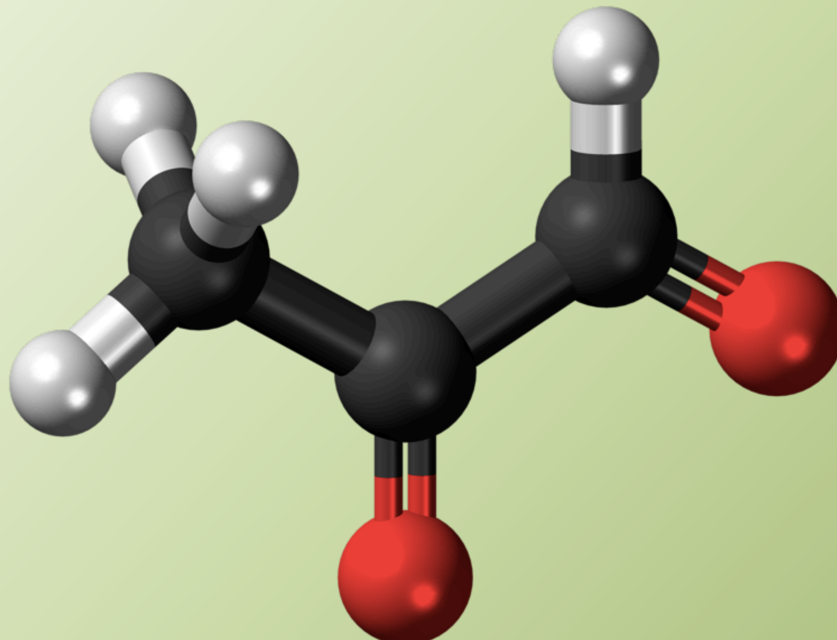
Gas Phase Hydration of Methylglyoxal to Form the Geminal Diol



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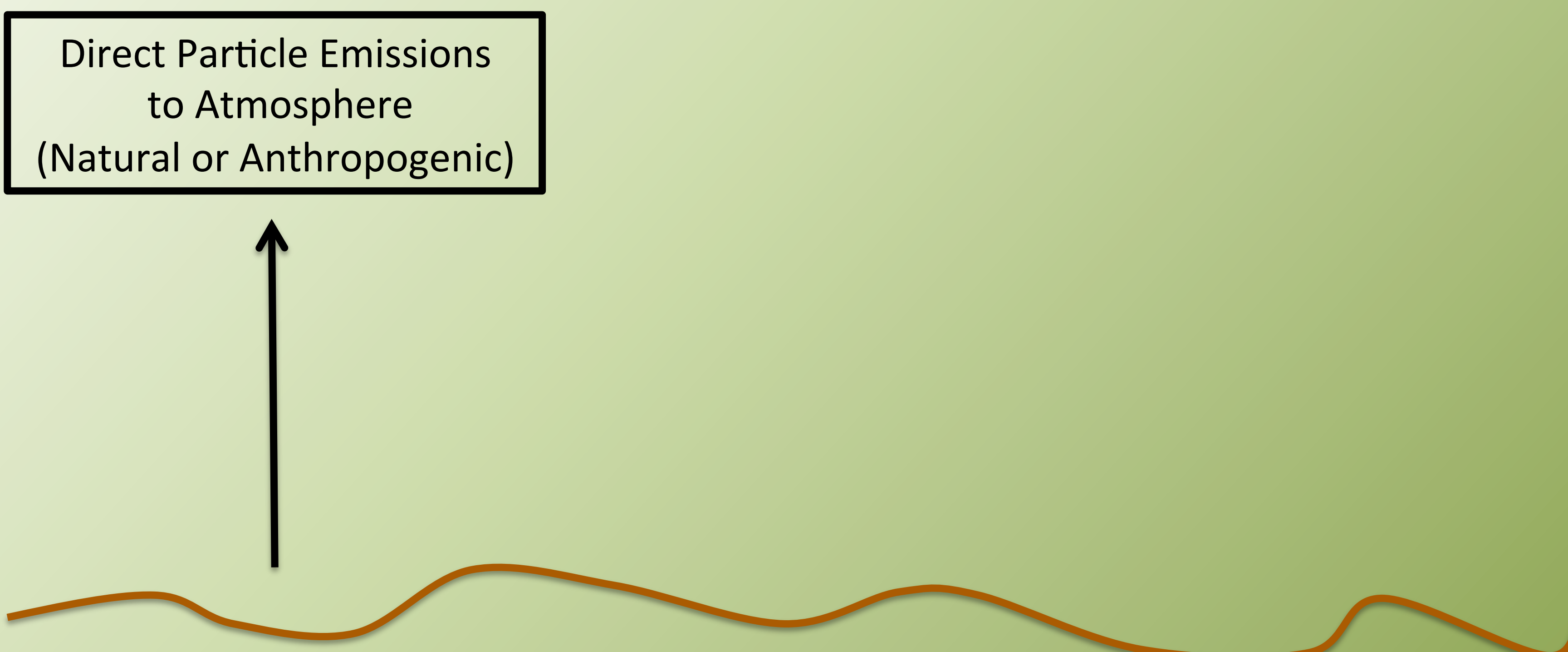
*Department of Chemistry and Biochemistry, University of Colorado, Boulder CO
†Department of Environmental Health Sciences, University of Michigan, Ann Arbor MI

June 21st, 2016

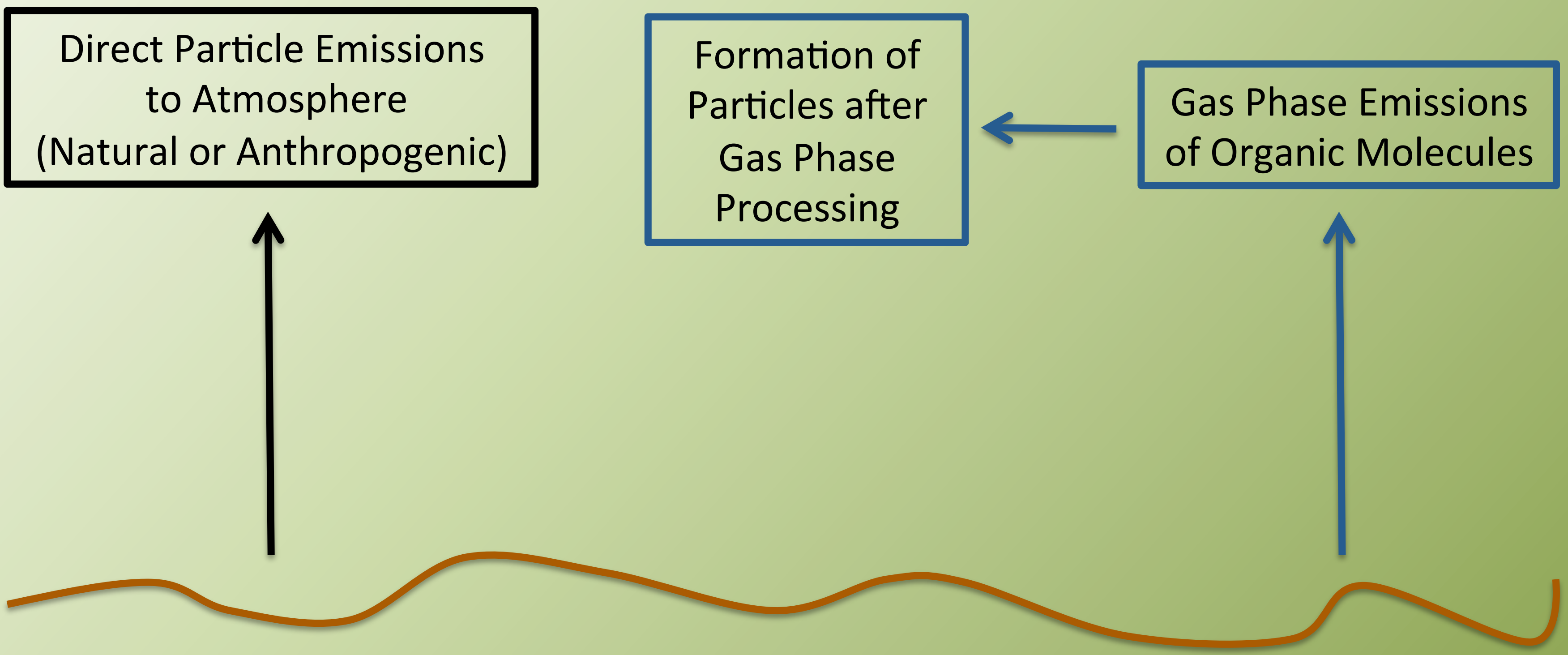
Organic Aerosols

- Two major types of organic aerosols
  - Primary (POA)



Organic Aerosols

- Two major types of organic aerosols
  - Primary (POA) and Secondary (SOA)

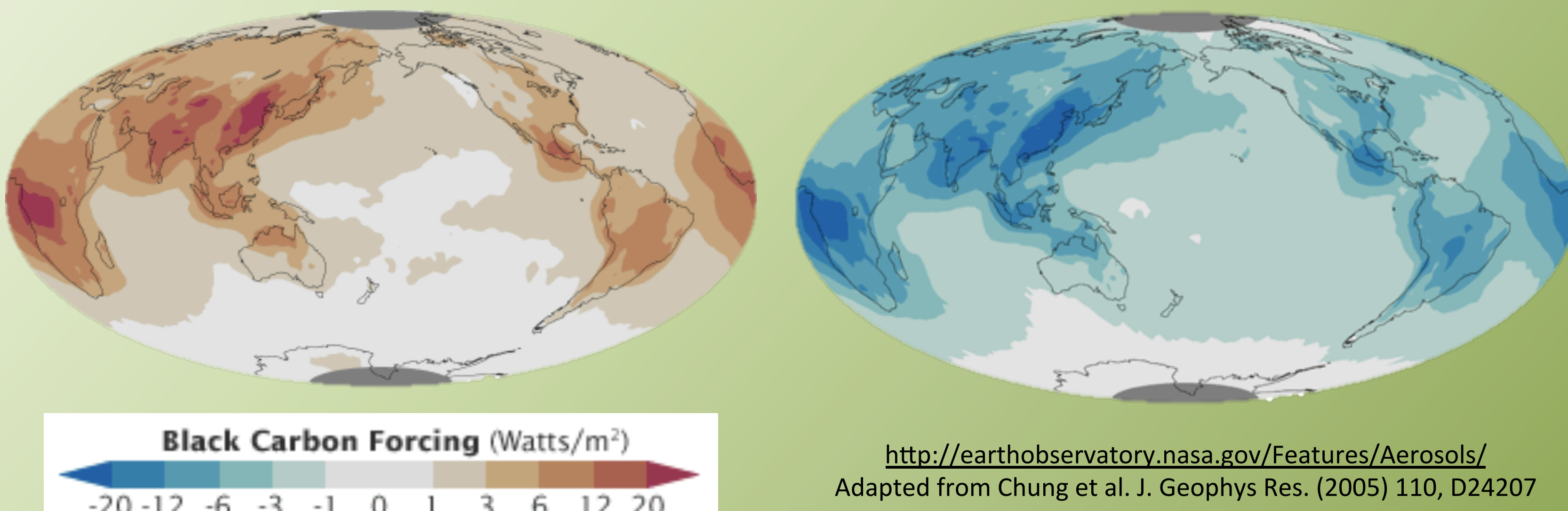


Organic Aerosols

- Two major types of organic aerosols
  - Primary (POA) or Secondary (SOA)
- Incredibly complex interaction with climate

Atmospheric Heating

Surface Cooling

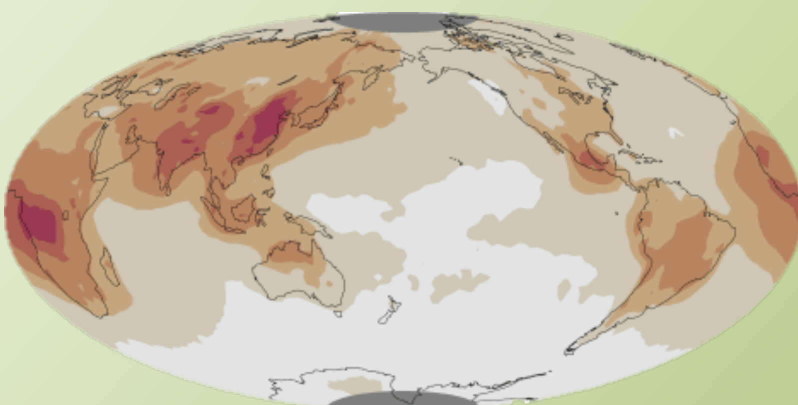


http://earthobservatory.nasa.gov/Features/Aerosols/
Adapted from Chung et al. J. Geophys Res. (2005) 110, D24207

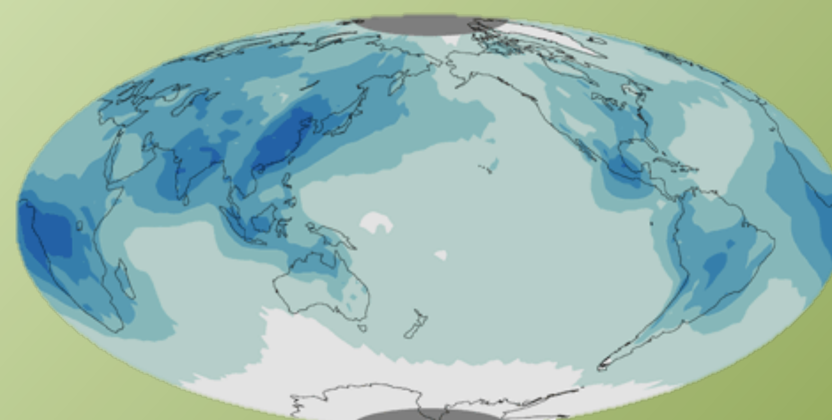
Organic Aerosols

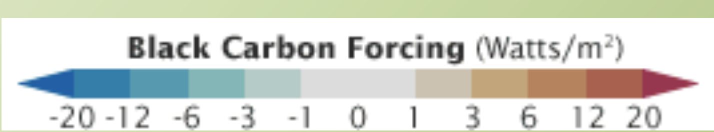
- Two major types of organic aerosols
  - Primary (POA) or Secondary (SOA)
- Incredibly complex interaction with climate
- Need for fundamental understanding of molecular processes that lead to organic aerosol formation

Atmospheric Heating



Surface Cooling





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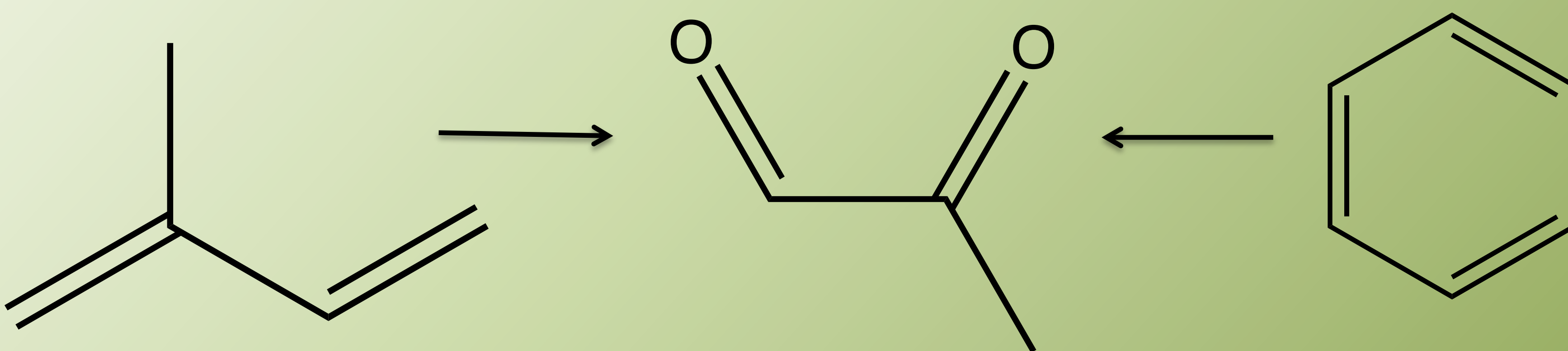
Methylglyoxal

- Produced from atmospheric processing of biogenic and anthropogenic volatile organic compounds (VOCs).
- One of the most abundant α-dicarbonyl compounds present in the atmosphere.
- Proposed as a major source of SOA



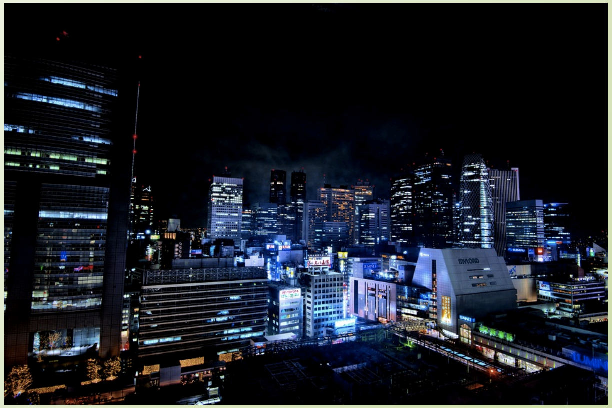
Isoprene Methylglyoxal Aromatic Hydrocarbons

Fu, T.-M., et al., *J. Geophys Res Atmos*,(2008), **113**(D15).
Grosjean et al. *Environ. Sci. Technol.*, (1993**)**, *27* (5) 830–840.
Carlton et al., *Atmos. Chem. Phys.*, (2009), 9, 4987–5005.

Methylglyoxal is Ubiquitous

Methylglyoxal is found in aerosol throughout the atmosphere.

Urban



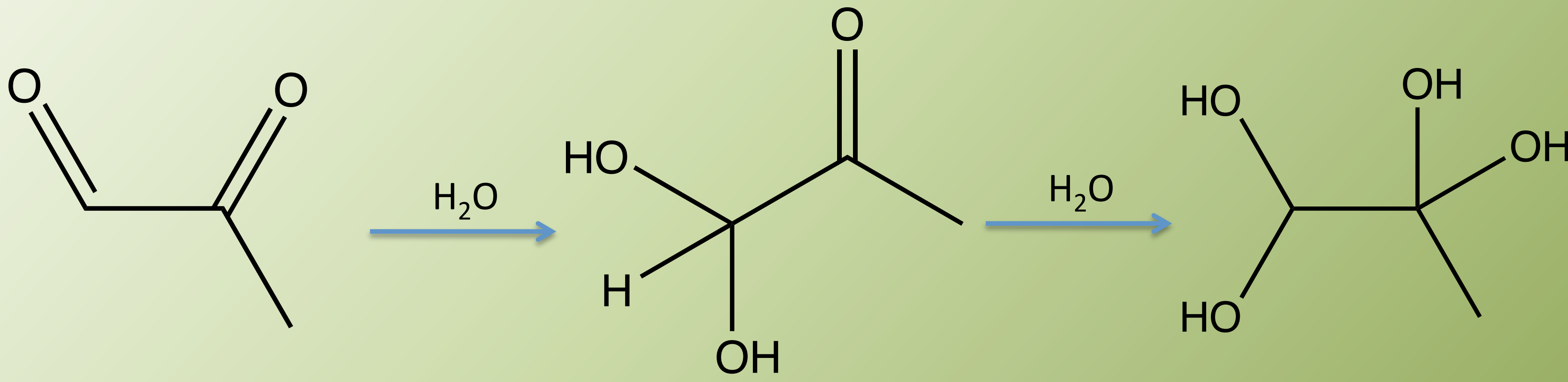
Rural

Remote

Kawamura, K., et al., *Atmos. Environ., (1996)* 30 (10–11): 1709-1722.
Kawamura, K. and O. Yasui, *Atmos. Environ.* (2005), 39 (10): 1945-1960.
VFu, T.-M., et al., *J. Geophys Res Atmos*,(2008), 113(D15).

Aqueous Phase Hydration

- Exists primarily as the diol and tetrol in the aqueous phase

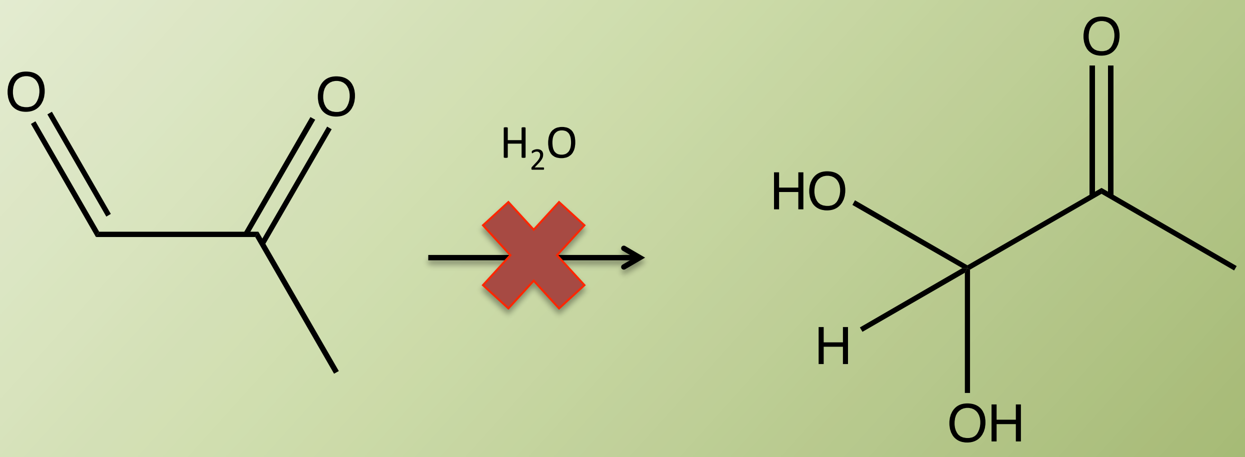


α-dicarbonyl 60% diol 40% tetrol

Krizner et al., *J. Phys Chem A*, (2009),113 (25) 6994-7001.
Nemet et al., *Bioorg Chem* (2004), 32 (6) 560-570.

Can Methylglyoxal undergo hydration to form the gem-diol in the gas phase?

- Theory suggests it is energetically unfavorable to form the methylglyoxal diol species in the gas phase.



Rayne and Forest, *J Phys Org Chem* (2016).
Barsanti and Pankow, *Atmos Environ.* (2005), 39, 6597–6607.
Axson, J. L., Takahashi, K., De Haan, D. O.,Vaida, V. *Proc Natl Acad Sci USA,* (2010), **107**, 6687-6692.

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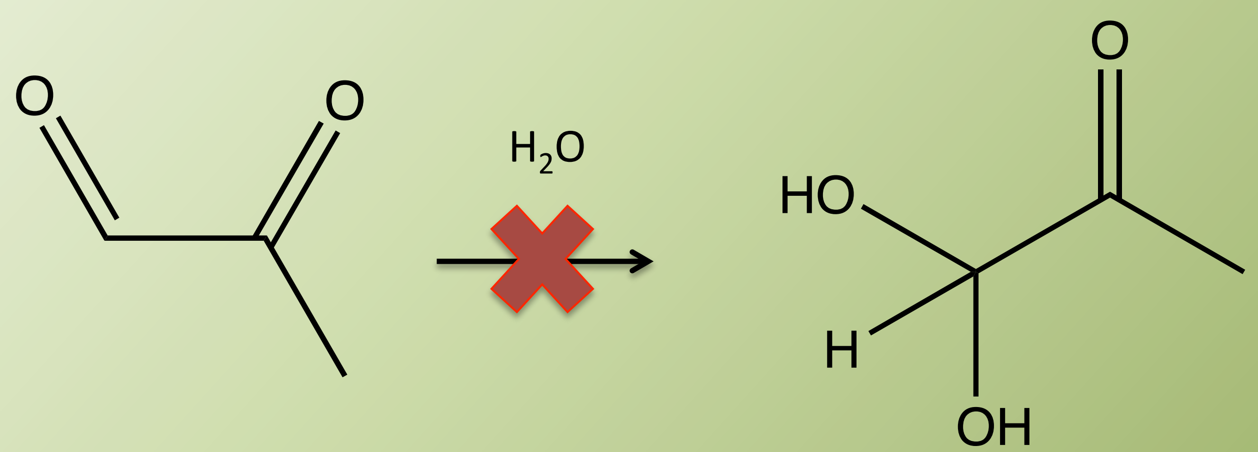
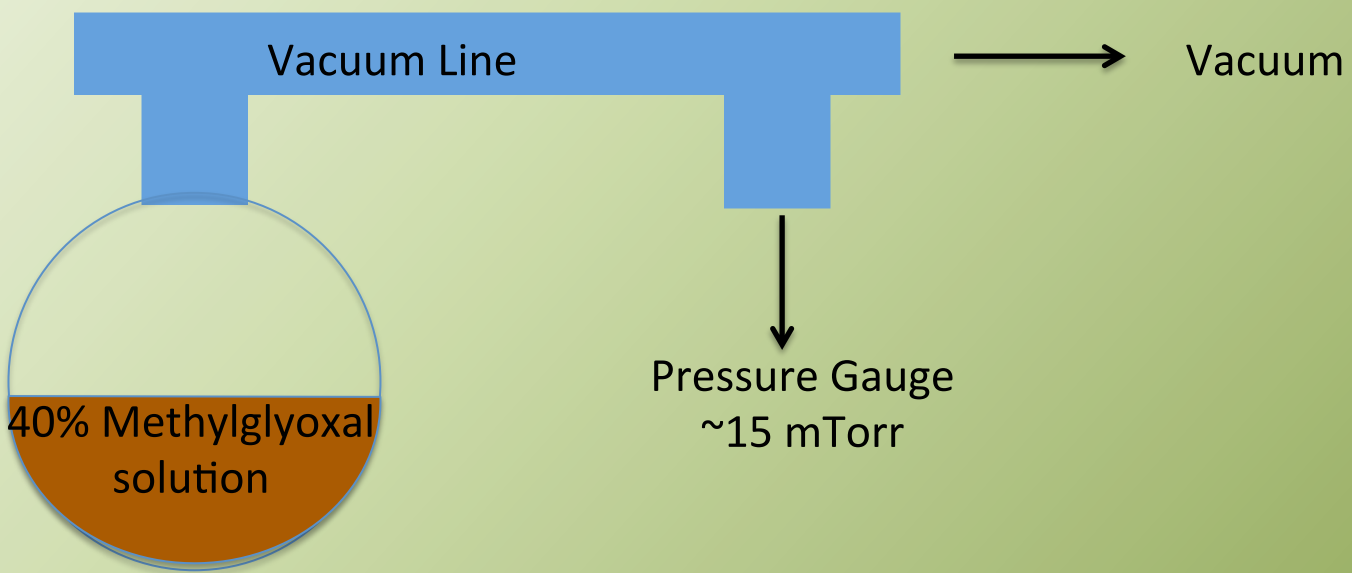


Experimental work done in our lab suggests this is incorrect and that the diol does form in the gas phase.

Rayne and Forest, *J Phys Org Chem* (2016).
Barsanti and Pankow, *Atmos Environ.* (2005), 39, 6597–6607.
Axson, J. L., Takahashi, K., De Haan, D. O.,Vaida, V. *Proc Natl Acad Sci USA,* (2010), **107**, 6687-6692.

Sample Purification

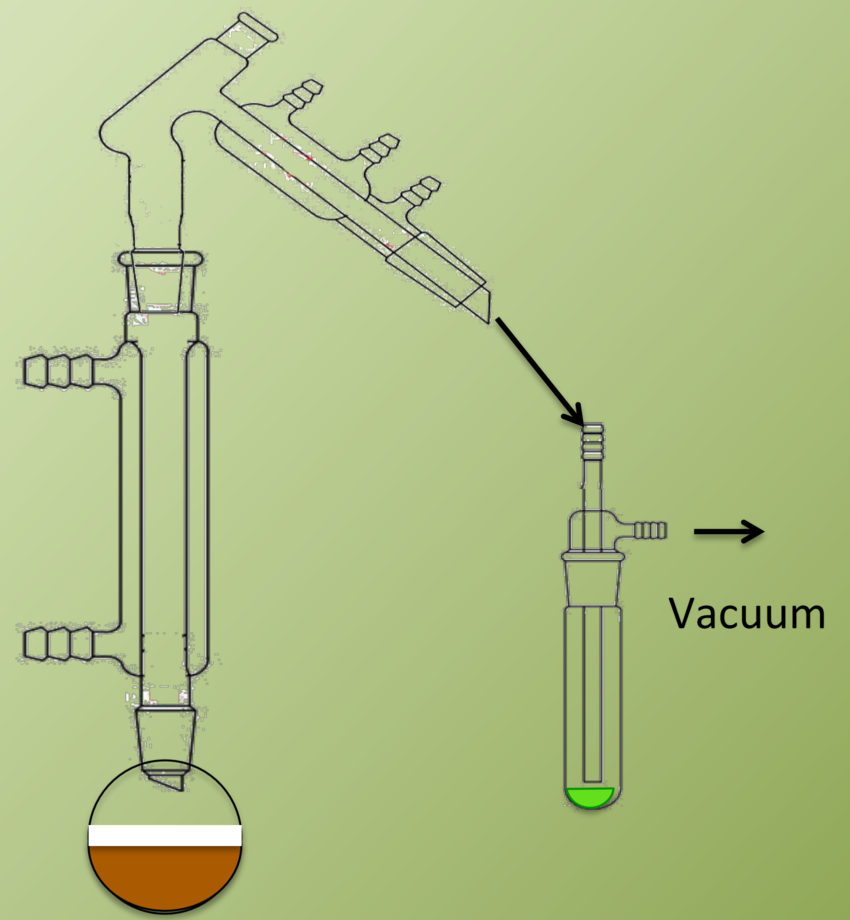
- In order to prepare pure methylglyoxal for gas phase experiments it must first be dehydrated and then distilled.
  - Sample is attached to a vacuum line and gently heated for 12-15 hours



Axson, J. L., Takahashi, K., De Haan, D. O.,Vaida, V. *Proc Natl Acad Sci USA,* (2010), **107**, 6687-6692.

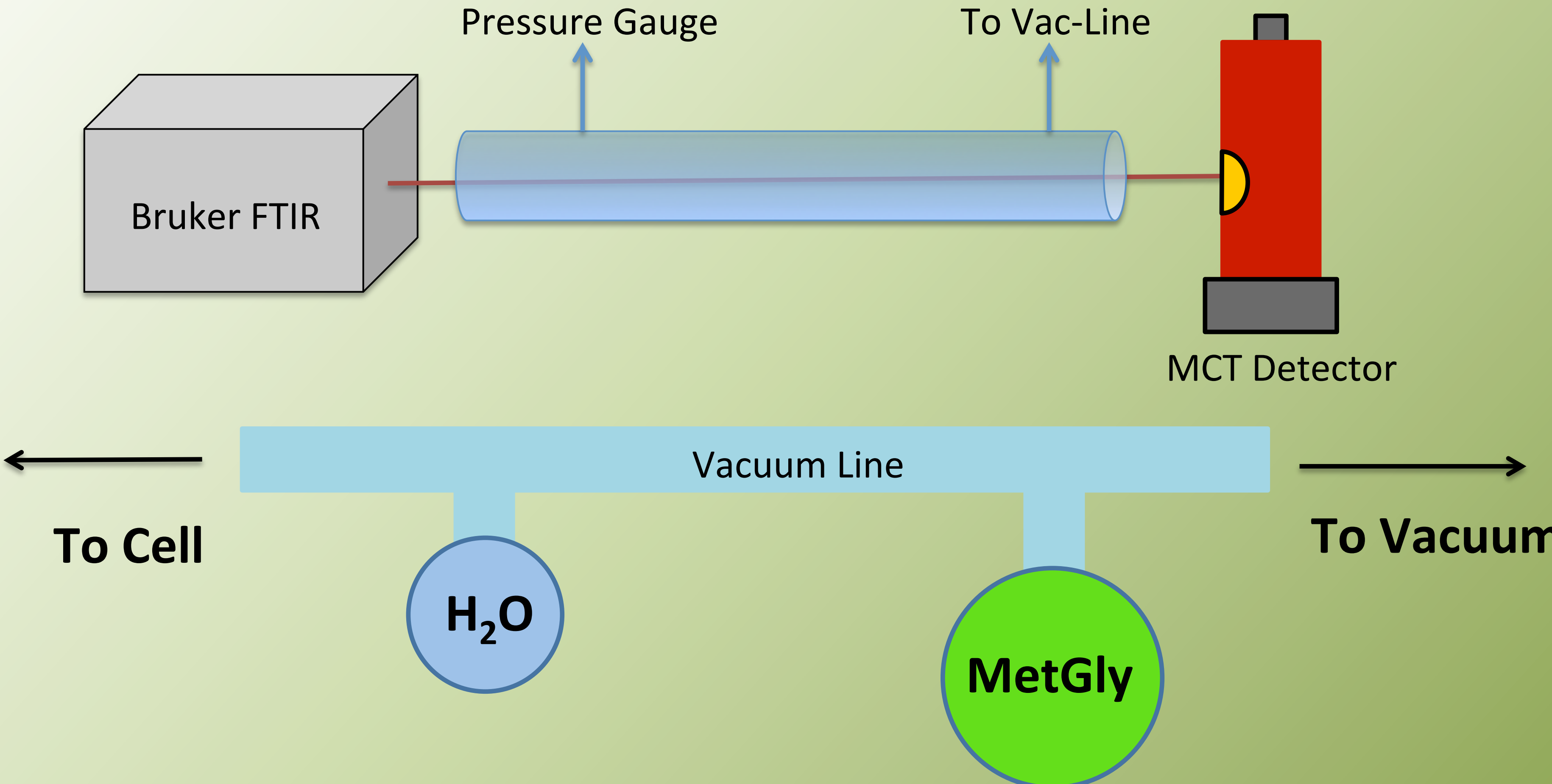
Sample Purification

- Add equimolar amount of P_2O_5 as drying agent
- Distill under vacuum using two cold water condensers
- Collect pure methylglyoxal using liquid nitrogen trap
- Pure sample is a bright green color



Axson, J. L., Takahashi, K., De Haan, D. O.,Vaida, V. *Proc Natl Acad Sci USA,* (2010), **107**, 6687-6692.

FTIR Setup



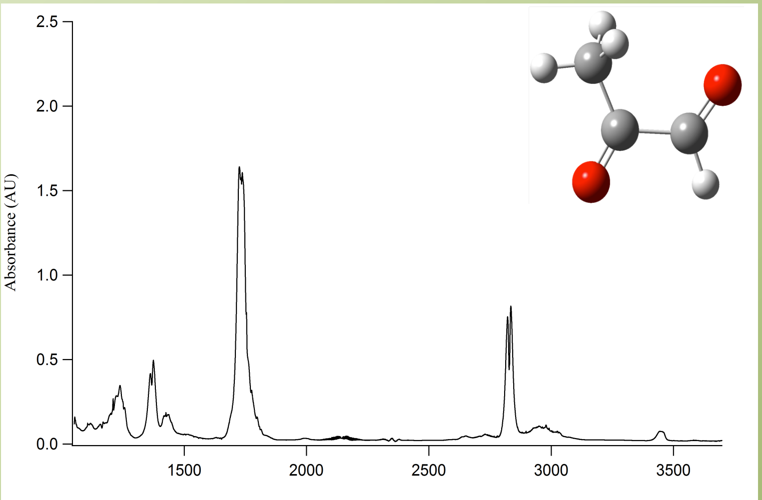
Spectra collected from 1000-8000 cm^{-1} at 0.5 cm-1 resolution.

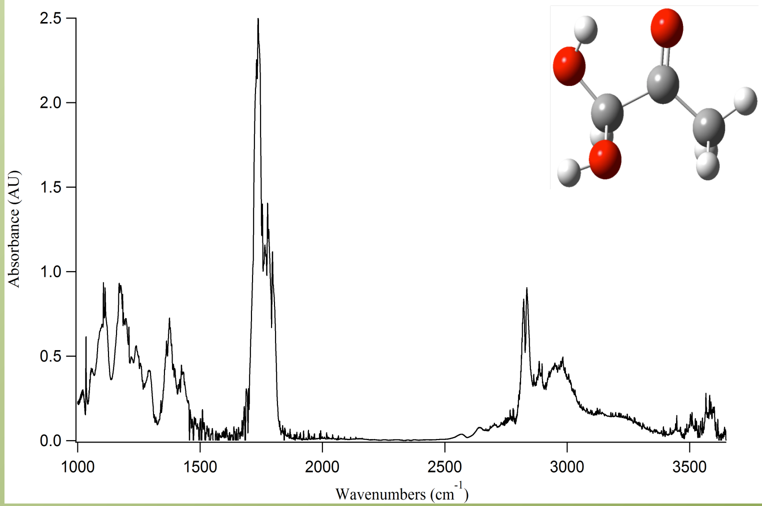
Axson, J. L., Takahashi, K., De Haan, D. O.,Vaida, V. *Proc Natl Acad Sci USA,* (2010), **107**, 6687-6692.

FTIR Results

Upon addition of water to methylglyoxal there is a clear change in the IR spectrum.

Spectra of methylglyoxal and a mixture of methylglyoxal and methylglyoxal diol





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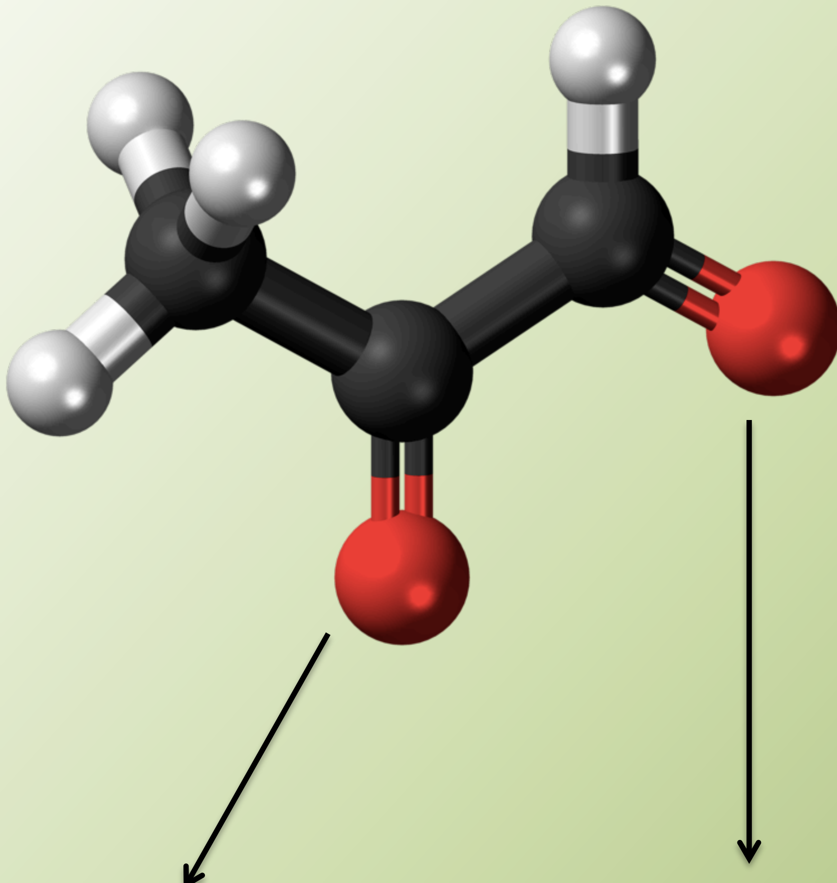
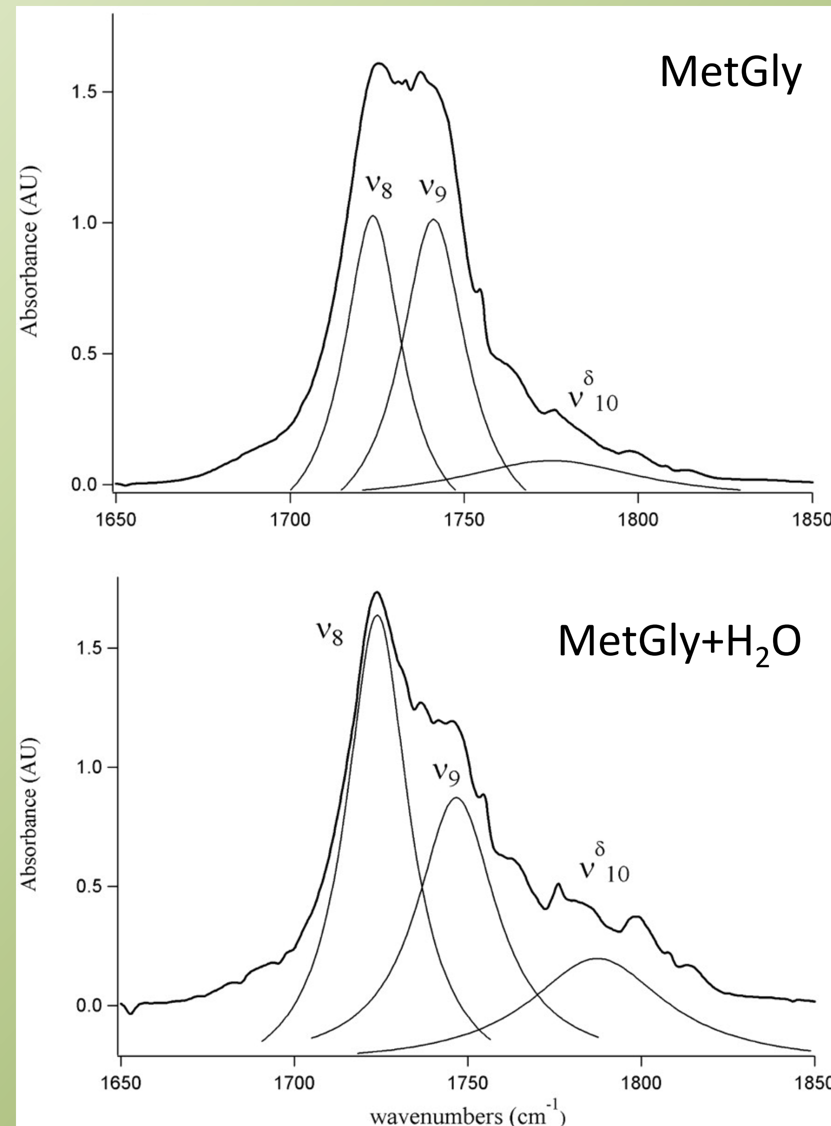
FTIR Results



v_8 = carbonyl stretch v_9 = aldehyde stretch



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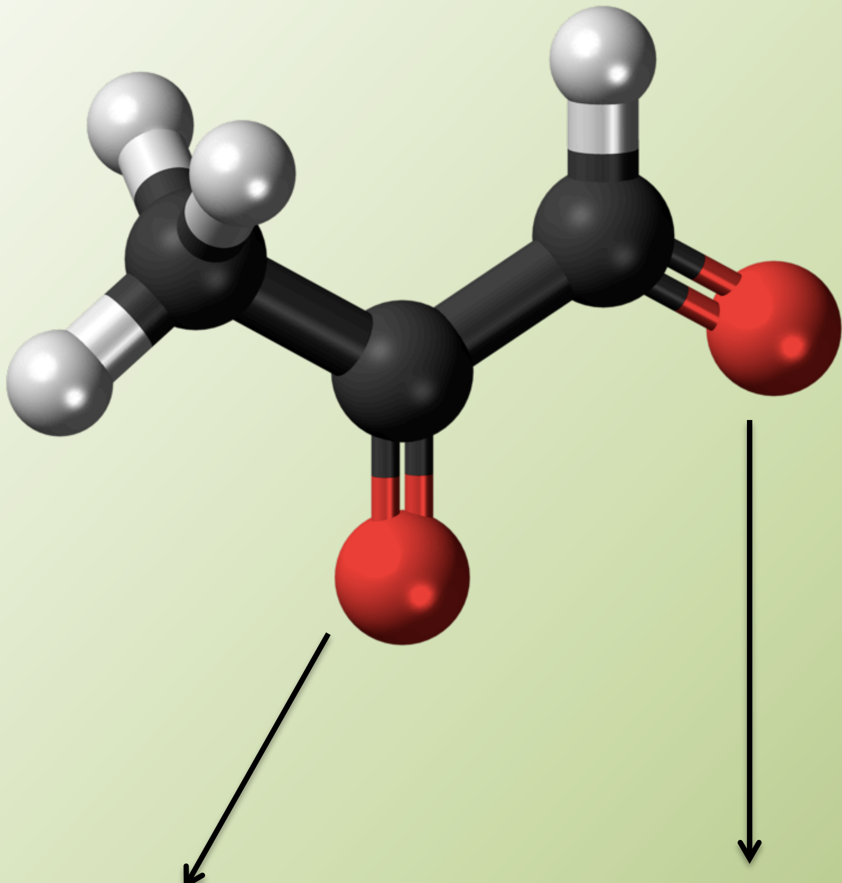

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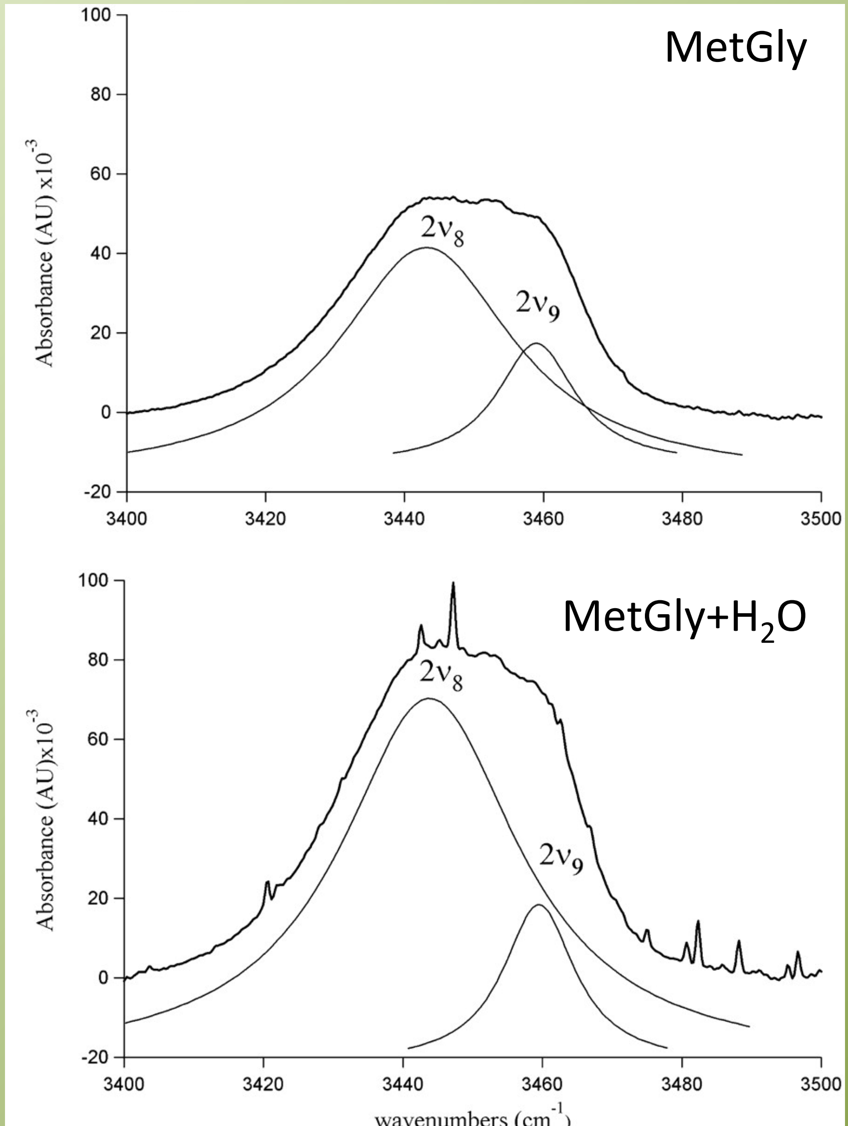
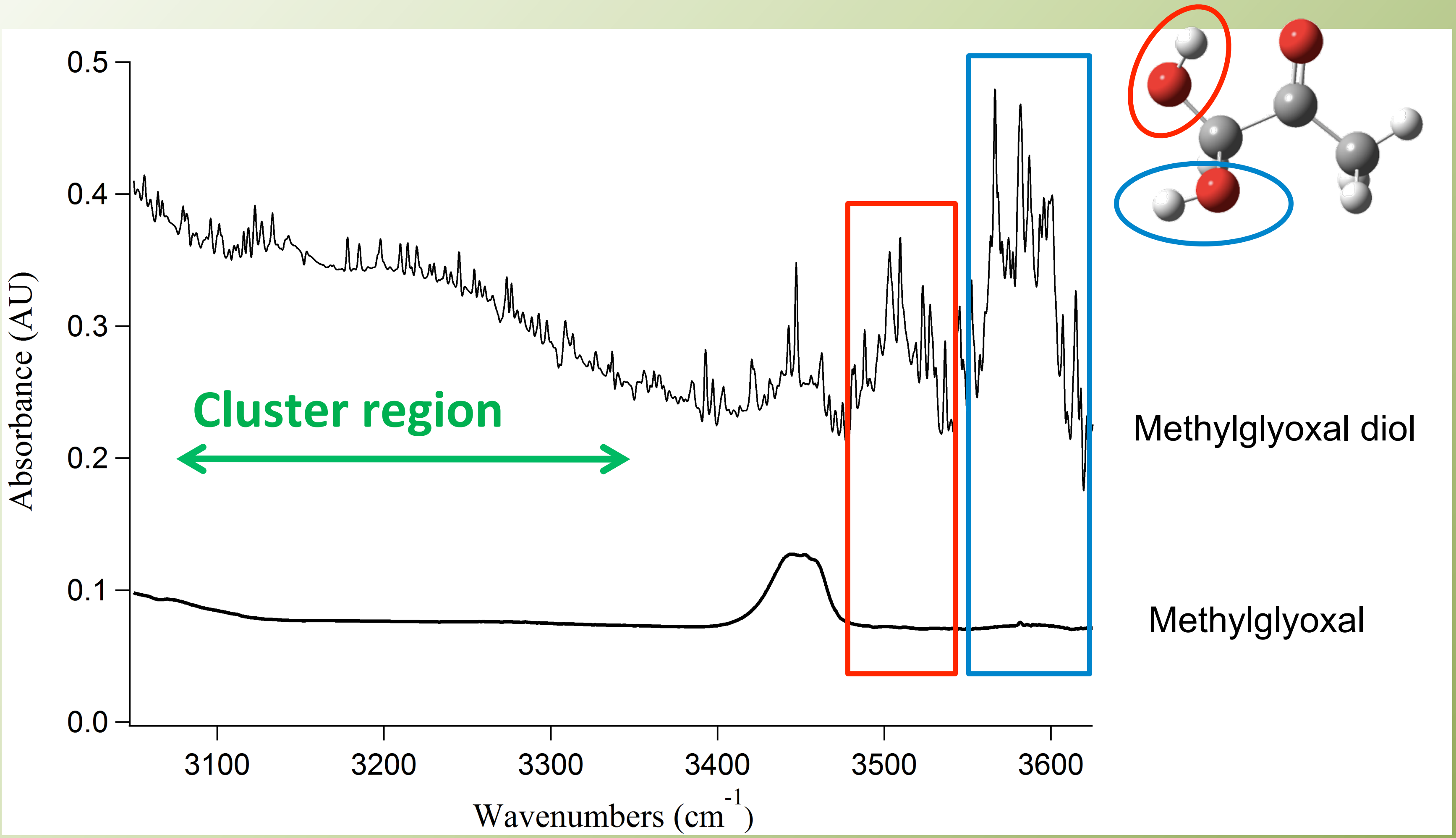


Axson, J. L., Takahashi, K., De Haan, D. O.,Vaida, V. *Proc Natl Acad Sci USA,* (2010), **107**, 6687-6692.

Methylglyoxal diol OH fundamental stretching region



Axson, J. L., Takahashi, K., De Haan, D. O.,Vaida, V. *Proc Natl Acad Sci USA,* (2010), **107**, 6687-6692.

FTIR Results

- Using the partial pressures of the methylglyoxal, diol, and water we can calculate an equilibrium rate constant
- The diol concentration was determined using the OH stretch and the theoretically determined cross section

$$K_P = \frac{P_{diol}}{P_{Mgly} P_{H_2O}}$$

$$\Delta G^\circ = -RT(\ln K_P)$$

Axson, J. L., Takahashi, K., De Haan, D. O.,Vaida, V. *Proc Natl Acad Sci USA,* (2010), **107**, 6687-6692.

FTIR Results

Experiment	P_{diol} (atm)	P_{water} (atm)	P_{mgly} (atm)	KP	ΔG° kcal mol-1
1	1.08×10^{-5}	1.25 × 10-3	5.40 × 10-5	159	-3.13
2	1.06×10^{-5}	1.24 × 10-3	5.40 × 10-5	157	-3.12
3	1.07×10^{-5}	1.23 × 10-3	5.40 × 10-5	161	-3.13
4	3.16×10^{-5}	1.59 × 10-3	1.29 × 10-4	154	-2.98

- The experimentally determined values for the Gibbs free energy of the reaction to form the diol show the reaction to be favorable.
- The values determined would suggest it is significantly more favorable than theoretical calculations predict, even when compared to calculations for hydration in aqueous solutions.

Rayne and Forest, *J Phys Org Chem* (2016).
Krizner et al. *J Phys Chem A* (2009), 113(25) 6994-7001.
Barsanti and Pankow, *Atmos Environ* (2005), 29 (35) 6597-6606.
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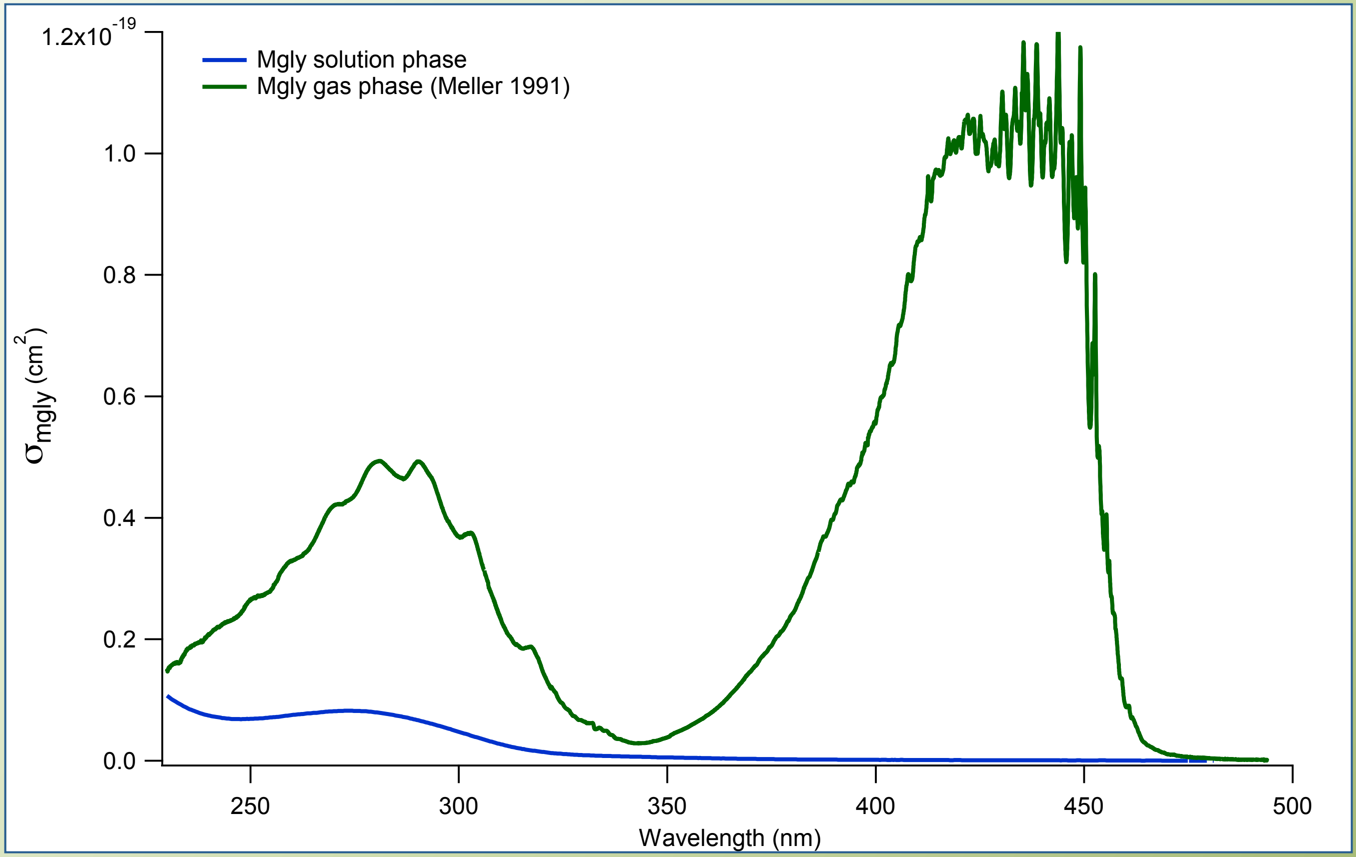
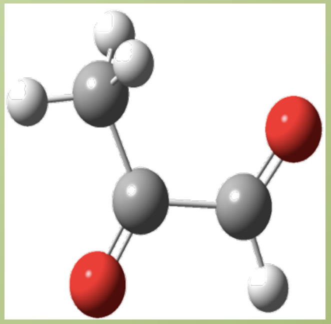
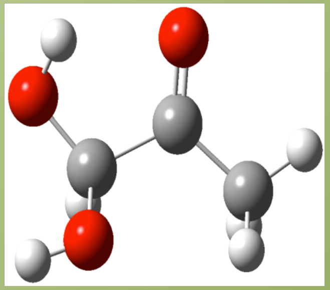
Gas phase vs. solution phase methlyglyoxal UV cross section







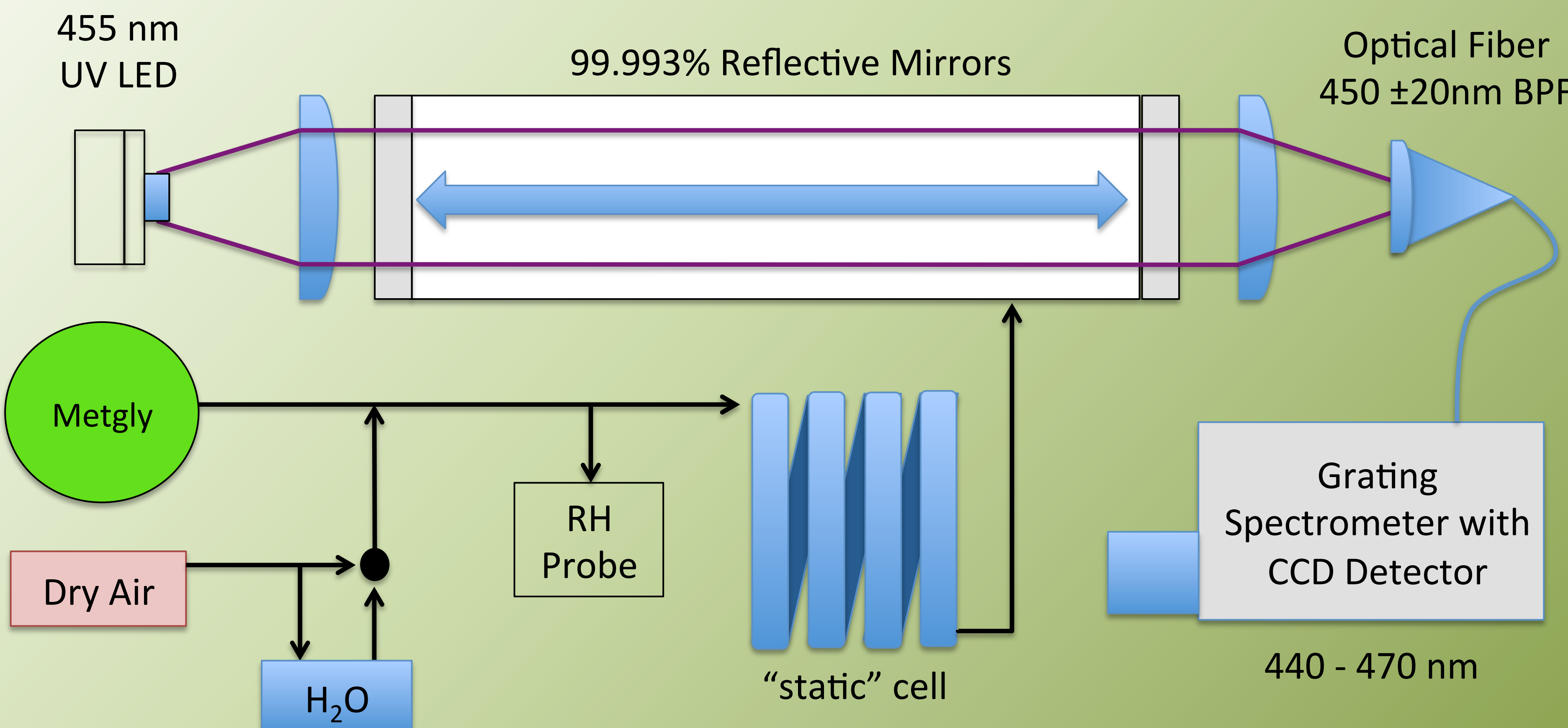
n → π* ketone

n → π* aldehyde

In solution, methylglyoxal is primarily present as the diol (60%)

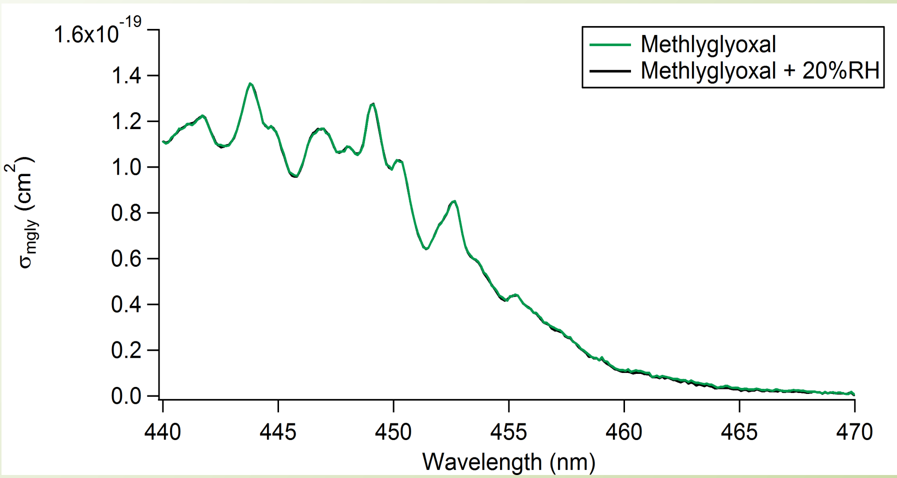
Meller, R., et al. *J. Photochem. Photobiol. A-Chem.,* (1991), **62**, 163-171.

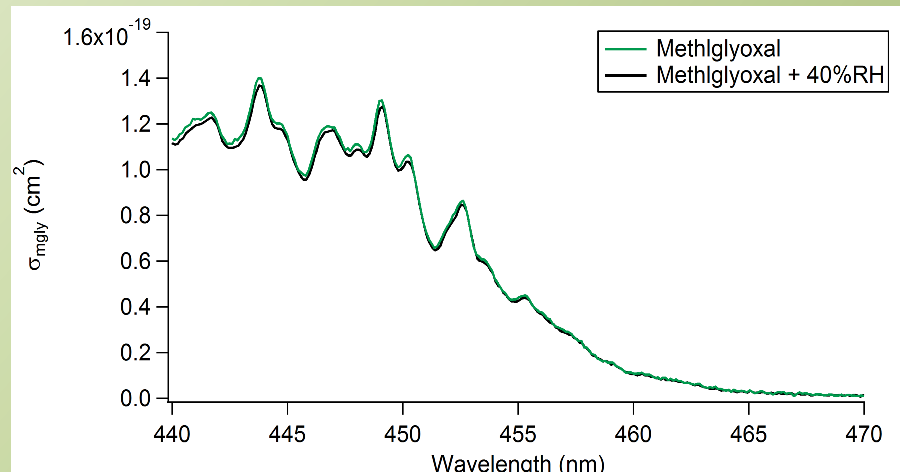
Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS)

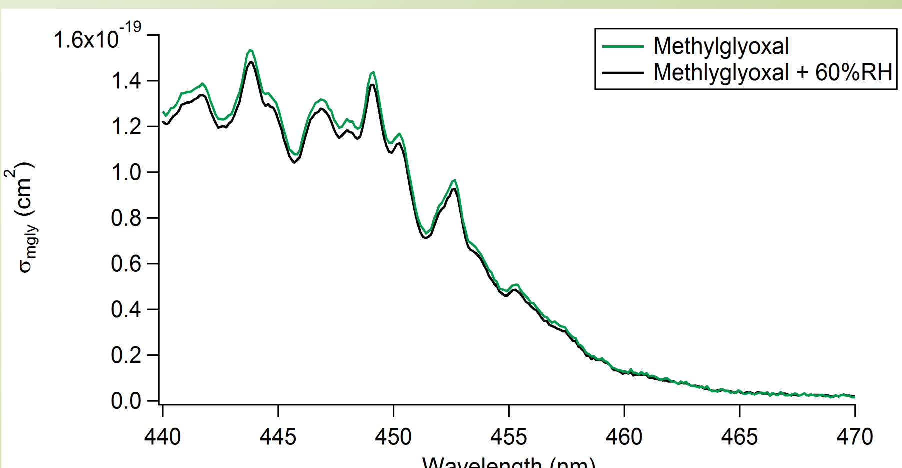


Jessica Axon Thesis

IBBCEAS Results

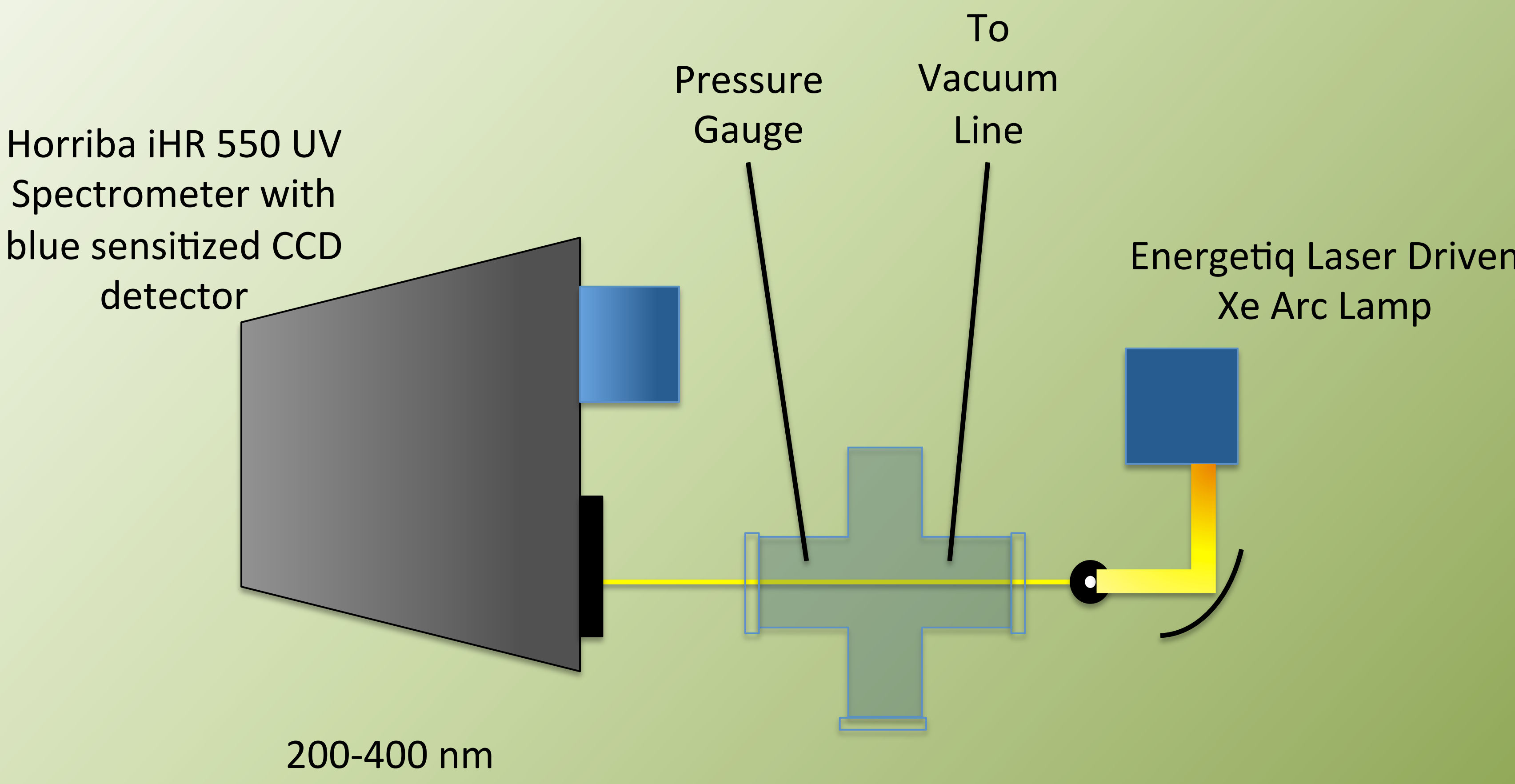






A small change is seen in the absorption cross section when relative humidity is increased.

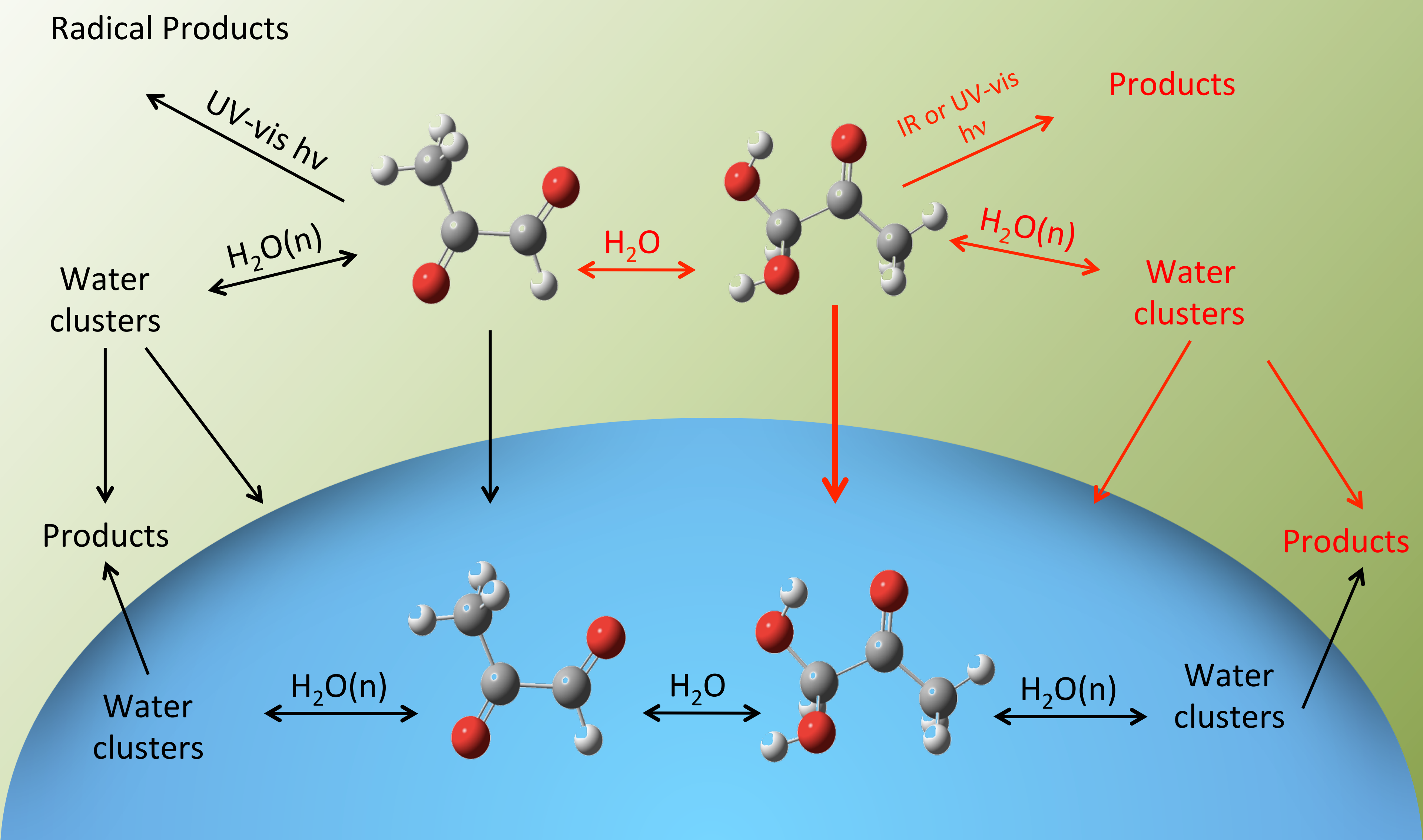
UV Direct Absorption Spectrometer



UV Direct Absorption Spectrometer

- 1 mtorr to >1 Atm
- λ>200 nm
  - Current typical experiments 200-400 nm
- Can go to visible wavelengths 400-700 nm
- 0.01 nm resolution

Implications for Atmospheric Chemistry



Acknowledgements

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  - Steve Brown
  - Rebecca Washenfelder
- NCAR
- Cooperative Institute for Research in Environmental Science (CIRES)
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  - NSF
  - NASA
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  - CIRES Graduate student fellowship- Jessica Axson
  - University of Colorado Boulder
- The Vaida group