Cavity-enhanced absorption spectroscopy: Transition from UV/VIS into the MIR using quantum cascade lasers

J.H. van Helden

Leibniz Institute for Plasma Science and Technology, Greifswald, Germany

16th International Symposium on Laser Aided Plasma Diagnostics
Madison, Wisconsin, September 25 2013
Outline

- Introduction of cavity enhanced techniques
- Moving to the mid-infrared: Quantum Cascade Laser
- DFB QCL off-axis cavity enhanced absorption spectroscopy
- External-cavity QCL based cavity enhanced absorption spectroscopy
- External-cavity QCL absorption spectroscopy for plasma studies
Motivation

Laser absorption spectroscopy:
+ Selective
+ Absolute
+ Non-invasive

Beer-Lambert Law
\[ \ln \left( \frac{I_0}{I} \right) = \sigma(\nu) c l \]
\[ \sigma(\nu) = \text{absorption cross-section (molecule specific)} \]
\[ c = \text{concentration of sample} \]
\[ l = \text{sample length} \]

Disadvantages
- Line-of-sight (spatial average)
- Not sensitive enough → maximise \( \sigma(\nu) \) by accessing mid-infrared
  → maximise \( l \) by optical cavities
Motivation

Mirror reflectometer based on optical cavity decay time

Dana Z. Anderson, Josef C. Frisch, and Carl S. Masser

Described is a reflectometer capable of making reflectivity measurements of low-loss highly reflecting mirror coatings and transmission measurements of low-loss antireflection coatings. The technique directly measures the intensity decay time of an optical cavity comprised of low-loss elements. We develop the theoretical framework for the device and discuss in what conditions and to what extent the decay time represents a true measure of mirror reflectivity. Current apparatus provides a decay time resolution of 10 nsec and has demonstrated a cavity total loss resolution of 5 ppm.

Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources

Anthony O’Keefe and David A. G. Deacon

Deacon Research, 900 Welch Road, Palo Alto, California 94304

(Received 28 March 1988; accepted for publication 27 July 1988)

We have developed a technique which allows optical absorption measurements to be made using a pulsed light source and offers a sensitivity significantly greater than that attained using stabilized continuous light sources. The technique is based upon the measurement of the rate of absorption rather than the magnitude of absorption of a light pulse confined within a closed optical cavity. The decay of the light intensity within the cavity is a simple exponential with loss components due to mirror loss, broadband scatter (Rayleigh, Mie), and molecular absorption. Narrowband absorption spectra are recorded by scanning the output of a pulsed laser (which is injected into the optical cavity) through an absorption resonance. We have demonstrated the sensitivity of this technique by measuring several bands in the very weak forbidden $b^1 \Sigma_g^+ \rightarrow X^1 \Sigma_g^+$ transition in gaseous molecular oxygen. Absorption signals of less than 1 part in $10^6$ can be detected.
## Optical cavities techniques

- **Pulsed CRDS** (O'keefe et al. 1988)  
  \( \alpha_{\text{min}} = 10^{-8} - 10^{-9} \text{ cm}^{-1} \)
- **PSCRD** (Engeln et al. 1996)  
  \( \alpha_{\text{min}} = 10^{-8} - 10^{-9} \text{ cm}^{-1} \)
- **cw-CRDS** (Romanini et al. 1997)  
  \( \alpha_{\text{min}} = 10^{-8} - 10^{-9} \text{ cm}^{-1} \)
- **Cavity-locked CRDS** (Paldus et al. 1998)  
  \( \alpha_{\text{min}} = 10^{-9} - 10^{-10} \text{ cm}^{-1} \)
- **CEAS/ICOS** (Engeln et al. 1998)  
  \( \alpha_{\text{min}} = 10^{-8} - 10^{-9} \text{ cm}^{-1} \)
- **NICE-OHMS** (Ye et al. 1998)  
  \( \alpha_{\text{min}} = 10^{-11} - 10^{-14} \text{ cm}^{-1} \)
- **Laser-locked CRDS** (Spence et al. 2000)  
  \( \alpha_{\text{min}} = 10^{-11} - 10^{-12} \text{ cm}^{-1} \)
- **OA-CEAS** (Paul et al. 2001)  
  \( \alpha_{\text{min}} = 10^{-9} - 10^{-10} \text{ cm}^{-1} \)
- **OF-CEAS** (Morville et al. 2004)  
  \( \alpha_{\text{min}} = 10^{-9} - 10^{-11} \text{ cm}^{-1} \)

Optical cavities techniques

Cavity ring-down spectroscopy: principles

Absorption per unit of pathlength (cavity loss):
1/\(c\tau = (1 - R + n\sigma L) / d\)

Density in one transition:
- Isolated (one single line)
- Known absorption cross section

Density in all transitions:
- Using Boltzmann equation
- Know rotational temperature
- Know vibrational temperature

\[
n_{\text{tot}} = n_i \sum_k g_k \cdot \exp\left(-\frac{E_{\text{rot},k}}{kT_{\text{rot}}}ight) \cdot \exp\left(-\frac{E_{\text{vib},k}}{kT_{\text{vib}}}ight)
\]

\[
n_i = \frac{1}{\sigma L} \left( \frac{d}{c\tau} - \frac{d}{c\tau_0} \right)
\]

CRDS: a versatile technique

Cavity ringdown spectroscopy on:
- Gas phase radicals
- Thin films (tf-CRDS)

I.M.P. Aarts et al
APL 84, 3079 (2004)

- Surface species (evanescent wave-CRDS)

A.C.R. Pipino et al
JCP 120, 2879 (2004)
# Measured radicals and molecules

<table>
<thead>
<tr>
<th>Particle</th>
<th>Used transition</th>
<th>$\lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$4s^3P_1 \leftarrow 3p^2^3P_0$</td>
<td>252</td>
</tr>
<tr>
<td>SiH</td>
<td>$A^2\Delta \leftarrow X^2\Pi(0 \leftarrow 0)Q_{11}(11.5)$</td>
<td>413</td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>$\tilde{A}^2A_1 \leftarrow \tilde{X}^2A_1$ band</td>
<td>215 &amp; 250</td>
</tr>
<tr>
<td>C</td>
<td>$3s^1P_1 \leftarrow 3s^1S_0$</td>
<td>248</td>
</tr>
<tr>
<td>C$_2$</td>
<td>$d^3\Pi_g \leftarrow a^3\Pi_u (0 \leftarrow 0)$</td>
<td>517</td>
</tr>
<tr>
<td>CH</td>
<td>$A^2\Delta \leftarrow X^2\Pi(0 \leftarrow 0)$</td>
<td>431</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>$\tilde{B}^2A_1 \leftarrow \tilde{X}^2A_2$ band</td>
<td>216</td>
</tr>
<tr>
<td>NH</td>
<td>$A^3\Pi \leftarrow X^3\Sigma^-(0 \leftarrow 0)P_{3,3}(9)$</td>
<td>340</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>$\tilde{A}^2A_1 \leftarrow \tilde{X}^2B_1(090 \leftarrow 000)\Sigma^pQ_{1,7}$</td>
<td>597</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>$\nu_1 + \nu_3$ combination band</td>
<td>1522</td>
</tr>
</tbody>
</table>

- **Growth a-Si:H**
- **Growth a-C:H**
- **NH$_3$ generation/**
- **NH$_3$ dissociation/**
- **growth a-SiN$_x$:H**
Cavity ring-down spectroscopy: system

- Highly reflective mirrors (97% in the UV - 99.9% in VIS), bandwidth 100 nm
- Cavity length ~ 112 cm
- Filter to block plasma light
- Small Ar flow to protect mirrors
- Laser power before cavity <100 μJ/pulse
- TU/eDACS: homebuild detection system: 100 MHz, 12 bit, every transient recorded
Cavity ring-down spectroscopy: example

CRD spectrum of SiH measured during a:Si-H deposition
Cavity ring-down spectroscopy: example

CRD spectrum of SiH measured during a:Si-H deposition

\[ \frac{1}{c \tau} = \frac{1 - R + n \sigma L}{d} \]
Cavity ring-down spectroscopy: example

SiH detection: $A^{2}\Delta \leftrightarrow X^{2}\Pi$, 405 – 430 nm

- line width
- temperature
- absorption + cross-section
- density

$T_{vib} = 3000\text{K}$
$T_{rot}(v=0) = 1800\text{K}$

Cavity Enhanced Absorption: Setup

Tunable cw diode laser (5 mW) @1520-1560 nm, line-width ~ 1MHz (~10^{-3} \times \Delta v_D)
Scanning 1 cm^{-1} at 31 Hz

During each scan several laser frequencies coincide with the frequency of one of the cavity modes and are coupled into the cavity

After several scans all frequencies are sampled

CEA spectrometer
(a simplified ‘mode-picture’)

Time dependence of the intensity in a single mode (during a laser scan)

Integrated intensity of one cavity mode as function of ring-down time

Lorentzian profile

\[
\begin{align*}
  I_{\text{max}} &\sim \tau^2 \\
  \Delta \nu &\sim \tau^{-1}
\end{align*}
\]

\[I_{\text{max}} \sim \tau\]
CEA: typical measurement

Ro-vibrational absorption spectrum of NH$_3$

Scanning frequency: 30 Hz
Frequency range: 30 GHz
Averages: 1000
Measurement time: 30 s

The absorption coefficient $\kappa(\nu)$ from intensity by:

$$\kappa(\nu) = \left( \frac{S_0(\nu)}{S(\nu)} - 1 \right) \left( \frac{1 - R}{d} \right)$$

Ro-vibrational absorption spectrum of NH₃

Line width

\[ T_{tr} = 600 \text{ K} \]

\[ \sigma \approx 10^{-22} \text{ m}^2 \]

\[ N \approx 10^{19} \text{ m}^{-3} \]

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Moving to the mid-infrared: Why?

- many molecular species
  - Only detectable in the 3 – 20 μm spectral range (MIR)
  - Strong fundamental rovibrational transitions
Moving to the mid-infrared: Why?

- Strong fundamental rovibrational transitions of many molecular species
- High degree of ro-vibrational structures
- Free of interference from molecules in the atmosphere in 3 - 5 µm and 8 – 13 µm regions
- Allows sensitive and selective spectroscopic measurements of many compounds
- **Quantum** – quantum wells created by sandwiching thin layers of different semiconductor materials; large wavelength range accessible.

- **Cascade** – applied electric field allows a single electron to cascade through a series of active regions to achieve a high optical gain.

- **Laser** – population inversion maintained due to relative speed of transitions between levels.

QCL: Properties

- Novel source of mid-IR radiation of $\lambda \approx 3 \, \mu m - 300 \, \mu m$

- Advantages over other mid-IR sources (e.g. non-linear frequency conversion or lead salt diode lasers):
  - Simplicity
  - High power of tens of mWs
  - Single mode operation
  - Continuously tuneable
  - Room temperature operation
  - Narrow intrinsic line-width $\Rightarrow \Delta \nu < 10 \, MHz \ (0.0003 \, cm^{-1})$

- Single mode operation is normally achieved by a DFB grating ($\sim 10 \, cm^{-1}$ tuning), although an external cavity is an alternative giving wide tunability ($\sim 200 \, cm^{-1}$)
## Comparison of MIR Absorption Techniques

<table>
<thead>
<tr>
<th></th>
<th>IR - TDLAS</th>
<th>IR – DFB-QCLAS</th>
<th>IR - EC-QCLAS</th>
<th>FT - IR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>sensitivity</strong> ((I_0 - I)/I_0)</td>
<td>☹ (10^{-3}...10^{-5})</td>
<td>☺ (10^{-3}...10^{-5})</td>
<td>☺ (10^{-3}...10^{-5})</td>
<td>☹ (10^{-2}...10^{-3})</td>
</tr>
<tr>
<td><strong>selectivity</strong> (\Delta \nu)</td>
<td>☺ (10^{-4}...10^{-3}) cm(^{-1})</td>
<td>☺ (10^{-4}...10^{-2}) cm(^{-1})</td>
<td>☺ (10^{-4}...10^{-3}) cm(^{-1})</td>
<td>☹ 0.1 cm(^{-1})</td>
</tr>
<tr>
<td><strong>tunability</strong></td>
<td>☹ (10...100) cm(^{-1})</td>
<td>☹ (1...10) cm(^{-1})</td>
<td>☺ (80...200) cm(^{-1})</td>
<td>☺ whole MIR</td>
</tr>
<tr>
<td><strong>time resolution</strong> (\Delta t)</td>
<td>☺ ms (... μs)</td>
<td>☺ ms...ns</td>
<td>☺ s (... ms)</td>
<td>☹ min...s</td>
</tr>
<tr>
<td><strong>operation/detection</strong></td>
<td>☹ (20 - 130) K LN(_2) detectors</td>
<td>☺ near room T TE detectors</td>
<td>☺ near room T TE detectors</td>
<td>☹ room T LN(_2) detectors</td>
</tr>
</tbody>
</table>
CW external cavity QCL laser

- Daylight Solutions 5.3 μm CW EC-QCL, water cooled
- Wide tuning range: 1776 – 1968 cm⁻¹ (5.1 – 5.6 μm)
- Mode hop free: 1870 – 1920 cm⁻¹
- 160 mW output power
- Laser bandwidth 20 MHz
- Grating tuning
- Piezo tuning over < 1.2 cm⁻¹ at 10 - 100 Hz ramp

G. Hancock, J. H. van Helden, R. Peverall, G.A.D. Ritchie, R.J. Walker,
Appl. Phys. Lett. 94 (2009) 201110
Wavelength modulation spectroscopy

- 2f data: 15 kHz modulation of laser current and thus laser frequency and demodulated by lock-in amplifier at 2\textsuperscript{th} harmonic
- Signal peaks at 700 mV = 0.005 cm\textsuperscript{-1} (142 MHz)
- Peak corresponds to S/N = 765
- $\alpha_{\text{min}}(\text{BW}_{\text{eff}}) = 1.9 \times 10^{-6}$ cm\textsuperscript{-1} Hz\textsuperscript{-1/2}
- Enhancement $\times 25$

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OA-CEAS of OCS: Experimental

- CW 9.7 μm Hamamatsu DFB QCL (20 mW) to detect OCS.
- Low power requires use of MCT detector and noise reduction using a mechanical chopper and lock-in amplifier.
- Input mirror in front of cavity is mounted on a stage so that $x_{\text{TRANS}}$, $\theta_x$ and $\theta_y$ can be altered.
Cavity methods: Off-axis approach

Starting on-axis: TEM\(_{00}\) and examples of higher order TEM\(_{nm}\) modes imaged from cavity.

- Off-axis path through the cavity spatially separate the multiple reflections within the cavity until the “re-entrant” condition is fulfilled.

- As the re-entrant condition increases in length, the effective FSR of the cavity decreases and mode spacing is reduced.

- Limiting factor of this alignment tends to be power.
CEAS of OCS: Aligning the cavity using the input mirror

- Begin with “on-axis” arrangement:

Alignment procedure

Simulation

Experimental
CEAS of OCS: Aligning the cavity using the input mirror

- Applying a 5 mm translation in the x-plane:
CEAS of OCS: Aligning the cavity using the input mirror

- Applying $\theta_y$:

Alignment procedure

Simulation

Experimental
CEAS of OCS: Aligning the cavity using the input mirror

- Applying $\theta_x$ such that $\theta_x = -\theta_y$:
CEAS of OCS: Effect of cavity alignment on signal

Mode structure as alignment varies
CEAS of OCS: Improving the output signal even further....

- Setup still dominated by mode structure, which could normally be minimised by mechanical dithering.

- In this case, the mode structure was further reduced by dithering of the input current.
- The disadvantage of this is broadening of the lineshape.
CEAS of OCS: Initial results

- Example data taken over 50 seconds of 0.77 Torr OCS at 1031.109 cm\(^{-1}\) \((\sigma_{\text{INT}} = 2.58 \times 10^{-21} \text{ cm}^2 \text{ cm}^{-1})\) and 1031.146 cm\(^{-1}\) \((\sigma_{\text{INT}} = 4.52 \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1})\)

- Cavity length 48 cm
- The fit returns an effective pathlength of 108 \(\pm\) 3.5 m
- Corresponds to \(R = 99.56\%\)
- From baseline noise can calculate: \(\alpha_{\text{min}} = 7.7 \times 10^{-6} \text{ cm}^{-1}\)
Restrictions on available equipment

Limited availability on detectors, usually resulting in the use of small surface area detectors, coupled with lower detectivity than in NIR (approx. $10^3$)

Divergence $= \frac{\lambda}{\pi \omega_0}$

Diffraction $\sin \theta = 1.22\lambda/d$

No change in optic size to compensate for this

Overall, the result is poorer coupling into the cavity
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CEAS setup

- EC-QCL 1305 – 1445 cm\(^{-1}\) (mode-hop free 1345-1400 cm\(^{-1}\)), 150 mW
- Isolator to prevent back reflections into laser from the optical cavity
- Lens to mode-match the laser beam to the modes in the cavity
- Optical cavity of 32 cm consisting of HR mirrors, R = 0.9998, r = -0.5 m, 1” diameter.

J.H. van Helden, N. Lang, U. Macherius, H. Zimmermann, J. Röpcke,
Accepted for publication in Appl. Phys. Lett. (2013)
Results: Calibration Measurement

- Piezo scanning: 80 Hz, 9V ($\Delta\nu \sim 1.2$ cm$^{-1}$)
- Current modulation at 85 kHz with an amplitude of about $2.33 \times 10^{-3}$ cm$^{-1}$ (70 MHz) < Free spectral range (FSR) of the cavity ($\sim 0.015$ cm$^{-1}$)
- Calibration with 10 ppm N$_2$O at 1326.779 cm$^{-1}$ ($S = 1.52 \times 10^{-21}$ cm$^2$ cm$^{-1}$): $R=0.99982 \pm 0.00001$ corresponding to $L_{eff} = 1780 \pm 100$ m

![Graph showing calibration measurements with different current modulation amplitudes.](image)
Results: CH₄ measurement

Linestrengths CH₄ transitions

<table>
<thead>
<tr>
<th></th>
<th>v (cm⁻¹)</th>
<th>S (cm² cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1327.074</td>
<td>9.616 x 10⁻²⁰</td>
<td>R(3)</td>
</tr>
<tr>
<td>2</td>
<td>1327.256</td>
<td>5.771 x 10⁻²⁰</td>
<td>R(3)</td>
</tr>
<tr>
<td>3</td>
<td>1327.410</td>
<td>5.771 x 10⁻²⁰</td>
<td>R(3)</td>
</tr>
<tr>
<td>4</td>
<td>1348.042</td>
<td>3.479 x 10⁻²⁰</td>
<td>R(7)</td>
</tr>
</tbody>
</table>

Mode-hop free region

From measurements on air:

CH₄ concentration = 1.8 ± 0.1 ppm

Agrees with previous measurements:
Results: CH$_4$ Measurement at 1348.042 cm$^{-1}$

- From slope of integrated CEAS signal versus concentration of CH$_4$ in air: $R = 0.99982$

- From Allen Variance: $\alpha_{\text{min}} = 2.6 \times 10^{-8}$ cm$^{-1}$ in 625 seconds corresponding to 6 ± 2 ppb CH$_4$ in 10 mbar total pressure
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Plasma Chemistry and Reaction Kinetics

- Planar Microwave Plasma Reactor

→ basic research of non-stationary excitation and relaxation phenomena and of plasma chemistry

Sideview of a Double Microwave Plasma Source

Arrows pointing to the plasma region below the microwave window.
EC-QCL spectrometer at a MW plasma reactor
D1, D2, D3: detectors, RGC: reference gas cell, DP: diaphragm

D. Lopatik, N. Lang, U. Macherius, H. Zimmermann and J. Röpcke,
Absorption spectrum in an Ar/N₂/CH₄ MW plasma
absorption lines of CH₄, C₂H₂ and HCN, l= 30 m

D. Lopatik, N. Lang, U. Macherius, H. Zimmermann and J. Röpcke,

Ar=17 sccm
N₂=1 sccm
CH₄=2 sccm
p=0.5 mbar
P=0.2 kW
Concentrations of CH$_4$ (■, □) and C$_2$H$_2$ (●, ○) and HCN (▲, △) as a function of gas mixture, p = 0.5 mbar and P = 0.2 kW

D. Lopatik, N. Lang, U. Macherius, H. Zimmermann and J. Röpcke,
Plasma Diagnostics with EC-QCLs, No. 1

Temperature determination using CH₄ line
MW plasma, P = 0.2 kW, 10% N₂ + 10% CH₄ in Ar, p = 0.5 mbar

D. Lopatik, N. Lang, U. Macherius, H. Zimmermann and J. Röpcke,
$T_g$ as a function of power calculated from line profiles

MW plasma, $P = 0.2$ kW, 10% $N_2$ + 10% $CH_4$ in Ar, $p = 0.5$ mbar
instrumental profile: 0.00127 cm$^{-1}$ (38.1 MHz)

D. Lopatik, N. Lang, U. Macherius, H. Zimmermann and J. Röpcke,
## Table 1. Plasma diagnostic applications of mid-IR QCLs.

<table>
<thead>
<tr>
<th>Species</th>
<th>Spectral range (cm⁻¹)</th>
<th>Type of plasma</th>
<th>Application¹</th>
<th>Pressure (mb)²</th>
<th>Type of QCL</th>
<th>Tuning method</th>
<th>Method of absorption¹</th>
<th>Time resolution</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>~1275</td>
<td>MW</td>
<td>Res.</td>
<td>&gt;-50</td>
<td>Pulsed</td>
<td>Intra</td>
<td>DAS/SP</td>
<td>1 s</td>
<td>2006</td>
<td>[66]</td>
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<tr>
<td>NO</td>
<td>1897</td>
<td>dc</td>
<td>Res.</td>
<td>2.7</td>
<td>Pulsed</td>
<td>Intra</td>
<td>DAS/SP</td>
<td>5 μs</td>
<td>2007</td>
<td>[67]</td>
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<tr>
<td>SiF₆</td>
<td>1028</td>
<td>RF</td>
<td>Ind.</td>
<td>0.33</td>
<td>Pulsed</td>
<td>Inter</td>
<td>DAS/DP</td>
<td>~1 s</td>
<td>2007</td>
<td>[46]</td>
</tr>
<tr>
<td>CH₃⁺</td>
<td>1253</td>
<td>RF</td>
<td>Res.</td>
<td>0.23</td>
<td>Pulsed</td>
<td>Intra</td>
<td>DAS/SP</td>
<td>n.a</td>
<td>2008</td>
<td>[68]</td>
</tr>
<tr>
<td>CF₃⁺</td>
<td>1253</td>
<td>Photolysis</td>
<td>Res.</td>
<td>2.6-5.4</td>
<td>Pulsed</td>
<td>Intra</td>
<td>DAS/SP</td>
<td>5 μs</td>
<td>2008</td>
<td>[69]</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>~1275</td>
<td>MW</td>
<td>Res.</td>
<td>1013</td>
<td>Intra</td>
<td>DAS/SP</td>
<td>5 μs</td>
<td>2009</td>
<td>[70]</td>
<td></td>
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<tr>
<td>NF₃</td>
<td>1028</td>
<td>RF</td>
<td>Ind.</td>
<td>0.33</td>
<td>Pulsed</td>
<td>Inter</td>
<td>DAS/DP</td>
<td>~1 s</td>
<td>2009</td>
<td>[71]</td>
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<tr>
<td>CH₃⁺</td>
<td>~1275</td>
<td>MW</td>
<td>Res.</td>
<td>199.5</td>
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<td>2009</td>
<td>[72]</td>
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<tr>
<td>C₂H₅⁺</td>
<td>2244</td>
<td>VHF⁴</td>
<td>Res. (Ind.)</td>
<td>3.5-4.5</td>
<td>cw</td>
<td>DAS/SP</td>
<td>n.a</td>
<td>2009</td>
<td>[48]</td>
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<tr>
<td>BC₁</td>
<td>964</td>
<td>MW</td>
<td>Ind.</td>
<td>2</td>
<td>Pulsed</td>
<td>Inter</td>
<td>DAS/DP</td>
<td>3 s</td>
<td>2009</td>
<td>[46]</td>
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<tr>
<td>NO</td>
<td>1900</td>
<td>DPBPR⁸</td>
<td>Res.</td>
<td>1000</td>
<td>cw</td>
<td>DAS/SP</td>
<td>&gt;1 s</td>
<td>2009</td>
<td>[73]</td>
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<tr>
<td>CF₃⁺</td>
<td>1271</td>
<td>RF</td>
<td>Res.</td>
<td>0.1</td>
<td>Intra</td>
<td>DAS/SP</td>
<td>5 ms</td>
<td>2009</td>
<td>[74,75]</td>
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<td>DAS/DP</td>
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<td>CH₄</td>
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<td>CO</td>
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<td>&lt;1 μs</td>
<td>2012</td>
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</table>

¹ Application type: Res. = Resonant, Pulsed = Pulsed, DC = Direct Current, ICP-RF = Inductively Coupled Plasma - Radio Frequency
² Pressure in mbar
³ Time resolution in seconds
⁴ VHF = Very High Frequency
⁵ DAS = Distributed Amplifier System, SP = Spectroscopic Package, DP = Diode Pumped, DP = Diode Pumped, MP = Multi-Path, EC = External Cavity
Summary

EC-QCLAS – useful for multiple species detection

EC-QCL CEAS – detection of low concentrations

First application of EC-QCLs for plasma diagnostics

General properties for plasma spectroscopy

+ wide tuning range
+ small line width
+ compact system
+ high power
+ collimated beam

- limited general tuning speed
- Piezo frequency low
- no pulsing possible
- often power too high
- no power regulation
- sensitive for back reflections
Acknowledgement

INP Greifswald
- U. Macherius
- D. Lopatik
- H. Zimmermann
- S. Glitsch
- F. Weichbrodt
- M. Spiller
- M. Wiese
- N. Iang
- J. Röpcke

Eindhoven University of Technology
- R. Engeln
- P.J. van den Oever
- P. Vankan
- J.P.M. Hoefnagels
- S. Mazouffre
- W.M.M. Kessels
- M.C.M. van de Sanden
- D.C. Schram

University of Oxford
- R.J. Walker
- J. Kirkbide
- S.J. Horrocks
- B. Cummunings
- D. Weidmann
- R. Peverall
- G.A.D. Ritchie
- G. Hancock

Collaborative Research Centre “Complex Plasmas” (B2)
Leibniz Institute for Plasma Science and Technology
Address: Felix-Hausdorff-Str. 2, 17489 Greifswald
Phone: +49 - 3834 - 554 300, Fax: +49 - 3834 - 554 301
E-Mail: welcome@inp-greifswald.de, Web: www.inp-greifswald.de