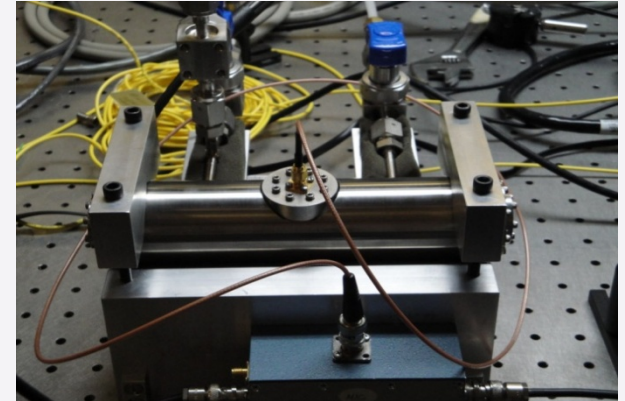
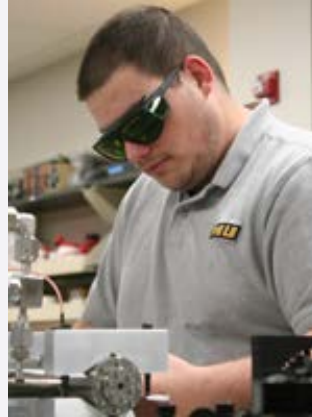
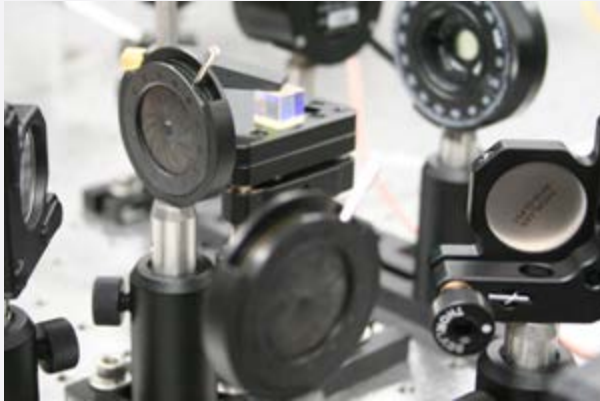


OPTICAL PROPERTIES AND ENERGY TRANSFER DYNAMICS OF ATMOSPHERIC SPECIES



Daniel K. Havey
Department of Chemistry and Biochemistry
James Madison University

Presented to the Science Enabled by Photon Sources: Local
Research Interests in Virginia workshop
May 15th, 2012

The Havey Group at James Madison University



Eric Vess
Chemistry '13
(2010 – Present)



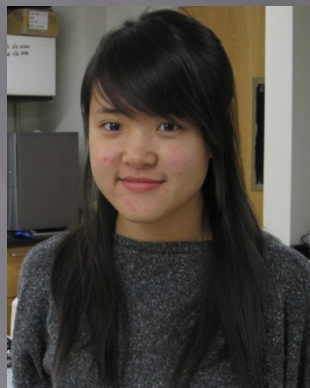
Heidi Campbell
Chemistry '12
(2011 – Present)



Colin Wallace
Chemistry '14
(2010 – Present)



Victoria Awadalla
Nursing '14
(2010 – Present)



Chae yeun Jeon
Chemistry '14
(2010 – Present)



Meg Goodale
Chemistry '15
(2011 – Present)



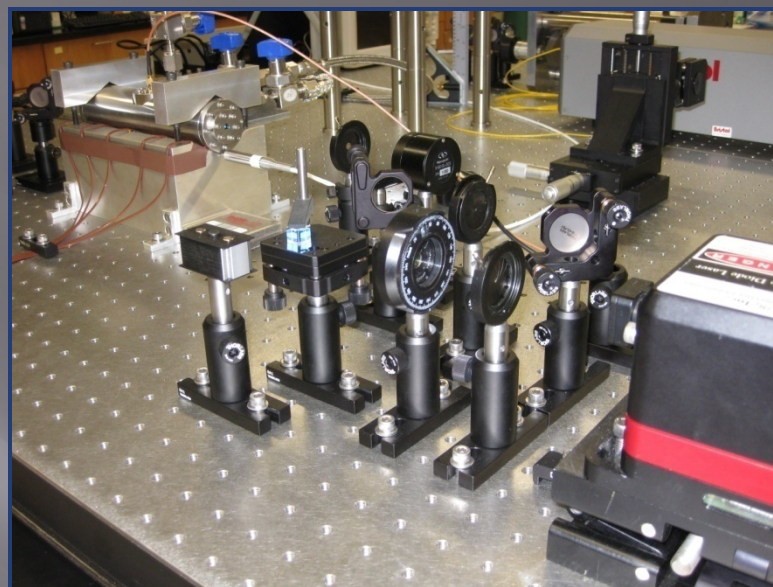
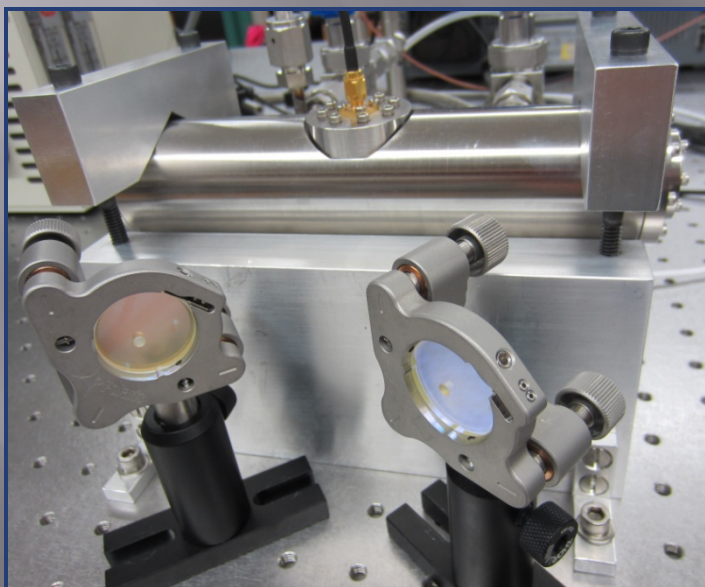
Esther Park
Nursing '14
(2012 – Present)

The Havey Group at James Madison University

Our Discipline: Physical Chemistry

Our Approaches: Optical spectroscopy,
Line Shape Theory, Lorenz-Mie Theory
Calculations

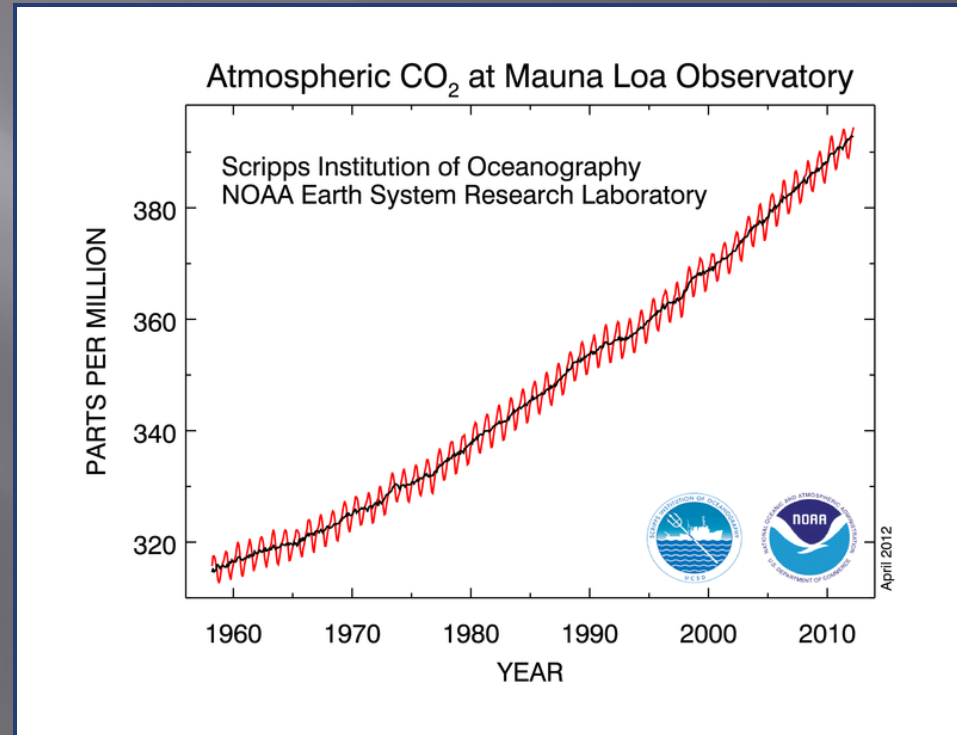
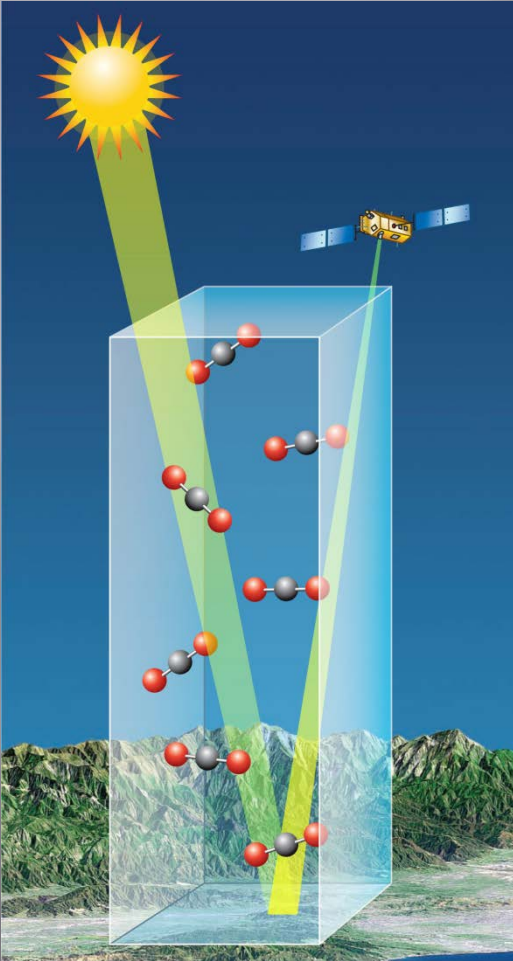
Current Systems of Interest: Carbon
Dioxide, Oxygen, Soot particles



We use laser spectroscopy to measure the optical properties of gases and aerosol particles that are important in atmospheric remote sensing.

We use laser spectroscopy to measure the optical properties of gases and aerosol particles that are important in atmospheric remote sensing.

Remote Sensing: Get information about something without coming in contact with it.



Remote sensing of carbon dioxide is important because it provides information about changes in local, regional, and global concentrations.

This research is important for the environment. It is also important for industrial profit margins.



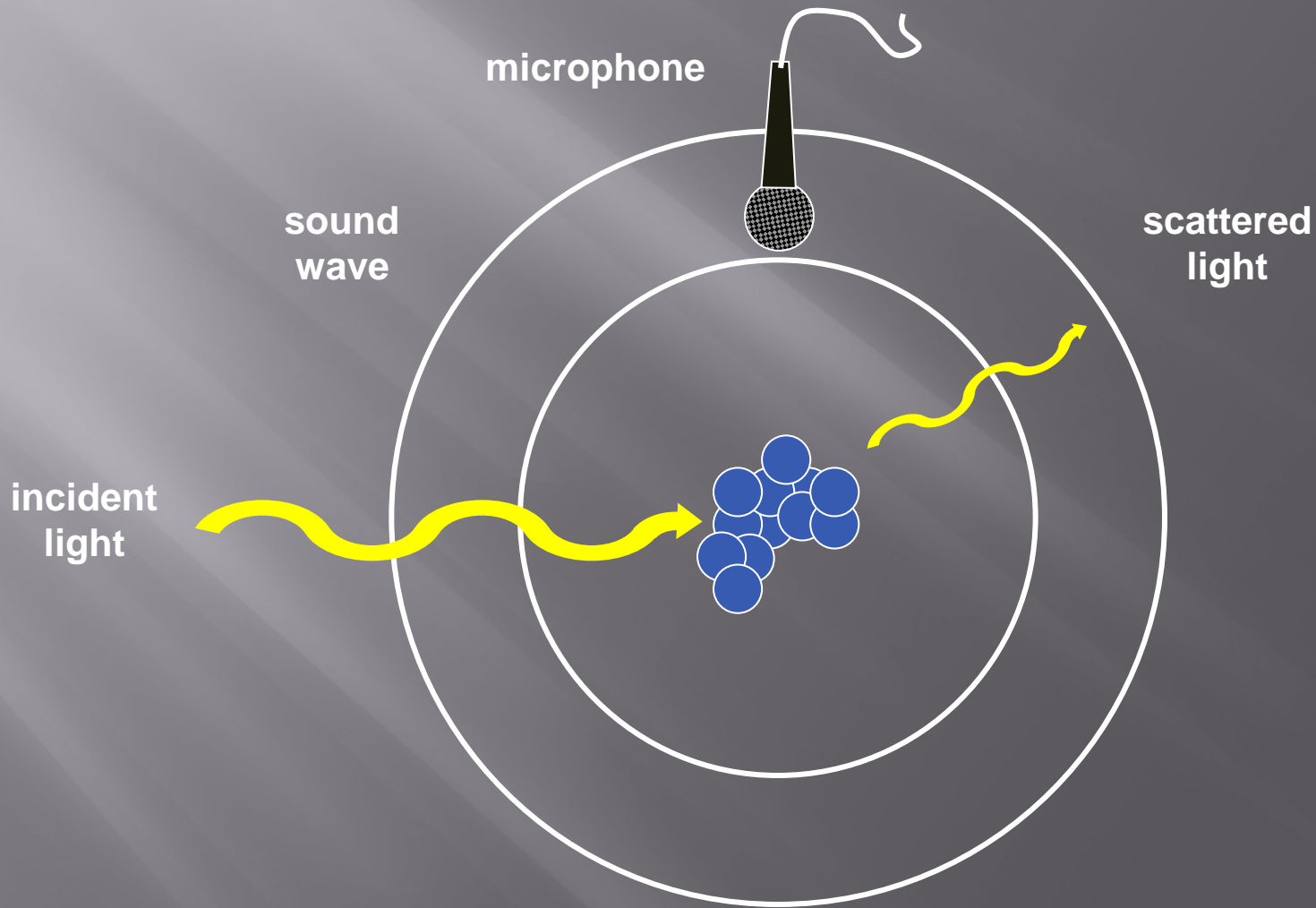
Consider an emissions trading system... If the success of your company is tied to large sums of money paid to offset pollution then there needs to be some sort of validation.



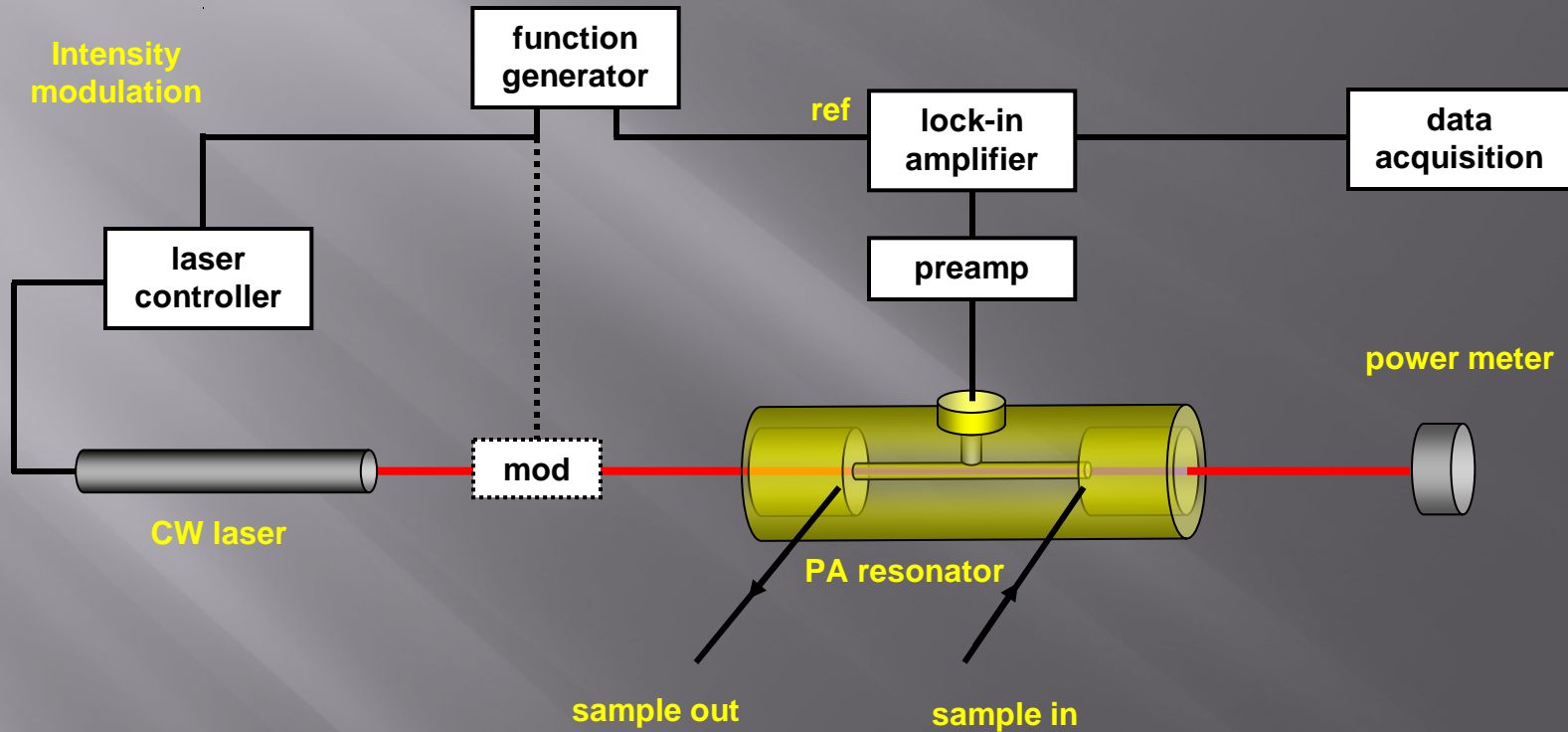
Remote sensing can be the “validation.”

However, for remote sensing campaigns to be successful they need high-fidelity spectroscopic reference data.

Photoacoustics: Light is switched on and off periodically; periodic light absorption causes periodic thermal expansion in the buffer gas, which generates sound that a microphone detects



Photoacoustic Spectroscopy: Study a sample's optical absorption as a function of wavelength by detecting the generated sound



The absorption coefficient we measure, $\alpha(\lambda)$, is the product of $\sigma(\lambda)$ and N . $\sigma(\lambda)$ is the absorption cross-section which is fundamental optical reference data.

$$\alpha(\lambda) = \sigma(\lambda) \times N$$

Photoacoustic Spectroscopy: Study a sample's optical absorption as a function of wavelength by detecting the generated sound

To “get the right answer” the instrumental response needs to be deeply understood.

$$\alpha = \frac{S_M}{R_{UL} W_L C_c \beta_m}$$

α = Absorption coefficient (cm⁻¹)

S_M = Magnitude of the photoacoustic microphone signal (Volts)

R_{UL} = Relaxation parameter

W_L = Peak-to-peak modulated laser power (Watts)

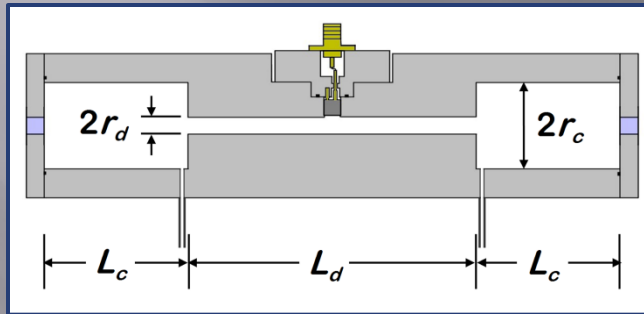
C_c = Cell constant (Pa/W-cm⁻¹)

β_m = Calibrated microphone sensitivity (V/Pa)

$$C_{sys} = C_c \beta_m$$

C_{sys} = System constant (V/W-cm⁻¹)

We have designed and implemented a new type of photoacoustic resonator



$$2r_c = 30 \text{ mm}$$

$$L_c = 50 \text{ mm}$$

$$2r_d = 6 \text{ mm}$$

$$L_d = 100 \text{ mm}$$

$$\alpha = \frac{S_M}{R_{UL} W_L C_c \beta_m}$$

This design has a very useful property. It's significance lies in the fact that we can calculate C_c really well.

We don't use a very sensitive microphone ($\sim 12 \text{ mV/Pa}$ @ f_{mod}).

We don't have a very large resonator Q factor (~ 30).

We have a very predictable system.

Example Recent Results

Remote sensing reference data:

E.M. Vess, C.J. Wallace, H.M. Campbell, V.E. Awadalla, J.T. Hodges, D.A. Long, D.K. Havey, “*Measurement of H₂O Broadening of O₂ A-Band Transitions and Implications for Atmospheric Remote Sensing*,” *Journal of Physical Chemistry A* **116** (2012) 4069-4073.

Wallace, C.J., C. Jeon, C.N. Anderson, D.K. Havey, “*H₂O Broadening of a CO₂ Line and its Nearest Neighbors Near 6360 cm⁻¹*,” *Journal of Physical Chemistry A* **115** (2011) 13804-13810.

Instrument development:

E.M. Vess, C.N. Anderson, V.E. Awadalla, E.J. Estes, C. Jeon, C.J. Wallace, X.F. Hu, D.K. Havey, “*Investigation of an energy-gap model for photoacoustic O₂ A-band spectra: H₂O Calibration Near 7180 cm⁻¹*,” *Chemical Physics* (2012) In Press.

K.A. Gillis, D.K. Havey, J.T. Hodges, “*Standard Photoacoustic Spectrometer: Model and Validation Using O₂ A-band Spectra*,” *Review of Scientific Instruments* **81**, 064902 (2010).

Soot particle absorption measurements:

D.K. Havey, P.A. Bueno, K.A. Gillis, J.T. Hodges, G.W. Mulholland, R.D. van Zee, M.R. Zachariah, “*Photoacoustic Spectrometer with a Calculable Cell Constant for Measurements of Gases and Aerosols*,” *Analytical Chemistry* **82** (2010) 7935-7942.

P.A. Bueno, D.K. Havey, G.W. Mulholland, J.T. Hodges, K.A. Gillis, R.R. Dickerson, M.R. Zachariah, “*Photoacoustic Measurements of Amplification of the Absorption Cross Section for Coated Soot Aerosols*,” *Aerosol Science and Technology*, **45** (2011) 1217.

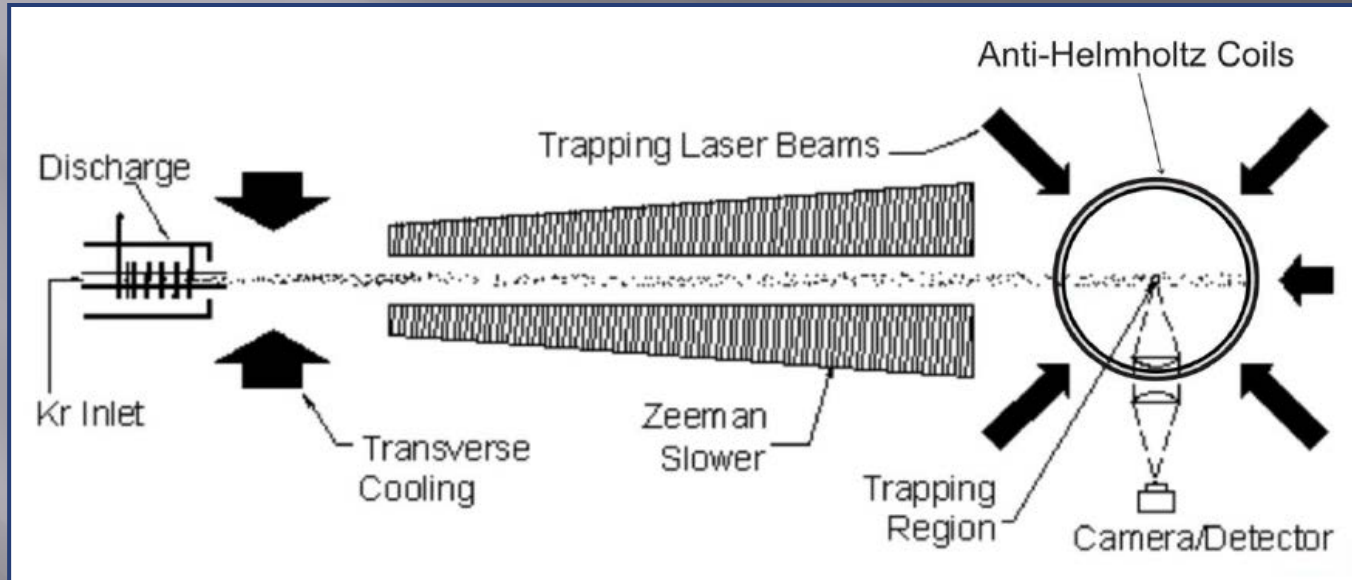
Future Work – Ultrasensitive Trace Analyzers of Noble Gas Isotopes

^{81}Kr is an important tracer for dating water and ice in the range of approximately 10^6 years. Additionally, ^{85}Kr appears as a result of nuclear fission. Monitoring the isotope can be performed in order to gauge nuclear weapons treaty compliance.



Future Work – Ultrasensitive Trace Analyzers of Noble Gas Isotopes

A new technique called Atom Trap Trace Analysis (ATTA) can be used to measure Kr isotopes. **Problem** – It currently requires a lot of water!

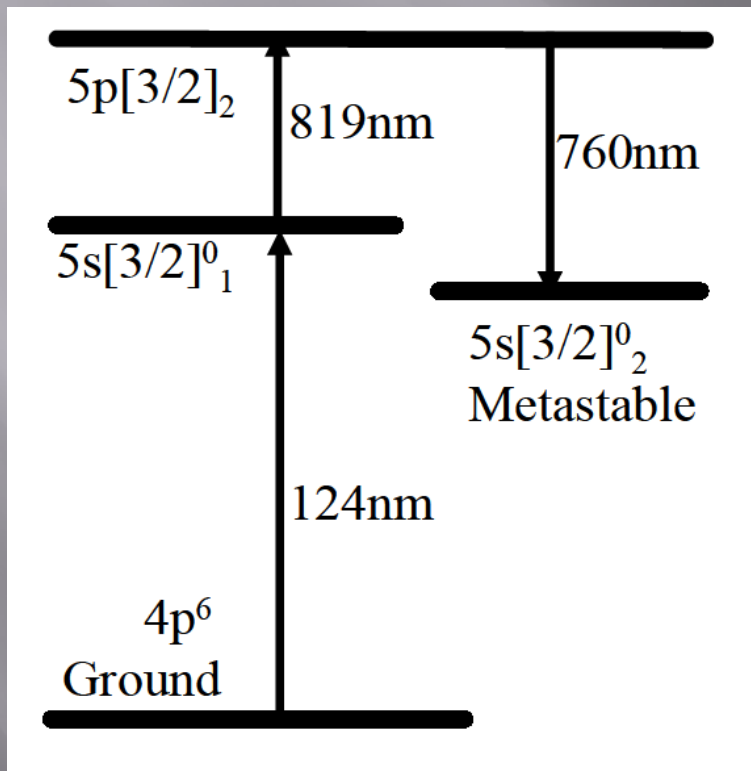


N.C. Sturchio, X. Du, R. Purtschert, B.E. Lehmann, M. Sultan, L.J. Patterson, Z.-T. Lu, P. Mueller, K. Bailey, T.P. O'Conner, L. Young, R. Lorenzo, B.M. Kennedy, M. van Soest, Z. El Alfy, B. El Kaliouby, Y. Dawood and A.M.A. Abdallah (2004) One million year old groundwater in the Sahara revealed by krypton-81 and chlorine-36, *Geophys.Res. Lett.* **31**, L05503.

X. Du, R. Purtschert, K. Bailey, B.E. Lehmann, R. Lorenzo, Z.-T. Lu, P. Mueller, T.P. O'Conner, N.C. Sturchio and L. Young (2003), A new method of measuring ^{81}Kr and ^{85}Kr abundances in environmental samples, *Geophys. Res. Lett.* **30**, 2068.

Future Work – Ultrasensitive Trace Analyzers of Noble Gas Isotopes

A high power VUV photon source will improve ATTA considerably and may enable routine analysis.



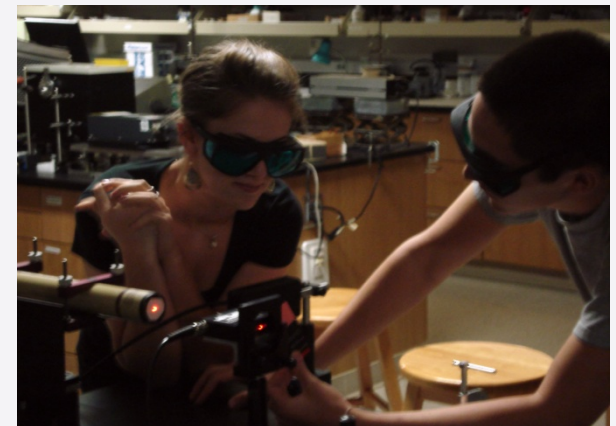
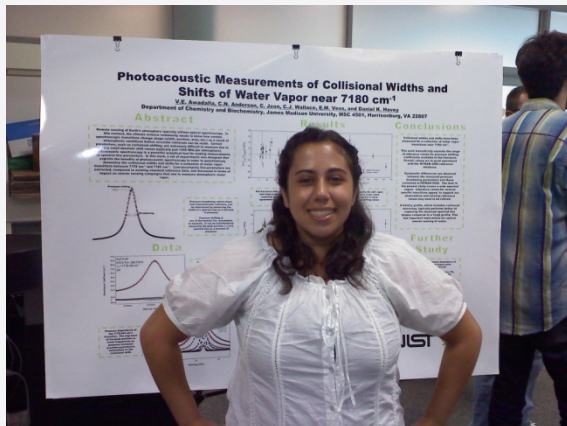
Energy level diagram for Kr
(reproduced from JLAMP VUV/Soft
X-Ray User Facility proposal)

Our proposed contribution: Support the development of ATTA with the precise determination of Kr-H₂O collisional energy transfer rates between the $5p[3/2]_2$ and $5s[3/2]^0_2$ states. Also perform basic fundamental research to understand relaxation from $5s[3/2]^0_2$ to $4p^6$, $5p[3/2]_2$ to $5s[3/2]^0_1$, and $5p[3/2]_2$ to $5s[3/2]^0_2$.

Experimental method: Perform two-photon photoacoustic spectroscopy with a 124 nm VUV source and a tunable 819 nm diode laser.

Summary

- Our group uses lasers to study how small molecules and particulate matter interact with light. Primary applications of interest to us are atmospheric chemistry and climate change.
- At JMU, we have constructed a novel and powerful photoacoustic spectrometer which can be used to obtain high-fidelity spectroscopic reference data as well as to measure collisional relaxation rates.
- Access to an advanced photon light source would enable an interesting collisional relaxation project on Krypton isotopes. Results would support the development of “next-generation” environmental isotope sensors.





Acknowledgements



External Collaborators

- J.T. Hodges (NIST)
- M.R. Zachariah (UMD)
- M. Okumura (Caltech)
- D. Lisak (UMK, Poland)
- K.A. Gillis (NIST)
- G.W. Mulholland (UMD)
- C.E. Miller (NASA)
- R.D. van Zee (NIST)

Internal Collaborators

- B.M. Boardman (JMU Chemistry)
- T.C. DeVore (JMU Chemistry)
- E.A. Johnson (JMU Geology)

Funding Sponsors

- NIST Measurement Science Grant (2010-2012)
(Grant No. 70NANB10H250)
- National Science Foundation Research Experience for Undergraduates Grant (Grant No. CHE-1062629)
- James Madison University Department of Chemistry and Biochemistry (Start-up support)