11th International
User Meeting and Summer School
on Cavity Enhanced Spectroscopy

June 16 – 19, 2015
Boulder, Colorado

www.esrl.noaa.gov/csd/events/ces2015/

National Institute of
Standards and Technology
U.S. Department of Commerce

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Conference Program

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NOAA, Boulder, Colorado, USA

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Plenary Speakers

Jonathan Reid
University of Bristol, Bristol, UK

Yinon Rudich
Weizmann Institute, Rehovot, Israel

Shailendhar Saraf
Stanford University, Palo Alto, California, USA

Jun Ye
University of Colorado, Boulder, Colorado, USA

Invited Speakers

David Chandler
Sandia National Laboratories, Albuquerque, New Mexico, USA

John Hall
University of Colorado, Boulder, Colorado, USA

Harold Linnartz
University of Leiden, Leiden, the Netherlands

Terry Miller
The Ohio State University, Columbus, Ohio, USA

Dan Murphy
National Oceanic and Atmospheric Administration, Boulder, Colorado, USA

Scott Papp
National Institute of Technology, Boulder, Colorado, USA

Sheila Rowan
University of Glasgow, Glasgow, UK

Matthew Sellars
Australian National University, Canberra, Australia

Helen Waechter
Tiger Optics, Warrington, Pennsylvania, USA

Yun-Feng Xiao
Peking University, Beijing, China

GENERAL INFORMATION

Meeting Webpage

The meeting agenda, abstracts, and information are available electronically at
http://www.esrl.noaa.gov/csd/events/ces2015/

Meeting Location

Session will be held at the National Institute of Standards and Technology (NIST) main auditorium. The address is 325 Broadway, Boulder, Colorado, USA.

Transportation from Denver International Airport to Boulder

Airport Shuttle

SuperShuttle (303-227-0000) provides service from the airport to locations in Boulder, and will deliver you directly to your destination.

Public Transportation

Regional bus service to Boulder is available through the Regional Transportation District (RTD). The AB bus (westbound) provides service from Denver International Airport to Boulder. It departs hourly and costs $13. Exact change is required. This option will likely require a local bus within Boulder or walk to reach your hotel. The schedule is available here: http://www3.rtd-denver.com/schedules/getSchedule.action?routeId=AB

Driving

Exit Denver International Airport via Peña Boulevard.
Take Peña Boulevard to I-70 West.
Split right on I-270 North (Exit 279), toward Ft. Collins and follow across I-25 to US-36 (West) toward Boulder.
Exit US-36 at Baseline Road (University of Colorado Main Campus exit).
Keep left and turn left (West) onto Baseline.
Keep left and turn left at the first light onto 27th Way.
Stay in the middle lane and turn left onto Broadway.
Take the second right at the light onto Rayleigh Road then right into the Visitors Center parking lot.

Travel within Boulder

Walk

The recommended Boulder hotels are within a 3 km walk of the NIST auditorium.

Bicycle

Local bike rentals are available at Boulder B-Cycle stations throughout the city. After you pay a daily or weekly fee, unlimited free 30-minute trips are included. Conference participants can use the promotion code NOAASS (case sensitive) to receive a $10 / week rental rate. There is a convenient B-Cycle station in front of the NIST auditorium where bicycles can be borrowed or returned.

Bus

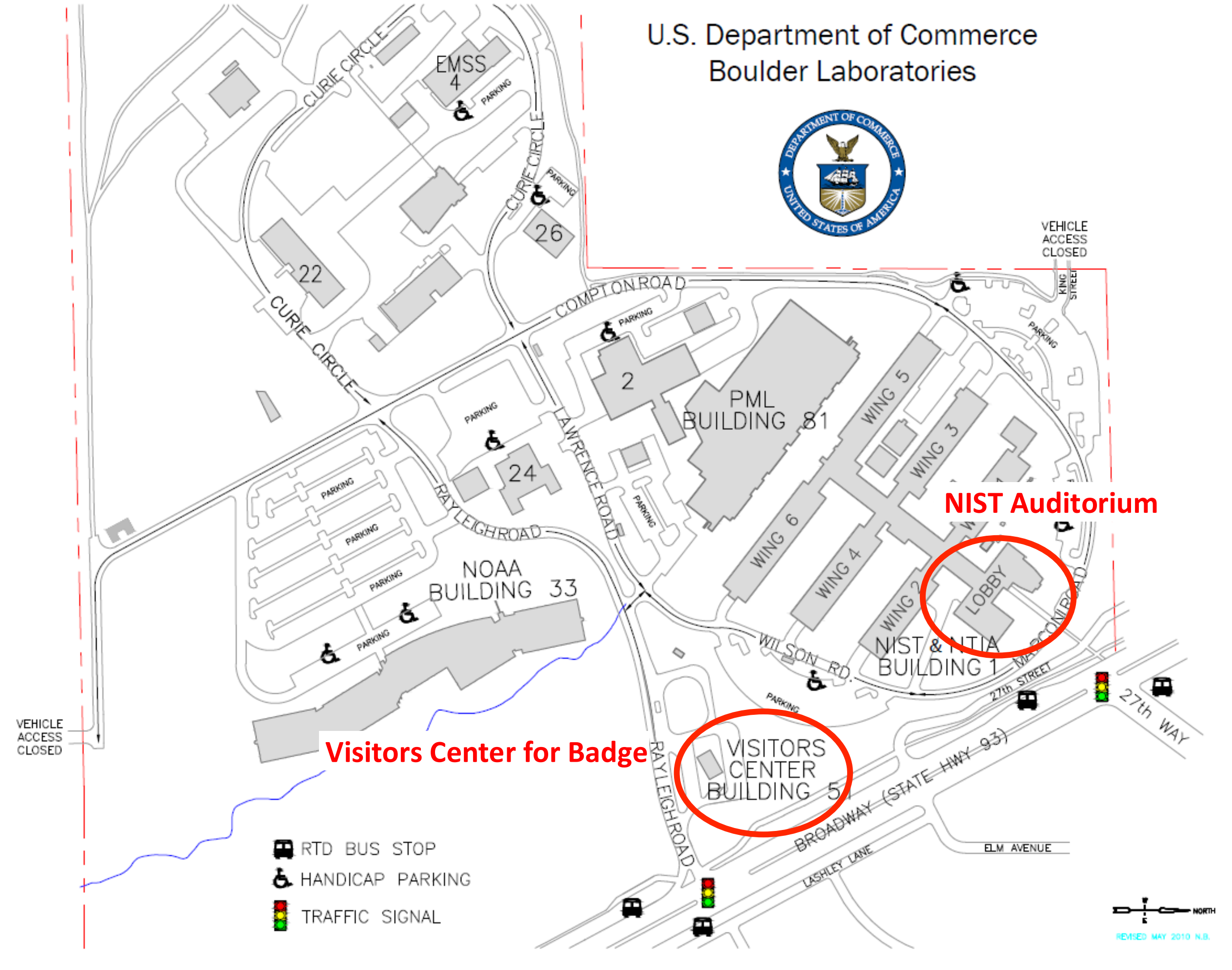
Rayleigh Road and Broadway is the closest RTD bus stop to the visitor center and is served by the SKIP, DASH, AB, B, DD, DM, GS, and J bus routes. The Flatiron Park-n-Ride (Broadway and 27th Way) is also nearby and is served by the BOUND and the 204 routes.

Arrival and Badging

Please arrive 45 minutes before the first session. You can save time by going to the visitor center on Monday June 15 (or Tuesday June 16, if you are not attending the summer school) to receive your badge in advance.

The Visitors Center is located on Broadway at Rayleigh Road. All visitors, including pedestrians and bike riders, are required to check in at the Visitors Center to receive a badge, before proceeding to the auditorium. To receive a visitor badge, U.S. visitors must present a valid photo ID (federally approved State issued driver's license, Federal ID, or original passport). International visitors must present a valid passport or green card.

Drivers must bring their vehicle registration card or rental agreement.



Registration Fee Includes

Admission to scientific sessions
Coffee breaks and lunches on June 16, 17, 18, and 19
Conference dinner on Thursday June 18

Coffee Breaks and Lunches

Food will be served in the main lobby, outside the auditorium.
Lunch menus with meal choices will be included in your arrival packet. Please complete the forms and return them at the NIST auditorium.

Wednesday and Thursday Poster Preview Talks

Each poster presenter is asked to give a brief presentation to highlight their work, in a special oral session immediately before the poster session. Each presenter will have one minute to speak and may present one slide, which has been submitted in advance. The poster presenters will be introduced in alphabetical order.

Wednesday Afternoon Laboratory Tours

Following the scientific program on Wednesday, there is a choice of two laboratory tours. One tour will visit laboratories at the National Institute of Standards and Technology (NIST) and the other tour will visit laboratories at the National Oceanic and Atmospheric Administration (NOAA).

Wednesday Dinner

Dinner is on your own, with bus tickets provided to visit Pearl Street in downtown Boulder. Pearl Street is a four-block pedestrian mall in the center of the city. You can catch the Skip bus on the east side of Broadway (across the street from the NIST auditorium), and exit the bus at Pearl Street.

Thursday Evening Poster Session and Dinner

The Thursday night poster session and dinner will be held in the beautiful NCAR Mesa Laboratory, at the base on the Flatiron mountains in Boulder. Group transportation from the NIST auditorium to the poster session and dinner will be provided. Buses will depart at 3:15 pm and return after dinner at 7:30 pm. If you prefer to drive yourself, the address is 1850 Table Mesa Drive, Boulder, Colorado.

Audiovisual Facilities

The auditorium is equipped with a laptop and projector. Speakers are asked to upload their presentation to the shared laptop at the beginning of the day or during one of the conference breaks.

Meeting Sponsors

We are appreciative of the support by our sponsors. Please visit their tables in the main lobby to learn more about their products. Silver and Gold level sponsors will make short presentations prior to the lunch break each day.

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11th International User Meeting and Summer School on Cavity Enhanced Spectroscopy
16 - 19 June 2015
Boulder, Colorado, USA

Tuesday 16 June 2015

Time	Agenda	Speaker	Lecture Title
	Registration and coffee in the NIST Main Lobby		
9:00	*Welcome*	**Steve Brown**	*Introduction to **Summer School***
9:15	Lecture 1	**Joseph Hodges**	Assessing the precision and accuracy of cavity ring-down spectroscopy measurements
10:05	*Coffee Break*		
10:20	Lecture 2	**Kevin Lehmann**	The properties of Optical Cavities and how they effect CES
11:10	Lecture 3	**Frans Harren**	Off-Axis Integrated Cavity Output spectroscopy for trace gas detection
12:00	*Lunch*		
13:00	Lecture 4	**Aleksandra Foltynowicz**	Cavity-Enhanced Optical Frequency Comb Spectroscopy
13:50	Lecture 5	**Alejandro Farinas**	Industrial Applications of Cavity-Enhanced Spectroscopy Instruments
14:40	*Coffee Break*		
14:55	Lecture 6	**Rebecca Washenfelder**	Atmospheric Field Measurements Using Cavity Enhanced Spectroscopy
15:45	*Tour Science On a Sphere at NOAA*		

Wednesday 17 June 2015

Time	Agenda	Speaker	Presentation Title
	Registration and coffee in the NIST Main Lobby		
8:30	*Welcome*	**Rebecca Washenfelder**	*Introduction to the **User Meeting***
	Morning Session Chair: Hans Osthoff		
8:40	Plenary talk	**Shailendhar Saraf**	Cavity Enhanced Molecular Spectroscopy for Developing Ultrastable Frequency Standards and Generating Frequency Combs in the Mid-IR
9:20	Invited talk	**David Chandler**	Dual Etalon Frequency Comb Spectrometer
9:45	Contributed talk	**Jerome Morville**	A Very Broadband Direct Frequency Comb - Cavity Enhanced Vernier Spectrometer
10:05	*Coffee Break*		
10:20	Contributed talk	**Garwing Truong**	Towards Fieldable Dual-Comb Spectroscopy For Greenhouse Gas Monitoring in Outdoor Air
10:40	Invited talk	**Scott Papp**	Microresonator optical frequency combs
11:05	Contributed talk	**Leonid Sheps**	Time-Resolved Broadband Cavity-Enhanced Absorption Spectroscopy: A New tool for Chemical Kinetics
11:25	Contributed talk	**Albert A. Ruth**	Laser-Induced Plasmas in Ambient Air for Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy
11:45	Sponsor talk	**Brent Wheelock**	*Menlo Systems*
11:55	Sponsor talk	**Brian Siller**	*Tiger Optics*
12:00	*Lunch*		

	Afternoon Session Chair: Jong Chow		
13:00	Invited talk	**Yunfeng Xiao**	Microcavity Raman Laser and Its Application in Single-Nanoparticle Detection
13:25	Contributed talk	**Dean James**	Open-Access Optical Microcavities for Lab-on-a-Chip Spectroscopy
13:45	Contributed talk	**Meez Islam**	Bioanalytical Applications of Liquid Phase BBCEAS
14:05	Invited talk	**Sheila Rowan**	Low Noise Cavities in Interferometric Gravitational Wave Detectors
14:30	**Poster Previews (A - L)**		
14:55	**Poster Session (A - L)**		
16:55	*Lab Tours at NIST or NOAA*		
17:55	*Dinner on your own in downtown Boulder*		

Thursday 18 June 2015

Time	Agenda	Speaker	Presentation Title
8:30	*Welcome in the NIST Auditorium*		
	Morning Session Chair: Solomon Bililign		
8:35	Plenary talk	**Yinon Rudich**	Measurements of Aerosol Optical Properties using Broadband Cavity Enhanced Spectroscopy
9:15	Invited talk	**Terry Miller**	Near-Infrared Cavity Ringdown Spectroscopy of Intermediates in Complex Chemical Reactions
9:40	Contributed talk	**Guillaume Genoud**	Quantum Cascade Laser Spectroscopy for Radiocarbon Detection
10:00	Contributed talk	**Giovanni Giusfredi**	Spectroscopic detection of 14CO2: Towards Parts Per Quadrillion Sensitivity
10:20	*Coffee Break*		
10:35	Contributed talk	**Kevin Lehmann**	Combining several spectroscopic techniques, including cw-CRDS and IR-IR double resonance to analyze the first C-H overtone region of CH3D
10:55	Invited talk	**Helen Waechter**	Fiber-Loop Cavity Ring-Down Analyzer for Cryogenic Liquids
11:20	Contributed talk	**Sze Tan**	Investigation of Backscattered Wave Effects on Cavity Ring-Down Spectrometers with Ring Cavities
11:40	Contributed talk	**Laurie McHale**	Development of Open-Path Cavity Ring-Down Spectroscopy Sensors for Methane and Ammonia
12:00	Sponsor talk	**Malcolm Gray**	*Liquid Instruments*
12:10	Sponsor talk	**Thomas Kraft**	*LayerTec*
12:15	*Lunch*		
	Afternoon Session Chair: Norbert Lang		
13:00	Invited talk	**John Hall**	The realistic prospect of being able to separate the cavity and absorber resonances very strongly: expecting an optical molecular frequency standard with a stability and reproducibility at the Hz level
13:25	Contributed talk	**Aleksandra Foltynowicz**	Optical Frequency Comb Fourier Transform Spectroscopy with Resolution beyond the Path Difference Limit
13:45	Contributed talk	**Ibrahim Sadiek**	Saturation Dynamics and Working Regimes of Saturated Absorption Cavity Ringdown Spectroscopy (Sat.-CRDS)
14:05	Contributed talk	**Erin McDuffie**	The Dark Side of Cavity Ring Down - Measurements of Nocturnal Reactive Nitrogen Species, NO3 and N2O5

14:25	Contributed talk	**Roland Fleddermann**	Cavity Enhanced Amplitude Modulated Laser Absorption Spectroscopy
14:45	**Poster Previews (M - Z)**		
15:10	*Travel to NCAR Mesa Lab and poster setup*		
16:00	**Poster session (M - Z)** with drinks at NCAR Mesa Lab		
18:00	***Banquet dinner*** *at NCAR Mesa Lab*		

Friday 19 June 2015

Time	Agenda	Speaker	Presentation Title
8:30	*Welcome in the NIST Auditorium*		
	Morning Session Chair: Adam Fleischer		
8:35	Plenary talk	**Jonathan Reid**	Cavity Ringdown Spectroscopy of Single Aerosol Particles
9:15	Invited talk	**Dan Murphy**	Opening Up and Miniaturizing Cavity Enhanced Spectroscopy
9:40	Contributed talk	**Jiahao Dong**	Cavity Polarization Mode Impedance Matching Spectroscopy
10:00	Contributed talk	**Antonio Giorgini**	An Optical-Cavity Microbalance for Surface-Plasmon-Resonance Bio-Chemical Sensing
10:20	*Coffee Break*		
10:35	Contributed talk	**Andrew Freedman**	Measuring Soot Optical Properties Using Cavity Attenuated Phase Shift (CAPS) Techniques
10:55	Invited talk	**Harold Linnartz**	Tools for Molecular Astrospectroscopy: os-BBCEAS, CESAS and CRDS
11:20	Contributed talk	**Luca Ciaffoni**	Using Cavity-Enhanced Spectroscopy to Improve Healthcare: In-Airways O2 Consumption Sensing Based on OA-CEAS
11:40	Contributed talk	**Frans Harren**	Sensitivity Enhancement in Off-Axis Integrated Cavity Output Spectroscopy
12:00	Sponsor talk	**Darren Berns**	*IDEX / Advanced Thin Films*
12:!5	Sponsor talk	**Quentin Turchette**	*Research Electro-Optics, Inc.*
12:20	*Lunch*		
	Afternoon Session Chair: Hendrik Nahler		
13:10	Invited talk	**Matthew Sellars**	Cavity enhanced rephased spontaneous emission
13:35	Contributed talk	**Patrick Dupre**	Photo-Dissociation Resonances of Jet-Cooled NO2 by CW-CRDS
13:55	Contributed talk	**Dean Sheppard**	Cavity-Enhanced Methods for Optical Detection of Magnetic Field Effects in Biological Systems
14:15	Contributed talk	**James Hodges**	Advances in Sensitive, Accurate, Precise, Ion Spectroscopy through Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy
14:35	Contributed talk	**Ove Axner**	Optimum conditions for Doppler-broadened NICE-OHMS – How to reach an Allan deviation in the 10^14 cm-1 range using a tunable laser
14:55	Plenary talk	**Jun Ye**	Cavity-Enhanced Frequency Comb Spectroscopy
15:35	*Presentation of student awards*	**Hans Osthoff**	
15:45	*Final remarks and conclusion*	**Steve Brown**	

Poster Session Wednesday 17 June 2015, 3 - 5pm at NIST

Presenter		Abstract Title
Ove	**Axner**	Doppler-broadened NICE-OHMS beyond the cavity-limited weak absorption condition
Solomon	**Bililign**	Measuring Aerosol Scattering and Absorption - Limitations of the Extinction-Minus-Scattering Method
Mixtli	**Campos-Pineda**	Study of the Ozonolysis of Ethene and 2,3-Dimethyl-2-Butene using Cavity Ring-down Spectroscopy
Idil	**Cazimoglu**	Cavity Enhanced Absorption Spectroscopy for the Detection of Plant Volatile Organic Compounds
Sean	**Coburn**	Measurements of diurnal variations and eddy covariance (EC) fluxes of glyoxal over the tropical Pacific Ocean during the TORERO 2012 field experiment
Sean	**Coburn**	Determining optical path lengths for aerosol-free cavity enhanced spectroscopy: theoretical calculations based on mirror characterization and Rayleigh scattering vs determination from measurements of collision induced absorption of oxygen molecules
Kirstin	**Doney**	Infrared cavity ring-down measurements of astronomically relevant cations
Patrick	**Dupre**	Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectrometry Modeling under Saturated Absorption
Dorothy	**Fibiger**	First Aircraft Measurements of NOy by Cavity Ring-Down Spectroscopy
Al	**Fischer**	A UV-visible Broadband Cavity Enhanced Spectrometer for Atmospheric Aerosol Extinction
Adam	**Fleisher**	Cavity Ring-Down Spectroscopy in the Quantum-Noise Limit
Aleksandra	**Foltynowicz**	Cavity-Enhanced Optical Frequency Comb Spectroscopy of High-Temperature Water in a Flame
Elizabeth	**Foreman**	High Resolution Spectroscopy of CH2OO and the Kinetics of its Reactions with Inorganic Acids
Timothy	**Gordon**	Design Of A Novel Open-Path Aerosol Extinction Cavity Ringdown Spectrometer and Data From Recent Field Deployments
James	**Hargrove**	A Portable NX and particle analyzer
Thomas	**Hausmaninger**	Doppler-broadened mid-infrared NICE-OHMS system based on an optical parametric oscillator
John	**Hoffnagle**	CRDS with cavity mode-based frequency axis for ppm-level quantitative spectroscopy
Tara	**Kahan**	Cavity-enhanced measurements of hydrogen peroxide absorption cross sections at long wavelengths: Implications for hydroxyl radical production indoors and outdoors
Jay	**Kroll**	Cavity Ring-Down Spectroscopy in Exploration of the Reactivity of Atmospheric Systems
Norbert	**Lang**	RES-Q-Trace: a mobile CEAS-based demonstrator for multiple-component trace gas detection in the MIR
Olivier	**Laurent**	ICOS ATC Metrology Lab: a facility for metrological performance assessment of prototypes and commercialized GHG analyzers
Mingyun	**Li**	Fiber Loop Supercontinuum Cavity Enhanced Absorption Spectroscopy
Elizabeth	**Lunny**	Frequency-Stabilized Cavity Ring-Down Spectroscopy of CO2 in Support of Remote Sensing

Poster Session Thursday 18 June 2015, 4 - 6pm at NCAR Mesa Lab

Presenter		Abstract Title
Georgia	**Mansell**	An in-vacuum optical parametric oscillator squeezer for gravitational wave detectors
Davide	**Mazzotti**	High-Q resonant cavities in the terahertz range: optical feedback effects on quantum cascade lasers
Hendrik	**Nahler**	CELIF: Cavity-enhanced laser-induced fluorescence
Chris	**Nichols**	Pre-excitation CRDS for Mercury
Hans	**Osthoff**	Vapor detection of nitrogen oxide containing explosives by catalytic thermal dissociation blue diode laser cavity ring-down spectroscopy
Bin	**Ouyang**	An airborne three-channel LED-based broadband cavity enhanced absorption spectrometer for measurements of atmospheric trace gases
Inga	**Piller**	A novel NIR ew-cw-CRD spectrometer for investigating heterogeneous processes at the quartz-air/water interface: Characterization and first measurements
Mary	**Rad**	Detection of S-nitrosocompunds in biological samples
Lucile	**Rutkowski**	Noise-Immune Cavity-Enhanced Optical Frequency Comb Spectroscopy
Linhan	**Shen**	Laboratory Measurements of Temperature Dependent 13C and D Kinetic Isotope Effect in The Oxidation of CH4 by O(1D) and OH
Matthew	**Smarte**	Simultaneous Kinetics and Ringdown Study of Peroxy Radical Reactions
Jean-Pierre	**van Helden**	Optical feedback cavity-enhanced absorption spectroscopy with a 3.24 µm interband cascade laser
Nick	**Wagner**	Analysis of multi-exponential decays in cavity ringdown spectroscopy
Haichao	**Wang**	Broadband absorption spectrometers using LED for the detection of NO2, NO3 and N2O5
Rebecca	**Washenfelder**	Measurements of formaldehyde using broadband cavity enhanced spectroscopy at 315 - 360 nm
Jonas	**Westberg**	Cavity-enhanced Faraday rotation spectroscopy for oxygen detection
Robert	**Wild**	Cavity ring-down system for measurement of trace gases in high vibration environments
Nick	**Yordanov**	A cyan-light-emitting diode cavity-enhanced absorption spectrometer for the measurement of reactive iodine species
Kyle	**Zarzana**	Aerosol Optical Properties Derived using Optical Spectroscopy

Assessing the precision and accuracy of cavity ring-down spectroscopy measurements

Joseph T. Hodges, David A. Long, Adam J. Fleisher, Zachary D. Reed
National Institute of Standards and Technology, Gaithersburg, MD 20899

Three attributes of CRDS: immunity to intensity fluctuations, spectra that comprise data pairs based on observations of laser frequency and cavity decay time, and long effective pathlengths, make it the method of choice in many applications requiring spectrum fidelity, high accuracy and high sensitivity. In this context, I will discuss how the precision and accuracy of ring-down spectra can be optimized and quantified. This point of view requires that one consider numerous real-world effects which lead to measured decay signals and line profiles that deviate from those predicted using overly simplistic models. I will introduce basic concepts of relative precision in decay signals, Allan deviation analysis, technical- and shot-noise-limited statistics, as well as systematic effects linked to transverse-mode-beating, finite extinction ratio, detector nonlinearity, coupled-cavities (etalons), mirror birefringence, polarization-dependent losses and optical saturation. I will also address how uncertainty in the *x*-axis (frequency) can determined and minimized using active stabilization methods. These concepts will be illustrated using a variety of cavity ring-down experiments.

Off-Axis Integrated Cavity Output spectroscopy for trace gas detection

Frans Harren
Molecular and Laser Physics, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, the Netherlands

There is a growing interest to use coherent light (from non-linear generation or lasers) from molecular trace gas detection. As the strongest molecular absorptions are in the mid-infrared wavelength region Quantum Cascade lasers, Interband Cascade lasers, Optical Parametric Oscillators, Difference frequency Generation systems are used for this. On the other hand Semiconductor lasers in the near infrared wavelength region (Telecom lasers) are also successfully used thanks to their mature technology, although the absorption strength in that wavelength region is a factor 100-100 times weaker. Such trace gas detection systems are used in environmental sciences, biology, agriculture and medical sciences. Nowadays, such coherent systems provide relatively high output power, narrow linewidth and emit almost at any desired wavelength within the infrared wavelength. Accurate detection of specific gases becomes into reach thanks to the known infrared fingerprint absorption spectrum of many molecular gases and the exact tuning capabilities of lasers. When the lasers are combined with sensitive spectroscopic techniques, such as photoacoustic spectroscopy and Off-Axis-Integrated Cavity Output Spectroscopy (OA-ICOS), gases can be determined extremely sensitive under atmospheric conditions.
Here, the performance of OPOs and Quantum cascade lasers for trace gas sensing is demonstrated in combination with OA- ICOS, we demonstrate the analysis from breath detecting CH_4, C_2H_6, CO, HCN and NO. The advantages are a rapid, sensitive, multicomponent trace gas detector for gases at sub-second time scale in single exhalations of human breath at the low part per billion levels. We present the real-time HCN production from *P. aeruginosa* strains *in vitro*, using laser-based photoacoustic spectroscopy and compare this with OA-ICOS using a near-infrared semiconductor laser.

Cavity-Enhanced Optical Frequency Comb Spectroscopy

Aleksandra Foltynowicz
Physics Department, Umeå University, Sweden

Cavity-enhanced optical frequency comb spectroscopy combines high spectral resolution and broad spectral coverage with high absorption sensitivity. It allows measurements of entire molecular bands and simultaneous detection of multiple molecular species in short acquisition times. I will describe the principles of the technique, including the various comb-cavity coupling schemes and broadband detection methods, and I will give examples of performance and applications in different wavelength ranges.

Industrial Applications of Cavity-Enhanced Spectroscopy Instruments

Alejandro Farinas
Picarro, Inc.

This lecture will focus on the commercialization of analytical instruments based on cavity-enhanced spectroscopy (CES). CES technologies offer numerous benefits when compared with incumbent solutions, and these will be described in detail. I will also touch on how the design of commercial CES instruments is constrained by required function and measurement goals. These topics will be supported via relevant case studies of CES techniques as applied to industrial applications. These applications include industrial emissions monitoring, process control, and safety; with particular reference to semiconductor manufacturing and continuous emissions monitoring for compliance. In addition to an expanding array of commercial applications, commercial CES instruments continue to be applied to scientific tasks. These types of applications, such as the deployment and management of large-scale greenhouse gas monitoring networks, will also be discussed.

Atmospheric Field Measurements Using Cavity Enhanced Spectroscopy

Rebecca Washenfelder
NOAA and University of Colorado, Boulder, CO, USA

Field measurements of atmospheric trace gases and aerosol particles are necessary to understand the chemistry and radiative properties of the atmosphere. The key trace gases are present at small concentrations, ranging from parts per trillion (pptv; approximately 2×10^7 molecules cm^{-3}) to parts per million (ppmv; approximately 2×10^{13} molecules cm^{-3}), and their detection requires sensitive analytical techniques. During the past two decades, cavity ringdown spectroscopy and other cavity enhanced spectroscopy techniques have provided important new measurements of trace gas concentrations and aerosol optical extinction. I will give an overview of atmospheric field instruments and the scientific problems they are being used to address.

Cavity Enhanced Molecular Spectroscopy for Developing Ultrastable Frequency Standards and Generating Frequency Combs in the Mid-IR

Shailendhar Saraf, Alireza Marandi, John Lipa and Robert Byer
Stanford University

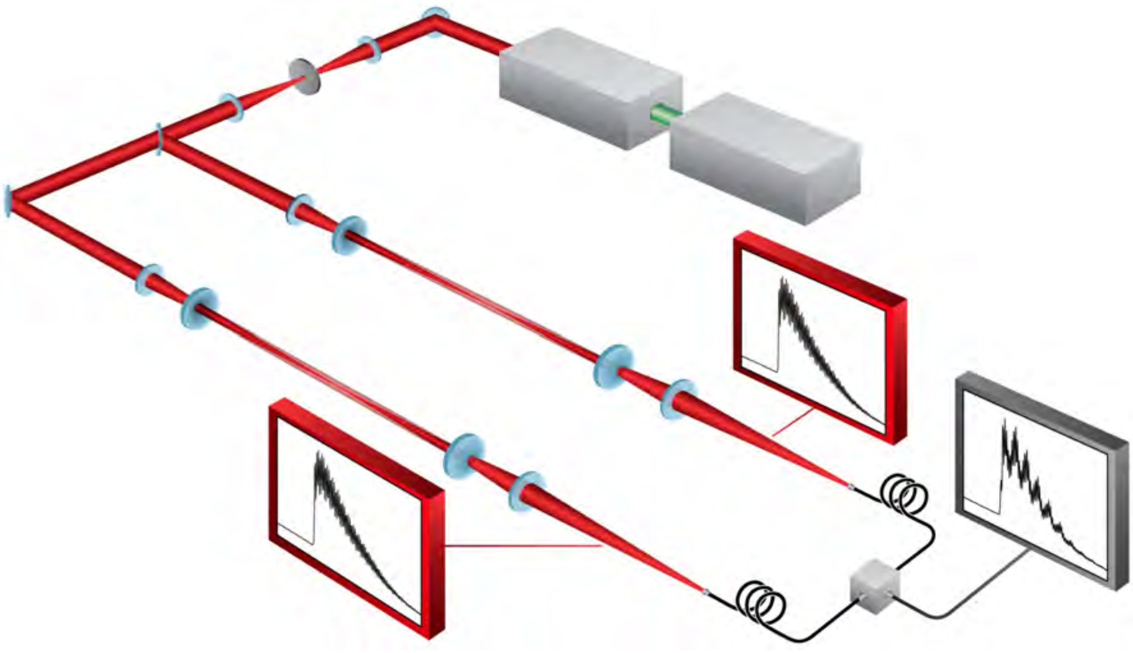
We discuss the development of a NICEOHMS-based clock at 10-15 stability using an overtone of carbon monoxide interrogated at telecom wavelengths. This robust, compact, ultrastable frequency standard with magnetic insensitivity will be flown on a future satellite mission to test for violations of Lorentz Invariance under boost conditions (Kennedy Thorndike experiment).

We also present recent results in broadband molecular spectroscopy for developing frequency combs in the mid_IR using optical parametric oscillators (OPOs) at degeneracy, where the generated signal is at half the frequency of the input pump. This technique can be used to coherently translate well-established near-IR frequency comb sources to the mid-IR spectral region between 2 and 6 micrometers.

Dual Etalon Frequency Comb Spectrometer

David W. Chandler and Kevin E. Strecker
Sandia National Laboratory

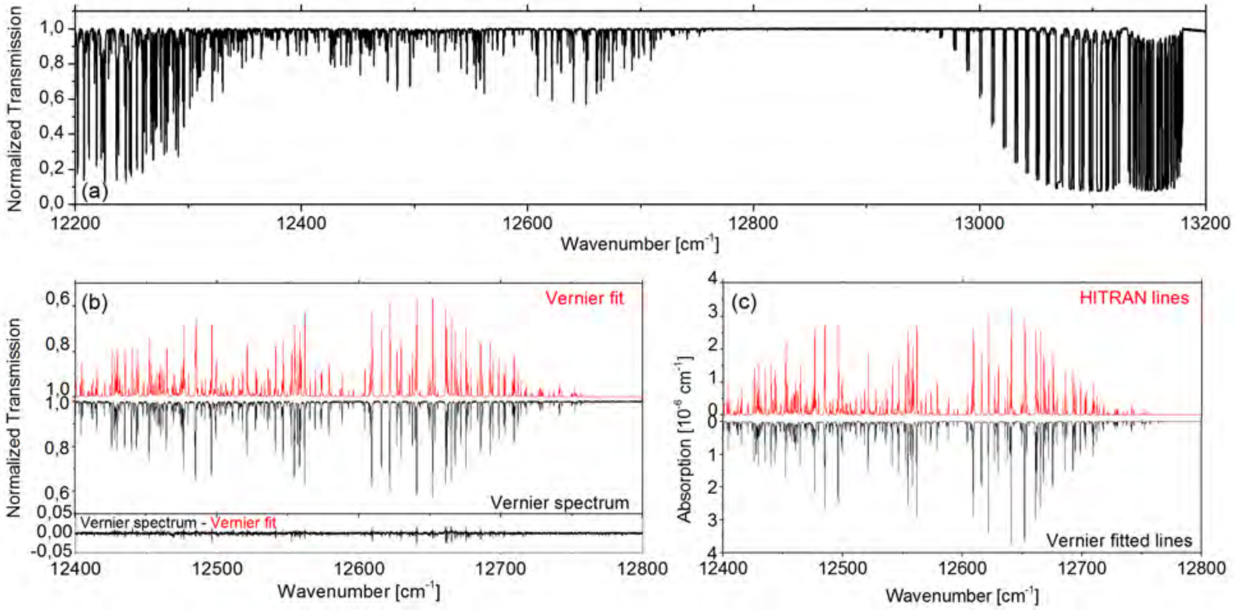
A new concept for time-resolved Fourier-transform spectroscopy has been demonstrated. This spectrometer is based on the interference between two transient frequency combs and has many potential uses including time-resolved, "broad-band" spectroscopy with a nanosecond time scale, high-resolution spectroscopy and remote sensing. The Dual Etalon Frequency Comb (DEFCOM) spectrometer utilizes two independent etalons to generate two frequency combs. The bandwidth of the combs is set by the bandwidth of the laser beam used to excite the etalons. The etalon lengths are set such that the free spectral ranges (~300 MHz) of the two etalons are slightly different, approximately 250 kHz apart in our initial demonstration. An atom or molecule placed inside of one or both of the etalons possessing an optical transition resonant with some of the frequencies present within the etalons will absorb some of the light associated with some of the frequency-comb teeth. In order to quantitatively determine the intensity of each of the frequency comb teeth, the outputs of the etalons are combined onto a single photo detector. At the detector the outputs interfere producing a transient interferogram. The spectrum is retrieved by Fourier transforming the interference pattern. As the light "rings down" from the etalons for over 100 micoseconds, and every time segment of the interferogram contains the entire spectrum, one may obtain sequential spectra with a time resolution that one chooses by selectively Fourier transforming segments of the interferogram. We demonstrate this by Fourier transforming 5 microseconds time segments sequentially for approximately 100 microseconds. In the first demonstration the (1,1,3) overtone spectrum of H_2O and the R(7) line of the weak gamma band of O_2 were recorded. A single laser pulse provided a 3 GHz spectrum across a transition with a frequency resolution of 300 MHz. This is a simultaneous multi-frequency cavity-ring-down spectrometer.



A Very Broadband Direct Frequency Comb - Cavity Enhanced Vernier Spectrometer

Lucile Rutkowski, Jérôme Morville
Institut Lumière Matière, UMR 5306 CNRS - Université Claude Bernard Lyon1

In Vernier spectroscopy an optical frequency comb (OFC) is coupled to a cavity with a free spectral range (FSR) slightly mismatched from the OFC repetition rate (frep)[1], creating a beating pattern between the cavity transmission and the OFC, with a periodicity proportional to the inverse of the FSR/frep mismatch, in the THz range, easily resolved with a standard grating. In the case of small mismatch, this comb-like pattern (the Vernier comb) offers a continuous transmission when it is spectrally swept, as one order of the Vernier comb contains several OFC modes partially transmitted by the cavity. We use a Titanium:Sapphire femtosecond laser (frep of 90 MHz), coupled to an open air cavity with a finesse of 3000. A rotating grating is placed right after the cavity, translating any frequency fluctuation of the Vernier orders in spatial displacement. The cavity length is stabilized in regards of the OFC by detecting the position of one of the Vernier orders with a split-photodiode, enabling also a precise spectral sweeping of this order across the entire OFC (tens of THz) when the grating is rotated[2]. We show in Fig.(a) Vernier spectra from the $3\nu+\delta$ band of H_2O and the A-band of O_2 around 800 nm. Taking care of the absorption and dispersion effects induced by a molecular transition on the Vernier signal, we are able to fit the parameters of the 300 water lines in the 12400-12800 cm^{-1} range, the result being presented in Fig.(b) together with the Vernier spectrum and the residuum. The retrieved absorption spectrum showed in Fig.(c) is in good agreement with the calculated spectrum under the same conditions using the HITRAN database[3]. We will further discuss the Vernier lineshapes and other significant properties of the Vernier spectrometer.



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Towards Fieldable Dual-Comb Spectroscopy For Greenhouse Gas Monitoring in Outdoor Air

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Dual Frequency-Comb Spectroscopy (DCS) is a technique akin to Fourier Transform Spectroscopy but offers faster acquisition times and simultaneous sampling over a broad band of wavelengths with negligible instrumental linewidth contribution. The coherent output of the comb permits the technique to be used for point-sensing applications with cavity enhancement to provide high sensitivity, or over open-air paths to provide column-averaged measurements over long distances. In a recent demonstration of DCS, two mutually coherent optical frequency combs centered at 1.6 μm with slightly differing repetition rates were transmitted through outdoor air over a 2 km open path[1]. CO_2 concentrations were retrieved with a precision of <1 ppm and an accuracy of ~7 ppm, whilst CH_4 concentrations were measured to <3 ppb precision with comparable absolute accuracy. In this talk, we will discuss our efforts to develop a fieldable DCS system, without compromising the performance demonstrated from the laboratory system. This will enable a range of high-precision, low-systematic error atmospheric carbon measurements. The main challenges towards a robust and fieldable dual-comb spectrometer are to reduce the overall system size, reduce its sensitivity to environmental perturbations, maintain mutual coherence between the two combs in the field (for coherent signal averaging), and maintain the absolute frequency calibration of the system (for low systematics). The planned fieldable system will cover CO_2 bands at 1.6 μm and 2.1 μm coinciding with the OCO-2 and ASCENDS missions. In addition, this broadband source will also cover H_2O, CH_4 in the 1.65μm band. We will present the current prototype dual-comb spectrometer, which has been significantly reconfigured from the laboratory design to support field operation.

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Microresonator optical frequency combs

Scott Papp
National Institute of Standards and Technology

Femtosecond-laser frequency combs have revolutionized metrology at optical frequencies and have introduced or advanced numerous applications from precision spectroscopy to quantum information. A new direction in experiments is to create frequency combs using parametric-nonlinear optics in microresonators. Such micro-combs offer a range of advantages including miniature size, low turn-on power, broadband spectra, and ultimately the potential for a fully integrated frequency comb system-on-a-chip.

I will report on experiments that explore the microcomb generation process, including modelocking dynamics and phase noise of the comb teeth, and that demonstrate applications of microcomb devices, including self-referenced optical frequency metrology. Microcombs are governed by the balance of intracavity power, microcavity mode dispersion, and Kerr-nonlinear optical mode interactions apart from a saturable absorber mechanism. Our work characterizes the rich phase diagram that describes the interplay between these physical parameters.

Time-Resolved Broadband Cavity-Enhanced Absorption Spectroscopy: a new tool for Chemical Kinetics

Leonid Sheps
Sandia National Lab, Livermore, CA

I will describe a new apparatus, constructed recently with the goal of developing novel probe methods for the study of short-lived radical intermediates in a wide range of gas-phase reactions. This approach brings a unique combination of capabilities to our experimental chemical kinetics toolkit: good time resolution, simultaneous detection of multiple species, sufficient sensitivity for dilute gas samples, and fast data acquisition. The apparatus is based on a moderate-finesse optical cavity that uses a continuous white-light probe radiation source (Xe arc lamp) and operates over broad wavelength ranges of 300 - 450 nm or 370 - 700 nm. The cavity is integrated into a flow chamber, where chemical reactions are initiated by laser photolysis. The cavity output is monitored by a CCD detector that records the time evolution over the entire spectral range for every photolysis laser shot. The spectra are averaged directly on the CCD chip, enabling the acquisition of transient absorption data with sub-nm spectral resolution and microsecond time resolution at high repetition rates in a simple, robust, and inexpensive experimental setup. I will also cover the application of this technique to our studies of Combustion and Atmospheric Chemistry. I will focus specifically on the spectroscopy and reactivity of Criegee intermediates - an elusive class of carbonyl oxides, formed in ozonolysis reactions of unsaturated hydrocarbons in the Earth's troposphere. These highly reactive transient species may influence the global budgets of VOCs, NO_x, SO_x, and OH, yet direct studies of their reactivity have only recently became feasible. Our work on the transient UV spectroscopy of two prototype Criegee intermediates, formaldehyde oxide (CH_2OO) and acetaldehyde oxide (CH_3CHOO), sheds light on their complex electronic structure and allows direct measurements of their reactions with SO_2, water, carboxylic acids, and other potentially important tropospheric compounds.

Laser-Induced Plasmas in Ambient Air for Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy

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The emission from a laser-induced plasma in ambient air, generated by a high power femtosecond laser, was utilized as pulsed incoherent broadband light source in the center of a quasi-confocal high finesse cavity. The time-dependent spectra of the light leaking from the cavity was compared with those of the laser-induced plasma emission without the cavity[1]. It was found that the light emission was sustained by the cavity despite the initially large optical losses of the laser-induced plasma in the cavity. The light sustained by the cavity was used to measure part of the S1 <- S0 absorption spectrum of gaseous azulene at its vapour pressure at room temperature in ambient air as well as the strongly forbidden gamma-band in molecular oxygen at 628 nm.

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Microcavity Raman Laser and Its Application in Single-Nanoparticle Detection

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Peking University

Stimulated Raman scattering holds great potential for various photonic applications, such as label-free high sensitivity biomedical imaging, and for extending the wavelength range of existing lasers, as well as for generating ultra-short light pulses. In high Q microcavities, stimulated Raman scattering, also called Raman lasing, has been experimentally demonstrated to possess ultra-low thresholds, due to the greatly increased light densities in microcavities. Such microcavity Raman lasers have great potential for sensing applications, using the following mechanisms. Raman lasing can initially occur in any of the two initially degenerate counter-propagating traveling wave modes. These two traveling wave modes couple to each other due to backscattering when a nanoscale object binds to the microcavity surface. For a sufficiently strong coupling, in which the photon exchange rate between the two initial modes becomes larger than the rates of all the loss mechanisms present in the system, two new split modes form and can lase simultaneously. Thus, by monitoring the mode splitting, i.e., the beat frequency of the split-mode Raman lasers, ultrasensitive nanoparticle detection can be realized. In this talk, we report the experimental demonstration of single nanoparticle detection using split-mode microcavity Raman lasers. The principles underlying this Raman lasing sensor are first analyzed and demonstrated in air, by controllably binding or removing single 50-nm-radius polystyrene (PS) nanoparticles to and from the cavity surface using a fiber taper, and measuring the changes in the beat frequency of the two split Raman lasers. We then perform real-time single nanoparticle detection in an aqueous environment using this method.

Open-Access Optical Microcavities for Lab-on-a-Chip Spectroscopy

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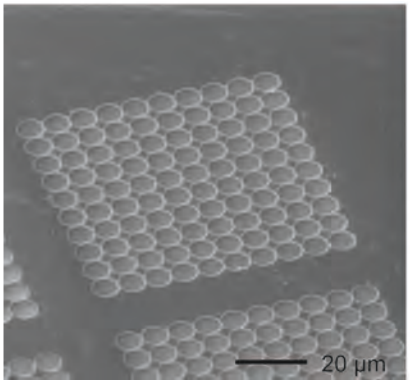
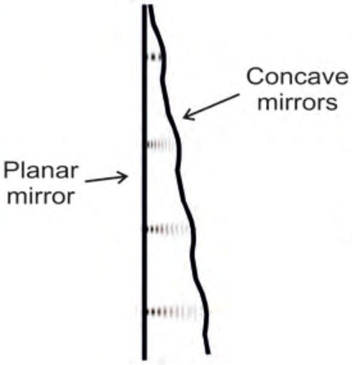
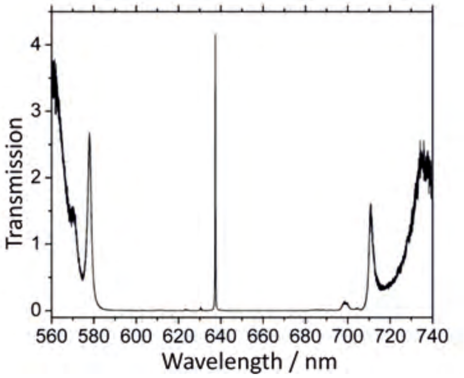
Open-access optical microcavities provide a novel approach to performing label-free on-chip spectroscopic measurements in a microfluidic environment. Arrays of concave micromirrors are fabricated by focused ion beam milling of a suitable substrate followed by deposition of a suitable dielectric mirror coating. Arrays of microcavities are constructed by positioning a micromirror array a few microns from a planar dielectric mirror. The resulting cavities have mode volumes of tens of femtolitres, with cavity finesse on the order of 10^3 to 10^4. The small cavity lengths result in a large free spectral range, such that only one or a few wavelengths are resonant inside the cavity within the reflection bandwidth of the mirrors. This property is key to the use of the cavities in chemical sensing applications. The mirror separation can be controlled with sub-nanometre precision using piezoelectric actuators, providing a simple mechanism for tuning the cavity resonances to any desired wavelength. For initial proof-of-concept work, the microcavity arrays have been incorporated into a flow cell, allowing liquid samples to be flowed into and out of the cavities. To date, we have demonstrated both refractive index and absorption sensing down to the level of a few thousand molecules, as well as the ability to track the motion of individual nanoparticles within the cavities through their interaction with the various longitudinal and transverse cavity modes. Recent results from these studies will be presented.







Bioanalytical Applications of Liquid Phase BBCEAS

Meez Islam, Zuzana Bajuszova, Godfrey Pasarayi and Zulf Ali
Teesside University, School of Science and Engineering, Borough Road, Middlesbrough, TS1 3BA, United Kingdom

We present new results from the ongoing EU FP7 project CE-microArray on the application of BBCEAS to the measurement of bio assays in 96 well microtitre plates. Multiplexed measurements from up to 4 wells simultaneously have been demonstrated in a prototype cavity enhanced microplate reader.

Low Noise Cavities in Interferometric Gravitational Wave Detectors

Sheila Rowan
University of Glasgow, UK

The first upgraded detectors in the global network of interferometric gravitational wave antennae will start taking data in the next few months, initiating a new program of searches for gravitational waves from astrophysical sources via sensing the effects of the waves on the relative displacements of suspended mirrors. These detectors represent the most sensitive displacement measuring devices ever constructed, with core parts of the instruments being formed from optical cavities incorporating mirrors and mirror coatings of ultra-low thermal noise. Improving detector sensitivities further will require further improvements to the thermal noise performance of the cavities, making this a highly active research area in the field. This talk will discuss briefly the status of the current instruments, the performance of the optical cavities used, and cover some of the avenues of research being explored in aiming for even better thermal-noise-limited sensitivities.

Measurements of Aerosol Optical Proeprties Using Broadband Cavity Enhanced Spectroscopy

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The optical properties of organic aerosols are important for determining their radiative forcing in the atmosphere and, subsequently, their impact on climate. The high abundance of natural and anthropogenic volatile organic compounds in the atmosphere leads to formation of secondary organic aerosols (SOAs) via photochemical reactions with OH, NO_3, and O_3. In the atmosphere, aerosols undergo further processing with oxidizing species, thus changing their chemical, physical, and optical properties. Despite their acknowledged importance, understanding the optical properties of aerosols with good precision, and how these properties depend on chemical composition and structure remain poorly understood. We will describe the use of broadband cavity enhanced spectroscopy to investigate the optical properties of different model aerosols upon atmospheric reactions. We will describe a newly developed broadband aerosol spectrometer that can retrieve aerosol optical properties at short wavelengths, from 320 nm, a less explored wavelength range. We will describe closure studies between this instrument and a photoacoustic cell and cavity ring down spectrometer. Finally, we will present an overview summary of SOA optical properties from several sources and aging pathways.

Near-Infrared Cavity Ringdown Spectroscopy of Intermediates in Complex Chemical Reactions

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A difficult challenge for any spectroscopic technique is the observation, characterization, and quantification of weakly absorbing molecular species in complex chemical mixtures. The species of interest may be weakly absorbing due to either low concentration or low oscillator strength, or a combination of both. Complex chemical mixtures have the additional difficulty of interference from typically stronger absorptions from other molecules. Near-infrared cavity ringdown spectroscopy (NIR-CRDS) offers a powerful tool to address these challenges. The NIR is a convenient spectral window, lower in frequency that the electronic transitions of most non-reactive molecules and containing only weak combination and overtone vibrational bands. However electronic transitions of many reactive chemical species fall into the NIR due to their open-shell electronic nature. The lowest singlet-triplet transitions of molecules are often in this region, e.g. the singlet-triplet transition of O_2 which is important in fields as far separated as atmospheric chemistry and photochromatic cancer therapy. Key oxidation intermediates in combustion often have low-lying electronic transitions, e.g. the peroxy radicals, RO_2, where R is any hydrocarbon functional group, like methyl, ethyl, etc. Atmospheric pollutants, like NO_3, likewise have a NIR electronic transition. This talk will discuss NIR-CRDS of both room temperature and jet-cooled reactive chemical intermediates. It will show the nature of the spectra at both temperatures. It will further discuss the analyses of the spectra and the information resulting therefrom as well as its significance for several areas, including chemical diagnostics and the benchmarking of electronic structure calculations.

Quantum Cascade Laser Spectroscopy for Radiocarbon Detection

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[3] *National Physical Laboratory, Teddington, UK*

An instrument based on mid-infrared laser spectroscopy and a quantum cascade laser for the detection of radiocarbon is presented. The measurement is based on cavity ring-down spectroscopy, and a high sensitivity is achieved with a simple setup[1]. By using a tunable narrow-linewidth continuous-wave laser, and by selecting a suitable mid-infrared absorption line of radiocarbon dioxide at 4527 nm, it is possible to minimize spectral interference from other isotopes of carbon dioxide. In addition, issues related to optical feedback and interference fringes have been considered in order to achieve high sensitivity. The instrument was tested using a standardized sample containing elevated levels of radiocarbon. Radiocarbon dioxide could be detected from samples with an isotopic ratio $^{14}C/C$ as low as 50 parts-per-trillion, corresponding to an activity of 5 kBq/m3 in pure carbon dioxide, or 2 Bq/m3 in air after extraction of the carbon dioxide from an air sample. While radiocarbon has a natural abundance of 1.2 parts-per-trillion relative to the total amount of carbon, much higher levels are present in nuclear power environment. Radiocarbon is present in all parts of nuclear power plants and is mostly released in the form of carbon dioxide. This instrument is therefore aimed at the monitoring of radioactive gaseous emissions, during the operation and decommissioning of nuclear power plants. Its high sensitivity also makes it the ideal tool for the detection of leaks in radioactive waste repositories, where radiocarbon is present at high abundance and released as radiocarbon dioxide through biodegradation. The instrument is simple, compact, and robust, making it the ideal tool for on-site measurements.

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Spectroscopic Detection of $^{14}CO_2$: Towards Parts Per Quadrillion Sensitivity

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Measurement of radiocarbon concentration has important and countless applications in several fields of investigation, e.g. environmental monitoring, nuclear security, dating of biological samples, pharmacology. Our group has already demonstrated that saturated-absorption cavity ring-down (SCAR) spectroscopy[1], performed on the very strong transitions of radiocarbon dioxide ($^{14}CO_2$) around 4.5 micron[2], enables the detection of this isotopologue at extremely low concentrations, well below the natural abundance of 1.2 ppt, and even at high enrichment values[3]. Recently, we have been improving the experimental apparatus in order to simplify it, to increase the achievable sensitivity and to move towards a field-deployable analyzer. The comb-referenced difference-frequency-generated source has been replaced by a pair of quantum cascade lasers directly emitting at 4.5 micron and referenced to a molecular transition. The dry-ice cooling of the spectroscopic cavity has been replaced by a Stirling cryo-cooler operated at a lower temperature. Preliminary results show that this new setup is very promising in terms of overall sensitivity, robustness, compactness and simplicity in view of field-deployable instrumentation.

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Fiber-Loop Cavity Ring-Down Analyzer for Cryogenic Liquids

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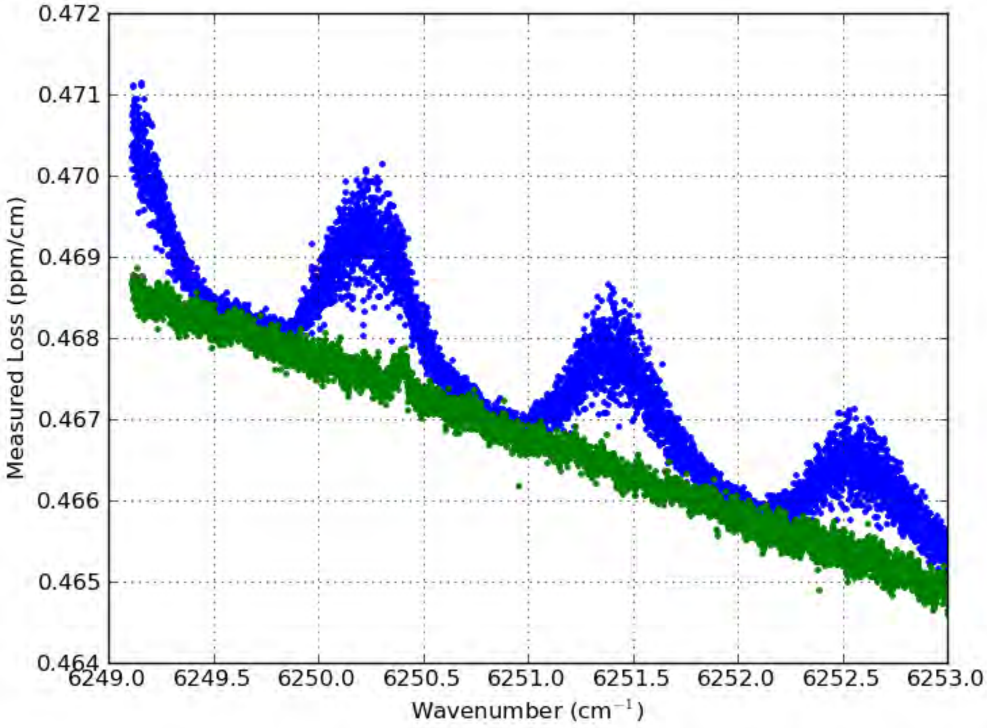
Cryogenic liquids are used for many purposes, from freezing food to hydrogen fuel cells to MRIs. All of these applications share a common need to measure impurities in cryogenic liquids. For example, water contamination can cause filters and transfer lines to ice up, and accumulation of oxygen and hydrocarbons condensing in cryogenic liquids poses a serious risk of explosion. Nonetheless, there is currently no technology to directly measure the concentration of impurities in the liquid phase inside air separation units, cryogenic storage tanks, or filling stations. Instead, contamination is measured in the gas phase by various instruments. But, the gas phase does not necessarily have the same impurity concentrations as the liquid phase due to different boiling-point temperatures of the contaminants and the matrix. Therefore, the levels of contamination can be considerably larger in the liquid phase, allowing impurities to accumulate and yet go undetected in gas phase measurement. Combining the robustness of fiber sensors with the sensitivity of CRDS, Fiber-Loop Cavity Ring-Down Spectroscopy has been proven to be a promising alternative to gas-phase analyzers. We will present a ring-cavity formed by a strand of optical fiber bent into a loop, with one section of the fiber loop replaced by a sensing element where the light can interact with the sample. Similar to mirror-based CRDS, light is coupled into the loop and its decay time is measured. We compared the performance of several types of sensing elements: fiber tapers, side-polished fibers, and core-only fibers; and we examined their potential to reach detection limits of contaminants in the parts-per-million range. Our results indicate that Fiber-Loop Cavity Ring-Down Spectroscopy is suitable for measuring contaminants in cryogenic liquids.

Investigation of Backscattered Wave Effects on Cavity Ring-Down Spectrometers with Ring Cavities

Sze Meng Tan, Yonggang He
Picarro, Inc.

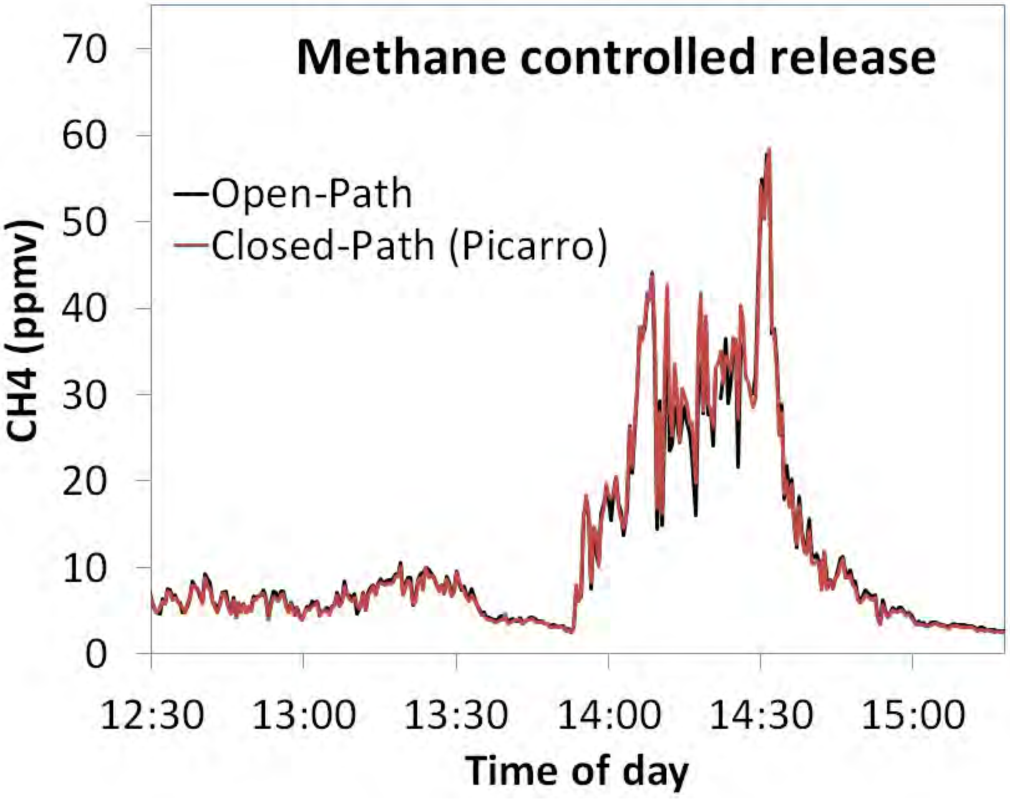
Imperfections on the surfaces of intra-cavity elements in optical ring resonators can cause scattering of light from one mode to a nearly degenerate counter-propagating mode. This can cause well-known problems such as mode locking in laser gyroscopes. We present theoretical and experimental results showing how backscattering affects CRDS measurements made with high-finesse ring cavities. Coupling between counter-propagating modes gives rise to a non-exponential ring-down waveform which biases the loss measurement. A stochastic simulation of the build-up of the mode amplitudes shows that it also increases the shot-to-shot variability, limiting the overall sensitivity. The frequency-dependence of the backscattering process can also be analyzed and is found to produce a ripple in the empty cavity spectrum whose form is determined by the cavity geometry. Under appropriate assumptions about the nature of the scattering process, it is found that improved results may be obtained by measuring the intensities of both counter-propagating waves and adding these together electronically. The sum of intensities decays exponentially, and the stochastic fluctuations in the individual mode intensities are anti-correlated, reducing the shot-to-shot noise. Figure 1 shows an empty cavity spectral scan from a ring cavity when using conventional processing (forwards wave only, in blue) and when the forwards and backwards intensities are added together (in green). This technique has been used in the manufacture of cavity ring-down spectrometers for measuring the isotopic composition of carbon dioxide and methane at near atmospheric concentrations. It has led to a significant improvement in the measurement precision and product yield.



Development of Open-Path Cavity Ring-Down Spectroscopy Sensors for Methane and Ammonia

Laurie McHale, Soran Shadman, Azer Yalin
Colorado State University, Fort Collins, Colorado, USA

We present the development of open-path cavity ring-down spectroscopy (CRDS) for the measurement of atmospheric methane and ammonia in the mid-infrared (MIR). In comparison to more common closed-path instruments, open-path CRDS sensors have the potential for lower mass (<5kg) and power (<50W), enabling more remote deployments and use on small unmanned aerial systems (sUAS). Such sensors are useful for studies of emissions from oil and gas extraction, and agricultural operations. An initial proof of principle open-path methane CRDS sensor has been developed at 1.73µm to investigate sensitivity, effects of mirror reflectivity degradation and aerosol particles. A simple purge system, utilizing a small HEPA filter and diaphragm pump (<50 g) was developed to maintain mirror reflectivity. Mirror reflectivity (R>0.99995) was preserved over long duration testing (>100 hrs) in the laboratory, outside and in the presence of high aerosol concentrations. Aerosol particles in the cavity contribute to quasi-constant background absorption (particles <1 µm) as well as fluctuations (varying presence of particles >1µm). A software filtering technique, which bins points by frequency and time, was implemented to mitigate the particle induced fluctuations. Binning absorption measurements in a small frequency range, outliers due to aerosols are removed and the spectral signal preserved. Using these approaches, a noise equivalent sensitivity of ~3 x 10^{-10} cm^{-1} (in 1 s) has been demonstrated, within a factor of ~3 of closed-path measurements. Comparisons were made against a commercial closed-path CRDS instrument (Picarro 2203) during a controlled release of methane in a warehouse, partially open to the outdoors, with good agreement. Ongoing efforts to develop open-path CRDS sensors utilizing strong fundamental vibration bands in the MIR will also be discussed, specifically an ammonia sensor at 10.3 µm (with a quantum cascade laser) and methane sensor at 3.65 µm (using an interband cascade laser).



The realistic prospect of being able to separate the cavity and absorber resonances very strongly: expecting an optical molecular frequency standard with a stability and reproducibility at the Hz level

John Hall
JILA, NIST and University of Colorado

Detailed analysis shows that saturated absorption of CO2 in a proper cavity can give ~3% increased cavity-transmitted power at the molecular resonance frequency near 1560 nm. While the JILA vertical vibration-resistant cavity design was demonstrated to give sub-Hz linewidth of the locked laser, the calculated high molecular resonance S/N promises absolute frequency stability at the Hz level at 1s and beyond. In addition to NICE-OHMS, the toolbox now contains a new anti-RAM solution, the "RAM-Buster", which has shown Residual AM control of < 3 ppm for days, where the non-zero limit came from spurious rf pickup in the photodetector of the first setup.

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Optical Frequency Comb Fourier Transform Spectroscopy with Resolution Beyond the Path Difference Limit

Aleksandra Foltynowicz[1], Alexandra C. Johansson[1], Amir Khodabakhsh[1], Lucile Rutkowski[1], Piotr Maslowski[2], Grzegorz Kowzan[2], Kevin F. Lee[3], Martin E. Fermann[3]
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Fourier transform spectrometers (FTS) based on optical frequency combs (OFC) allow detection of broadband molecular spectra with high signal-to-noise ratios within acquisition times orders of magnitude shorter than traditional FTIRs based on thermal sources[1]. Moreover, high absorption sensitivity is obtained using optical enhancement cavities[2]. Due to the pulsed nature of OFCs the interferogram consists of a series of bursts rather than a single burst at zero optical path difference (OPD). The comb mode structure can be resolved by acquiring multiple bursts in both mechanical FTS systems[3] and dual-comb spectroscopy[4]. However, in all existing demonstrations the resolution was limited either by the maximum OPD between the interferometer arms or by the total acquisition time. We show that it is sufficient to acquire an interferogram in a symmetric range around a single burst with length precisely matched to the comb line spacing in order to exceed the spectrometer's OPD-limited resolution and measure the intensity change of the individual comb lines. Our method allows measurements of broadband spectra with absorption lines narrower than the OPD-limited resolution without any influence of the instrumental lineshape function, and reduces the acquisition time and interferometer length by orders of magnitude. We demonstrate this by measuring undistorted low pressure CO_2 and CO absorption lines with linewidths narrower than the OPD-limited resolution using OFC-based mechanical FTS in the near- and mid-infrared wavelength ranges. The near-infrared system is based on an Er:fiber femtosecond laser locked to a high finesse cavity, while the mid-infrared system is based on a Tm:fiber-laser-pumped optical parametric oscillator coupled to a multi-pass cell.

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Saturation Dynamics and Working Regimes of Saturated Absorption Cavity Ringdown Spectroscopy (Sat.-CRDS)

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In contrast to the well-established CRDS procedures in the linear absorption regime, no mature implementation for trace gas measurements in the presence of absorption saturation has been introduced yet. Modeling the saturation process is complex: it depends on the characteristics of the absorbing species, its interaction with the surrounding gas as well as on the temporal and spectral characteristics of the laser beam. Recently, a new approach of CRDS has been developed that relies on saturating the gas absorption using narrow linewidth continuous-wave (cw) laser sources[1]. Sat.-CRDS allows one to extract both the gas absorption and the cavity loss from a single ringdown signal simultaneously, resulting in lower detection limits. This is possible because the degree of sample saturation changes during the ringdown event causing non-exponential behavior. In this work, a new cw-CRDS experiment based on a high power cw-IR-OPO system has been setup. The dynamics of the saturation process, which is controlled by the degree of saturation as well as the relaxation rate relative to the empty cavity decay rate, has been investigated in detail. The transition from the highly saturated absorption regime to a lower degree of saturation has been studied. Both the intracavity intensity as well as the saturation intensity have been varied independently. Moreover, the saturation intensity was tuned either by changing the relaxation rate or by selecting absorption lines with different line strengths. A statistical analysis that provides the ultimate working conditions of Sat.-CRDS method will be introduced. The optimal values for the degree of saturation, which strongly controls the standard error as well as the sensitivity of the method, have been determined. Finally, the validity of the Sat.-CRDS model to retrieve the gas absorption and the empty cavity loss at different concentrations of the absorbing species has been tested.

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The Dark Side of Cavity Ring Down - Measurements of Nocturnal Reactive Nitrogen Species, NO_3 and N_2O_5

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[3]*NOAA Earth System Research Laboratory - Chemical Sciences Division*
[4]*NSF Geospace Sciences Postdoctoral Fellow*

The nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) are important nocturnal trace gases in the troposphere. While NO_3 photolysis leads to moderate daytime levels (<1 pptv) of both species, nighttime conditions allow these species to build to higher mixing ratios (>10 pptv) and participate in further nocturnal chemistry. NO_3 is important for the oxidation of VOCs (volatile organic compounds) and sulfur compounds, while N_2O_5 can react heterogeneously with aqueous aerosol to form nitric acid (HNO_3) or nitryl chloride ($ClNO_2$). The nocturnal chemical pathways of NO_3 and N_2O_5 greatly impact the tropospheric reactive nitrogen budget, which has larger consequences and implications for both air quality and climate. Cavity Ring-Down Spectroscopy (CRDS) is the only current method for simultaneous measurements of NO_3 and N_2O_5. Here we present the latest developments in a real-time high sensitivity instrument that has been designed and developed for field deployment, specifically for mobile platforms such as aircraft. Ambient NO_3 is measured directly in the first channel by probing its strong absorption peak with a diode laser centered at 662 nm. In a second channel, N_2O_5 is thermally converted into NO_3 and then measured using the same spectral feature. Subtraction of these two channels provides a simple quantitative measurement of ambient N_2O_5. This presentation will discuss the operational details of this instrument, the current calibration procedure for N_2O_5, and applications to current topics in the atmospheric community regarding N_2O_5 chemical mechanisms.

Cavity Enhanced Amplitude Modulated Laser Absorption Spectroscopy

Roland Fleddermann[1], Jiahao Dong[1], Ya J. Guan[1], Timothy T-Y. Lam[1], Malcolm B. Gray[2], and Jong H. Chow[1]
[1]*Australian National University, Canberra, Australia*
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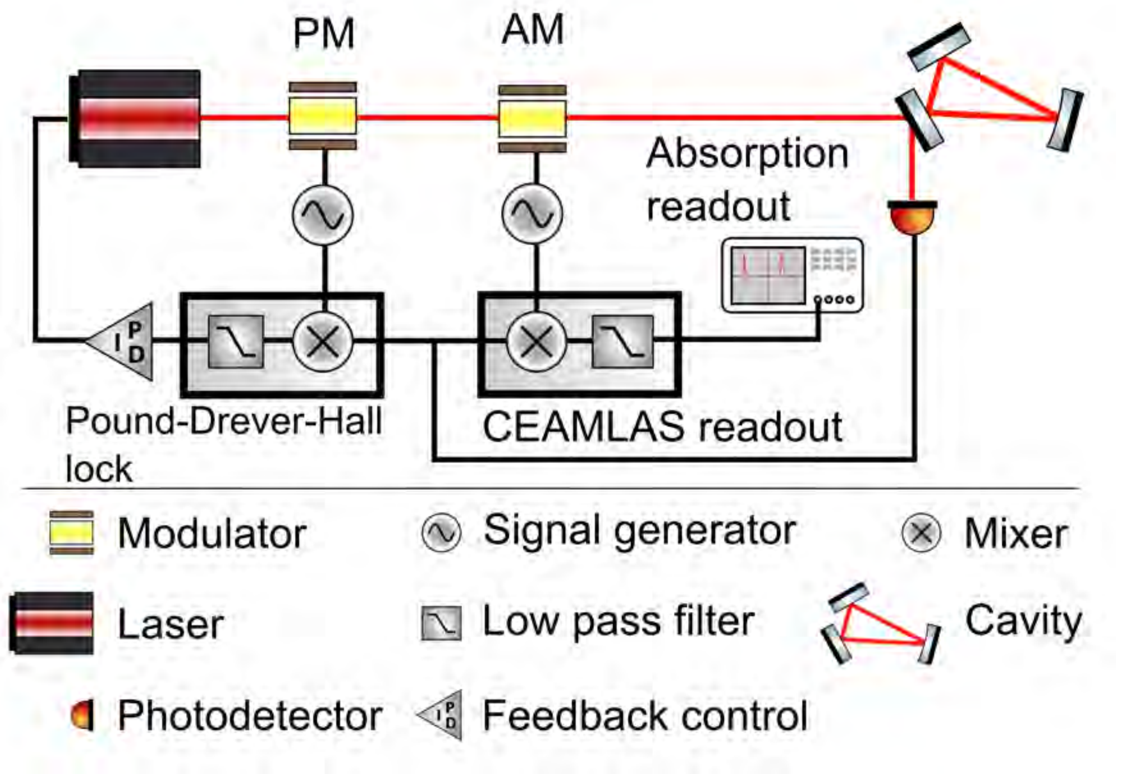
Over the past decade, laser absorption spectrometers have attracted plenty of research interest because of their potential to act as field-deployable gas/isotope analyzers. For this technique, a long interaction length between interrogating light and the gas sample is desirable to improve sensitivity. The most sensitive laser absorption spectrometer to date is noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS). It combines absorption enhancement from a 100000 finesse cavity with laser frequency modulation to achieve a quantum shot-noise limited sensitivity. We have developed another absorption readout technique named cavity enhanced amplitude modulated laser absorption spectroscopy (CEAMLAS) using a lower finesse while still maintaining excellent absorption sensitivity. This improves usability in field deployed applications by avoiding the strict cleanliness requirements associated with high finesse cavities. We report the implementation of a CEAMLAS spectrometer, demonstrating that it can be readily used as a gas sensor or an isotope analyzer delivering real-time and continuous absorption data. We also discuss current noise limits and improvements made to achieve better sensitivity in a real life setup, as well as potential future developments for this technique.



Cavity Ringdown Spectroscopy of Single Aerosol Particles

Jonathan P. Reid[1], Andrew J. Orr-Ewing[1], Michael I. Cotterell[1], Bernard J. Mason[1], Thomas C. Preston[2], Rose Willoughby[1] and Jim S. Walker[1]
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Light scattering and absorption is widely used to probe the properties of dispersed colloidal particles (e.g. aerosol), providing information on size, shape and composition. Indeed, optical extinction by aerosols plays a key role in atmospheric optics, directly influencing the radiative balance of the atmosphere and impacting climate. Typically, light scattering is measured over a wide range of scattering angles and absorption can be inferred from a photoacoustic response. To determine optical cross-sections directly, cavity ringdown is widely used to probe an ensemble of particles. In many instances, rather than inferring the properties of particles from a single snapshot of optical extinction by a disperse ensemble, measurements of the evolving properties of a single particle are desirable. For example, to constrain and improve model predictions of light extinction by atmospheric aerosol, new tools should provide refined information on the dependence of light extinction on relative humidity, particle composition and heterogeneous aging, requiring time-dependent measurements. We will present a new technique using a combination of a Bessel beam to manipulate individual particles (200 to >3000 nm radius) and cavity ringdown spectroscopy for ultrasensitive measurements of their optical cross-section. Particles are spatially separated along the propagation direction of a Bessel beam according to their size and refractive index and the interplay of the forces arising from Stokes drag and radiation pressure, referred to as optical chromatography. Once captured, a particle can be moved into an optical cavity formed by two highly reflective mirrors. The time constant for the ringdown in light coupled within the cavity is used to measure the optical cross-section of the individual particle with extremely high accuracy. Thus, an individual particle can be captured indefinitely and its change in optical cross-section measured with change in environmental conditions.

Opening Up and Miniaturizing Cavity Enhanced Spectroscopy

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NOAA ESRL Chemical Sciences Divsion, Boulder, Colorado, US

I will discuss a method to open up cavity ring down spectroscopy to ambient conditions rather than conditions inside of an instrument. This is useful for maintaining relative humidity or for reactive molecules that would be lost in an inlet line leading into a conventional instrument. The instrument allows us to study the nearly exponential growth in light scattering at humidities above 90%, an area not accessible to other instruments. I will also discuss efforts to simplify and miniaturize a cavity ring down system for aerosol extinction. A complete instrument weighing 1 or 2 kg is feasible.

Cavity Polarization Mode Impedance Matching Spectroscopy

Jiahao Dong[1], Timothy T-Y. Lam[1], Roland Fleddermann[1], Ya Jie Guan[1], Malcolm B. Gray[1,2], and Jong H. Chow[1]
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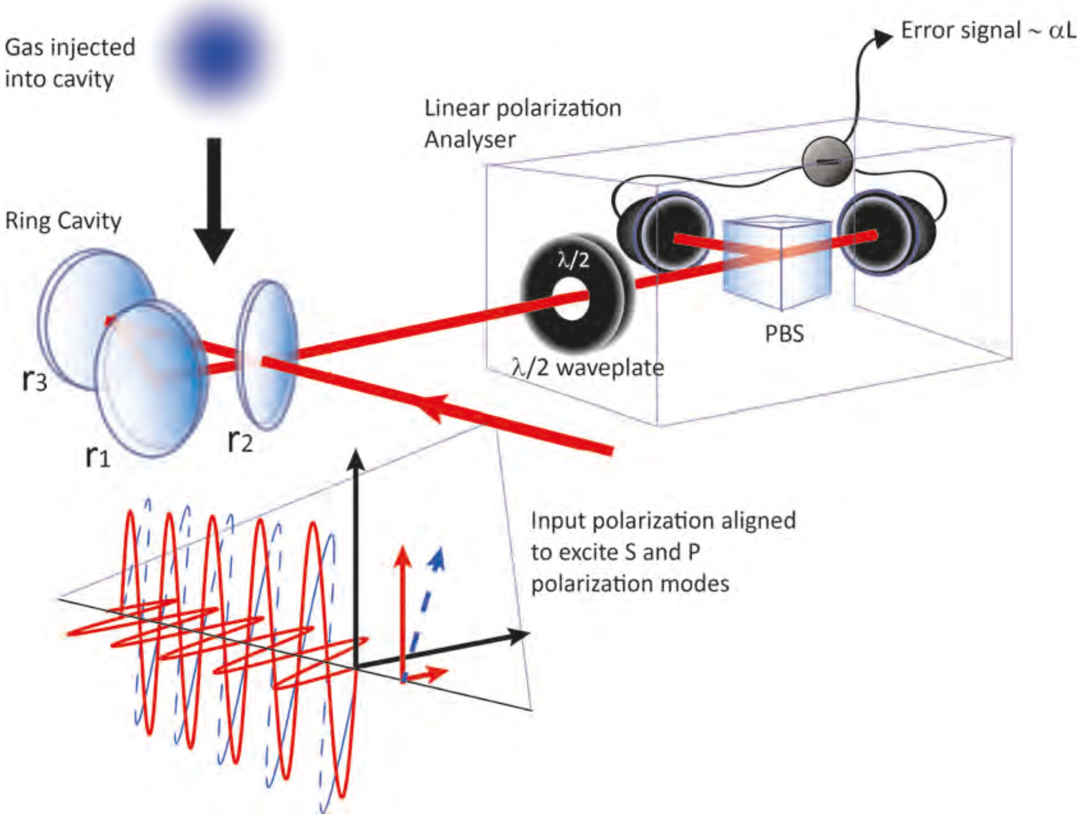
Cavity enhanced gas analyzers have been used in many research areas, and are now finding their way into industrial applications. Here we present a new cavity enhanced spectroscopy technique named Cavity Polarization Mode Impedance Matching Spectroscopy (PIMS). Besides being a real-time readout and having high absorption sensitivity, PIMS also uses a low complexity, modulation-free setup, making it a promising candidate for both field-deployable and laboratory-based applications. PIMS belongs to a new family of techniques that measures gas absorption by probing the impedance matching condition (also known as coupling condition) of an optical cavity. It uses the intrinsic characteristic of a birefringent cavity with nondegenerate polarization modes to provide the desired impedance matching readout. Light in one polarization is used to probe the intra-cavity gas absorption. The orthogonally polarized light becomes a reference as it is not resonant with the cavity. A linear polarization analyzer is used to interfere these two polarization modes. The resulting interference signal is linearly proportional to the intra-cavity absorption. This analyzer also provides common-mode rejection of laser intensity noise, largely removing its influences on the absorption signal. We conducted a proof of concept experiment by using this PIMS spectrometer to measure a rovibrational overtone of CO_2 at 1572.992 nm. An absorption line was obtained which accurately reconstructed the predicted Voigt line profile. This proof of concept spectrometer exhibits a low noise equivalent absorption (NEA) that is already comparable to some existing cavity enhanced systems. As these results demonstrate, PIMS offers an elegant alternative architecture for cavity enhanced high sensitivity gas absorption measurements.



An Optical-Cavity Microbalance for Surface-Plasmon-Resonance Bio-Chemical Sensing

Antonio Giorgini[1], Rosa Zullo[1], Saverio Avino[1], Pietro Malara[1], Gianluca Gagliardi[1], Paolo De Natale[2]
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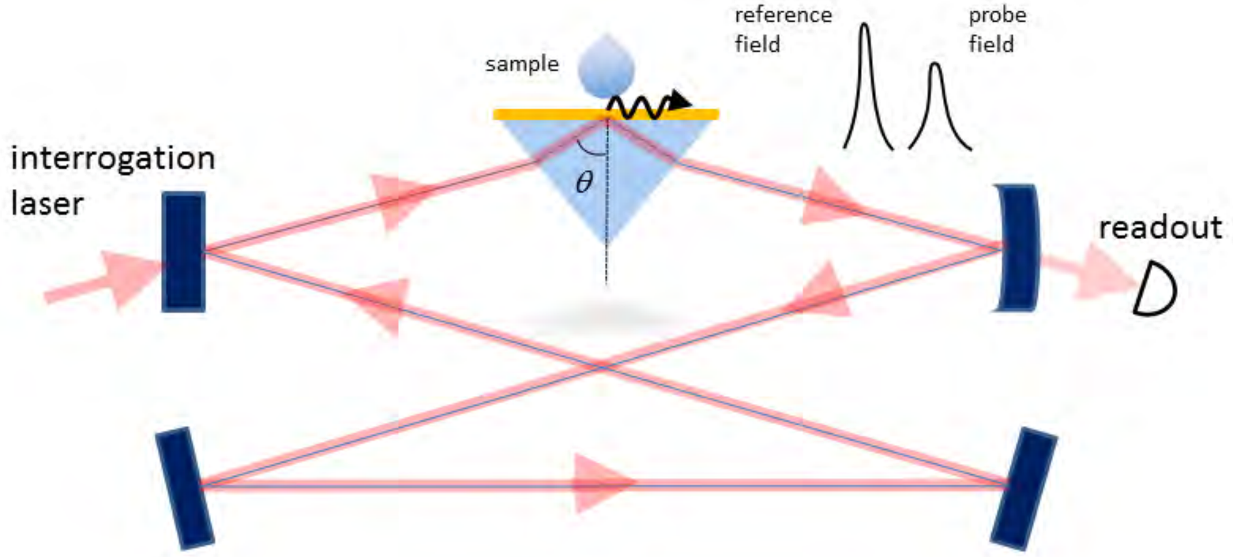
Surface Plasmon Resonance (SPR) based sensors play a leading role in chemical and biochemical sensing due to their high sensitivity and the ability to implement real-time label-free, selective sensing protocols. Plasma waves can be coupled at the interface between a metal layer and a dielectric medium under given condition of incidence angle, polarization, wavelength and permittivity. Due to their short penetration depth, near the interface, plasma waves probe directly the surface chemical activity. Although the best techniques can ultimately measure refractive-index changes down to 10-7RIU, detection of low weight molecules (< 400Da) at low concentrations (pM) or low-copy number heavier targets is still challenging. Many efforts have been spent in pushing SPR detection limit further, through improved chip engineering and/or immobilization protocols. The fundamental limiting factor is still represented by the intrinsic light source and detector noise. In this work, we present experimental investigations on new methods for SPR sensors interrogation. The starting point is the integration of the sensing element, mounted on a prism (Kretschmann configuration), as an intermediate mirror of an optical resonator. This setup allows readout of the surface-plasmon coupling changes from new physical observables related to the intracavity radiation, including time, polarization and resonant frequency[1,2]. The work has focused on noise-immune interrogation methodologies based on differential measurements on the orthogonally-polarized SPR fields that are simultaneously resonating in the cavity.



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Measuring Soot Optical Properties Using Cavity Attenuated Phase Shift (CAPS) Techniques

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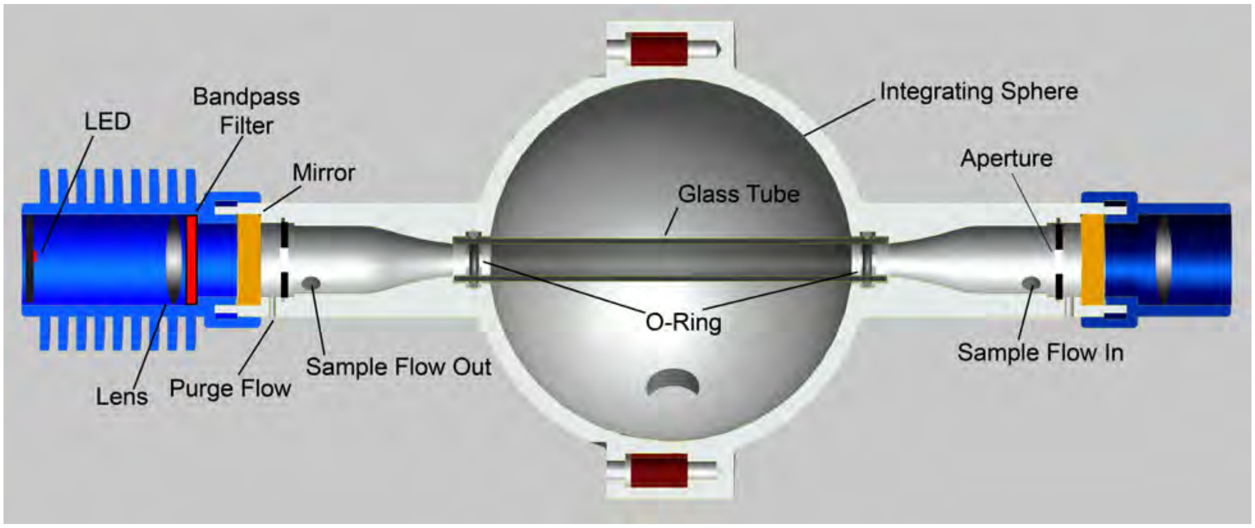
Center for Sensor Systems and Technology, Aerodyne Research, Inc., Billerica, MA, U.S.A.

We describe a robust, field deployable monitor which employs cavity attenuated phase shift techniques to simultaneously measure both ambient particle optical extinction and scattering (and thus single scattering albedo, SSA) on the same sample volume with high precision and accuracy. In order to measure the scattering, a Lambertian integrating sphere is incorporated within the optical cavity. The scattering measurement is calibrated using small salt particles and using the extinction channel as an absolute standard. Typical precision levels in both channels are less than 1 Mm^{-1} (1s, 1σ). With an appropriate change in mirrors and LED, measurements can be made at wavelengths ranging from 450 to 780 nm. This range is limited at long wavelengths by the availability of suitable detectors and at short wavelengths by the availability of suitable mirrors. We will present results of optical measurements of flame-produced soot, both in nascent form and with organic and inorganic coatings. The aim of this study is to understand the influence of such coatings on the absorption properties of ambient "black carbon" as compared to primary soot emissions. At low SSA, determination of absorption using the subtraction technique (extinction - scattering) offers a viable alternative to traditional methodology employing photoacoustic or filter-based techniques for the measurement of primary emission sources such as diesel, gasoline and aircraft engines.



Tools for Molecular Astrospectroscopy: os-BBCEAS, CESAS and CRDS

Dongfeng Zhao[1], Kirstin Doney[1], Xavier Bacalla[1,2], Wim Ubachs[2], Harold Linnartz[1]
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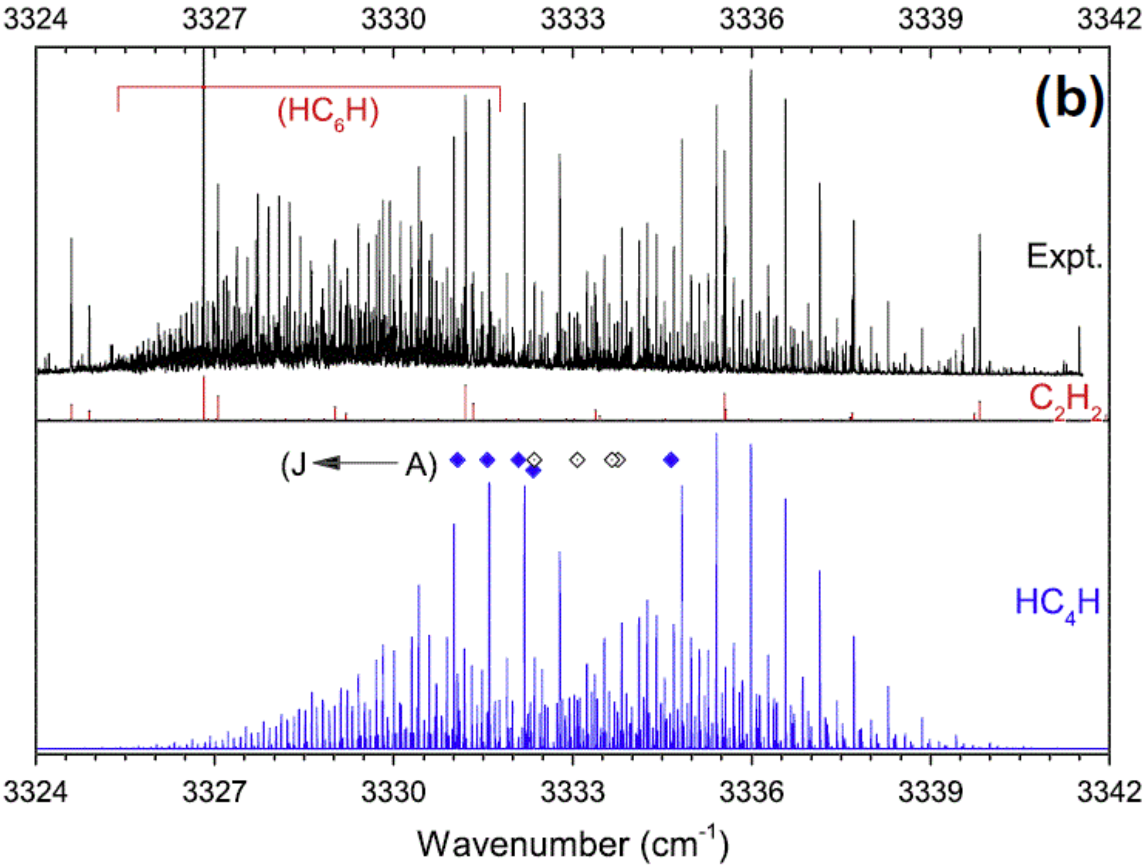
[2]Department of Physics and Astronomy, LaserLaB, VU University, Amsterdam, the Netherlands

Light from space carries all the information it takes to identify molecules in the highly dilute regions in between and around stars, the interstellar medium (ISM). More than 180 different species, meanwhile, have been identified and show that the chemical processes in the ISM follow exotic chemical routes. Unambiguous identifications of these molecules only has become possible following dedicated laboratory experiments, providing accurate line positions and molecular parameters that are needed to interpret and to guide astronomical observations. In this talk several CES-based techniques are discussed with the aim to collect high resolution spectra of astrophysically relevant molecules. The focus is on unstable species; radicals and ions. Regular CRDS, both pulsed and cw (in the IR) allows to record highly precise rovibronic and rovibrational transitions of molecular transients. Broadband applications (optical shutter modulated broad band cavity enhanced spectroscopy - os-BBCEAS - and cavity enhanced self absorption spectroscopy - CESAS) allow to cover large wavelength domains with high sensitivity. Several molecules are discussed to illustrate the potential of the methods used here.



The cw IR CRDS spectrum of di- and triacetylene in the CH stretch region.

Using Cavity-Enhanced Spectroscopy to Improve Healthcare: In-Airways O_2 Consumption Sensing Based On OA-CEAS

L. Ciaffoni[1], D. O'Neill2, J. Couper[1], G. Hancock[1], G.A.D. Ritchie[1], P.A. Robbins[2]
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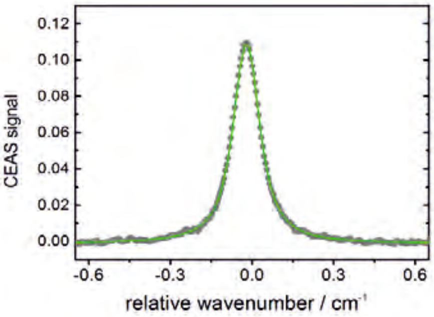
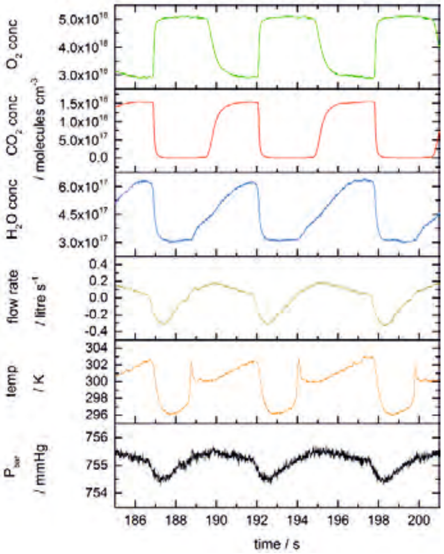
Directly interfacing cavity-enhanced spectrometers with a hot, humid, and turbulent gas mixture such as exhaled breath is a difficult task. So far, the general approach has been to opt for side-stream configurations that rely on a small portion of the respired gas mixture to be diverted via a sampling tube or bag to the measuring site, where pre-conditioning of the pressure, temperature, and relative humidity of the sample is often required. These strategies raise a number of issues when it is necessary to combine synchronous measurements of molecular concentration with those of respiratory flow for calculating the rate of gas uptake by the lungs. The impact of monitoring on-going oxygen consumption in a range of clinical settings (anaesthesia, intensive care) where current side-stream technology is not applicable, [1, 2] has prompted the development of an O_2 sensor that can offer high accuracy (< 2000 ppm at 1 atm), fast response (<50 ms), large dynamic range (0-100%), and operates directly within the airways. We present a compact, off-axis cavity-enhanced absorption spectrometer (OA-CEAS) constructed from a 764 nm VCSEL and a 27 mm optical cavity with re-entrant configuration. RF noise perturbation of the laser current was employed to improve the sensitivity by promoting the non-resonant properties of the cavity. [3] The O_2 sensor is integrated into a purpose-built CO_2 and water vapour absorption spectrometer and respiratory flow sensor, from which the O_2 consumption rate is calculated. The performance and challenges in achieving high accuracy and precision when dealing with a gas sample with time-varying physical properties (composition, temperature, humidity, flow) will be presented, alongside with data collected from patients undergoing surgical procedures.





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Sensitivity Enhancement in Off-Axis Integrated Cavity Output Spectroscopy

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Molecular and Laser Physics, Radboud University, Nijmegen, the Netherlands

In cavity-enhanced techniques the absorption path length can be increased up to several kilometers, hence enhancing the sensitivity significantly. The development of off-axis integrated cavity output spectroscopy (OA-ICOS) offered mechanical robustness and relatively simple alignment for field measurements, being used for race gas detection in numerous studies during recent years, such as atmospheric studies and breath analysis. The method can straightforward be implemented, making it less technically demanding and more cost effective than other laser-based methods. A major drawback of OA-ICOS is the significantly reduced cavity transmitted power due to highly reflective mirrors, which impact on the sensitivity of the sensor. It becomes critical when low power lasers and room-temperature detectors with limited detectivity are the only suitable or available devices for the designed system. To overcome this drawback, we report on a model of a three mirror OA-ICOS setup that re-injects the light reflected by the optical cavity. We present a detailed model on how the optimization process can be performed to achieve optical enhancement. The influence of different re-injection parameters and their effect on the signal-to-noise ratio (SNR) are presented and compared to the experimental results of real-time detection of ethylene with a pulsed distributed feedback Quantum Cascade Laser at a wavelength of 10 micrometer.

Cavity enhanced rephased spontaneous emission

Matthew Sellars
Australian National University

One of the key components required for optical quantum computation and communication technologies is a high efficiency, triggerable single photon source. We are developing such a source based on the rephasing of the spontaneous emission from an ensemble of rare-earth ions in a crystal.

The protocol uses a photon echo technique to rephase the coherence generated in an ensemble of ions during a spontaneous emission event, causing the ensemble to emit a second photon identical to the initial spontaneously emitted photon. The release time of the second photon is controlled by choosing when the coherence is rephased. Critical to achieving a high fidelity source is the use of an optical cavity, impedance matched to the ensembles coherent emission.

Recent results will be presented demonstrating that the spontaneously emitted emission is entangled with the rephased emission and that this entangled quantum state can be stored on the nuclear spin states of the ions.

Photo-Dissociation Resonances of Jet-Cooled NO2 by CW-CRDS

Patrick Dupré
Laboratoire de Physico-Chimie de l Atmosphere, University of Littoral, Cote d Opale

Around 398 nm, the jet-cooled NO_2 spectrum exhibits a well identified dissociation threshold (D_0). Combining LIF detection and continuous-wave absorption-based CRDS technique a frequency range of $\sim 25\ cm^{-1}$ is analyzed at high resolution around D_0. In addition to the usual rovibronic transitions towards long-lived energy levels, ∼ 115 wider resonances are observed. Over this energy range, the resonance widths spread from $\sim 0.006\ cm-1$ (∼ 450 ps) to $\sim 0.7\ cm^{-1}$ (∼ 4 ps) with large fluctuations. At least two ranges of resonance width can be identified when increasing the excess energy. They are associated with the opening of the dissociation channels $NO_2 \rightarrow NO\ (X^2\Pi_{1/2}, v = 0, J = 1/2) + O\ (^3P_2)$ and $NO_2 \rightarrow NO\ (X^2\Pi_{1/2}, v = 0, J = 3/2) + O\ (^3P_2)$. Weighted mean unimolecular dissociation rate coefficients k uni are calculated. The density of reactants (following the RRKM predictions) is deduced, and it will be discussed versus the density of transitions, the density of resonances and the density of vibronic levels. The data are analyzed in the light of time-resolved data previously reported. This analysis corroborates the existence of loose transition states along the reaction path close to the dissociation energy in agreement with the phase space theory predictions.

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[1]Accepted in J. Chem. Phys.

Cavity-Enhanced Methods for Optical Detection of Magnetic Field Effects in Biological Systems

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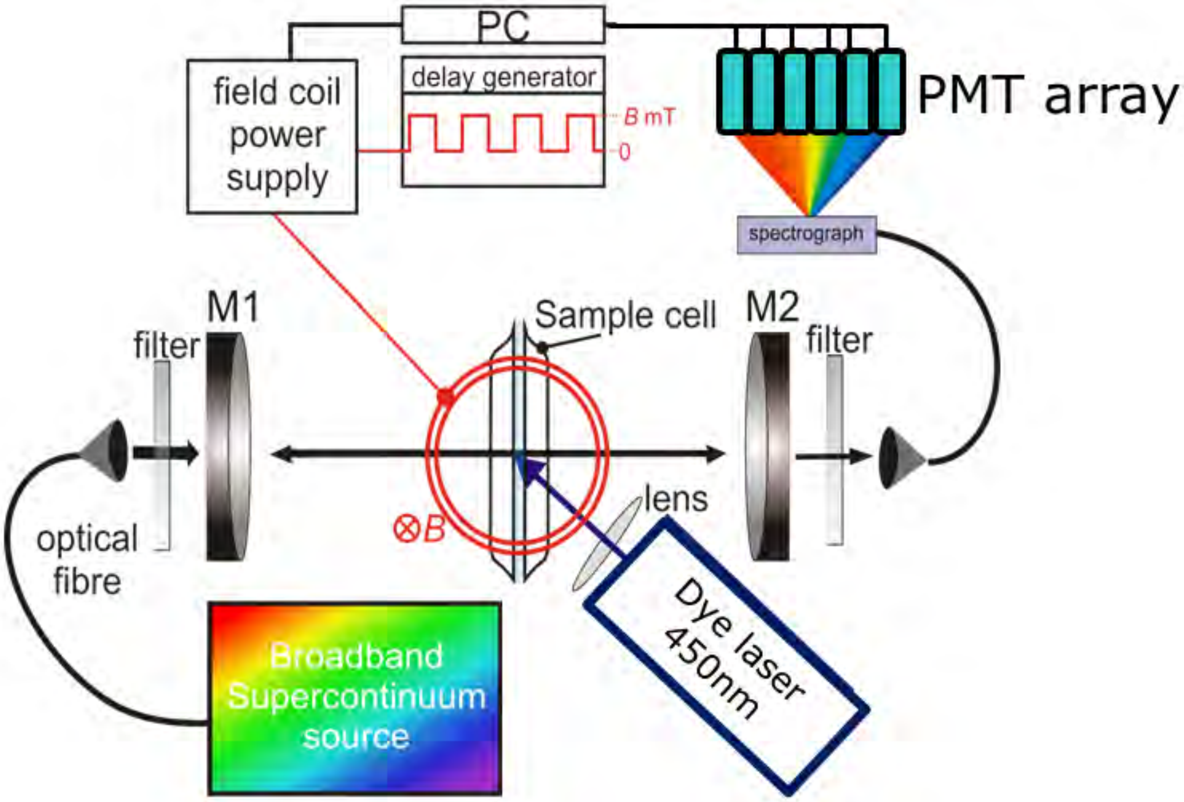
The underlying physical mechanisms of magnetosensitivity in animals remain unclear, in part due to the lack of suitable techniques for detecting the tiny effects of magnetic fields on biological systems in solution. Experiments investigating magnetic field effects (MFEs) have traditionally used flash-photolysis transient absorption techniques to detect short-lived radical species which are hampered in their application to real biological systems by their requirement for large sample volumes (cm^3), high precursor concentrations (>µM), and high photolysis pulse energies, which lead to problems of photo-degradation. Here, we report on recent developments in our application of highly sensitive optical techniques to the detection of MFEs in solution. Two well-known cavity-based variants, Cavity Ring-Down Spectroscopy (CRDS) and Cavity Enhanced Absorption Spectroscopy (CEAS), have been adapted from their usual application in the gas phase and optimised for the study of condensed phase systems. In addition, a new instrument has been developed which harnesses the major advantages of both of these two powerful techniques. Optical Cavity-based Transient Absorption Spectroscopy (or OCTAS) combines the wide spectral coverage and high sensitivity of broadband-CEAS with microsecond time-resolution.



Advances in Sensitive, Accurate, Precise, Ion Spectroscopy through Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy

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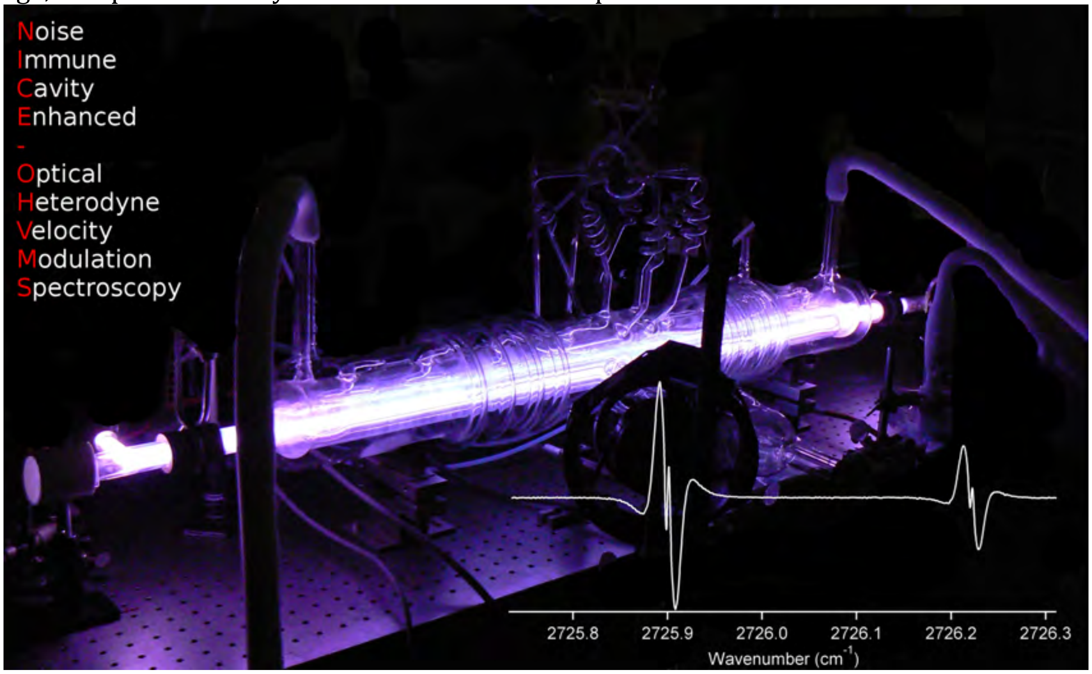
[2]*Department of Chemistry and Departments of Astronomy and Physics, University of Illinois, Urbana, Illinois*

Noise immune cavity enhanced optical heterodyne velocity modulation spectroscopy (NICE-OHVMS) is the implementation of velocity modulation spectroscopy with cavity enhanced optical heterodyne spectroscopy. NICE-OHVMS combines the advantages of pathlength and power enhancement of the cavity, reduced 1/f noise as a result of heterodyne modulation, and ion selectivity due to velocity modulation. Our lab developed this technique to measure molecular ion transitions with high precision, which allows us to support astronomical observations and challenge the predictive power of ab initio theory. Our spectrometer consists of an optical parametric oscillator (OPO) and a low finesse external optical cavity, which contains a liquid nitrogen cooled positive column discharge cell.[1] The sensitivity of the spectrometer is approximately 10^{-9} cm^{-1} Hz$^{-1/2}$. Coupling our OPO into a cavity results in a tremendous amount of power, about 10 to 12 watts, which allows us to optically saturate ion transitions. Optical saturation results in Lamb dips in the spectra which can be fit with a high degree of frequency precision. When the OPO is referenced to an optical frequency comb, we can determine transition frequencies with an uncertainty of 500 kHz to a few MHz depending on the signal to noise ratio of the Lamb dip. We have measured transitions from a variety of ions including H_3^+, HeH^+, HCO^+, CH_5^+, and OH^+,[2,3] and have successfully reduced the errors on these linecenters by two orders of magnitude. Additionally, ongoing work is focused on describing NICE-OHVMS lineshapes, in order to infer the saturation parameter, which can be used to better understand the relaxation rates in a positive column discharge, and provide a way to measure transition dipole moments.



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Optimum Conditions for Doppler-Broadened Nice-Ohms – How to Reach an Allan Deviation in the 10^{-14} cm^{-1} Range Using a Tunable Laser

Isak Silander[1], Thomas Hausmaninger[1], Patrick Ehlers[1], Weiguang Ma[1,2], and Ove Axner[1]
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NICE-OHMS has demonstrated exceptional detection sensitivity (DS). In its first realization, based upon a well-stabilized fixed-frequency Nd:YAG laser, targeting C_2HD by its sub-Doppler (sD) mode of detection, it demonstrated a noise equivalent absorption per unit length (NEAL) of 10−14 cm^{-1} over 1 s. The realization of Doppler-broadened (Db) NICE-OHMS based on tunable lasers, which is the preferred mode when the technique is used for trace gas detection, has, up to now, not produced comparable DS. To remedy this, we have methodically scrutinized the technique and identified actions to reduce the amount of background signals and noise and assessed the conditions that maximize the signal and the signal-to-noise conditions. In particular, background signals from residual amplitude modulations (RAM) have been reduced by identification of the origin of RAM from fiber-based EOMs and the optimum use of such. Signals from etalons have been reduced by the introduction of etalon-immune distances (EID), which constitute separations between optical components for which an etalon will contribute equally to each mode of the light, which implies that they will not contribute to the NICE-OHMS signal. The optimum conditions for Db NICE-OHMS with respect to modulation index, frequency, and order, demodulation phase, cavity length, and scanning range have been assessed. By constructing a NICE-OHMS system around a tunable fiber-laser that adheres to most of these conditions, a white noise equivalent absorption coefficient (NEAC) of 2.6×10^{-13} cm^{-1} $Hz^{-1/2}$ and a minimum NEAC of 8.8×10^{-14} cm^{-1} at 30 s have been obtained. This is similar to that of the first NICE-OHMS demonstration using a fixed-frequency laser (since the NEAL value assessed by sD detection corresponds to a NEAC of 8×10^{-14} cm^{-1}). This demonstrates that Db NICE-OHMS based on tunable lasers can achieve similar NEAC as sD NICE-OHMS assessments based on well-stabilized fixed-frequency lasers.

Cavity-Enhanced Frequency Comb Spectroscopy

Jun Ye
JILA, NIST and University of Colorado

With our recent development of novel frequency combs in the mid infrared and extreme ultraviolet, we have opened the door for sensitive and high-resolution spectroscopy in these spectral regions. Cavity-enhanced direct frequency comb spectroscopy provides simultaneous and precise measurements of many types of molecules, analyzing their spectral strengths and patterns, and thus forming global, signatory identifications of trace presence at an unprecedented level of specificity and confidence. With the integration of a powerful capability for time-resolved transient absorption at high spectral resolution, we demonstrate the utility of this technique for identifying transient chemical species and studying reaction kinetics. Combined with the technology of cold molecules, we can unravel complex spectra from large molecules and obtain new insights to molecular structure and dynamics. Finally, with an XUV comb produced inside an enhancement cavity we can directly manipulate molecules and probe the extreme nonlinear physics, opening future high-precision measurements in strong-field phenomena.

Doppler-Broadened NICE-OHMS Beyond the Cavity-Limited Weak Absorption Condition

Weiguang Ma[1,2,] Thomas Hausmaninger[1], Isak Silander[1], and Ove Axner[1]
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[2]State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China

NICE-OHMS is a laser-based technique that has demonstrated an extraordinary high sensitivity for detection of molecules in gas phase. Its Doppler-broadened (Db) response is usually described by an expression that is restricted to the conventional cavity-limited weak absorption (CCLWA) condition, i.e. when the single pass absorbance is much smaller than the empty cavity losses. However, with the realization of NICE-OHMS in the Mid-IR range, in which the transition line strengths can be huge, often around 10^{-18} cm^{-1}/(molecule cm^{-2}), and with the use of high finesse cavities, it has become more and more common that assessments and calibrations are no longer performed under cases for which this condition is valid. So far, no analytical expression for the Db NICE-OHMS signal for the situations when the CCLWA condition is not fulfilled has been derived. Nor is the principle of Db NICE-OHMS under such conditions well known. We have therefore scrutinized in detail the principles of Db NICE-OHMS. Based on this, we have been able to provide a description of the technique that is based solely upon a few general assumptions and thus not limited to the CCLWA condition (termed the FULL description). Unfortunately, this description constitutes a set of equations to which there is no closed form solution. Hence, it needs to be solved numerically. To circumvent this, two analytical expressions have been derived; one based on an extended locking & extended transmission (ELET) description, and another on an extended locking & full transmission (ELFT) description, valid under close-to CCLWA conditions. By use of simulations and experiments, the extended descriptions have been verified and their ranges of applicability have been assessed. Access to these increases considerably the dynamic range of the technique, by at least two orders of magnitude, and facilitates calibration using certified reference gases, which significantly broadens the applicability of the Db NICE-OHMS technique.

Measuring Aerosol Scattering and Absorption - Limitations of the Extinction-Minus-Scattering Method

Solomon Bililign[1], Damon Smith[2], Marc Fiddler[1], Sujeeta Singh[1]
[1] *North Carolina A&T State University*
[2] *High Point University, High Point, NC*

Aerosols from biomass burning represent a significant source of particles in the atmosphere. An accurate measurement of the optical properties of these aerosols is critical for measuring their effect on climate, since they represent a large uncertainty. Optically dark aerosols, such as soot, affect the climate system by both cooling (due to scattering) and by warming (due to absorbing), depending on the aerosol's size, composition, and shape. The aim of this work is to quantitatively determine the absorption and scattering cross-sections, single scattering albedo, and angstrom coefficient of soot. Particle extinction (absorption + scattering) was measured with a cavity ring-down spectrometer (CRDS), scattering was measured with an integrating nephelometer, and a condensation particle counter (CPC) measured particle number density. In this work, we perform an assessment of the contributions to systematic and random errors for CRDS, nephelometer, and combined measurements. Extinction cross section measurements are limited by the accuracy of the CPC and, to a lesser extent, measurement variability and cell geometry. Statistical fluctuations of aerosol particles, recapturing of forward-scattered light, laser mode noise, and laser bandwidth effects are negligible. For nephelometer measurements, scattering cross section errors are mostly limited by CPC counting accuracy and the truncation angle correction factor. A comparison between CRDS, nephelometery, and Mie Theory predictions for non-absorbing polystyrene latex spheres shows mean measured cross section values at 584 nm to have an excellent agreement, though all were systematically larger than predicted values. The resulting effects of propagated errors on the accuracy of absorption cross section and single scattering albedo are discussed along with preliminary measurements on absorbing polystyrene.

Study of the Ozonolysis of Ethene and 2,3-Dimethyl-2-Butene Using Cavity Ring-down Spectroscopy

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Ozonolysis is one of the main oxidation channels of alkenes in the atmosphere, as well as a significant source of secondary organic aerosol (SOA) and hydroxyl and organic radicals. Carbonyl oxides, also known as Criegee intermediates (CIs), are key products in the ozonolysis of alkenes, being produced with a broad internal energy distribution. While CIs with high internal energy can dissociate and produce OH, RO, and other organic radicals, CIs with low internal energy (known as stabilized CIs) react rapidly to form other carbonyl compounds involved in the SOA production. In this work, indirect measurements of the yield of stabilized Criegee intermediates (SCIs) from the ozonolysis reaction of ethene and 2,3-dimethyl-2-butene were carried out at low pressures using cavity ring-down spectroscopy (CRDS). Determination of the yield of SCIs was performed by chemical titration using SO_2. In the case of ethene ozonolysis, the formation of formaldehyde by reaction of SCI with SO_2 was also monitored. Chemical kinetic modeling was performed to estimate the kinetic rate constants of the reactions between SCIs and SO_2. The yield of SCIs was found to decrease with decreasing pressure and reach a minimum value at the low pressure limit, which corresponds to the fraction of CI formed with internal energy below that of dissociation.

Cavity Enhanced Absorption Spectroscopy for the Detection of Plant Volatile Organic Compounds

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We are using cavity enhanced absorption spectroscopy to develop a sensor to detect and quantify plant volatile organic compounds (VOCs). Plants constantly emit a variety of VOCs, with the composition of the mixture changing in response to external stresses such as water deficiency, nutrient deficiency, and herbivore and pathogen attacks. Understanding the correspondence between the emitted VOCs and the various environmental triggers, and developing sensors to detect and quantify these VOCs, has the potential to yield a step change in agricultural sustainability. Such sensors will be used by crop farmers to monitor crops at a local level, allowing the provision of targeted nutrition and pest control as well as early intervention in the event of drought, disease or pest infestation. We will report our progress on a proof-of-concept study on detection of the compound geraniol. Geraniol has been chosen as a suitable first target molecule due to the availability of genetically-modified crop plants that emit geraniol at increased concentrations relative to wild-type plants. Such plants should therefore yield relatively high signal levels for our first prototype sensor.

Measurements of Diurnal Variations and Eddy Covariance (Ec) Fluxes of Glyoxal Over the Tropical Pacific Ocean During the Torero 2012 Field Experiment

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Here we describe a Fast Light Emitting Diode Cavity Enhanced Differential Optical Absorption Spectroscopy (Fast LED-CE-DOAS) instrument to measure diurnal variations and EC fluxes of glyoxal, and inform about its unknown sources. The Fast LED-CE-DOAS is a multispectral sensor that selectively and simultaneously measures glyoxal (CHOCHO), nitrogen dioxide (NO_2), oxygen dimers (O_4) and water vapor (H_2O) with ~2 Hz time resolution. The instrument was deployed during the Tropical Ocean Troposphere Exchange of Reactive Halogens and OVOC (TORERO) field experiment (January to March 2012) on a cruise from Honolulu, Hawaii, USA to Puntarenas, Costa Rica, probing a large portion of the Eastern tropical Pacific Ocean. Glyoxal is the smallest α-dicarbonyl product of hydrocarbon oxidation, and a precursor for secondary organic aerosol (SOA). The unique physical and chemical properties of glyoxal, i.e., high solubility in water (Henry's Law constant, KH = 4.2×10^5 M atm^{-1}) and short atmospheric lifetime (~2 hrs at solar noon) make it a unique indicator species for organic carbon oxidation in the marine atmosphere. Previous reports of elevated glyoxal over oceans remain unexplained by atmospheric models. Eddy covariance (EC) fluxes are a well-established and widely used technique to measure surface-atmosphere gas exchange. The EC flux method provides insight into sources and sinks of atmospheric parameters (physical, chemical state variables) suitable to test our process level understanding. Our findings are discussed in context with measurements of glyoxal from remote sensing (ship-based MAX-DOAS and satellite) and implications for our current understanding of sources and sinks of this tracer gas over the open ocean.

Determining Optical Path Lengths for Aerosol-Free Cavity Enhanced Spectroscopy: Theoretical Calculations Based On Mirror Characterization and Rayleigh Scattering Vs Determination from Measurements of Collision Induced Absorption of Oxygen Molecules

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Cavity enhanced absorption spectroscopy (CEAS) presents a powerful analytical method with the demonstrated capability to measure numerous trace gases over a wide range of wavelengths. One critical aspect of this technique is the determination of the optical path length within the cavity. Two methods for determining this parameter are discussed and compared here for a CEAS instrument coupled to a broadband LED light source and utilizing the differential optical absorption spectroscopy (DOAS) retrieval method, which has the capability to simultaneously measure multiple trace gases over a wide wavelength range (>30 nm) and has been demonstrated to be insensitive to broadband processes such as lamp drift (and thus does not require explicit knowledge of lamp intensity). The first method is the through the characterization of the cavity mirrors (measuring reflectivity) and calculating extinction due to Rayleigh scattering within the cavity, and the second uses measurements of oxygen molecule collision induced absorption within the cavity when sampling air (rather than calibration gases such as N_2, He, or Ar). Results of a comparison of these two methods is presented for several laboratory campaigns all representing aerosol free measurements, but with different configurations of the instrument described above (i.e., different mirrors, base cavity lengths, set-up personnel). Overall, these methods show good agreement with percent differences typically (<7%), even under conditions where extinction due to the absorption of other trace gases starts to become relevant.

Infrared Cavity Ring-Down Measurements of Astronomically Relevant Cations

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Interstellar cations play a role in ion-molecule interactions, and can be used a tracers for centrosymmetric molecules, e.g. HO_2^+ or CH_5^+, as well as tracers of the formation pathways of larger species. For example, current astronomical models predict that hydrocarbon cations, e.g. $C_2H_3^+$, act as key intermediates in the formation pathways of larger species, such as those for long carbon chains or polycyclic aromatic hydrocarbons (PAHs). However, currently many key cations have yet to be observed in space. While new astronomical flagship facilities, e.g. ALMA (Atacama Large Millimeter Array), can now probe even trace molecules (abundances of $\sim 10^{-6}$ - 10^{-10} with respect to H_2), a shortage of accurate laboratory spectroscopic data complicates the identification of such species. We present new high resolution infrared (IR) spectra in the C-H stretch region obtained using ultra-sensitive and highly precise IR continuous wave cavity ring-down spectroscopy (cw-CRDS), combined with supersonic plasma expansions[a]. In particular, we show recent studies of cations, including the first gas phase detection of the smallest aromatic molecule[b], c-$C_3H_3^+$, which have yield molecular parameters accurate enough for astronomical applications.

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Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectrometry Modeling under Saturated Absorption

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The Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectrometry (NICE-OHMS) is a modern technique renowned for its ultimate sensitivity, because it combines long equivalent absorption length provided by a high finesse cavity, and a detection theoretically limited by the sole photon-shot-noise. One fallout of the high finesse is the possibility to accumulating strong intracavity electromagnetic fields (EMF). Under this condition, molecular transitions can be easy saturated giving rise to the usual Lamb dips (or hole burning). However, the unusual shape of the basically trichromatic EMF (due to the RF lateral sidebands) induces nonlinear couplings, i.e., new crossover transitions. An analytical methodology will be presented to calculate spectra provided by NICE-OHMS experiments. It is based on the solutions of the equations of motion of an open two-blocked-level system performed in the frequency-domain (optically thin medium). Knowing the transition dipole moment, the NICE-OHMS signals ("absorption-like" and "dispersion-like") can be simulated by integration over the Doppler shifts and by paying attention to the molecular Zeeman sublevels and to the EMF polarization[1]. The approach has been validated by discussion experimental data obtained on two transitions of C_2H_2 in the near-infrared under moderated saturation[2]. One of the applications of the saturated absorption is to be able to simultaneously determine the transition intensity and the density number while only one these 2 quantities can only be assessed in nonlinear absorption.

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First Aircraft Measurements of NO_y by Cavity Ring-Down Spectroscopy

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The sum of total reactive, oxidized nitrogen, commonly referred to as NO_y is important for understanding emissions of reactive nitrogen species to the atmosphere and for photochemical production and chemical loss of ozone. NO_y has traditionally been measured by chemical conversion to nitric oxide, NO, followed by chemiluminescence detection. NO_y was measured during the WINTER (Wintertime Transport, Emissions and Reactivity, February – March 2015) campaign conducted on the NCAR C-130 via Cavity Ring-Down Spectroscopy (CRDS). NO_y was measured by immediately passing the sampled air through a quartz tube heated to 650°C, which will decompose any higher oxidized nitrogen species into NO or NO_2. Ozone was added to the NO/NO_2 mixture to convert any NO to NO_2. The NO_2 was measured via multi mode diode laser CRDS near 405 nm. These were the first aircraft-based measurements of NO_y via CRD and, as such, there were aspects of the data that require farther analysis. As these measurements were conducted during a campaign with a rich suite of other measurements to compare with, we can determine the accuracy of the new method for NO_y measurements. By looking at reactive nitrogen budgets with other measurements that had already been aircraft-tested, we can determine if there are conditions when NO_y may be under- or over-measured. This presentation will describe the advantages and disadvantages of the new method for NO_y detection from aircraft.

A UV-visible Broadband Cavity Enhanced Spectrometer for Atmospheric Aerosol Extinction

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Atmospheric aerosols directly affect Earth's radiative balance by absorbing and scattering incoming solar radiation, and the aerosol direct effects contribute some of the largest uncertainties to predictions of Earth's future climate. Thus, understanding the optical properties of aerosols is vital to the development of appropriate policies attempting to tackle the issues of climate change and air pollution. The cavity enhanced spectroscopies, such as cavity ringdown spectroscopy and broadband cavity enhanced spectroscopy, provide sensitive methods for measuring light extinction by aerosols in-situ. However, due to the narrow spectral coverage of highly reflective mirrors and the lasers often used as light sources, aerosol extinction measurements have been traditionally limited from 1 to 50 nm wide regions of the spectrum. Aerosol extinction follows a power law relationship with wavelength, with increased extinction in the UV, and it is therefore desirable to measure extinction throughout the UV-visible spectrum. We have built an instrument composed of 4 parallel cavities coupled into a single grating spectrophotometer, in which each cavity contains its own LED light source. The robust and portable instrument provides access to wavelength-resolved measurements of aerosol extinction in four ~50nm wide regions spanning from 350 to 690 nm.

Cavity Ring-Down Spectroscopy in the Quantum-Noise Limit

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We report two cavity ring-down spectrometers capable of recording cavity losses with sensitivity limited by quantum (shot) noise. The first instrument based on emerging mid-infrared quantum-cascade laser (QCL) technology operated at a center wavelength of 4.53 μm by observing passive cavity decays at DC on a low-noise liquid-nitrogen cooled InSb photodetector. The passive decays exhibited significantly more noise at early times when more light was present on the photodetector, thus revealing a characteristic funnel shape to the exponential fit residuals. In addition to achieving a low noise-equivalent absorption coefficient (NEA) of 2.6×10^{-11} cm^{-1} $\text{Hz}^{-1/2}$ in the quantum-noise limit, we also observed direct evidence of interference (i.e., mode beating) in the mid-infrared cavity decays due to a small intrinsic supermirror birefringence. The second instrument to perform in the quantum-noise limit was a heterodyne-detected cavity ring-down spectrometer [1] which utilized high-bandwidth frequency-agile rapid scanning components to reach an ultimate sensitivity of NEA = 6×10^{-14} cm^{-1} $\text{Hz}^{-1/2}$ with 1 mW of detected near-infrared (1.55-1.6 μm) laser power [2].

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Cavity-Enhanced Optical Frequency Comb Spectroscopy of High-Temperature Water in a Flame

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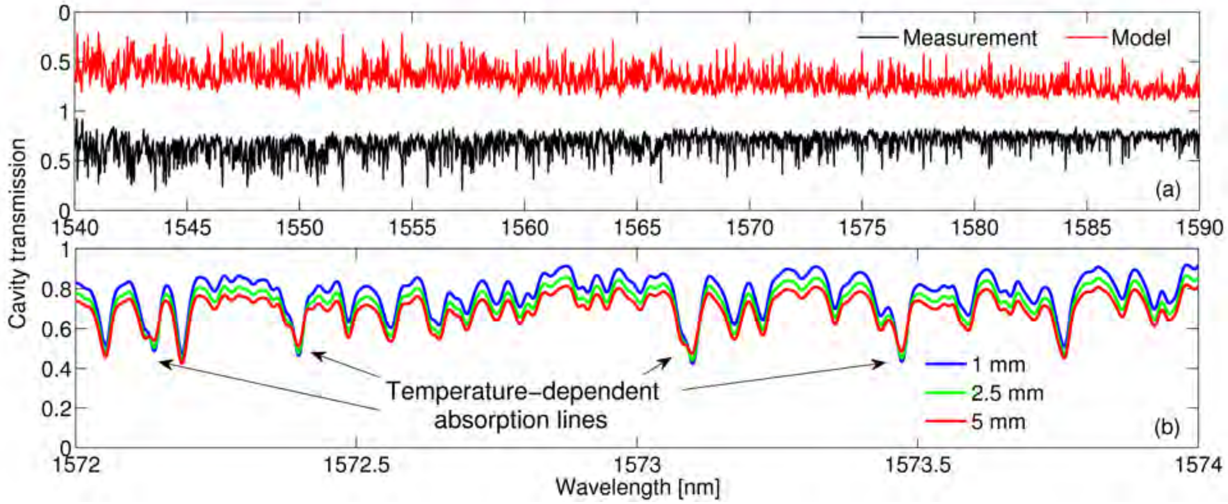
Laser-based absorption techniques are often used as a non-intrusive tool for combustion diagnostics to determine parameters such as reactant/product concentrations and temperature. However, the limited tunability of continuous wave lasers imposes restrictions on the number of detected species and the choice of absorption line pairs for thermometry. We present, for the first time, cavity-enhanced optical frequency comb spectroscopy (CE-OFCS) in a combustion environment by detecting high-temperature water spectra in a premixed methane/air flat flame[1]. The technique combines broad bandwidth with high spectral resolution and opens up the possibility for simultaneous multispecies detection and improved flame thermometry. Our comb source is an Er:fiber femtosecond laser locked to an open-to-air cavity with a finesse of ~1100. The burner[2] is placed below the intracavity beam on a vertical translation stage, which allows adjustment of the beam height above the burner (HAB). The light transmitted through the cavity is analyzed with a fast-scanning Fourier transform spectrometer equipped with an auto-balancing detector. The system allows acquiring high-temperature spectra with a bandwidth of 50 nm and resolution of 1 GHz in 0.4 s, with absorption sensitivity of 4×10^{-9} cm^{-1} Hz$^{-1/2}$ per spectral element. Figure (a) shows a normalized high-temperature H2O spectrum measured at HAB of 5 mm (black) compared to a model based on parameters from the HITEMP database for temperature of 2000 K and water concentration of 18% (red, inverted for clarity). Figure (b) shows a zoom of H_2O spectra around 1573 nm taken at three different HABs, revealing four groups of absorption lines with strong temperature dependence. We will present recent improvements to the stability of the system and the modeling of absorption spectra.



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High Resolution Spectroscopy of CH_2OO and the Kinetics of its Reactions with Inorganic Acids

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Carbonyl oxides, or Criegee Intermediates (CIs), are formed from the gas phase ozonolysis of alkenes and play a pivotal role in night-time and urban area atmospheric chemistry. There are significant discrepancies between existing measurements of the strong $\tilde{B}1A'$-$\tilde{X}1A'$ electronic transition of CH_2OO in the visible/near-UV. We report high-resolution spectra of the $\tilde{B}1A'$-$\tilde{X}1A'$ electronic absorption band of CH_2OO using both single-pass broadband transient absorption spectroscopy and cavity ring-down spectroscopy, which will help to resolve current debate over the excited state lifetime and the origin of discrepancies amongst previous spectroscopic measurements. We have also investigated the kinetics of reactions between CH_2OO and inorganic acids and evaluated their significance with respect to reactions with other trace gases (SO_2, NO_2) that are present in the atmosphere with comparable number densities.

Design of a Novel Open-Path Aerosol Extinction Cavity Ringdown Spectrometer and Data from Recent Field Deployments

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We present the key elements of a new open-path cavity ringdown spectrometer (CRDS) design as well as comparisons with a conventional closed-path CRDS and data obtained during two recent field campaigns: FRAPPE at NOAA's Boulder Atmospheric Observatory and HAGiS at NOAA's Earth System Research Laboratory. CRDS has been employed previously to quantify aerosol extinction at relative humidities <90%. At very high humidities (as found in and near clouds), however, existing CRDSs perform poorly, diverging significantly from theoretically predicted extinction values. The new open-path CRDS measures extinction as aerosol is drawn directly through the optical cavity transverse to the axis of the laser. With no inlet/tubing, particle losses due to impaction of coarse particles and condensation of highly humidified particles on transfer lines is eliminated, improving aerosol extinction measurements where such conditions exist. During FRAPPE the open-path CRDS recorded very large extinction enhancement (f(RH) > 50) due to highly humidified aerosol in low-lying rainclouds, demonstrating the instrument's utility in characterizing extinction in extremely high relative humidity conditions. During HAGiS the accuracy of aerosol hygroscopic growth parameterizations was investigated by comparing the extinction they predict to the extinction measured by the open-path CRDS.

A Portable NX and Particle Analyzer

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We present a portable Cavity Ring-Down Spectrometer at 405 nm with a pathlength of approximately 1 kilometer that achieves near photon limit resolution under ideal conditions. Applications include ambient NO_2, species that can be converted to NO_2, such as explosives and oxidizers, and particle attenuation.

Doppler-Broadened Mid-Infrared NICE-OHMS System Based on an Optical Parametric Oscillator

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Although detection sensitivities in the 10^{-14} cm^{-1} range recently has been demonstrated by fiber laser based Doppler broadened (Db) NICE-OHMS in the near-infrared (NIR) region, it has so far not been possible to utilize the full power of the technique for trace gas detection since molecular species in general only have weak overtone bands in this wavelength region. The realization of a Db NICE-OHMS instrumentation working in the mid-IR (MIR) region, in which many molecules have strong fundamental vibrational bands, is however not straightforward due to the lack of electro-optic modulators (EOMs) in this wavelength range. To circumvent such problems, we have realized a MIR NICE-OHMS system around a resonant optical parametric oscillator (OPO) pumped by a narrow linewidth fiber laser lasing in the 1064 nm region. By modulating the pump laser light by an ordinary EOM, and letting the signal wave be locked to a cavity mode of the OPO, a frequency modulated idler output in the 3.2-3.9 μm region results. This opens up for NICE-OHMS detection of not only trace of gases to low concentrations, but also their isotopologues. The laser was first locked to a low finesse cavity (F = 500). An Allan-Werle analysis revealed a white noise equivalent absorption per unit length (NEAL) of 3×10^{-9} cm^{-1} $Hz^{-1/2}$ and a minimum NEAL of 1.5×10^{-9} cm^{-1} for a 20 s integration time, which corresponds to 90 ppt of CH4 detected at 40 Torr. Further improvement of this system, e.g. by improving the locking by the use of an acousto-optic modulator (AOM) so that a higher finesse cavity (F = 5000) could be implemented, have since then been pursued, and we are presently approaching a NEAL of 1×10^{-10} cm^{-1}. This opens up for a number of interesting applications. Since the origin of the methane in nature can be assessed by the relative concentration of its isotopologues, we aim, as a first application, for detection of $^{13}CH_4$ and CH_3D, which exist in ppb and sub-ppb concentrations, with good accuracy.

Crds with Cavity Mode-Based Frequency Axis for PPM-Level Quantitative Spectroscopy

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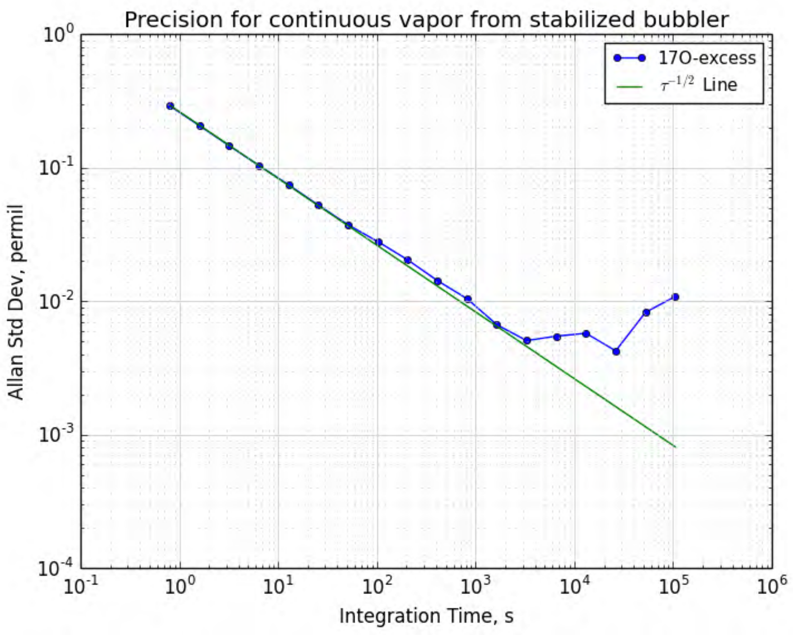
When acquiring absorption spectra for quantitative analysis of molecular mole fractions or isotope ratios, it is essential that the spectrometer have a stable, precise frequency axis. This presents a special challenge for the design of compact, field-deployable analyzers for environmental monitoring and similar applications. We describe the operation of a CRDS spectrometer that uses the ring-down cavity as its own optical frequency scale. While it is clear that a high-finesse cavity provides a convenient comb of longitudinal modes, the implementation of a spectrometer that relies on the CRDS cavity itself for its frequency axis has to contend with several practical obstacles: (1) the mode spacing of cavities of convenient length is generally substantial compared to the width of molecular absorption lines at moderate temperature and pressure; (2) the cavity modes are generally not aligned to the molecular features of interest; and (3) long-term stability of the longitudinal mode frequencies is not assured, especially when sampling gases of variable composition and therefore varying index of refraction. These difficulties can be overcome by a combination of measures: least-squares fitting of (relatively sparse) experimental spectra to a high-resolution spectral model; fine tuning of the cavity optical path length (OPL) to align the mode spectrum to the molecular spectrum; and stabilization of the cavity OPL using spectroscopic feedback from the measured spectrum of the analyzed gas sample. The CRDS spectrometer with cavity mode-based frequency axis reports molecular concentrations with very little sensitivity to undesired perturbations in cavity pressure, and improves in precision with averaging for intervals on the order of hours, permitting measurements with relative precision better than 10^{-5}. Examples of precise analyses that have been demonstrated using this method include 17O-excess in water and molecular oxygen concentration in air.



Cavity-Enhanced Measurements of Hydrogen Peroxide Absorption Cross Sections at Long Wavelengths: Implications for Hydroxyl Radical Production Indoors and Outdoors

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We used incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) to measure hydrogen peroxide (H_2O_2) absorption cross sections between 353 and 410 nm. These measurements expand previously published cross sections by 60 nm. We used these measured cross sections to calculate H_2O_2 photolysis rate constants in the lower troposphere at a range of solar zenith angles. Our results suggest that photolysis at wavelengths longer than those included in the current JPL recommendation may account for up to 28% of hydroxyl radical (OH) production from H_2O_2 photolysis under some conditions. We have also measured photon fluxes from several commonly-used indoor light sources including fluorescent, incandescent, and halogen bulbs, and have calculated OH production rates from H_2O_2 photolysis indoors. We predict that after certain cleaning events, OH production rates will be orders of magnitude greater than under background conditions.

Cavity Ring-Down Spectroscopy in Exploration of the Reactivity of Atmospheric Systems

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Cavity ring-down (CRD) spectroscopy provides a sensitive tool for the study of spectra and the reactivity of atmospheric molecular systems. Specifically we employ CRD to investigate vibrational overtone spectra and vibrational overtone initiated chemical dynamics. CRD is uniquely equipped for these sorts of problems due to the weak observed cross sections for vibrational overtone spectra. Spectroscopic studies have looked at cross sections for different X-H chromophores and concluded that the OH stretch has the largest cross section in the area of interest. Our system has been used to study the OH overtone stretches of various acids found in the Earth's atmosphere. Furthermore, it has provided spectroscopic information about hydrogen bonding in X-H chromophores. The CRD system in our lab is optimized to cover wavelength ranges from 610-680 nm and 740-795 nm in order to look at the vOH =4,5 overtone transitions. This is the turning point for concerted reactions in acids which will be demonstrated with the overtone driven dynamics of sulfuric acid (H_2SO_4) and pyruvic acid. Consequences of this overtone initiated chemistry in the Earth's atmosphere will be discussed.

Res-Q-Trace: A Mobile CEAS-Based Demonstrator for Multiple-Component Trace Gas Detection in the MIR

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Laser spectrometers based on quantum cascade lasers (QCLs) operating in the mid-infrared are an exciting prospect for trace gas sensing as they enable access to strong fundamental vibrational bands of many compounds with absorption cross sections that are typically two orders of magnitude larger than in the near-infrared. A further increase in sensitivity can be achieved by combining QCLs with cavity-enhanced techniques based on optical cavities. The importance of sensitive trace gas detection is manifold. Not only during the development, optimization and control of technological processes and for the monitoring of pollutant emissions, but also in medical breath analysis and for the detection of drugs and explosives a sensitive detection of trace gases down to part per billion (ppb) and part per trillion (ppt) levels is needed. For example exhaled human breath contains a few atmospheric molecules in relatively high concentrations such as H_2O, CO_2, N_2, O_2, several volatile organic compounds (VOCs) at part per million (ppm) or sub-ppm levels, and about four hundred major VOCs at ppb or ppt levels. The application of laser spectroscopic techniques promises the potential for small, portable, reliable and selective sensor systems which are sensitive enough for the online and in situ detection of trace gases. In order to proof and validate this concept, we will present a mobile demonstrator system comprising of four QCLs and CEAS measurement cells, two off-axis variants and two optical feedback variants respectively. The measurement cells are connected on the vacuum side, so that multi-component detection in one gas sample could be realized. Exemplarily species relevant not only for breath analysis but also for the detection of explosives were selected and will be presented with achieved sensitivities in the range of ppb and below: NO, N_2O, CH_4, C_2H_4, C_2H_6 and C_3H_6O.

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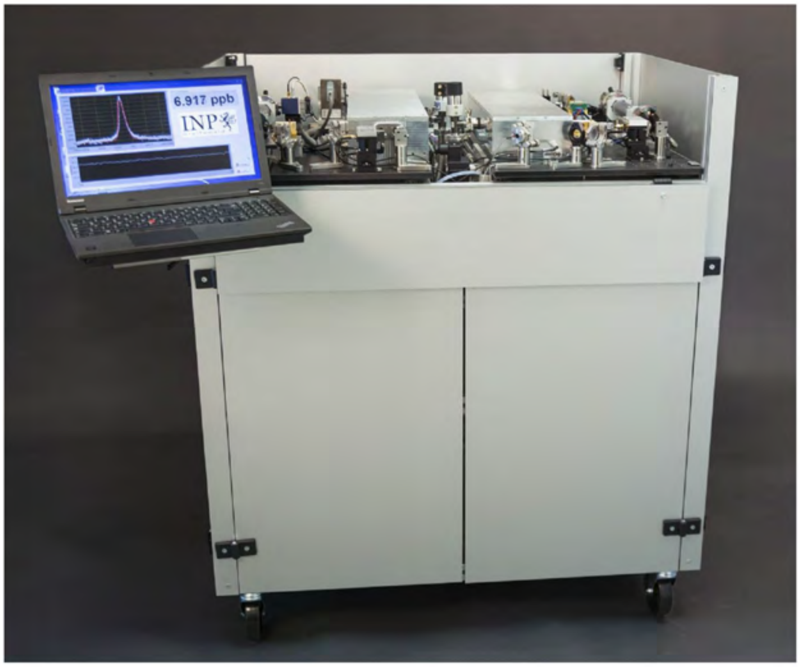

Demonstrator system RES-Q-Trace

Icos ATC Metrology Lab: A Facility for Metrological Performance Assessment of Prototypes and Commercialized GHG Analyzers

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In the framework of ICOS, an European research infrastructure aiming to provide harmonized high precision data for advanced research on carbon cycle and greenhouse gas (GHG) budgets over Europe, the Atmosphere Thematic Centre (ATC), located at LSCE in Gif-sur-Yvette, France, includes the Metrology Lab, a facility mainly dedicated to elaborating measurement protocols and evaluating performance of GHG analyzers. The Metrology Lab assesses the ICOS compliance of the analyzers before deployment in the ICOS monitoring station network, but also carries out a technology watch by testing the performance of new instrument, prototype and emerging technology from company and research group. The current species handled by ICOS for continuous measurement are CO_2, CH_4 and CO. However ICOS is targeting in a near future other species such as N_2O and isotopologues of CO_2 and CH_4. Most of the analyzers tested at the Metrology Lab are based on Cavity Enhanced Spectroscopy. The conducted tests consist in characterizing the metrological performance in term of precision, repeatability, linearity, drift, cross sensitivity with other species, thermal sensitivity, water vapor correction (to derive the dry mixing ratio) among others. For that purpose, the Metrology Lab has at its disposal a lot of sources of stable air (tanks) with different mixing ratios of the targeted trace gas and all the required equipment such as a humidifying bench able to humidify a known mixing ratio gas at different stable H_2O levels.

Fiber Loop Supercontinuum Cavity Enhanced Absorption Spectroscopy

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Supercontinuum is a technique developed in recent decades to generate a stable spatial coherent broadband light source from a very narrowband pump source. In this work, a 15-meter-long Photonic Crystal Fiber (PCF) is connected to a laser source as a Supercontinuum generator. The pump source is a Q-switched solid state Nd:YVO4 laser working at 1064 nm. By tuning the pump laser to work at a power between 300mW and 1 W, a Supercontinuum is generated to cover a region from 450nm to 1600nm. With different pump laser power, the output Supercontinuum power differs, and usually a higher power can give a broader spectrum. Using this Supercontinuum source, we intend to build a fiber loop by fusion splicing a long single mode fiber to the PCF. A tapered fiber is fabricated on the loop to work as a sensor in liquid phase. It is put into liquid samples like water and organics (methanol, ethanol, isopropanol, acetone, etc.). By comparing different spectra with a spectrum without samples, we are able to tell what each sample is and finally tell the concentrations of different components in a mixed sample. A fiber taper is fabricated by heating a single mode fiber and pulling it along two ends at the same time. It is made to become narrower in the tapered region so that fiber cladding can be thinner. The evanescent wave is easier to get outside the fiber to be absorbed by whatever around it. The reaction of evanescent wave with different samples gives different spectra, so we are able to tell what kind of samples we have.

Frequency-Stabilized Cavity Ring-Down Spectroscopy of CO_2 in Support of Remote Sensing

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The carbon dioxide (20013)←(00001) band at 2.06 um was measured with frequency-stabilized cavity ring down spectroscopy. The high signal to noise ratio of these measurements allows for line shape analysis, including Dicke narrowing and speed dependence. Proper line shape choice and parameterization of these values is critical for remote sensing retrievals including OCO-2, a NASA satellite measuring global sources and sinks of carbon dioxide.

An In-Vacuum Optical Parametric Oscillator Squeezer for Gravitational Wave Detectors

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Australian National University

We present the first optical parametric oscillator (OPO) squeezer operating under vacuum. The aim of this experiment is to demonstrate a prototype squeezed light source at audio Fourier frequencies for injection into the advanced laser interferometer gravitational wave detectors (LIGO). This is to enable metrology below the quantum noise limit set by shot noise and radiation pressure noise in an optical interferometer. LIGO is the most sensitive metrology experiment in the world, consisting of two Michelson interferometers with optical cavity arms each at 4 km in length. A squeezer for operation with LIGO needs to produce ~10 dB of squeezing below the shot noise level in the audio frequency band, have low cavity length noise, and be housed in the vacuum envelope with the interferometer. Injection of such a squeezed light source permits both enhancement of the strain sensitivity of the instrument and a lower required intracavity circulating intensity in the interferometer. The OPO cavity is in a medium finesse bowtie ring configuration, producing vacuum squeezing at 1064 nm using PPKTP as the nonlinear crystal. The cavity is quasi-monolithic and the spacer is glass based for length stability. Cavity mirrors are glued to glass tombstones, which are optically contacted to the glass breadboard base. To maintain dual resonance at the 532 nm pump and 1064 nm fundamental wavelengths, the crystal is kept at 33 degrees Celsius, in a translatable vacuum-compatible oven. Operating the experiment under vacuum presents several technical challenges, such as different thermal characteristics in the crystal oven, and a difference in the intracavity dispersion. We will present our latest squeezing results from the collaborative experiment between the Australian National University and the Massachusetts Institute of Technology.

High-Q Resonant Cavities In The Terahertz Range: Optical Feedback Effects On Quantum Cascade Lasers

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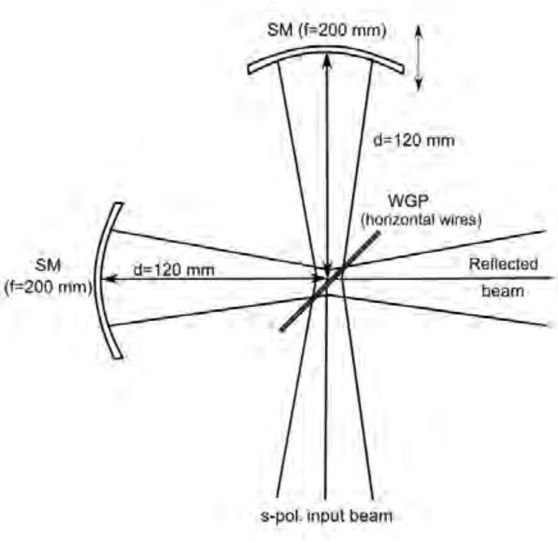
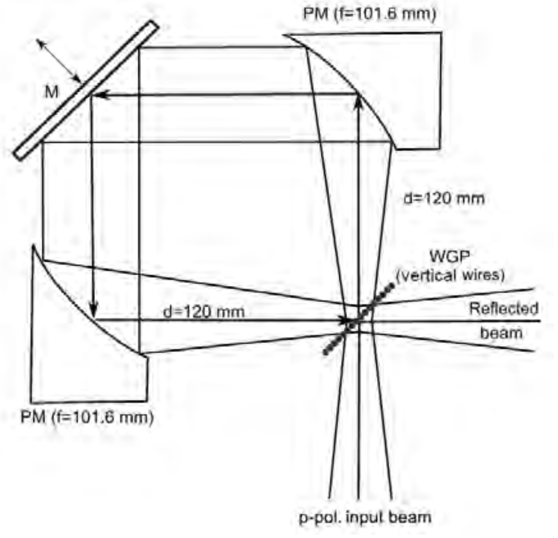
Optical resonators are well-established tools used in spectroscopy. The underexploited portion of the electromagnetic spectrum ranging from 0.1 to 10 THz, known as "terahertz", is still lacking of such tools. Recent advances in generation and detection of THz radiation, as well as the advent of THz quantum cascade lasers (QCLs), are now making THz light emerge as a new promising frontier for many research areas. Cavity resonators represent an attractive tool to further increase the sensitivity of a spectroscopic system, but design and fabrication of cavities resonating at THz frequencies are challenging. We report on the realization and characterization of two different designs (V-shaped and ring-shaped) for resonant THz cavities injected by a continuous-wave QCL emitting at 2.55 THz. We used wire-grid polarizers as high-reflectivity/low-transmission input/output couplers and equipped each cavity with a shifting mirror, in order to tune the cavity length. With the best values achieved for their finesse (F=63) and quality factor (Q=260,000), these cavities showed resonant peaks as narrow as few MHz, comparable with the typical Doppler linewidth of THz molecular transitions and slightly broader than the free-running QCL emission spectrum. In particular, the V-shaped resonator, when in resonance condition, generated optical feedback to the QCL, that, broadening the resonance peak profiles, prevented accurate finesse measurements. By simultaneously coupling the same THz QCL to both cavities, the effect of optical feedback from the V-shaped cavity to the laser was investigated. We injected both the resonators at the same time: the V-shaped cavity was swept across its resonances, while the ring cavity was kept fixed at a resonance half-height. In these conditions, any shift of the laser frequency induced by the optical feedback from the V-shaped cavity was measured as a variation of the signal retrieved from the ring-shaped cavity.





CELIF: Cavity-Enhanced Lase-Induced Fluorescence

N Hendrik Nahler[1], Arin Mizouri[2], Scott E Sanders[2], Oliver R Willis[1,2], Thomas Messider[2], David Carty[2], Eckart Wrede[2]
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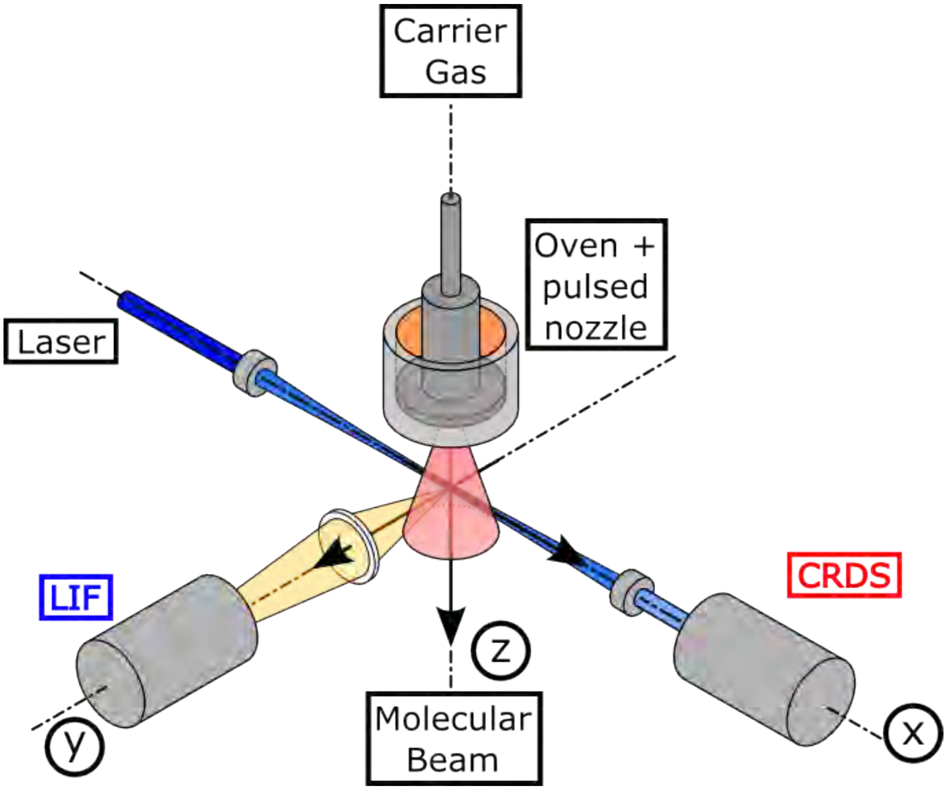
We describe a novel experimental setup that combines the advantages of both laser-induced fluorescence and cavity ring-down techniques. We perform a simultaneous and correlated ring-down and fluorescence measurement of the same sample in a single, pulsed laser beam. The combined measurement provides the calibration to extract absolute absorption coefficients from the fluorescence measurement which extends the dynamic range of a stand-alone cavity ring-down setup from typically three to at least six orders of magnitude. The presence of the cavity improves the quality of the signal, in particular the signal-to-noise ratio. The methodology, dubbed cavity-enhanced laser-induced fluorescence (CELIF), is developed and rigorously tested against the spectroscopy of 1,4-bis(phenylethynyl)benzene in a molecular beam and density measurements in a cell. We outline how the method can be utilised to determine absolute quantities: absorption cross sections, sample densities and fluorescence quantum yields.[1] In a further study, the absolute density of SD radicals in a supersonic jet has been measured down to $(1.1 \pm 0.1)\mathrm{x}10^{5}$ cm^{-3}. Such a density corresponds to 215 ± 21 molecules in the probe volume at any given time. The minimum detectable absorption coefficient was quantum noise-limited and measured to be $(7.9 \pm 0.6)\mathrm{x}10^{-11}$ cm^{-1}, in 200 s of acquisition time, corresponding to a noise- equivalent absorption sensitivity for the apparatus of $(1.6\pm0.1)\mathrm{x}10^{-9}$ cm^{-1} Hz$^{-1/2}$.[2]



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Pre-Excitation CRDS for Mercury

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Absorbance at 254 nm is traditionally used for detection of mercury. However, mercury shows significant cross sectional absorption area for the excited state transition at 405 nm, an optical region where higher reflectivity mirrors are available. We have produced a novel design using 254 nm light as a pre-excitation source for 405 nm mercury CRDS.

Vapor Detection of Nitrogen Oxide Containing Explosives by Catalytic Thermal Dissociation Blue Diode Laser Cavity Ring-Down Spectroscopy

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University of Calgary, Calgary, Alberta, Canada

The ubiquitous threat of terror attacks on airplanes, trains, and important infrastructure has led to a strong demand and interest in new instrumentation for detection of explosives. To avoid disrupting the flow of individuals and goods instrumentation is posed with the difficulty of rapidly detecting low vapor-pressure compounds in the gas phase requiring detection limits below the parts-per-billion by volume (ppbv) level. Many explosives contain nitrogen oxides, such as the nitroalkanes (e.g., ethylene glycol dinitrate, EGDN), nitroaromatic compounds (e.g., 2,4,6-trinitrotoluene, TNT), and the nitramines (e.g., hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX). Here, a compact 2-channel (55 cm optical path length) blue diode laser catalytic thermal dissociation cavity ring-down spectrometer (cTD-CRDS) for detection of nitroaromatic vapors is presented. The instrument utilizes a 405 nm cw diode laser which is square-wave modulated at a frequency of 2000 Hz. A heated quartz tube containing platinum (IV) oxide catalyst is used to dissociate nitrogen containing organic compounds to NO_2, which is detected via its absorption at 405 nm. Any NO generated is oxidized to NO_2 via addition of excess ozone prior to detection. The cTD-CRDS detection limit (3σ) is sufficiently low (0.3 ppbv) to allow direct detection of 2,4-dinitrotoluene (DNT) and TNT in real-time. We have recently constructed an automated preconcentration trap for detection of less volatile compounds, including RDX.

An Airborne Three-Channel LED-Based Broadband Cavity Enhanced Absorption Spectrometer for Measurements of Atmospheric Trace Gases

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We report the development and deployment of a three-channel airborne Broadband Cavity Enhanced Absorption Spectrometer using light emitting diodes (LEDs) as the light source, capable of covering the broad UV-vis spectrum by adapting the wavelength-sensitive components such as the ringdowm mirrors, LEDs and CCD detectors to the target wavelengths. The instrument has been deployed in a few field campaigns, with focuses on the nighttime NO_3/N_2O_5/NO_2 and on IO, respectively. Results from these campaigns are presented, with atmospheric implications discussed.

A Novel NIR ew-cw-CRD Spectrometer for Investigating Heterogeneous Processes at the Quartz-Air/Water Interface: Characterization and First Measurements

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Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Germany

Many cavity designs utilizing the evanescent wave (ew) have been developed such as monolithic resonators, fiber loop schemes and setups with an additional prism inside the cavity. Common to all implementations is that the attenuation of the ew resulting from total internal reflections (TIR) yield information about absorbing species adsorbed on the TIR surface. A novel ew-cw-CRD spectrometer has been built allowing us to observe vibrational overtone absorption bands in the near-infrared (NIR) region between 1600-1700 nm. A tunable external cavity diode laser served as a narrowband light source. The spectrometer was designed for this wavelength region due to 1.) the possibility to detect organic compounds based on their C-H overtone vibrations, 2.) the availability of high-quality mirrors and quartz prisms with low absorption and scattering losses and 3.) low disturbances caused by interfering water absorption bands, hence enabling the investigation of liquid water systems. A further advantage of our reactor is a modular design providing the possibility of both gas phase and interfacial measurements including photolysis. The performance of the spectrometer has been characterized by measuring empty cavity signals and by using Trichloroethylene (TCE) as a test substance. Spectra and adsorption isotherms are presented. As expected for single mode excitation of the ringdown cavity using narrow bandwidth radiation, measured spectra are affected by resonance effects stemming from the additional etalons arising from the configuration of the mirrors and the prism. Beating frequencies can be clearly related to the different intrinsic cavities. Several cavity modulation schemes and special fitting and averaging procedures have been tested to overcome the overlaying beating structure and therefore to increase the quality of the spectra. Nevertheless, despite long ringdown times (up to 3.7 μs in a 0.5 m cavity), minimum detectable absorbance is limited to $A\_min,10 = 2.7\times10^{-6}$.

Detection of S-Nitrosocompounds in Biological Samples

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S-nitrosocompunds are of strong biochemical interest due to their role as nitric oxide donors and their potential role in cardiovascular and pulmonary signaling. To elucidate the role of S-NO in proteins, exact concentrations must be measured in healthy and diseased tissues and cells throughout the body. Further understanding would benefit from metabolic studies of S-NO groups utilizing isotopic labeling. Levels of S-NO groups in cell and organ systems are typically 10-1000 nM, however this number is not known exactly for many tissues due to the potential breaking or formation of these bonds during sample preparation. Currently the most sensitive technique available for S-NO detection, chemiluminescence, has a limit of detection of 50 nM. However, chemiluminescence has the significant drawback of lack of specificity between ^{14}NO and ^{15}NO, making the technique not viable for use in metabolic studies. With the current cavity ring down (CRDS) set up in the Lehmann lab limits of detection of 2 pico moles and 5 pico moles for ^{14}NO and ^{15}NO respectively, which corresponds to concentrations of 20-50 nM in a typical 100 muL sample. Progress toward measuring S-NO groups in biological samples will be presented.

Noise-Immune Cavity-Enhanced Optical Frequency Comb Spectroscopy

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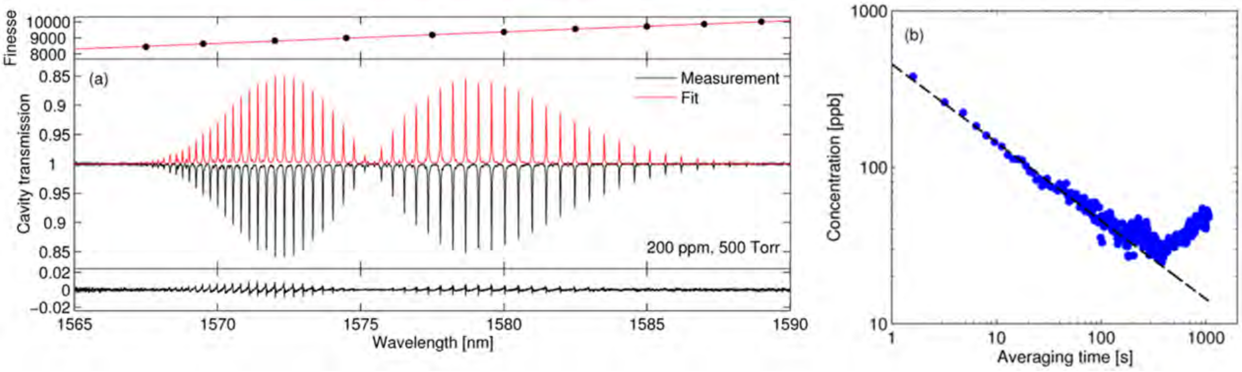
We present noise-immune cavity-enhanced optical frequency comb spectroscopy (NICE-OFCS), a new technique of sensitive, broadband, and high resolution spectroscopy [1]. In NICE-OFCS a frequency comb is locked to a high-finesse cavity and phase-modulated at a frequency equal to (a multiple of) the cavity free spectral range (FSR). Since each comb line and sideband is transmitted through a separate cavity mode in exactly the same way, residual frequency noise on the comb relative to the cavity affects each component equally. The transmitted intensity contains a beat signal at the modulation frequency that is immune to frequency-to-amplitude noise conversion by the cavity, similar to continuous wave NICE-OHMS [2]. Our NICE-OFCS system is based on an Er:fiber femtosecond laser (repetition rate of 250 MHz), a cavity (FSR of 187.5 MHz, finesse of ~9000 [Fig. (a)]), and a fast-scanning Fourier-transform spectrometer with a high-bandwidth commercial detector. The comb is locked to the cavity using the two-point Pound-Drever-Hall technique [3] and phase-modulated at a frequency of 562.5 MHz, generated by a direct digital synthesizer referenced to a harmonic of the comb repetition rate [4]. The NICE-OFCS signal is obtained by fast Fourier transform of a synchronously demodulated interferogram. We measured NICE-OFCS signals from the $3\nu1+\nu3$ overtone band of CO_2 around 1.57 μm [shown in Fig. (a) together with a fit and residual], and achieved absorption sensitivity of 6.4×10^{-11} cm^{-1} $Hz^{-1/2}$ per spectral element, corresponding to a minimum detectable CO_2 concentration of 25 ppb after 330 s [Fig. (b)]. We will describe the principles of the technique and its technical implementation, and discuss the spectral lineshapes of the signals.



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Laboratory Measurements of Temperature Dependent ^{13}C and D Kinetic Isotope Effect in the Oxidation of CH_4 by $O(^1D)$ and OH

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In this work, we utilized the frequency stabilized cavity ringdown spectroscopy (FS-CRDS) technique to study the temperature dependence of kinetic isotope effect (KIE) during the oxidation of methane by $O(^1D)$ and OH radicals. We demonstrated a dual wavelength technique by coupling two orthogonally polarized CW lasers into a ringdown cavity simultaneously to measure the full wavelength range of 1.45 to 1.65 um. The spectrometer is capable of measuring major isotopologues of methane ($^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$) of enriched samples to very high precision (D < 0.03% and ^{13}C < 0.01%). The photochemistry was initiated by photolyzing a mixture of N_2O, isotope enriched methane, H_2, and He at 193 nm in a temperature controlled cell between 155 K and 300 K. The concentrations of all major methane isotopologues before and after photolysis were analyzed using a frequency stabilized cavity ringdown (FS-CRDS) spectrometer. Our measurements observed D-KIE(155 K) = 1.133(20), and ^{13}C-KIE(115 K) = 1.149(22).

Simultaneous Kinetics and Ringdown Study of Peroxy Radical Reactions

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Peroxy radicals are key intermediates formed in the low temperature combustion and atmospheric oxidation of volatile organic compounds. Over the past decade, spectroscopic and kinetic investigations have increasingly employed near-infrared cavity ringdown spectroscopy to detect these radicals through their forbidden A-X electronic transition. Absorption features associated with distinct organic peroxy radicals exhibit greater spectral isolation in the near-infrared than their more traditional detection in the ultraviolet, thereby aiding the interpretation of time-resolved absorption signals for kinetic studies. In this work, we use near-infrared pulsed cavity ringdown spectroscopy and the Simultaneous Kinetics and Ringdown (SKaR) technique to study the production and decay of organic peroxy radicals. The SKaR technique (S.S. Brown, A.R. Ravishankara, and H. Stark, J. Phys. Chem. A, 2000, 104, 7044-7052) was developed as a way to measure a reaction rate that occurs on the same timescale as a ringdown event. We employ this method and report rate constants for the formation ($R + O_2 \rightarrow RO_2$) of organic peroxy radicals and their principle loss reaction in polluted environments ($RO_2 + NO \rightarrow$ products). We present progress toward measuring these rate constants for the peroxy radicals formed in the OH and Cl initiated oxidation of ethene, propene, 1-butene, 2-butene, 1,3-butadiene, and isoprene.

Optical Feedback Cavity-Enhanced Absorption Spectroscopy with a 3.24 µm Interband Cascade Laser

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The development of interband cascade lasers (ICLs) has made the strong C-H transitions in the 3 µm spectral region increasingly accessible. We present the first, to our knowledge, demonstration of a single mode distributed feedback ICL coupled to a V-shaped optical cavity in an optical feedback cavity-enhanced absorption spectroscopy (OF-CEAS) experiment. A typical cavity transmission spectrum averaged over 100 scans of a 25 kPa sample with 180 ppb CH_4 is shown in Fig. 1(a). Over 20 ms, the ICL locked to 40 successive cavity modes with a locking time, estimated by the FWHM, of 120 µs, much longer than the ring-down time (typically 3.2 µs). The time between modes was ~ 300 µs (Fig. 1(b)). We achieved a minimum detectable absorption coefficient, α_{min}, of $(7.1 \pm 0.2) \times 10^{-8}$ cm^{-1} for a spectrum of CH_4 at 3.24 µm with a two second acquisition time (100 scans averaged). This corresponds to a detection limit of 3 ppb CH_4 at atmospheric pressure, which is comparable to previously reported OF-CEAS instruments with diode lasers or quantum cascade lasers [1, 2]. The ability to frequency lock an ICL source in the important 3 µm region to an optical cavity holds great promise for future spectroscopic applications.

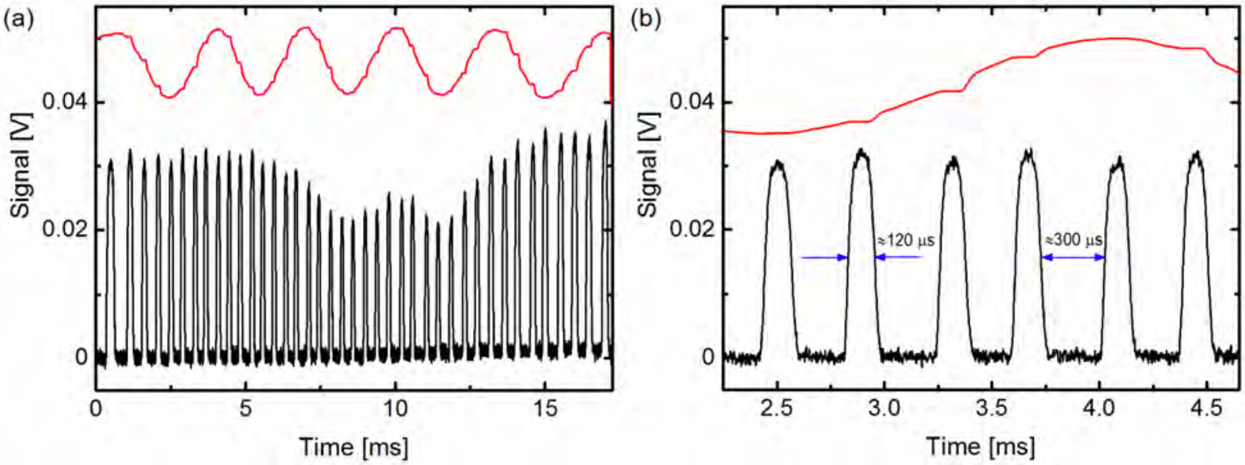

Fig. 1: (a) Cavity transmission for 180 ppb CH_4 in buffer gas at a total pressure of 25 kPa while the laser is scanning to lower wavenumber. This transmission spectrum is the average of 100 scans. (b) A magnification of the modes around 3 ms. In both figures, the upper trace is an etalon trace showing flat sections when locking to the modes occurs (shifted for clarity).

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Analysis of Multi-Exponential Decays in Cavity Ringdown Spectroscopy

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In cavity ringdown spectroscopy, the decay of optical power in a high finesse cavity is typically described by a single exponential, and cavity ringdown instruments are designed and operated to minimize any multi-exponential character. However, multi-exponential decays are frequently encountered in several situations: higher-order spatial modes from misalignment, non-optimal mode-matching, absorption features with spectral details that are finer than the laser spectrum, non-uniform mirror reflectivity, and co-adding of many decays. In this report, we analyze ringdown decays using a multi-exponential fit function and quantify errors arising from non-exponential decays. Specifically, we use an aerosol extinction cavity ringdown spectrometer to quantify aerosol extinction at elevated relative humidity. At 662 nm, water vapor, which has spectral features finer than laser bandwidth, interferes with the aerosol measurement. We show how a multi-exponential fit function can be used to remove this interference and to quantify errors due to misalignment.

Broadband Absorption Spectrometers Using LED for the Detection of NO_2, NO_3 and N_2O_5

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We developed a three channel IBBCEAS instrument for simultaneous measurement of NO_2, NO_3 and N_2O_5. For all channels, we used single color LED from LedEngin as light source and Ocean Optics QE65000 as detectors. In characterization experiments, we tried HR mirrors with 99.99% (in some cases 99.999%) reflectivity from Layertec, CRD optics and Sigmakoki. We calibrated the mirror reflectivity with pure nitrogen and helium, and the calibration results were further validated by observation of NO_2 compared to a commercial CLD NO_2 instrument. The spectral analysis is currently achieved by DOASIS but we are also developing an IDL software package for fast and on-line data analysis based on SVD algorithm. In the lab, if we produce NO_3 inside the cavity, the optical detection limit is found to be around a few ppt. In field test experiments, we recognized that the detection limit are strongly degraded by other factors and there were several major issues we have to overcome to deliver meaningful results of both NO_3 and N_2O_5. First is to minimize the losses on the aerosol filters especially the urban air in China is mostly with high aerosol loadings. Second is to minimize the inlet and cavity losses of them. Third is to subtract the extinction of H_2O correctly and precisely. To overcome the first and the second problems, we are developing an automatic filter exchanger, a new design to shorten the inlet and minimize the cavity volume so that most of NO_3 and N_2O_5 can survive into the cavity. For the third problem, we are setting up a lookup table of the H_2O absorption cross section at different concentrations at room temperature for our current detectors. This lookup take may be extended to other temperature regime according to theoretical calculations. We plan to use the newly developed IBBCEAS system to measure ambient NO_3 and N_2O_5 in both urban and rural Beijing. And therefore, to test and develop the nighttime chemical mechanism under highly polluted Chinese megacity areas.

Measurements of Formaldehyde Using Broadband Cavity Enhanced Spectroscopy at 315 - 360 nm

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Formaldehyde is the simplest aldehyde, and the most abundant in the atmosphere. Its sources include primary emissions and secondary photochemical production from anthropogenic and biogenic organic compounds. In many parts of the atmosphere, formaldehyde photolysis makes an important contribution to oxidation by providing a large source of HO_x (=OH + HO_2) radicals. We describe a laboratory instrument for simultaneous measurements of formaldehyde and nitrogen dioxide using broadband cavity enhanced spectroscopy. The output from a laser-driven Xenon arc lamp is coupled into a 1-m optical cavity, and the light exiting the cavity is recorded by a grating spectrometer with a charge-coupled device (CCD) array detector. Using cavity mirrors with 595 ppm loss at 330 nm, we obtain absorption spectra across the 315 - 360 nm spectral region. Mirror reflectivity as a function of wavelength is determined from the known Rayleigh scattering cross sections of He and dry zero air (N_2 + O_2). We use least-squares fitting with published reference spectra to simultaneous retrieve formaldehyde and nitrogen dioxide concentrations. For 1-min sampling at ambient conditions, the precision ($\pm 1\sigma$) on signal is better than 2 ppbv formaldehyde. We will discuss instrument improvements that would be required to reach sub-ppbv levels for atmospheric measurements.

Cavity-Enhanced Faraday Rotation Spectroscopy for Oxygen Detection

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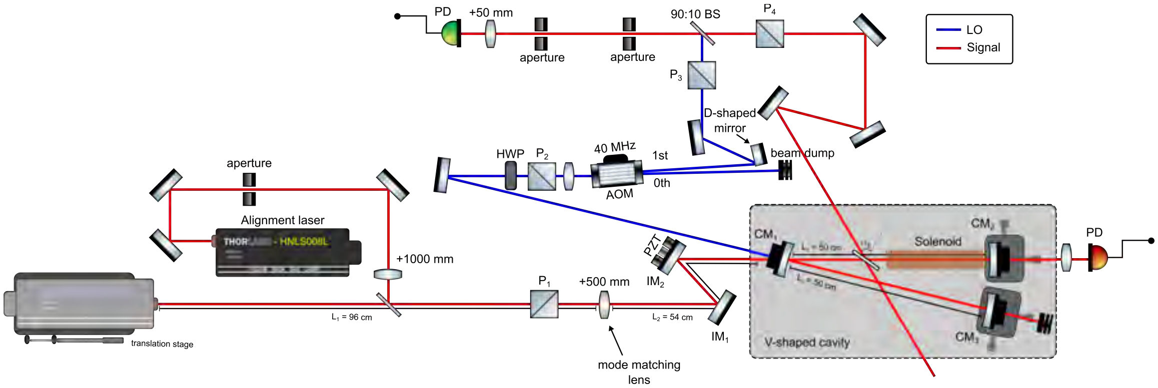
[2]*Pacific Northwest National Laboratory, Richland, Washington*

Indirect spectroscopic techniques such as photoacoustic spectroscopy or laser induced fluorescence (LIF) are known to benefit from increased optical power that directly affects the measured signal and improves the sensitivity. This is rarely the case for direct methods that rely on transmitted radiation through the sample. In this category, Faraday rotation spectroscopy (FRS), is one of the few techniques, in which the signal is directly proportional to the optical power, and hence benefits from large intra-cavity power build-ups. In this work we investigate the application of high-finesse cavities to effectively build up intra-cavity optical power to perform cavity enhanced FRS (CE-FRS). FRS utilizes an external magnetic field to induce a rotation of light polarization in the proximity of a magnetically sensitive molecular transition. The rotation angle is proportional to the sample concentration, which can be detected using a conventional polarimetric setup. Since FRS is sensitive only to paramagnetic species, unwanted interferences from diamagnetic molecules, such as CO_2 and H_2O, are largely suppressed. In recent years, this technique has been thoroughly investigated and several system have reached shot-noise limited performance. In order to perform CE-FRS, we propose a polarized cavity containing an intra-cavity polarization selector (e.g. a Brewster window). In this configuration, Faraday rotation results in an out-coupling of non-resonant polarization on every round-trip. Optical feedback with active laser-frequency locking and heterodyne detection are implemented for measurement of the out-coupled signal, and efficient suppression of background birefringence is obtained through a sinusoidal modulation of the magnetic field followed by lock-in detection. We will demonstrate an experimental setup with possible cavity build-up powers of up to several hundreds of mW, or even W, and theoretical modeling with prospects for obtaining enhanced FRS detection limits.



Cavity Ring-Down System for Measurement of Trace Gases in High Vibration Environments

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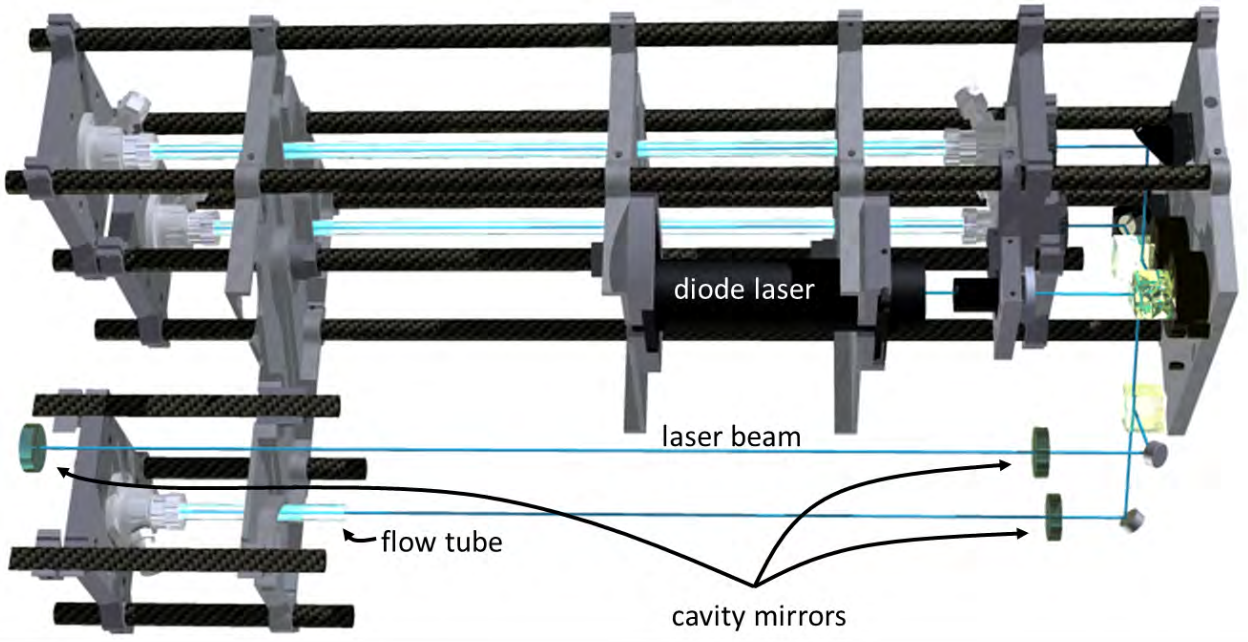
Cavity ring-down spectroscopy has established itself in the trace gas measurement community as a versatile and reliable measurement method. Field studies, as for studies of atmospheric chemistry and composition, often require mobile measurement platforms such as on-road vehicles or aircraft. These measurements add size, weight, and power restrictions to the instrument as a whole, but also subject the optical system to large mechanical vibrations within a broad frequency range. We present a custom-built cavity ring-down system adapted to these conditions, consisting of 4 separate 50 cm long optical cavities measuring NO, NO_2, NO_y, and O_3. The optics are mounted on a custom-built cage system made of carbon fiber rods and aluminum plates as shown in the figure below (sections have been removed for ease of illustration). The mounting system for the cavity mirrors contains no moving parts, providing the necessary immunity to misalignment. We use a single 405 nm diode laser for all four cavities, and achieve ring-down times of approximately 26 µs with noise of 5 ns/sqrt(Hz) in the laboratory and 8 ns/sqrt(Hz) while measuring in-flight on the NOAA P3, a large propeller aircraft. This results in 20-30 parts per trillion/sqrt(Hz) of in-flight noise on NO_2 mixing ratio measurements. Additionally, the alignment of the cavity mirrors has not needed readjustment over the last two years, which included multiple field campaigns and cross-country shipments by truck.



A Cyan-Light-Emitting Diode Cavity-Enhanced Absorption Spectrometer for the Measurement of Reactive Iodine Species

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Atomic iodine (I), molecular iodine (I_2) and iodine oxides (e.g., IO, OIO, I_2O_3, I_2O_5) are important trace gas constituents of the troposphere, in particular in coastal regions and at the poles. Even though the natural abundances of iodine species are often quite low (typically less than 100 parts per trillion by volume, pptv), iodine species have been found to contribute to the production and destruction of ozone (O_3) and to new particle formation. A recent review paper has identified the need for more ambient measurements to gain a better understanding of the global tropospheric distribution of iodine species. Mixing ratios of I_2, IO and OIO have been quantified using their visible absorption lines (between 400 and 600 nm) by open path differential optical absorption spectroscopy (DOAS) and cavity enhanced absorption spectroscopy (CEAS) in both open and closed cells. In this spectral region other molecules (e.g. O_4, NO_2, glyoxal, methyl glyoxal) and aerosols also extinguish light. In this presentation, a CEAS spectrometer to quantify NO_2, I_2, and OIO in ambient air is described. The instrument uses a cyan light emitting diode (LED) mounted on a temperature stabilized driver circuit. The absorption cell consists of a pair of concave (radius of curvature, r = 1 m) highly reflective mirrors that are situated approximately 1 m apart in a stable resonator configuration. The light source is coupled passively to the cavity. Light exiting the optical cavity is digitized using a Czerny-Turner spectrograph equipped with a CCD camera controlled using software written in National Instruments Labview. The instrument response to NO_2 was verified by blue diode cavity ring-down absorption spectroscopy (CRDS).

Aerosol Optical Properties Derived using Optical Spectroscopy

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A large fraction of aerosol is composed of organic compounds and understanding how these compounds interact with light is crucial to understanding their role in affecting climate. The bulk of organic aerosol is non-absorbing, but a significant fraction is composed of compounds that absorb at shorter wavelengths. The amount of light that a compound absorbs and scatters can be quantified using the complex refractive index, $m = n + ki$, where the real part n describes the scattering and the imaginary part k describes the absorption. While the refractive index cannot be directly measured, optical methods such as photoacoustic spectroscopy and cavity ring-down spectroscopy can be used in tandem to retrieve the refractive index. In this work details of the retrieval method will be presented, along with refractive indices for compounds formed via the reaction of glyoxal with ammonium sulfate, which could be a potential source of absorbing organic aerosol in the atmosphere.