Laboratory Studies of Atmospheric Chemical Processes
Kinetics and Photochemistry of Acetone

Role of Laboratory Measurements

Kinetic and photochemical parameters, needed in chemical models for predicting capability of Air Quality and Climate, can be determined under isolated and controlled conditions in the laboratory.

Example: **Acetone**, $CH_3C(O)CH_3$

- ubiquitous key species
- large abundance (~1ppb)
- source of PAN ($CH_3C(O)O_2NO_2$) and HOx

Focus: Evaluate it as a source of HOx

Atm Loss processes: OH Reaction and Photolysis

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Evaluation of Acetone as source of HOx in the UT

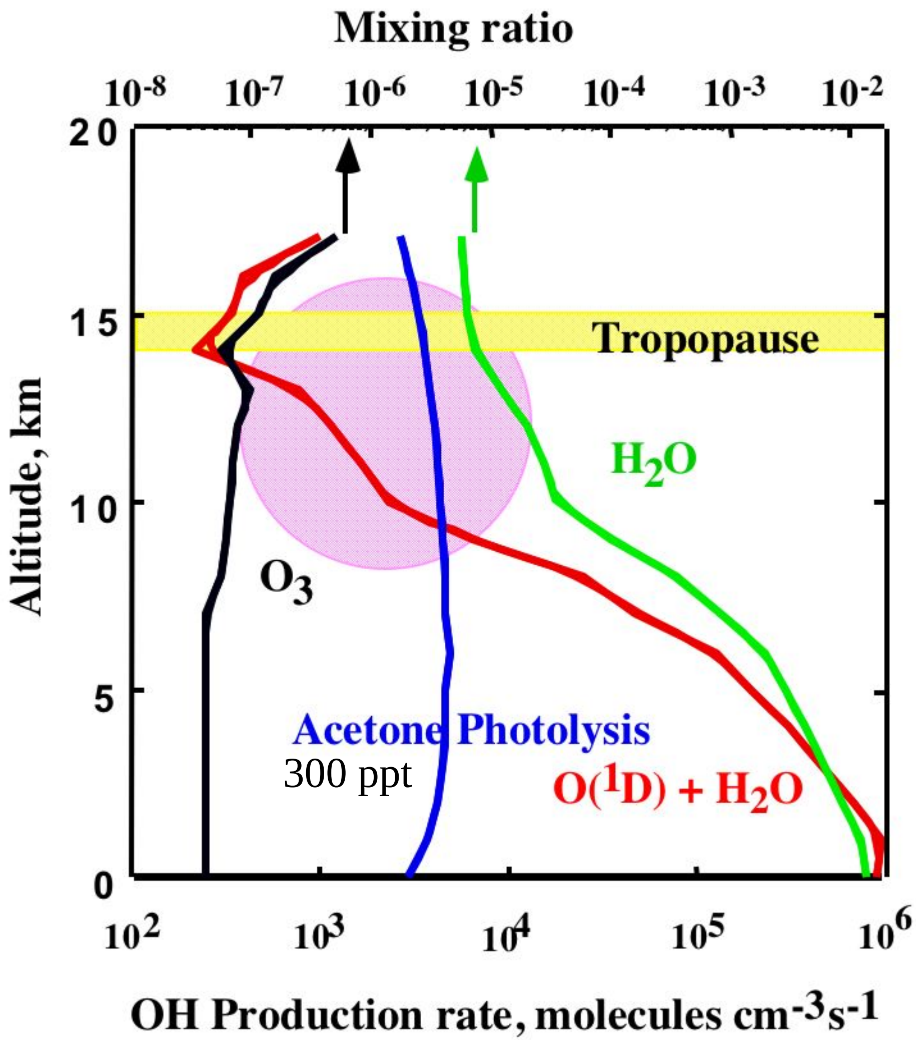
Net HO_x Production

•Photolysis

$$CH_3C(O)CH_3 \xrightarrow{h\nu/O_2/NO} 3HO_2$$

•OH Reaction

$$CH_3C(O)CH_3 \xrightarrow{OH/O_2/NO} HO_2$$



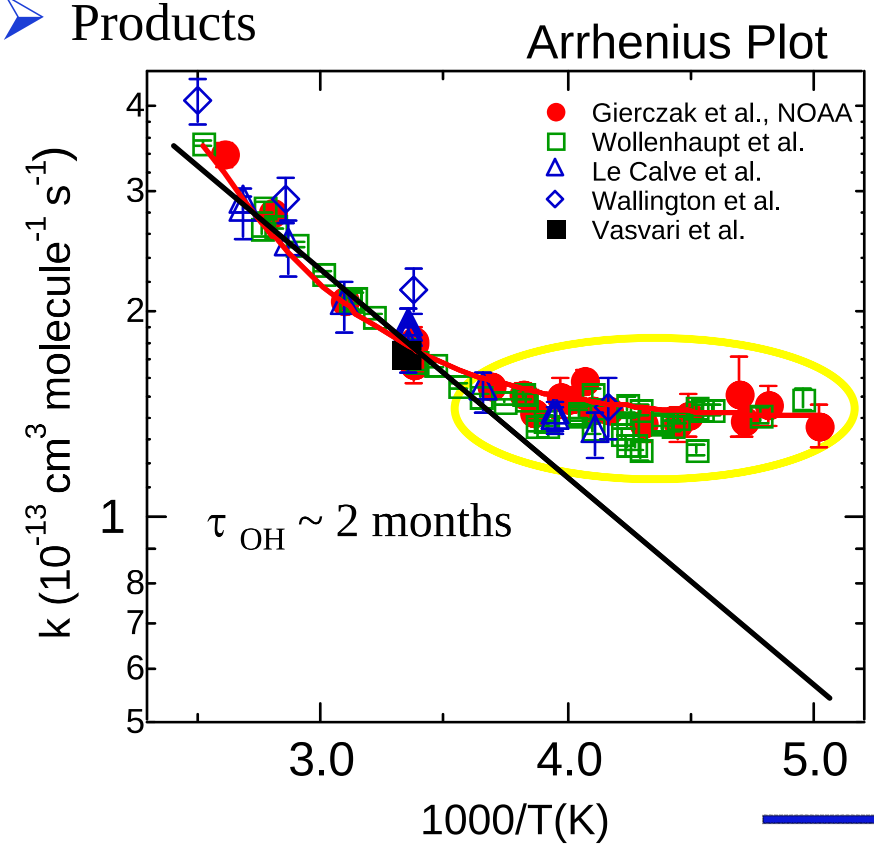
•Upper Troposphere is dry

Use laboratory measurements to Evaluate the Relative Significance of OH Reaction and Photolysis

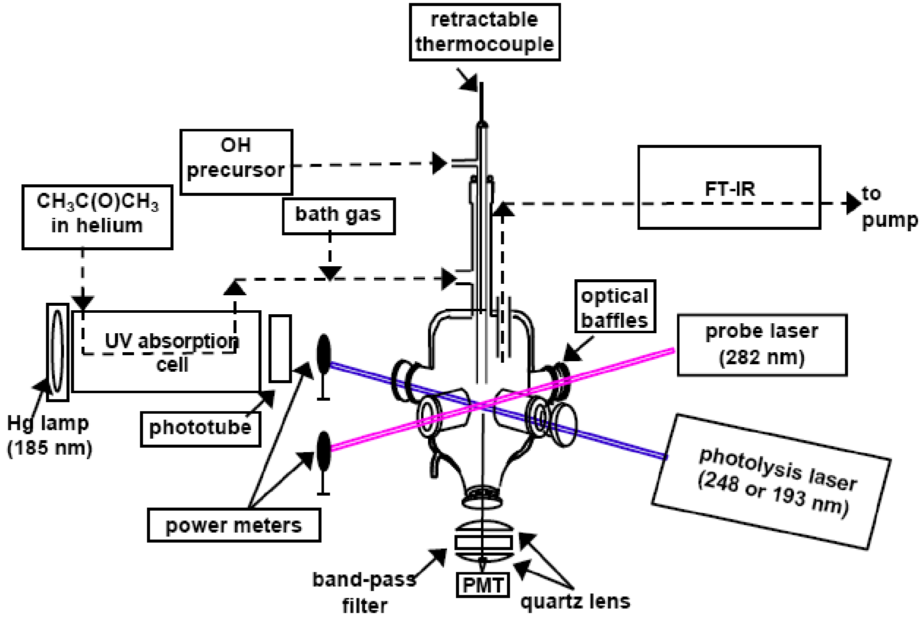
Atmospheric Loss: OH Reactivity

$OH + CH_3C(O)CH_3 \rightarrow$ Products

- OH rate coefficient
- Products



Pulsed Laser Photolysis- Laser Induced Fluorescence Apparatus



OH rate coefficient √

T. Gierczak, M.K. Gilles, S. Bauerle, A.R. Ravishankara, J. Phys. Chem. A, 107, 5014, 2003

Wollenhaupt and Crowley, 2000

$CH_3C(O)CH_3 + OH \rightarrow CH_3C(O)CH_2 + H_2O$ 50 %

$\rightarrow CH_3C(O)OH +$ **CH_3** 50 %

OH Reaction Products - Atmospheric Impact

Direct detection of products:

$CH_3C(O)CH_3 + OH \rightarrow$ **$CH_3C(O)CH_2$** $+ H_2O$ **96 ± 11 %**

$\rightarrow$ **$CH_3C(O)OH$** $+ CH_3$ **<1%**

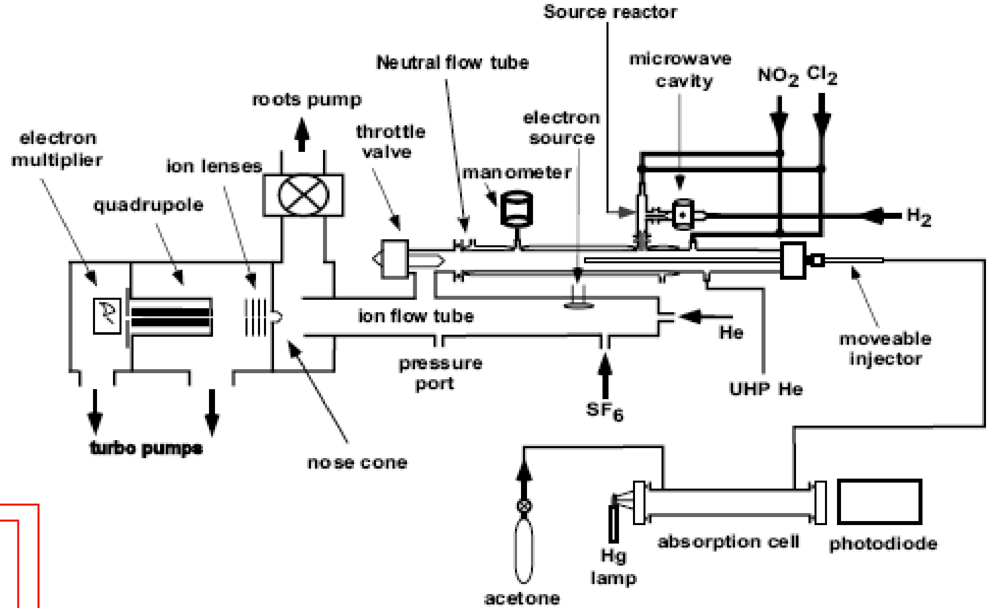
➢ Branching Ratio: Independent of Temperature (237 - 353 K)

■ Reaction occurs via H-abstraction pathway under all atmospheric conditions.

✓ $CH_3C(O)OH$ is not produced

-Degradation products stay in the atmosphere and lead to HOx

Flow Tube-Mass Spectrometer



OH Reaction Products √

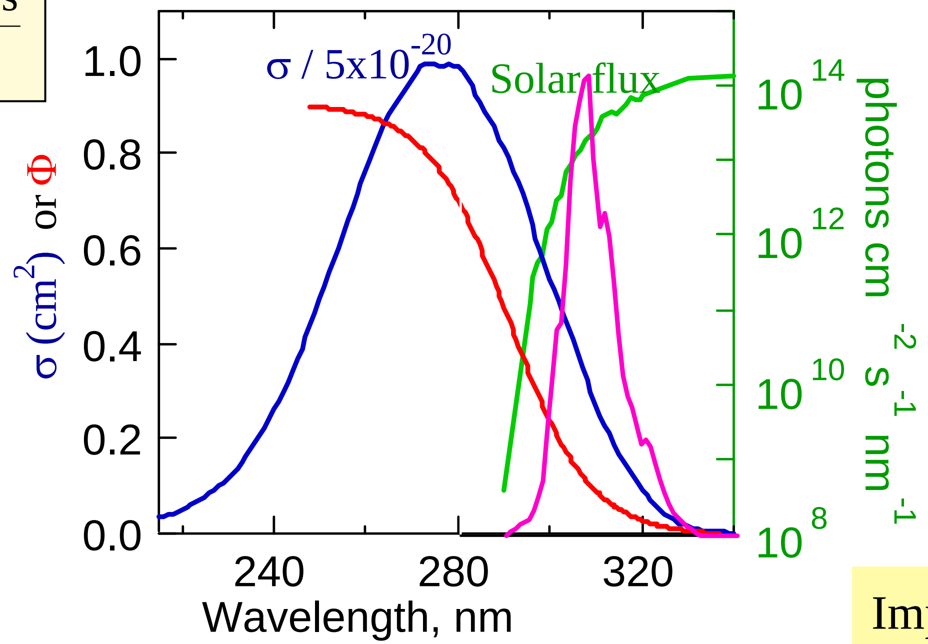
R.K. Talukdar, T. Gierczak, D.C. McCabe, A.R. Ravishankara, J. Phys. Chem, A, 107, 5021, 2003

Atmospheric Loss: UV Photochemistry

$$J\ \text{value} = \int_{\lambda} \sigma(\lambda,T) \times \Phi(\lambda,[M],T) \times F(\lambda,z,\chi)$$

UV abs cross section — Quantum yield — Solar flux

$$\Phi = \frac{\#\ \text{of destroyed molecules}}{\#\ \text{of photons absorbed}}$$



Important λ range: 290-330 nm

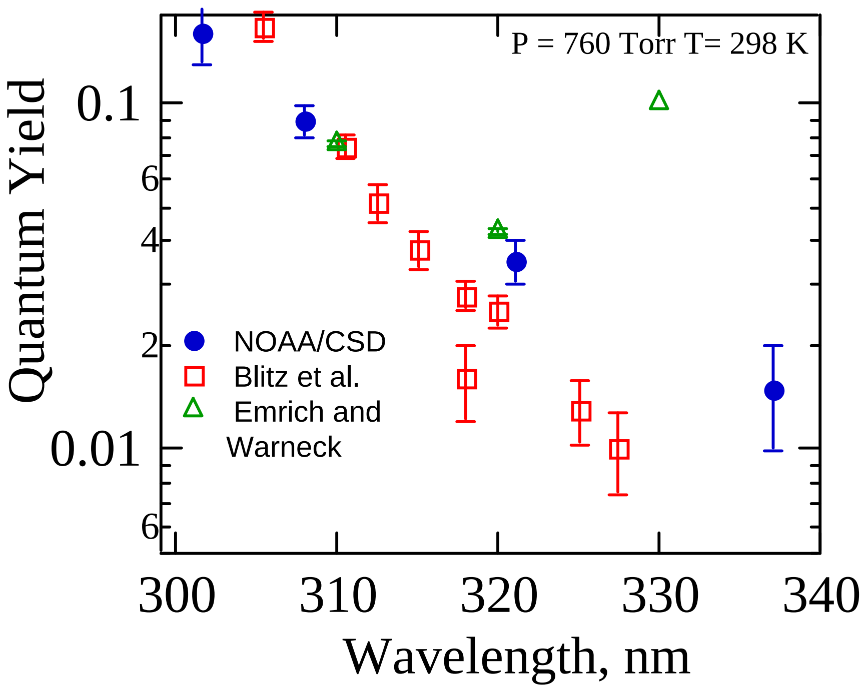
Quantum yield, $\Phi(\lambda, [M], T)$

$CH_3C(O)CH_3 \xrightarrow{h\nu}$ **$[CH_3C(O)CH_3]^*$** $\rightarrow CH_3CO + CH_3$ Dissociation, k_d

$[CH_3C(O)CH_3]^* \xrightarrow{M} CH_3C(O)CH_3$ Quenching, k_q

QY needs to be measured as function of (λ, [M], T)

Quantum Yields from Earlier Studies



- Φ is small and σ is small-- difficult to measure
- Sensitive technique has been developed in our laboratory.

- Uncertainties in QY exist.
  - Impacts J
  - Impacts HOx production rate
- Primary products were not measured.

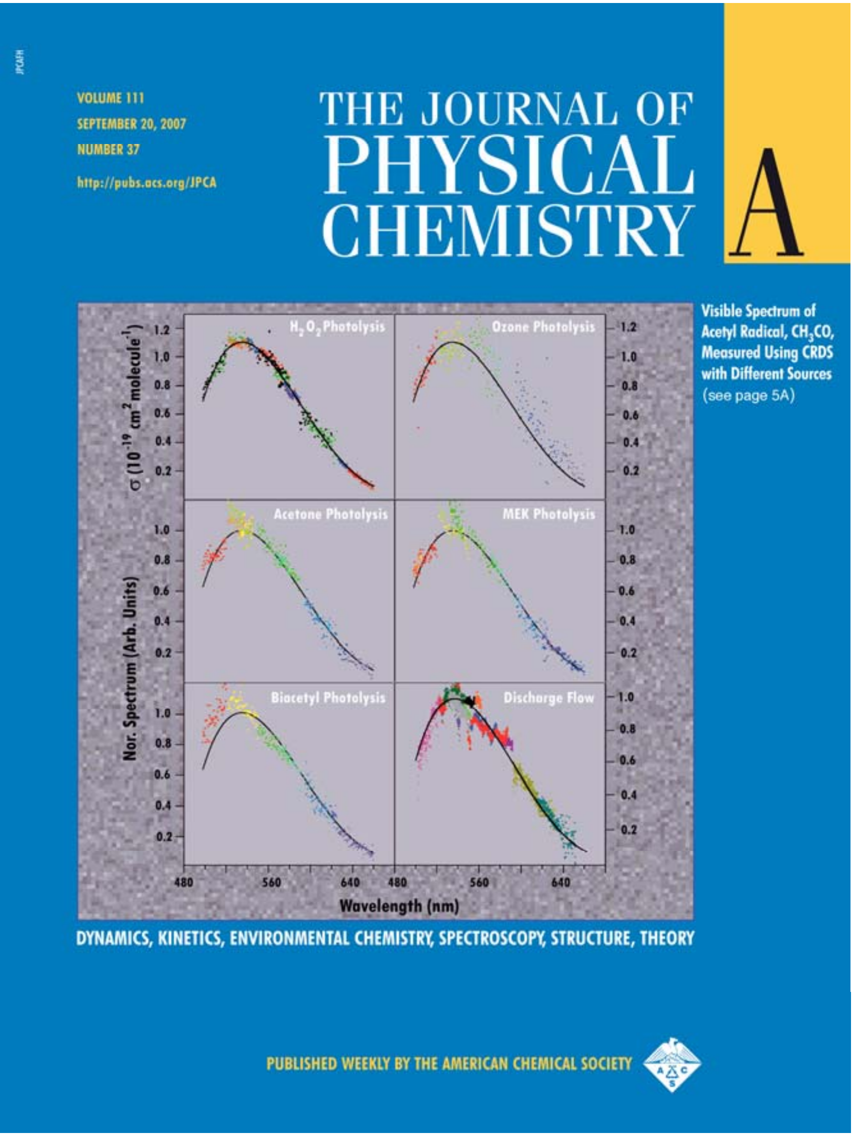
- Detect the primary photolysis product, CH_3CO

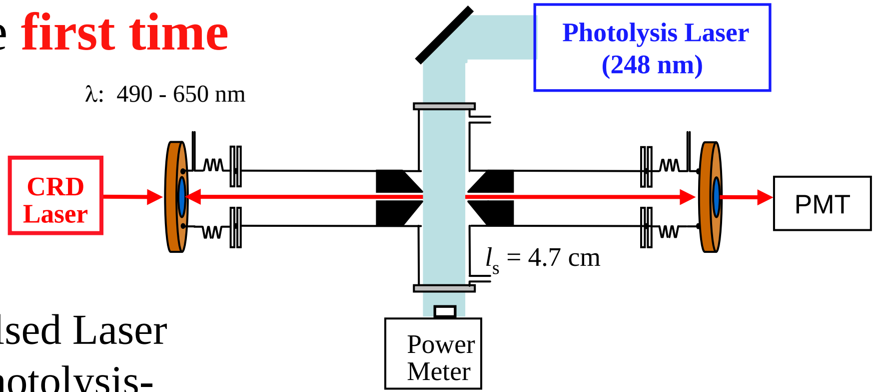
$$CH_3C(O)CH_3 \xrightarrow{h\nu} CH_3CO + CH_3$$

- Developed spectroscopic method.

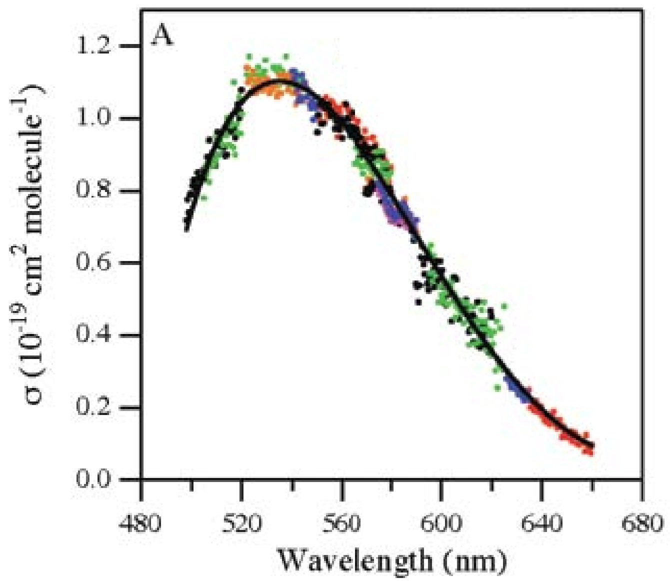
Direct Sensitive Detection of Acetyl Radical, CH_3CO

- CH_3CO Visible spectrum measured for the **first time**





Pulsed Laser Photolysis-Cavity Ring Down Spectroscopy

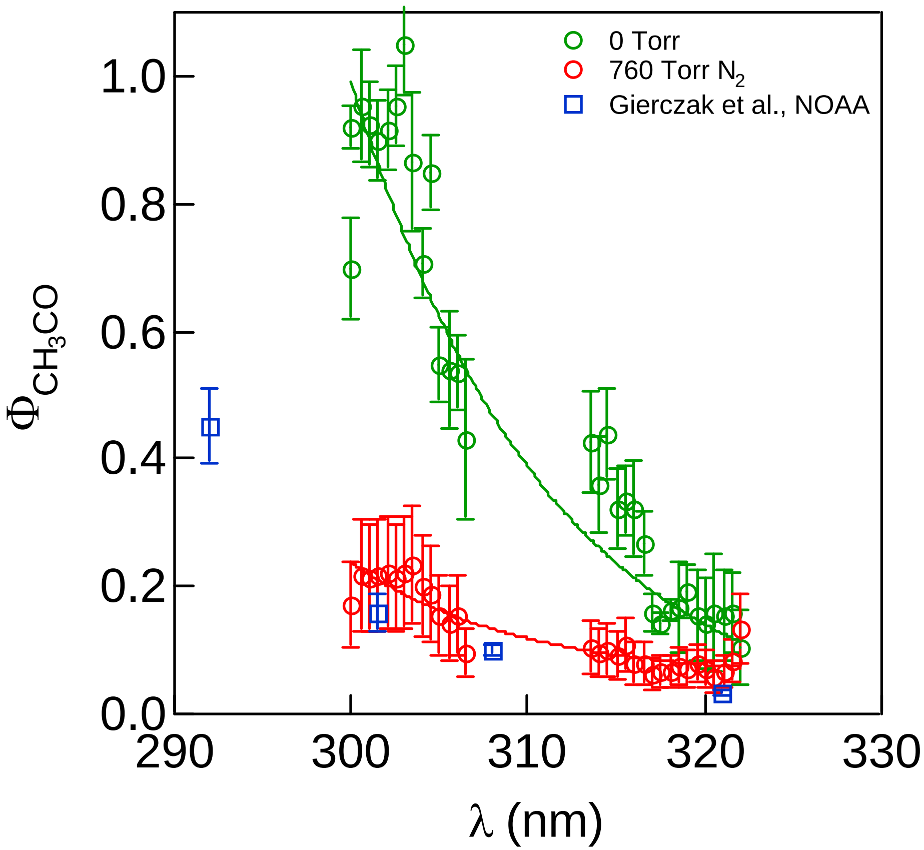


- New way to detect acetyl radical
- Enables direct measurement of a primary photolysis product

B. Rajakumar, J.E. Flad, T. Gierczak, A.R. Ravishankara, J.B. Burkholder, J. Phys. Chem. A, 111, 8950, 2007

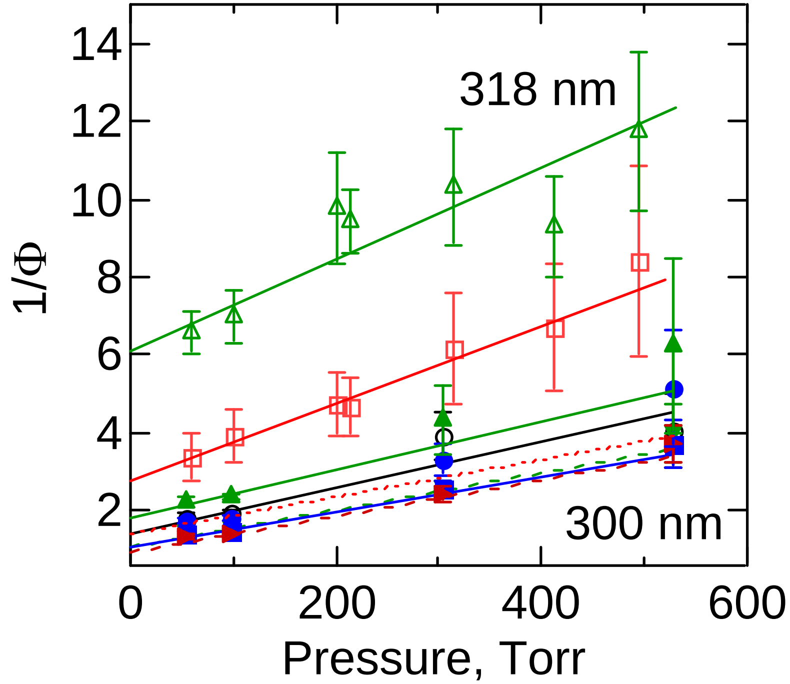
CH_3CO Quantum Yields in the Actinic region

Results from ongoing Experiments



Stern-Volmer Plots

$$\frac{1}{\Phi} = \frac{1}{\Phi_0} + P\left(\frac{k_q}{k_d}\right)$$



Pressure and Temp dependence of QY at each λ are required for atmospheric photolysis rate calculations

Summary and Conclusions

- **Determined the OH rate Coefficients accurately under atmospheric conditions** √
- **Quantified the Products of OH reaction** √
- **Characterized and quantified the Visible spectrum of CH_3CO for the first time.** √
- **We are currently measuring the Photolysis quantum yields under atmospheric conditions.** ..

Once the Quantum Yields are determined under atmospheric conditions, we can evaluate the HOx production efficiency of acetone

Laboratory studies of reactivity and mechanisms of elementary processes provide key building blocks for understanding atmospheric chemistry.