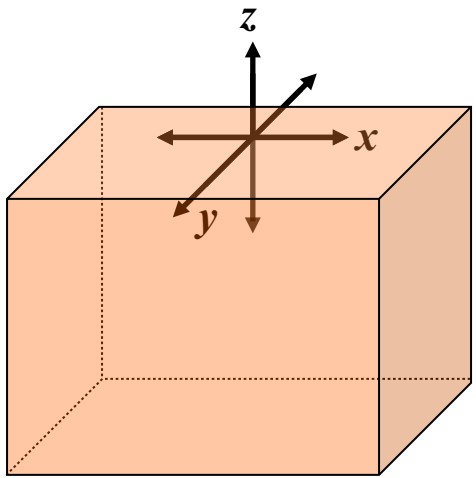

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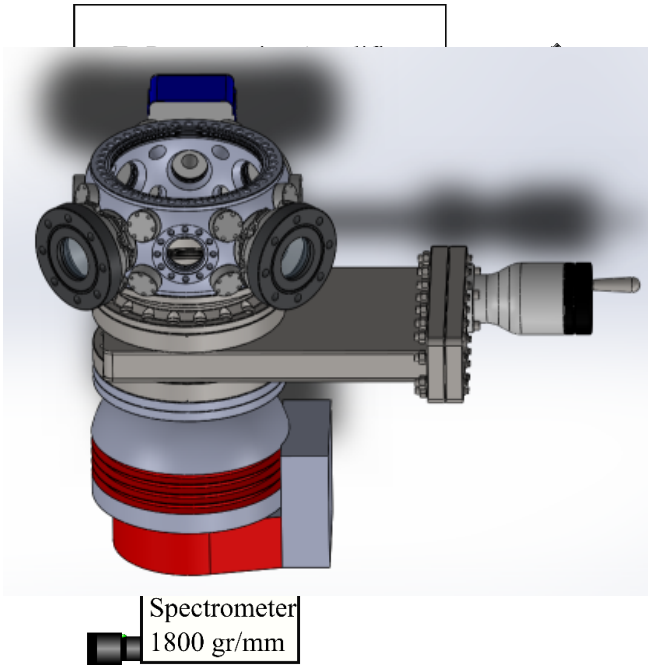
Building the experiment: a new UHV to ambient pressure surface science / spectroscopy chamber



- We built single cell UHV prep chamber / ambient pressure reaction chamber
- Ion sputtering, surface annealing, Auger electron spectrometer, sample heating/cooling (~100 K – 800 K), RGA
- Retractable CaFl2 Windows for IR-based spectroscopy
- ~1E-9 Torr one day after open to atmosphere

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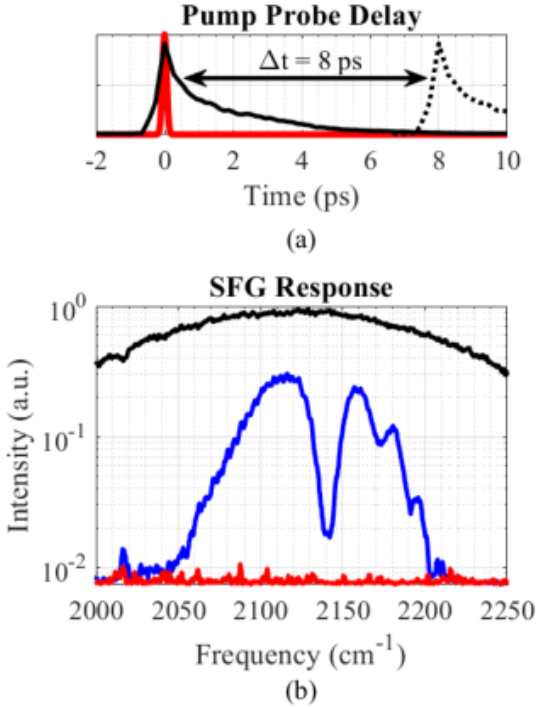
The case of CO adsorbed on Au(111)



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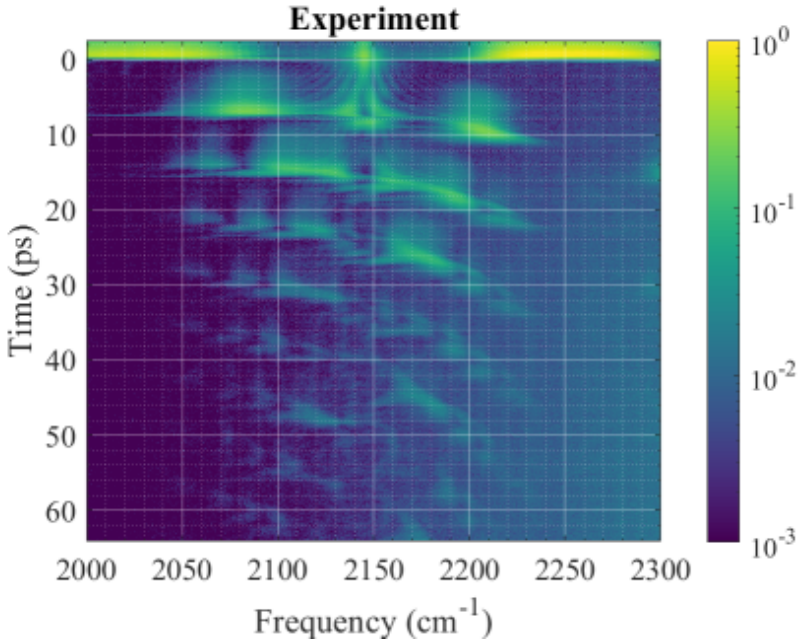

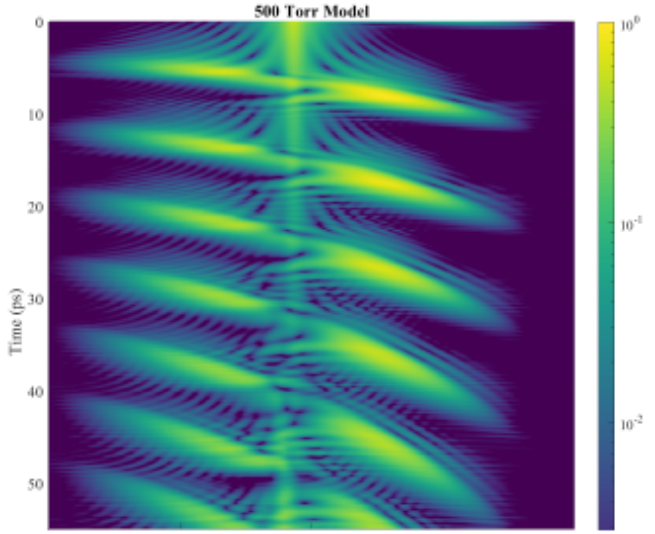

First time free rotors observed in a surface sum-frequency experiment

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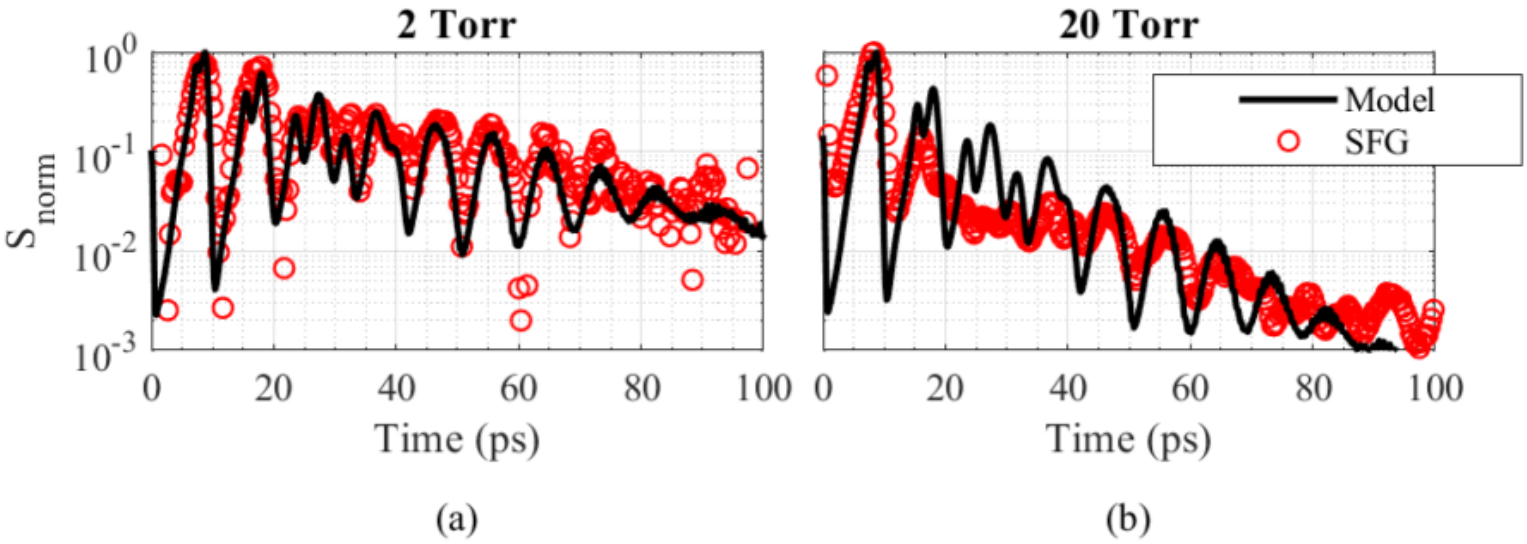
Long-lived rovibrational lifetime observed for free-rotor-like physisorption of CO



Rovibrational SFG coherence dephasing more than 50X faster than a gas-phase collisional energy transfer model, but lasts 1-2 orders of magnitude longer than vibrational excitation in chemisorbed modes. 70 (+/- 10) ps dephasing at 2 Torr. 30 (+/- 5) ps at 20 Torr

How does one know the SF signal is not, somehow, simply arising from gas phase molecules?

- Higher order wave-mixing in the gas phase (linear dependence on both IR and upconversion pulse power)
- Bulk SFG from quadrupolar terms
- Open question in the SFG community – how far from an interface is probed? Interfacial quadrupolar terms…

$$\tau_{SFG} = 30\text{-}70\ ps \quad \tau_{gas} = \text{several ns}\ldots\ \tau_{SFG} \ll \tau_{gas}$$

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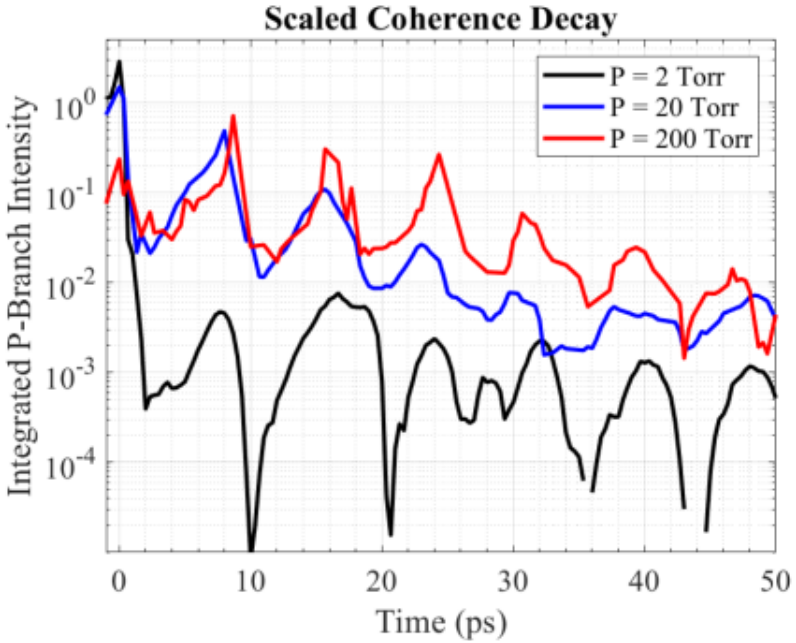
Pressure scaling provides compelling evidence…



- Strong deviation from Pressure^2 behavior at higher pressures

- Absorption is kept low, but the spectra are corrected for completeness
- Sensitivity of the decay rate to the pressure at low pressures (2-20 Torr) on the 10's of ps timescale is further direct proof this is not a gas-phase phenomenon. The gas phase is "collision free" in that time-scale.

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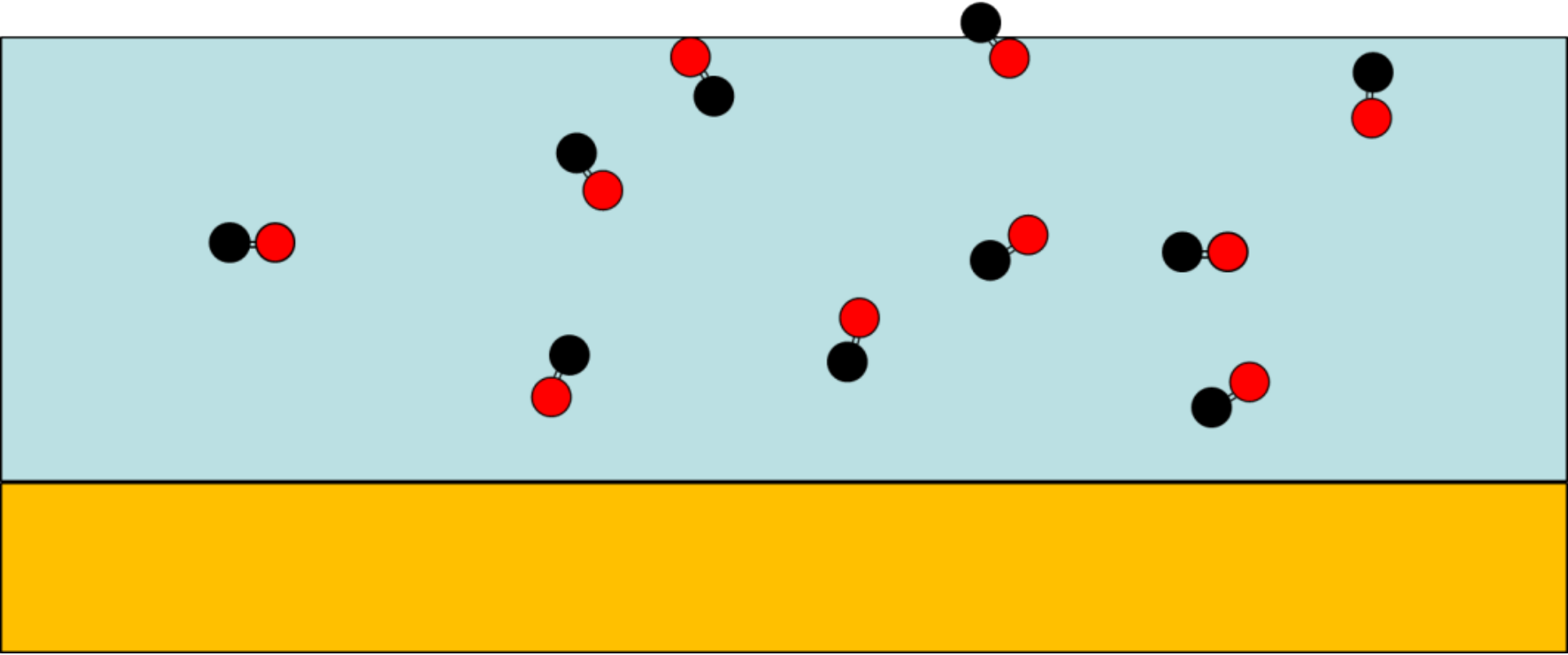
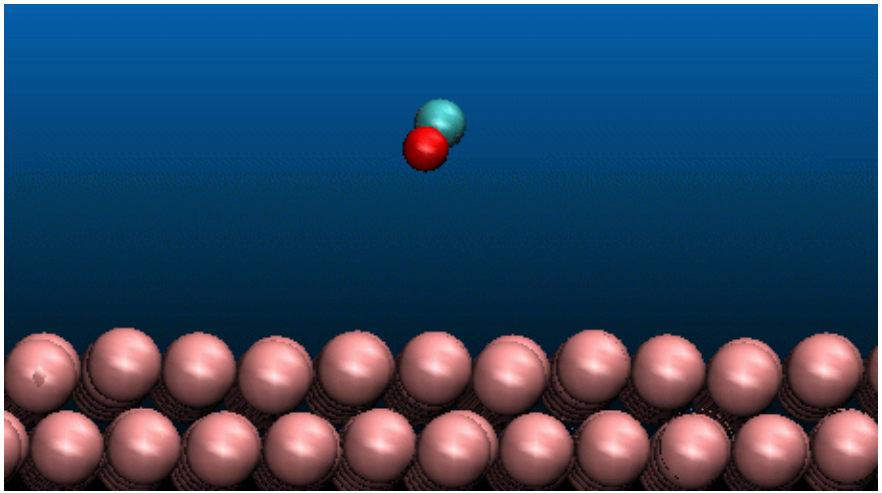
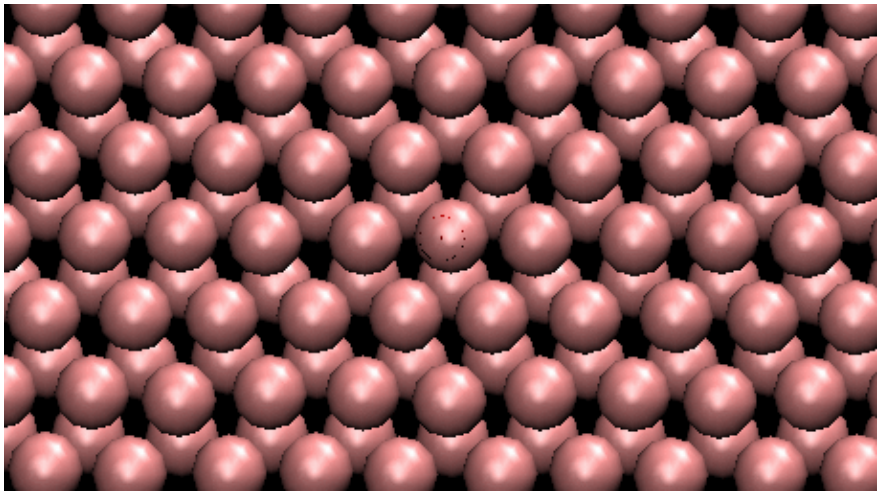
Pressure dependence of coherence decay suggests a surface state is probed…



Physisorption trapping during recoil from surface collision. Simulation from Hua Guo.





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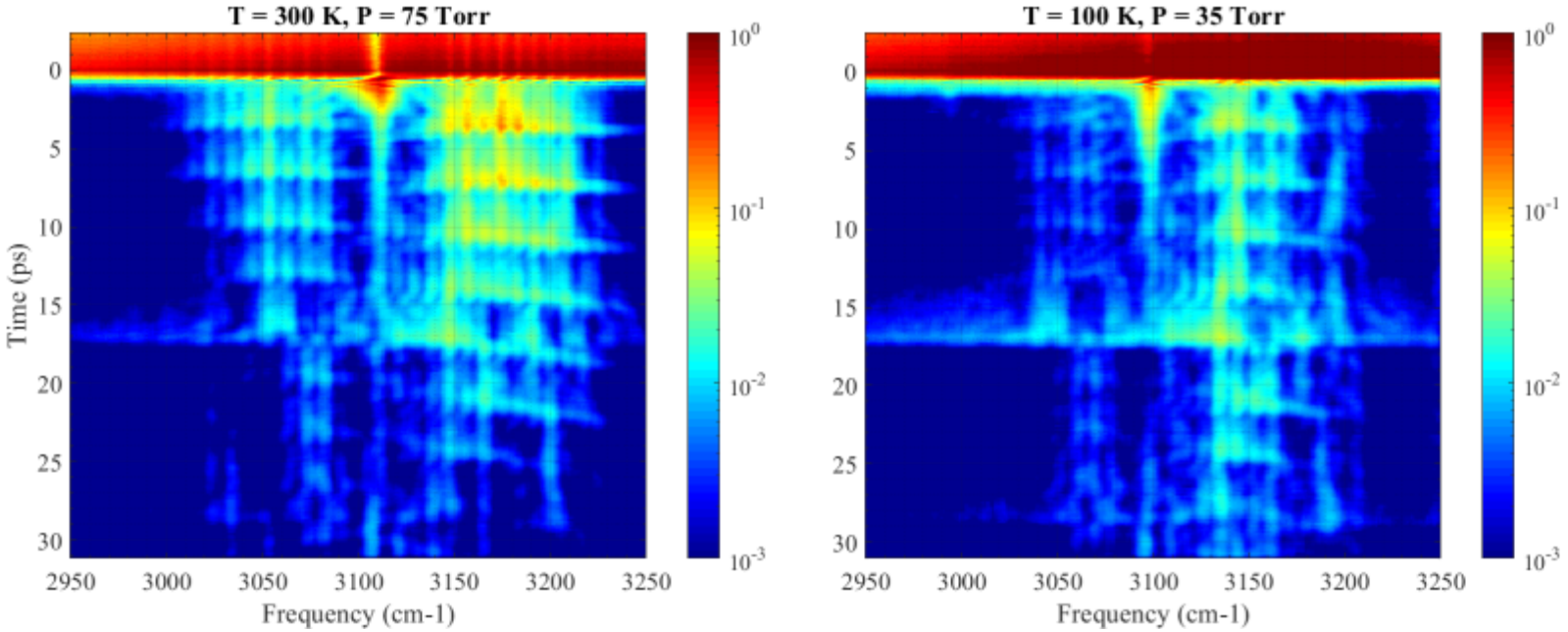
Methane significantly rotationally thermalizes to Au(111) while CO does not



Current preliminary fits show 300K methane & surface, and ~120K methane for cooled surface, but work in progress…

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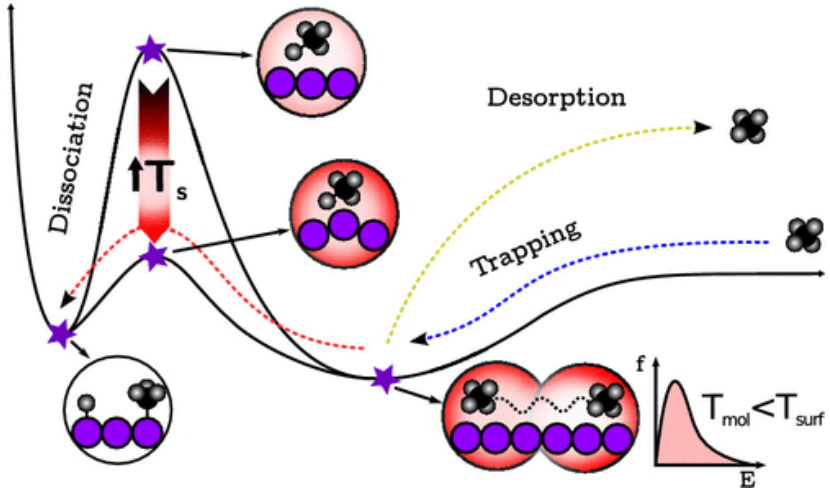
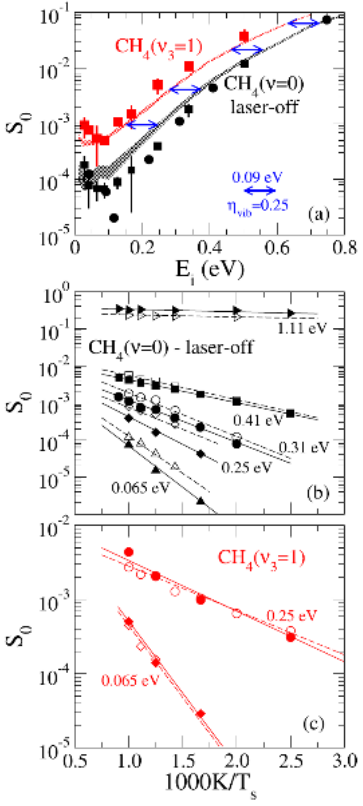
Important discovery for gas-surface kinetics:

- The assumption of modal thermalization to the surface temperature upon physisorption of gas-phase molecules is not always valid.
- Considering rotationally active physisorption and non-thermalized modes can significantly alter the assessment of entropy change upon adsorption, and therefore temperature dependence of the microkinetic model.
- Our experiments show that rotationally and vibrationally nonthermalized molecules reside in the surface layer for significant time-intervals. Energy exchange between these molecules and more tightly bound chemisorbed species in a reactive system must be considered.

Thermal fluctuations in metal phonon modes may activate physisorption precursors



J. Phys. Chem. Lett. 2020, 11, 6, 2211–2218
February



Future Directions

- Full polarization assessment of susceptibility tensor – such signals have never been observed in SFG-VS before. Incorporate model for dynamic image dipole cancellation at larger physisorption distances (e- screening as image moves into the surface)

- Move to different surfaces/interactions: Stepped Au and Ir surfaces. Rovibrational lifetime dependence. Thermalization to the surface temperature.

- Move to reactive systems.

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