CAVITY RING-DOWN USER MEETING 2005

September 20th/21st

Physical and Theoretical Chemistry Laboratory
The University of Oxford, UK

Book of Abstracts

Sponsored by:

EPSRC

Sacher Lasertechnik Group

TigerOptics

Invited Contributions

Selected Short Presentations

Posters

Detection of soot in an atmospheric propane flame using cavity ring-down spectroscopy

Jens Ekengren*, Johan Sjöholm*, Stina Hemdal*, Mats Andersson** and Arne Rosén**

*Dept. of Applied Physics, Chalmers University of Technology, Göteborg, Sweden
**Dept. of Physics, Göteborg University, Göteborg, Sweden

Soot particles in the environment is a serious concern to health and high levels of soot and other types of particulate matter is a problem in many cities. Most of the soot particles come from combustion, often combustion engines in vehicles. In order to be able to improve engines and other combustion devices it is necessary to be able to measure the formation and abundance of soot with high sensitivity, good accuracy and high time resolution. Cavity ring-down spectroscopy (CRDS) is one method with the potential to achieve that [1,2], and which can be applied both in fundamental flame studies and to the analysis of emissions in practical applications.

In this study soot formation was investigated in atmospheric propane flames using two types of optical spectroscopy. Emission and single-pass extinction using a monochromator with a CCD-detector and cavity ring-down spectroscopy for determination of the soot volume fraction and absorption. Emission and single-pass extinction spectra between 200 nm and 1000 nm have been collected. Based on the results from these measurements, a wavelength interval to be investigated using cavity ring-down spectroscopy was selected.

For the CRDS experiment the light from an excimer-pumped dye laser with 10-ns pulses was used. The light was filtered to avoid that the weak intensity of other wavelengths was transmitted to the detector. Mirrors with a reflectivity maximum at 510 nm were used for the cavity. The light transmitted through the cavity was detected by a photo-multipler tube, and the signal was recorded with a digital oscilloscope.

Ring-down times have been measured at two heights in sooting and premixed atmospheric flames for wavelengths between 494.0 nm and 498.2 nm, and for different heights for two wavelengths of special interest. The maximum soot volume fraction was for the sooting flame found 23 mm above the burner edge and was calculated to 50 ppb. This value was calculated using the ring-down time for the premixed flame as the "empty-cavity" reference to compensate for thermal lensing effects influencing the ring-down time.

R.L. Vander Wal and T. Ticich, Appl. Opt. 38, 1444 (1999).
C. Schoemaecker Moreau, E. Therssen, X. Mercier, J.F. Pauwels, P. Desgroux, Appl. Phys. B 78, 485 (2004).

CRDS at RF- and microwave-generated hydrogen plasmas

M. Berger*, U. Fantz, S. Christ and IPP NBI Team

Max-Planck-Institut für Plasmaphysik Boltzmannstrasse 2, 85748 Garching, Germany

CRDS is being used more and more also as a diagnostic tool for plasma sources. In Hydrogen plasmas e.g. the species H^- and H_3^+ can be measured using this method. One of the main plasma heating mechanisms in fusion research used today is the neutral beam injection, where protons produced in a hydrogen discharge are first accelerated in an electric field and then neutralized for injection through the confining magnetic field into the plasma volume. For future fusion devices the need for sources producing large amounts of negative hydrogen ions (H^-) emerged, because it is possible to almost completely neutralize the accelerated beam even at high energies, which is not the case for protons. At one of the test facilities at the IPP the extraction of H^- from a pulsed high power (up to 140 kW) RF-driven hydrogen discharge is studied. A CRDS is being set up at the source for absolute density measurement of H^- inside the source by photodetaching the additional electron with the pulse of a Nd:YAG-laser coupled into the high finesse cavity. This kind of pulsed CRDS for determining the H^--density has already been successfully applied under laboratory conditions, but is much more difficult to realize in the rough environment of large high-power test facility, i.e. a large vacuum system, high power load on components, mirror degradation by plasma impact and excessive EM-disturbances induced by the RF-transmitter. The progress on the CRDS-setup at is shown and different issues and workarounds concering CRDS under these conditions are discussed.

In a second setup the density of H_3^+ was measured in a low-pressure (10-100 Pa) continuously operating surface wave discharge with a microwave heating power of up to 2 kW by means of a wavelength-resolved cw-CRDS, using an external cavity diode laser tunable around 1469 nm. An absorption line of H_3^+ was measured and a method for deriving the absolute H_3^+-density from H_3^+ molecular data is presented. The setup was shown to be working, but still suffers from e.g. thermal misalignment of the ringdown cavity during plasma operation due to the high power load to the vacuum vessel. Plans for future improvements of the setup are discussed.

F^- detection by CRDS in a dual-frequency capacitive plasma in $Ar/C_4F_8/O_2$

Garrett Curley, Cormac Corr and Jean-Paul Booth

Laboratoire de Physique et Technologie des Plasmas, Ecole Polytechnique, Palaiseau France

Dual-frequency capacitively coupled plasmas in Ar/fluorocarbon mixtures are widely employed for etching of holes in SiO_2-based dielectrics in integrated circuit manufacture. Negative ions can dominate the structure and dynamics of discharges if their density is high enough, yet no experimental data is available for dual-frequency plasmas. They may also play a role in etching if they can reach the surface. The determination of the negative ion density via the detection of photo-detached electrons is difficult to implement in such reactors due to the large RF fluctuations of the plasma potential. Therefore we have implemented the cavity ring-down spectroscopy (CRDS) technique to measure the density of fluorine negative ions in a customized industrial dual-frequency capacitive etch reactor operating with $Ar/C_4F_8/O_2$. A pulsed laser beam from a tuneable dye laser was scanned over the wavelength range 340 to 360 nm and injected into an optical cavity formed by two high-reflectivity concave mirrors (> 99.95 %). The temporal behaviour of the decaying pulse at the cavity exit allows the density of absorbing F^- ions to be determined from the known photo-detachment cross-section. The negative ion density will be investigated as a function of input power and gas mixture.

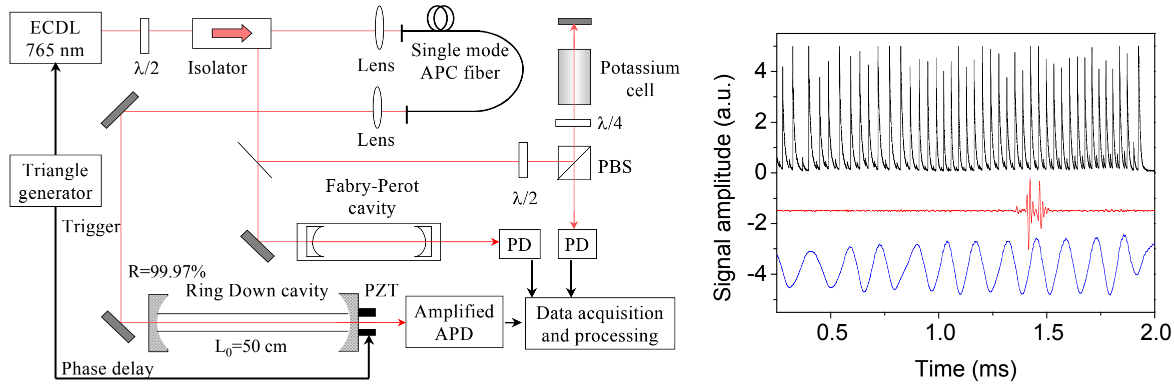
High-speed Cavity Ringdown Spectroscopy with increased spectral resolution by simultaneous laser and cavity tuning

I. Debecker, A. K. Mohamed
Office National d'Etude et de Recherches Aérospatiales (ONERA), Chemin de la Hunière, 91761 Palaiseau Cedex, France
D. Romanini
Centre National de la Recherche Scientifique (CNRS), LSP (UMR 5588), 38402 Saint Martin d'Hères Cedex, France

We present a new cw-CRDS design based on a fast tuning of the laser frequency and a simultaneous sweep of the cavity length. The ringdown events, consisting in the cavity injection and the subsequent intensity relaxation, are obtained while continuously passing through the successive resonance conditions. An absorption spectrum is recorded during a single laser sweep, without any extinction of the laser beam or averaging procedure of the signals.

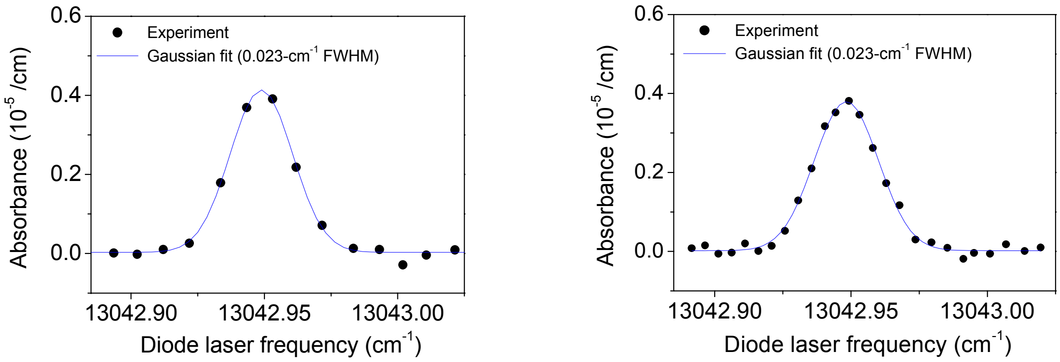
This method offers low integration times but also presents an interesting potentiality to increase spectral resolution. Considering only the excitation of the TEM_{00} modes of a static cavity, the maximum achievable frequency resolution corresponds to the free spectral range of the cavity. To overcome this limitation, the laser frequency is rapidly tuned through the probed absorption line, while the cavity resonance frequencies are synchronously swept in the opposite direction. This leads to an increased number of frequency-matched events between the laser and the cavity, thus to points on the absoption feature that are sampled at intervals smaller than the cavity free spectral range.

The experimental setup devoted to the detection of a weak transition of O_2 in air near 766 nm is depicted in Fig. 1(a). The typical signals recorded during a single positive-going ramp of the laser current within 2 ms are shown in Fig. 1(b). The combination of a 0.2-cm^{-1} laser frequency sweep and a synchronized 7.5-µm cavity sweep results in a refined resolution of almost 0.005 cm^{-1}, whereas the resolution is 0.01 cm^{-1} for the static 50-cm-long cavity (see Fig. 2). Our CRDS system thus offers a high acquisition rate and an increased resolution for probing fast chemical processes with accuracy and minimal instrumental complexity.



(a) (b)

Fig. 1. (a) Experimental setup. ECDL: external cavity diode laser, PBS: polarizing beam splitter, PD: photodiode, APD: avalanche photodiode, PZT: piezo translator. (b) Typical signals recorded during a single laser sweep. The ringdown peaks are obtained during a single 2-ms frequency sweep and the relative calibration is provided by a saturated absorption line of potassium and a Fabry-Perot etalon.



(a) (b)

Fig. 2. Experimental absorption line profiles of the weak $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-(0, 0)$ transition of O_2 in room air, around 10 mbar. The measurements are obtained using a 0.2-cm^{-1} laser frequency sweep within 2 ms, (a) without cavity tuning and (b) with a simultaneous 7.5-µm cavity sweep to increase the frequency resolution.

Universal water quality sensors based on long-period gratings and fiber-loop ring-down spectroscopy

Jenny Du, Cathleen Crudden†
Jun Zhang, Krista Laugesen, Stephen Brown,‡
Nick Trefiak, Jack Barnes, Hans-Peter Loock*

Queen's University, Dept. of Chemistry, Kingston, ON, Canada, K7L 3N6

Fiber-loop ring-down spectroscopy (FLRDS) is suited to measure very small optical losses in loops made of single-mode optical fiber. In this contribution the optical losses are induced by the insertion of a long-period grating into the waveguide loop. The long-period grating, has recently received attention as an inexpensive, robust and sensitive means to determine refractive indices.
Long-period gratings (LPGs) have attenuation spectra that depend strongly on the refractive index of the immediate environment of the fiber. A sensor for contaminants in water was made by coating the LPG with an index matched material that also permits solid phase microextraction of the desired analyte from an aqueous solution. The contaminant is enriched in the fiber coating by 2-7 orders of magnitude, changing the refractive index of the coating considerably. This change is detected by a change in the attenuation spectrum using FLRDS. Detection limits of better than 10ppm for a variety of hydrocarbons have been demonstrated, and work on sensors for specific metal cations is underway.
Applications in remote environmental monitoring of organic pollutants are discussed.

†CruddenC@chem.QueensU.CA ‡BrownS@chem.QueensU.CA
*HPLoock@chem.QueensU.CA

INCOHERENT BROAD-BAND CAVITY ENHANCED ABSORPTION SPECTROSCOPY (IBBCEAS) OF LIQUID SAMPLES.

S.E. FIEDLER, A. HESE, *Institut für Atomare Physik und Fachdidaktik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany*; A.A. RUTH, *Department of Physics, National University of Ireland, University College Cork, Cork, Ireland.*

IBBCEAS is a new very sensitive method for broad-band absorption measurements[1]. The sensitivity of classical spectrometers (white light source, sample-chamber, monochromator, CCD-array) can be enhanced using an optical cavity by orders of magnitude. The calculated enhancement of the sensitivity by the cavity mirrors as well as examples of IBBCEA spectra in the liquid phase will be presented.

---

[1] S.E. Fiedler, A. Hese, A.A. Ruth, *Chem. Phys. Lett.*, **371**, 284-294 (2003).

Development of an LED based broadband cavity enhanced absorption spectrometer for atmospheric studies

Justin M. Langridge*, Stephen M. Ball and Roderic L. Jones

Department of Chemistry, University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

A new instrument adopting a broadband variant of cavity enhanced absorption spectroscopy has been demonstrated at visible wavelengths using incoherent light from arrays of red and green light emitting diodes. The broadband CEAS spectrum of a mixture of molecular oxygen and water vapour has been recorded with a bandwidth of 60nm centred at 675nm allowing simultaneous measurement of the b $^1\Sigma_g^+$ (v'=1) ← X $^3\Sigma_g^-$ (v''=0) overtone of molecular oxygen and the water vapour 4ν and 4ν +δ polyads. In addition, quantitative amounts of 3 atmospherically important absorbers have been recovered from broadband CEAS spectra of laboratory samples at high dilution using spectral fitting techniques adapted from differential optical absorption spectroscopy. The nitrate radical, NO_3, was measured at a concentration of 40.3 ± 2.5pptv (255s exposure, 0.45nm FWHM resolution), NO_2 at 64.8 ± 0.7ppbv (500s exposure, 0.09nm FWHM) and I_2 at 991 ± 11pptv (300s exposure, 0.09nm FWHM). Hence, this first generation proof of principle instrument already has sufficient sensitivity to detect ambient levels of NO_2, NO_3 and N_2O_5 (via thermal decomposition to NO_3) present under polluted conditions and elevated levels of I_2 occasionally observed in the marine boundary layer. Collectively, these results demonstrate progress made towards the development of a compact, portable and power-efficient field instrument capable of providing highly sensitive in-situ trace gas measurements.

Combining pre-concentration of air samples with cavity ring down spectroscopy

Ruth E. Lindley, Alistair M. Parkes and Andrew J. Orr-Ewing

University of Bristol, Department of Chemistry, Cantock's Close, Bristol, BS8 1TS.

Cavity ring down spectroscopy is a highly sensitive laser absorption technique that can be used to detect gaseous species at very low concentrations (ppbv and pptv mixing ratios). Using continuous wave diode lasers in the near infrared allows detection of a number of atmospherically important molecules via excitation of overtone and combination bands. Although these features have relatively small absorption cross-sections (typically of the order of 10^{-21} cm^2 $molecule^{-1}$ cm^{-1}) detection limits are approaching the atmospheric concentrations of many species.

Sample pre-concentration can be achieved by passing a large volume sample through a trap containing an absorbent material which retains the species of interest. The trap can then be heated to desorb this species and a small volume of carrier gas used to flow the molecules into a small volume ring down cavity. The concentration of the sample within the cavity can then be determined and the concentration of the original sample obtained. This combination of techniques has been shown to improve the detection limit by a factor of 34 and allowed detection of ethene (C_2H_4) at 6150.3 cm^{-1} in urban air samples as low as 6 ppbv without the need for calibration.[1]

The pre-concentration system is now being applied to acetylene. Early experiments have shown that the efficiency of trapping and desorption is ~ 60 %. This efficiency must be quantified to a high degree of accuracy and the reproducibility of the process analysed. Optimisation of the experiment to improve the efficiency would also improve the detection limit and hopefully provide a technique sensitive enough to measure atmospheric acetylene in both urban and rural environments.

References

1. A. M. Parkes, R. E. Lindley and A. J. Orr-Ewing, *Anal. Chem*. 76, 7329-7335 (2004)

Cavity ring-down spectroscopy diagnostics of a DC arcjet plasma system for diamond CVD

Christopher J. Rennick, Jie Ma, Richard Engeln,[a] Andrew J. Orr-Ewing,
Michael N. R. Ashfold and Yuri A. Mankelevich,[b]

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK
[a] Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.
[b] Nuclear Physics Institute, Moscow State University, 119899 Moscow, Russia

Cavity ring down spectroscopy (CRDS) has proved to be one of the best methods at present for measuring the absolute concentrations of species in the plasma because of its non-invasive character, its high sensitivity and accuracy.
The DC arcjet technique is an important diamond CVD technique, in which a plasma jet is formed by using a high dc voltage to break down the feedstock gas mixture of H_2/Ar; the resultant gases then expand through a small nozzle into a vacuum chamber. Methane can be added downstream into the plasma as the carbon source, the active carbon-containing species generated in the plasma can then react on the substrate and finally lead to diamond growth.
Hydrogen plays an essential role in diamond deposition. Here, experiments on measuring the column density of excited hydrogen atoms H (n=2) in an Ar/H_2 plasma jet by CRDS have been performed and at the same time compared with a 2D theoretical model, in order to gain a deep understanding of the hydrogen chemistry. The absorption was measured at 486.13 nm, the hydrogen Balmer-β absorption line. Electron densities are obtained simultaneously, simply by deconvolution of the Stark broadening from the measured spectrum. Direct absorption measurement of the spatial variation of H (n=2) atom concentration have also been made using a cw diode laser tuned to the Balmer-α absorption feature.

Combining evanescent wave cavity ringdown with scanning electrochemical microscopy to study dynamical interfacial phenomena.

M. Mazurenka, J.V. Macpherson, P.R. Unwin and S.R. Mackenzie

Department of Chemistry, University of Warwick, Coventry, UK

We have very recently begun development of a hybrid technique combining Evanescent Wave Cavity Ring-Down Spectroscopy (EW-CRDS) with Scanning Electrochemical Microscopy (SECM) in order to investigate dynamical interfacial phenomena. In essence ultra-microelectrode SECM will be used to trigger local perturbations in solid-liquid and liquid-liquid interfaces the evolution of which will be monitored by EW-CRDS.

A simple blue diode laser, ring cavity variant has been built and the initial results of its characterization are presented. The instrument performance and sensitivity will be tested using the mass transport-limited oxidation of ferrocyanide $[Fe(CN)_6^{4-}]$ to ferricyanide $[Fe(CN)_6^{3-}]$ in aqueous solution using a disc-shaped UME. Detection will be via cavity ring-down detection of $[Fe(CN)_6^{3-}]$ at 417 nm, close to the minimum in the absorption spectrum of water. The high spatial resolution provided by the UME-SECM (typical microelectrode diameters of 10 μm can be produced routinely) coupled with the sensitivity and temporal characteristic provided by EW-CRDS should make for a very powerful instrument capable of investigating a wide range of interfacial phenomena. Envisaged applications of the instrument include studies of lateral proton diffusion in supported lipid bilayers, liquid-liquid mixing kinetics, charge propagation in ultra-thin conducting polymer films and nanocomposite materials, reaction kinetics at immiscible liquid/liquid interfaces, and particle nucleation and growth (controlled deposition) at surfaces.

CRDS as a non-invasive diagnostic tool in medicine

B.W.M. Moeskops, S.M. Cristescu and Frans J.M. Harren

Department of Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University Nijmegen, The Netherlands

For correspondence: E-mail B.Moeskops@science.ru.nl
Webpage: www.ru.nl/tracegasfacility

Breath testing is the least invasive of all diagnostic tests. Our challenge is to develop a cost-effective and non-invasive diagnostic tool for medical diagnostics, by real-time analysis of trace gas concentrations in human breath.. Examples are given of detection schemes and applications. A CO_2 laser based photoacoustic instrument is used to determine the pharmacokinetics of ethylene. A pulsed quantum cascade laser is used for the detection of carbon monoxide at ppbv levels. And a peltier cooled continuous wave quantum cascade laser will be used for cavity enhanced absorption spectroscopy of nitric oxide.

Preliminary studies of photolytic and discharge products of methane using CRDS technique

C. Romanzin[(a)], Y. Bénilan[(a)], S. Boyé-Péronne[(b)], S. Douin[(b)], D. Gauyacq[(b)], M.-C. Gazeau[(a)], A. Jolly[(a)]

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Universités Paris 7 & 12, Créteil, France.
Laboratoire de Photophysique Moléculaire (LPPM), Université Paris 11, Orsay, France.

As methane is the main precursor of Titan's photochemistry, its photolytic behaviour is of great importance for the understanding of Titan's atmospheric system. For this reason, an experimental simulation program of Titan's atmosphere, named SET-UP (Experimental and Theoretical Simulations Useful for Planetology), is being developed at LISA. In Titan's atmosphere, methane is mainly photolysed by the solar Lyman-α radiation. Therefore, one major goal of the laboratory experimental simulations is to extract branching ratios and abundances of the primary fragments from the Ly-α photolysis of CH_4, since these radical fragments will be responsible for the active chemistry in the Titan atmosphere. The starting step of these simulations, carried out at LPPM, consists of probing by CRDS the CH produced from methane photodissociation, through its A-X transition. In order to validate a photolytic scheme of methane by using a commercial KrF excimer laser at 248 nm, the two-photon photolysis at this wavelength will be compared with the one-photon photolysis at Ly-α, on the CH fragment production.
A preliminary CRDS study of CH has been performed by using $CHBr_3$, a well-known precursor of CH radicals, both via discharge and two-photon dissociation. These experiments have allowed to optimize the experimental conditions for CH observation by using effusive beams, supersonic beams, or bulk conditions. Comparison of both precursors, $CHBr_3$ and CH_4, shows significant differences: it turns out that discharge in a free jet of methane, in contrast to that of bromoform in similar conditions, leads to vibrationally hot CH fragments. Nevertheless, two-photon photolysis of methane has failed to produce enough CH fragments to be observable via CRDS, probably because of energetics of the two-photon excitation scheme which notably differs in both precursor molecules.

Porphyrin detection in solution: A comparison between pulsed cavity ring-down and integrated cavity output spectroscopy

K.T. Lynch, D. O'Leary, A.A. Ruth*

Physics Department, National University of Ireland, University College Cork, Cork, Ireland

So far only a few studies considered pulsed cavity ring-down (CRD) absorption measurements of samples in bulk liquids [1-6]. Due to large inherent losses in liquids and at surfaces of appropriate cuvettes, the ring-down transients and their changes due to the sample absorption are typically rather short (ns-time scale), which ultimately affects the signal-to-noise limit in these experiments. Moreover, the dynamic range of absorptions, which can be measured in solution using the CRD principle is limited, since ring-down rates can become too large at reasonably strong absorbances to be readily detectable. Therefore absorption measurements based on pulsed integrated cavity output spectroscopy (ICOS) [7] were performed at 532 nm in the Q-band of platinum-octaethylporphyrin (PtOEP) in toluene and compared with conventional pulsed CRD experiments. A procedure to determine absolute concentrations in the 10^{-9} molar regime of PtOEP was established and a systematic study was undertaken to quantify the inherent losses of several commonly used organic solvent at 532 nm. The possibility of detecting extremely forbidden singlet-triplet transition ($T_1 \leftarrow S_0$) in aromatic hydrocarbons in solution will be also be discussed.

[1] A.J. Hallock, E.S.F. Berman, and R.N. Zare, Anal. Chem. 74 (2002) 1741.
[2] S.C. Xu, G.H. Sha, and J.C. Xie, Rev. Sci. Instrum. 73 (2002) 255.
[3] A.J. Hallock, E.S.F. Berman, and R.N. Zare, Appl. Spectr. 57 (2003) 571.
[4] K.L. Snyder and R.N. Zare, Anal. Chem. 75 (2003) 3086.
[5] Z.G. Tong, M. Jakubinek, A. Wright, A. Gillies, and H.-P. Loock, Rev. Sci. Instrum. 74 (2003) 4818.
[6] B. Bahnev, L. van der Sneppen, A.E. Wiskerke, F. Ariese, C. Gooijer, and W. Ubachs, Anal. Chem. 77 (2005) 1188.
[7] A. O'Keefe, Chem. Phys. Lett. 293 (1998) 331.

* Corresponding author. E-mail: a.ruth@ucc.ie

Photochemistry of formaldehyde under tropospheric conditions

Carina A. Smith, Francis D. Pope, Dudley E. Shallcross, Michael N.R. Ashfold, Andrew J. Orr-Ewing.

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK.

Absorption cross sections of the $\tilde{A}^1A_2 \leftarrow X^1A_1$ electronic transition of formaldehyde in the wavelength range 300 – 320 nm have been measured[1] at resolutions close to the Doppler broadening limit at 294 K of 0.07 cm^{-1} FWHM, for isolated rotational lines. Lifetime broadening effects contribute a further ~0.5 cm^{-1}. In this wavelength region, absorption cross sections peak at 2.3 x 10^{-19} cm^2 $molecule^{-1}$, but band-integrated values are in excellent accord with previous measurements.[2] Accurate values are of considerable importance for atmospheric monitoring and to understand the photochemistry of this compound. HCO absorption coefficients, measured by cavity ring-down spectroscopy following UV photolysis of HCHO generally mimic the parent absorption band profiles over the wavelengths measured. We present first data[3] on the photochemical yields of the H + HCO channel following UV excitation of HCHO. In determining relative quantum yields, the radical products of this important photochemical step in the pathway to HO_x production have been measured directly for the first time.

[1] F.D. Pope, C.A. Smith, M.N.R. Ashfold, A.J. Orr-Ewing, *Phys. Chem. Chem. Phys.*, 2004, **6**, 1.
[2] C.A. Cantrell, J.A. Davidson, A.H. McDaniel, R.E. Shetter, J.G. Calvert, *J. Chem. Phys.*, 1990, **94**, 3902.
[3] F.D. Pope, C.A. Smith, P.R. Davis, D.E. Shallcross, M.N.R. Ashfold, A.J. Orr-Ewing, *Faraday Discuss*, 2005, **130**, 59.

Study of the reactivity of calcium with halogenated compounds by CRDS

C. Bahrini*, J. Rostas** and G. Taieb**

*Laboratoire de Spectroscopie Atomique, Moléculaire et Applications, Université El Manar, Campus Universitaire, Tunis 1060 Tunisie
**Laboratoire de Photophysique Moléculaire du CNRS, Université Paris Sud, bat.210, 91405 Orsay France

The reaction of Calcium atoms with halogenated compounds ($CHBr_3$, C_3H_7I) has been studied by simultaneous recording of the absorption (CRDS technique) and fluorescence (LIF technique) of nascent CaX radical. The analysis of absorption and emission spectra involving excited electronic states has provided evidence of predissociations. Observation of strong auto-absorption of the first resonance line of Ca (^1S – ^1P transition at 422.67 nm) will be reported and discussed.

Fibre-optic ring-down absorption detectors

Nick Trefiak, Dan Courtney, Richard Walford, Hans-Peter Loock*

Queen's University, Dept. of Chemistry, Kingston, ON, Canada, K7L 3N6

In the past decade the telecom industry has produced an enormous variety of specialized lightsources, waveguides, detectors and other optical components. Chemists are now making use of these developments by adapting waveguide techniques to chemical measurements. A recently developed technique (fibre-loop ring-down spectroscopy: FLRDS) that is based on the measurement of the photon lifetime in a waveguide loop appears to be particularly suited to sensitive measurements of optical loss. FLRDS has been used by a number of groups to measure mechanical strain, optical absorption losses in picoliter sized volumes formed by gaps in the waveguide, and absorption of the evanescent wave. This contribution highlights the use of FLRDS as a sensitive absorption detector for microfluidic devices. Combined with capillary electrophoresis or "labs-on-a-chip" FLRDS permits the separation and detection of unlabelled analytes. Advantages and limitations of FLRDS as a universal absorption detector are discussed.

trefiakn@chem.queensu.ca / *HPLoock@chem.QueensU.CA

Phase and amplitude detection in phase-shift cavity ring-down spectroscopy

J.H. van Helden*, J.J.A. van den Dungen, P. Vankan, D.C. Schram, R. Engeln

Department of Applied Physics, Center for Plasma Physics and Radiation Technology (CPS), Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Cavity ring-down detection schemes are nowadays widely used for measuring electronic and
vibrational transitions in gases, plasmas and even solids [1]. In most CRD schemes, a pulsed laser is used.

In this contribution, we show the results of a study of the use of a continuous wave CRD scheme, i.e. phase-shift cavity ring-down (PSCRD) [2], to determine densities of species in plasma. In the phase-shift cavity ring-down technique, a narrow-band diode laser is used in combination with a high-finesse optical cavity to perform sensitive high-resolution, direct absorption spectroscopy. The absorption spectrum is extracted from a measurement of the phase-shift that an intensity modulated continuous laser beam experiences upon passing through an optical cavity. At the same time also the amplitude of the detected signal gives information about the absorption spectrum.

Recently, we demonstrated that with PSCRD spectroscopy absolute line intensities of the spinforbidden transitions in the $b^1\Sigma_g$ + (v'=0) $\leftarrow X^3\Sigma_g$ + (v''=0) band of molecular oxygen, the so-called 'Aband,' can be measured within 4% of the line intensities given by the HITRAN molecular spectroscopic database [3]. We also showed that in case the laser emission contains a large amount of amplified spontaneous emission, a simple model can be used to correct the measurements for this. From our results obtained, we concluded that with phase-shift cavity ring-down absorptions down to $2\cdot10^{-8}$ cm^{-1} can be recorded in an integration time of 500 millisecond.

The high sensitivity together with its simplicity and high duty cycle makes phase-shift cavity ring-down spectroscopy a very promising diagnostic technique. Moreover, the PSCRD technique could specifically be very helpful in plasma measurements, since the use of a frequency modulated laser would allow to filter out the light emission of the plasma. Currently, we are investigating the possibilities to reduce the total measurement time per spectrum of a transition together with cheaper detection systems, without loss of sensitivity.

We will present results of measurements of the phase and amplitude obtained with the PSCRD technique using different ways of recording an absorption spectrum. In particular, a comparison between performing a scan in step-mode or by fast continuous scanning over the wavelength range of interest. Also the detection system was analyzed, i.e. if a state-of-the-art lock-in amplifier could be replaced by a simple homemade detection system. The measurements revealed that the experimental setup used previously [3], could be simplified without loss of sensitivity.

[1] G. Berden, R. Peeters, G. Meijer, Int. Rev. Phys. Chem., 19 (2000) 565.
[2] R. Engeln, G. von Helden, G. Berden, G. Meijer, Chem. Phys. Lett. 262 (1996) 105.
[3] J.H. van Helden, D.C. Schram, R. Engeln, Chem. Phys. Lett., 400 (2004) 320.

Cascaded arc as a light source for broadband CRD-like measurements

R.A.B. Zijlmans, J. Goudsmits, D.C. Schram, R. Engeln

Dept. Of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, the Netherlands

Various types of pulsed lasers have been used in many different CRD-like experiments. These types of lasers exhibit a high light output power of typically 10^6 W during the laser pulse. This is enough light to permit a CRD scheme using a high finesse optical cavity (high Q-factor, e.g. 3000) and thus a signal reduction of the same order as the Q-factor. CW diode lasers show a high total intensity (10 – 100 mW) over a small spectral range, which can be scanned. Together with time integration, this permits the use of a relatively high finesse optical cavity. Broadband CW light sources generally show a significantly lower spectral light output intensity, which makes the combination with a CRD-like detection scheme more challenging.

Fiedler implemented a xenon short-arc as a light source in a cavity enhanced absorption detection scheme on jet-cooled azulene [2]. We also showed the possibility of using a cascaded arc as an extremely bright light source (an etendue of xxx) to perform broadband CRD-like absorption measurements on methane [1]. We conclude that these types of variants on the CRD detection scheme with intermediate Q-factors (e.g. 100) are useful for broadband absorption experiments in which the single pass detection limit is just not good enough.

We used the cascaded arc light source in combination with a Fourier transform spectrometer in order to use the highest possible fraction of the emitted light beam. The etendue of the light beam was matched to the FT spectrometer by improving the geometry of the arc channel (110 W cm^{-2} sr^{-1} nm^{-1}). By using an optical cavity with a relatively low Q-factor (100), the sensitivity has been increased with a factor of five compared to single-pass measurements. Recently, we introduced the possibility of modulating the light output of the cascaded arc by directly modulating the current through the arc channel and we improved the detection system.

A thorough characterization of the cascaded arc, operated on argon is presented. Furthermore this contribution aims to give guidelines for experimental conditions in which the use of an incoherent, broadband light source combined with a CRD-like detection method can give extra information compared to single-pass or multi-pass measurements.

[1] Fiedler et al., Incoherent broad-band cavity-enhanced absorption spectroscopy, CPL 371 (2003) 284-294

[2] Zijlmans et al., Fourier transform cavity enhanced absorption with a cascaded arc Poster CRD user meeting 2004