Amplitude modulated **multimode-diode-laser-based** cavity enhanced absorption spectroscopy with a **phase-sensitive detection** for high-sensitivity NO_2 detection

Weixiong Zhao, Jiacheng Zhou, Yang Zhang, Bo Fang, Feihu Cheng,

Xuezhe Xu, Shichuan Ni, Weijun Zhang

Anhui Institute of Optics and Fine Mechanics, HFIPS, Chinese Academy of Sciences, Anhui, China

wxzhao@aiofm.ac.cn, http://lapc.aiofm.ac.cn/

Chunxiang Ye

College of Environmental Sciences and Engineering, Peking University, Beijing, China

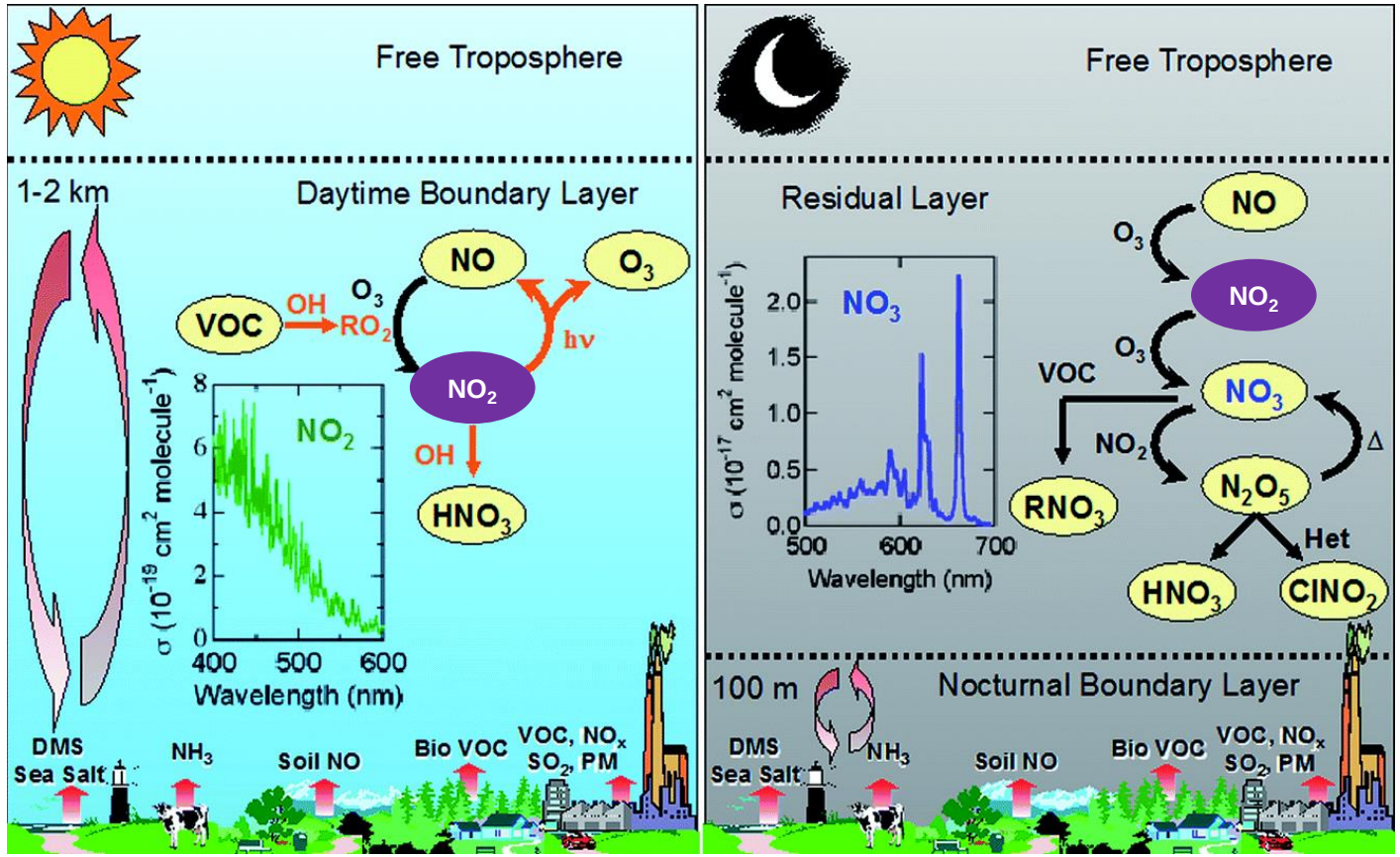
Weidong Chen

Laboratoire de Physicochimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France

Dean S. Venables

School of Chemistry and Environmental Research Institute, University College Cork, Cork, Ireland

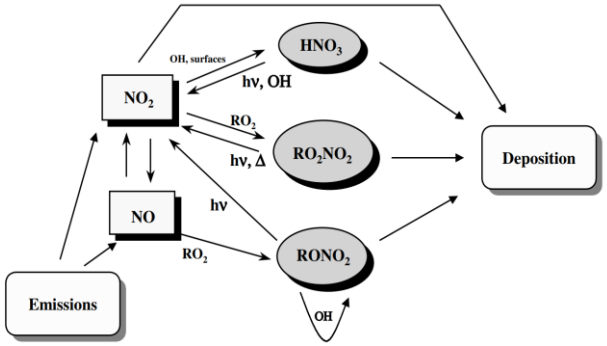
The need for high sensitivity and accurate measurement of NO_2 (1)



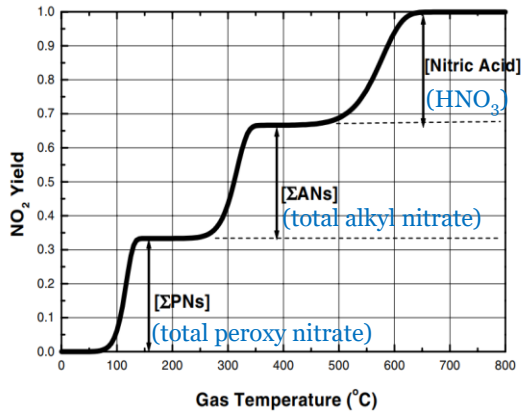
Brown, S. S. et al., Faraday Discuss. 2017, 200, 529–557
Perring, A. E.; Pusede, S. E.; Cohen, R. C., Chem. Rev. 2013, 113, 5848-5870

- Nitrogen dioxide (NO_2): one of the most important molecules in the formation of ozone (O_3), acid deposition, and secondary particulate pollutants, which has a profound impact on human health, the environment, and climate change.
- Daytime: acts as a catalyst that produces O_3;
- Nighttime: oxidizes to NO_3 radical (a strong oxidant for unsaturated VOCs).

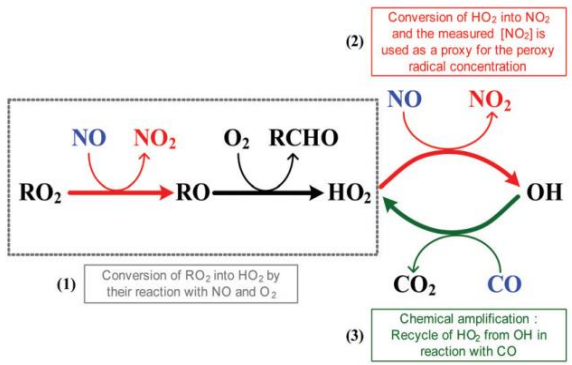
The need for high sensitivity and accurate measurement of NO_2 (2)



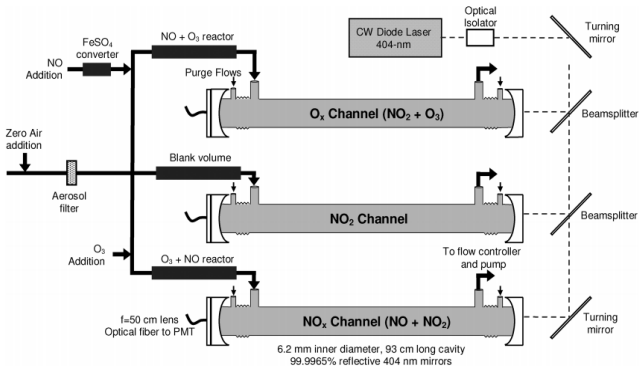
Day et al., JGR 2002, 107, ACH 4



- In tandem with thermal dissociation, NO_2 measurement can be used for the precision measurement of total reactive nitrogen.
- Combined with chemical amplification for the measurement of total peroxy radicals.
- With chemical titration, for NO and O_3 measurement.



Chen et al., Analyst 2016, 141, 5870

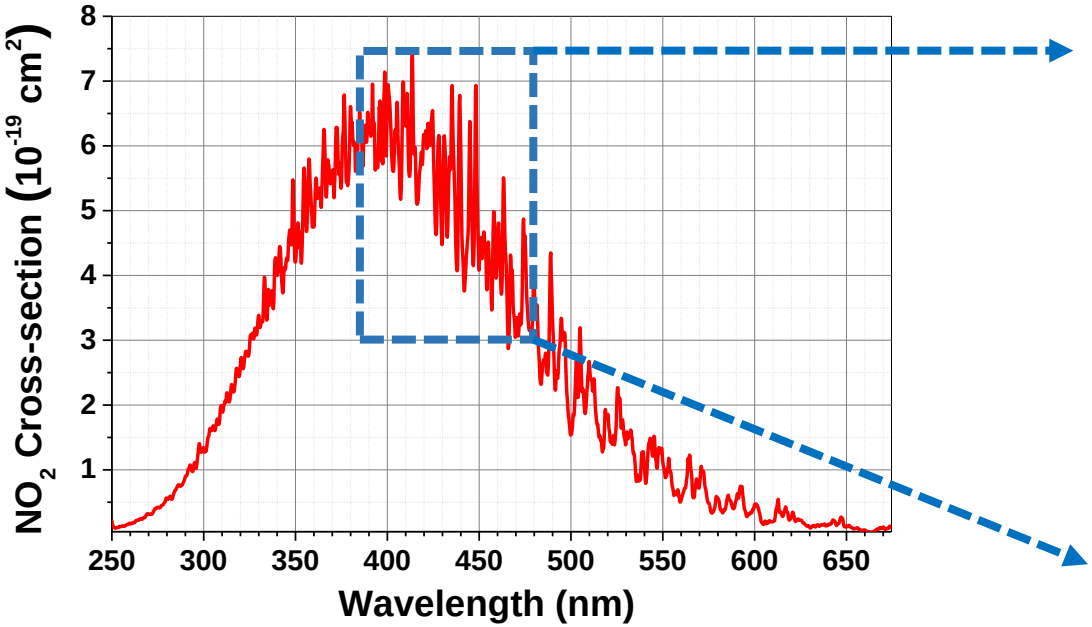


Washenfelder et al., EST 2011, 45, 2938

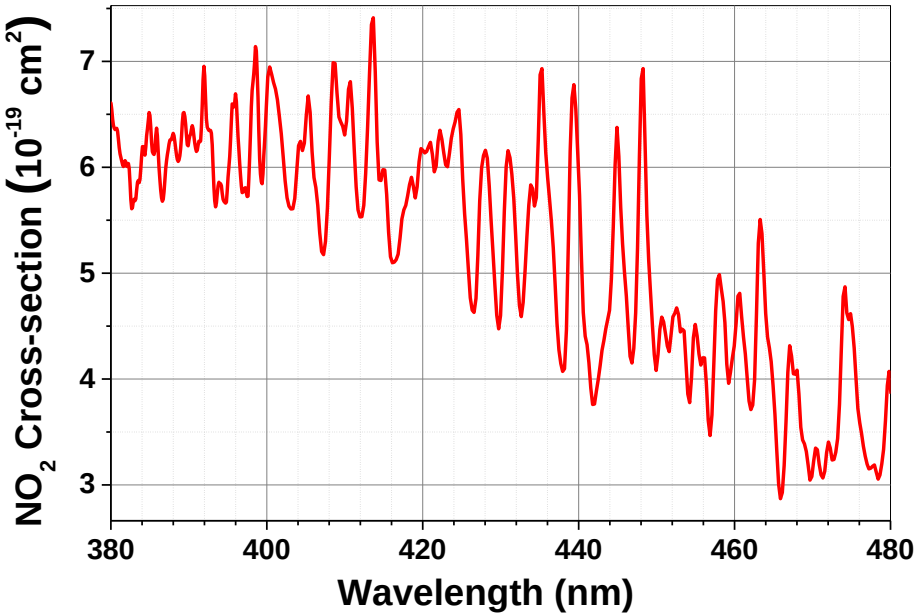
Sensitive and accurate measurements of NO_2 play an extremely important role in atmospheric studies, which have enhanced our understanding of nitrogen chemistry, free radical chemistry, and atmospheric oxidation capacity.

Optical detection of NO_2 in the visible spectral range

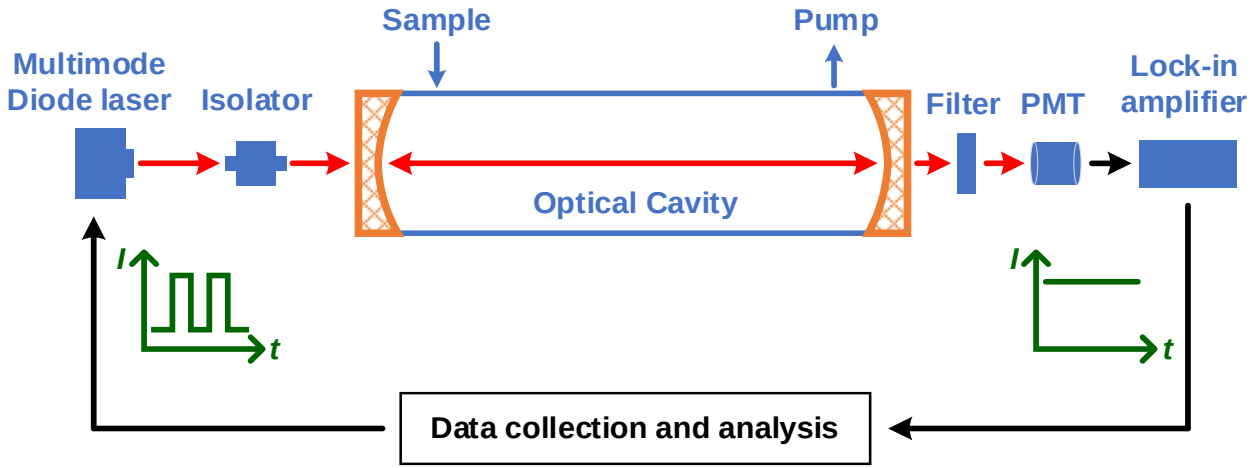
The MPI-Mainz UV/VIS Spectral Atlas

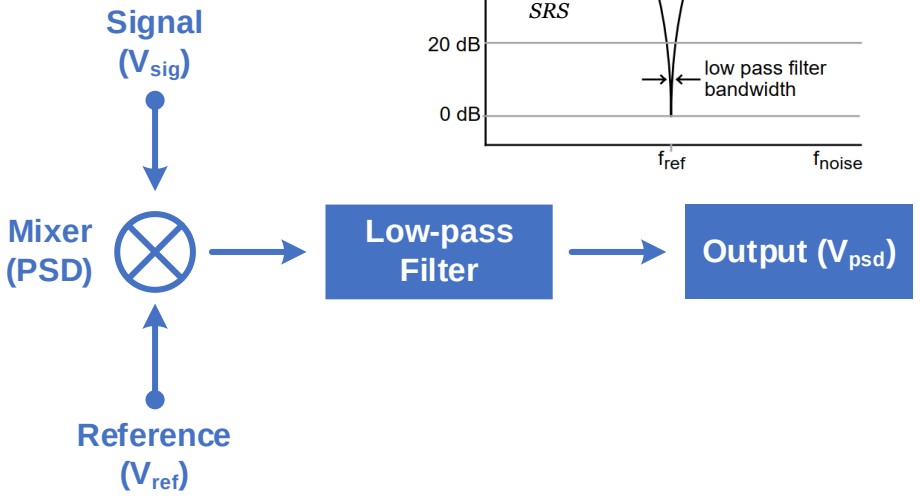


Strong absorption between 400 and 480 nm



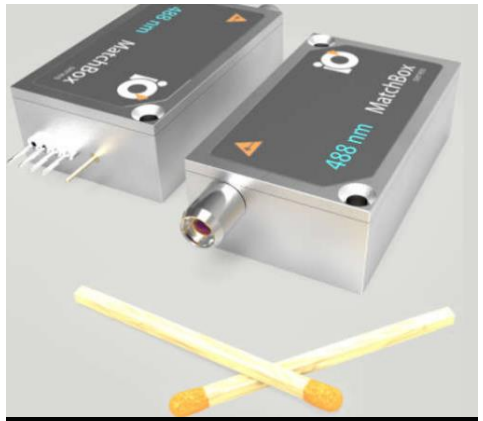
Multimode-diode-laser-based cavity enhanced absorption spectroscopy (AM-CEAS)

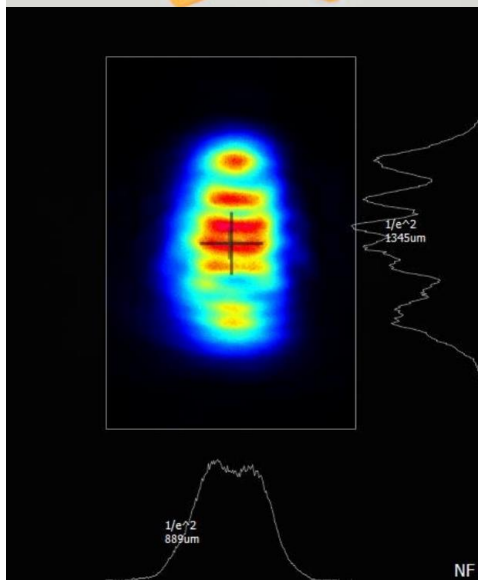




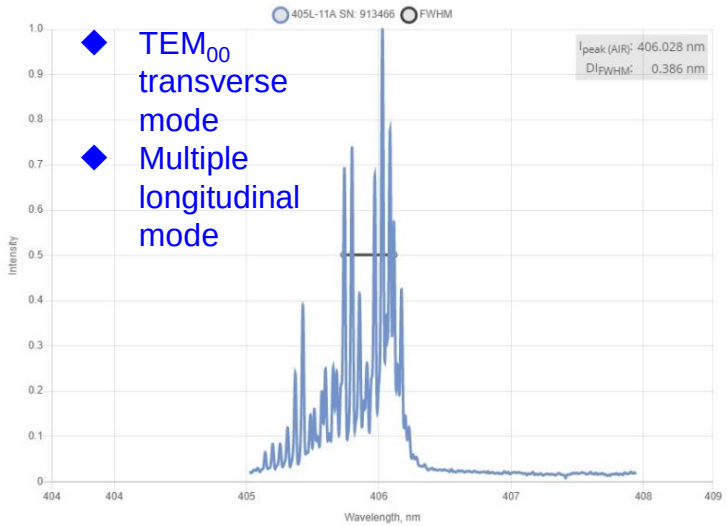
- Phase sensitive detection provides a powerful and simple method for weak signal detection.
- Using PSD, signal at a frequency of interest is selected within a narrow bandwidth by using a low-pass filter, which can be measured accurately even when the magnitude of the signal is thousands of times smaller than that of the noise.

The (match box) multimode-diode-laser





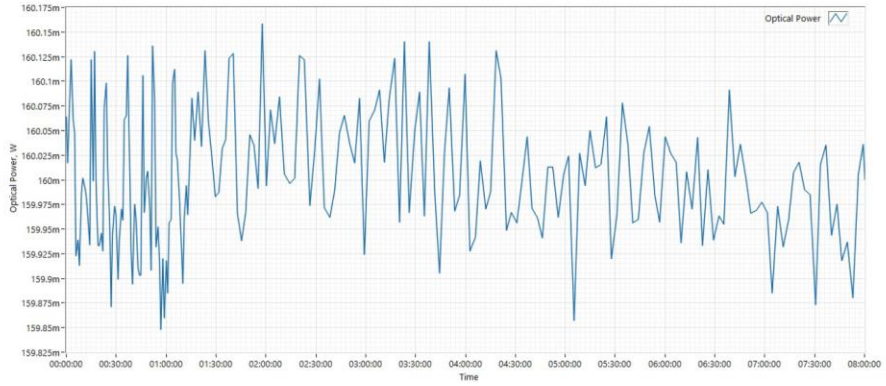
Integrated Optics



- TEM$_{00}$ transverse mode
- Multiple longitudinal mode

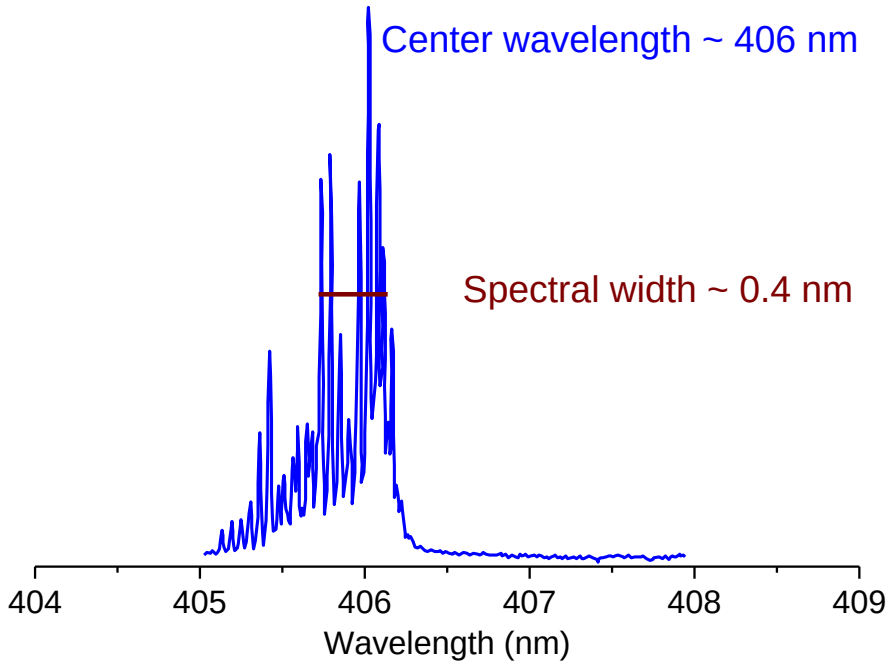
Power Stability

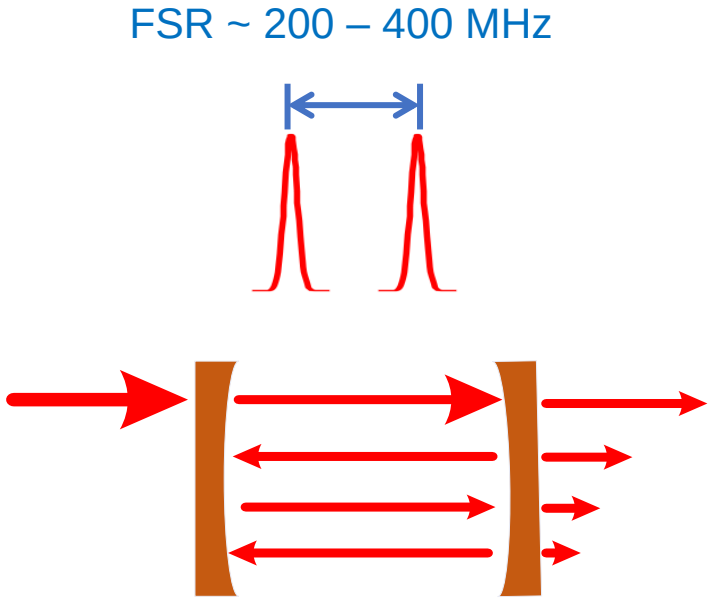
Set optical power	Power DAC value	Noise 200Hz - 20MHz	8 Hour Test			
			RMS	Peak-to-peak	Std. deviation	Mean power
150.9 mW	4612	0.21 %	0.04%	0.194%	0.07 mW	160.0 mW



- ➢ Spectrum and Polarization: Center wavelength: 406.03 nm; Spectral width: < 0.386 nm; Polarization ratio: 1:2500;
- ➢ Beam Properties:
  - Vertical beam dia. (near field) 1.3 mm, full angle divergence 0.7 mrad, M^2 = 1.5;
  - Horizontal beam dia. (near field) 0.9 mm, full angle divergence 0.9 mrad, M^2 = 1.11;
  - Effective M^2 = 1.35;
- ➢ Power stability: typical noise 0.2% rms.

Multimode-diode-laser approach greatly simplify the cavity-based instruments (with high injection efficiency and low cavity mode noise)

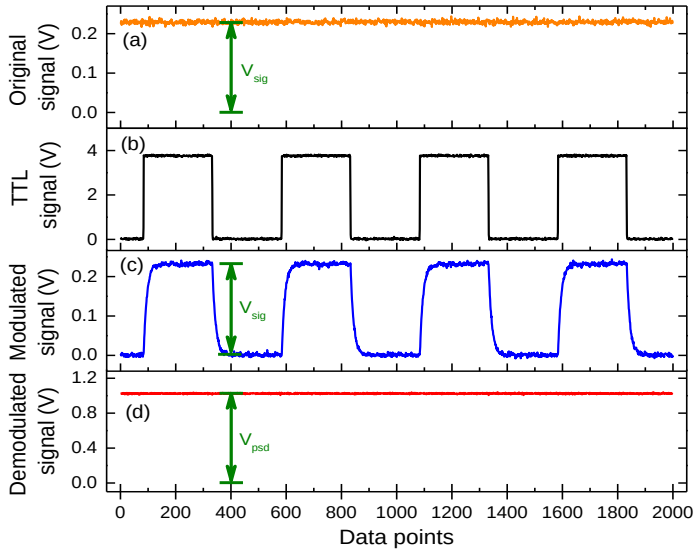


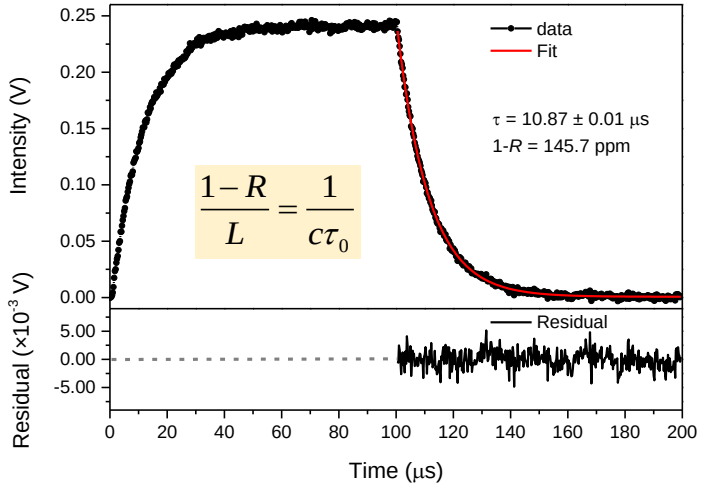


- About 2000 – 4000 cavity modes can be simultaneously excited; Slight mode changes have negligible impact on the laser injection, thus avoiding the need for mode matching between the laser and the cavity, high mechanical stability, and complex electronic control.

Fuchs et al., EST 43, 7831 (2009); Thieser et al., AMT 9, 553 (2016); Karpf et al., Appl. Opt. 55, 4497 (2016)

Data retrieval method of AM-CEAS: self-calibration approach





- Without modulation: $\alpha = n\sigma = \left(\frac{1-R}{L}\right)\left(\frac{I_0}{I}-1\right)$
- The laser is modulated with an external TTL signal (rise time of 14.4 ns, fall time of 28.4 ns).
- TTL modulated laser intensity can be represented by a Fourier series of many sine waves at odd multiples of the modulation frequency f_m.

$$V_s(t) = \frac{V_{sig}}{2} + \frac{2V_{sig}}{\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)}\sin\left[(2n+1)2\pi f_m t + \theta_{sig}\right]$$

- With 1f harmonic detection, only the first harmonic is singled out.

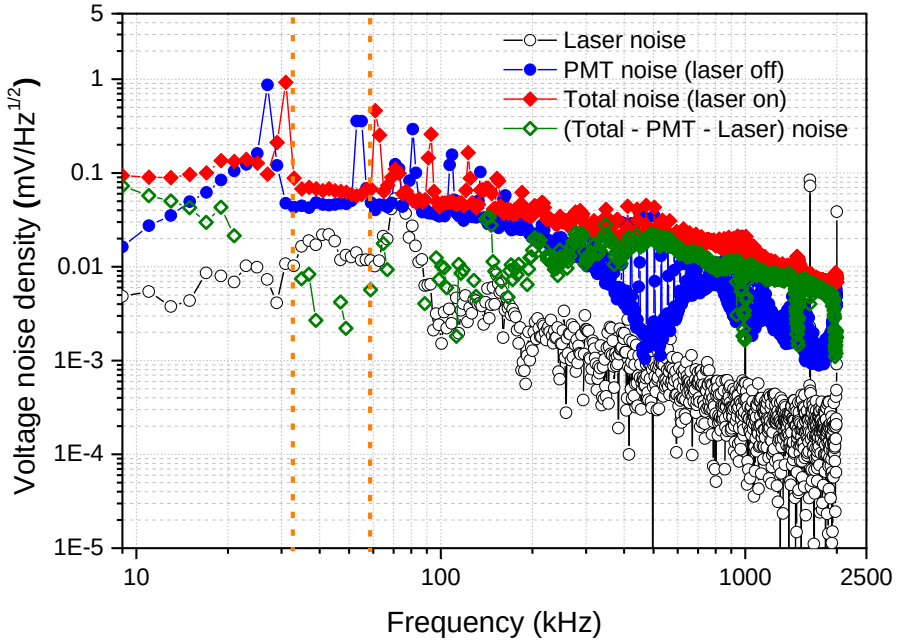
$$V_{psd} = \frac{V_{sig}}{\pi}V_{ref}\cos\theta$$

V_{psd} is proportional to the laser transmission intensity (I).

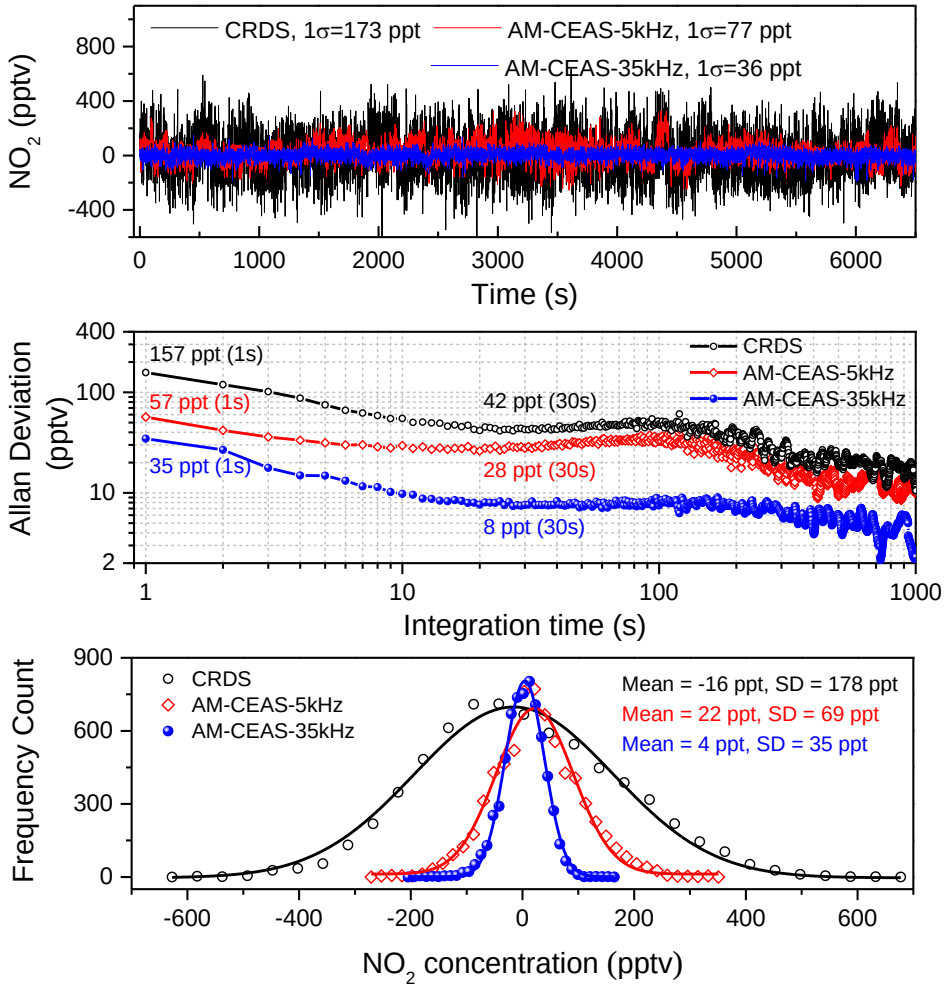
$$\alpha = \frac{1}{c\tau_0}\left(\frac{V_{psd\_0}}{V_{psd}}-1\right)$$

The AM-CEAS system has the advantage of a **straightforward** and reliable **self-calibration** method for quantitative extinction/absorption measurements.

Performance evaluation (over 4 times better than CRDS method)

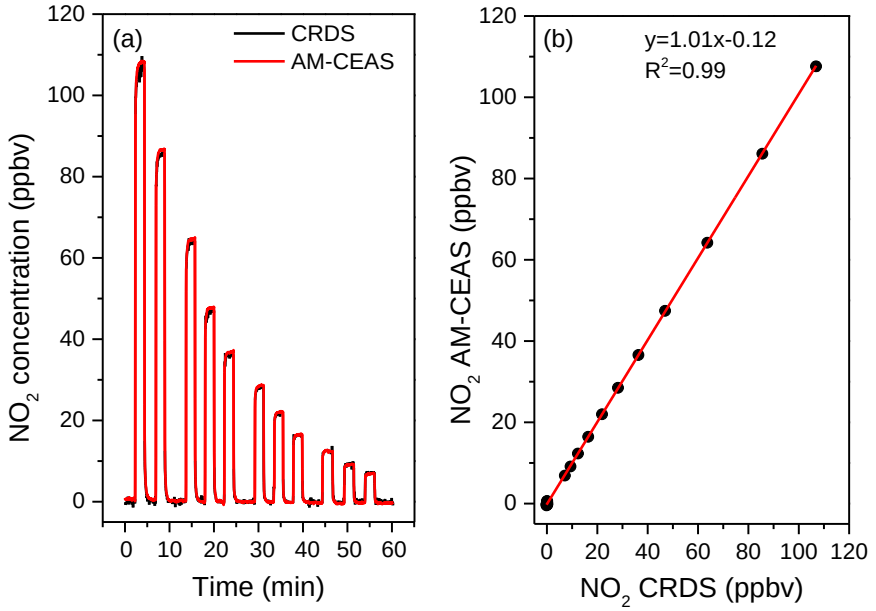


- By selecting the modulation and demodulation frequency in a low noise level region of the noise spectrum (35 kHz here), the precision can be effectively improved.
- As PSD has the advantages of weak signal detection, we expected that higher detection sensitivity can be achieved using higher reflectivity mirrors.

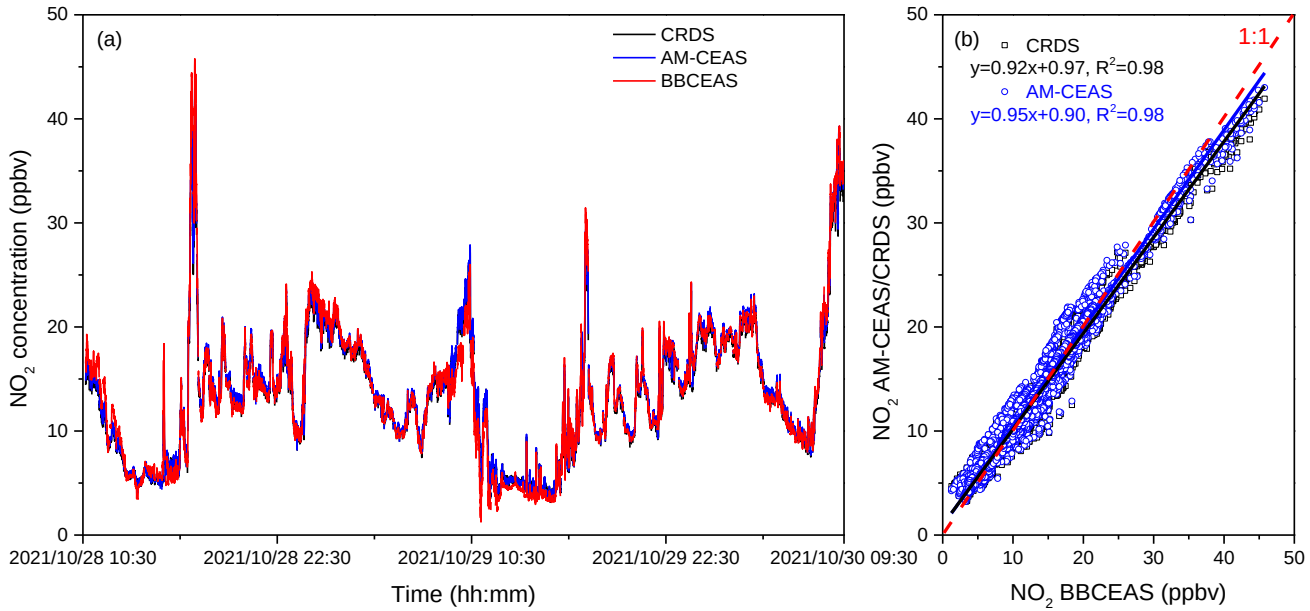


R ~ 99.985%, d = 47.5 cm, L_{eff} = 3.26 km

Laboratory test and field application



Comparison of NO_2 measurement with AM-CEAS and CRDS with laboratory generated diluted samples.



Comparison of ambient NO_2 measurement with AM-CEAS, CRDS and BBCEAS. All data were acquired at a time resolution of 10 s.

Conclusion

- **AM-CEAS provides a simple, reliable, and self-calibration method for absolute concentration measurement.**
- **The sensitivity and precision are competitive and attractive.**
- **Custom-developed lock-in circuits could replace the commercial lock-in amplifier, reducing the instrument cost and promoting a wider range of applications to NO_2 and other species.**

Jiacheng Zhou, et al., Amplitude-Modulated Cavity-Enhanced Absorption Spectroscopy with Phase-Sensitive Detection: A New Approach Applied to the Fast and Sensitive Detection of NO2, Anal. Chem. 2022, 94, 3368−3375.

Thank you for your attention !

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