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
- Reaction observed after freeze-thaw or drying
- Droplet interior is unchanged
- Phase-separated crust is mostly organic, with pyruvic acid and reaction products
- Pyruvic acid gem diol is present at the surface

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

Bulk Solutions, Calculations, & Spectral Assignments
- 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\(^{-1}\)
- 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

Surface Spectra
- 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

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