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Noise-immune, Cavity-enhanced, Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) for Trace Gas Detection

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Session: Cavity and Frequency Comb Based Precision Sensing

Trace Gas Detection – application sectors

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Industrial

Airborne Molecular Contamination (**AMC**)
- chemical contamination from vapours or aerosols
- adverse effects on products, processes or instruments (safety, efficiency, revenue)
- semiconductor, nanotechnology, photovoltaic and high brightness and organic LED industries

Environmental

Clean energy / Greenhouse gases
- biomethane / hydrogen fuel contaminants
- methane monitoring and source tracking

Medical

Disease diagnostics
- exhaled breath analysis
- key metabolic markers

Growing need for improved methods of **real-time**, **calibrated measurement** of trace-level gases across multiple sectors

NICE-OHMS

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Noise-Immune,

Cavity-Enhanced,

Optical Heterodyne

Molecular Spectroscopy

First demonstration:

Ultrasensitive detections in atomic and molecular physics: demonstration in molecular overtone spectroscopy, J. Ye, L. Ma, and J. L. Hall, *Journal of the Optical Society of America B* **15**, 6-15 (1998).

Detection of acetylene and carbon dioxide molecules

- 1.064-mm Nd:YAG laser
- 46.9-cm-long cavity
- High finesse cavity, F = 100,000

Further reading: developments in NICE-OHMS

Aleksandra Foltynowicz *et al.* "Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy: Current status and future potential," *Appl. Phys. B* **92,** 313 (2008).

Patrick Ehlers, Isak Silander, and Ove Axner, "Doppler broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry: optimum modulation and demodulation conditions, cavity length, and modulation order," J. Opt. Soc. Am. B 31, 2051-2060 (2014).

NICE-OHMS: Molecular Spectroscopy

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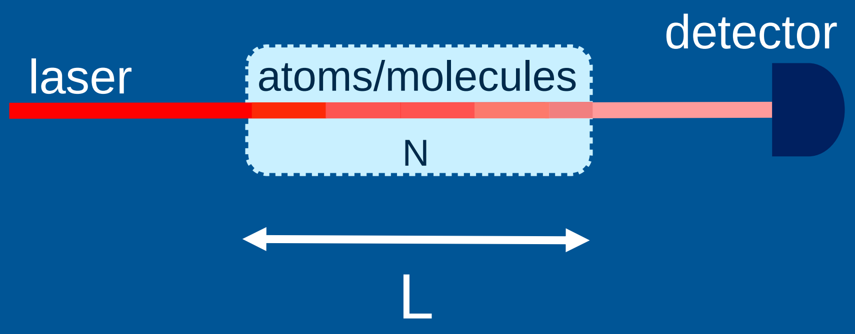
Gas sensing with lasers:

Absorption spectroscopy



Linear absorbance (A) over a path length L

$$A = NL\sigma$$

with number of atoms or molecules N, interaction path length L, and cross section σ.

absorption profile

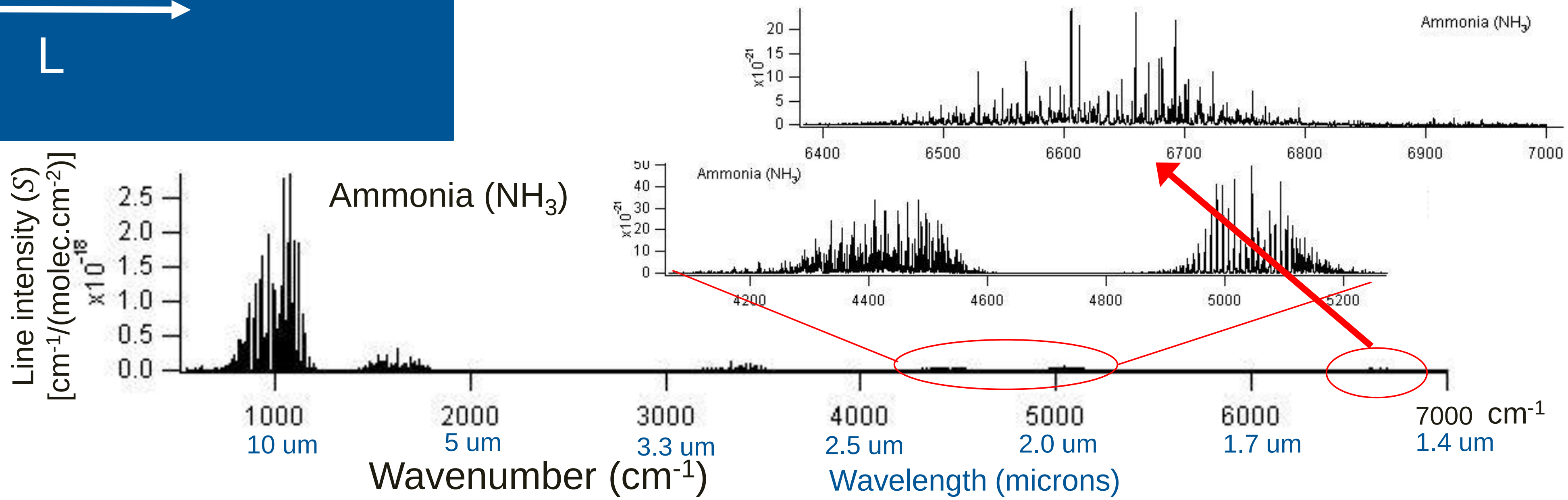
$$\sigma = S\,\chi_{abs}(\nu)$$

line intensity

Transmission, T, through a sample is described by the Beer-Lambert law

$$T = \exp(-A)$$

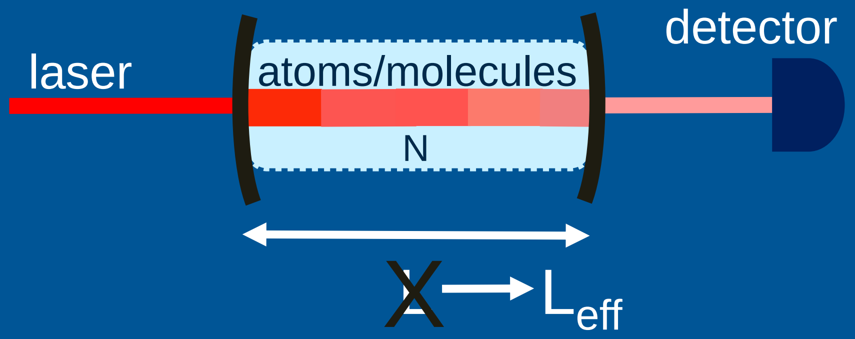
HITRAN database



NICE-OHMS: Cavity-Enhanced

Gas sensing with lasers:

increase the laser path length



$$\mathrm{FSR} = \Delta\nu_{\mathrm{FSR}} = c/2L$$

(resonant cavity mode spacing)

$$\mathcal{F} = \frac{\mathrm{FSR}}{\Delta\nu_c} = \pi\frac{\sqrt{\mathcal{R}}}{1-\mathcal{R}}$$

Cavity enhancement

- interaction length L is increased

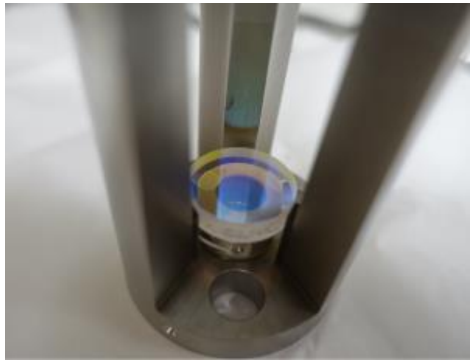
$$L_{\mathrm{eff}} = \frac{2\mathcal{F}}{\pi}$$

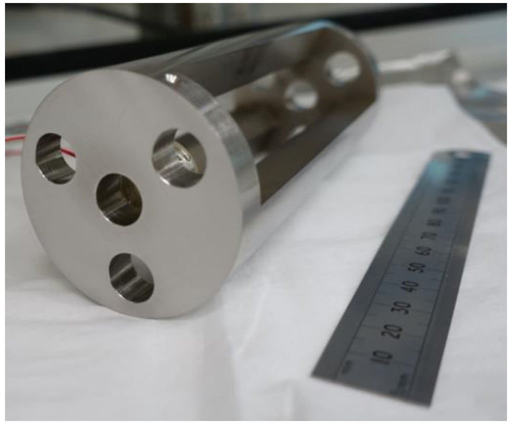
$\mathcal{F}$ = cavity Finesse
$\Delta\nu_c$ = cavity linewidth
$\mathcal{R}$ = mirror reflectivity

Our cavity Finesse ~ 169,000
Effective distance light travels inside cavity = 10.8 km
(within a 10 cm cavity)
2 x Finesse / π = 108,000 enhancement factor

Cavity challenges:

- Sourcing high-reflectivity mirrors at certain wavelengths
- Narrow cavity linewidth
  - Frequency noise to amplitude noise conversion (FM to AM)
  - Coupling noisy lasers to narrow cavities in an "open" cavity [MHz to kHz linewidth differential / gas flow]

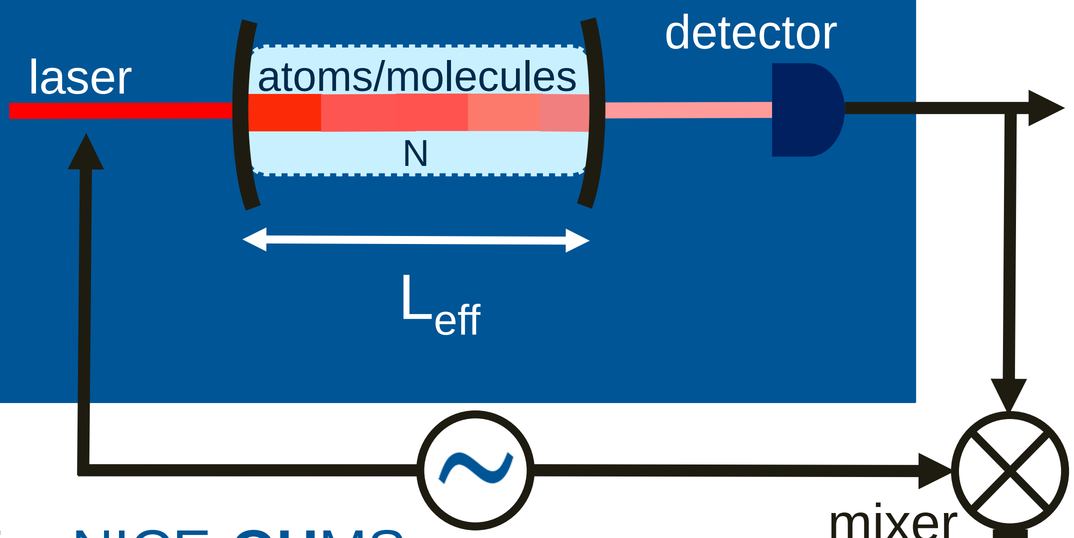




NICE-OHMS: Noise-Immune

Gas sensing with lasers:

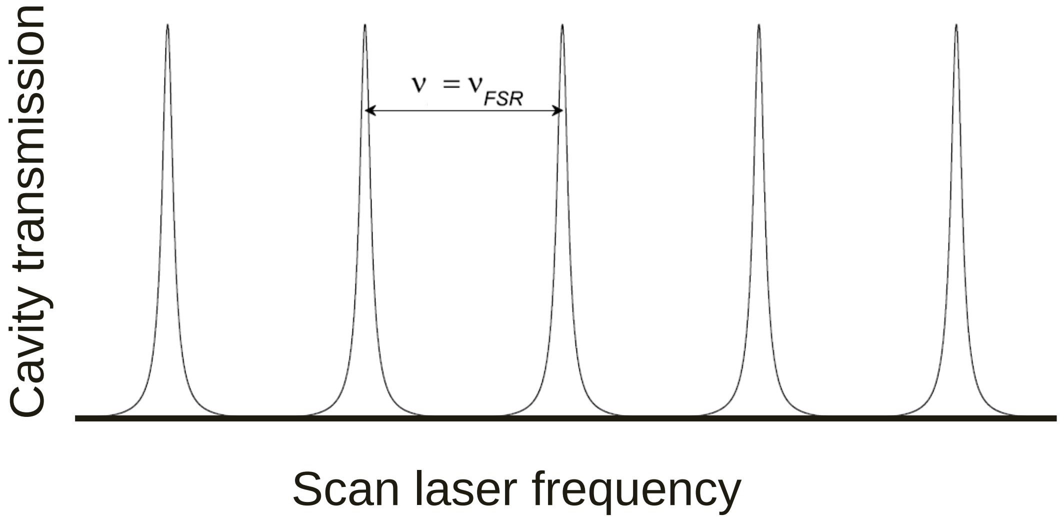
(laser) noise immune detection



For NICE-**OHM**S
- relative interaction of sidebands and carrier with molecules is the spectroscopic signal

Optical Heterodyne

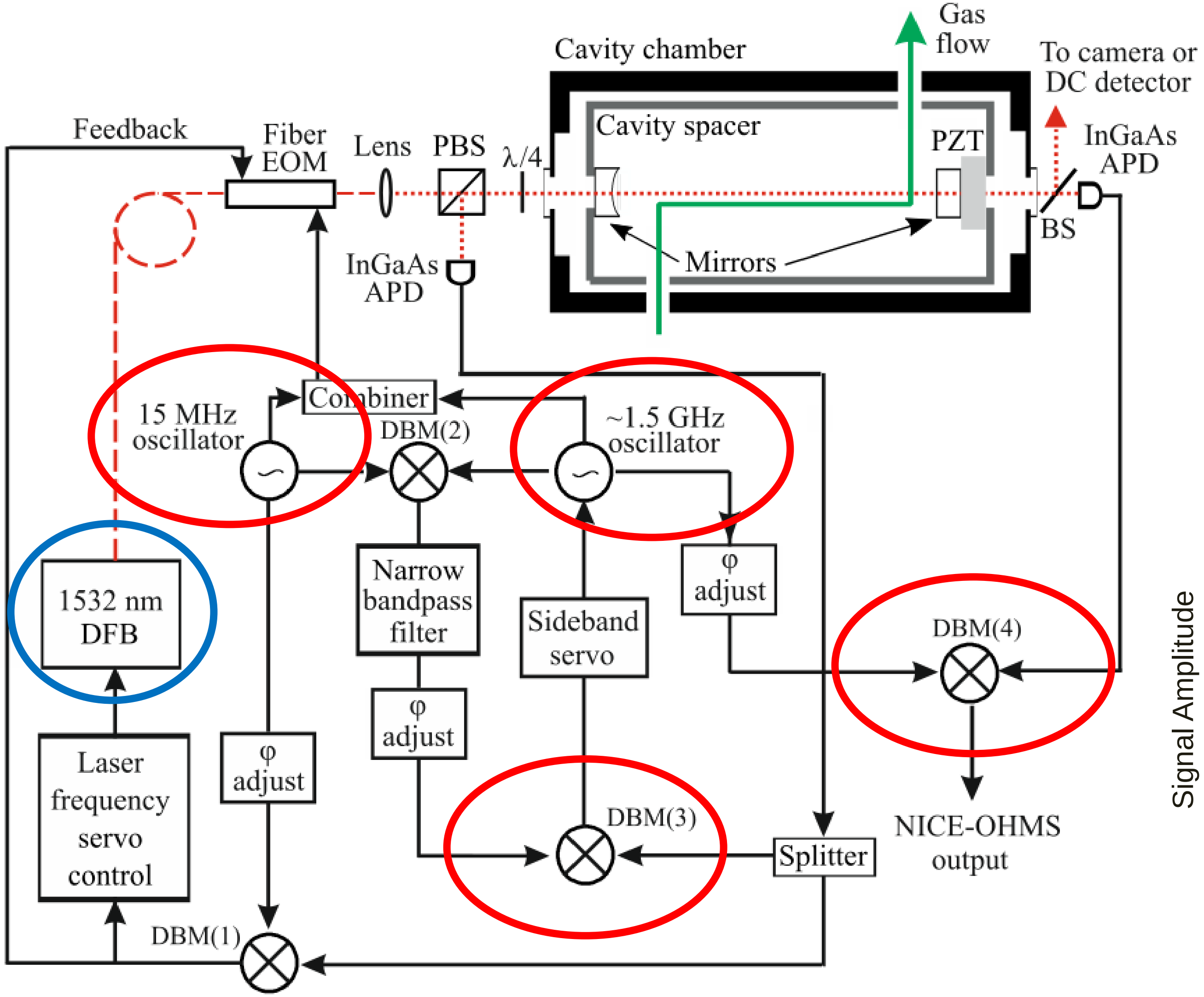
$$FSR = \Delta\nu_{FSR} = c/2L$$

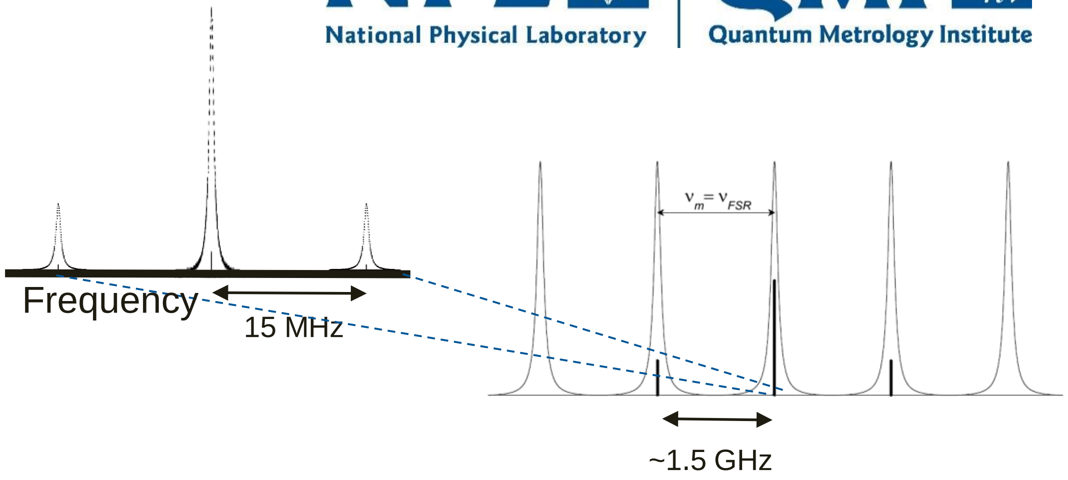


- FM to AM conversion still occurs, but now also affecting the sidebands in the same way, as they pass through the cavity

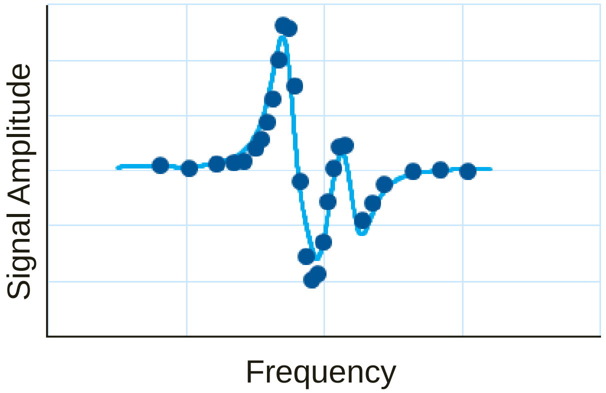
Relative frequency triplet amplitudes are preserved and enhanced

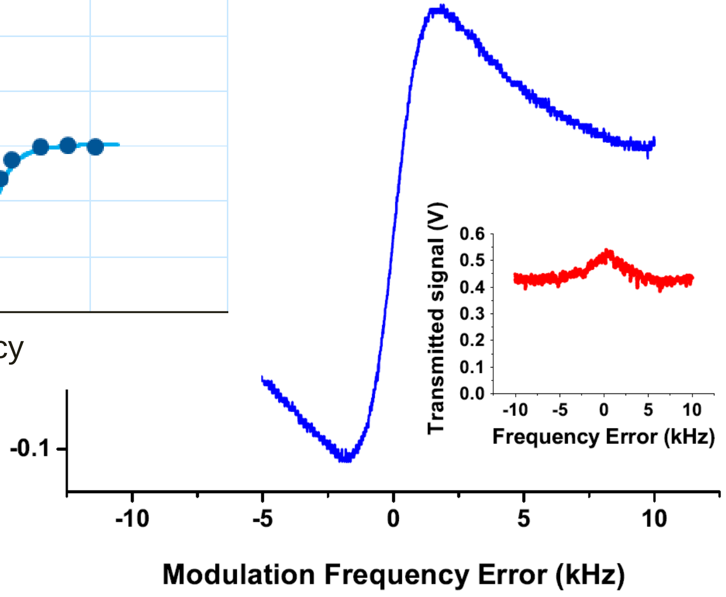
NICE-OHMS System Schematic





5 µmol/mol data





R. G. DeVoe and R. G. Brewer, "Laser-frequency division and stabilization," Physical Review A **30**, 2827–2829 (1984).

NICE-OHMS results:
Calibrated ammonia measurements

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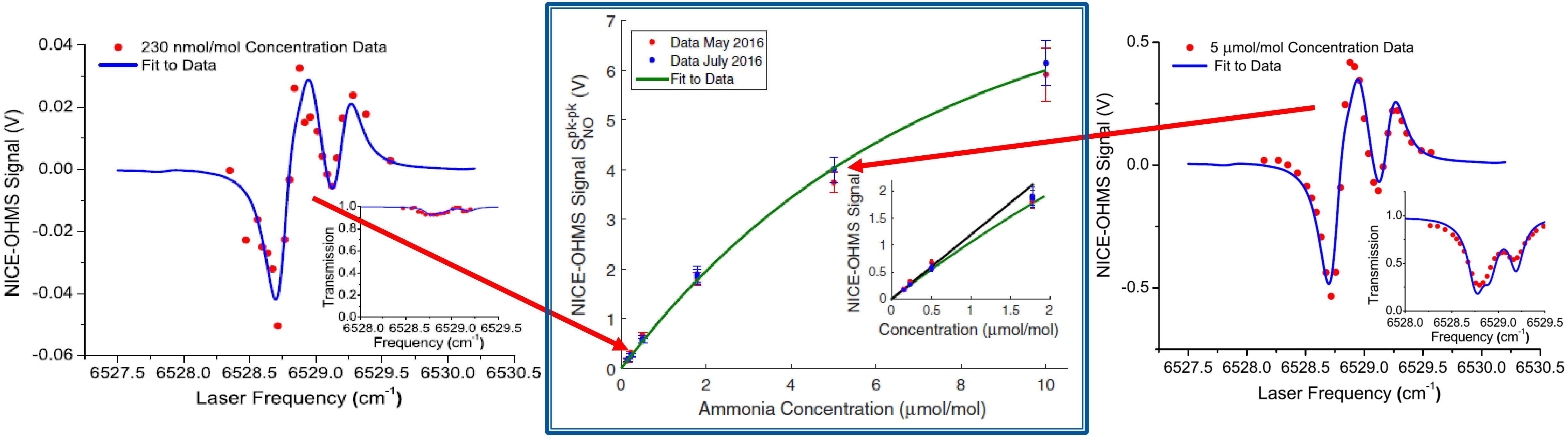

E. A. Curtis, G. P. Barwood, G. Huang, C. S. Edwards, B. Gieseking, and P. J. Brewer, "Ultra-high-finesse NICE-OHMS spectroscopy at 1532 nm for calibrated online ammonia detection," J. Opt. Soc. Am. B 34(5), 950-958 (2017).

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MetAMC NH_3 Detection requirement: 100 nmol/mol in 5 min

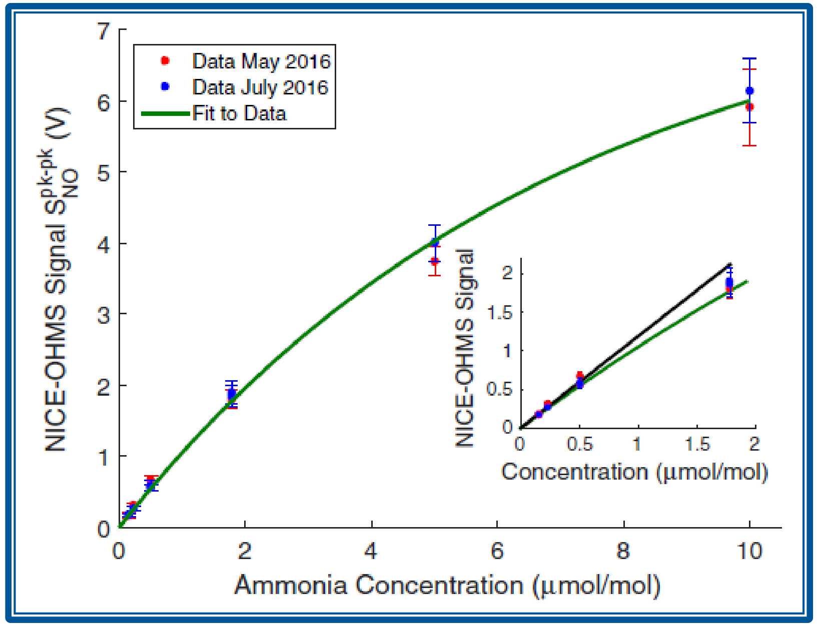
MetAMCII (NH_3), HCl Detection requirement: 1 nmol/mol in 1 min

Metrology for
Airborne Molecular Contaminants

NICE-OHMS:
Future directions at NPL

Where does NICE-OHMS make the most impact?

- sensitivity
- speed (real-time/online)



Metrology for Airborne Molecular Contaminants

Other industrially-relevant contaminant measurements

- HCl (stronger line / improved electronics)
- corrosive/sticky
- water vapour

Hydrogen fuel / biomethane contaminants

METROLOGY for HYDROGEN VEHICLES

Environmentally- and medically-relevant applications, e.g. ammonia and methane

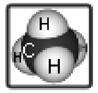


Table 1 Maximum impurity levels that should not be exceeded for PEM fuel cell hydrogen as specified by ISO 14687-2:2012

Anal. Methods, 2014, **6**, 5472–5482

Impurity	Maximum amount fraction (µmol mol^{-1})
Water	5
Total hydrocarbons	2
Oxygen	5
Helium	300
Nitrogen	100
Argon	100
Carbon dioxide	2
Carbon monoxide	0.2
Total sulphur compounds	0.004
Formaldehyde	0.01
Formic acid	0.2
Ammonia	0.1
Total halogenated compounds	0.05

NH_3 100 nmol/mol

includes HCl in 50 nmol/mol total

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NPL Emissions & Atmospheric Metrology Group

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For more information on this work, please contact Anne Curtis, anne.curtis@npl.co.uk

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