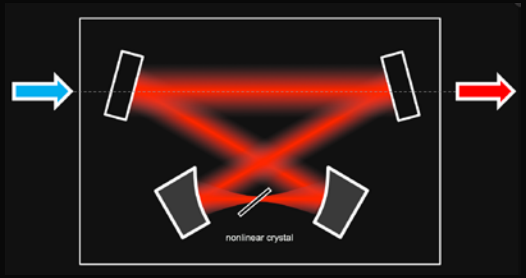
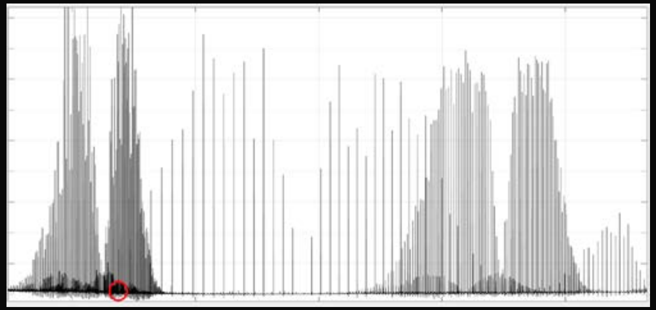
Massively parallel sensing of molecules with mid-infrared frequency combs

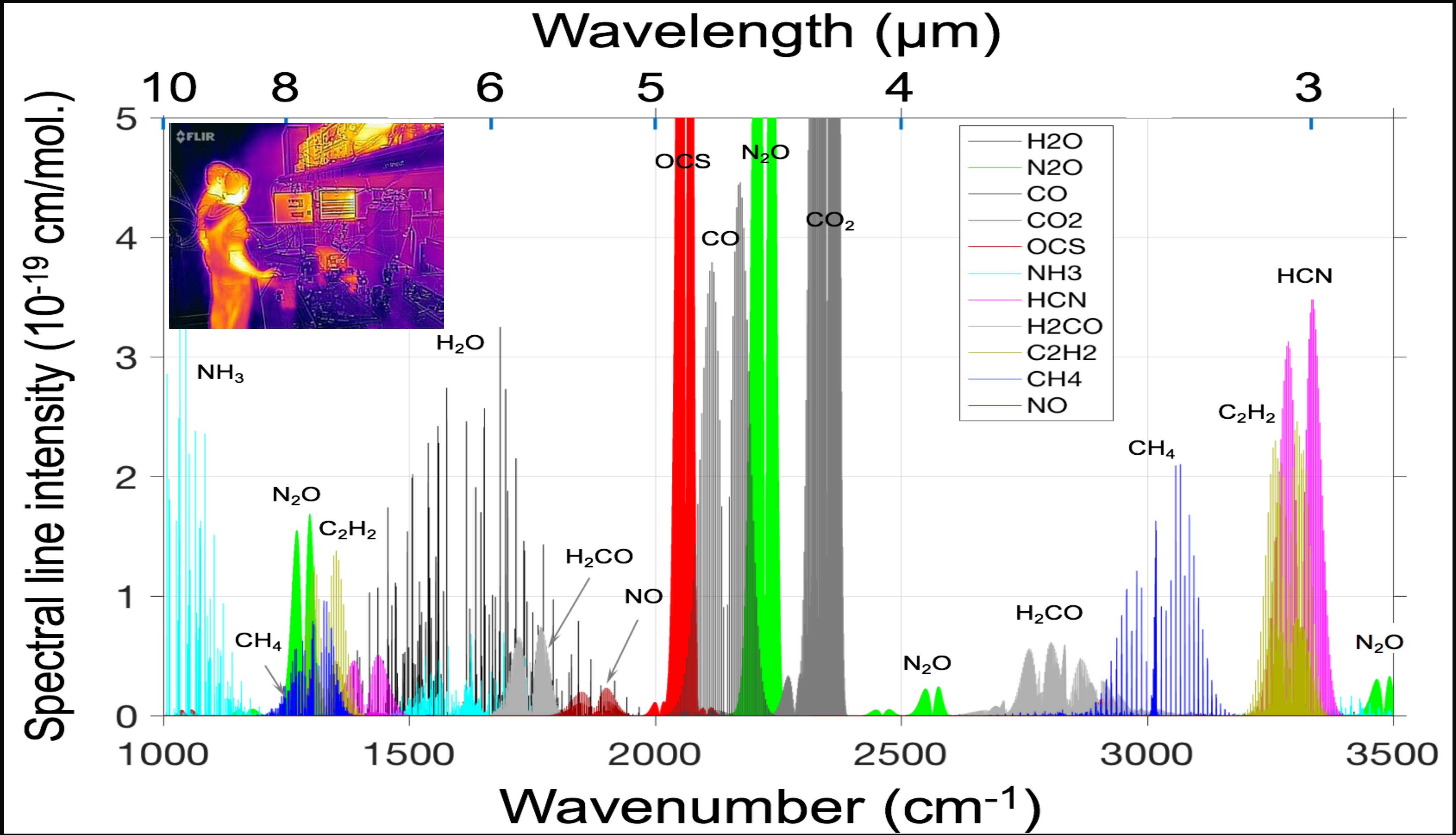




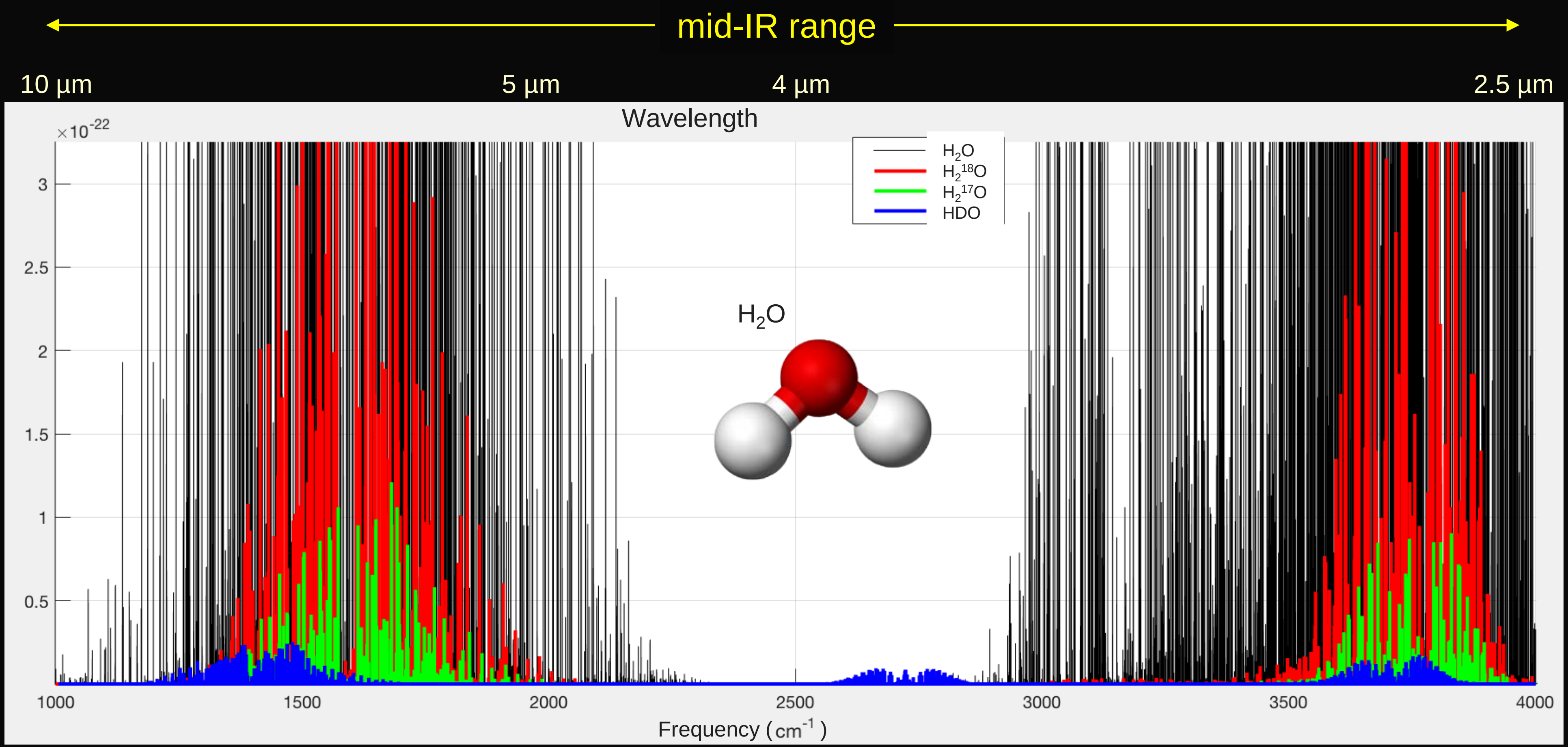
Konstantin Vodopyanov
CREOL, The College of Optics and Photonics, Univ. of Central Florida

Purdue Bircks talk 21-June 2018

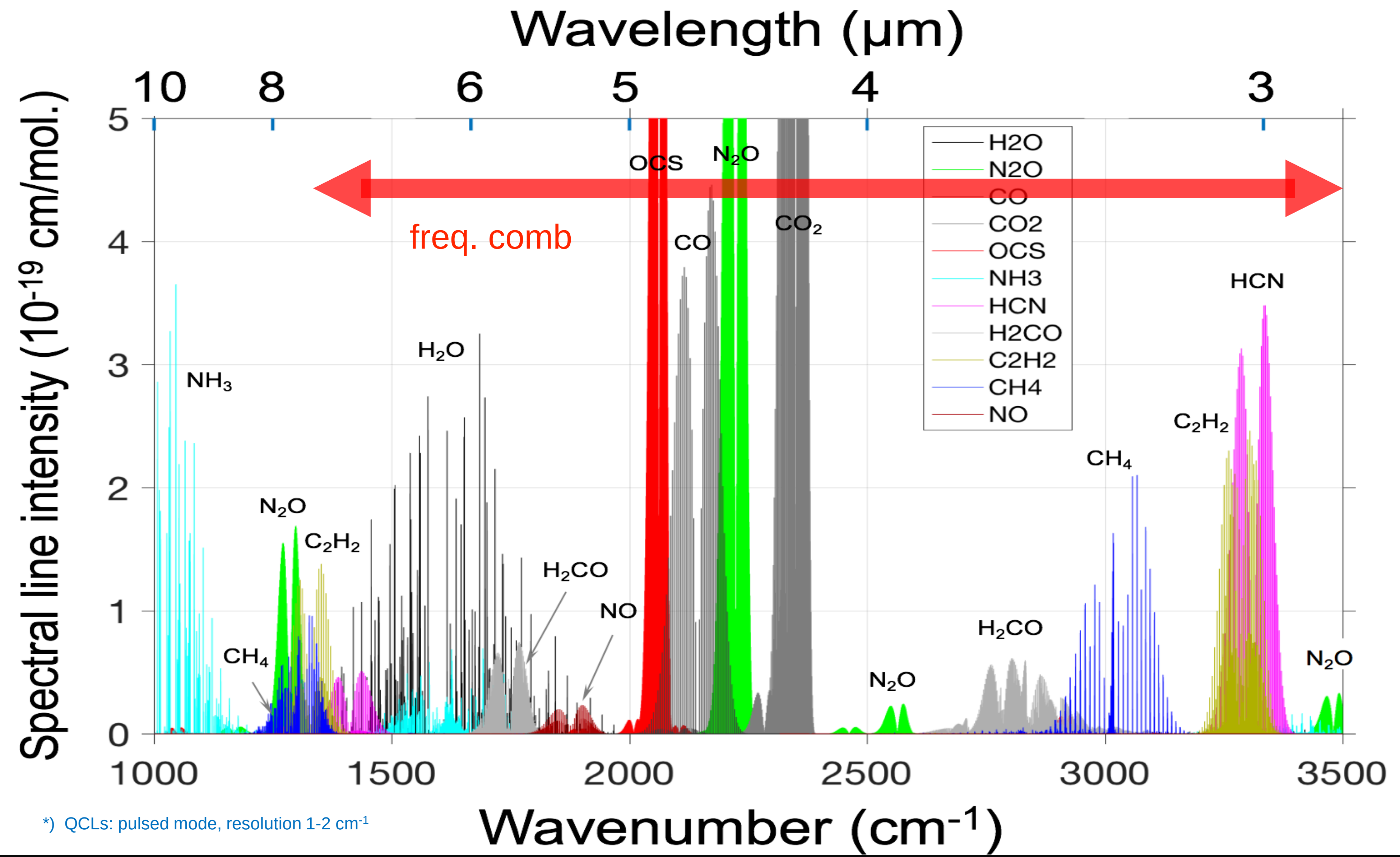
Mid-IR molecular 'signature' refgion



Absorption resonancs of water molecule



Molecular spectra in the spectral range of 3-10 μm

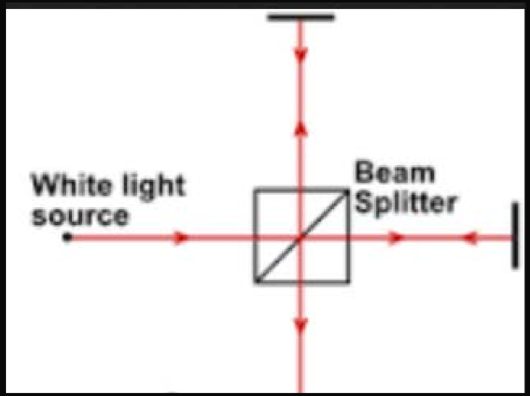


Fourier-transform spectroscopy
(Michelson-interferometer spectroscopy)

A. Michelson
Nobel Prize in Physics 1907

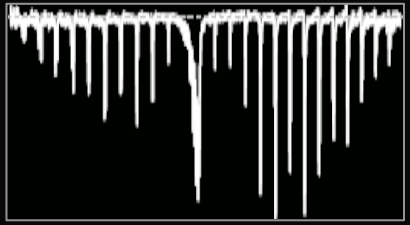
Fourier transform of the autocorrelation is the optical power spectrum

Wiener-Khinchine theorem

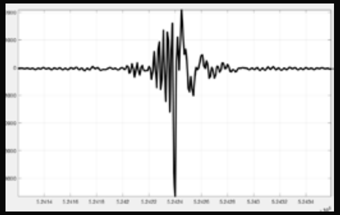


Detector

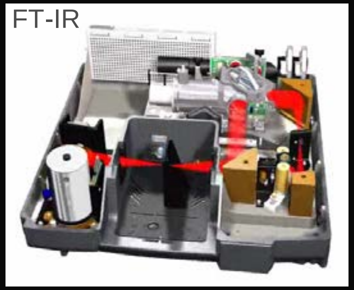
spectrum



detector signal

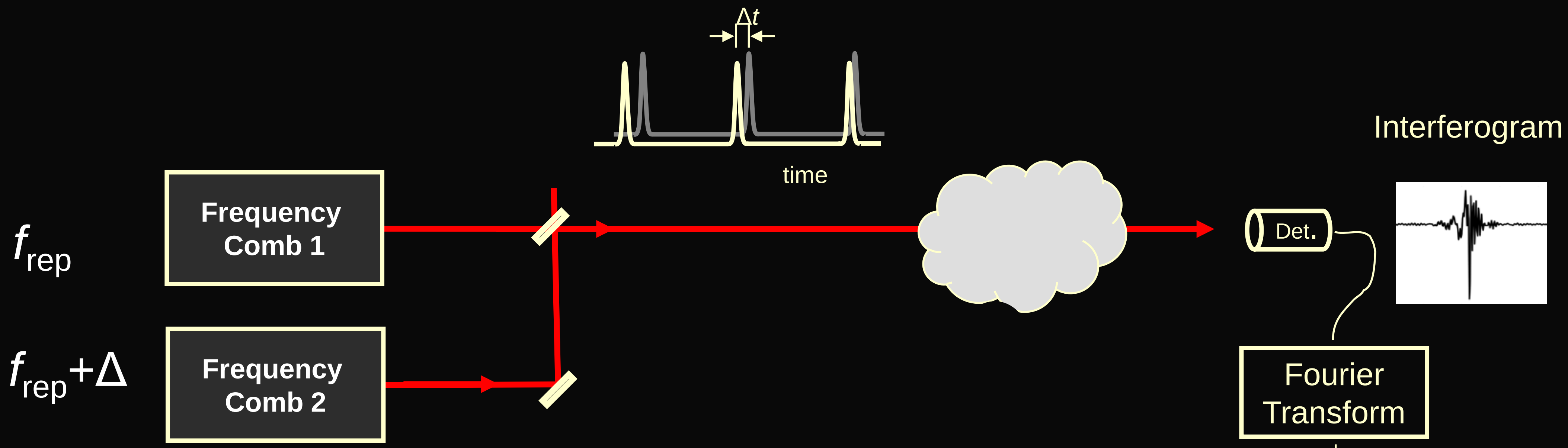


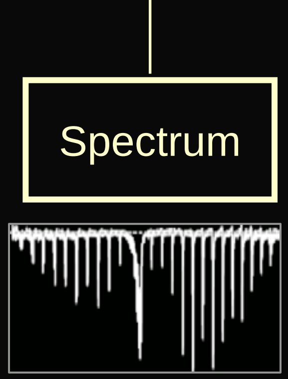
FFT



Optical spectrum is encoded in the dependence of detector signal vs. beam path difference.

Dual-comb Fourier-transform spectroscopy



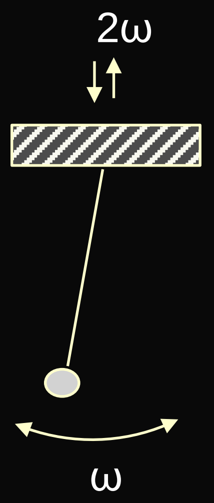


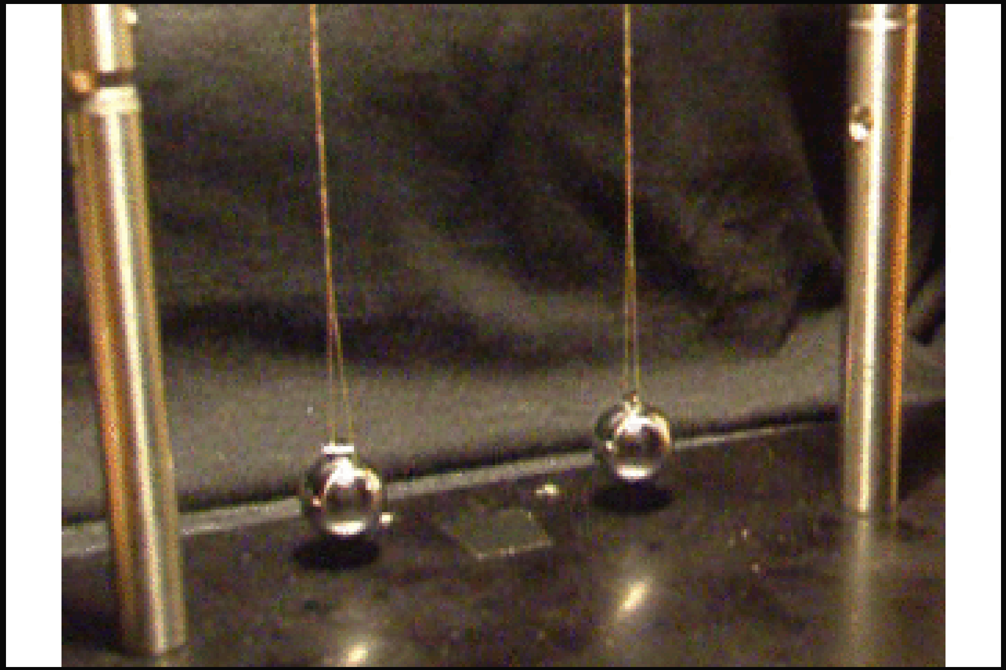
Repetition rates of Comb 1 and Comb 2 have small offset of Δ ~ 100 Hz

Up to 1 000 000 spectral points in 10 ms with resolution ~ 100 MHz (0.003 cm^{-1})

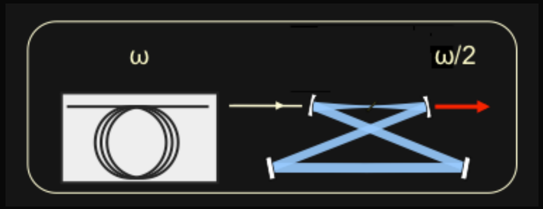
D. W. van der Weide, F. Keilmann, Coherent periodically pulsed radiation spectrometer, US Patent 5,748,309 (1998) (filed 1995)
S. Schiller, Spectrometry with frequency combs, Opt. Lett. 27, 766 (2002).
F. Keilmann, C. Gohle, and R. Holzwarth, Time-domain mid-infrared frequency-comb spectrometer, Opt. Lett. 29, 1542 (2004).

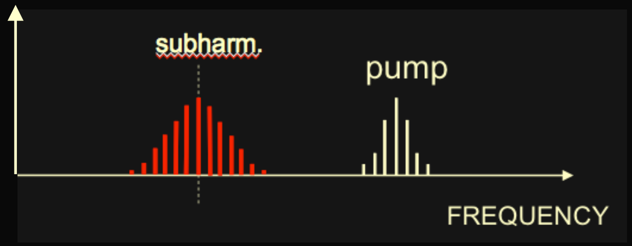
Frequency-divide-and-conquer approach to producing broadband mid-IR combs



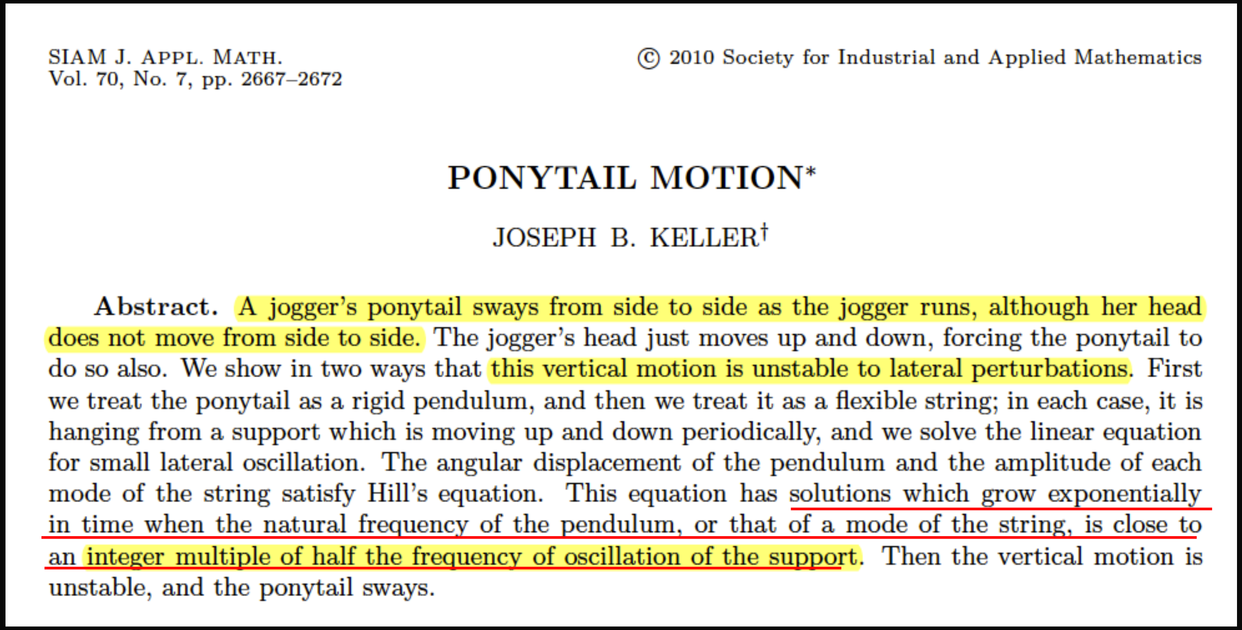


Ponytail motion





The 2012 Ig Nobel Prize in Physics

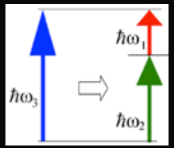

SIAM J. APPL. MATH.
Vol. 70, No. 7, pp. 2667–2672

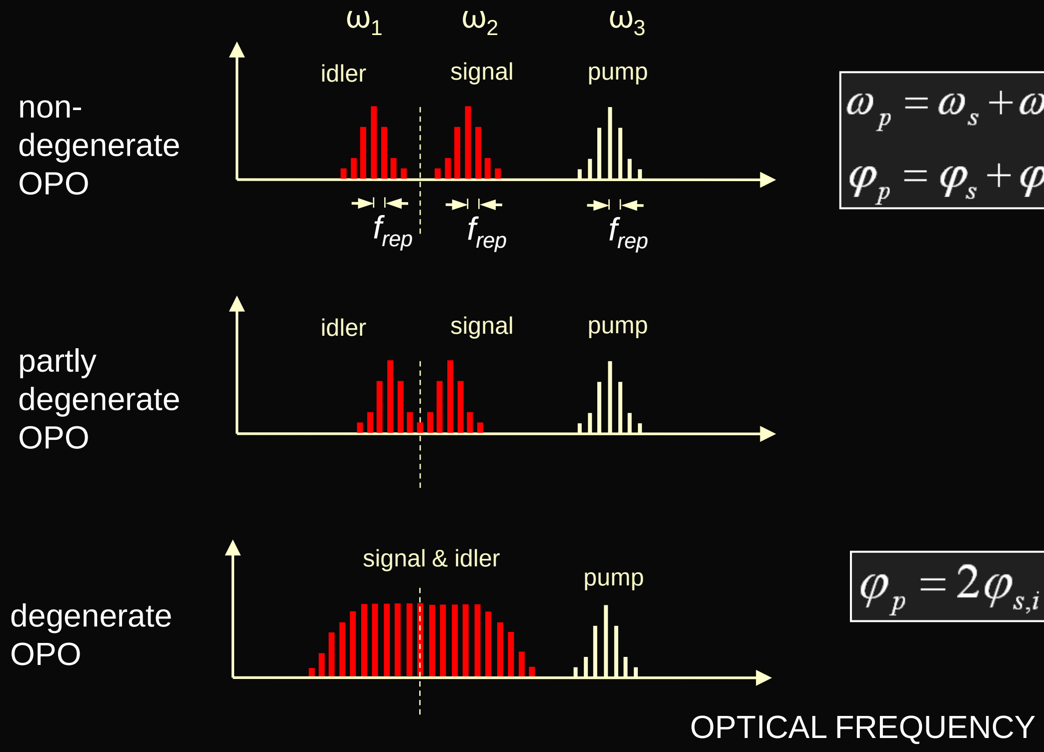
PONYTAIL MOTION*

JOSEPH B. KELLER†

Abstract. A jogger's ponytail sways from side to side as the jogger runs, although her head does not move from side to side. The jogger's head just moves up and down, forcing the ponytail to do so also. We show in two ways that this vertical motion is unstable to lateral perturbations. First we treat the ponytail as a rigid pendulum, and then we treat it as a flexible string; in each case, it is hanging from a support which is moving up and down periodically, and we solve the linear equation for small lateral oscillation. The angular displacement of the pendulum and the amplitude of each mode of the string satisfy Hill's equation. This equation has solutions which grow exponentially in time when the natural frequency of the pendulum, or that of a mode of the string, is close to an integer multiple of half the frequency of oscillation of the support. Then the vertical motion is unstable, and the ponytail sways.

Concept of a subharmonic ‘frequency-divide-by-two’ OPO





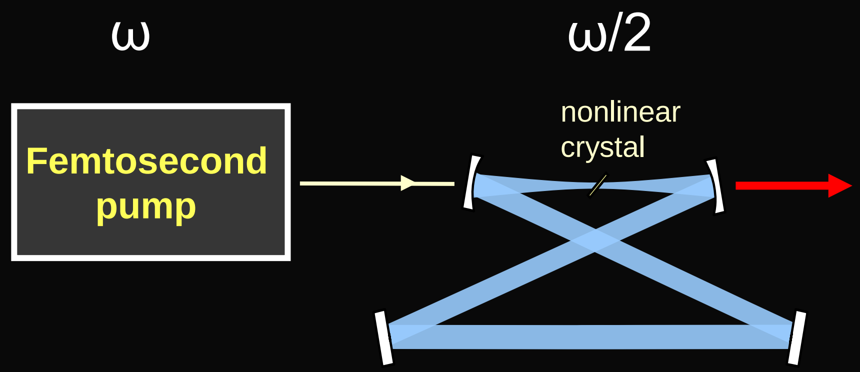
$$\omega_p = \omega_s + \omega_i$$

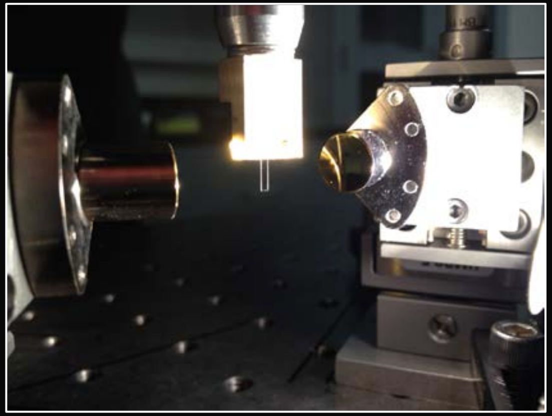
$$\varphi_p = \varphi_s + \varphi_i + \pi / 2$$

$$\varphi_p = 2\varphi_{s,i} + \pi / 2$$

Wong, Vodopyanov, Byer, JOSA B 27, 876 (2010)

Subharmonic mid-IR OPO combs with a variety of pump lasers and NL crystals

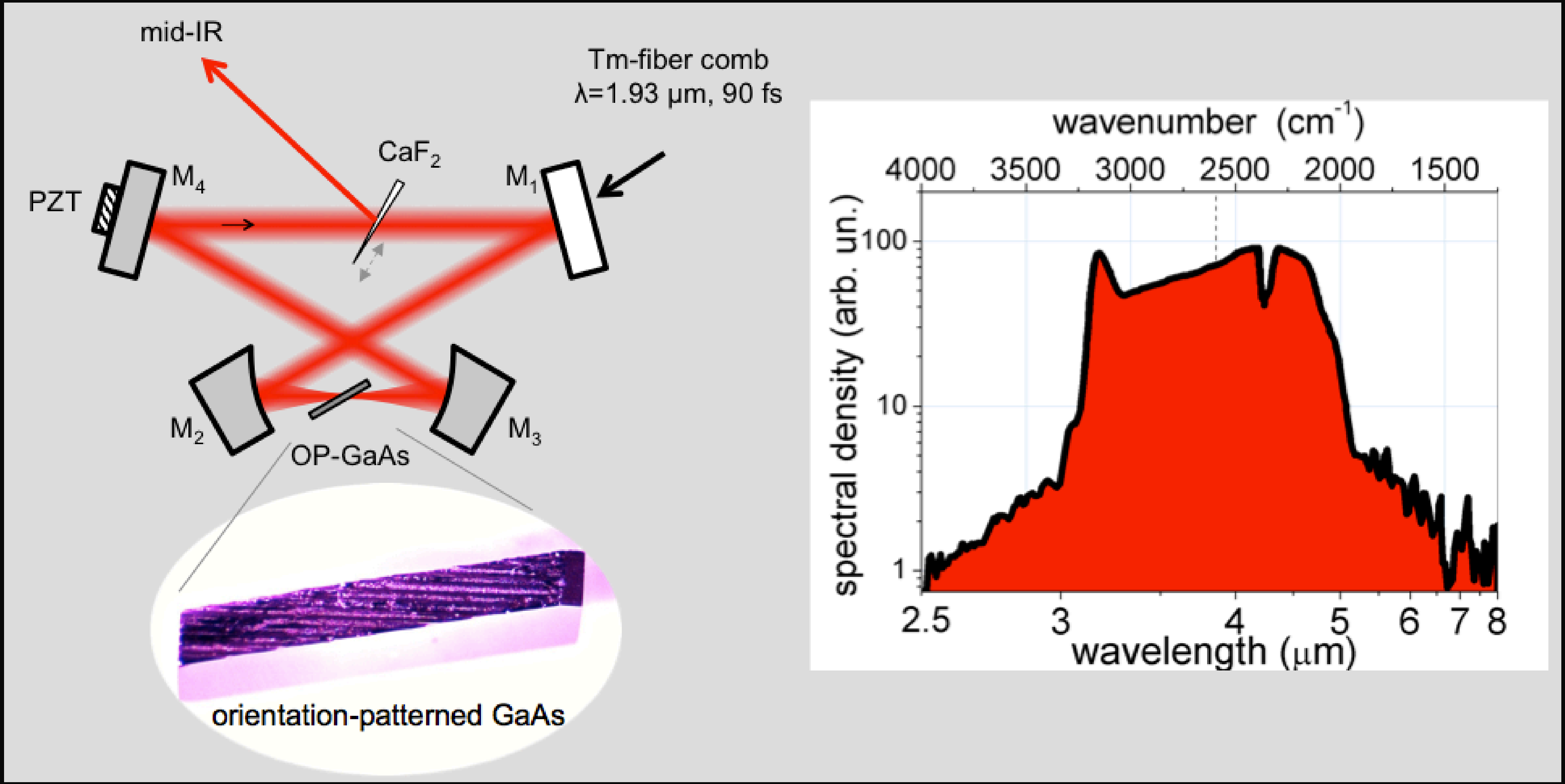




Femtosecond pump laser	Nonlinear crystal	Spectral span	Ref.
Er-fiber at 1560 nm	Periodically-poled **lithium niobate**, 200-500-µm long	2.5 - 3.8 µm	Leindecker et al., Opt. Express. 19, 6296 (2011)
Cr:ZnSe at 2425 nm	Orientation-patterned **GaAs** 500-µm long	4.4 - 5.4 µm	Vodopyanov et al., Opt. Lett. 36, 2275 (2011)
Tm-fiber at 2050 nm	Orientation-patterned **GaAs** 500-µm long	2.6 - 6.1 µm	Leindecker et al., Opt. Express. 20, 7046 (2012)
Cr:ZnS at 2380 nm	Orientation-patterned **GaAs** 500-µm long	3.6 – 5.6 µm	Smolski et al., Opt. Lett. 40, 2906 (2015)
Tm-fiber at 1930 nm	Orientation-patterned **GaAs** 500-µm long	2.6 – 7.5 µm	Smolski et al., Opt. Lett. 41, 1388 (2016)
Er-fiber at 1560 nm	Orientation-patterned **GaP** 500-µm long	2.3 - 4.8 µm	Q. Ru et al., Opt. Lett. 42, 4756 (2017)

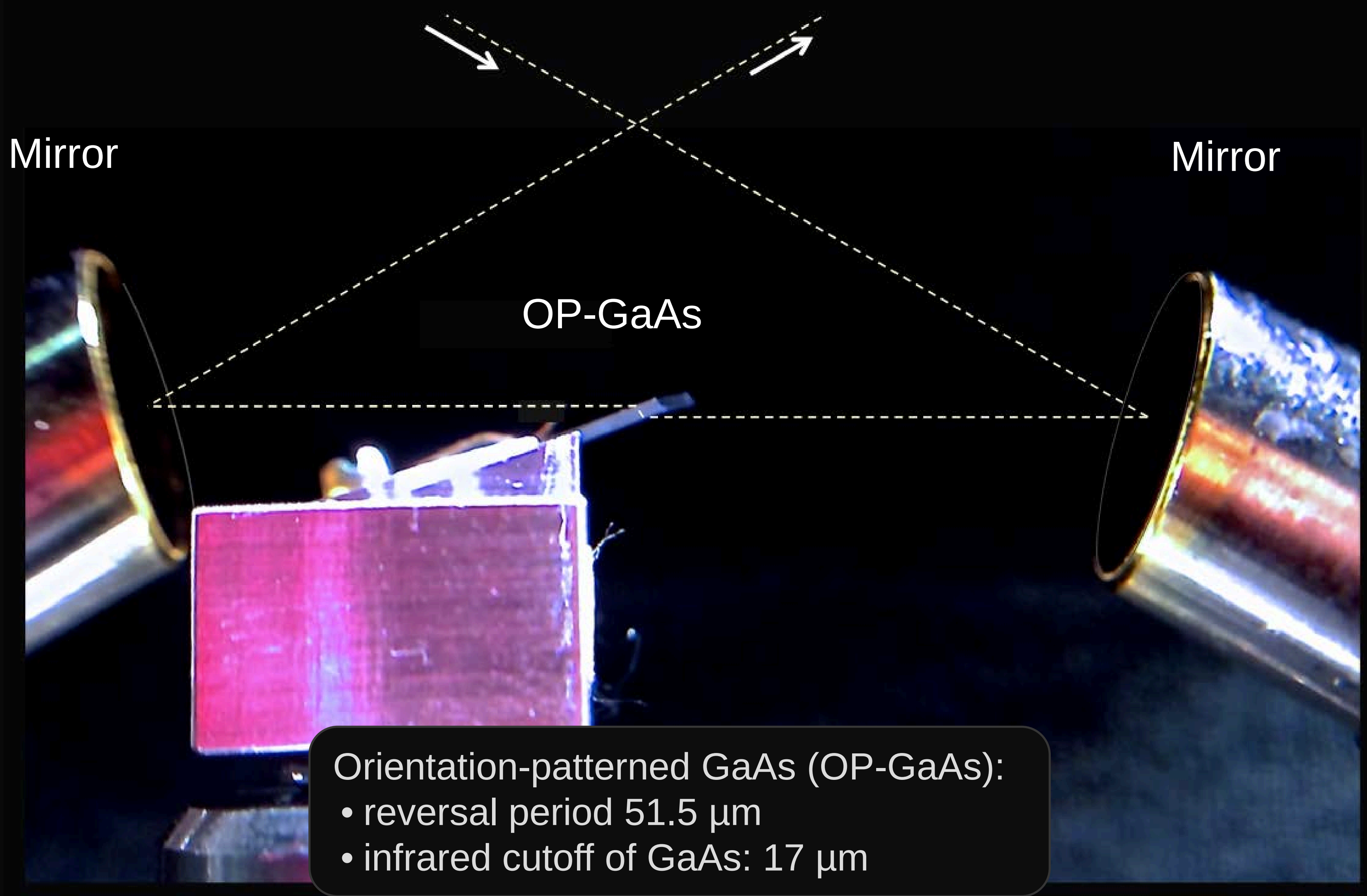
Pump threshold ~ 10mW. Conversion officiency can be > 60%

Tm-fiber pumped 2.6–7.5 μm frequency comb based on OP-GaAs



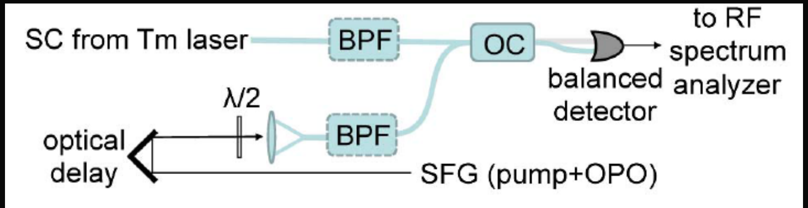
Smolski, Yang, Gorelov, Schunemann, Vodopyanov, Opt. Lett. 41, 1388 (2016)

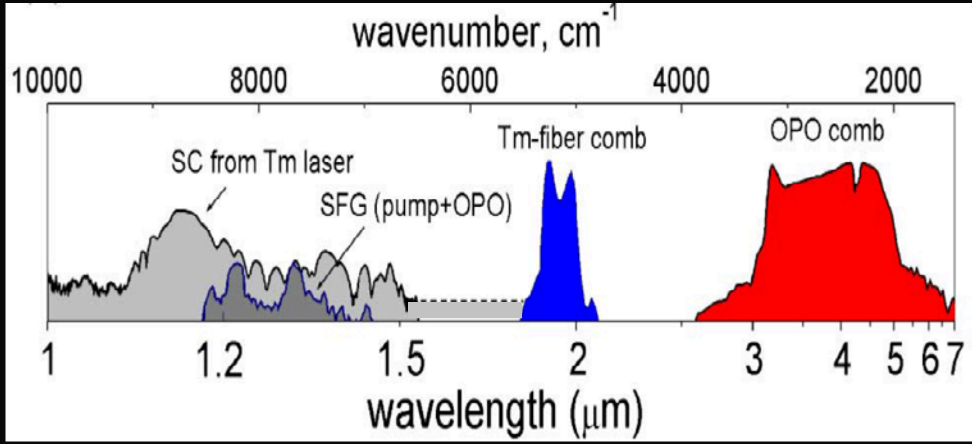
OPO engine

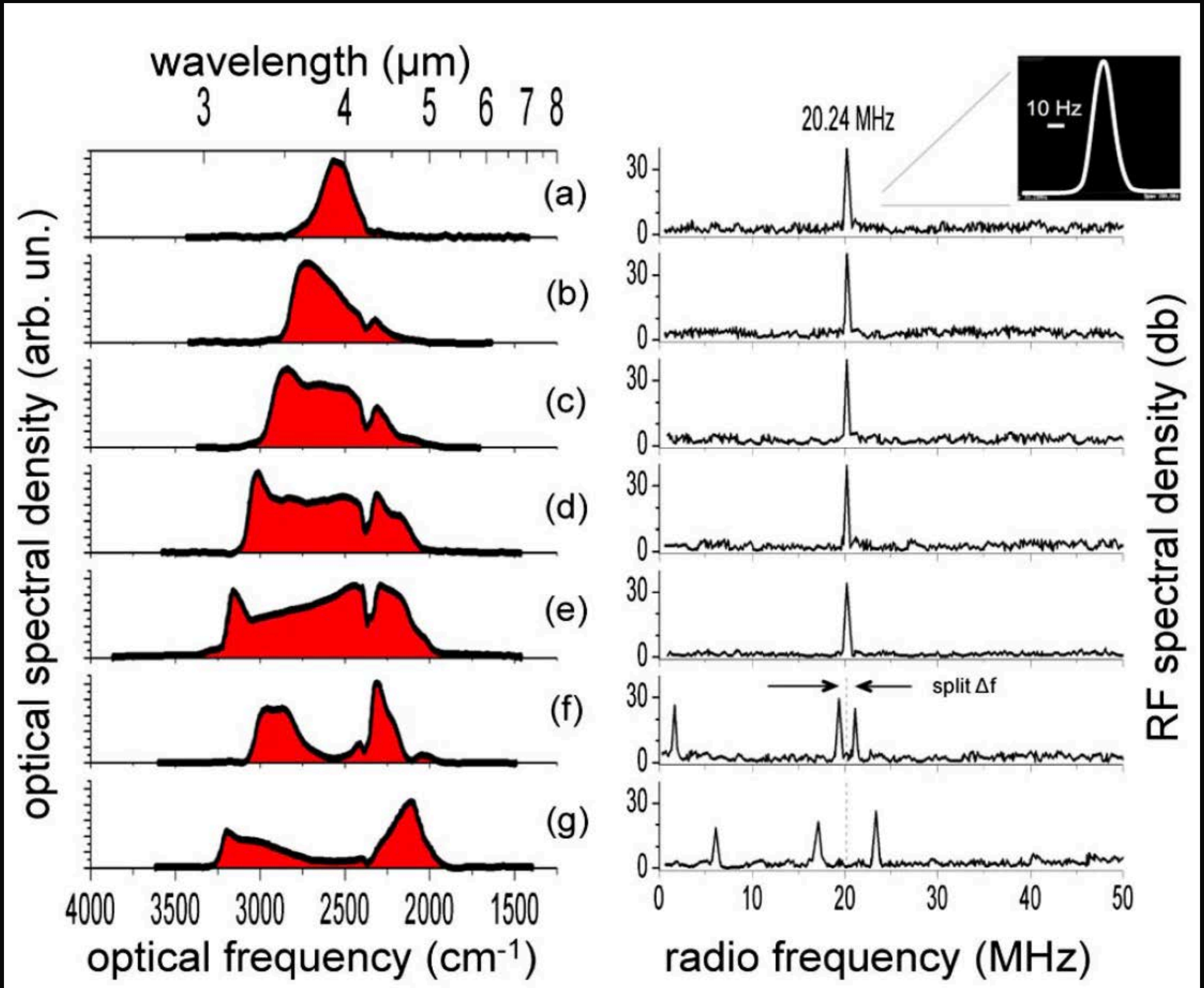


Orientation-patterned GaAs (OP-GaAs):
- reversal period 51.5 µm
- infrared cutoff of GaAs: 17 µm

Coherence properties of a Tm pumped subharmonic OPO

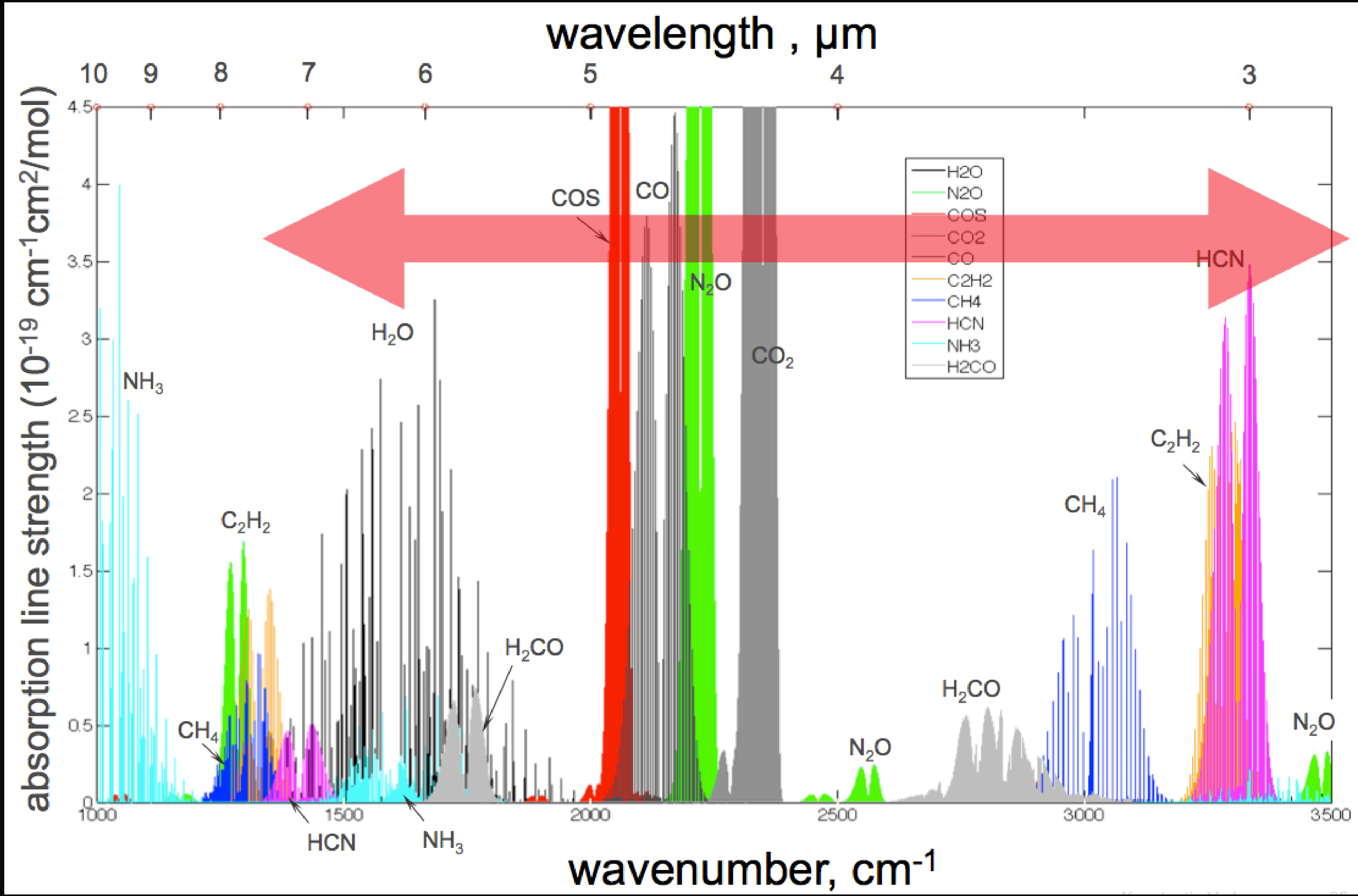






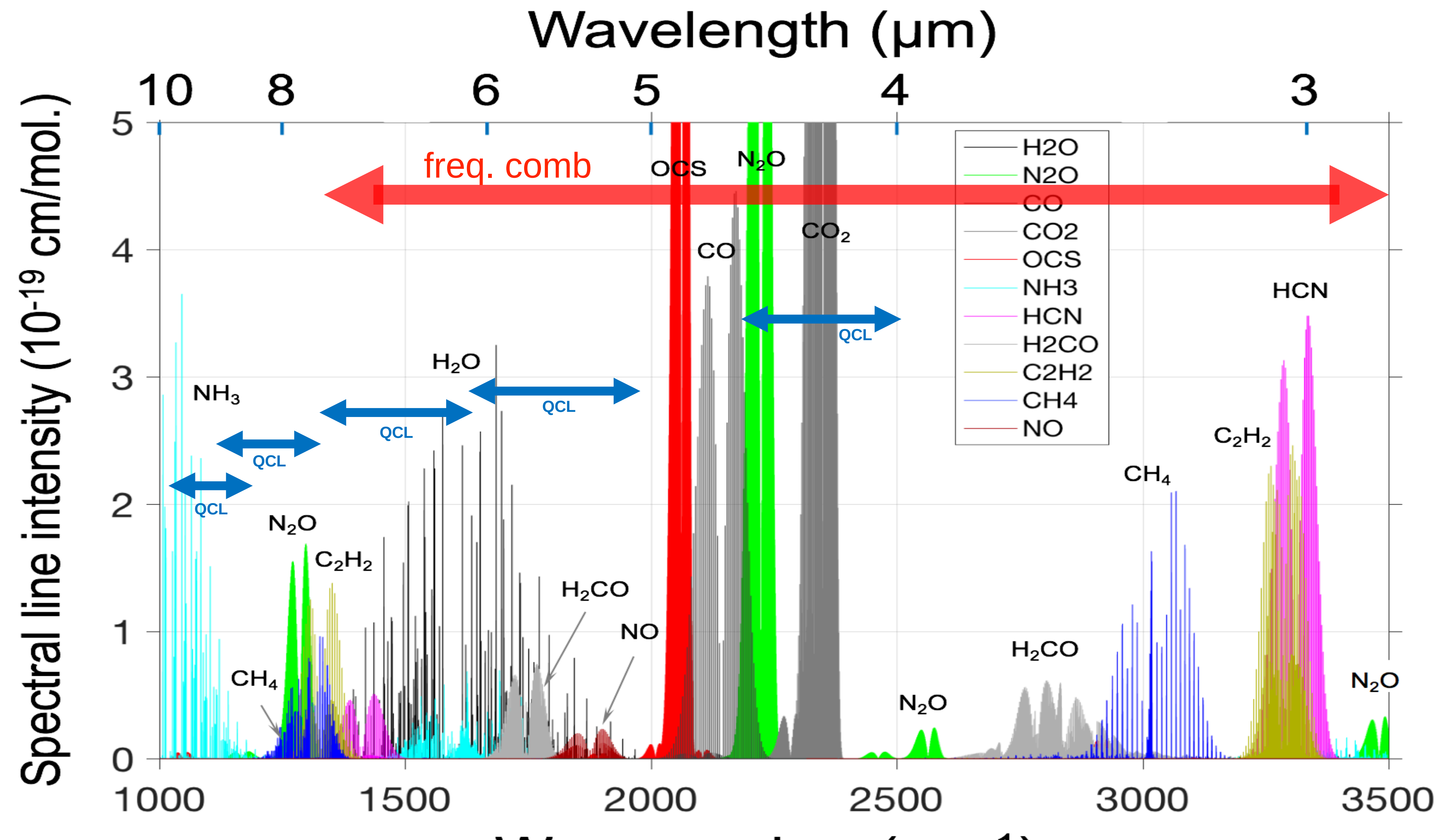
Smolski, Yang, Gorelov, Schunemann, Vodopyanov, Opt. Lett. 41, 1388 (2016)

Spectral span, Tm-fiber pumped subharmonic GaAs OPO



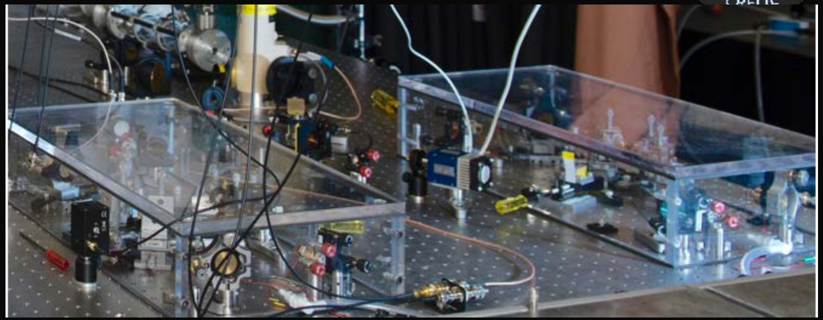
Smolski, Yang, Gorelov, Schunemann, Vodopyanov, Opt. Lett. 41, 1388 (2016)

Molecular spectra in the spectral range of 3-10 μm

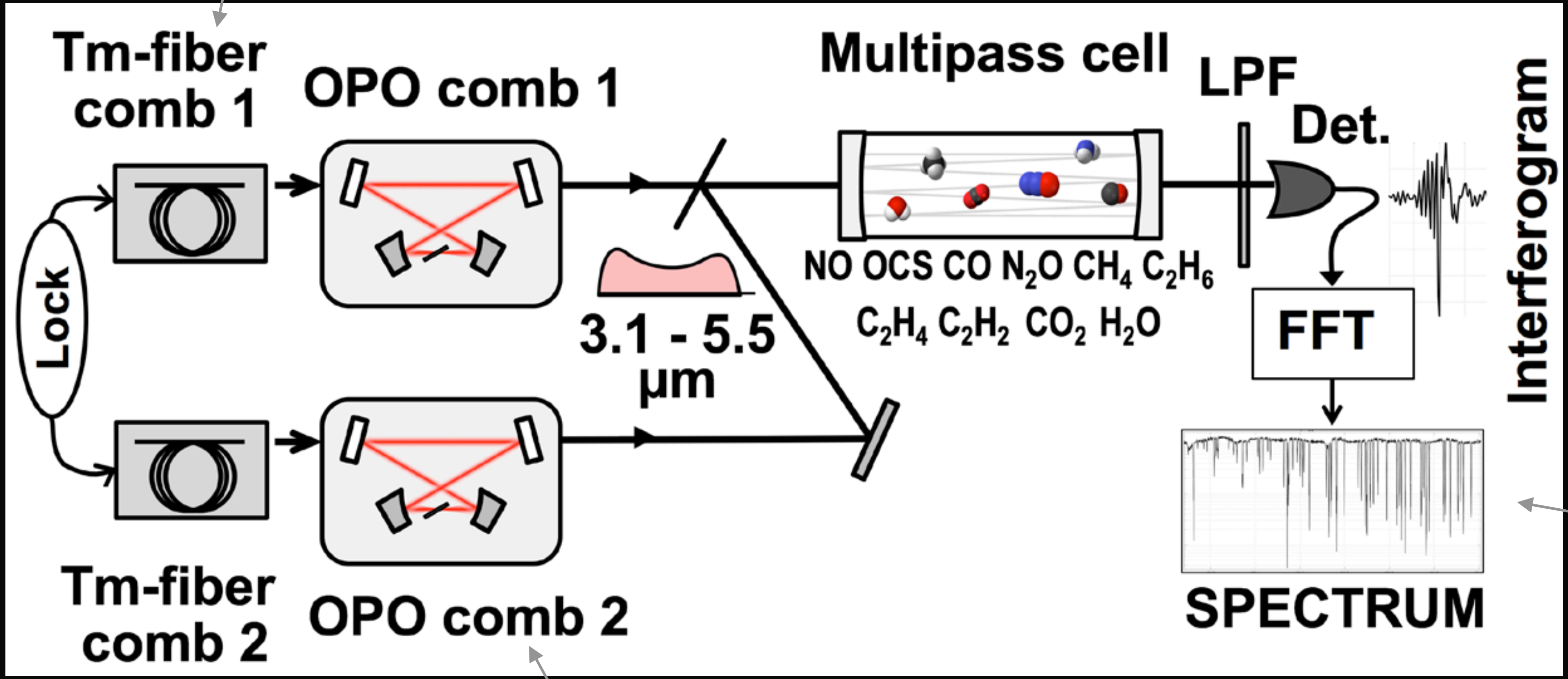


*) QCLs: pulsed mode, resolution 1-2 cm^{-1}

Dual-comb spectroscopic system



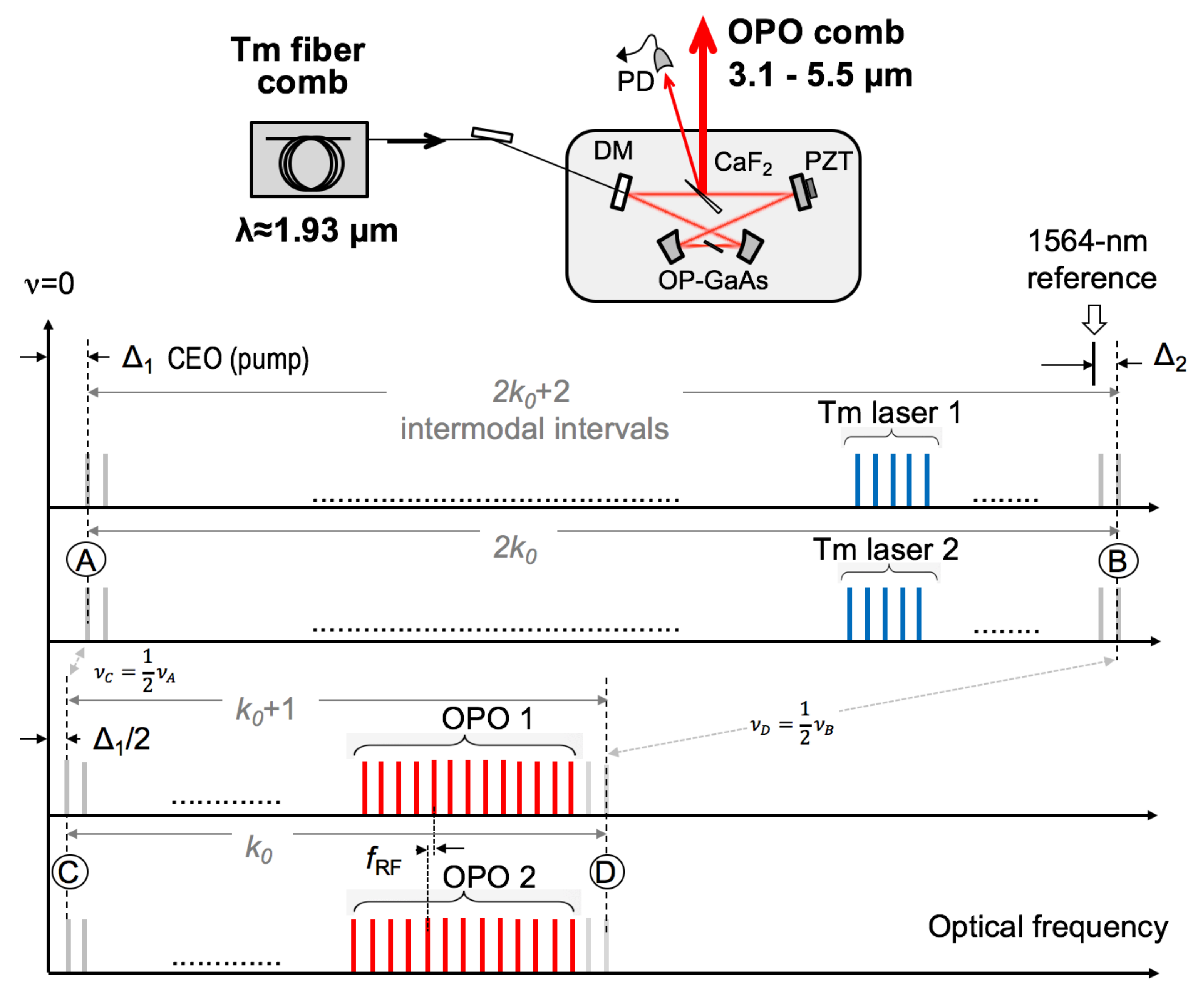
A pair of mutually coherent Tm-fiber combs (λ≈2 μm) with slightly different mode spacing are f_{ceo} locked and referenced to the same CW laser



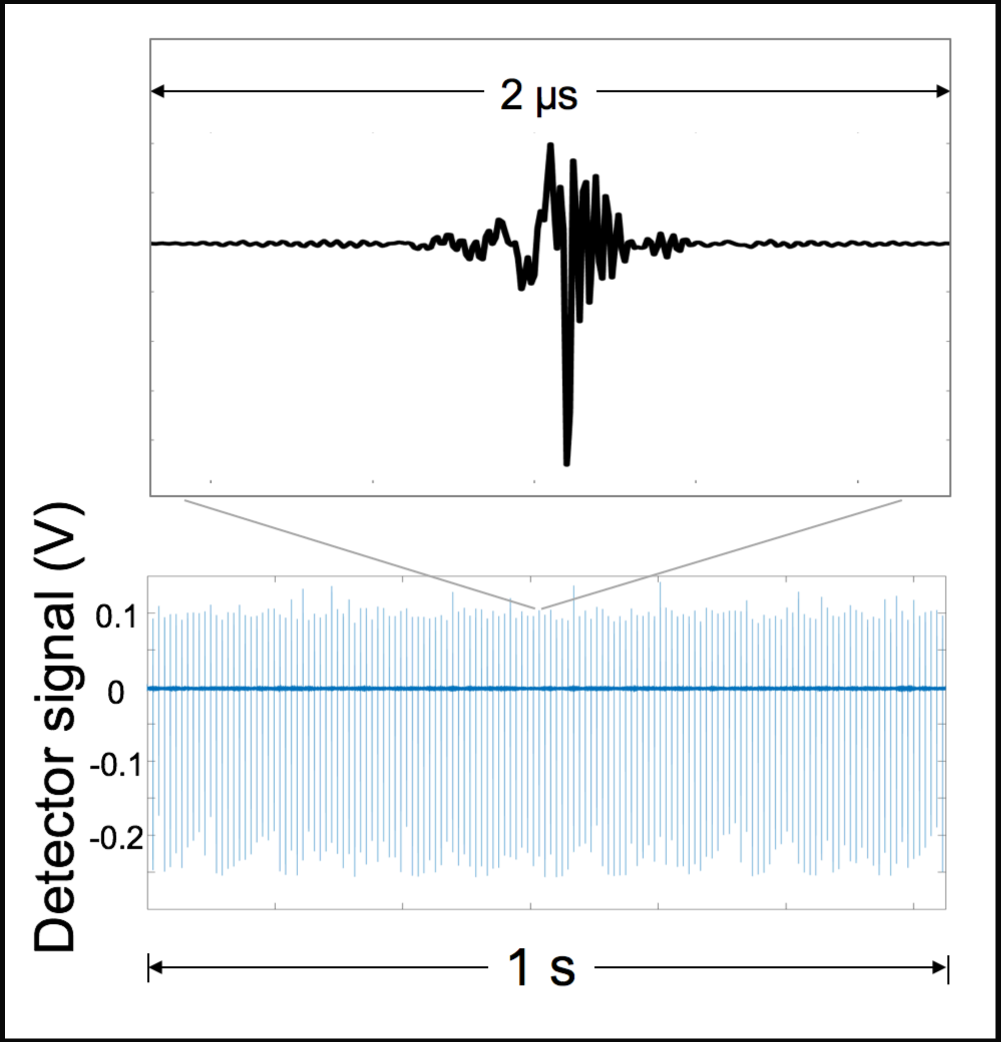
Two subharmonic OPOs are phase and frequency locked to the pump lasers; the mutual coherence time between the two OPOs is **40 sec**.

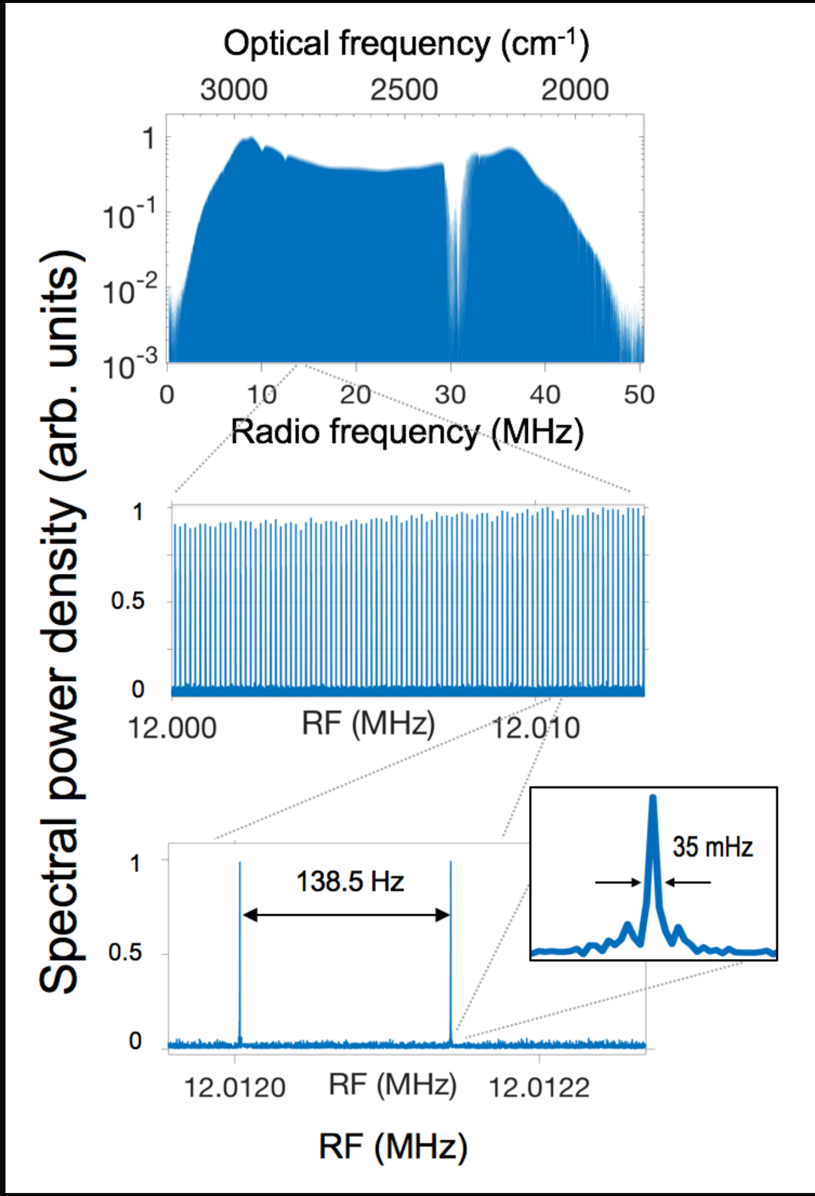
The optical spectra were referenced to radio frequencies only: the frequency counters for measuring f_{rep} and Δf_{rep}, the frequency synthesizers that generated offsets for Tm-fibre combs, and the clock of the A/D card – were all stabilized against **Rb-clock**.

Muraviev, Smolski, Loparo, Vodopyanov, *Nature Photon.* 12, 209 (2018)


Tm fiber comb
λ≈1.93 µm
PD
OPO comb
3.1 - 5.5 µm
DM
CaF2
PZT
OP-GaAs
1564-nm reference
ν=0
Δ1 CEO (pump)
Δ2
2k0+2 intermodal intervals
Tm laser 1
2k0
Tm laser 2
A
B
νC = 1/2 νA
k0+1
OPO 1
νD = 1/2 νB
Δ1/2
k0
fRF
OPO 2
C
D
Optical frequency

We can resolve all 350,000 modes with the finesse of 4,000

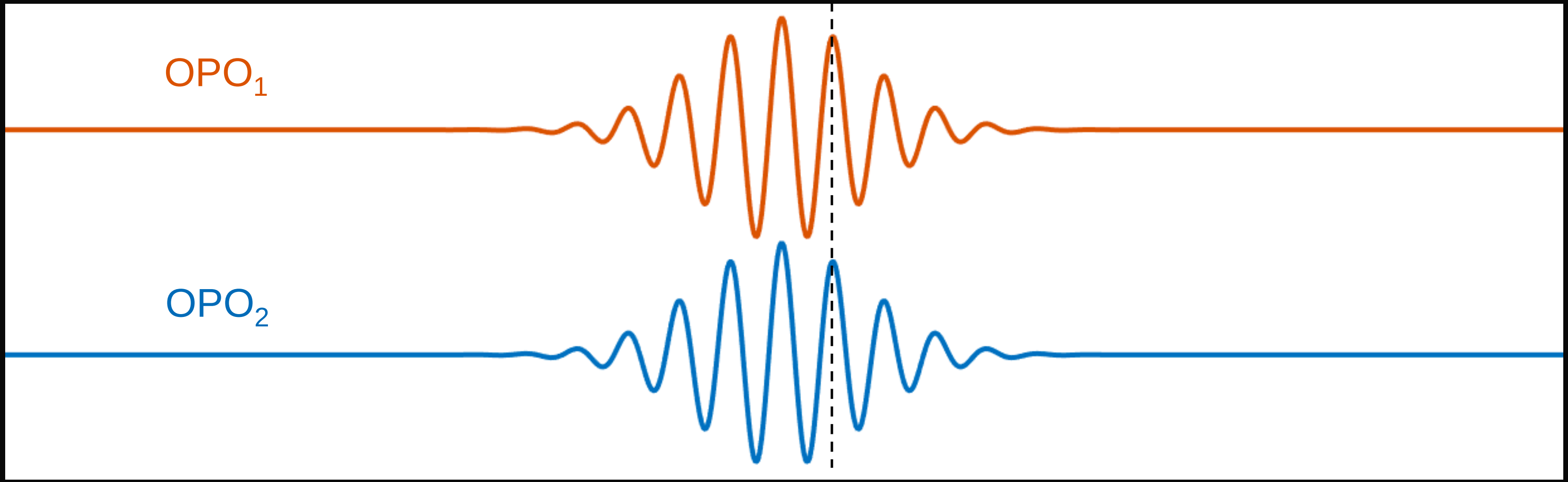




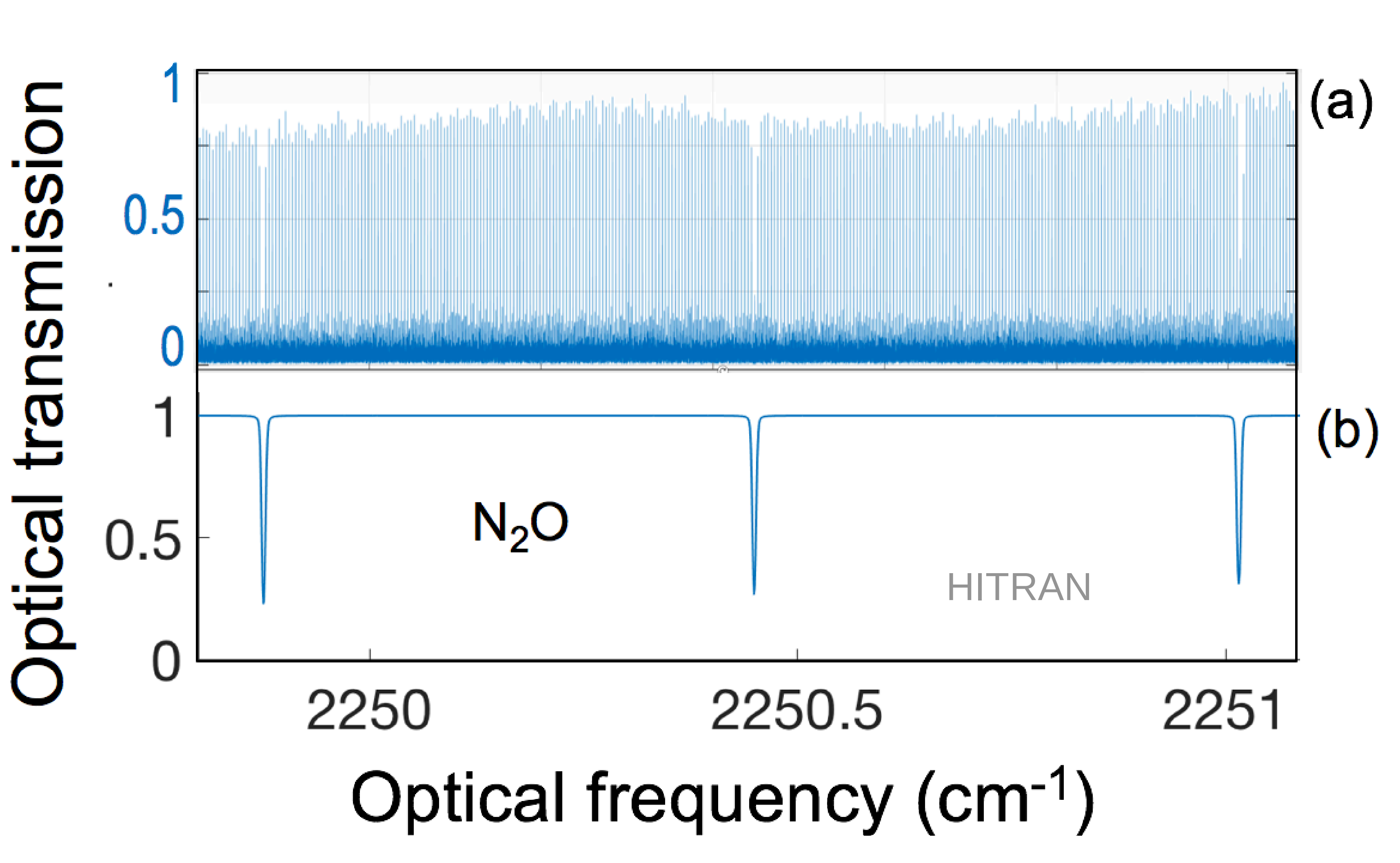
Muraviev, Smolski, Loparo, Vodopyanov, *Nature Photon.* 12, 209 (2018)

Mutual coherence **40 sec**

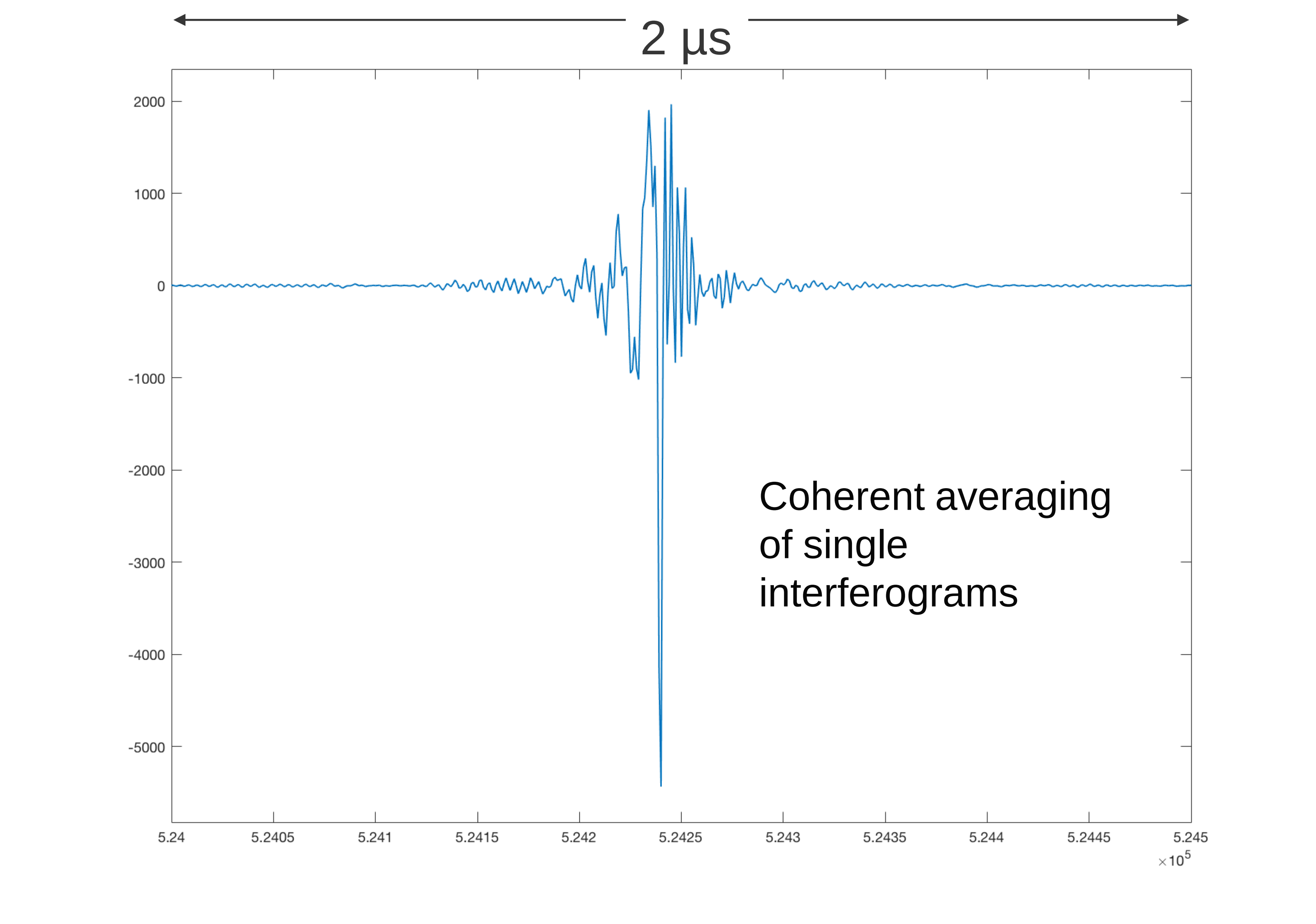
The moon is about 1.3 light-seconds away from the Earth.
40 sec is about 30 distances to the moon



Mode resolved spectrum: N_2O

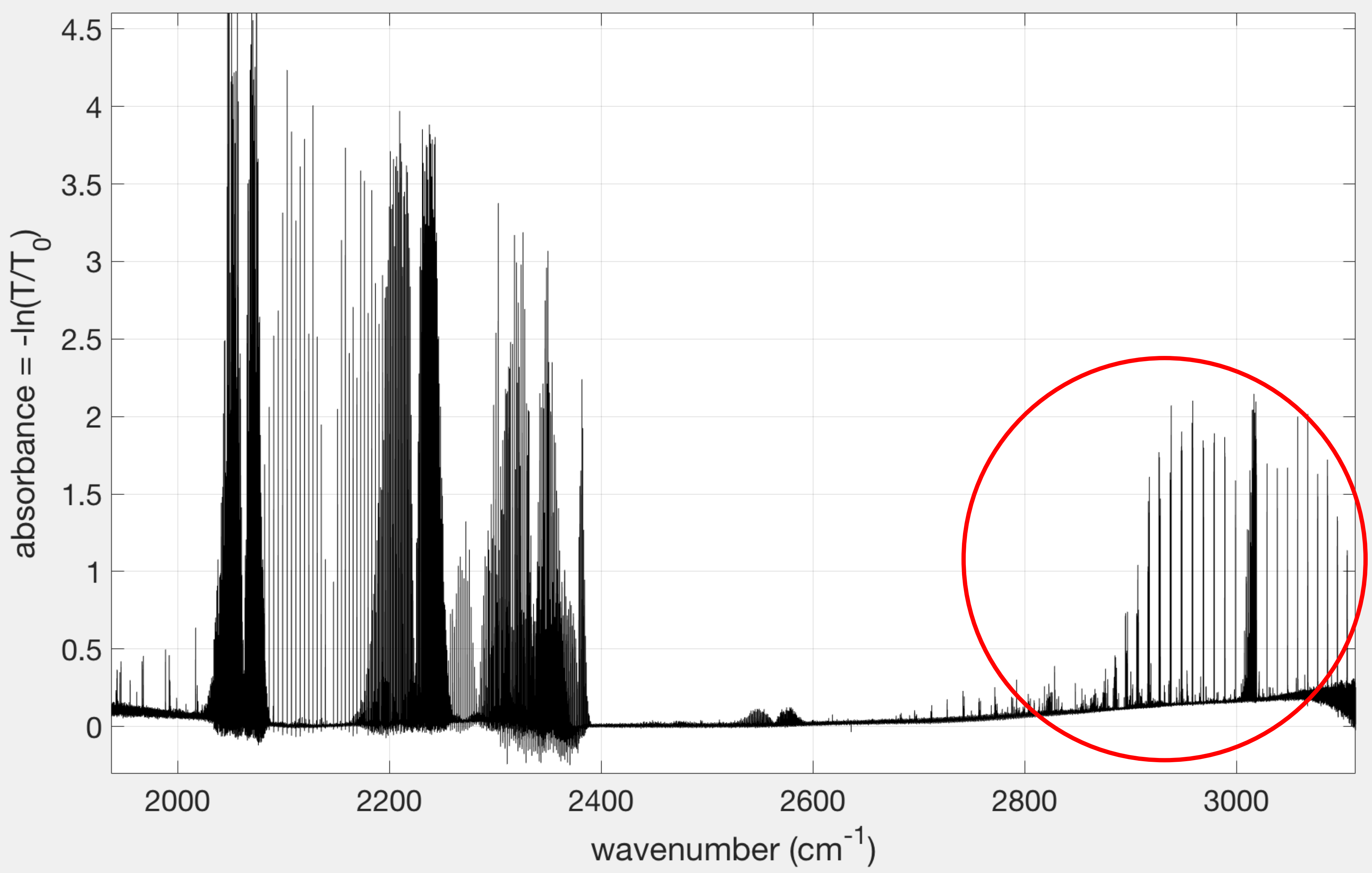


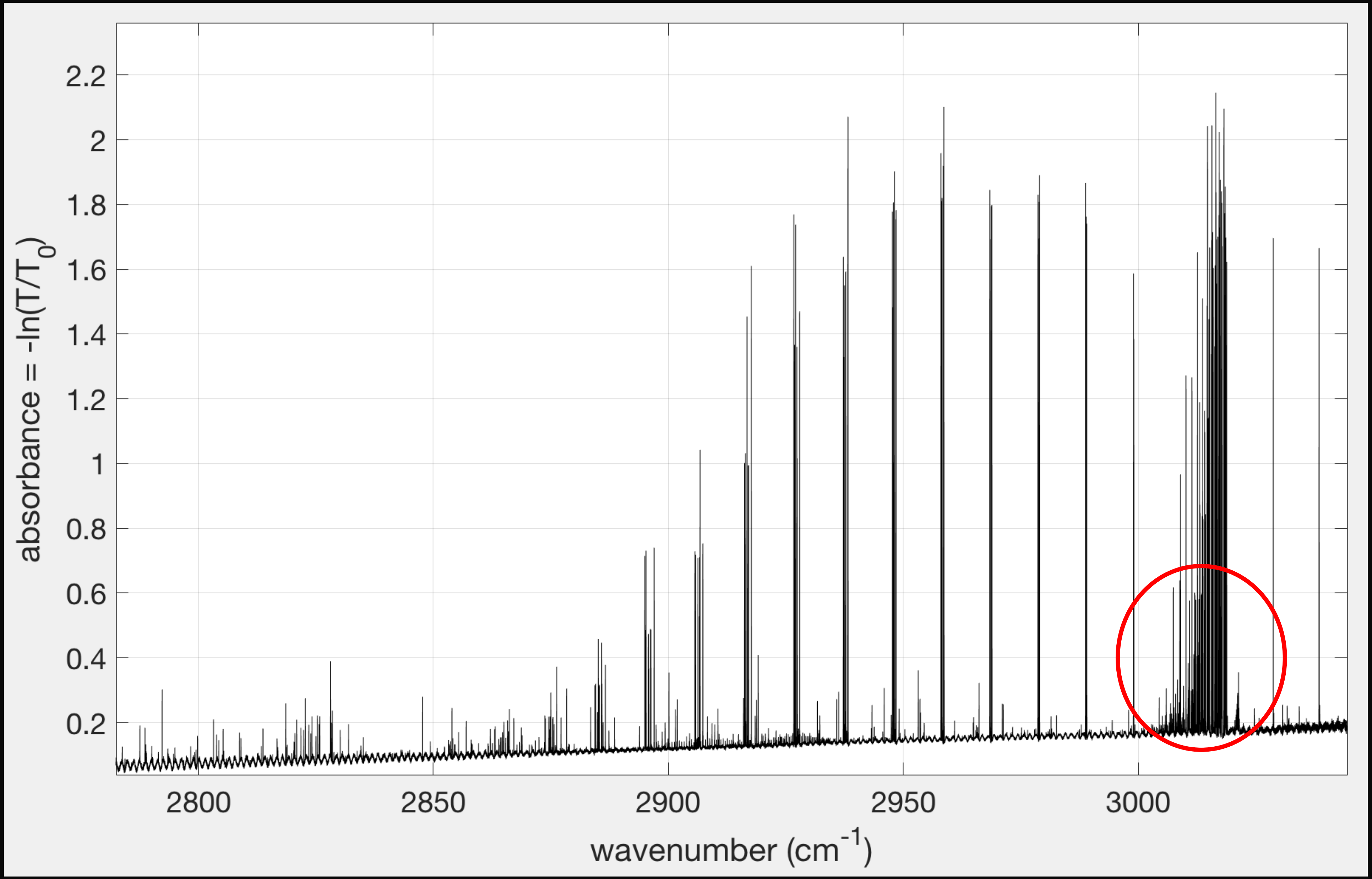
Muraviev, Smolski, Loparo, Vodopyanov, *Nature Photon.* 12, 209 (2018)



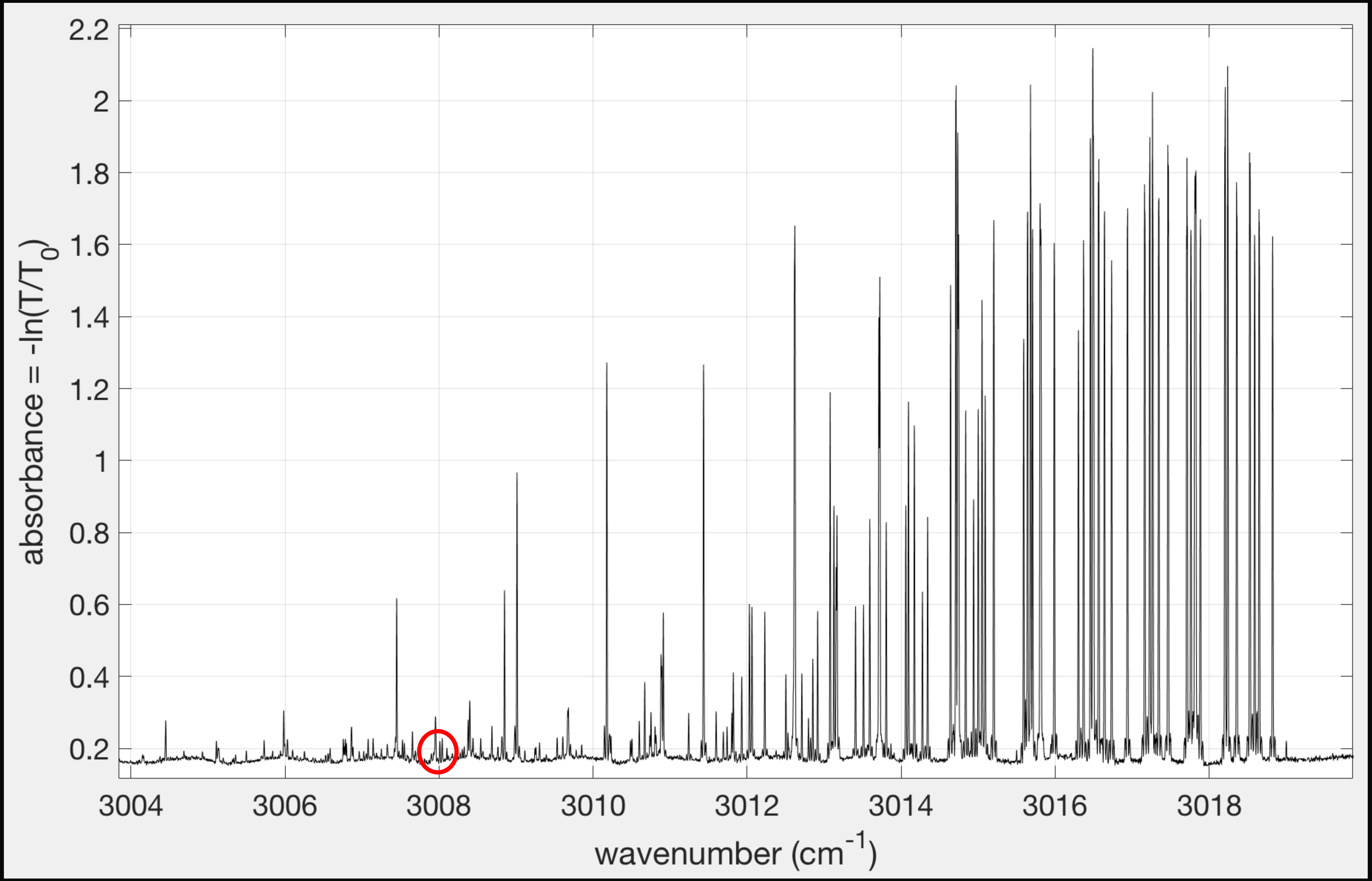
2 µs
2000
1000
0
-1000
-2000
-3000
-4000
-5000
5.24
5.2405
5.241
5.2415
5.242
5.2425
5.243
5.2435
5.244
5.2445
5.245
×10^5
Coherent averaging of single interferograms

Normalized spectrum after taking Fourier transform

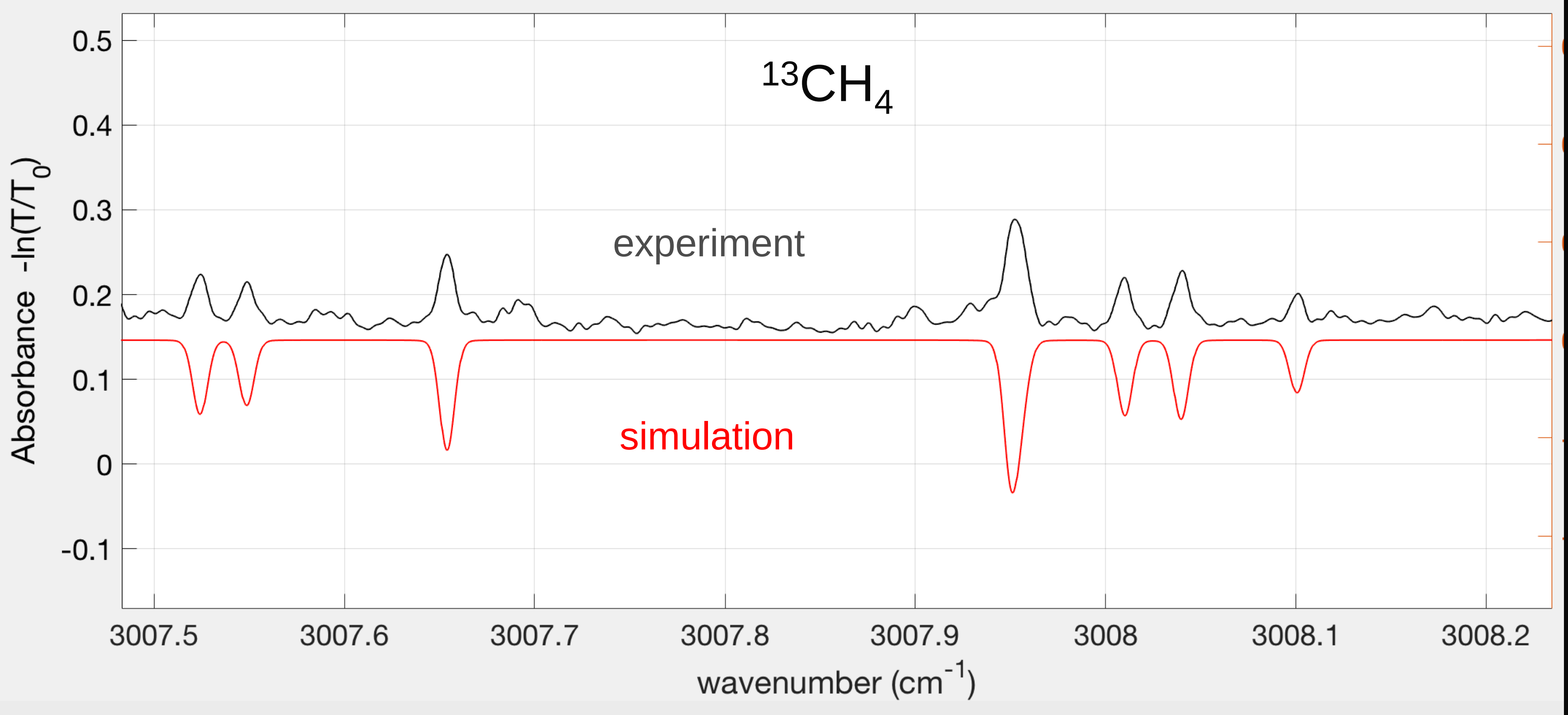




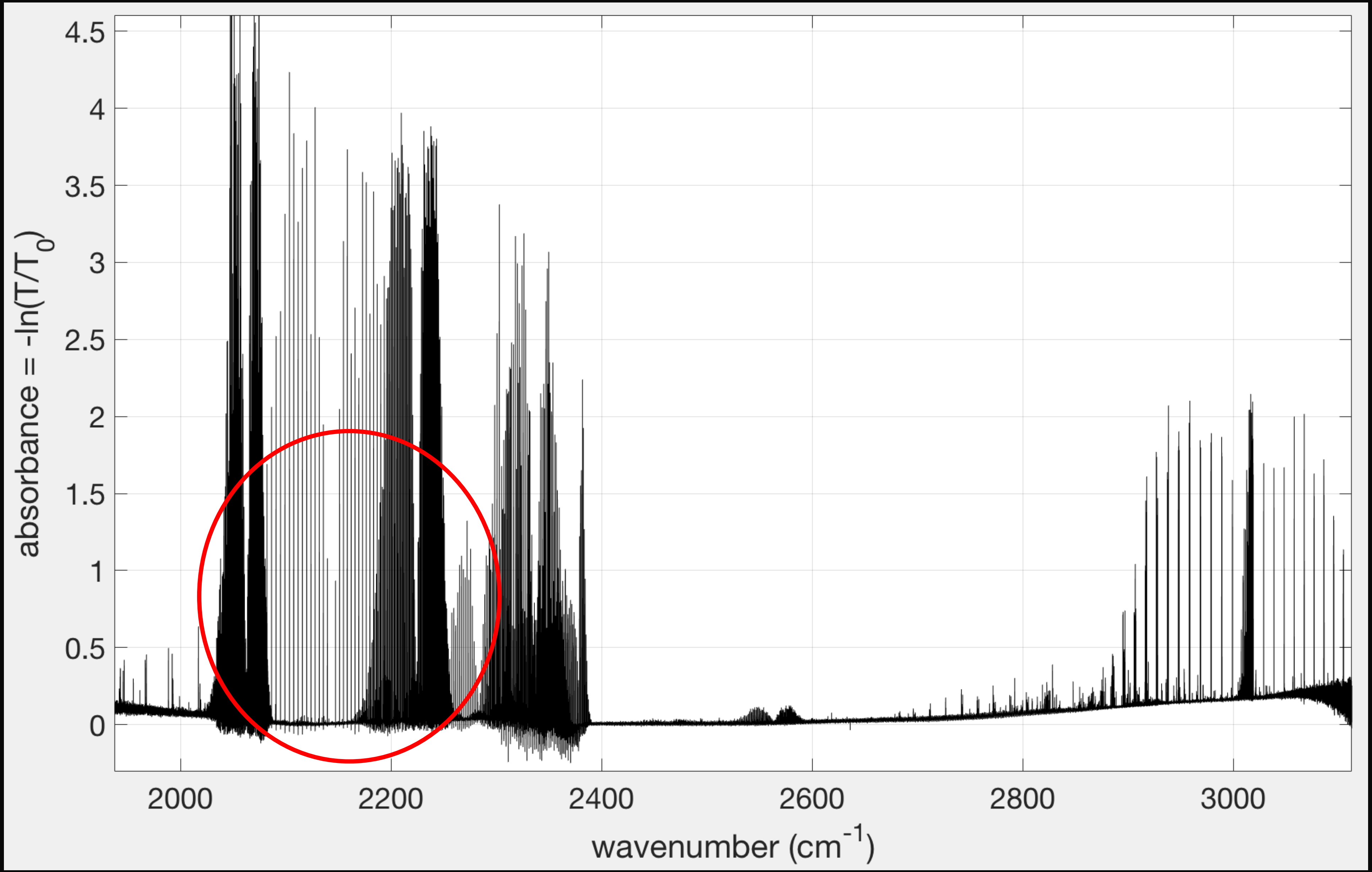
absorbance = -ln(T/T0)
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
2800
2850
2900
2950
3000
wavenumber (cm-1)



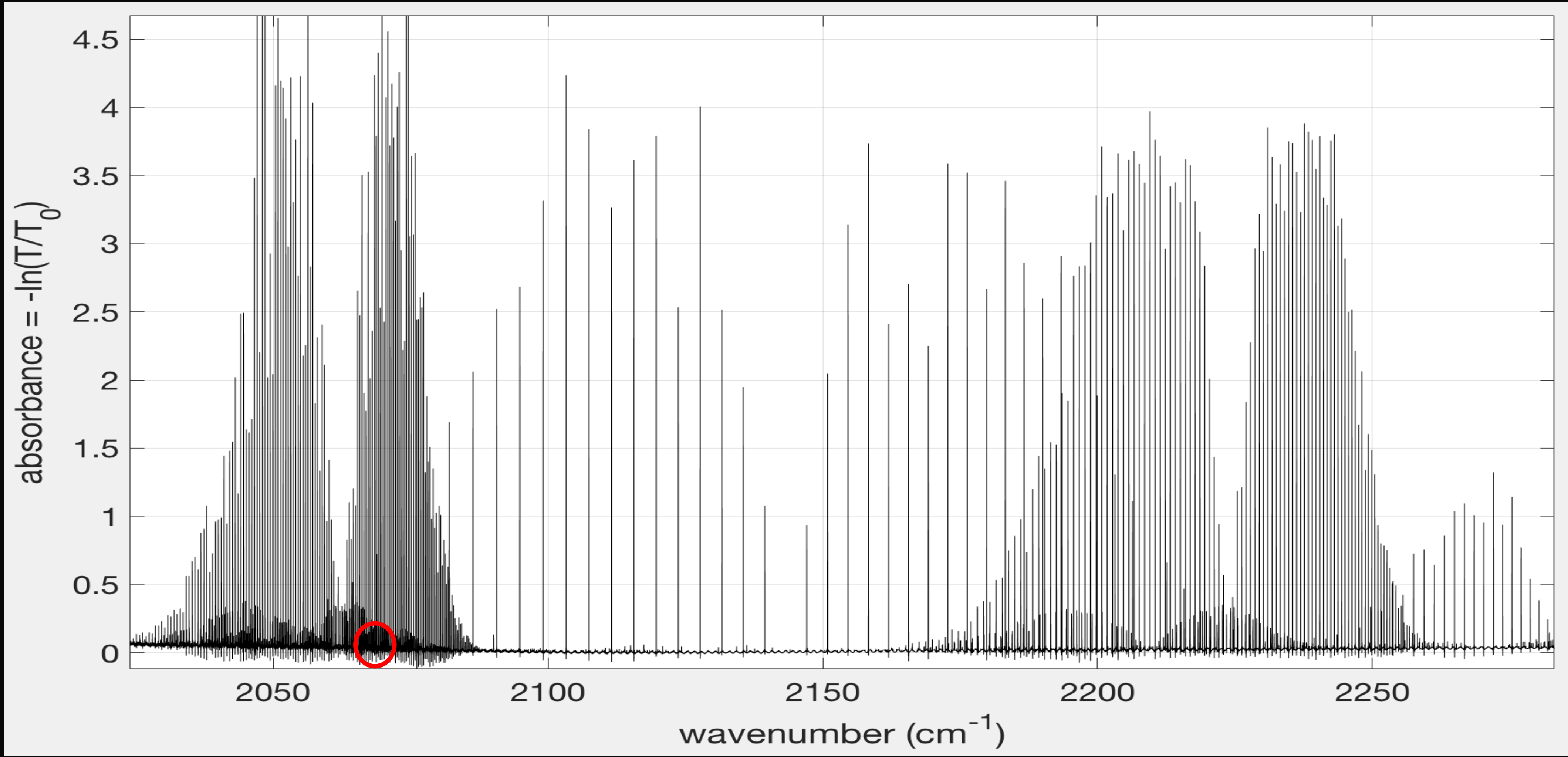
absorbance = -ln(T/T0)
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
3004
3006
3008
3010
3012
3014
3016
3018
wavenumber (cm-1)



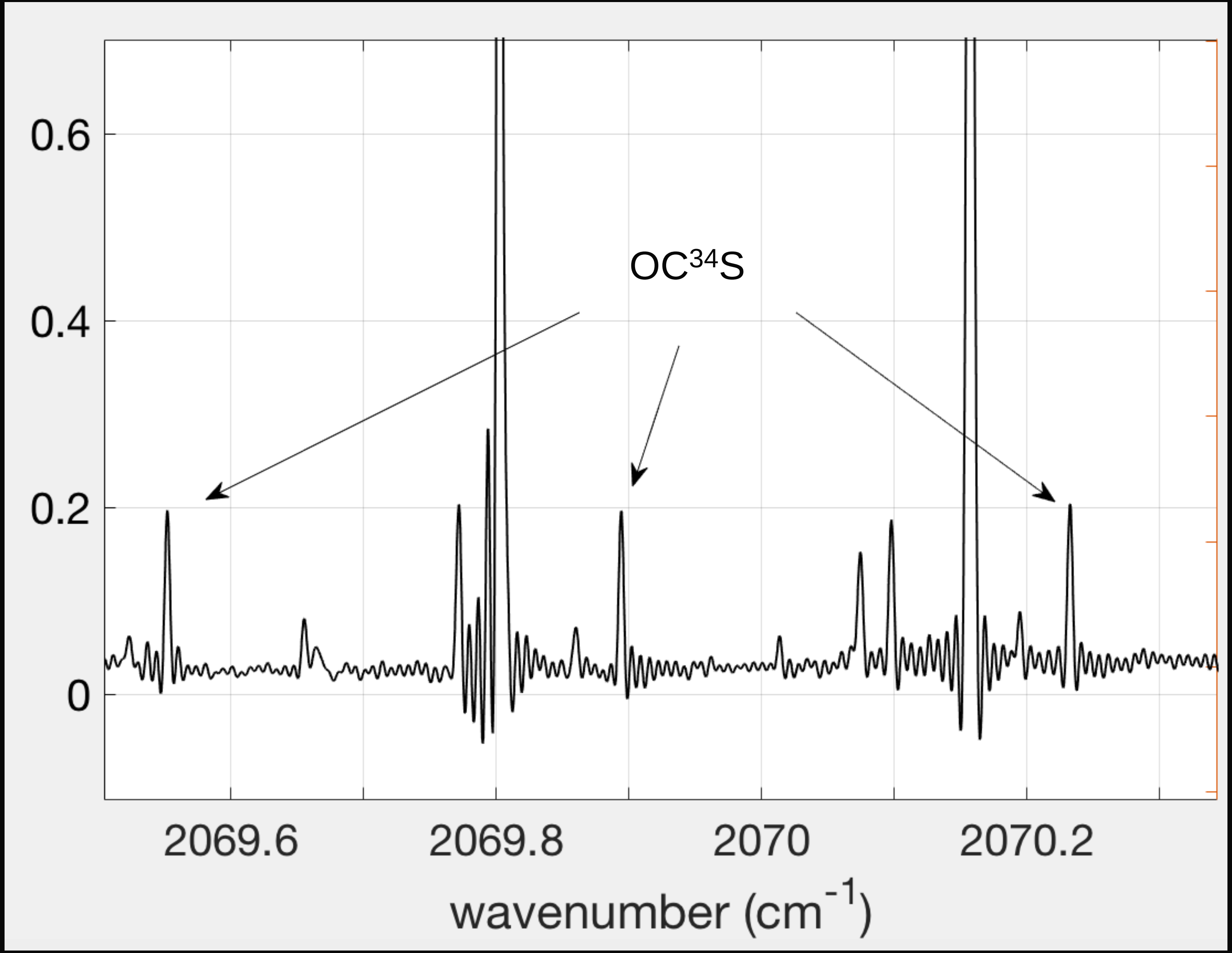
$^{13}CH_4$
experiment
simulation
Absorbance -ln(T/T$_0$)
0.5
0.4
0.3
0.2
0.1
0
-0.1
3007.5
3007.6
3007.7
3007.8
3007.9
3008
3008.1
3008.2
wavenumber (cm^{-1})



absorbance = -ln(T/T0)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
2000
2200
2400
2600
2800
3000
wavenumber (cm-1)

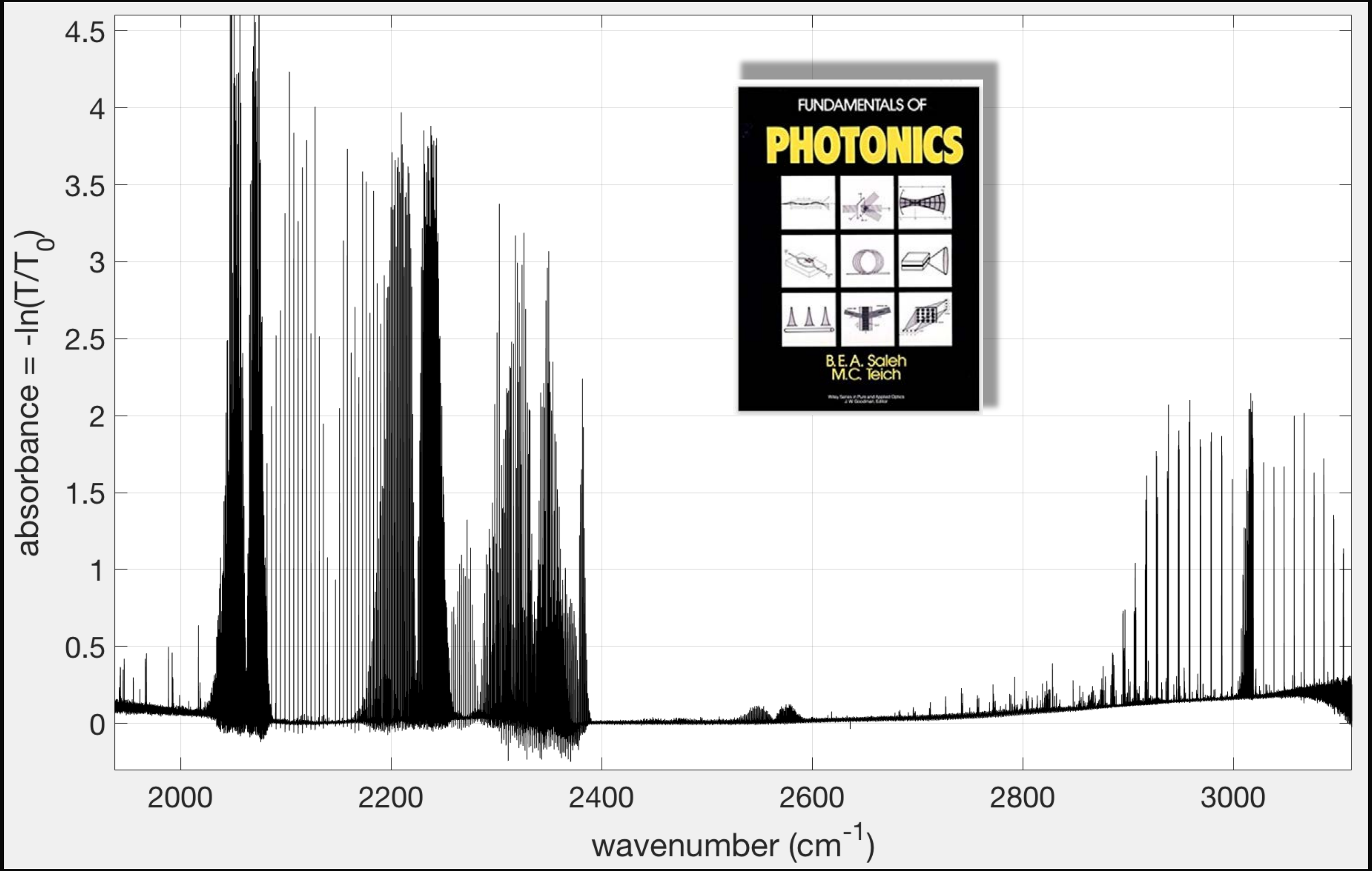


4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
absorbance = -ln(T/T0)
2050
2100
2150
2200
2250
wavenumber (cm-1)



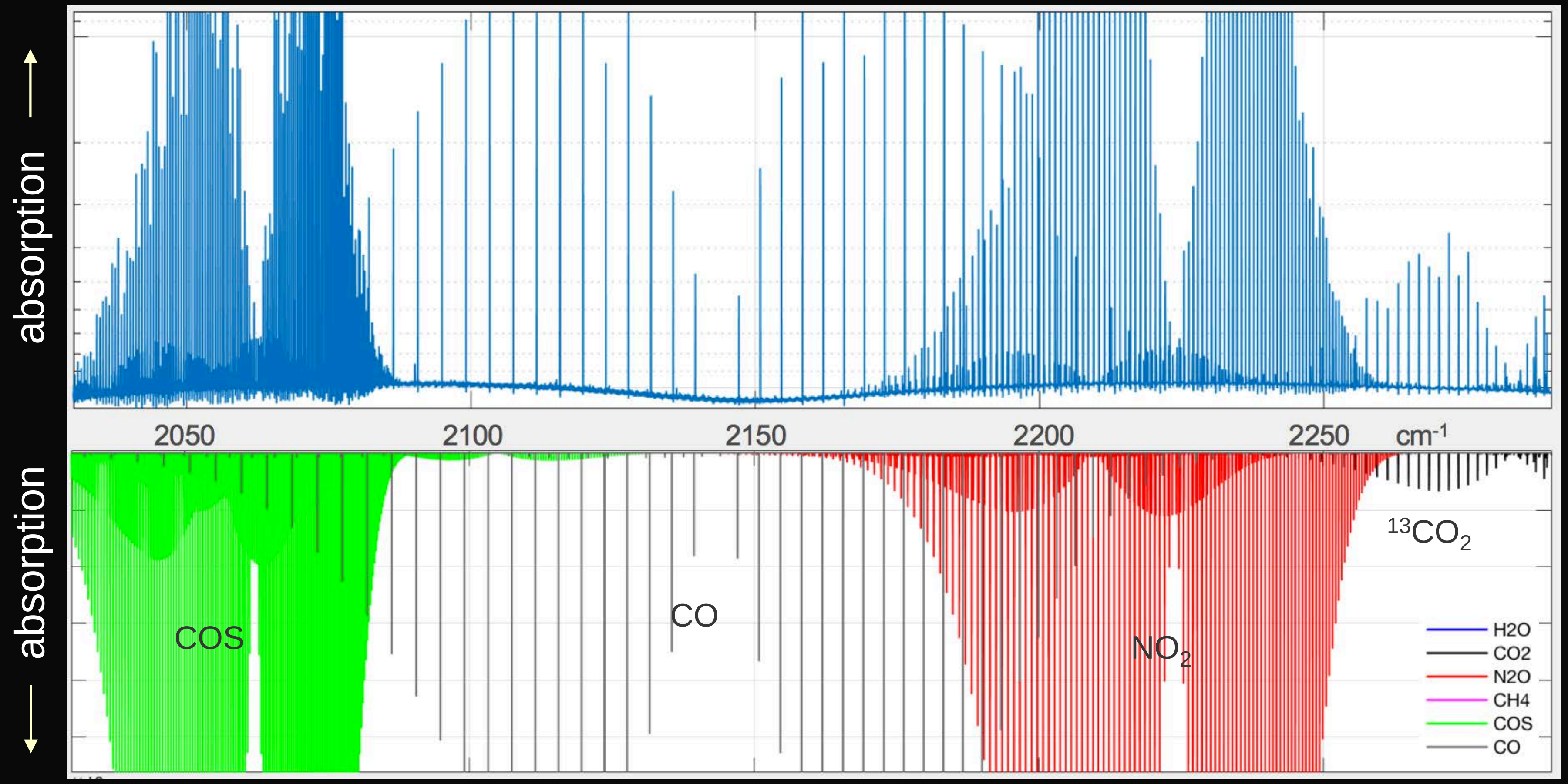
OC34S
0.6
0.4
0.2
0
2069.6
2069.8
2070
2070.2
wavenumber (cm-1)

The amount of information obtained in ~1 sec is equivalent to a thick book



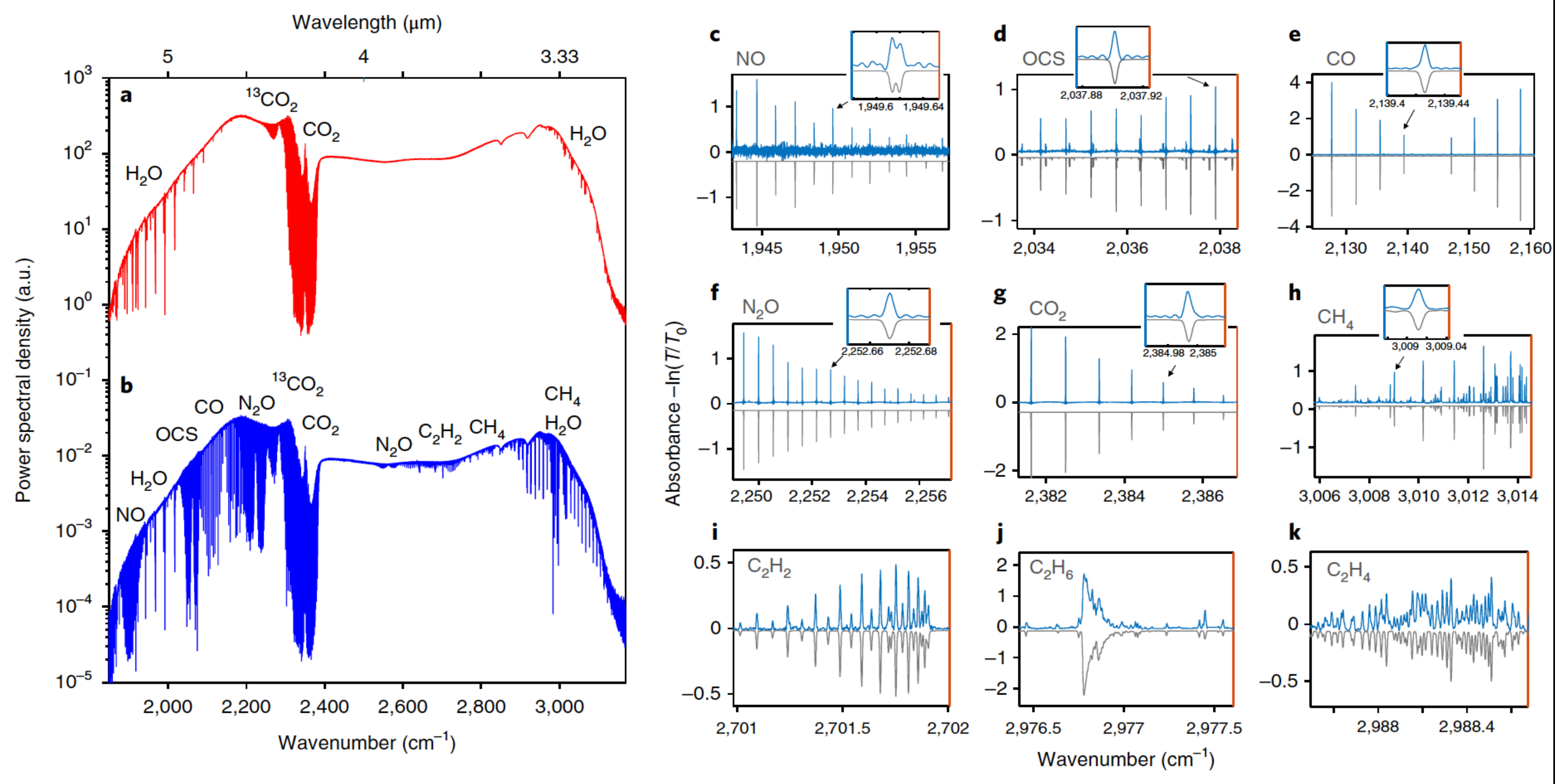
Experiemnt vs. theory (HITRAN)

experiment



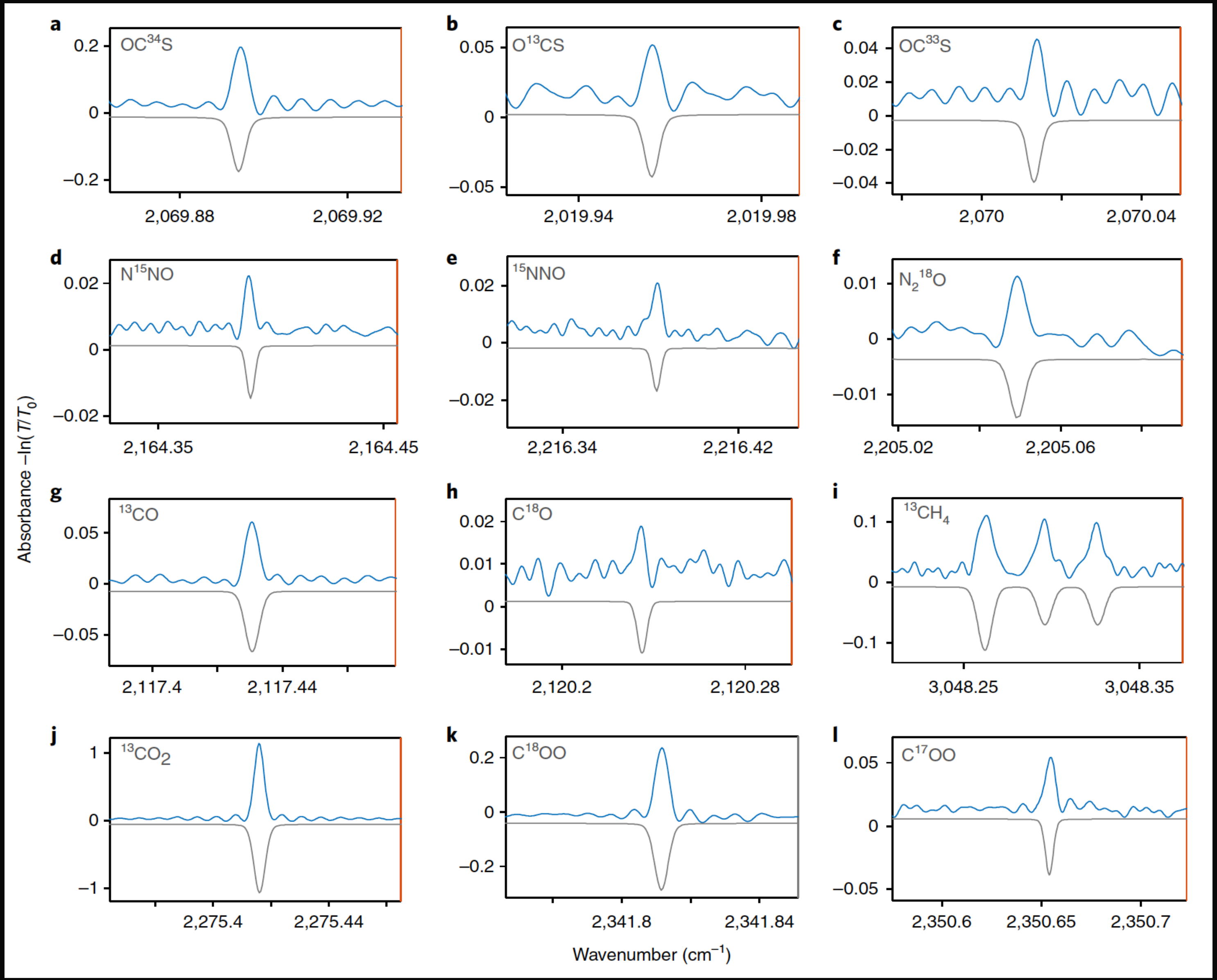
HITRAN

Dual-comb spectra of a mixture of gases at 3 mbar



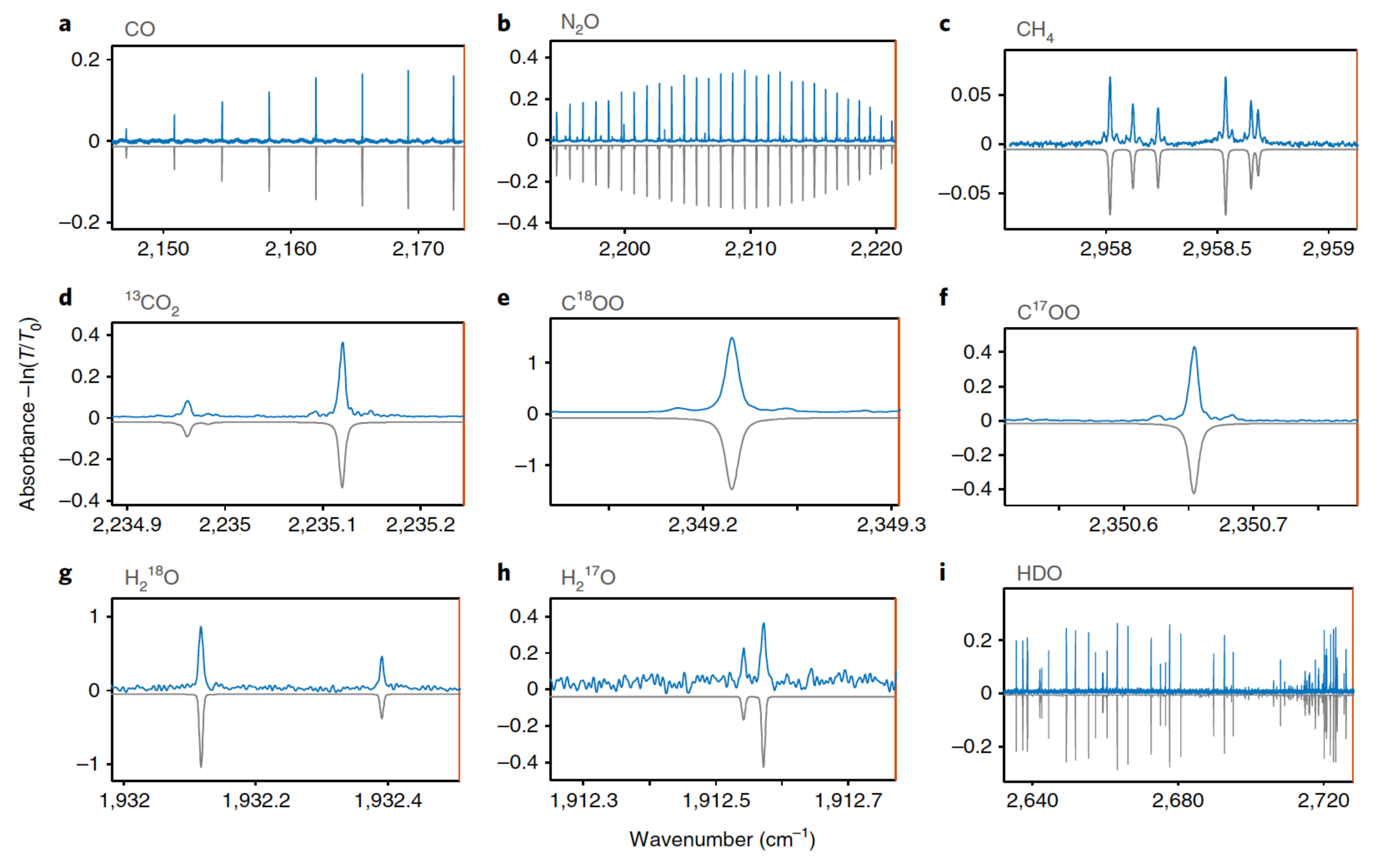
Muraviev, Smolski, Loparo, Vodopyanov, *Nature Photon*. 12, 209 (2018)

Spectra of isotopologues detected in a mixture of gases at 3 mbar

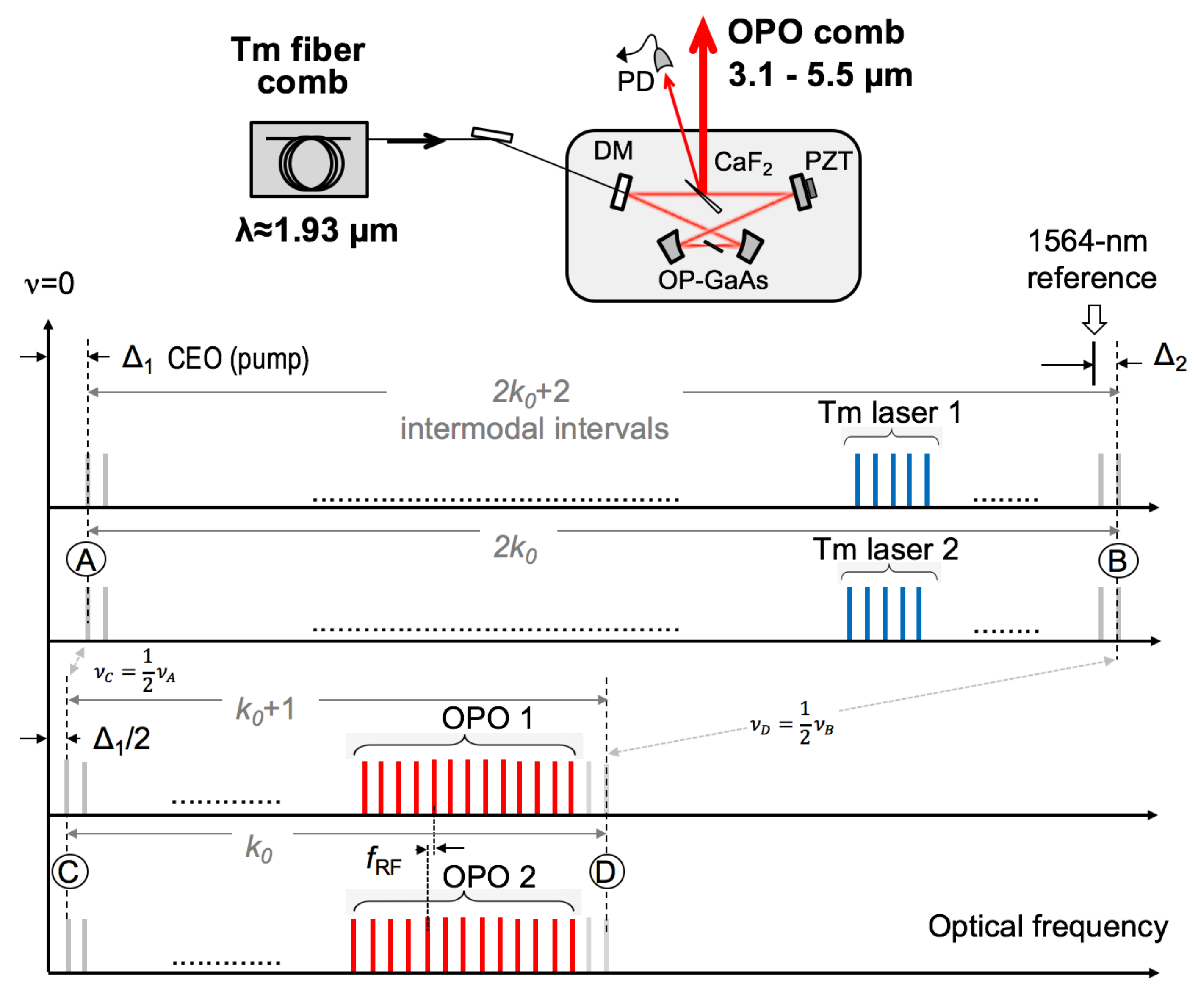


Muraviev, Smolski, Loparo, Vodopyanov, *Nature Photon*. 12, 209 (2018)

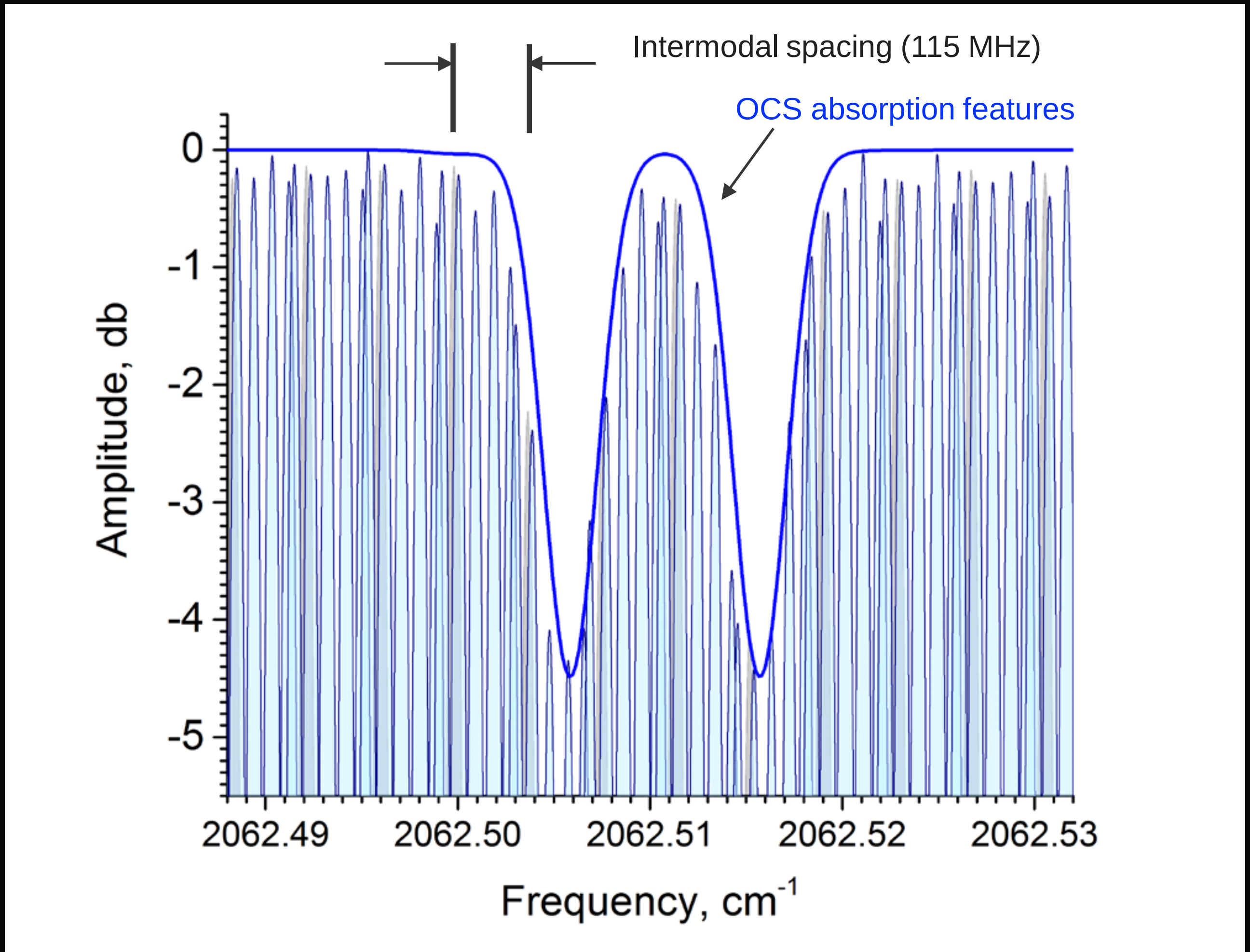
Spectra of trace molecules in ambient air at 10 mbar



Muraviev, Smolski, Loparo, Vodopyanov, *Nature Photon.* 12, 209 (2018)


Tm fiber comb
λ≈1.93 µm
OPO comb
3.1 - 5.5 µm
PD
DM
CaF2
PZT
OP-GaAs
1564-nm reference
ν=0
Δ1 CEO (pump)
Δ2
2k0+2 intermodal intervals
Tm laser 1
2k0
Tm laser 2
A
B
νC = 1/2 νA
k0+1
OPO 1
Δ1/2
νD = 1/2 νB
k0
fRF
OPO 2
C
D
Optical frequency

Acquiring spectral data at interleaved comb frequencies



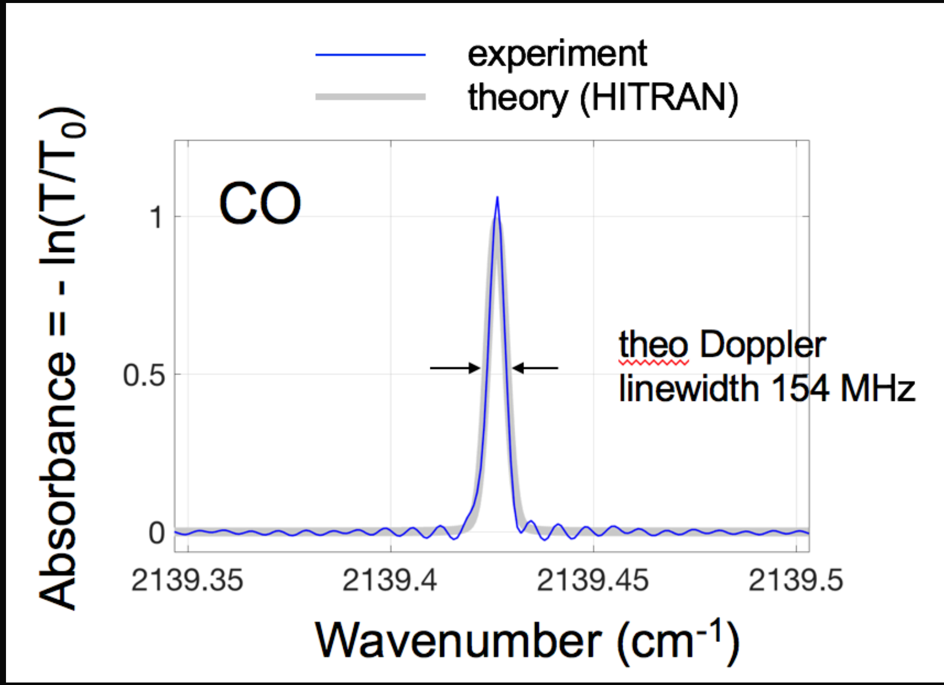
Tuning the frequency of the CW reference laser and thus shifting the combs allowed resolution below intermodal spacing (f_{rep})

Absolute frequency referencing

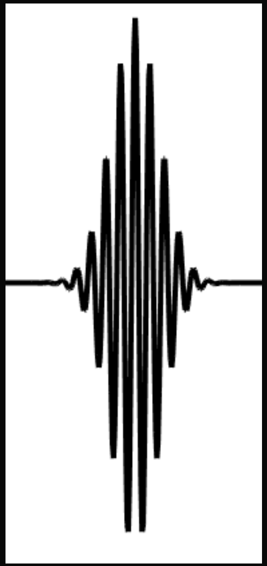
FS725 — 10 MHz Rb frequency standard
accuracy ± 5×10^{-11}

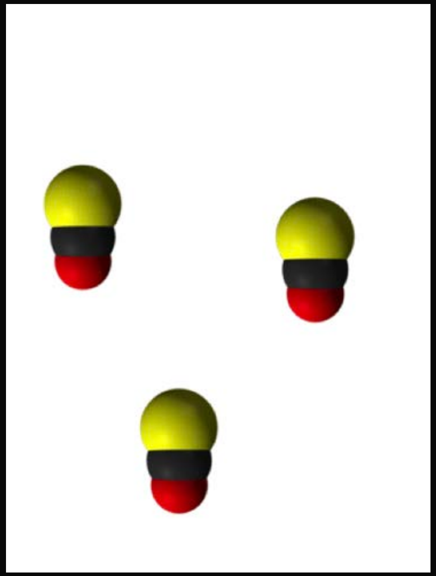
This converts to 4 kHz absolute referencing

Frequency counters



Time picture: free induction decay of molecules





The angular momentum of molecules is quantized:

$$I\omega = J\hbar$$

I - momentum of inertia
J = 0,1,2, ...

Hence the rotation speeds are quantized; the molecules periodically rephase (every $T=2\pi/\Delta\omega$) to generate additional pulses of coherently forward-scattered light called commensurate echoes.

Free induction decay of molecules

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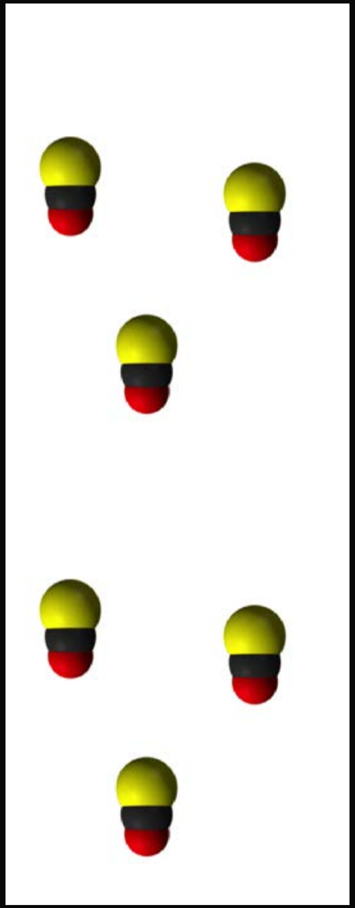
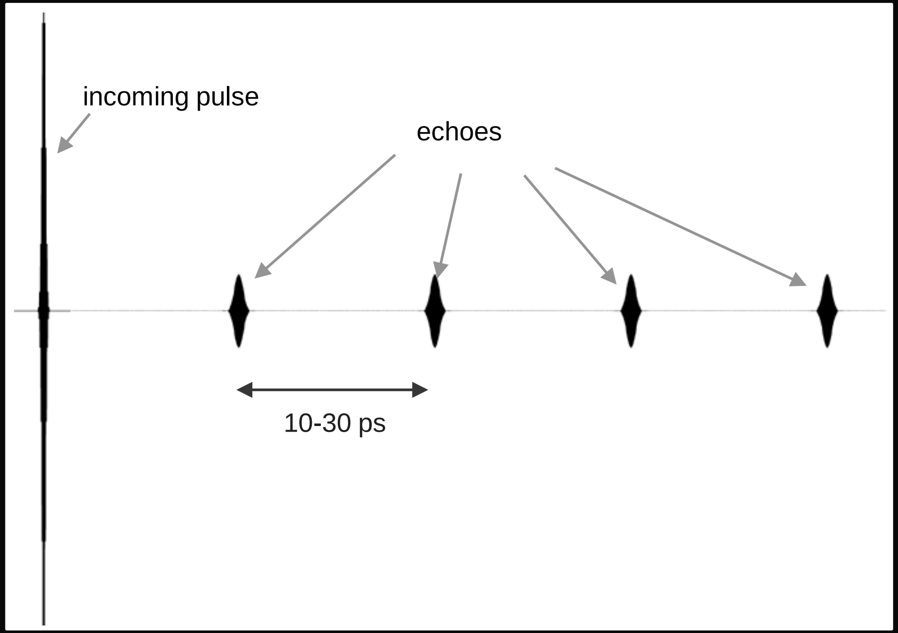
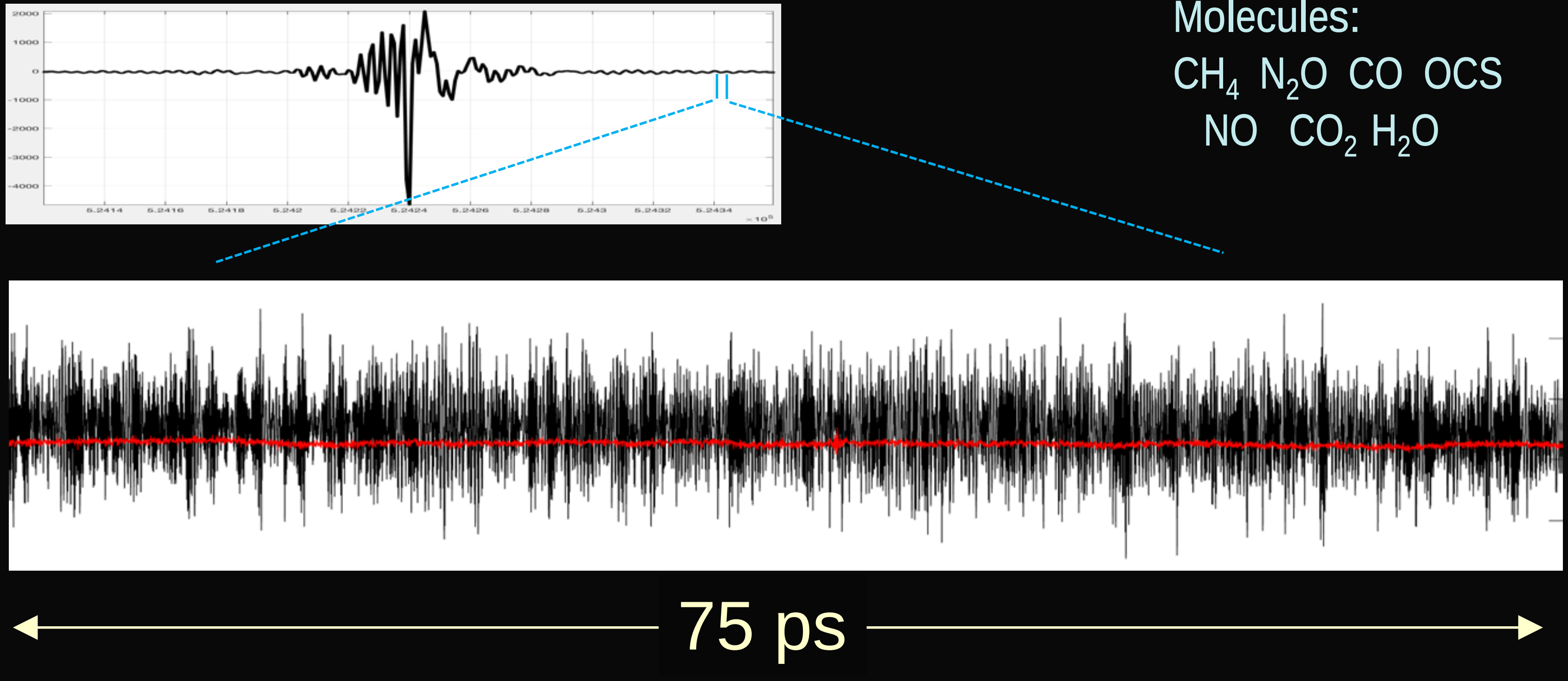


Hence the rotation speeds are quantized; the molecules periodically rephase (every T=2π/Δω) to generate additional pulses of coherently forward-scattered light called commensurate echoes.

Eeach type of molecules emits a train of subpicosecond pulses



Hearing the molecules



Molecules:
CH_4 N_2O CO OCS
NO CO_2 H_2O

mixture of molecules

vacuum

Molecular vibrations were slowed down by 25 billion times (2.5×10^{10})

Towards two-octave-wide span: Cr:ZnS - pumped OP-GaAs system

Kerr-lens mode-locked Cr:Zns laser at ~ 2.35 µm


5054 Vol. 40, No. 21 / November 1 2015 / Optics Letters **Letter**

Optics Letters

Three optical cycle mid-IR Kerr-lens mode-locked polycrystalline Cr^{2+}:ZnS laser

Sergey Vasilyev,[1,*] Igor Moskalev,[1] Mike Mirov,[1] Sergey Mirov,[1,3] and Valentin Gapontsev[2]

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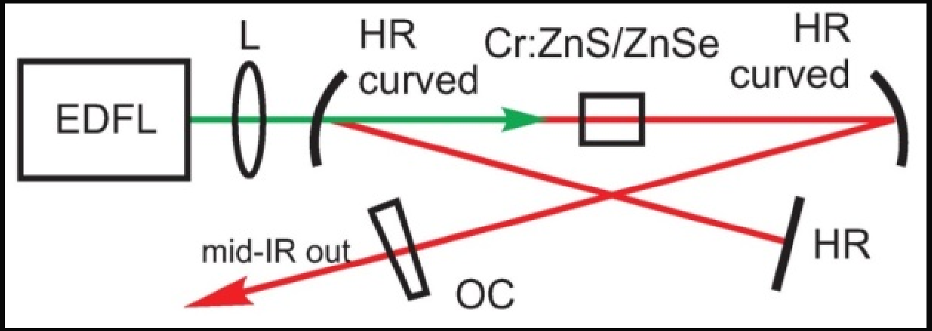
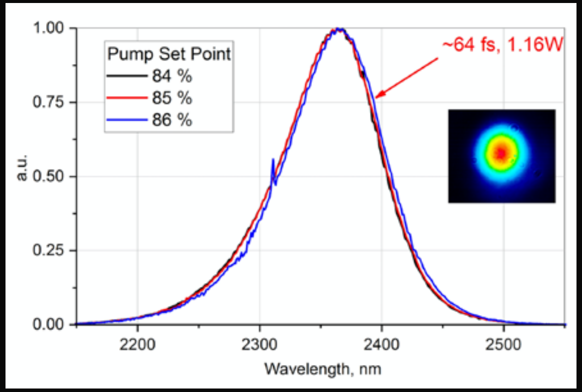
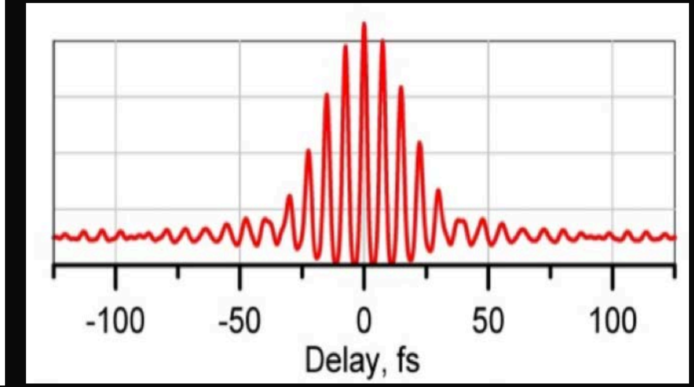
[3]Center for Optical Sensors and Spectroscopies, University of Alabama at Birmingham, 1530 3rd Avenue South, Birmingham, Alabama 35294, USA





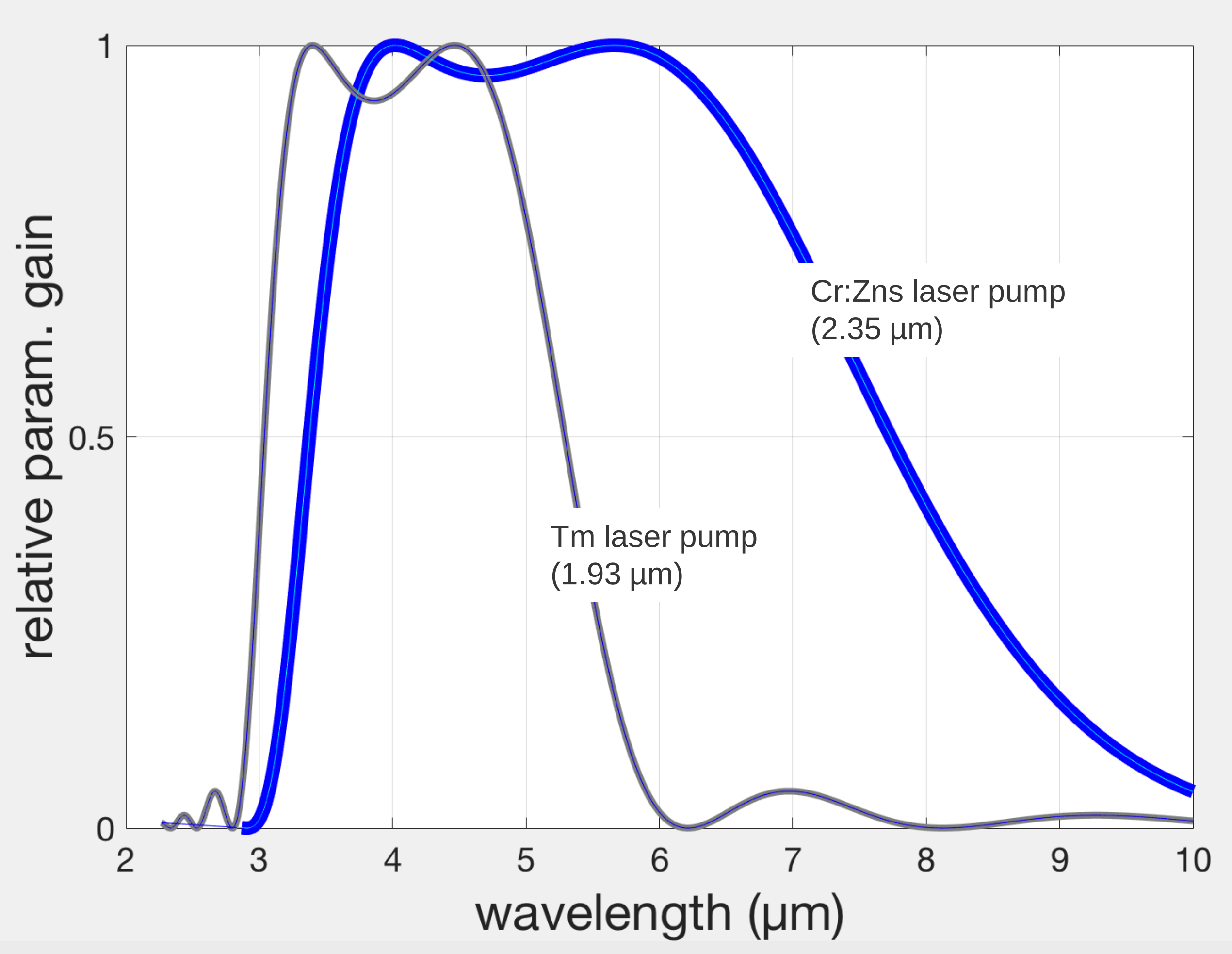


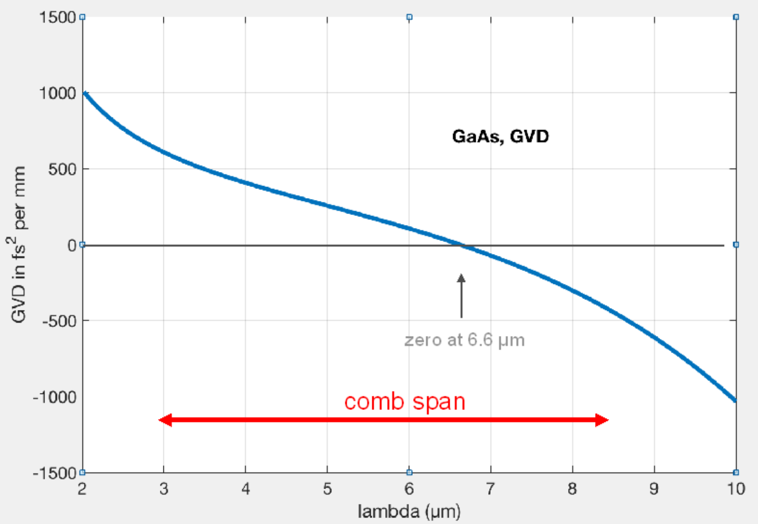
"Ti:Sapphire of the mid-IR"

Broadband,
High Kerr coefficient (3 times Ti:Sapph.)
Convenient pumping: Er-fiber, Tm- fiber

Rep. rate: 80 MHz – 1.2 GHz
Duration: from 100 fs down to 19 fs
Ave. power: up to 1.8 Watts from an oscillator

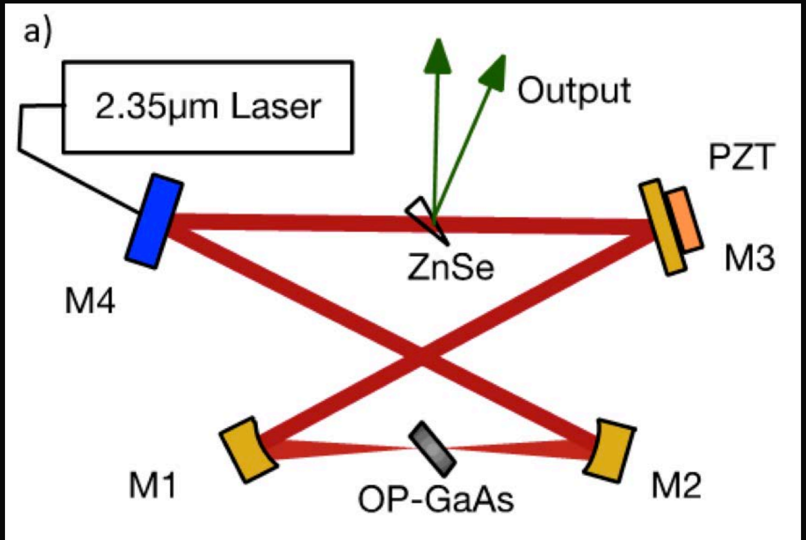
Parametric gain bandwidth for 500-µm-long GaAs

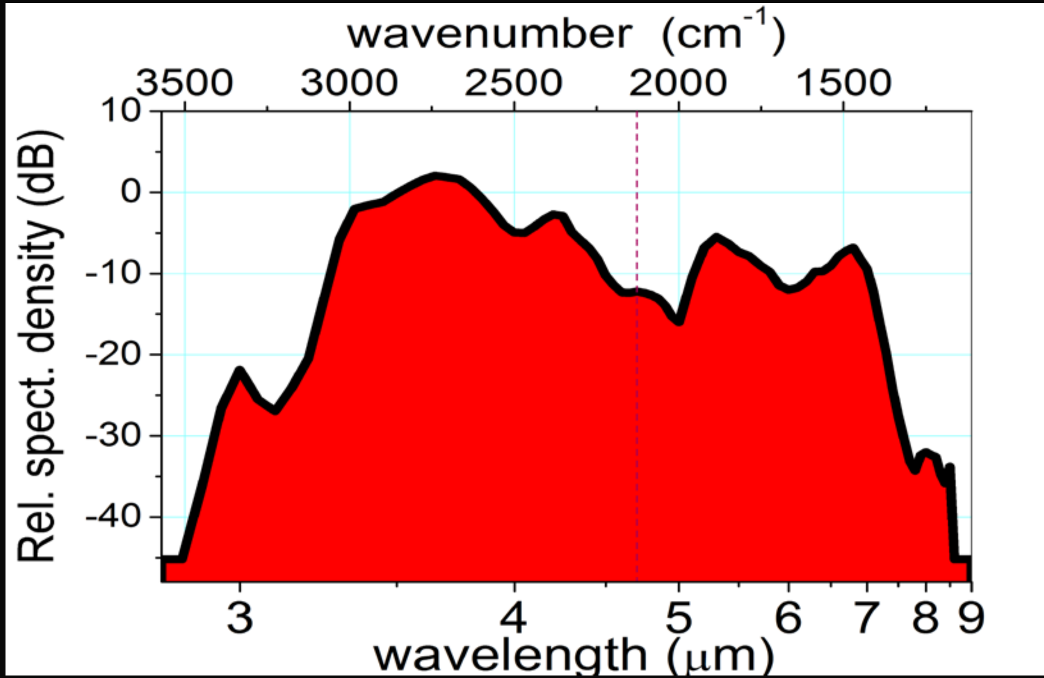




Cr:ZnS - pumped OP-GaAs system

Collaboration with Sergey Mirov's group (UAB / IPG)



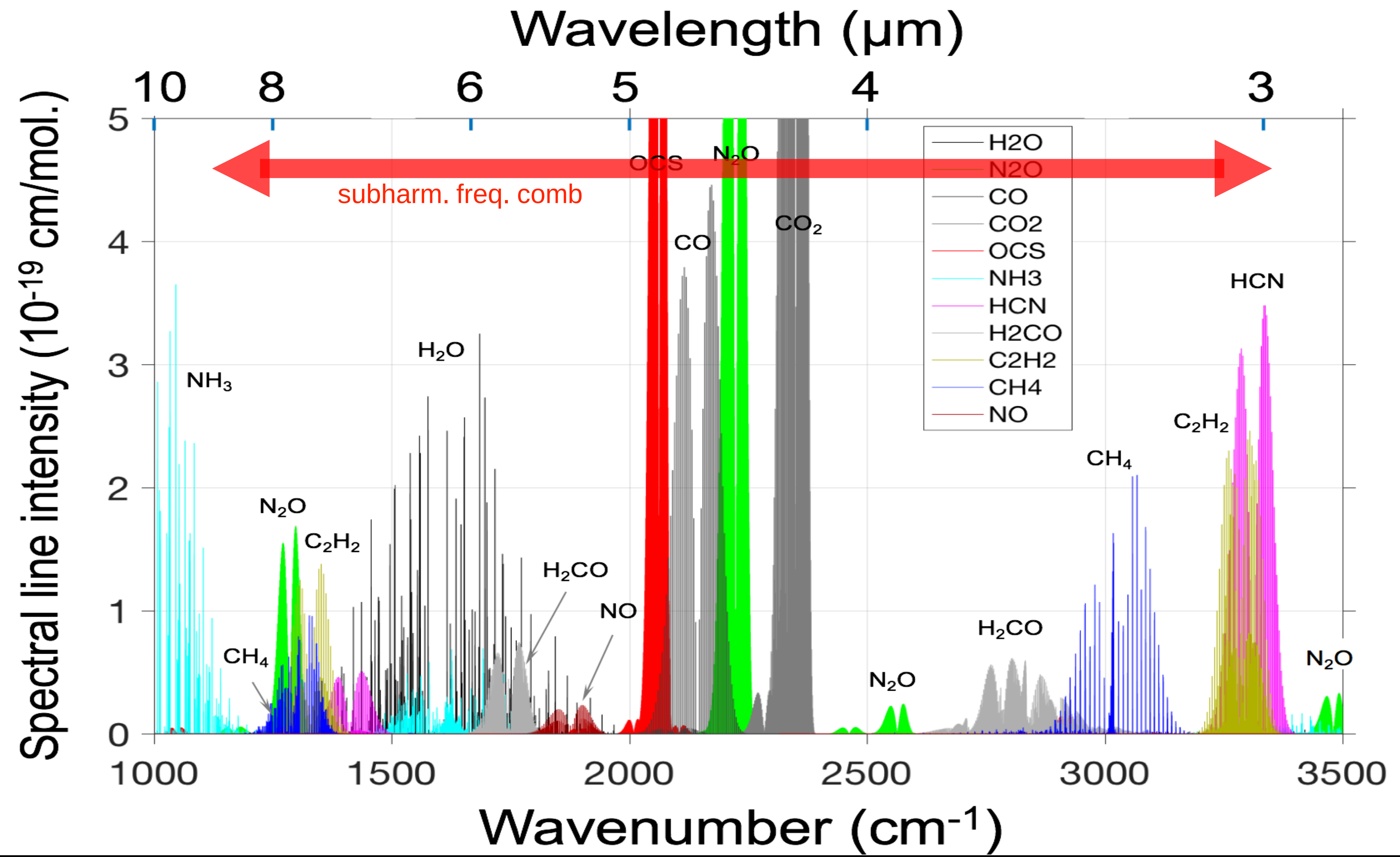


A subharmonic OPO based on 0.5-mm-thick OP-GaAs pumped by a 62-fs Kerr-lens mode-locked Cr:ZnS oscilaltor (2.35 µm, 79 MHz, 800 mW).

Broadband (3–9 µm) output.
120 mW average power
(Subharmonic conversion efficiency ~ 20%).
OPO pump depletion 85%.

Ru, Zhong, Lee, Loparo, Schunemann4, Vasilyev, Mirov, Vodopyanov, CLEO '2017

Spectral span, Cr:ZnS (2.35 µm) pumped subharmonic GaAs OPO

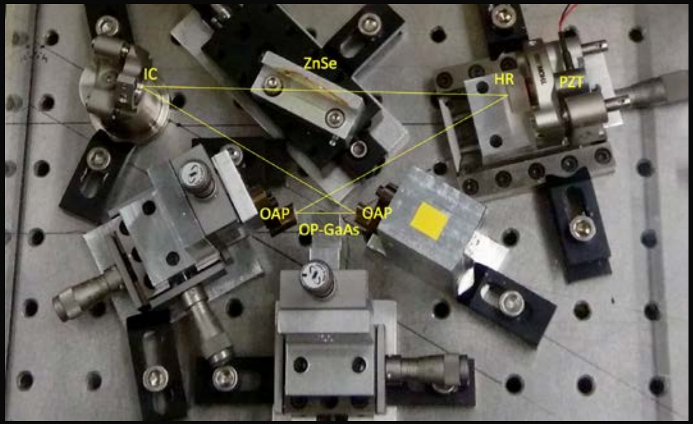


High-power GHz system, span 3–8 μm

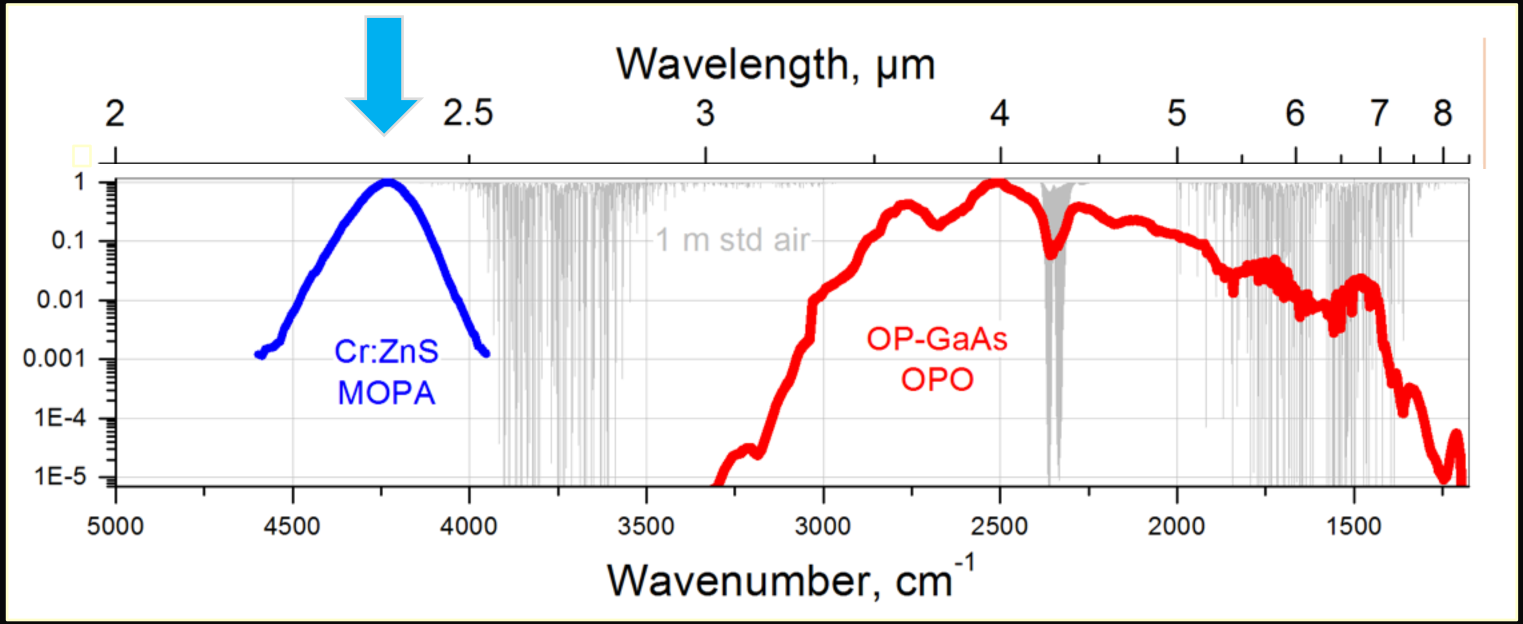
Pump: KLM Cr^{2+}:ZnS laser 2.35 μm, 77 fs, **0.9 GHz**, 6 W

Subharmonic OPO based on a QPM OP-GaAs crystal.

0.5-W output in the form of a broadband (3–8 μm) spectrum



KLM Cr:ZnS laser 2.35 μm



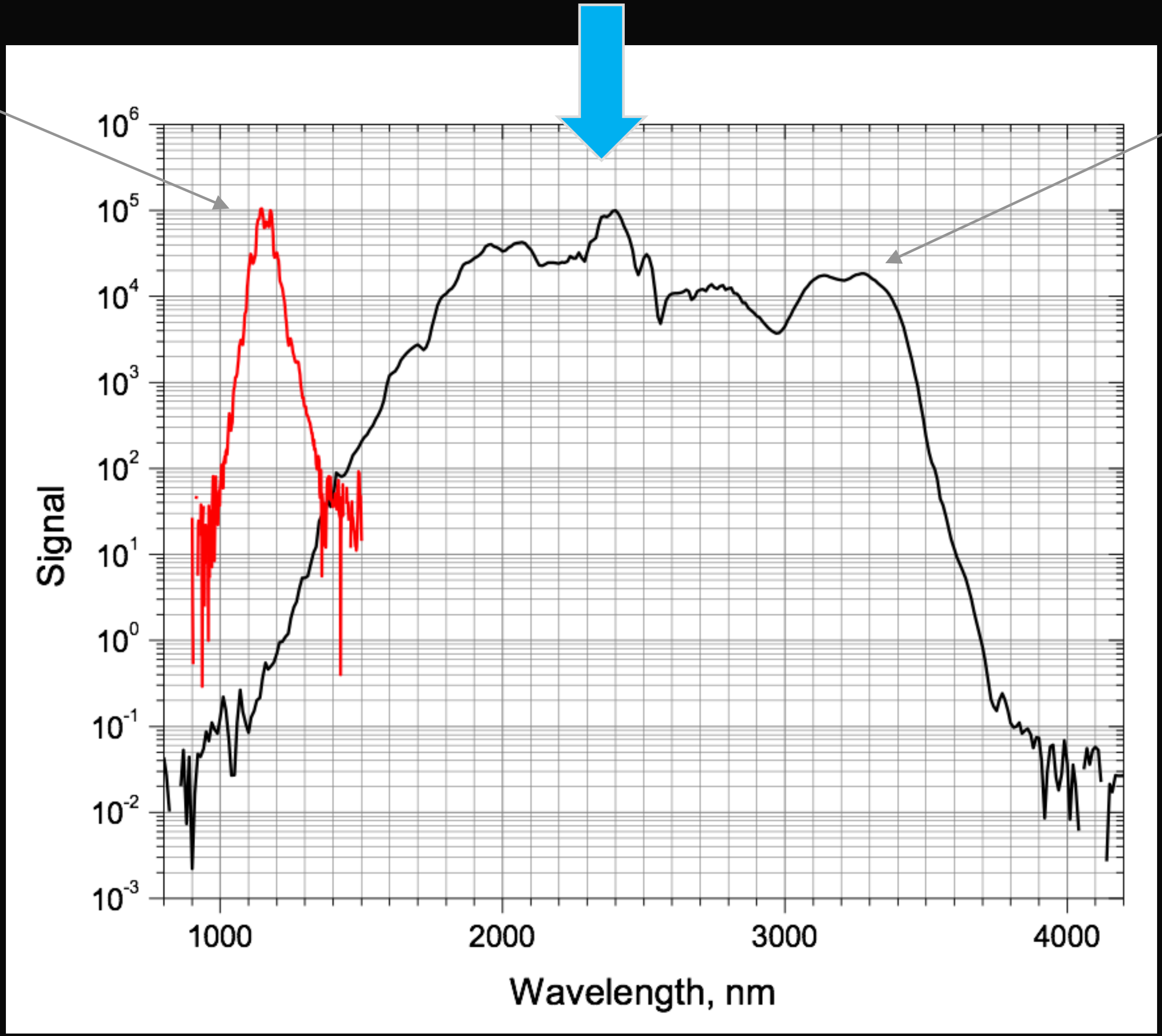
Smolski, Vasilyev, Moskalev, M. Mirov, Ru, Muraviev, Schunemann, S. Mirov, Gapontsev, Vodopyanov, Appl. Phys. B (in press)

Two octaves-wide supercontinuum in SiN waveguide

KLM Cr:ZnS laser 2.35 μm

Second harmonic of the Cr:ZnS laser

Supercontinuum spectra generated in SiN waveguide



Collaboration:

S. Mirov group
T. Kippenberg group

Non-invasive diagnostics via breath

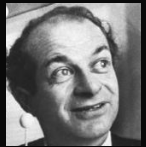
Breath testing is probably the least invasive of all diagnostic tests. For centuries, physicians used a “sniff test” of patient’s breath to diagnose conditions like diabetes. Breath is most informative medium: it contains a rich assortment (> 200) of volatile metabolites (usually in trace amounts) that carry enough information about the body’s metabolism for an accurate diagnosis for many conditions.

Biomarkers in human breath

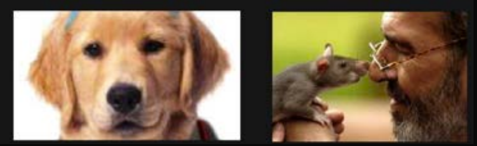
... concept that breath contains molecules that originated from normal or abnormal physiology...

Hippocrates of Kos

Antoine Lavoisier



Linus Pauling



Animals can be used for sensitive diagnostics

nitric oxide - asthma

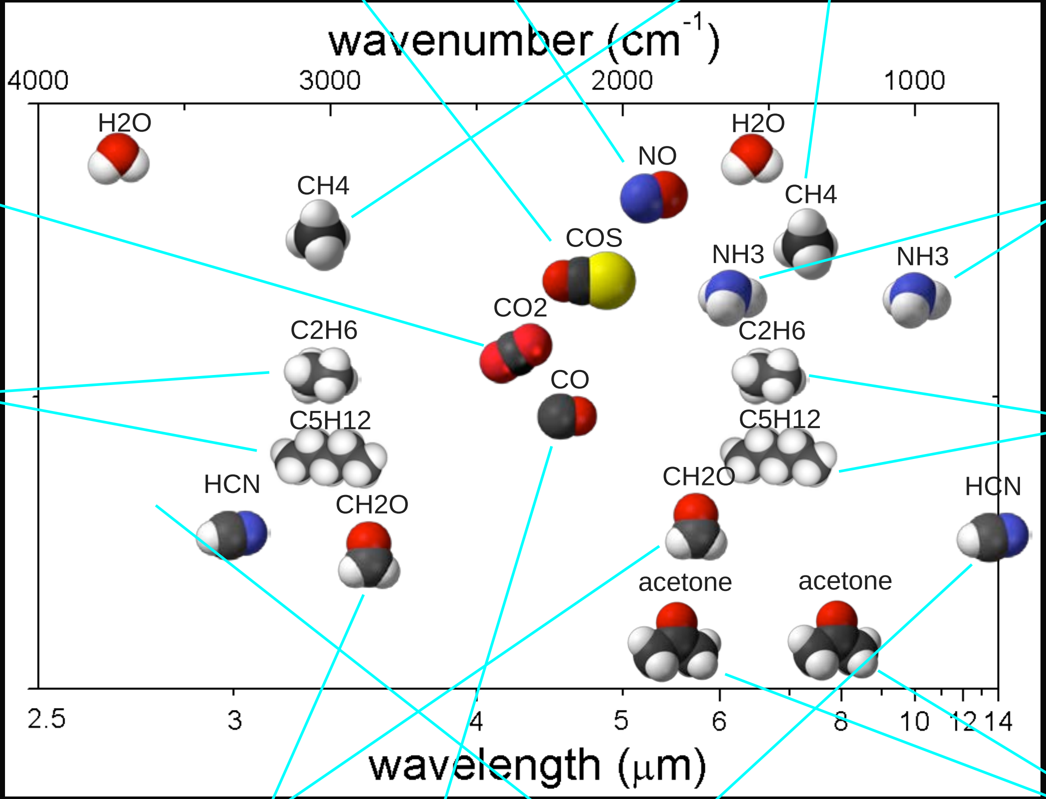
methane - gut bacteria

carbonyl sulfide - liver disease, transplant rejection

carbon dioxide – stomach ulcer

ammonia – liver disease, renal failure

ethane, pentane – lipid peroxidation



ethane, pentane – lipid peroxidation

formaldehyde - breast cancer

carbon monoxide - asthma, hyperbilirubinemia

hydrogen cyanide - cystic fibrosis

acetone - diabetes

Conclusion

- Highly coherent dual-comb subharmonic OPO system pumped by phase-locked Tm-fiber combs
- Simultaneous acquisition of 350,000 spectral data points over 3.1–5.5 μm
- Parallel detection of 22 trace molecular species in a mixture including isotopes: ^{13}C, ^{18}O, ^{17}O, ^{15}N, ^{34}S, ^{33}S and ^{2}H (deuterium)
- Part-per-billion level sensitivity and sub-Doppler resolution.
- Absolute optical frequency referencing to atomic clock
- Feasibility for kilohertz-scale spectral resolution
- Subharmonic combs - extendable to 2 octaves with 2.35 μm fs pump

Special thanks:

Andrey Muraviev
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Martin Fermann
IMRA America, Inc., USA

Sergey Mirov
Sergey Vasilyev
Viktor Smolski
IPG Photonics

Peter Schunemann
BAE Systems, Inc., USA