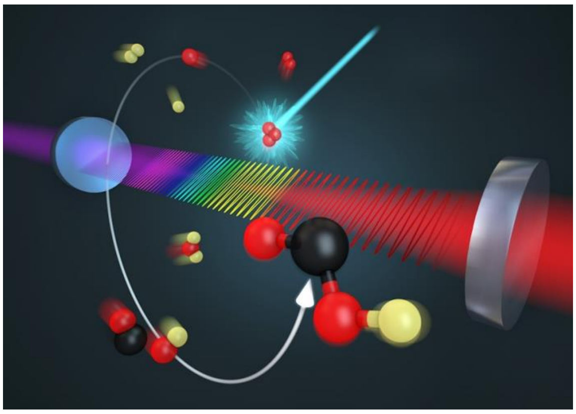
Dr Julia H. Lehman

This proposal is representative of the projects currently on offer in our group starting in January 2017. For more details on active research projects, please contact Dr Lehman.

Methylmercapto radical reactions: kinetics and spectroscopic identification

This project involves the spectroscopic identification of intermediates and products from reactions of methylmercapto radicals.

Thionitrites, or s-nitrosothiols, have the form RSNO, where R is any organic group. Thionitrites are proposed atmospheric intermediates in the oxidation of reduced sulphur compounds in the presence of NO. For example, CH_3SNO was experimentally observed as a reaction intermediate in high NO_x environments following the OH oxidation of dimethylsulphide (DMS).[1] Reduced sulphur compounds, such as H_2S, DMS, dimethyl disulphide (DMDS) and alkyl substituted mercaptans (RSH), are generated primarily from biogenic sources and supply a net flux of sulphur in the atmosphere. These reduced compounds are oxidized, becoming a source for atmospheric SO_2 (contributing to tropospheric aerosol formation) and carbonyl sulphide (contributing to the stratospheric sulphate layer). This project will focus on the radical-radical reaction, CH_3S + NO, in the synthesis of methyl thionitrite, CH_3SNO.



Example of cavity-enhanced frequency comb spectroscopy: conceptualized view of a mid-infrared frequency comb used to monitor the OD + CO reaction, forming the DOCO transient reaction intermediate.
Credit: The Ye Group and Steve Burrows, JILA, University of Colorado, Boulder USA[2]

In this project, you will measure reaction rate constants at room temperature using laser photolysis combined with a cutting-edge laser-based detection method: cavity-enhanced mid-infrared frequency comb vibrational absorption spectroscopy. As just recently demonstrated by the Ye group at JILA (University of Colorado, Boulder, USA),[2] cavity-enhanced frequency comb spectroscopy can be used to simultaneously obtain a broadband, high-resolution vibrational absorption spectrum, as well as reaction rate constants. This powerful technique, made possible by the pioneering work of Jan Hall and Ted Hänsch for which they were awarded the 2005 Nobel Prize in Physics, will be applied to the radical-radical reaction of CH_3S + NO, forming CH_3SNO. You will measure the vibrational absorption spectra of reactants, products, and intermediates in this reaction. You will also use this technique as a detection method to monitor the reaction progress and derive room temperature reaction rate coefficients. You will interpret the laboratory measurements with the aid of theoretical methods, including quantum chemical calculations, spectroscopic modelling, and the opportunity to collaborate within the *Atmospheric and Planetary Chemistry* group to use your results in atmospheric modelling.

This PhD will provide a broad spectrum in training, particularly covering vibrational absorption spectroscopy, kinetic methods, high-resolution laser-based spectroscopic techniques, optics, vacuum systems, and quantum chemical calculations. You will also receive training in writing and implementing computer controlled data acquisition and analysis programs. You will be part of the well-funded, active, and highly collaborative *Atmospheric and Planetary Chemistry* group within the School of Chemistry.

Please contact Dr Julia Lehman (julia.lehman@colorado.edu) for further details about this opportunity.

References

[1] H. Niki *et al*, *J. Phys. Chem.* **1983**, *87*, 7.
[2] B. J. Bjork *et al*, *Science*, **2016**, *354*, 444.