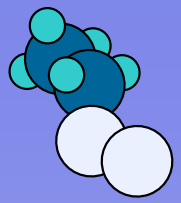
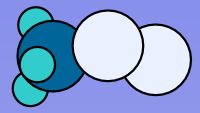
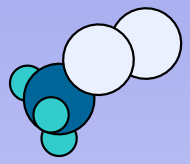
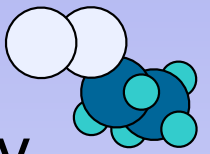




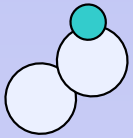
Towards NICE-OHMS for the detection of peroxy radicals



Nicola van Leeuwen



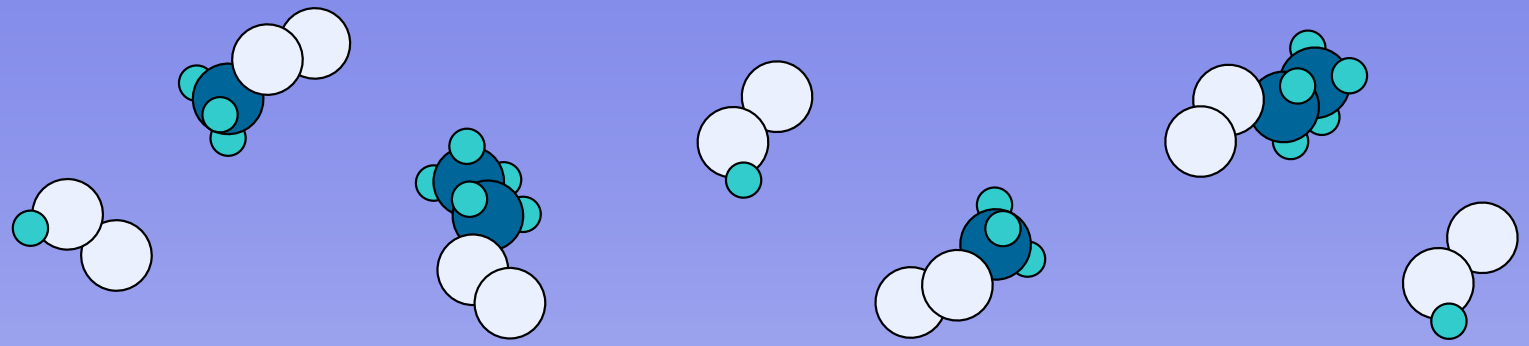
Physical and Theoretical Chemistry Laboratory
University of Oxford



Outline

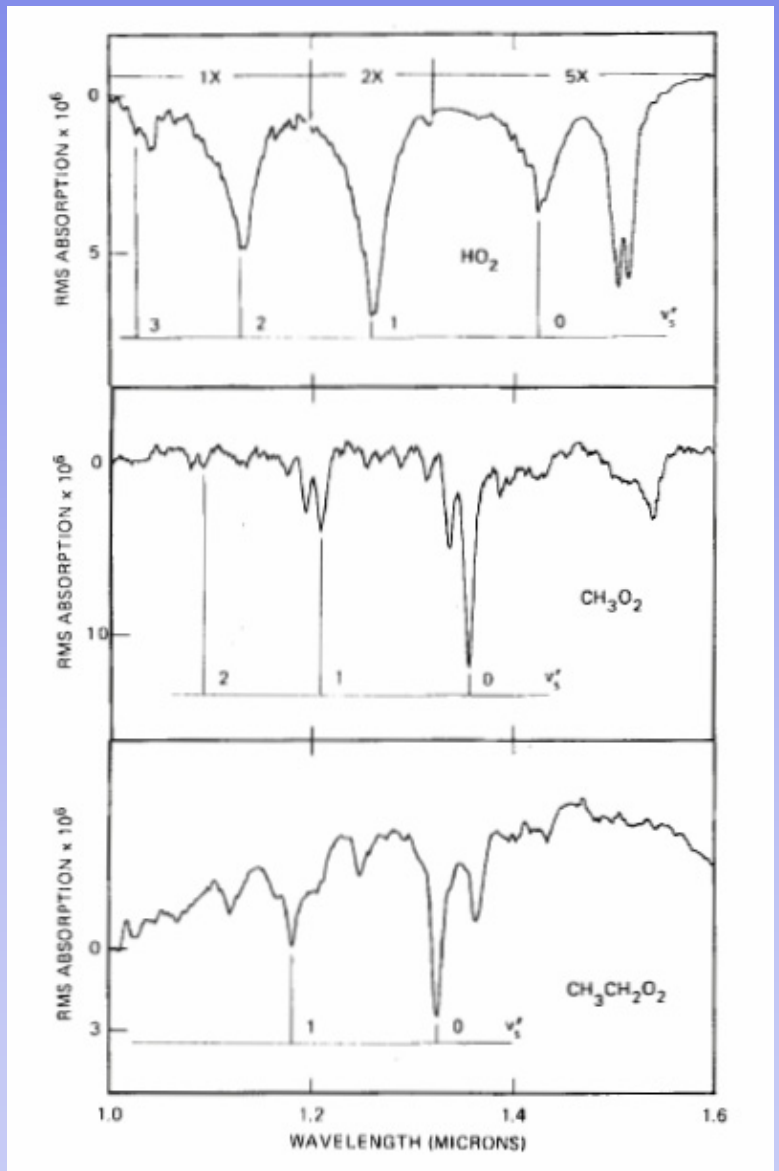
- Peroxy radicals
  - Requirements for direct detection
- NICE-OHMS and the Oxford setup
  - Steps towards NICE-OHMS
  - Initial results
  - Improving the system
- Plans and Prospects

Peroxy radicals



- RO_2 molecules (HO_2 , CH_3O_2 etc)
- Important intermediate in breakdown of organic pollutants
- Concentrations of 10^7 – 10^8 molecules cm^{-3}
- Current measurements by PERCA and FAGE

Direct detection of peroxy radicals



Hunziker, HE and Wendt HR,
J. Chem. Phys., **64**, 8, 3488 (1976)

- Distinct absorption bands in the near infra-red
- Need to detect in one of the atmospheric windows
- HO_2 at ~ 1510 nm
- Atmospheric detection of HO_2 at 1510 nm requires sensitivity of order 10^{-13} to 10^{-14} cm^{-1}

NICE-OHMS

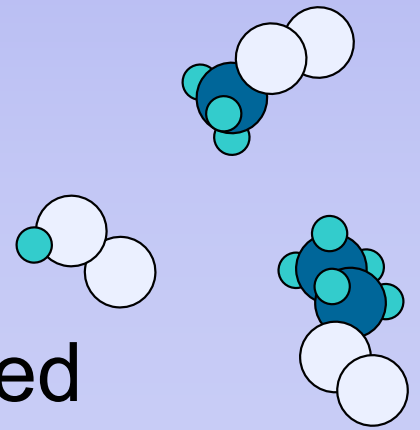
Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy

NICE-OHMS combines

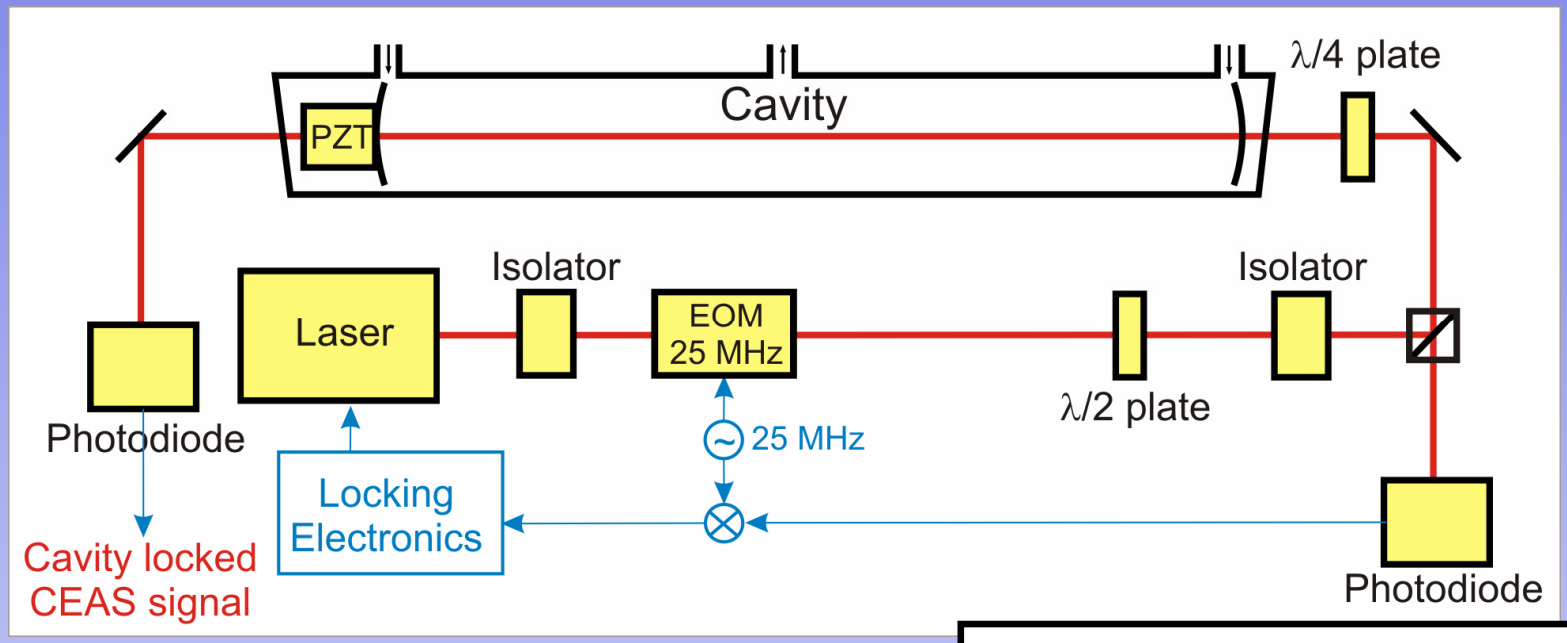
- Cavity enhanced spectroscopy
  - Increase absorption path length
- Frequency modulation spectroscopy
  - Decrease noise level

To Give

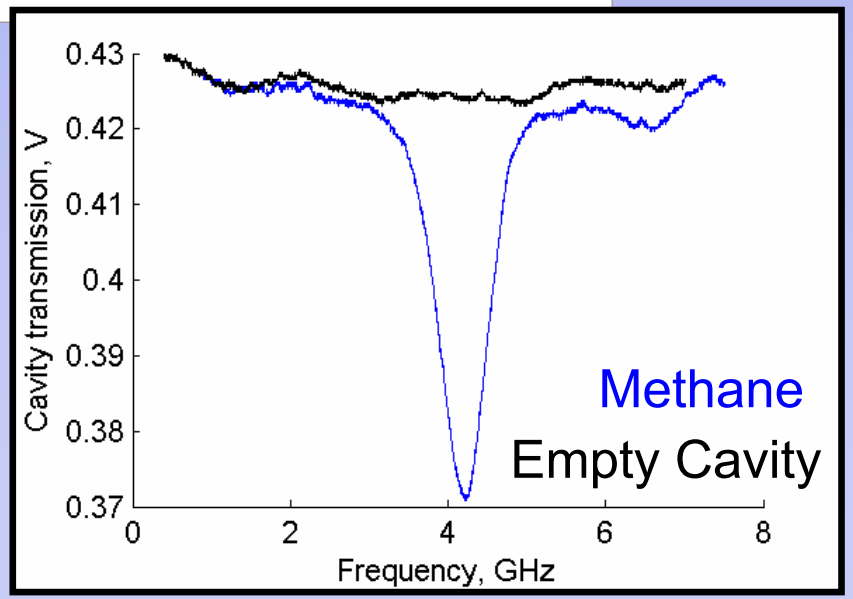
- Ultra high sensitivity
  - 10^{-14} cm^{-1} in 1s demonstrated



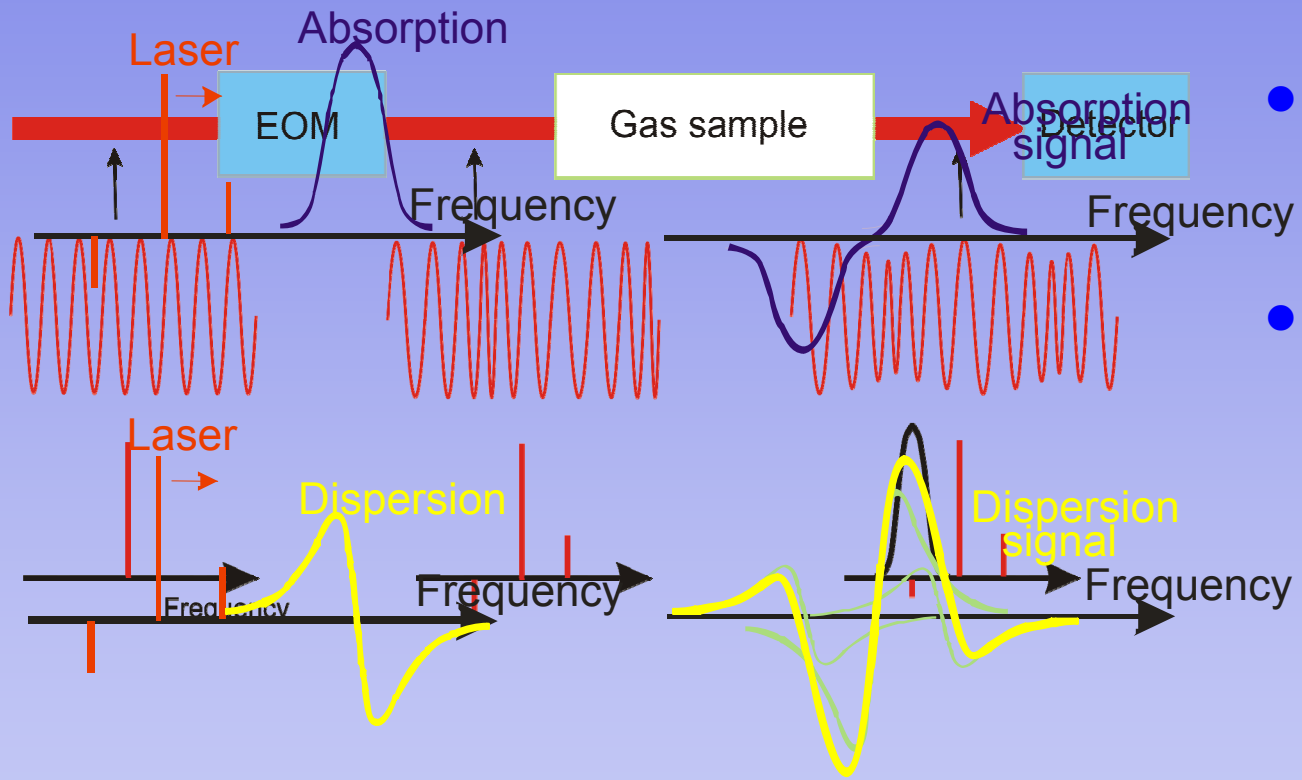
Oxford Experiment – Step 1
Cavity locked CEAS



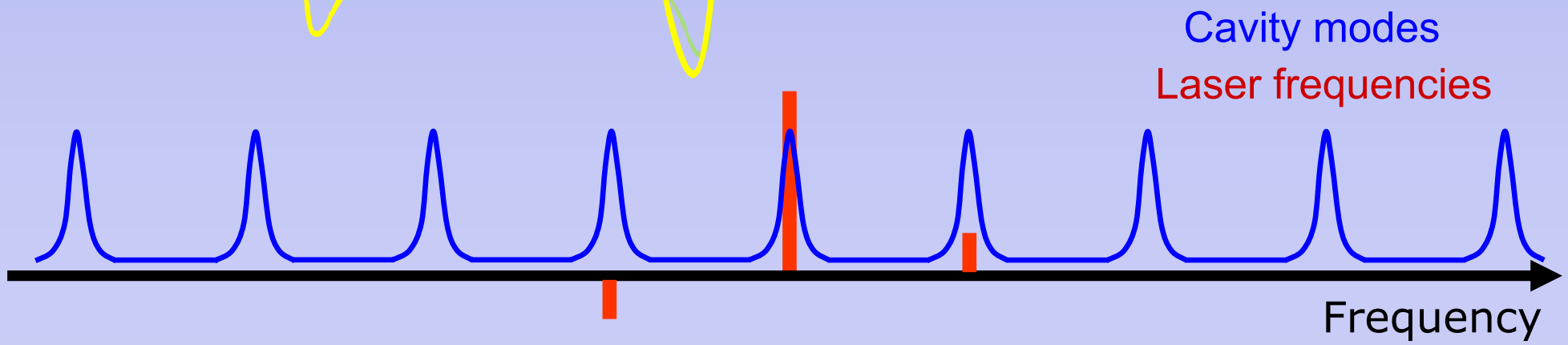
- Laser electronically locked to high finesse cavity
- Cavity transmission gives absorption profile
- Sensitivity of 8.37×10^{-9} cm^{-1}



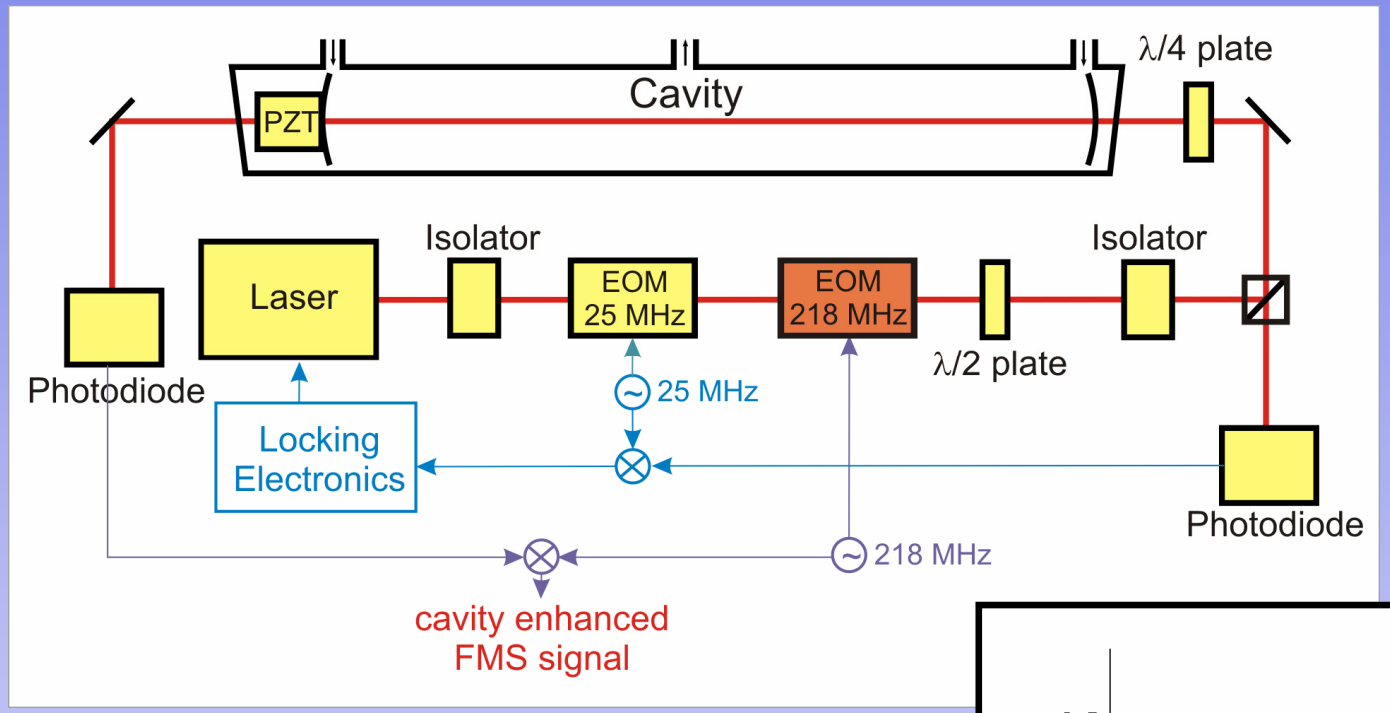
Oxford Experiment – Step 2
Cavity enhanced FMS



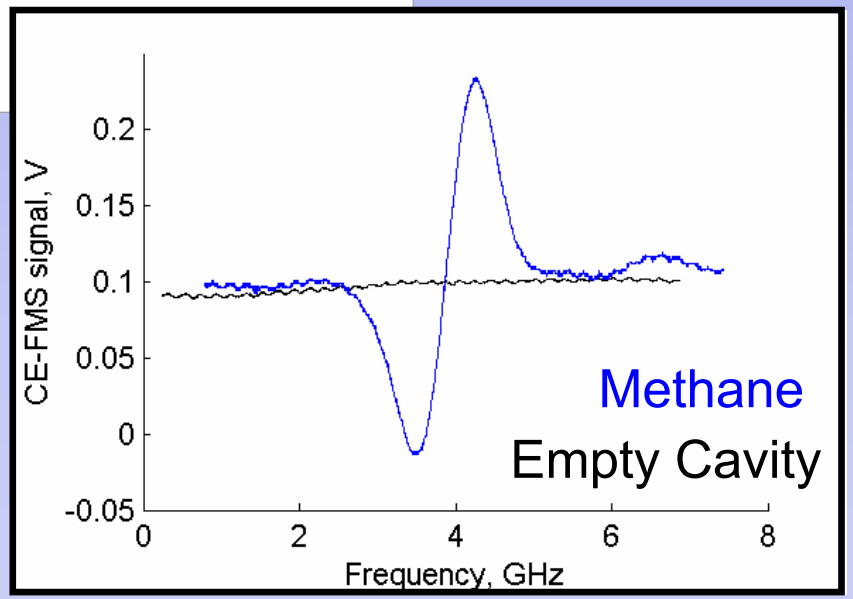
- Frequency modulation spectroscopy (FMS)
- Decreased noise with detection at high frequency



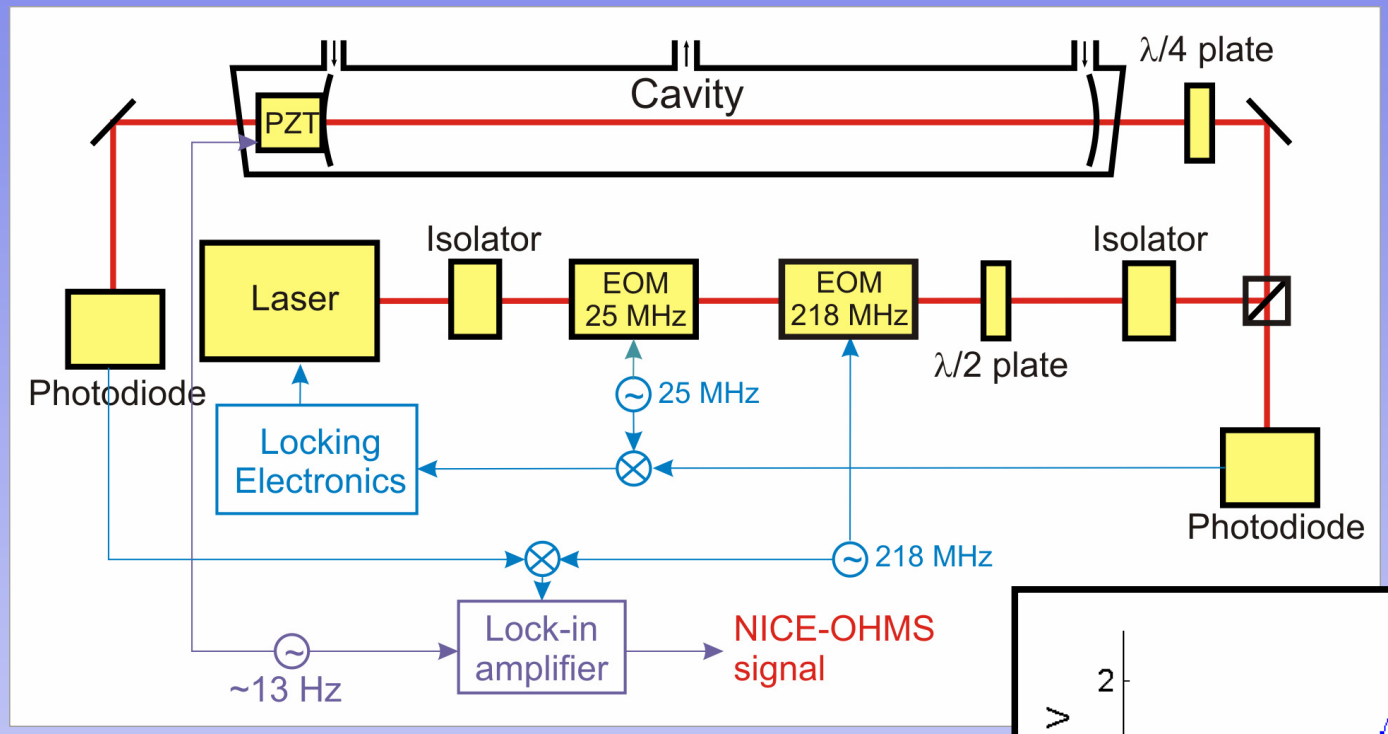
Oxford Experiment – Step 2
Cavity enhanced FMS

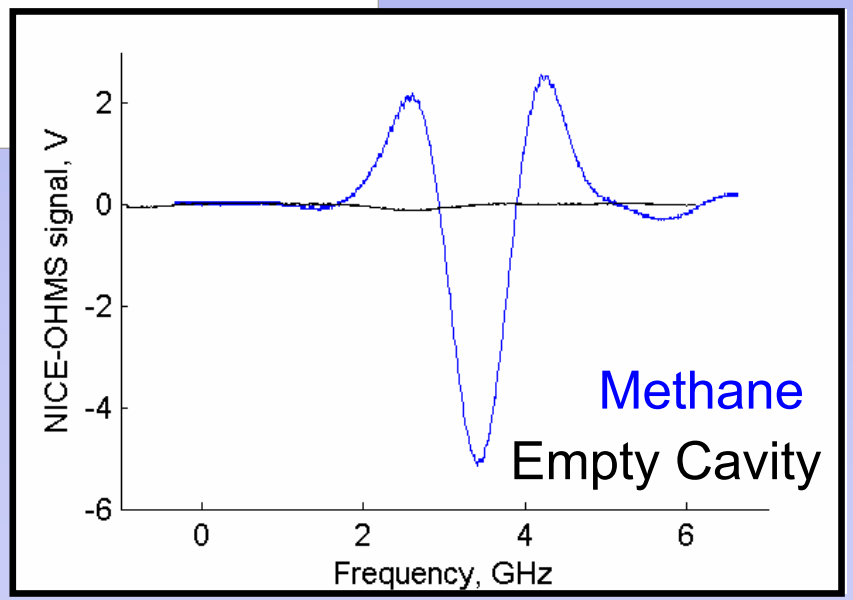


- FMS signal decoded in normal way for absorption profile
- Sensitivity of 5.13×10^{-9} cm^{-1}



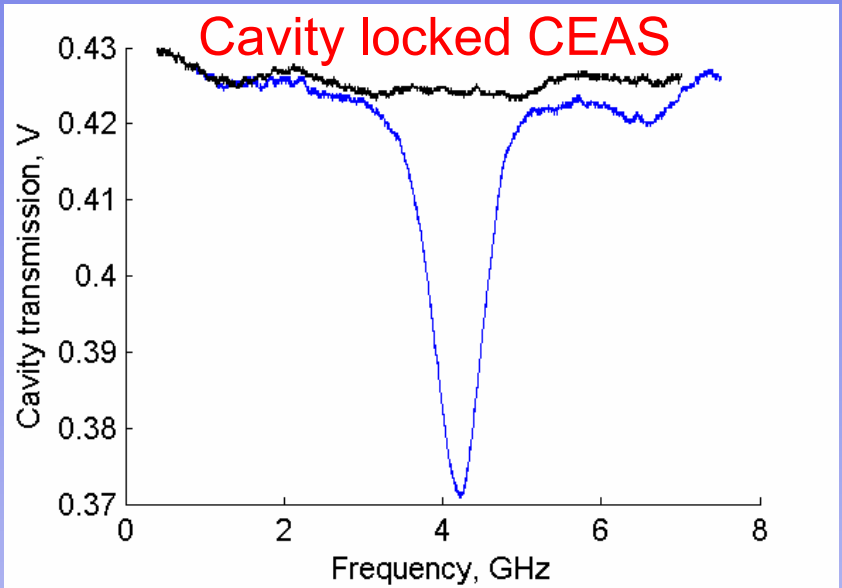
Oxford Experiment – Step 3
NICE-OHMS





- Extra layer of modulation removes noise source inherent to cavity enhanced FMS
- α_{min} of 1.58×10^{-9} cm^{-1}

Cavity locked CEAS → NICE-OHMS

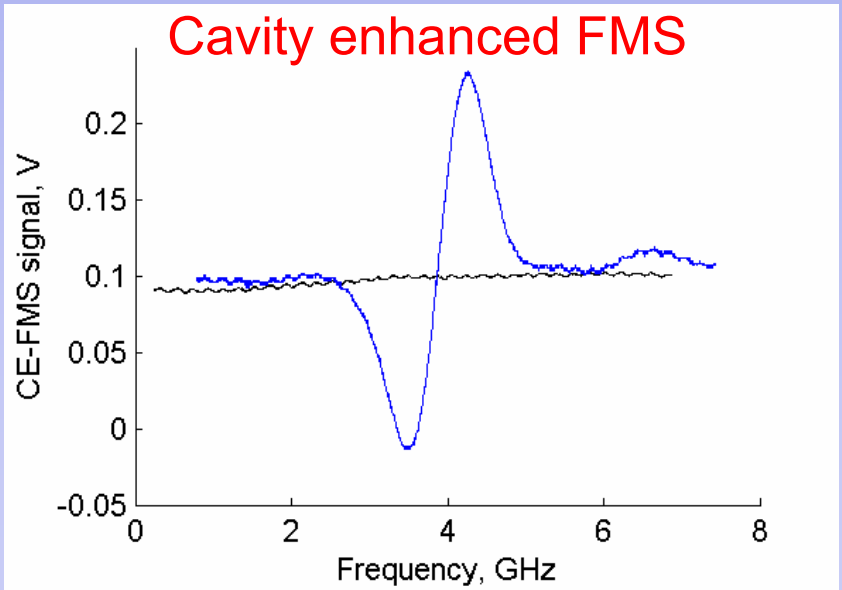


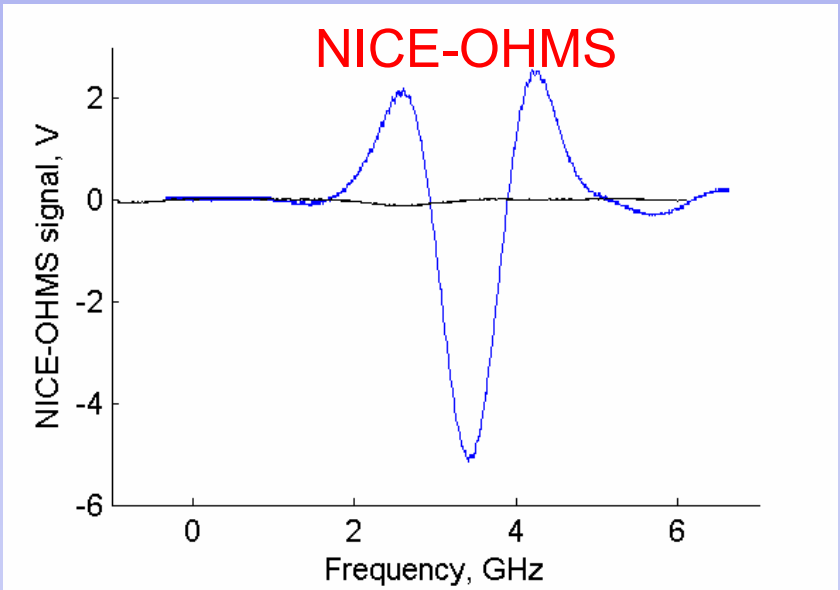
Methane Detection

- 4.9 Torr
- unassigned transition at 6595.90 cm^{-1}
- Peak absorption of 7.7×10^{-8} cm^{-1}

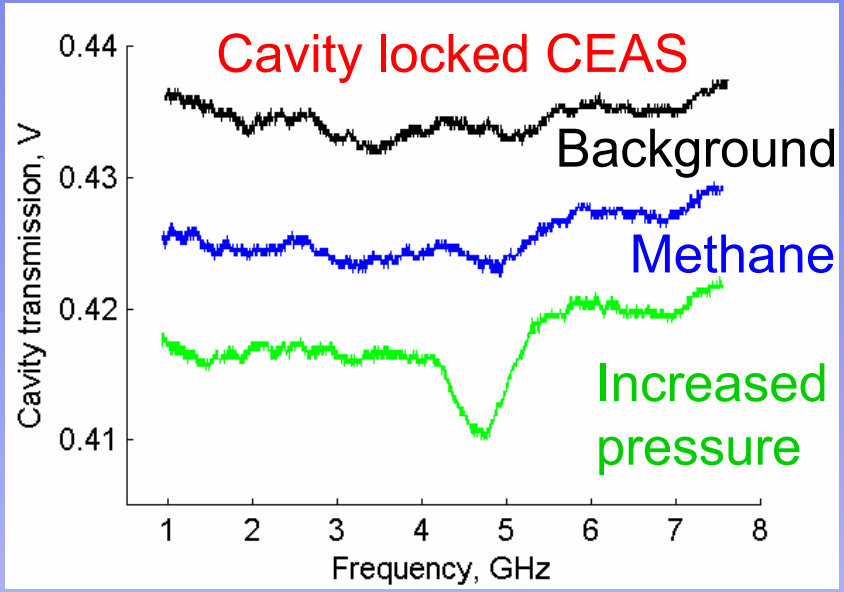
Minimum detectable absorption

- CL-CEAS 8.37×10^{-9} cm^{-1}
- CE-FMS 5.13×10^{-9} cm^{-1}
- NICE-OHMS 1.58×10^{-9} cm^{-1}
  (9.83×10^{-10} cm^{-1} $Hz^{-1/2}$)





What is limiting the sensitivity?

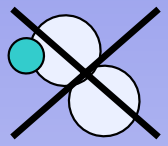


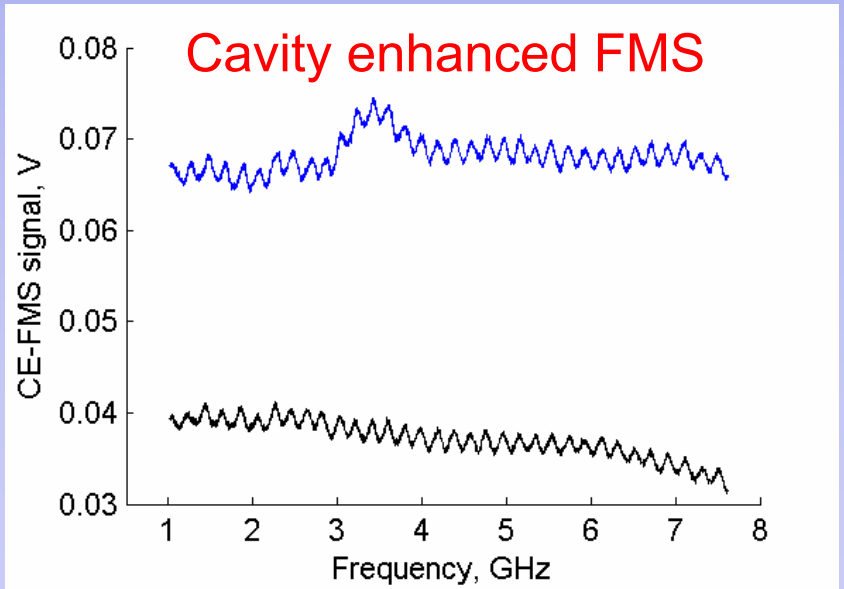
- Reduce pressure to 160 mTorr
- Limiting noise sources become clear

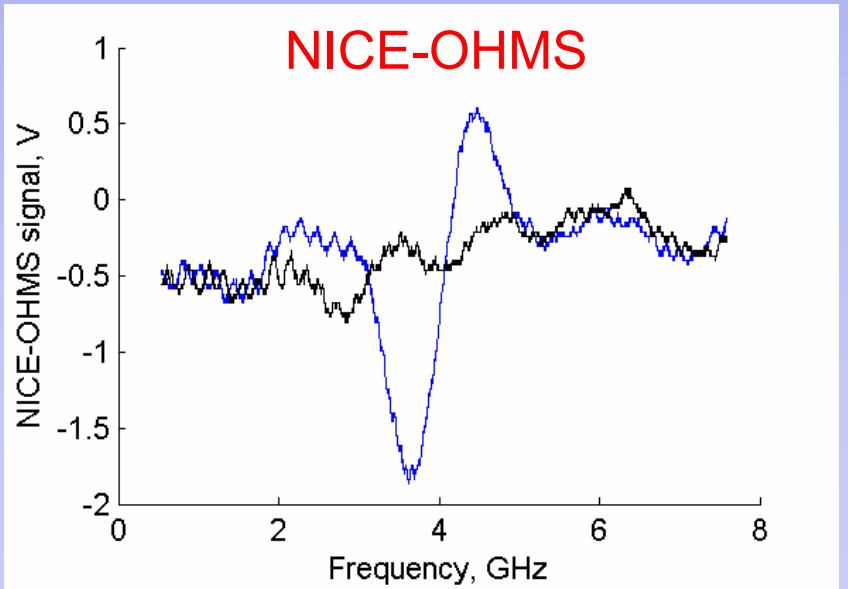
Minimum detectable absorption

- NICE-OHMS 1.58×10^{-9} cm^{-1}

~~$(9.83 \times 10^{-10}$ cm^{-1} Hz$^{-1/2})$~~



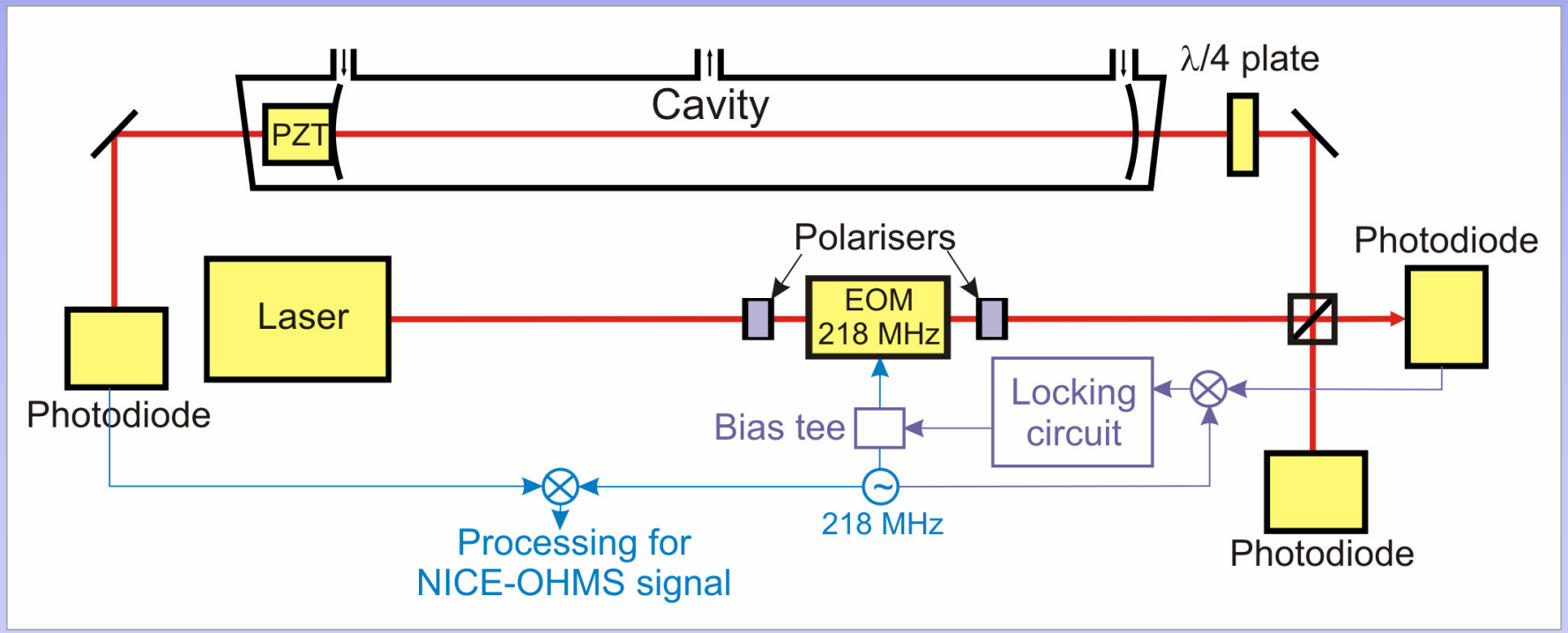




Planned Improvements 1
Removing RAM

Residual amplitude modulation (RAM)

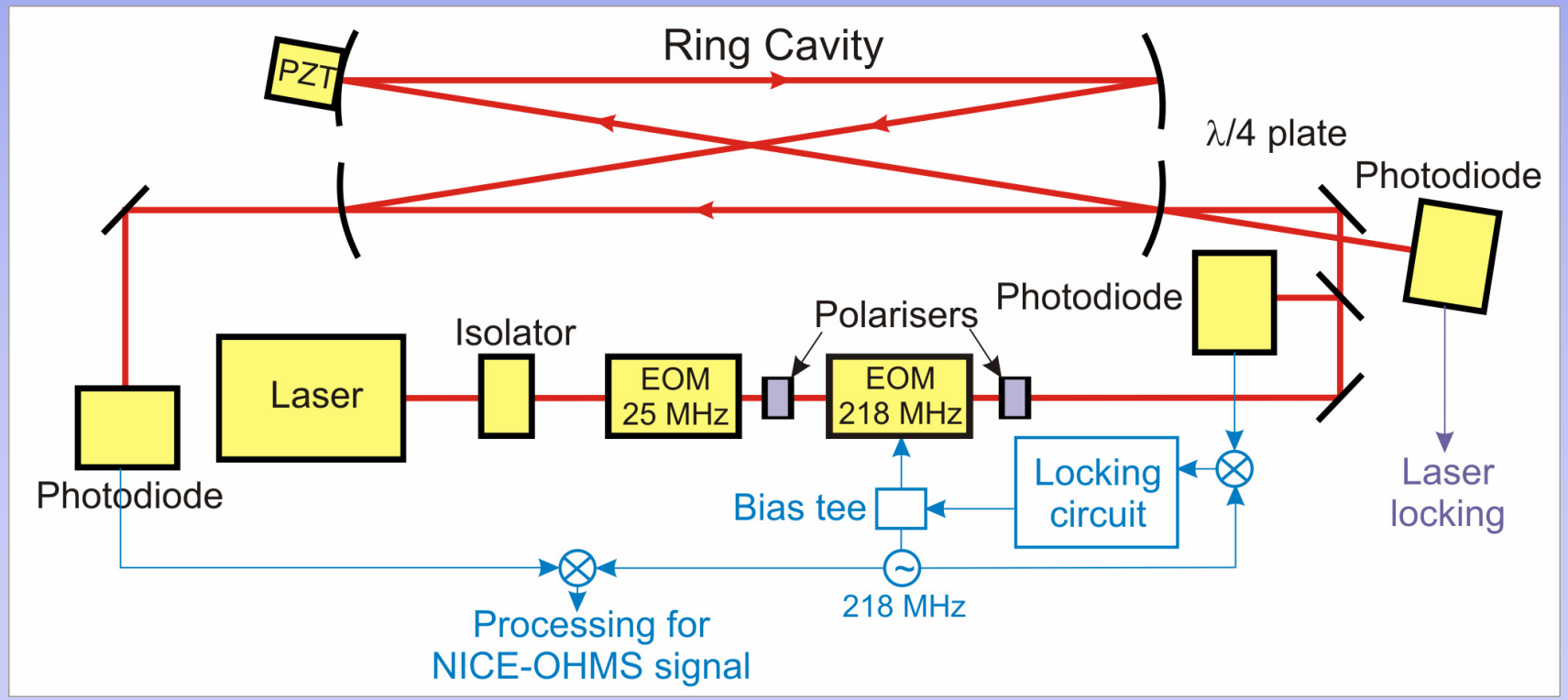
- EOM provides phase modulation
- … can provide amplitude modulation too!

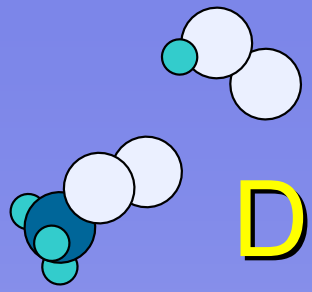


Planned Improvements 2
Ring Cavity

Etalons

- Replace linear cavity with ring cavity
- Stop formation of etalons involving cavity mirrors





Plans and Prospects: Detection of peroxy radicals

Plans

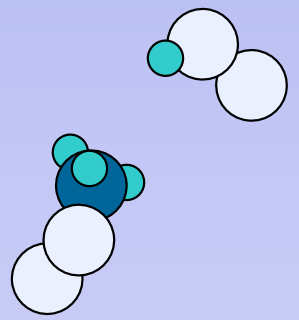
- Implement RAM removal locking and ring cavity
- Detect HO_2 at higher concentrations and investigate potential detection transitions

Prospects

- Potential sensitivity with ring cavity (Finesse 3300)?

$$\alpha_{\text{shot noise}} = 4.3 \times 10^{-13}\ \text{cm}^{-1}\ \text{Hz}^{-1/2}$$

- Enough for detection of atmospheric HO_2?
  - Yes! – with averaging or better mirrors
- Can we reach this ?
  - We don't know – but we can try



Acknowledgements

Thanks to

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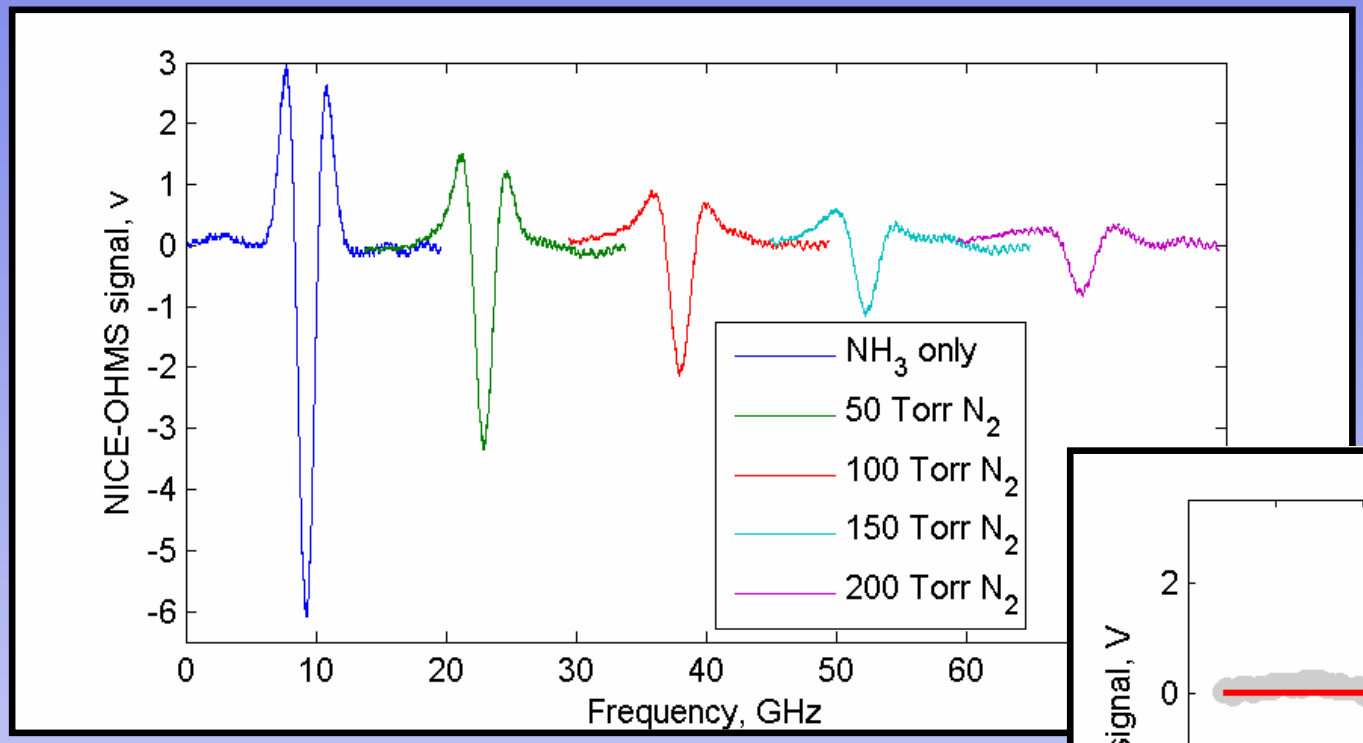
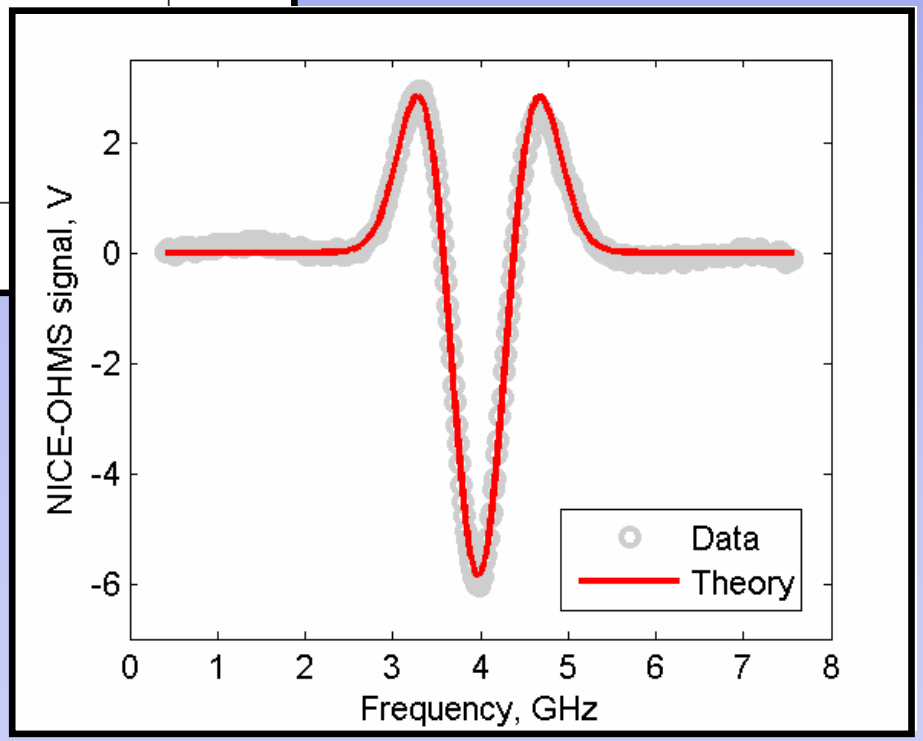
Paul Instrument Fund, Royal Society

EPSRC - Laser Portfolio Award

NICE-OHMS signals: Broadening and Fitting



- Effect of pressure broadening on NICE-OHMS signal



- Use frequency and wavelength modulation theories to determine NICE-OHMS signal shape

- Fitting allows line parameters to be quantitatively determined