Aqueous Pyruvic Acid: Insights from Surface and Bulk Vibrational Spectroscopy

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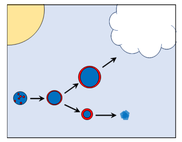
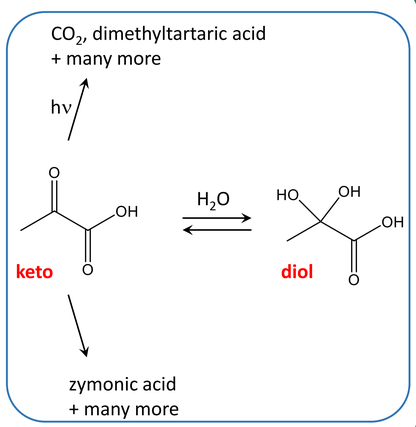
Motivations



- Aqueous surfaces are a unique chemical environment
- If small organics oligomerize, they may partition to the surface, changing aerosol properties
- Aerosol phase, cloud condensation propensity, and optical properties affect climate

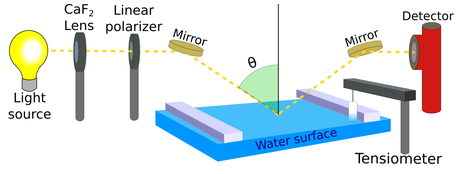
Aqueous Pyruvic Acid Chemistry

- Diol dominates in low-pH solution
- Keto is slightly enhanced at surface
- Diol is thought to be depleted at the surface
- Oligomers will have higher surface activity

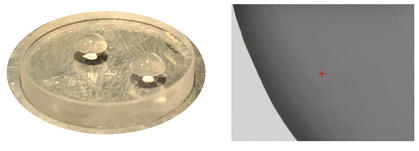


Experimental Methods

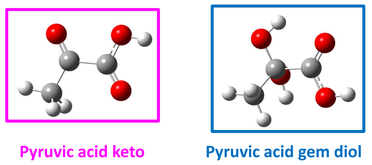
- Aqueous solutions 0.04 to 1.0 M not adjusted for pH
- ATR-IR Spectroscopy: bulk solution
- IR-RAS: solution surface



- Raman microscopy: bulk solution & droplet edges



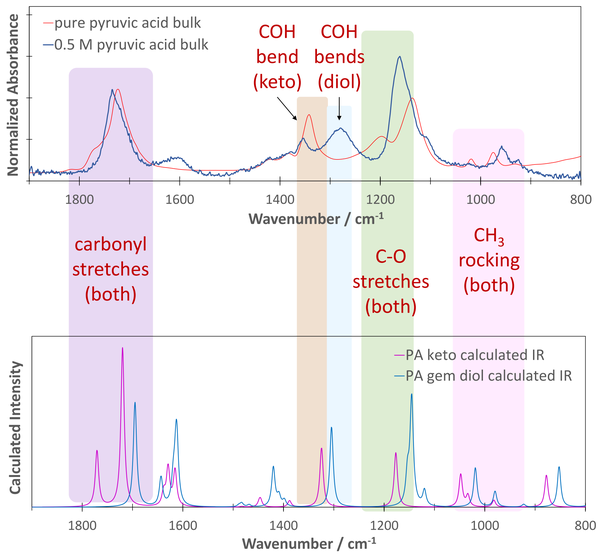
- DFT quantum calculations: harmonic frequencies of solvated species for pyruvic acid and its geminal diol



Pyruvic acid keto | Pyruvic acid gem diol

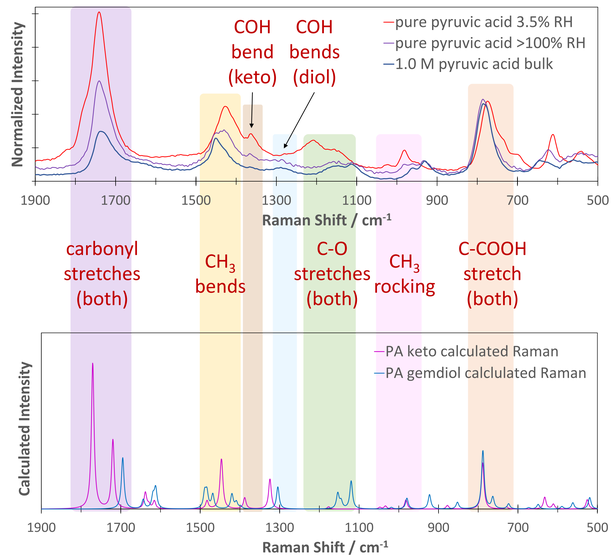
Bulk Solutions, Calculations, & Spectral Assignments

Infrared spectra of pure and aqueous PA



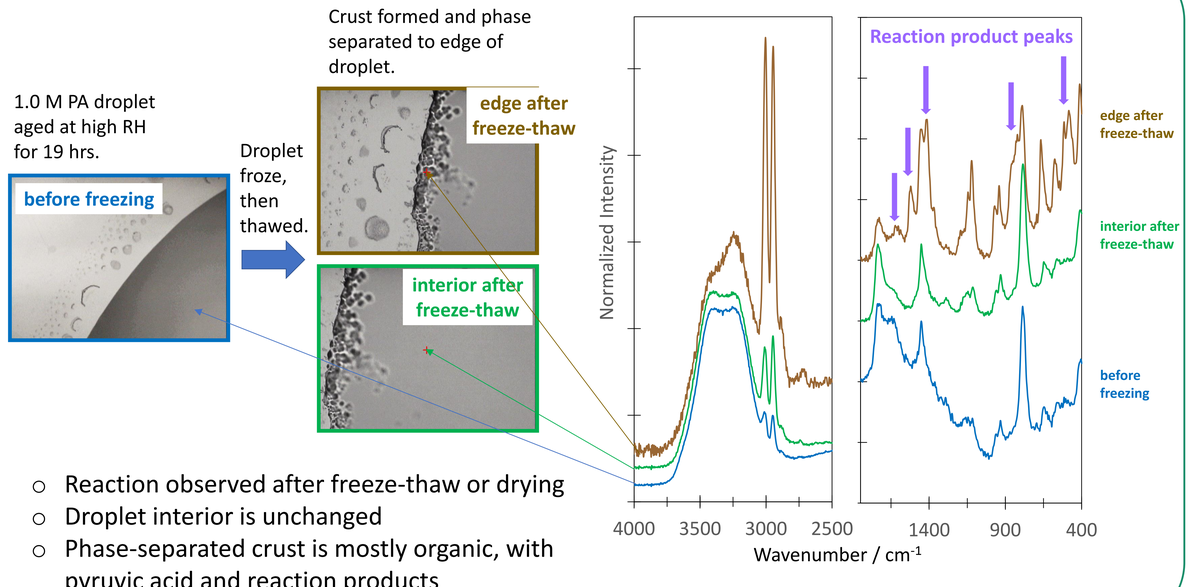
- Water was subtracted as the background
- Evidence of gem diol formation with addition of water:
  - New peak at 1278 cm^{-1}
  - Higher intensity at 1161 cm^{-1}

Raman spectra of pure and aqueous PA



- Evidence of gem diol formation with addition of water:
  - Lower intensity and red shift of carbonyl peak, relative to peak at 785 cm^{-1}
  - 1450 cm^{-1} is blue shifted relative to pure PA

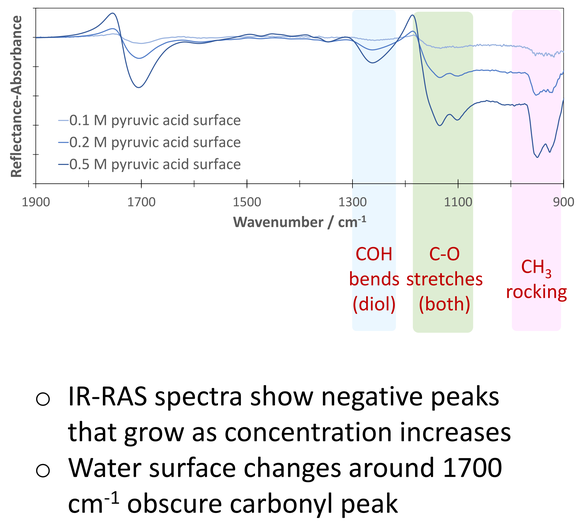
Reaction with Phase Separation



- Reaction observed after freeze-thaw or drying
- Droplet interior is unchanged
- Phase-separated crust is mostly organic, with pyruvic acid and reaction products

Surface Spectra

Infrared reflection-absorbance spectra of the aqueous PA surface



- IR-RAS spectra show negative peaks that grow as concentration increases
- Water surface changes around 1700 cm^{-1} obscure carbonyl peak
- Peaks in three regions can be assigned by comparison with bulk spectra and calculations
- Pyruvic acid gem diol is present at the surface

Conclusions and Implications

- Pyruvic acid geminal diol observed at the aqueous surface
- Presence of diol impacts possible reactions
  - Diol does not absorb sunlight
  - Diol will also have different dark chemistry
- Crust from reaction products seen at droplet edge
  - Drying
  - Freeze concentration effect
- Efforts to identify the phase separated material are ongoing

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