# Cavity Ring-Down User Meeting 2006

# Programme

18th and 19th September 2006

Physics Department
University College Cork
Ireland

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# Welcome to Cork and UCC

## – 6th CRDS User Meeting –

## Main Venue

Physics Department, Science Building (Sir Robert Kane Building)

*Registration:* In front of Lectures Theatre G2 – ground floor. (Sunday, Monday)
*Lectures:* Theatre G2 – ground floor. (Monday, Tuesday)
*Posters:* Room 117 – first floor Physics Department. (Monday, Tuesday)

***Oral Presentations:***

Invited: 45 & 5 minutes. Contributed: 20 & 5 minutes.
Hardware provided:

- Pentium PC (operating system is Windows XP) with data projector
- Overhead projector
- VCR or DVD player

Powerpoint presentations will be collected at registration and can be e-mailed in advance as a backup (CRDS2006@ucc.ie). Please mention any special requirements (*e.g.* use of own laptops) at registration or contact us by e-mail before the meeting.

***Poster Presentations:***

Poster board size is 90 cm × 120 cm (3ft × 4ft) and can be used in the orientations of portrait (preferred) or landscape. Velcro fastener will be provided.

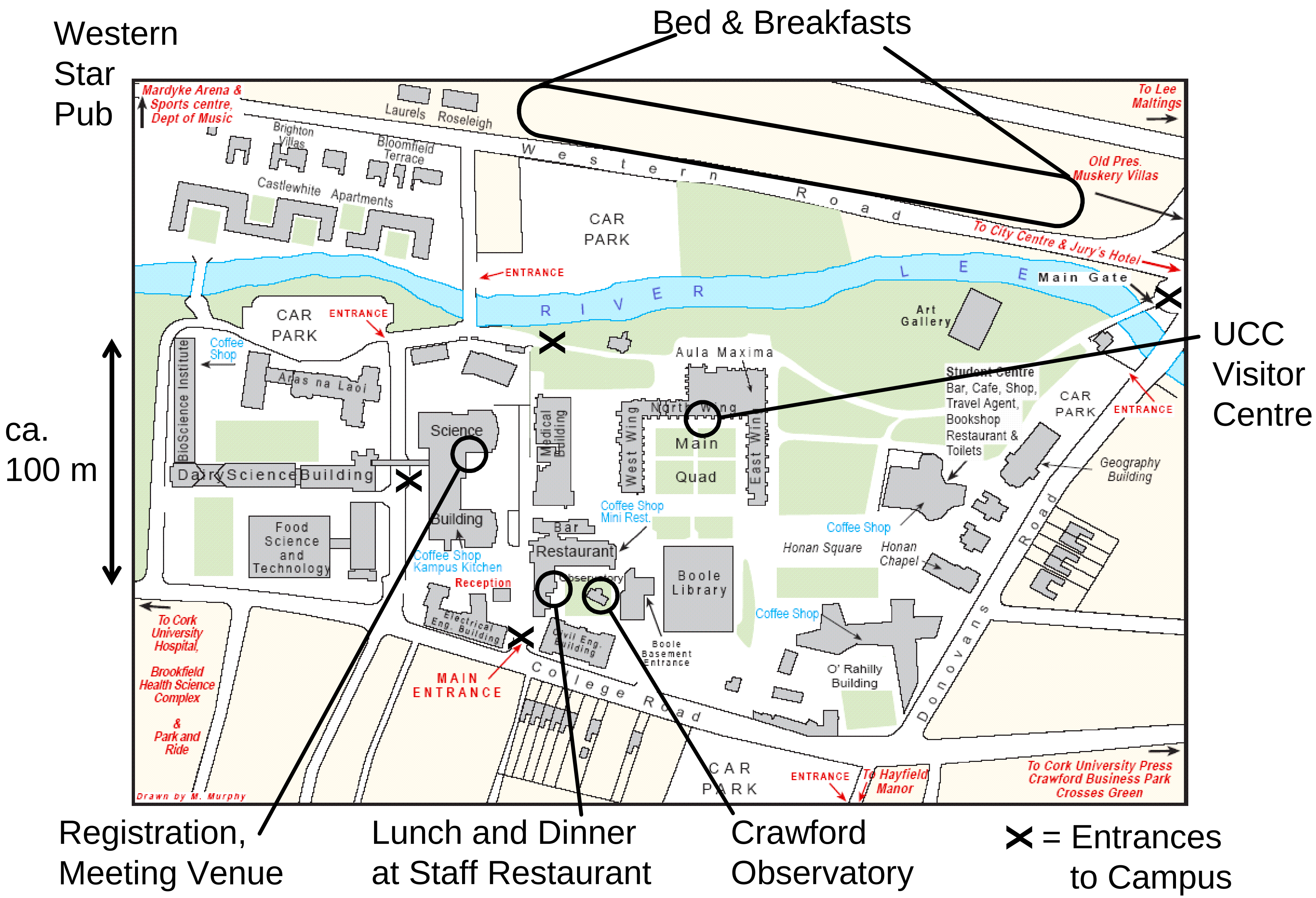
## Guided Campus Tour on Sunday 17th September

***– Meeting Point: UCC Visitor Centre in the main quadrangle on Campus, 6:15 p.m. –***

University College Cork (UCC) is one of four constituent universities of the federal National University of Ireland.

Founded in 1845, UCC is one of Ireland's oldest institutes of higher learning and was originally established as Queen's College. At the same time, two other Queen's Colleges were established in Ireland - one in Galway, the other in Belfast.

The original site chosen for the University is believed to have a connection with the patron saint of Cork, St Finbarr, who set up a monastery and school of learning in close proximity to the University. Hence the University's motto:
"*Where Finbarr Taught, Let Munster Learn*".

Western Star Pub
Bed & Breakfasts
UCC Visitor Centre
ca. 100 m
Registration, Meeting Venue
Lunch and Dinner at Staff Restaurant
Crawford Observatory
X = Entrances to Campus
Mardyke Arena & Sports centre, Dept of Music
To Lee Maltings
Old Pres. Muskery Villas
To City Centre & Jury's Hotel
Western Road
Main Gate
RIVER LEE
CAR PARK
ENTRANCE
Laurels
Roseleigh
Brighton Villas
Bloomfield Terrace
Castlewhite Apartments
Art Gallery
Aula Maxima
Student Centre Bar, Cafe, Shop, Travel Agent, Bookshop Restaurant & Toilets
Geography Building
North Wing
West Wing
East Wing
Main Quad
Medical Building
Coffee Shop Mini Rest.
Coffee Shop
Honan Square
Honan Chapel
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Boole Basement Entrance
O' Rahilly Building
Bar
Restaurant
Observatory
Civil Eng. Building
Electrical Eng. Building
Science Building
Coffee Shop Kampus Kitchen
Reception
MAIN ENTRANCE
College Road
Donovans Road
Áras na Laoi
BioScience Institute
Dairy Science Building
Food Science and Technology
To Cork University Hospital, Brookfield Health Science Complex & Park and Ride
To Hayfield Manor
To Cork University Press Crawford Business Park Crosses Green
Drawn by M. Murphy

## Transport

The centre of town is approximately 15 minutes by foot from UCC and the Meeting’s B&Bs.

| | |
|---|---|
| ***Buses UCC – City Centre:*** | Bus No.8. From the centre board bus marked “Bishopstown”, ca. every 15 min.) ask to get off at “Western Rd./UCC” or “Gaol Cross”. |
| ***Buses Airport – UCC:*** | Coaches depart Cork Airport from outside the Arrivals Hall every 30 minutes connecting with most city hotels, guest houses and city centre locations. (single journey € 5). |
| ***Taxis Airport – UCC*** | are more convenient and cost ca. €10 - €15. |
| ***Taxis UCC – City Centre*** | cost ca. €6 - €7. |
| ***Taxi Companies in Cork:*** | Shandon Taxi-Cabs, Tel. (021) 450 2255. ABC Cabs, Tel. (021) 431 1311. Cork Taxi Co-op, Tel. (021) 427 2222. |

## Restaurants (for Cork considered: €€€ expensive, €€ medium price range, € cheap)

***Cafe de la Paix***
16 Washington Street, Cork. Tel: +353-(021)-427 9556 (€€)

***Cafe Paradiso*** (http://www.cafeparadiso.ie/) exclusively VEGETARIAN (award winning)
16 Lancaster Quay, Cork. Tel: +353-(0)21-427 7939 (€€€)

***Fenn’s Quay Restaurant*** (http://www.fennsquay.ie/index_shw.html)
Sheares Street, Cork. Tel: +353-(0)21-427 9527 (€€)

***Il Padrino***
21 Cook Street, Cork. Tel: +353-(021)-4272160 (€€)

***La Boqueria*** (http://www.boqueriasixbridgest.com)
6 Bridge Street, Cork. Tel: +353-(021)-455 9049 (€€)

***Luigi Malones*** (http://www.luigimalones.com/)
Emmet Place, Cork. Tel: +353-(021)-427 8877 (€€)

***QuayCoop Restaurant*** (http://www.quaycoop.com/) exclusively VEGETARIAN
24 Sullivan's Quay, Cork. Tel:+353-(0)21-431 7026 (€)

***Ruen Thai***
17 Patricks Street, Cork. Tel: +353-(021)- 427-6127 (€€)

***Soho*** (http://www.soho.ie)
Grand Parade, Cork. Tel: +353-(021)-422 4040 (€€€)

***Wagamamas*** (http://www.wagamama.ie) many VEGETARIAN options
4-5 South Main Street, Cork. Tel: +353-(021)-427 8874 (€€)

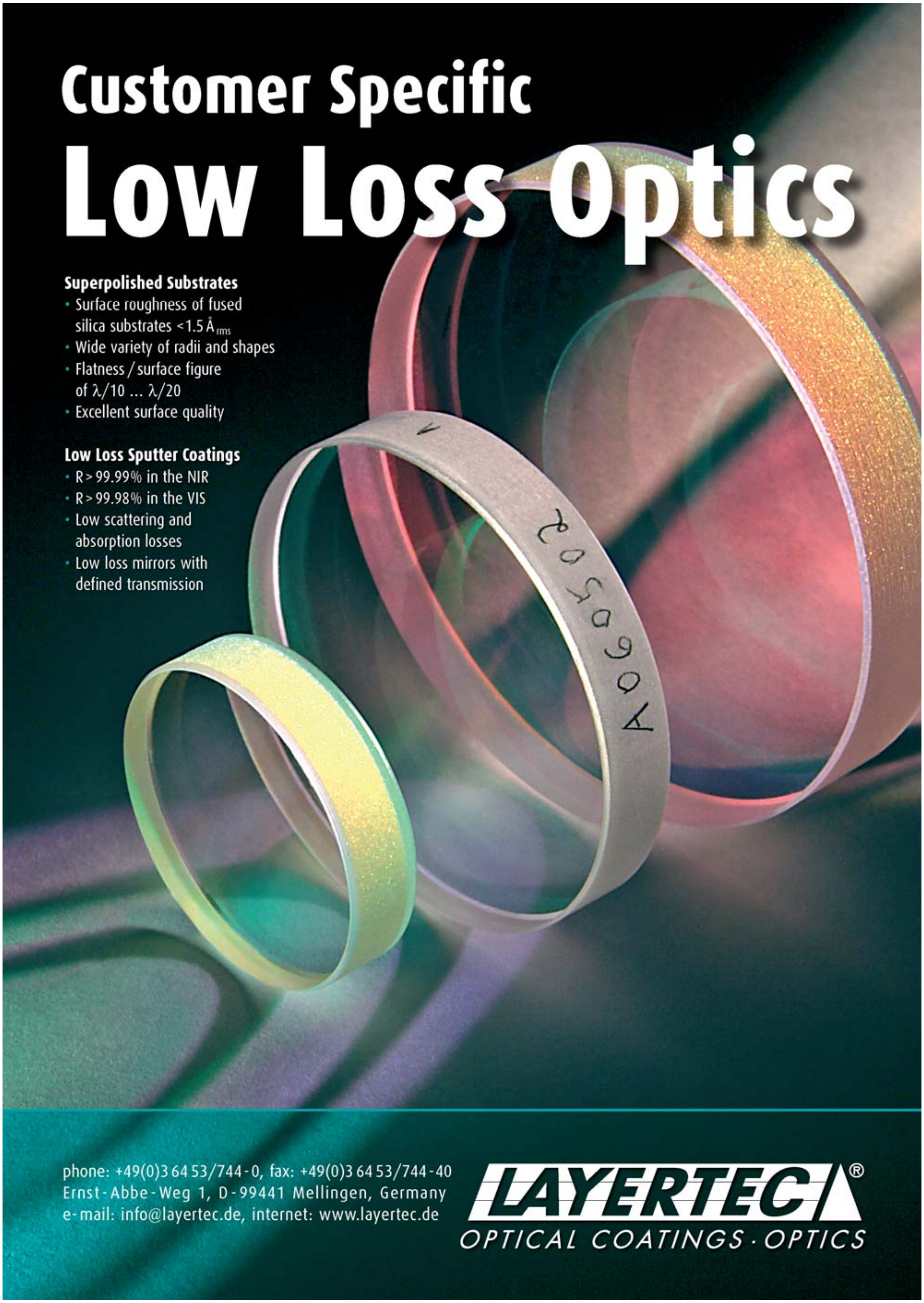
***WyLam Chinese Restaurant*** (many VEGETARIAN options)
Victoria Cross, Cork. Tel: +353-(021)-434 1063 (€€)

## Pubs

***Bodega Bar*** (Coal Quay), ***Dennehy's*** (Coal Quay), ***Spalpin Fanac*** (North Main St., Opposite Beamish Brewery, Trad.), ***The Corner House*** (Coburg Street, Trad.), ***Counihans*** (Pembroke Street), ***Franciscan Well Brewery*** (North Quay, home-brew), ***Tom Barry's*** (Barracks Street, beer garden in back), ***Thirsty Scholar*** (Western Road, student bar), ***Western Star*** (Western Road, student bar).

## Cork City Tourist Information Office (http://www.corkkerry.ie/?id=222)

Grand Parade, Cork. Tel: +353-(0)21-425 5100, Email: corkkerryinfo@failteireland.ie



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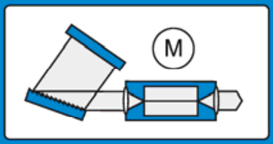

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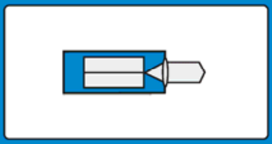

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Email: contact@sacher-laser.com
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# Programme

## Sunday, 17th September

| | |
|---|---|
| 16:00 – 18:00 | Registration / Coffee & Refreshments |
| 18:15 – 19:15 | Guided UCC Campus Tour – J.P. Quinn (supported by Alpes Lasers) |
| 20:30 … | Informal get-together in the Western Star (Pub on Western Road) |

## Monday, 18th September

| | | |
|---|---|---|
| 9:00 – 10:00 | Registration / Coffee & Refreshments | |
| 10:00 – 10:10 | A.A. Ruth<br>***'The welcome'*** | (University College Cork) |

### Session 1: **Chairman R. Engeln** (Eindhoven University of Techn.)

| | | |
|---|---|---|
| 10:10 – 11:00 | K.K. Lehmann (**invited**, L1)<br>***Recent advances in cavity ring-down spectroscopy and related methods*** | (University of Virginia) |
| 11:00 – 11:25 | H. Linnartz (not scheduled)<br>***Astrophysics and Astrochemistry: Cavity Ring Down Spectroscopy*** | (University of Leiden) |
| 11:25 – 11:50 | S. Rudic (L2)<br>***Optical properties of aerosol particles studied by cavity ringdown spectroscopy*** | (University of Bristol) |
| 11:50 – 12:15 | N.J. van Leeuwen (L3)<br>***Towards NICE-OHMS for the detection of peroxy radicals*** | (University of Oxford) |
| 12:10 – 14:15 | Lunch at Staff Restaurant on Campus | (supported by Layertec GmbH) |

### Session 2: **Chairman H.P. Loock** (Queen's University Kingston)

| | | |
|---|---|---|
| 14:30 – 15:20 | A. Orr-Ewing (**invited**, L4)<br>***Applications of cavity enhanced spectroscopy techniques in atmospheric chemistry*** | (University of Bristol) |
| 15:20 – 15:45 | M. Sigrist (L5)<br>***High resolution spectroscopic investigation of mono- and dimethyl amines employing a cw cavity ringdown spectrometer*** | (ETH Zürich) |
| 15:45 – 16:10 | J.H. van Helden (L6)<br>***The density of NH and $NH_2$ radicals in ammonia forming expanding plasmas*** | (Eindhoven University of Techn.) |
| 16:10 – 16:30 | Tea & Coffee Break | |
| 16:30 – 16:55 | D. Romanini (L7)<br>***High resolution cavity-enhanced absorption spectroscopy with a mode comb*** | (University J. Fourier of Grenoble) |
| 16:55 – 17:20 | J. Thiébaud (L8)<br>***cw-CRDS coupled to laser photolysis: an original set-up devoted to $HO_2$ time-resolved detection*** | (University of Lille) |

| | | |
|---|---|---|
| 17:20 – 19:30 | Poster Session & light refreshments | (supported by Sacher Lasertechnik) |
| 19:30 – 21:30 | Dinner at Staff Restaurant on Campus | (supported by Tiger Optics) |
| 21:30 ... | Get-together in an Irish Pub (to be announced) | |

## Tuesday, 19th September

| | | |
|---|---|---|
| **Session 3:** | **Chairman H. Linnartz** | (University of Leiden) |
| 9:30 – 10:20 | W. Ubachs (**invited**, L9)<br>***Cavity ring-down spectroscopy: from gases to liquids and to shorter wavelengths*** | (Vrije Universiteit Amsterdam) |
| 10:20 – 11:45 | M. Islam (L10)<br>***Broadband liquid phase cavity enhanced absorption spectroscopy*** | (University of Teesside) |
| 11:45 – 12:10 | A.J.L. Shillings (L11)<br>***Broadband CRDS laboratory studies of the near infra-red absorption of the water vapour dimer*** | (University of Cambridge) |
| 12:10 – 13:10 | Poster Session – continued<br>Tea & Coffee Break | |
| 13:10 – 14:10 | Lunch at Staff Restaurant on Campus | (supported by Layertec GmbH) |

| | | |
|---|---|---|
| **Session 4:** | **Chairman D. Romanini** | (University J. Fourier of Grenoble) |
| 14:10 – 15:00 | A. Pipino (**invited**, L12)<br>***Topics in evanescent wave cavity ring-down spectroscopy*** | (Eindhoven University of Techn.) |
| 15:00 – 15:25 | H.P. Loock (L13)<br>***Phase shift ring-down spectroscopy in optical wave guides*** | (Queen's University Kingston) |
| 15:25 – 15:40 | Tea & Coffee Break | |
| 15:40 – 16:05 | M. Mazurenka (L14)<br>***Combining evanescent wave cavity ringdown with scanning electrochemical methods to study dynamical interfacial phenomena*** | (University of Cambridge) |
| 16:05 – 16:30 | S. Gilb (L15)<br>***Optical absorption spectra of gold atoms deposited on*** $SiO_2$ ***from cavity ring-down spectroscopy*** | (Tech. University of Munich) |
| 16:30 – 16:55 | R. Faulkner (L16)<br>***A novel optical cavity technique for negative hydrogen ion density measurements (CANCELED !)*** | (Dublin City University) |
| 16:55 – 17:05 | A. Ruth<br>***'Concluding remarks'*** | (University College Cork) |
| 17:15 – 18:00 | P. Callanan<br>***Guided tour of the historic Crawford Observatory on Campus*** | (University College Cork) |

# Lectures

## Monday, 18th September

**Session 1:**

**L1:** Recent advances in cavity ring-down spectroscopy and related methods (**Kevin Lehmann**) - invited

**L2:** Optical properties of aerosol particles studied by cavity ringdown spectroscopy (**Svemir Rudic**)

**L3:** Towards NICE-OHMS for the detection of peroxy radicals (**Nicola van Leeuwen**)

**Session 2:**

**L4:** Applications of cavity enhanced spectroscopy techniques in atmospheric chemistry (**Andrew Orr-Ewing**) - invited

**L5:** High resolution spectroscopic investigation of mono- and dimethyl amines employing a cw cavity ringdown spectrometer (**Markus Sigrist**)

**L6:** The density of NH and $NH_2$ radicals in ammonia forming expanding plasmas (**Jean-Pierre van Helden**)

**L7:** High resolution cavity-enhanced absorption spectroscopy with a mode comb (**Daniele Romanini**)

**L8:** cw-CRDS coupled to laser photolysis: an original set-up devoted to $HO_2$ time-resolved detection (**Jerome Thiébaud**)

## Tuesday, 19th September

**Session 3:**

**L9:** Cavity ring-down spectroscopy: from gases to liquids and to shorter wavelengths (**Wim Ubachs**) - invited

**L10:** Broadband liquid phase cavity enhanced absorption spectroscopy (**Meez Islam**)

**L11:** Broadband CRDS laboratory studies of the near infra-red absorption of the water vapour dimer (**Alex Shilling**)

### Session 4:

**L12:** Topics in evanescent wave cavity ring-down spectroscopy (**Andrew Pipino**) - invited

**L13:** Phase shift ring-down spectroscopy in optical wave guides (**Hans-Peter Loock**)

**L14:** Combining evanescent wave cavity ringdown with scanning electrochemical methods to study dynamical interfacial phenomena (**Mikhail Mazurenka**)

**L15:** Optical absorption spectra of gold atoms deposited on $SiO_2$ from cavity ring-down spectroscopy (**Stefan Gilb**)

**L16:** A novel optical cavity technique for negative hydrogen ion density measurements (**Ronan Faulkner**)

# Posters

**P1:** Detection of atmospheric trace species by light emitting diode based broadband cavity enhanced absorption spectroscopy (**Justin Langridge**)
**P2:** Challenges in using quantum cascade lasers as a light source for CRDS (**Stefan Welzel**)
**P3:** Application and extension of cavity enhanced absorption spectroscopy (**Stuart Baran**)
**P4:** Rapid measurement of aerosol optical extinction using optical feedback cavity ring-down spectroscopy (**Tim Butler**)
**P5:** Influence of different cavity configurations on the signal-to-noise ration of IBBCEAS (**Sven Fiedler**)
**P6:** Cavity Enhanced Fourier Transform Absorption Spectroscopy using an Incoherent Broadband Light Source (**Andy Ruth & Johannes Orphal**)
**P7:** *In situ* monitoring of $NO_3$ using incoherent broadband cavity-enhanced absorption spectroscopy. A kinetic study of the $I_2/O_3/NO_x$ system (**Titus Gherman**)
**P8:** Application of spatially-resolved cavity ring down spectroscopy in plasma diagnosis (**Jie Ma**)
**P9:** Trace detection of acetylene in the atmosphere using cavity ring down spectroscopy combined with sample pre-concentration (**Manik Pradhan**)
**P10:** Quantitative Cavity Ring Down Spectroscopy with pulsed laser sources (**Hans Naus**)
**P11:** Off-axis, pulsed Cavity Ring Down Spectroscopy (**Hans Naus**)
**P12:** CRDS detection in the liquid phase: towards UV wavelengths (**Lineke van der Sneppen**)
**P13:** Prism Cavity Ring Down Spectroscopy (**Calvin Krusen**)
**P14:** $NO_2$ trace detection by Optical-Feedback Cavity-Enhanced Absorption Spectroscopy at 411nm (**Irene Courtillot**)
**P15:** Broadband Cavity Enhanced Absorption Spectroscopy of Thin film samples positioned at the Brewster Angle (**Alastair Smith**)
**P16:** Trace detection of water vapour using cw-CRDS (**Phyllis Fiadzomor**)
**P17:** The rotationally-resolved absorption spectra of formaldehyde and ammonia around 1450 nm (**Deirdre O'Leary**)
**P18:** Evanescent wave cavity enhanced absorption spectroscopy using a broad-band incoherent light source (**Kieran Lynch**)
**P19:** Line-mixing and collision-induced absorption in the A-band of molecular oxygen (**Maria Kiseleva & Wim van der Zande**)

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# Lectures

# Recent advances in cavity ring-down spectroscopy and related methods

**Kevin K. Lehmann***

Departments of Chemistry and Physics, University of Virginia,
Charlottesville VA, 22904 USA

E-mail: Lehmann@virginia.edu

Cavity Ring-down Spectroscopy (CRDS) and related cavity enhanced methods are increasingly used and further developed. A literature search retrieved almost a hundred publications in 2005 and nearly eighty already in 2006. In this talk, I will give a brief introduction to CRDS and its cousins and then describe recent areas that have advanced most rapidly in the past couple years, including measurements using optical fibers, measurements of optical activity, and broad bandwidth and super-broad bandwidth approaches. I will end with a personal perspective of important outstanding problems and opportunities.

*** invited**

# Optical properties of aerosol particles studied by cavity ringdown spectroscopy

**Svemir Rudić,***  **Rachael E.H. Miles,**  **Andrew J. Orr-Ewing,**
**Jonathan P. Reid**

School of Chemistry, University of Bristol, Bristol BS8 1TS, UK.

E-mail: s.rudic@bristol.ac.uk

Although aerosol particles have an important role in governing the radiative balance of the atmosphere, the nature of their contribution is not very well understood. Thus study of aerosol optical properties, in particular scattering and absorption, as a function of particle size, form, composition, mixing state and phase is of considerable interest. In this study the properties of non-absorbing spherical particles, such as pure water droplets and polystyrene beads were experimentally investigated by employing cavity ringdown spectroscopy in the micrometer and nanometer size ranges, respectively. Experimentally derived aerosol extinction coefficient as a function of size parameter was found to be in good agreement with theoretical calculations, and can be used for size determination of the particles probed. Results from the investigation of spherical and non-spherical absorbing aerosol particles will also be presented.

* presenting

# Towards NICE-OHMS for the detection of peroxy radicals

**W. Denzer**, **G. Hancock**, **R. Peverall**, **G. A. D. Ritchie**,
**L. Russell**, **N. J. van Leeuwen***

Physical and Theoretical Chemistry Laboratory, University of Oxford,
South Parks Road, Oxford, OX1 3QZ

E-mail: nicola.vanleeuwen@chem.ox.ac.uk

Noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy, or NICE-OHMS, is an extremely sensitive technique which combines the advantages of frequency modulation spectroscopy and cavity enhanced spectroscopy. The low noise level provided by the frequency modulation allows sensitivities well beyond those of standard cavity enhanced, and cavity ring-down spectroscopy to be achieved. While most NICE-OHMS apparatus constructed thus far have yielded sensitivities on order $10^{-10}$ $cm^{-1}$ $Hz^{-1/2}$ [1-3], a shot noise limited sensitivity of $10^{-14}$ $cm^{-1}$, in 1 second, has been reported by one group[4]. Thus, NICE-OHMS provides a unique tool for the detection of trace gases beyond the reach of other techniques.

Our aim is to produce a NICE-OHMS apparatus operating in the infra-red (around 1.5 μm) and investigate its potential for the species specific detection of peroxy radicals in the atmosphere. We have recently completed construction of the experiment and will present initial results on the performance of the NICE-OHMS spectrometer via detection of weak methane transitions in this region. A comparison of the sensitivity achieved using cavity enhanced absorption spectroscopy (CEAS), locked cavity (CEAS), and NICE-OHMS is made for the apparatus.

[1] L. Gianfrani, R. W. Fox, and L. Hollberg, J. Opt. Soc. Am. B. **16**(12), 2247 (1999).
[2] C. Ishibashi and H. Sasada, Jpn. J. Appl. Phys. Part 1. **38**(2A), 920 (1999).
[3] N. J. van Leeuwen and A. C. Wilson, J. Opt. Soc. Am. B. **21**(10), 1713 (2004).
[4] J. Ye, L. S. Ma, and J. L. Hall, Opt. Lett. **21**(13), 1000 (1996).

* presenting

# Applications of cavity enhanced spectroscopy techniques in atmospheric chemistry

**Andrew J. Orr-Ewing***

School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

E-mail: a.orr-ewing@bris.ac.uk

Cavity enhanced absorption spectroscopy techniques using both pulsed and cw lasers are very well suited to the study of atmospheric chemistry and photochemistry in the laboratory and in the open air. Our recent work includes development of diode laser based instruments and their application to the quantitative measurement of trace atmospheric constituents at mixing ratios of parts per billion and below. Laboratory studies of the ultraviolet photochemistry of carbonyl compounds under lower atmosphere conditions of temperature and pressure will also be described, focusing on quantum yield measurements for $HO_x$ (OH and $HO_2$) production and the consequences for formation of ozone in the troposphere. The talk will also present new techniques for studying the optical properties of micron sized atmospheric aerosol particles by CRDS.

*** invited**

# High resolution spectroscopic investigation of mono- and dimethyl amines employing cw cavity ringdown spectrometer

**D. Marinov,* J. Rey, D. Vogler, M. W. Sigrist**

ETH Zurich, Institute of Quantum Electronics, Laser Spectroscopy and Sensing Lab,
Schafmattstr. 16, 8093 Zurich, Switzerland

E-mail: marinov@phys.ethz.ch

Monitoring the concentrations of methyamines in exhaled human breath is of special medical interest, since some hepatic (cirrhosis, hepatitis) and renal (haemodialysis patients) diseases show clear correlation with increased concentrations of those gases, thus providing the possibility of convenient noninvasive diagnostics. Here we present a high resolution spectroscopic investigation of mono- (MMA, $CH_3NH_2$) and dimethyl (DMA, $(CH_3)_2NH$) amines in the region of the first overtone of the N-H stretch vibration in the near-infrared.

We performed our measurements with a laser spectrometer based on the cw cavity ringdown (CRD) detection technique. The light source is a fiber-coupled external cavity diode laser (ECDL) with an output power of 3 mW, tunable in the range between 1515 and 1550 nm. After collimation the laser radiation is coupled into the cavity of a 520 mm long home-built ringdown cell formed by two concave mirrors with 99.99% reflectivity in the spectral region of interest. After the alignment of the laser beam to match the $TEM_{00}$ mode of the ringdown cavity, the ringdown time of the cavity filled with pure nitrogen was around 40 μs. The standard deviation of the ringdown time is 1.07 μs resulting in a minimum detectable absorption coefficient $\alpha_{min}=2.3\cdot10^{-8}$ $cm^{-1}$ (for SNR=3), which corresponds to 350 ppt of MMA and 1.6 ppm of DMA in synthetic non-absorbing mixtures. With a cavity modulation frequency of 10 Hz and averaging over 100 CRD events, a sensitivity of $5\cdot10^{-8}$ $cm^{-1}$ $Hz^{-1/2}$ is achieved.

Unfortunately, even though the absorption lines of interfering $H_2O$ and $CO_2$ in human breath are rather weak in this near-infrared region, their high concentrations in the percent range significantly increase the detection limit of methylamines in a real-world application if no measures of preconcentration of methylamines are taken. An alternative approach would be spectroscopic investigations in the mid-infrared range around 3.3 μm where the methylamines exhibit strong absorption lines. However, in that range tunable laser sources are not readily available and powers are possibly too low for successful CRD measurements.

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* presenting

# The density of NH and NH2 radicals in ammonia forming expanding plasmas

**J. H. van Helden,* P. J. van den Oever, M. C. M. van de Sanden,**
**W. M. M. Kessels, D. C. Schram, R. Engeln**

Department of Applied Physics, Eindhoven University of Technology, PO Box 513, 5600 MB,
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Plasmas containing nitrogen and hydrogen are extensively studied because of their widespread applications in research and industry for the (surface) treatment of materials. Despite their widespread application, only limited information is available on the role of the $NH_x$ radical species in the plasma chemistry of $N_2$–$H_2$ plasmas. To obtain more insight in the role of the $NH_x$ species in $N_2$–$H_2$ plasmas, we measured the densities of NH and $NH_2$ radicals by cavity ring-down spectroscopy in $N_2$–$H_2$ plasmas expanding from a remote thermal plasma source and in $N_2$ plasmas to which $H_2$ was added in the background.

The $NH_2$ radical was observed via transitions in the (0, 9, 0) ← (0, 0, 0) band of the $\tilde{A}^2A_1 \leftarrow X^2B_1$ electronic transition. From a measured $NH_2$ spectrum, we determined the oscillator strengths of part of the transitions in the $^PQ_{1,N}$ branch of the $\Sigma$ vibronic sub-band. The NH radical was observed via transitions in the (0, 0), (1, 1) and (2, 2) vibrational bands of the $A^3\Pi \leftarrow X_3\Sigma^-$ electronic transition. Using CRDS, the density distribution of the rotational states of the NH radical in the plasma was determined. We found that most rotational levels in the three vibrational states were populated according to a Boltzmann distribution with a temperature of approximately 1775 K.

From the results, we conclude that the $NH_2$ radicals are formed by reactions of $NH_3$ molecules, produced at the walls of the plasma reactor, with H atoms emitted by the plasma source. The NH radicals are mainly produced via the reaction of N with $H_2$ with also a possible contribution of $N^+$ ions with $H_2$. The NH radicals can also be produced by H abstraction of $NH_2$ radicals. The flux densities of the $NH_x$ radicals is appreciable in the first part of the plasma expansion. Further downstream in the expansion they are further dissociated and the densities become smaller than those of the atomic radicals. It is concluded that $NH_x$ radicals play an important, though indirect, role in the ammonia production at the surface.

* presenting

# High resolution cavity-enhanced absorption spectroscopy with a mode comb

**T. Gherman,**[b] **S. Kassi,**[a] **J. C. Vial,**[a] **N. Sadeghi,**[a] **D. Romanini***[a]

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As is now well-known, Mode-Locked (ML) femtosecond lasers recently came out as a means to produce ultrastable optical frequency rulers (Optical Combs-OC's) very valuable in the measurements of optical frequencies with unprecedented accuracy. We exploited the high coherence properties of OC's in order to obtain the efficient ecxitation of a high finesse cavity over a broad spectral range with a single transverse mode (TEM00). This permits high performance Cavity Enhanced Absorption Spectroscopy when coupling the cavity output to a spectrograph equipped with a CCD detector array. We will present this OC-CEAS technique (we propose this name in place of our previous 'ML-CEAS') and illustrate its simplicity and robustness with several applications: The real time (0.1s) measurement of broad spectra with rotational resolution [1]; Its use with a mode-locked VECSEL semiconductor laser source [2]; The spectroscopy of very weak overtone vibrational transitions at blue wavelengths, at high resolution [3]; and finally, its use for plasma diagnostics, also in the near UV, with the measurement of densities of ionic or metastable species in a low pressure plasma discharge.

This technique holds a high promise for future applications, especially as modelocked femtosecond lasers are becoming a widespread laboratory tool: Their high peak power allows the effective use of nonlinear optical techniques to extend (by self phase modulation) or convert (by harmonic generation) their emitted spectrum to cover all the visible and the near UV or IR spectral ranges with sufficient power density for CEAS measurements (depending on cavity finesse).

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* presenting

# cw-CRDS coupled to laser photolysis: an original set-up devoted to $HO_2$ time-resolved detection

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The $HO_2$ radical plays a central role in both atmospheric and combustion chemistry due to its oxidizing capacity. Monitoring its concentration in laboratory experiments has long been a goal but its short lifetime and consequently low concentration provided a serious challenge. Therefore, the techniques used to study the $HO_2$ radical must present a suitable balance between time resolution and sensitivity.

Because it achieves this requirement, the UV absorption spectroscopy has become a widely used technique to monitor the $HO_2$ radical in photolysis reactor. However, its broad and structureless absorption in this wavelength range leads to many overlaps within the absorption features of other species like peroxy radicals. This lack of selectivity is an important limitation that encouraged the development of spectroscopic measurements in the infrared region where we can find narrow and resolved absorption lines for small species like the $HO_2$ radical. Over the past ten years, a few experiments have been reported using laser diode in the near-IR to detect $HO_2$ radicals in a photolysis reactor [1-3]. Even though they enabled successful investigations, the experimental set-ups are demanding (sensitive phase detection, multipass configuration, calibration procedure) and allow only limited overlap between the absorption path and the photolyzed volume (< 20 meters).

We have coupled a continuous wave Cavity Ring-Down Spectrometer to a photolysis system to perform time-resolved $HO_2$ detection [4] leading to an effective pathlength of several kilometers. During this presentation, the experimental set-up will be detailed with emphasize on the different timing strategies developed for both spectroscopic and kinetic measurements. Our first results will be presented.

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* presenting

# Cavity ring-down spectroscopy: from gases to liquids and to shorter wavelengths

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Since the invention of cavity ring-down spectroscopy, now almost two decades ago, the field has matured and a wide variety of applications is pursued. The original idea of pulsed CRD has been extended by a number of optical novelties involving lasers of all kinds. Also the spectroscopic targets have diversified from gas phase spectroscopic studies, to the liquid phase, to solids and to surface layers. I will report on developments in our laboratory with examples of determining Rayleigh scattering and collisional features in dense gases, in studying the spectroscopy of rare isotopologues available only in small samples, in extending CRD methods to the wavelength range of the deep ultraviolet, and to combining CRD detection with chemical separation techniques such as liquid chromatography.

*** invited**

# Broadband liquid phase cavity enhanced absorption spectroscopy

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Preliminary results will be presented of liquid phase measurements using a broadband implementation of the cavity enhanced absorption spectroscopy technique (CEAS). This relatively simple experimental setup involved using a high powered LED as the broadband light source and an inexpensive CCD spectrograph as the broadband detector. The cavity was formed by 2 concave >99.9% high reflectivity mirrors in the range 400-700 nm (3 mirror sets). In one implementation the cavity mirrors formed the ends of a 20.4 cm pathlength liquid cell in which a sample could be introduced. In separate experiments a 1cm glass cuvette contained the liquid sample and was placed between the cavity mirrors. Experiments have been performed on a number of common dye molecules dissolved in methanol and in some cases acetonitrile. By comparing with single pass experiments the cavity enhancement at a particular wavelength could be determined straightforwardly. Currently cavity enhancements corresponding to about 70 passes have been obtained. This is far less than the number of passes possible with the mirrors in the gas phase and is probably due to a combination of increased scattering/interface losses in the liquid phase experiments.

* presenting

# Broadband CRDS laboratory studies of the near infra-red absorption of the water vapour dimer

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While CRDS is now well established as an ultra sensitive tool for measurements of optical absorption properties in the laboratory, and it is being increasingly used for measurements of composition in the atmosphere, the presence of multiple absorbing species can limit its use for atmospheric studies. Multi wavelength or broad band CRDS (BBCRDS) is a development of single wavelength CRDS which combines the sensitivity and selectivity of the long path differential optical absorption spectroscopy (lp-DOAS) technique with the in-situ characteristics and long absorption path lengths of CRDS.

The role of water dimers in atmospheric processes is a controversial issue that has not been clearly resolved despite considerable effort. The excess absorption of solar radiation by the atmosphere has been ascribed to water dimers because these seem to be the only species present under most atmospheric conditions in sufficient densities to produce the measured effects. Similarly, the water dimer has been proposed as the source of “the water continuum” absorption in the far-infrared. Water dimers are also postulated to have an affect on many chemical species in the atmosphere. Nevertheless, and despite various experimental and theoretical attempts, there remains considerable uncertainty in atmospheric water dimer concentrations.

Here we report on BBCRDS laboratory studies of the near infra-red absorption of the water vapour dimer in the vicinity of the water monomer 4th overtone OH stretch bands around 745 nm. Experiments have been performed over a range of temperature and relative humidity conditions, allowing the investigation of the thermodynamic properties of the water dimer.

* presenting

# Topics in Evanescent Wave Cavity Ring-Down Spectroscopy

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Miniature monolithic optical resonators enable surface and interface diagnostics by evanescent wave cavity ring-down spectroscopy (EW-CRDS) with high sensitivity and arbitrary polarization. A minimum detectable optical loss of $\approx 10^{-8}$ has so far been routinely achieved, while improvements appear feasible. At this sensitivity level, a rich variety of vibration-combination and overtone bands as well as electronic transitions become accessible for surface species at sub-monolayer coverage. While multi-quanta vibrational transitions have been detected on metal surfaces in a few cases with established absorption techniques, EW-CRDS enables smooth oxide surfaces to be studied, which is unprecedented for these technologically important systems. For example, on atomically smooth $SiO_2$ - the intrinsic resonator surface, the 2νOH+δOH combination bands of surface hydroxyl groups and H-bonded water have been studied, in addition to the 2νOH and 3νOH overtones of $HNO_3$ and the 2νC-H overtone of physisorbed hydrocarbons. Other surfaces or interfacial systems can also be studied on prepared thin-film surfaces by exploiting the disparate length scales for evanescent field decay and surface chemical response. Currently, we are exploring the application of EW-CRDS to atomic layer deposition (ALD) processes, where the intrinsic absolute loss capability of a CRDS-based measurement may ultimately permit absolute surface reaction rates to be determined. An EW-CRDS-based variant of temperature-programmed desorption (TPD) spectrometry is also being explored in which the evanescent wave serves as an in-situ probe of surface coverage on a temperature-controlled monolithic resonator. The advantages and challenges of using monolithic resonators for novel surface science studies will be discussed, along with new directions in progress.

*** invited**

# Phase shift ring-down spectroscopy in optical wave guides

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In the past few years an effort has been made to adapt CRD to the detection of dilute analytes in liquids. Using a loop made of fiber-optic cable one create a “cavity” that shows the ring-down of an injected laser pulse. By placing a sample between the two ends of a fiber strand we were able to use fiber-loop ring-down spectroscopy (FLRDS) to detect attomole quantities of absorber in picoliter sized volumes. Applications of this technique to microfluidics and mechanical signal transduction are discussed. Because of its high time resolution, its simplicity, and low cost we prefer phase-shift detection over time-resolved detection. As a demonstration for the high time resolution, the ring-down spectra of microsphere resonators (with $\tau < 60$ns) will be presented.

A related sensor makes use of a long-period grating (LPG) that is inserted into the fiber loop. The optical loss of the LPG changes dramatically as a function of refractive index and is hence suited as an inexpensive, portable, robust and real-time sensor for a large variety of organic and inorganic pollutants in ground water, including PAHs, PCBs, mercury, copper, chromium and lead. The sensor presently consists of a Long Period Grating (LPG) element coated with a polymer films. The polymer film will selectively absorb and concentrate analytes of interest so that the LPG element can be modified to have different selectivity for specific contaminants. The absorbed analyte then causes a change in the refractive index of the coating, consequently altering the transmission properties of LPG.

* presenting

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

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We report progress in our efforts to develop hybrid micro-electrochemical / evanescent wave cavity ringdown techniques for the study of dynamical interfacial phenomena.

In a proof of concept study, the application of evanescent wave cavity ringdown spectroscopy (EW-CRDS) to monitor electrogenerated species within a thin layer electrochemical cell is demonstrated. In the proof of concept experiments described, ferricyanide, $Fe(CN)_6^{3-}$, was produced by the transport-limited oxidation of ferrocyanide, $Fe(CN)_6^{4-}$ in a thin layer solution cell (25-250 μm) formed between an electrode and the hypotenuse of a fused silica prism. The prism constituted one element of a high finesse optical cavity arranged in a ring geometry. The cavity was pumped with the output (*ca.* 417 nm) of a single mode external cavity diode laser which was continuously scanned across the cavity modes. The presence of electrogenerated ferricyanide within the resulting evanescent field, beyond the optical interface, was detected by the enhanced loss of light trapped within the cavity, as measured by the characteristic cavity ringdown. The cavity ringdown response accompanying both cyclic voltammetric and step potential chronoamperomerty experiments at a variety of electrode- surface distances are presented and the results are shown to be well reproduced in modeling by finite element methods. The studies herein thus provide a foundation for further applications of EW-CRDS to probe processes in thin films on the quartz surface, with an electrode positioned above used to initiate the physicochemical process of interest. Thus, processes such as adsorption, absorption, nucleation/growth, and lateral charge transport in films should all become amenable to study.

* presenting

# Optical Absorption Spectra of Gold Atoms Deposited on $SiO_2$ from Cavity Ringdown Spectroscopy

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Cavity ringdown spectroscopy is a highly sensitive photoabsorption technique which in the last decade has been employed to perform trace detection of molecules or to study weak electronic transitions in both the gas phase and in the liquid phase. We apply this technique in the solid phase in order to measure the absorption of gold nanoparticles on amorphous silica at low coverages. In particular, we explore the evolution of their optical properties in the visible range as their size varies from a single atom to the bulk.

Monodispersed samples of $Au_{n=1,2,4,8,20}$ where prepared by cluster deposition. Comparison of the gold monomer and dimer spectra demonstrates that soft landing conditions are fulfilled. Molecular-like optical transitions can be identified up to the tetramer, while larger clusters and particles show characteristic surface plasmon peaks. In addition, the optical properties of the small cluster are compared to time dependent TD-DFT calculation. Optically allowed electronic transitions were calculated, and comparisons with the experimental spectra show that silicon dangling bonds [≡Si•], nonbridging oxygen [≡Si─O•], and the silanolate group [≡Si─O─] act as trapping centers for the gold particles. [1,2]

Large gold particles with a diameter from 1.3 nm to 2.9 nm on $SiO_2$ where also fabricated by the reversed micelle method [3], the samples were measured in air. The measured extinction spectra can be well described by the Mie-Drude model of absorption for small particles.

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* presenting

# A novel optical cavity technique for negative hydrogen ion density measurements

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Optical cavities such as those used in the Cavity Ring Down (CRD) technique have been applied in the past to measure line-integrated negative hydrogen ion density in a hydrogen discharge [1,2]. While relatively straight-forward to apply to a laboratory chamber, cavity drift has made it difficult, in some cases, to apply this technique to high power, negative ion sources such as the KAMABOKO III source [3] on the MANTIS test-bed in CEA-Cadarache.

A novel alternative to the CRD technique, the "External Cavity Technique", has been developed which allows the coupling of high power energy into an optical cavity. The external cavity technique employs a polarisation sensitive beamsplitter and an electro-optic polarisation rotator (Pockels Cell) to capture the laser light within the cavity. This is in contrast to the standard CRD technique, which requires a low laser energy pulse to be coupled into the cavity via a highly reflective, low transmission input mirror.

The principal difference between these techniques is that the absorbing medium is no longer within the cavity mirrors but exterior to it where single pass absorption can be performed using the pulsed output from the external cavity. While this configuration loses some of advantages of a CRD technique, it has the distinct advantage that the highly reflective mirrors are no longer exposed to the plasma that may contain the absorbing species, as is often the case with CRD.

Furthermore, the output from the external cavity results in a relatively high energy train of laser pulses whose rate of decay is defined by the losses in the cavity, which are mainly due to the Pockels Cell and beamsplitter. The ability to detect this signal with high sampling rate and high bit rate allows for the precise characterisation of a time-varying light source which can then be used in absorption experiments.

This paper will discuss this novel optical cavity technique, which will endeavour to measure line-integrated negative hydrogen ion densities on KAMABOKO III, which is a high power, caesium seeded negative ion source and a small scale of the reference ion source for neutral beam injection (NBI) for the ITER fusion project.

This work is supported by the European Union under contract HPRI-CT-2001-50021 and through Association EURATOM DCU under contract ERB 5004 CT 96 0011.

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* presenting

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| Linewidth | - | 3 | - | MHz |
| Threshold current | 0.25 | 0.5 | 0.8 | A |
| Operation current | 0.3 | 0.6 | 1 | A |
| Average output power | 2 | 10 | 50 | mW |
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| Beam divergence perpendicular | 55 | 60 | 65 | deg |

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|---|---|---|---|---|
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| Frequency range | 2375 | - | 1033 | $cm^{-1}$ |
| Operation temperature | 80 | 100 | 160 | K |
| Linewidth | - | 3 | - | MHz |
| Threshold current | 0.15 | 0.3 | 0.5 | A |
| Operation current | 0.5 | 0.8 | 1.3 | A |
| Average output power | 2 | 10 | 100 | mW |
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| Operation temperature | 77 / 243 | 80 / 273 | - / 303 | K |
| Spectral width | 50 / 20 | 125 / 100 | 200 / 200 | $cm^{-1}$ |
| Threshold current | 0.4 / 0.6 | 0.6 / 1 | 0.8 / 1.4 | A |
| Operation current | 1.5 | 2.5 | 3.5 | A |
| Average output power | 1000 / - | 1010 / 100 | - / 250 | mW |
| Beam divergence parallel | 10 | 15 | 20 | deg |
| Beam divergence perpendicular | 25 | 30 | 40 | deg |
| Duty cycle | - | 10 | 20 | % |
| Pulse length | - | 50 | 150 | ns |

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# Posters

# Detection of atmospheric trace species by light emitting diode based broadband cavity enhanced absorption spectroscopy

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Broadband spectroscopic methods, such as long-pass differential optical absorption spectroscopy (DOAS), are widely used to quantify the concentrations of atmospheric trace species. The broadband approach enables the analysis of spectra recorded in the presence of multiple absorbing and scattering species, making it particularly well suited to atmospheric studies. Traditional DOAS gains its sensitivity by using extended absorption paths, typically across several kilometres of open atmosphere. Any *in situ* method capable of detecting species in the atmosphere with comparable sensitivity to DOAS would bring numerous advantages. In this paper we present an *in-situ* analogue of DOAS using broadband cavity enhanced absorption spectroscopy (a variant of cavity ringdown spectroscopy) based upon the emission from high intensity light emitting diodes and a high reflectivity optical cavity. The paper describes the development and validation of two field instruments: a compact detector for atmospheric $NO_2$ and a system for the detection of $N_2O_5$ based upon a mobile platform.

* presenting

Poster, P2

# Challenges in Using Quantum Cascade Lasers as a Light Source for CRDS

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Cavity Ring Down Spectroscopy (CRDS) has been applied as a highly sensitive absorption technique in the visible spectral range, with absorption lengths of hundreds of metres, for more than fifteen years. However, due to the lack of suitable light sources this technique has hardly been applied to the "fingerprint" mid infrared spectral region (MIR). However, the MIR region is of special interest for the investigation of stable and unstable molecules in several different fields, e.g. plasma diagnostics, biomedical applications and detection of traces of toxic gases. In the last few years a new light source in the MIR has become available namely quantum cascade lasers (QCLs) which exhibit higher output powers than other types of semiconductor lasers in this range. Therefore QCLs are possible candidate light sources for CRD experiments.

In order to function at room temperature commercially available QCLs are usually operated in a pulsed mode with low duty cycles. This opens up the possibility for the quite straightforward experimental scheme of pulsed-CRDS. The first measurements with a custom made compact quantum cascade laser measurement and control system (Q-MACS) demonstrated the potential of this approach as an extremely sensitive absorption technique in the MIR. However, the frequency chirp within the laser pulse, which is inherent to the QCL due to the heating of the semiconductor layers, causes some experimental obstacles. Usually, for low pressure applications, the frequency chirp is bigger than the width of the absorption line. As a result the calculated absorbance differs from the measured value for experiments with a reference gas.

Unfortunately, pulsed QCLs cannot be used with pulses long enough for cavity enhanced spectroscopy to take advantage of the frequency chirp. Recently, however, cw room-temperature QCLs have become available which could be used for cavity enhanced spectroscopy. First results of a room-temperature experiment using a cw QCL will be presented.

Poster, P3

* presenting

# Applications and extensions of Cavity Enhanced Absorption Spectroscopy

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Cavity enhanced absorption spectroscopy (CEAS) presents an experimentally simple technique for sensitive and selective detection of trace species at very low concentrations. We present our progress towards the development of a compact tool for the detection of hydrogen sulphide, $H_2S$. Hydrogen sulphide is a respiratory poison, often present in agricultural and mining environments. It is also of interest as a potential ailment-specific biomarker at low concentrations in human breath and headspace.

We have used CEAS to detect $H_2S$ absorption using an infrared distributed feedback diode laser (DFB-DL) centred at a wavelength around 1577 nm. Pressure broadening coefficients for $H_2S$ in methane and in air, along with relevant integrated cross sections, will be presented for a number of absorption lines in the 1576 – 1577 nm region.

We will also report progress towards the development of an Optical Feedback (OF-)CEAS system for sensitive quantitative detection of atmospheric carbon dioxide. We employ a DFB laser centred at approximately 1596 nm and a V-shaped three mirror cavity. This technique achieves a narrowed line width and increased sensitivity by allowing selective feedback of cavity-resonant light to the laser.

* presenting

# Rapid Measurement of Aerosol Optical Extinction Using Optical Feedback Cavity Ring-Down Spectroscopy

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Optical feedback cavity ring-down spectroscopy (OF-CRDS) is being used to study the optical properties of aerosol particles. OF-CRDS is a recently developed technique[1] that differs from a conventional CRDS technique in that a continuous wave distributed feedback laser is locked to the ring-down cavity via optical feedback, increasing the cavity injection efficiency. This technique retains the sensitivity of CRDS while conveniently enabling fast sampling rates in the kHz frequency range. The apparatus benefits from the simplicity of the optical set-up (as there is no need for fast optical switches or an optical isolator) as well as the compactness and high sensitivity of any diode laser based CRDS system, making it suitable for use in a portable instrument for in situ measurements.

The very fast accumulation rates make this technique especially attractive for the study of aerosol samples because of rapid quantification of the inherent statistical fluctuations. We present the first demonstration of the use of CRDS for the study of single aerosol particles, and propose a model which explains the observed phenomena. We show that the extinction losses are dependent on the position of a particle, as well as the total number of particles in the laser beam within the cavity. The extinction cross-section (the sum of absorption and scattering losses) is calculated and shown to be in good agreement with Mie theory scattering calculations. The extinction coefficients of a wide variety of aerosol types can be accurately measured, which will help to reduce the uncertainty of the role of aerosols in climate change and also provide a novel means of measuring air quality.

[1] J. Morville, D. Romanini, A. A. Kachanov, and M. Chenevier, Appl. Phys. B **78**, 465 (2004).

* presenting

# Influence of Different Cavity Configurations on the Signal-to-Noise Ratio of IBBCEAS

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In the recent years several publications presented experiments using the Incoherent Broad-Band Cavity-Enhanced Absorption Spectroscopy (IBBCEAS) scheme. Broad-band continuous light is transmitted through an optical cavity including an absorbing sample and then dispersed by a spectrometer. The intensity is observed spectrally resolved over a broad wavelength range by means of a CCD detector.

However, up to now the effects of a real optical setup on sensitivity and resolution of the measured spectra were not investigated in detail. On this poster we show first experimental measurements how different cavity configurations influence the signal-to-noise ratio of IBBCEAS measurements.

* presenting

# Cavity Enhanced Fourier Transform Absorption Spectroscopy using an Incoherent Broadband Light Source

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A cavity enhanced absorption setup employing an incoherent broadband light source was used in combination with a Fourier transform spectrometer to measure the spin-forbidden B-band of oxygen and several weak absorption transitions of water around ~ 688 nm at room temperature in ambient air. The experiments demonstrate that the detection sensitivity of a Fourier transform spectrometer can be significantly improved by increasing the effective pathlength (by a factor of several hundred in the present investigation) while retaining a reasonably small sample volume. The experimental advantages and limitation of this novel approach are outlined and potential applications briefly discussed.

* presenting

# *In situ* monitoring of $NO_3$ using incoherent broadband cavity-enhanced absorption spectroscopy

## A kinetic study of the $I_2/O_3/NO_x$ system

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We describe the application of Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy (IBBCEAS) for the *in situ* detection of atmospheric trace gases and radicals ($NO_3$, $NO_2$, $O_3$, $H_2O$) in an atmospheric simulation chamber under realistic atmospheric conditions [1]. Using a straightforward spectrometer configuration, we show that detection limits corresponding to typical atmospheric concentrations can be achieved using an optical cavity with a length of 4.5 m. Due to the length of the high finesse optical cavity it was possible to measure mixing ratios of 4 pptv of $NO_3$ in a 1 minute acquisition time with only moderate reflectivity mirrors ($R$=0.9977). The good spatial and temporal resolution of the IBBCEAS method and its pptv sensitivity to $NO_3$ makes it useful in laboratory studies of atmospheric processes as well as having obvious potential for field measurements.

A similar IBBCEAS set-up covering the 560-640 nm range was used to investigate the chemical kinetics of the $I_2/O_3/NO_x$ system, in particular to determine the rate constant of the $I_2+NO_3$ reaction which is significant in the chemistry of the marine boundary layer. The study involves the formation of iodine oxides (i.e. IO or OIO) and other iodine-containing species such as $INO_2$ or $IONO_2$.

[1] D.S. Venables, T. Gherman, J. Orphal, J.C. Wenger and A.A. Ruth, "High sensitivity *in situ* monitoring of $NO_3$ in an atmospheric simulation chamber using incoherent broadband cavity-enhanced absorption spectroscopy" *Environmental Science and Technology*, 2006, in press.

* presenting

# Application of spatially-resolved cavity ring down spectroscopy in plasma diagnosis

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Determining the structure of a plasma - *e.g.* the spatial distributions of its various constituent species and of temperature - can reveal a wealth of information about the physics and chemistry prevailing within the plasma. Furthermore, one of the toughest tests of the validity of any model of the plasma must be comparison of model outputs of species concentration profiles, *etc* with the corresponding, quantitative experimental measurement.

Cavity ring down spectroscopy (CRDS) is a highly sensitive, laser based technique for determining absolute column densities of species exhibiting well characterised absorption spectra at operationally convenient wavelengths. However, the stringent conditions associated with aligning the probe laser beam and the cavity has thus far limited the use of CRDS in spatially resolved concentration profiling applications. Here we report two different configurations whereby spatially resolved CRDS measurements have been demonstrated in the context of plasmas used for chemical vapour deposition (CVD) of thin film diamond. Using this technique, profiles of $C_2(a^3\Pi_u, v = 0)$ radicals (in a microwave plasma enhanced CVD reactor) and CH radicals (in an DC arc-jet plasma reactor) have been measured successfully.

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* presenting

# Trace detection of acetylene in the atmosphere using cavity ring down spectroscopy combined with sample pre-concentration

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The sensitive technique of cavity ring down spectroscopy (CRDS) coupled with sample pre-concentration has been used to measure the concentration of acetylene in the atmosphere in the parts per billion (ppbv) to parts per trillion order (pptv) range. Because of the very low abundances of this volatile organic compound (VOC) in the atmosphere, the use of pre-concentration serves as a tool to bring the concentration up in to the detection range of the instrument used. In such a way, trace acetylene concentrations can be measured quantitatively and precisely in the atmosphere. Monitoring the atmospheric level of this compound is of concern as it plays an important role in atmospheric chemistry, reacting with the OH radical, the main oxidising species in the atmosphere, as well as halogen atoms and the nitrate radical. Also acetylene has purely anthropogenic sources and so can be used as a chemical marker when determining the source of air packets in atmospheric measurements.

* presenting

# Quantitative Cavity Ring Down Spectroscopy with pulsed laser sources

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We will show preliminary results of an investigation how to solve the long standing, but often ignored problem of multi-exponential decays in Cavity Ring Down experiments with pulsed laser sources. Because the laser bandwidth of pulsed lasers is generally broader than, or comparable to, the absorption bandwidth, the light intensity leaking out of the optical cavity does not decay exponentially in time. Due to the convolution of the laser-and absorption line shape the light leaking out of the cavity is a ‘summation’ of numerous exponential decays with slightly different decay rates.

A mono-exponential fit to recorded decays will result in a too low estimate of the decay rate, and consequentially in an underestimation of the absorption strengths. Although it is possible to correct for this effect, this needs some kind of calibration. Our goal is to get quantitative and reliable results without corrections afterwards; first results look promising.

* presenting

# Off-axis, pulsed Cavity Ring Down Spectroscopy

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We will show that off-axis alignment of the optical resonator, with respect to the incoming laser beam, in a generic pulsed cavity ring down experiment is the solution to suppress oscillations in the background of the recorded spectrum. These oscillations often interfere with measured absorption spectra of molecules. The off-axis alignment is easy to achieve, robust, reproducible, and does not affect the sensitivity.

* presenting

# CRDS detection in the liquid phase: towards UV wavelengths

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The sensitivity of absorbance detection in liquid chromatography (LC) can be improved significantly by using cavity ring-down spectroscopy (CRDS). Thus far, liquid-phase CRDS experiments were performed using visible laser light at fixed standard wavelengths, such as 532 nm. However, since by far most compounds of analytical interest absorb in the UV, it is desirable to develop UV-CRDS. As a first step towards the deep-UV region, LC separations with CRDS detection (using a liquid-only cavity flow cell) at 457 and 355 nm are reported for standard mixtures of dyes and nitro-polyaromatic hydrocarbons (nitro-PAHs), respectively. For the measurements in the blue range a home-built optical parametric oscillator (OPO) system, tunable between 425 and 478 nm was used, achieving a baseline noise is $2.7 \times 10^{-6}$ A.U. at 457 nm, improving upon the sensitivity of conventional absorbance detection (typically around $10^{-4}$ A.U.). An enhancement of the sensitivity can be seen at 355 nm as well, but the improvement of the baseline noise ($1.3 \times 10^{-5}$ A.U.) is much less pronounced. Unfortunately, the sensitivity at 355 nm is limited by the quality of the UV-CRDS mirrors that are currently available.

* presenting

# Prism Cavity Ring Down Spectroscopy

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Although Cavity Ring Down Spectroscopy (CRDS) is a well proven tool for trace gas detection because of its high sensitivity and fast response, it has some clear limitations. Since it is based on high performance mirrors, which are only highly reflective over narrow spectral regions, measurements of multiple species in different spectral regions cannot be performed without changing the mirrors. This involves exposing the cell to ambient air and realignment of the optics. In addition, it is not yet possible to get highly reflective coatings for all spectral regions and the coatings may be damaged by extremely corrosive gases during measurements.

We recently introduced a prism cavity ring down method that can overcome these limitations. The cavity consists of two prisms - one having a curved surface - forming a stable ring resonator. A small portion of p-polarized laser light is coupled into the cavity by setting the angle of the incident beam near Brewster's angle. Working at exactly Brewster's angle with the second prism, we only get a very small, controlled loss for p-polarized light in the cavity. The optical beam undergoes two total internal reflections in each prism at 45°; therefore the spectral range is limited only by the absorption and the dispersion of the prism material itself. With this technology a single ring down cavity can be used over a wide spectral range, from the near UV to the mid-IR without any changes in optics or alignment. Thus providing a more versatile useable spectrometer, which combines the high sensitivity and fast response of conventional CRDS systems, with a very good broadband reflectivity.

* presenting

# $NO_2$ trace detection by Optical-Feedback Cavity-Enhanced Absorption Spectroscopy at 411nm

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Optical-Feedback Cavity-Enhanced Absorption Spectroscopy (OF-CEAS) relies on the laser sensitivity to Optical Feedback (OF) induced by a high finesse cavity [1]. Optical feedback enables laser frequency locking to the cavity resonances and laser bandwidth narrowing, resulting in optimal laser coupling and broad transmitted cavity modes. This allows fast spectra acquisition on small spectral windows (~1 $cm^{-1}$) over four decades in absorption unit with excellent linearity. Successive injection of all $TEM_{00}$ modes yields a mode-by-mode spectrum whose data points are highly defined in frequency and uniformly spaced by the cavity free spectral range. Absolute cavity losses are obtained by occasional ringdown time measurements on one cavity mode. OF-CEAS was initially developed in the IR domain, with distributed feedback diode lasers, where sensitivities of $10^{-10}$ $cm^{-1}$ are demonstrated [2].

We present preliminary results on the first application of OF-CEAS with a blue Extended Cavity Diode Laser for $NO_2$ detection. With a simple and compact optical set-up, the detection limit obtained at a pressure of 65 mbar corresponds to sub-ppb sensitivity at atmospheric pressure. Observed absorption spectra display more structure than previous spectra obtained at lower resolution by Fourier transform spectroscopy at the same wavelength (411nm). The present detection limit is obtained with a single laser scan (<0.1s). It should be further lowered by signal averaging. An alternate approach to be explored if we want to exploit the $NO_2$ spectral structure and achieve a more selective detection, requires specific data processing. Indeed, $NO_2$ absorption lines in the blue region are extremely dense and the observed spectrum does not present well isolated features even at low pressure.

[1] J. Morville, S. Kassi, M. Chenevier, and D. Romanini, Appl. Phys. B, 80, 1027 (2005).
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[3] I. Courtillot, J. Morville, V. Motto-Ros, and D. Romanini, Appl. Phys. B (in press).

* presenting

# Broadband Cavity Enhanced Absorption Spectroscopy of Thin film samples positioned at the Brewster Angle

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The use of a glass coverslip positioned at the Brewster Angle to the incident polarised light entering an optical cavity allows CRDS and CEAS measurements to be made of thin film samples at monolayer concentrations. The use of a broadband light source such as a Super LED and broadband dielectric mirrors allows the broad absorption features often displayed by these thin film samples to be probed in a fast and efficient manner without the associated problems of using multiple mirror sets and laser dyes that would be required for a pulsed laser CRDS set up.

I will present spectra of thin layers of dye molecules recorded by Broadband Brewster Angle CEAS as well as new results of monolayer samples of CdSe quantum dots which display a marked red shift from their solution spectra when prepared as a monolayer sample. This work will be backed up by previous results obtained by Brewster Angle CRDS as well as discussion as to possible reasons for the observed red shift.

* presenting

# Trace detection of water vapour using cw-CRDS

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A continuous wave cavity ring-down spectrometer with a compact design has been developed for the measurement of trace levels of water vapour using a 1358 nm DFB laser. As semiconductor processes become more sophisticated, moving to shorter wavelengths, the level of contamination in the vacuum environment becomes critical. The development of lithography beyond 193 nm increases the potential for photon-induced reactions with water vapour contamination which leads to irreversible oxidation of the lithography optics. Thus such systems demand ultra pure process gases and clean vacuum environments which give rise to the need for sensitive instruments for in-situ measurements.

A detection limit of $2.06\times10^{10}$ molecule $cm^{-3}$ has been determined at 1359.512 nm in a 37 cm long cavity from the mean ring-down time (RDT) $\tau_0$ = 20.55 μs of a set of measurements with a standard deviation of 0.6 %. The detection limit can be further improved by probing the stronger $H_2O$ absorption at 1392.534 nm.

The stability of the spectrometer has been determined using Allan-Variance analysis and its sensitivity and response time will be compared to those of current non-spectroscopic methods of trace water vapour detection.

* presenting

# The rotationally-resolved absorption spectra of formaldehyde and ammonia around IR (~1.45 µm)

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The high-resolution absorption spectrum of formaldehyde ($H_2CO$), measured from 6550 to 7050 cm$^{-1}$ (1527 to 1418 nm) at room temperature and 2 mbar, will be presented. The spectrum was obtained using diode-laser based cavity-enhanced absorption spectroscopy (CEAS) in off-axis alignment. The minimum detectable absorption coefficient was of $\alpha_{min}$ = $8\times10^{-8}$ cm$^{-1}$ and a sensitivity of $1.5\times10^{-9}$ cm$^{-1}$ Hz$^{-1/2}$ was achieved – the spectral resolution was approximately 0.001 cm$^{-1}$. The absorption cross-sections were calculated after calibrating the system using known absorption features of $H_2O$, $CO_2$ and $NH_3$. Several vibrational combination bands occur in the spectral region studied and give rise to a congested spectrum with several thousand observed absorption lines. The spectrum serves as a "finger print" for trace gas detection in the atmosphere and for the development of theoretical models which are based on the absorption of (urban) tropospheric pollutants. In addition, pressure broadening coefficients in $N_2$, $O_2$, and $H_2CO$ are reported for absorption lines at 6780.871 cm$^{-1}$ and 6684.053 cm$^{-1}$.

The same setup was used to study the near IR absorption spectrum of ammonia ($NH_3$) covering the region between 6900 and 7050 cm$^{-1}$ with the same resolution. This range has not been addressed before and relevant comparisons with the literature will be made.

* presenting

# Evanescent wave cavity enhanced absorption spectroscopy using a broad-band incoherent light source

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Total internal reflection (TIR) spectroscopy is a well established technique to provide information related to the chemical structure of biomaterials adsorbed on surfaces [1]. In TIR spectroscopy the absorption of a compound on the surface of a transparent internal reflection element (IRE) is measured using the evanescent wave of the totally reflected beam of light propagating inside the IRE.

In 1997 a TIR cavity, using a specially designed prism, was first applied in cavity ring-down spectroscopy by Pipino et al. [2]. So far most application of evanescent field cavity ring-down spectroscopy have been performed at a single or a narrow range of wavelengths. In this poster we combined incoherent broad-band cavity enhanced absorption spectroscopy (IBBCEAS) [3] with the evanescent wave approach in order to study the absorption spectra of metallo-porphyrins, Platinum-octaethyl porphyrin (PtOEP) and Palladium-octaethyl porphyrin (PdOEP), on a fused silica surface in the visible range of the spectrum. Broad-band light (470 – 620 nm) is coupled into a cavity consisting of a mirror-prism-mirror configuration. Since the amplitude and penetration depth of the evanescent wave are determined by the angle of incidence on the surface and the refractive index change between the two media, the setup is designed to be close to the critical angle in order to optimize the effective sampling depth. The time-integrated light transmitted by the cavity is dispersed and detected with a CCD detector. The experimental setup is characterized by a high time resolution, sufficiently high spectral resolution for measuring absorption spectra of surface species and has an improved sensitivity in comparison with conventional TIR spectroscopy.

Absorption spectra of PtOEP and PdOEP in a solution layer and on a fused silica surface will be shown. First results describing the anisotropy of these compounds on the interface will be discussed.

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A.C.R. Pipino, J.W. Hudgens, R.E. Huie, Rev. Sci. Instrum. **68**, 2978 (1997).
[3] S.E. Fiedler, A. Hese, A.A. Ruth, Chem. Phys. Lett. **371**, 284 (2003).

* presenting

# Line-mixing and collision-induced absorption in the A-band of molecular oxygen

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The A-band of molecular oxygen couples the ground-state $^3\Sigma_g^-(v=0)$ with the $^1\Sigma_g^+(v=0)$ state. This highly forbidden transition is still saturated in the Earth atmosphere. The fact, that oxygen is extremely well-mixed in the atmosphere, renders its spectral features useful for assessing cloud top heights by remote sensing. To do this quantitatively, line shapes, which are affected by pressure broadening, line-mixing effects and collision induced absorption (CIA), need to be known ideally within 1% accuracy.

We have started experiments in the A-band at the short wavelength side of the R-branch bandhead and in between the rotational lines in the P-branch in order to quantify both collision induced absorption as well as the far wing line-mixing induced line shapes. In a cell, in which the pressure can be varied between 0 and 10 bar, CRDS with a resolution of 0.03 to 0.1 cm$^{-1}$ is performed. Care has been taken to validate the absolute cross sections using Rayleigh scattering.

We find that we can obtain accurate and absolute information on the collision induced cross section and the pressure broadened line-shapes. The collision induced absorption spectrum is without structure and extends many wavenumbers to either side of the narrow resonances. The magnitude of the CIA coefficient is found to be ~ $1\cdot10^{-7}$ cm$^{-1}\cdot$atm$^{-2}$ at a wavelength of 758 nm (13192 cm$^{-1}$), ~ 25 cm$^{-1}$ from the R-branch bandhead. A spectrum build from a linear sum of Lorentzian lines does not reproduce the far wing line shapes of individual rotational lines, line-mixing is needed to account for the true line shape. In the far wing of the lines the cross section is reduced by line-mixing effects.

* presenting

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## The Cavity Ring-Down User Meeting (2007)

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