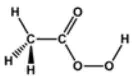
Determining the Absorption Coefficient of the Fourth O-H Stretching Overtone of Peracetic Acid using Cavity Ring-down Spectroscopy

Marc N. Fiddler[1], Stefan Boskovic[1], Solomon Bililign[1,2]

1) NOAA-ISET Center, 2) Department of Physics, North Carolina A&T State University

Importance

- Peracetic acid (PA):



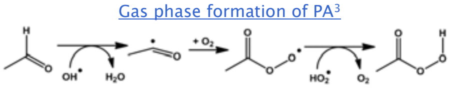
- **We are interested in characterizing photochemical reactions that are induced by the absorption of light by vibrational overtones.**
- Vibrations of X-H bonds (X=O, N, S, C) have are high frequency and have large dipole changes associated with stretching.[1,2]
- From this, the cross sections of their overtones are relatively intense and they occur at higher frequencies (energies) than other vibrations.
- Therefore, absorption of radiation by these vibrational overtones can have sufficient intensity and energy to produce chemical changes.[1,2]
- These chemical reactions can produce OH•, which is responsible for much of the oxidizing power of the atmosphere.[3]

Goal: Measure the absorption cross section of peracetic acid. From this, determine the photolysis rate constant (*J*) as a function of altitude and solar zenith angle.

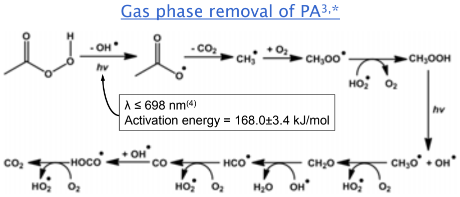
A + h*v* ⟶ products $\qquad d[A]/dt = J[A]$

Chemistry of Peracetic Acid

Gas phase formation of PA[3]

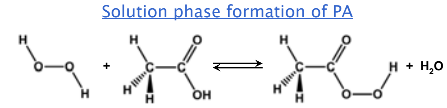


Gas phase removal of PA[3,*]



*Does not include wet and dry deposition processes of PA and its oxidation products.

Solution phase formation of PA

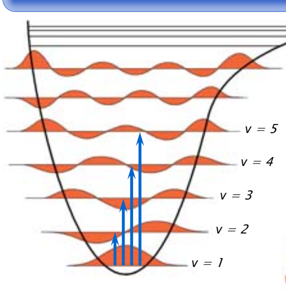


Hydrogen peroxide | Acetic acid | Peracetic acid | Water

Challenges of PA

- When procured from commercial sources, all of these components are in solution.
- Since the headspace is being sampled, all of these components (plus the monomeric and dimeric form of acetic acid) are in the gas phase.
- Acetic acid monomer and hydrogen peroxide absorb in the same region in the visible.[5]
- Acetic acid monomer and dimer, peracetic acid, and hydrogen peroxide all absorb in the in UV.[6]
- **All these factor contribute to difficult measurement of the number density of each component (most importantly peracetic acid).**

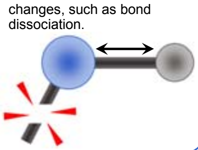
Vibrational Overtone-induced Photodissociation[1,2]



Energy $= h\nu$

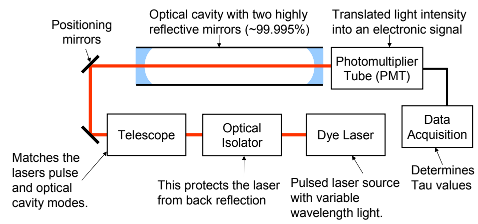
With increasing overtones, the energy associated with the absorbed photon increases.

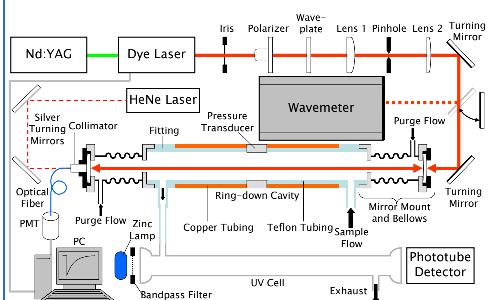
That energy can produce structural and chemical changes, such as bond dissociation.



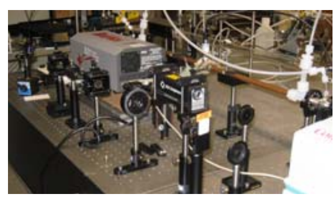
Cavity Ring-down Spectroscopy (CRDS)

Cavity ring-down spectroscopy (CRDS) is an ultra-sensitive absorption spectroscopic technique that is now being used in various atmospheric photochemistry studies.[8]



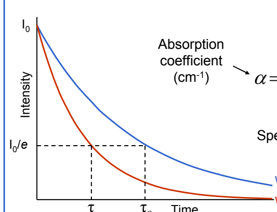


CRDS Setup:



Calculations

Ring-down Time[8]



$$\alpha = \frac{R_L}{c_{air}}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) = n_{abs}\sigma$$

Absorption coefficient (cm⁻¹) — α; Speed of light in air — c_{air}; Number density of absorber (molec•cm⁻³) — n_{abs}; Absorption cross section (cm²•molec⁻¹) — σ

- Using a well known cross sections CRDS can furnish the concentration (number density) of sample molecules in the cavity.
- On the other hand if a known concentration (number density) of the sample is introduced in the cavity, CRDS can easily provide its cross section.

Total UV Absorbance

$$A = \ln\left(\frac{V - V_{0\%T}}{V_{100\%T} - V_{0\%T}}\right)$$

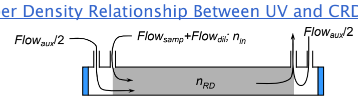
V: Voltage reading, sample; $V_{0\%T}$: Voltage reading, lamp off; $V_{100\%T}$: Voltage reading, no sample

Number Density in UV Cell

$$A = \sum_X (\sigma_{X,UV}\, n_{X,UV}\, \ell)$$

$\sigma_{X,UV}$: Cross section at 214 nm; $n_{X,UV}$: Number density in UV cell; ℓ: Path length (100 cm)

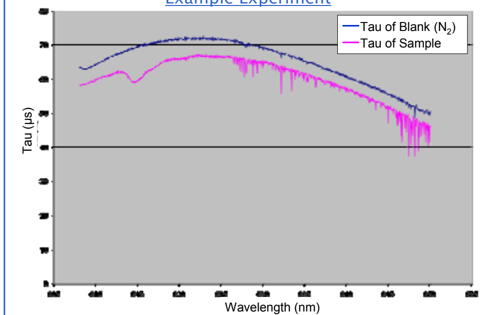
Number Density Relationship Between UV and CRDS Cell



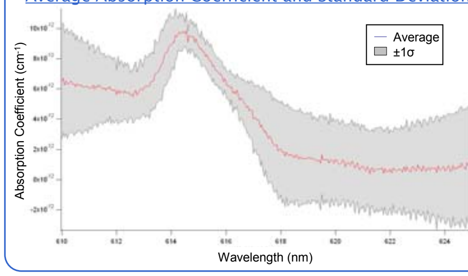
$$n_{RD} = (n_{UV})\left(\frac{Flow_{Sample} + Flow_{Dil} + Flow_{AUX}}{Flow_{Sample} + Flow_{Dil} + \left(\frac{Flow_{AUX}}{2}\right)}\right)$$

Preliminary Results

Example Experiment



Average Absorption Coefficient and Standard Deviation



Future Work

Simplifying the System

- Titration of hydrogen peroxide using 1 N Ceric (IV) sulfate. Since accuracy is not an issue, the end point would be reached when bubbles cease to form.

$$H_2O_2 + 2Ce(SO_4)_2 \rightarrow Ce_2(SO_4)_3 + H_2SO_4 + O_2$$

- Prevent acetic acid from entering the gas phase by deprotonating it with base (lye). This would also precipitate cerium by forming $Ce(OH)_3$.

$$AcOH + OH^- \rightarrow AcO^- + H_2O$$

- A pH meter would be used to determine the end point, since we do not want to also deprotonate peracetic acid.
- This will result in only peracetic acid and water in the gas phase.
- The water has no UV cross section, so the UV cell can be used to determine the peracetic acid concentration. Water features in this visible are sharp and easily differentiated from other absorbers.

Theoretical Calculations

- Determine the actinic flux (*I*) as a function of altitude and solar zenith angle using TUV, determine the quantum yield (Φ) with RRKM theory using Gaussian.

$$J = \int [\sigma(\lambda)\bullet\Phi(\lambda)\bullet I(\lambda)]d\lambda$$

$\sigma(\lambda)$: Absorption cross section (cm²•molecule⁻¹); $\Phi(\lambda)$: Quantum yield for photolysis; $I(\lambda)$: Solar actinic flux (cm⁻²•s⁻¹•nm⁻¹)

- From this, derive the photolysis rate constant (*J*) and the atmospheric lifetime of peracetic acid as a function of altitude and solar zenith angle.

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