Leveraging quantum calculations and independent spectroscopic measurement techniques to yield line intensities with relative uncertainties at the permille level

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Metrology for Climate Action, 26-30 September 2022

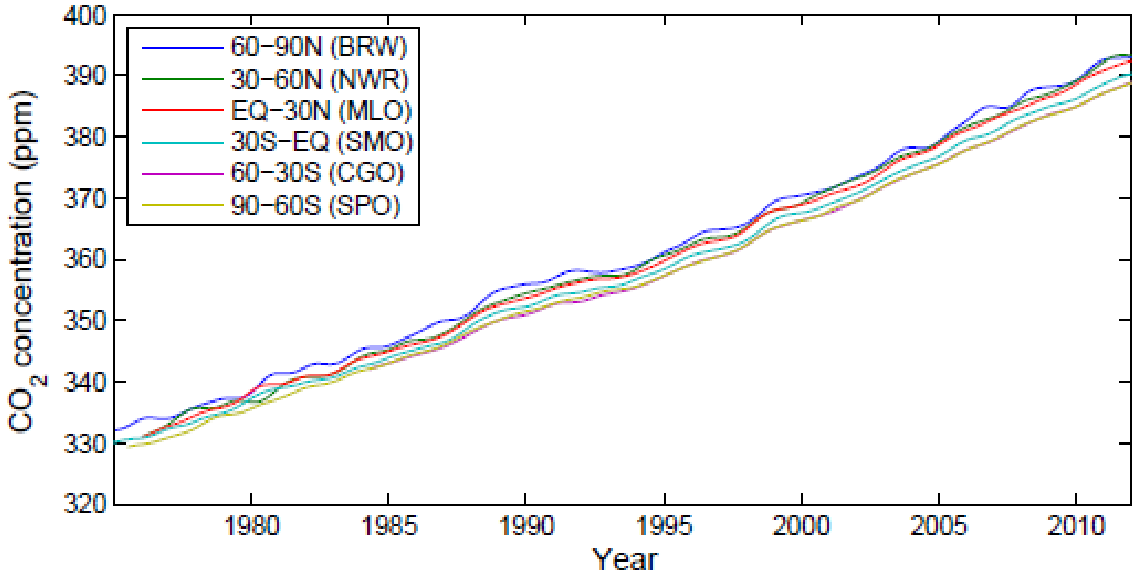
Outline

1. Motivation
2. Accuracy requirements
3. Lack of data compliance in literature data
4. Idea: theory + experiment
5. Previous study: CO_2 case
6. Present study: CO case
    - theory
    - three experiments
7. Comparisons between experiments and theory
8. Comparison with literature data
9. Conclusions & perspectives

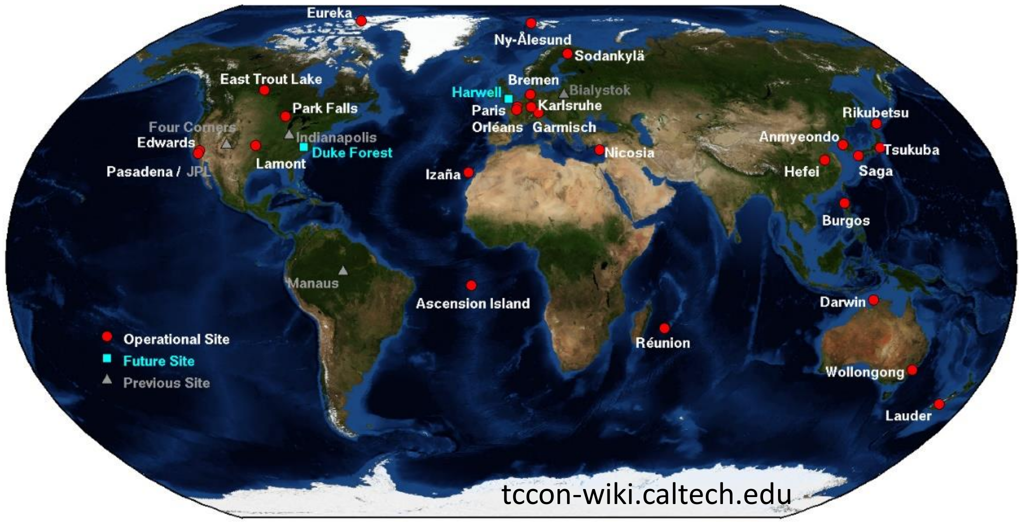
Motivation: atmospheric applications

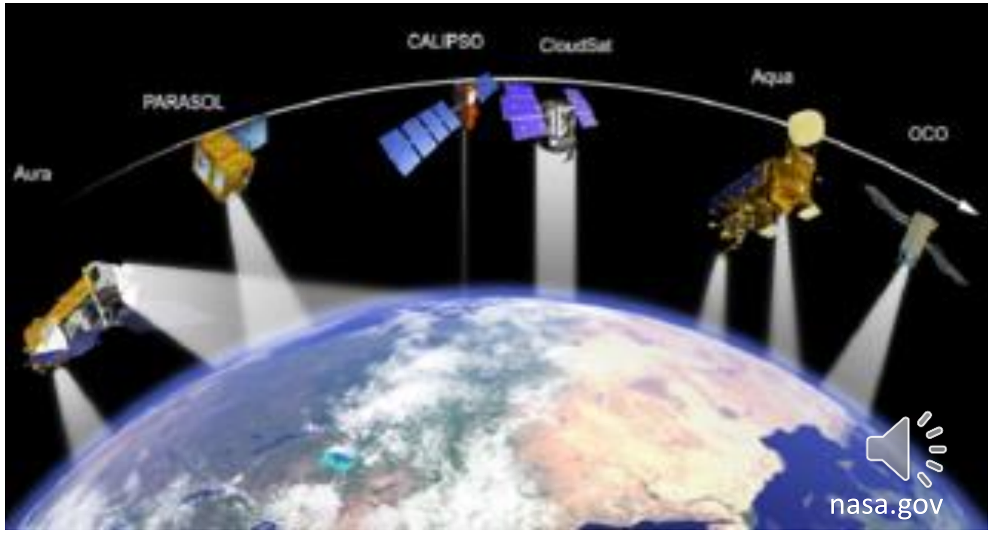
TCCON
total carbon column observing network

- transportation processes
- greenhouse gases
- sources of contaminants
- terrestrial vegetation
- chemical processes
- pressure and temperature profiles
- remote cloud detection
- stratospheric winds
- …



Barlow et al., Atmos. Chem. Phys. 15, 13739 (2015)





What accuracy is needed?

- Explanation of regional CO_2 fluxes requires accuracy of 1 ppm (2.5‰)

D. R. Thompson et al., J. Quant. Spectrosc. Radiat. T. 113, 2265 (2012); C. Miller et al., J. Geophys. Res. 112, D10314 (2007)

- CO: trace gas in the atmosphere, used for monitoring transportation processes, affects formation of greenhouse gases

World Meteorological Organization: inter-laboratory comparisons at 1 ppb or 5‰ level are needed

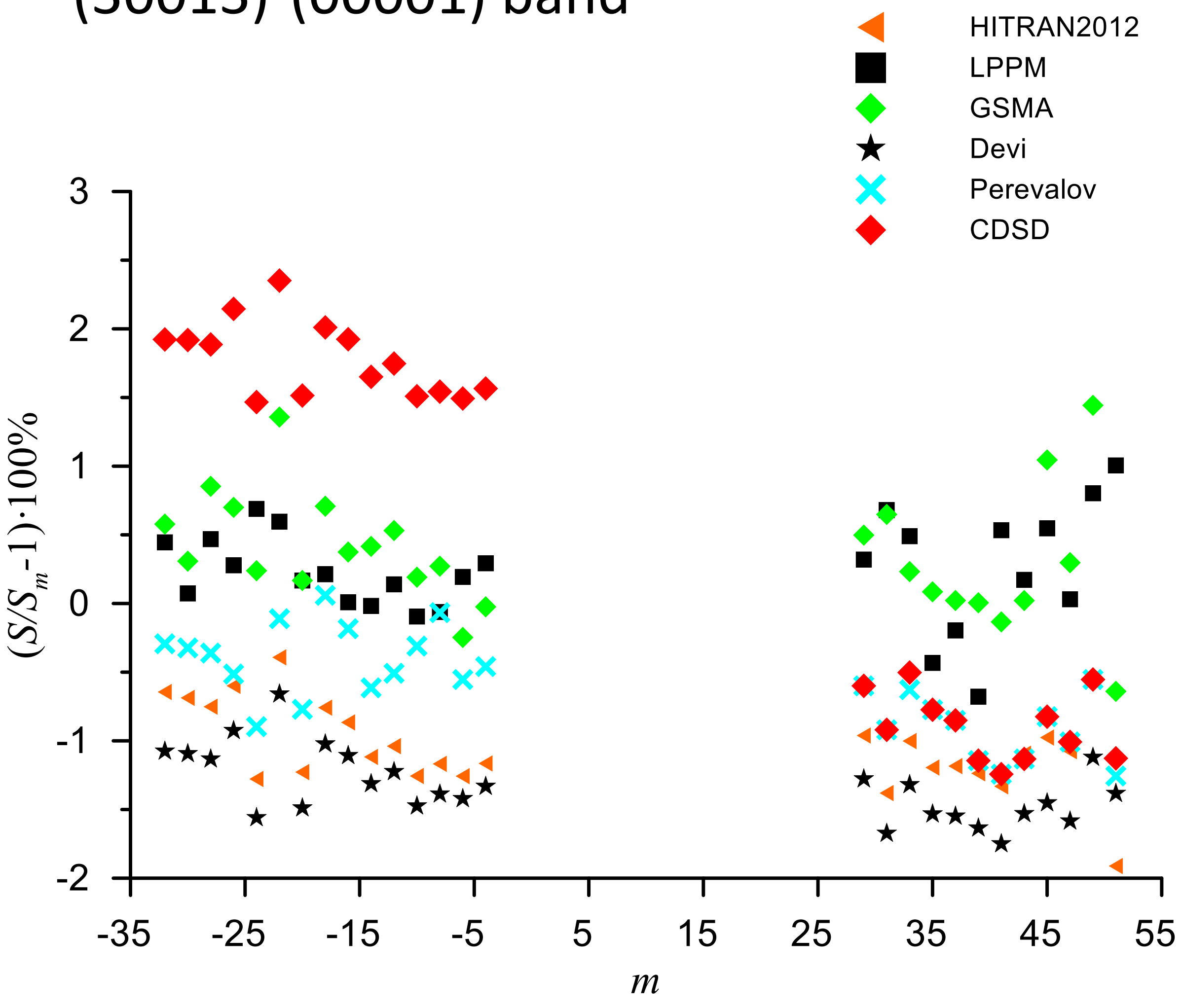
P. Tans, P. Zellweger (eds.), 18th WMO/IAEA meeting on carbon dioxide, other greenhouse gases and related measurement techniques (GGMT-2015). GAW Report No. 229: World Meteorological Organization (2016)

- Remote sensing claims measurement accuracy as good as ~2‰

Y. Yuan et al., Remote Sens. 11, 2981 (2019); D. Wunch et al., Phil. Trans. Roy. Soc. A 369, 2087 (2011)

Motivation: lack of data compliance

CO_2
(30013)-(00001) band



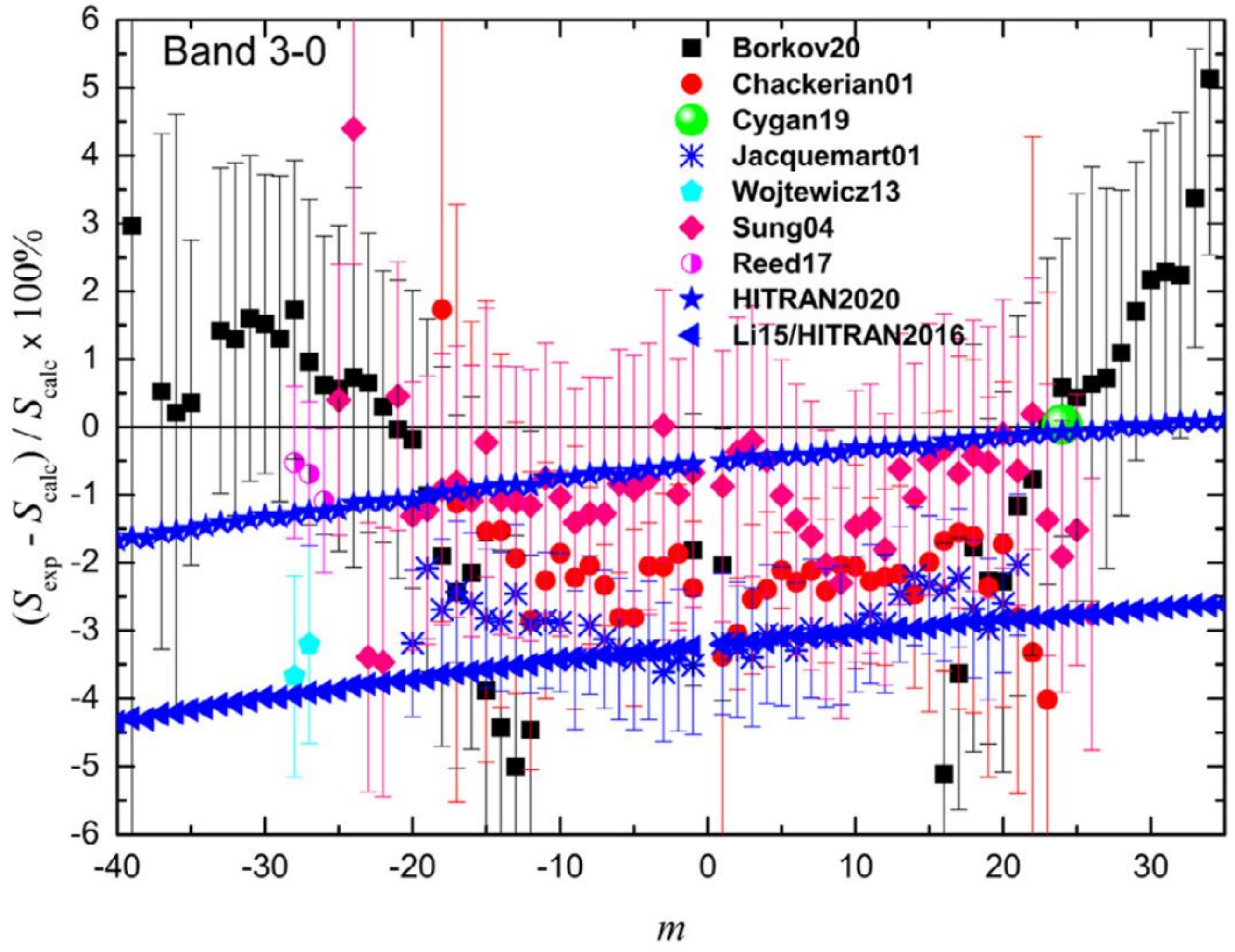
10x better accuracy is expected!

Theory:
V. I. Perevalov et al., J. Mol. Spectrosc. 252, 190 (2008)
S. A. Tashkun and V. I. Perevalov, JQSRT 112, 1403 (2011) (CDSD)
L. S. Rothman e al., JQSRT 130, 4 (2013) (HITRAN 2012)

Experiment:
V. M. Devi et al., J. Mol. Spectrosc. 245, 52 (2007)
D. Boudjaadar et al., J. Mol. Spectrosc. 238, 108 (2006) (GSMA, LPPM)

Motivation: lack of data compliance

CO (3-0) band



10x better accuracy is expected!

V. V. Meshkov et al., J. Quant. Spectrosc. Radiat. Transf. 280, 108090 (2022)

Our road to permille level line intensities: CO_2 case

Theory verified by experiment

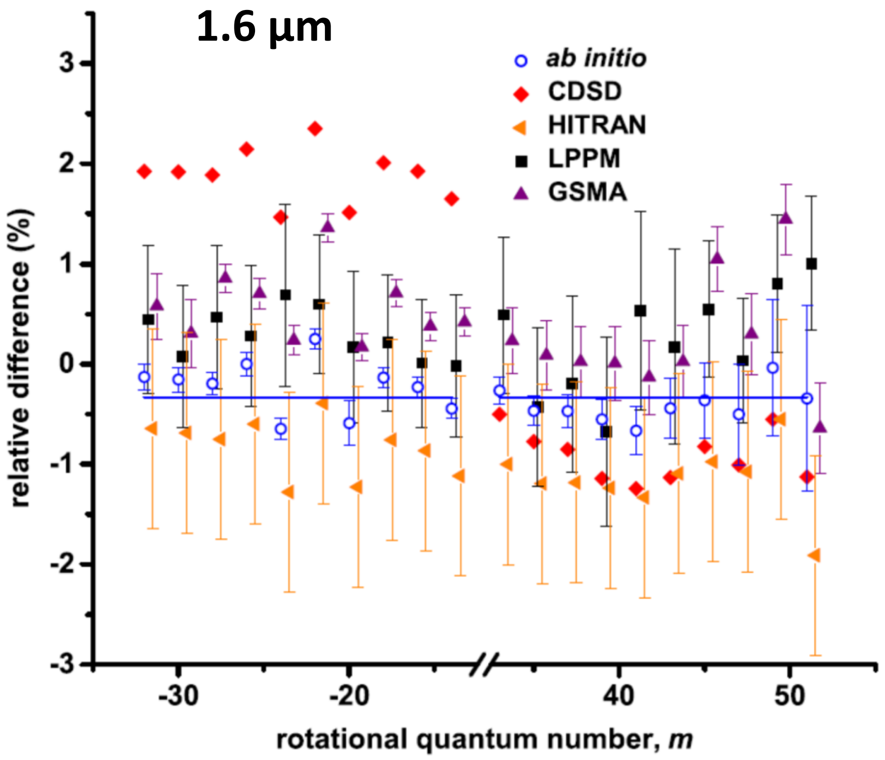
Highly-accurate calculations:

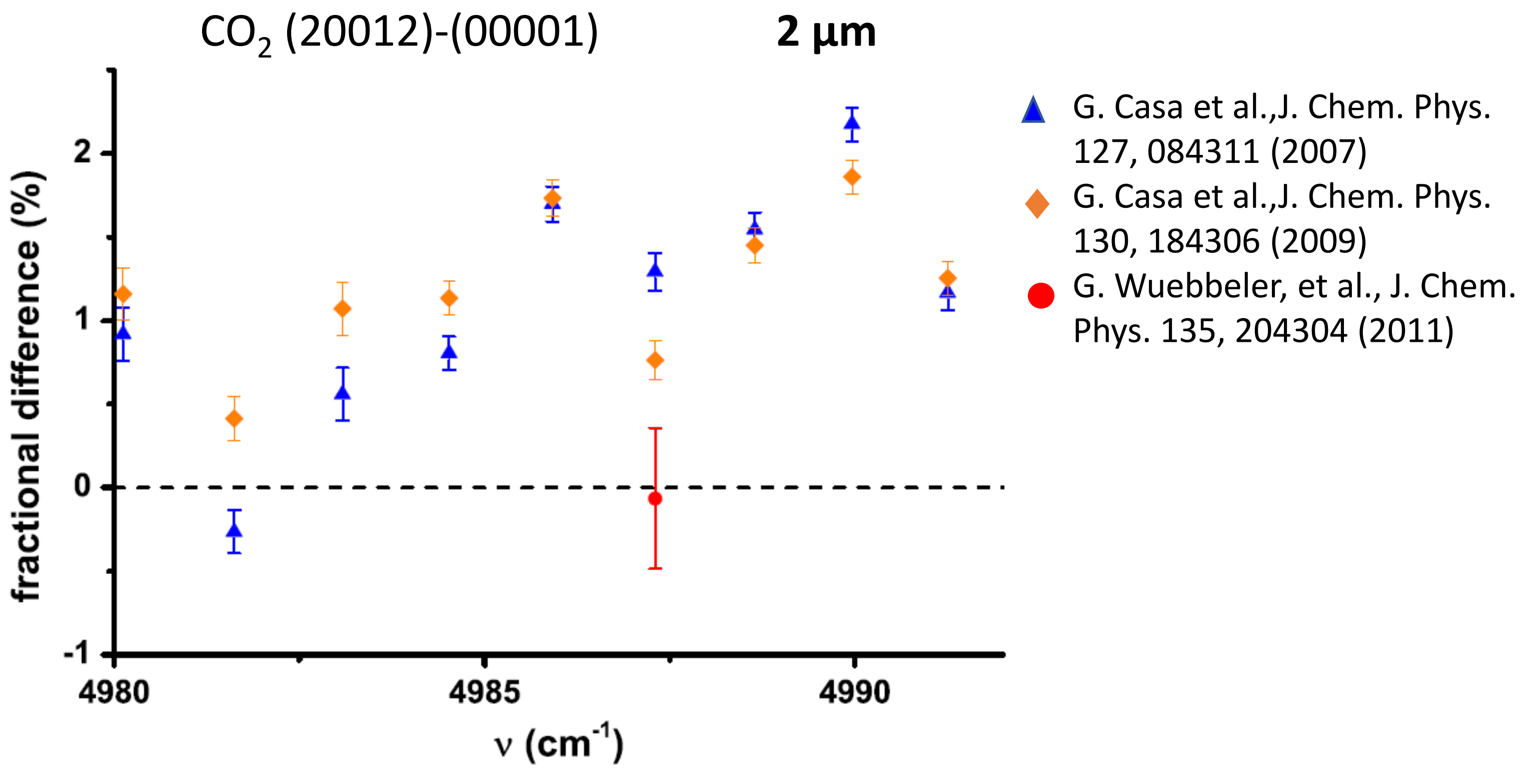
- *ab initio* dipole moment surface
- empirical potential energy surface

State-of-the-art measurements:

- cavity ring-down spectroscopy (CRDS)
- advanced line-shape analysis

CO_2 (30013)-(00001) band: comparison with theory





Mean difference: -3.3‰
Difference standard dev.: 0.5‰

PRL **114,** 243001 (2015) PHYSICAL REVIEW LETTERS week ending 19 JUNE 2015

High-Accuracy CO_2 Line Intensities Determined from Theory and Experiment

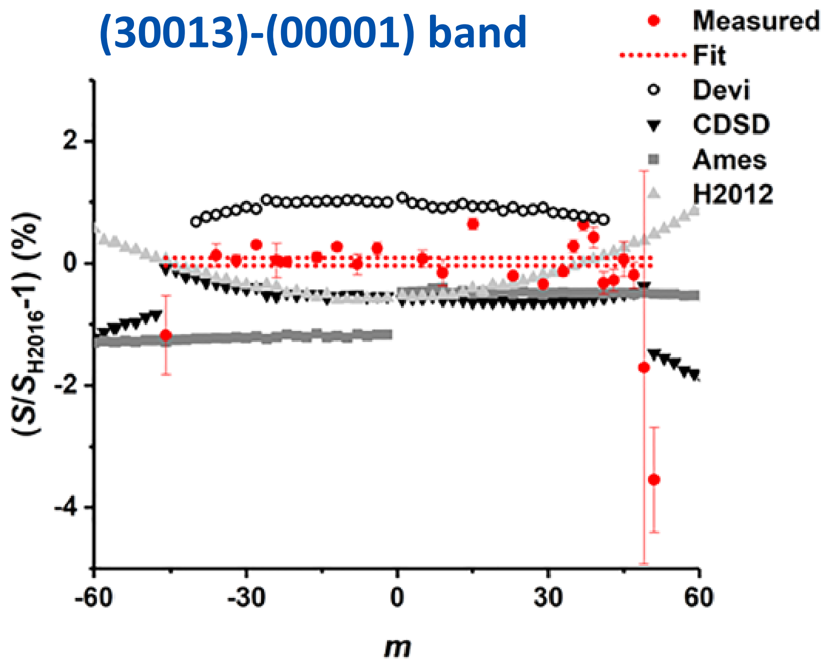
Oleg L. Polyansky,[1,2] Katarzyna Bielska,[3,4] Mélanie Ghysels,[3] Lorenzo Lodi,[1] Nikolai F. Zobov,[2] Joseph T. Hodges,[3] and Jonathan Tennyson[1,*]

CO_2: further results

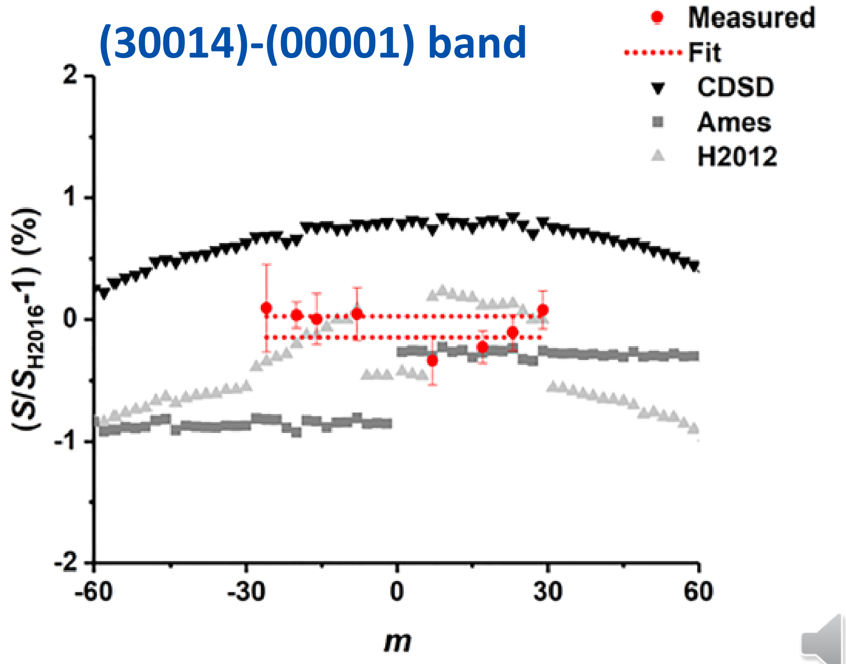
(20012)-(00001) band

Line	Present work	*Ab initio* calculations[11]	Relative deviation (%)
R(6)	8.355 ± 0.014	8.348	0.08
R(4)	6.235 ± 0.012	6.210	0.40
R(2)	3.844 ± 0.009	3.822	0.57

(30013)-(00001) band



(30014)-(00001) band



E. Zak et al., J. Quant. Spectrosc. Radiat. T. 177, 31 (2016) (calculations)
T.A. Oditsova et al., J. Chem. Phys. 146, 244309 (2017) (experiment)

D.A. Long et al., Geophys. Res. Lett. 47, e2019GL086344 (2020)

Our road to permille level line intensities: CO case

Why CO?

- smaller molecule - simpler structure - more accurate calculations possible
- good test case: diatomic, two different atoms
- experimentalist-friendly: non-sticky, relatively simple line structure

Theory verified by 3 experiments

Highly-accurate calculations:

- *ab initio* dipole moment curve
- empirical potential energy curve

Substantially different state-of-the-art measurements:

- cavity ring-down spectroscopy (CRDS, NIST)
- cavity mode-dispersion spectroscopy (CMDS, NCU)
- Fourier transform spectroscopy (FTS, PTB)

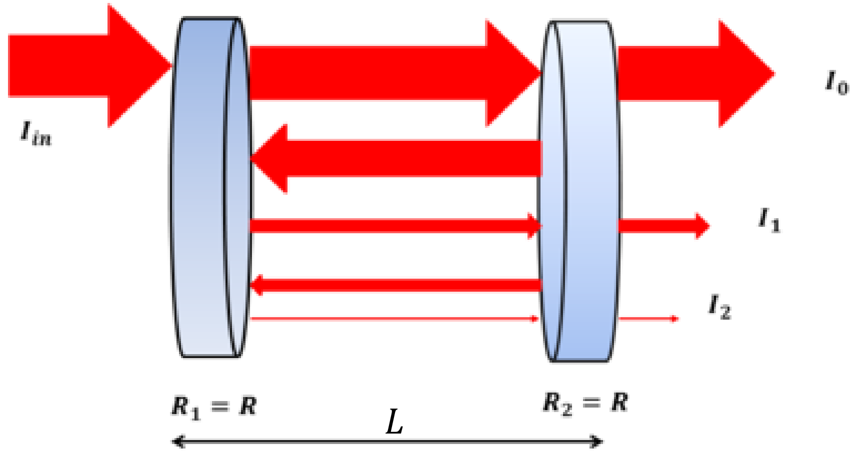
Theoretical calculations at UCL

Line strength:

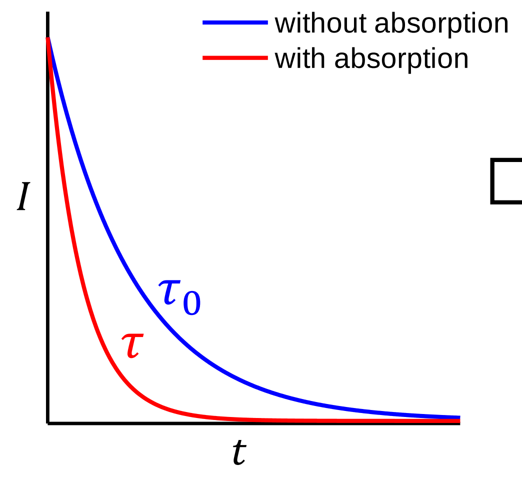
$$S_{ij} = \left[\int_V \psi_i^* M(\vec{r}) \psi_j dV \right]^2$$

$M(\vec{r})$ - dipole moment from *ab initio* calculations
ψ_i, ψ_j - wave functions corresponding to the lower and higher energy level, based on empirical potential energy curve from J. A. Coxon and P. G. Hajigeorgiou, J. Chem. Phys. 121, 2992 (2004)

Cavity ring-down spectroscopy (CRDS) at NIST



$0.9998 \leq R \leq 0.999998$



typically: $\tau_0 \sim 10 \div 500\ \mu s$

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right)$$

$$\frac{1}{c\tau} = \frac{1}{c\tau_0} + \alpha(\nu)$$

baseline ($\frac{1}{c\tau_0}$)

absorption coefficient ($\alpha(\nu)$)

A. O'Keefe, D.A.G. Deacon, Rev. Sci. Instrum 59, 2544 (1988)

PHYSICAL REVIEW LETTERS **123,** 043001 (2019)

Editors' Suggestion   Featured in Physics

Twenty-Five-Fold Reduction in Measurement Uncertainty for a Molecular Line Intensity

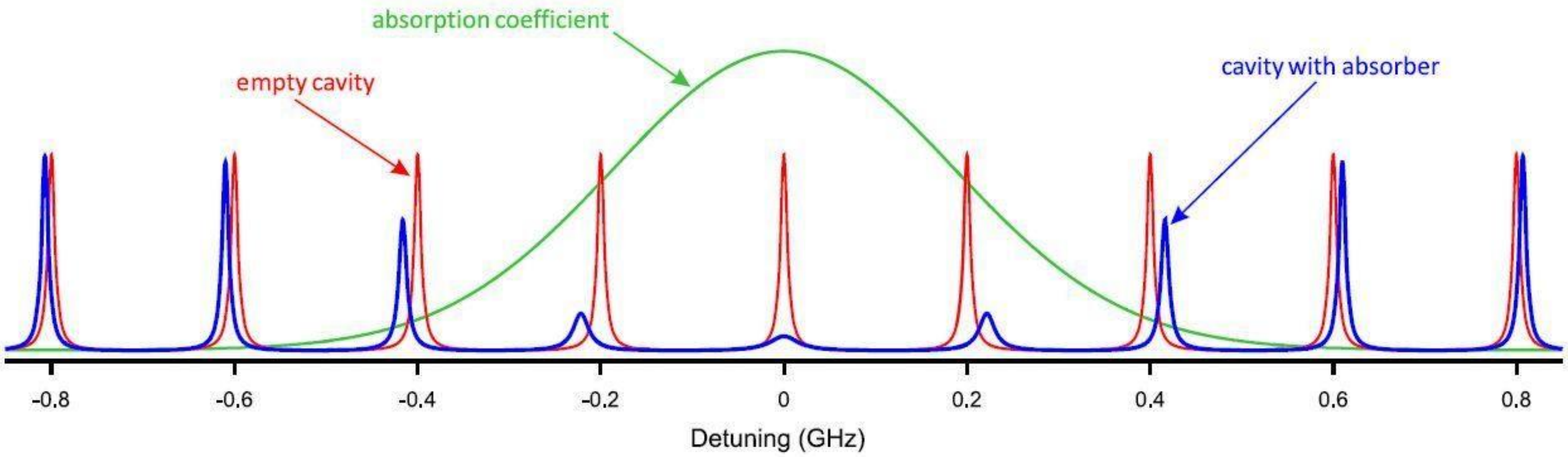
Adam J. Fleisher,* Erin M. Adkins, Zachary D. Reed, Hongming Yi, David A. Long, Hélène M. Fleurbaey, and Joseph T. Hodges†

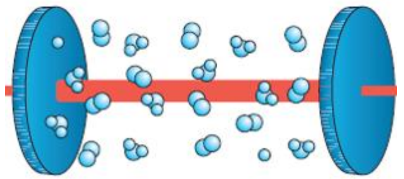
CRDS
+
reference metrology-grade digitizer

⇩

$u(S)/S < 1‰$

Spectroscopy in high-finesse optical cavity: CMDS at NCU





Measurement techniques:

- CRDS – cavity ring-down spectroscopy
  measurement of a photon life time in an optical cavity

$$\tau(\nu) \approx \frac{L}{c(1 - R + \alpha(\nu)L)}$$

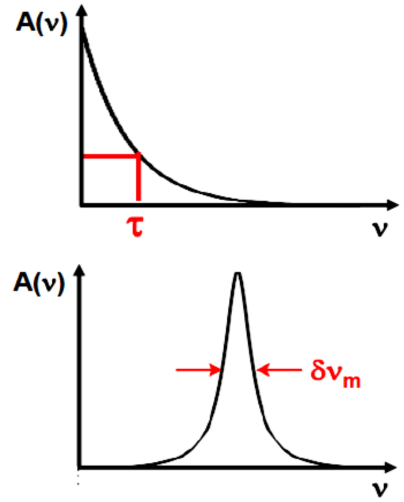
- CMWS – cavity mode-width spectroscopy
  measurement of the cavity resonance width

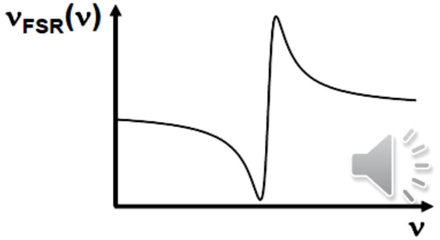
$$\delta\nu \approx \frac{1}{2\pi n \tau(\nu)}$$

- CMDS – cavity mode-dispersion spectroscopy
  measurement of the cavity mode shift due to dispersion
  Only frequency is being measured.

$$u(S)/S < 1‰$$

$$\nu_{\mathrm{FSR}}(\nu) = \frac{\nu_{\mathrm{FSR_{bg}}}(\nu)}{1 - \frac{\mathrm{Im}(I(\nu))}{4\pi k_0}}$$

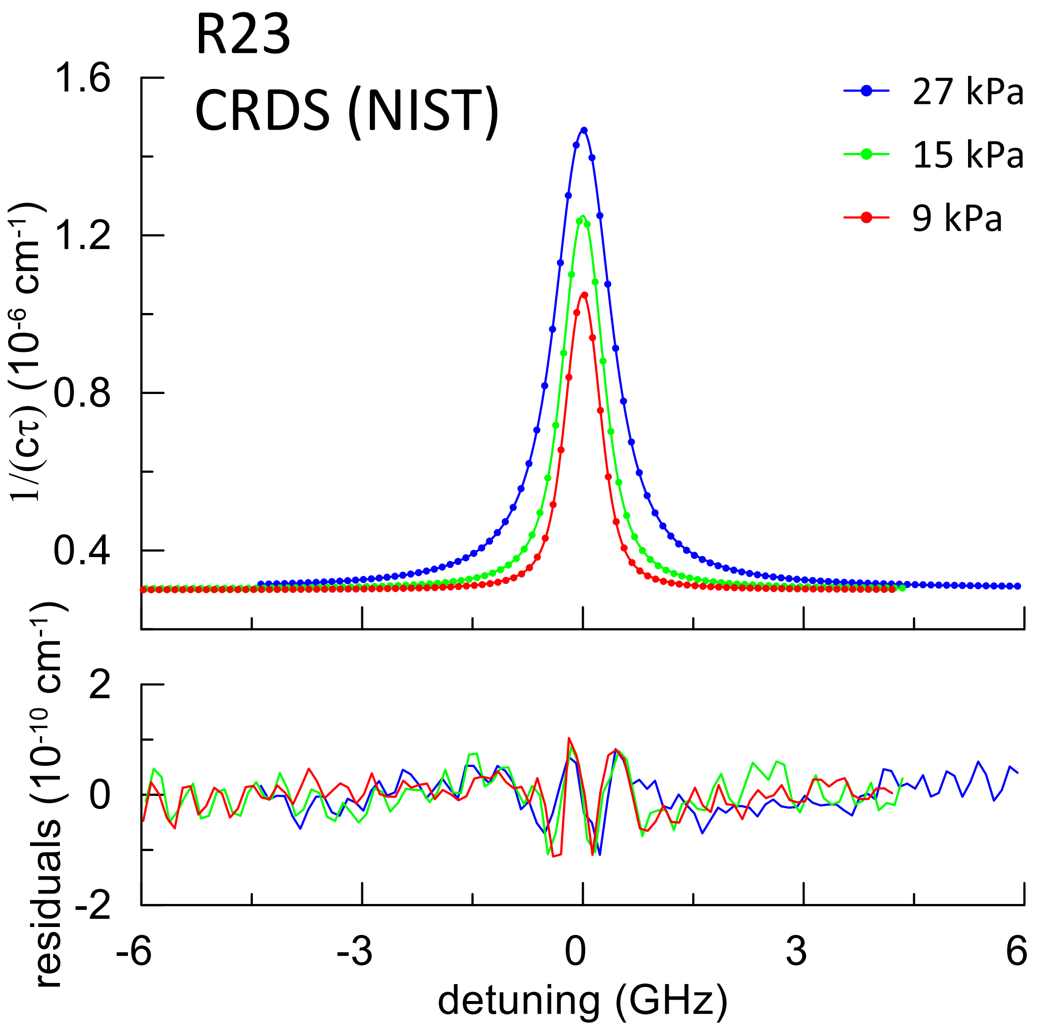




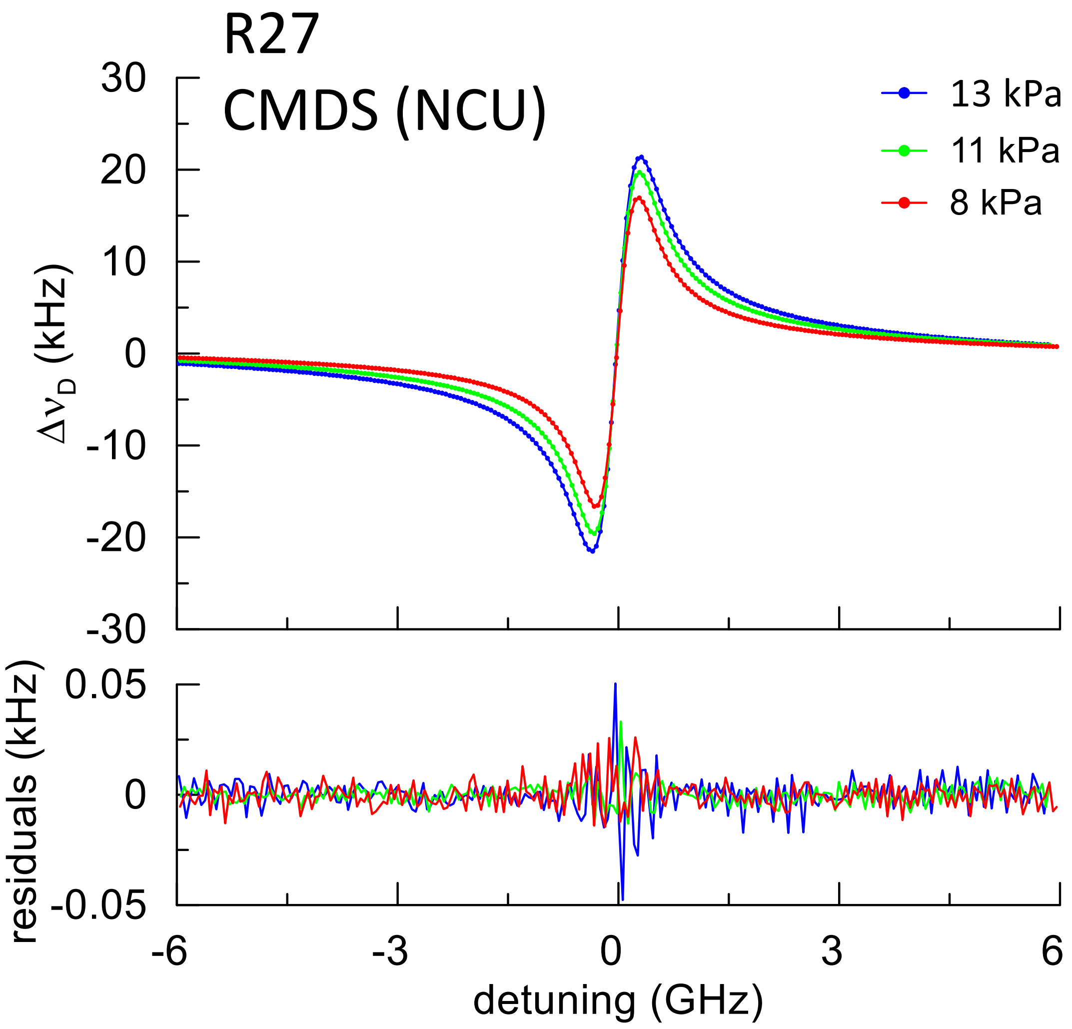
A. Cygan et al., Opt. Expr. 23, 14472 (2015)

A. Cygan et al., Opt. Expr. 27, 21810 (2019)

CRDS & CDMS spectra



$SNR \approx 34000$



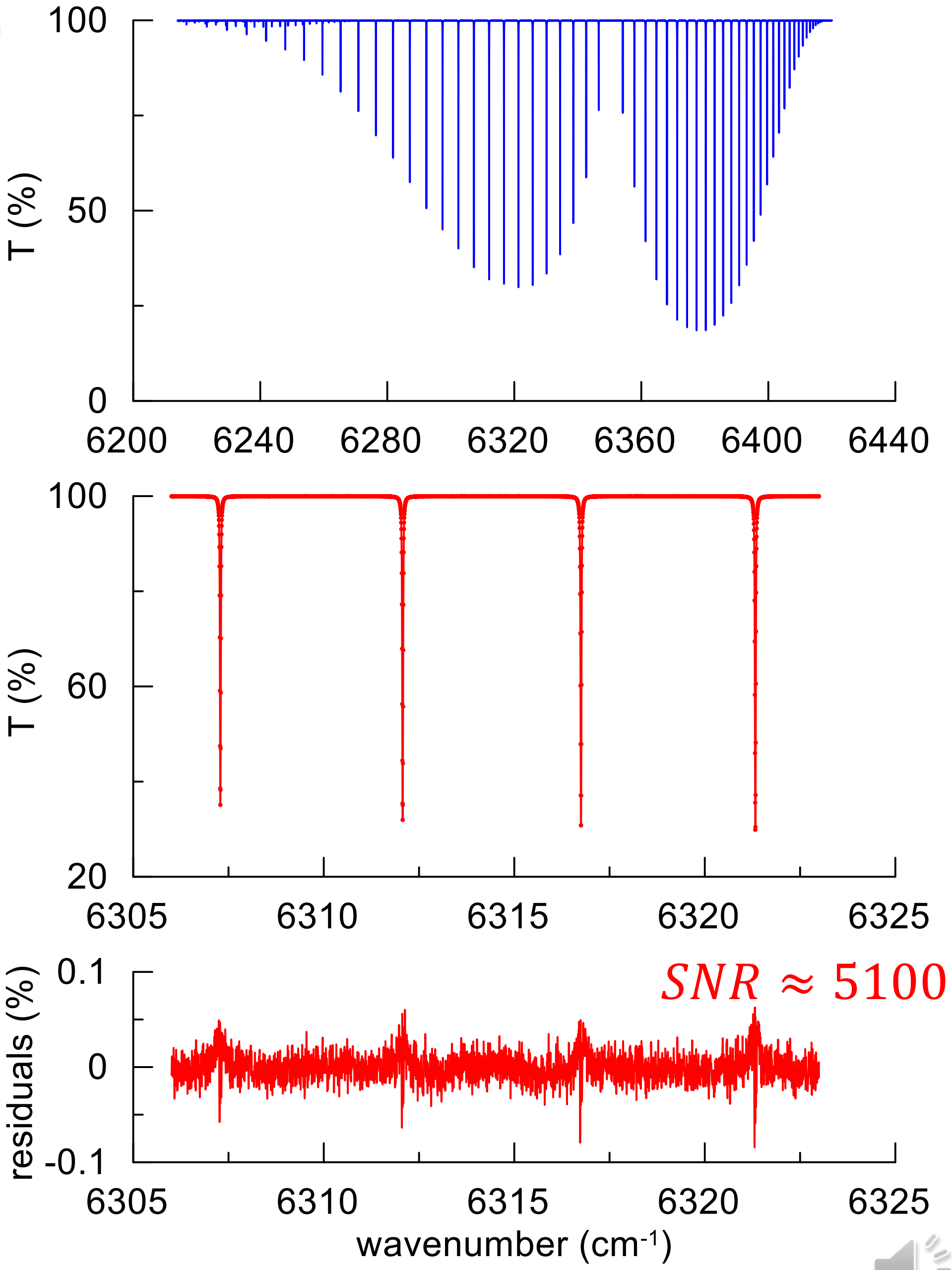
$SNR \approx 5400$

K. Bielska et al., Phys. Rev. Lett. 129, 043002 (2022), Supplemental Material

Fourier transform spectroscopy (FTS) at PTB

- multipass White cell
- calibrated absorption path length
- highly linear InGaAs detector

$$u(S)/S \approx 1.3‰$$



V. Werwein et al., Appl. Optics 56, E99 (2017)

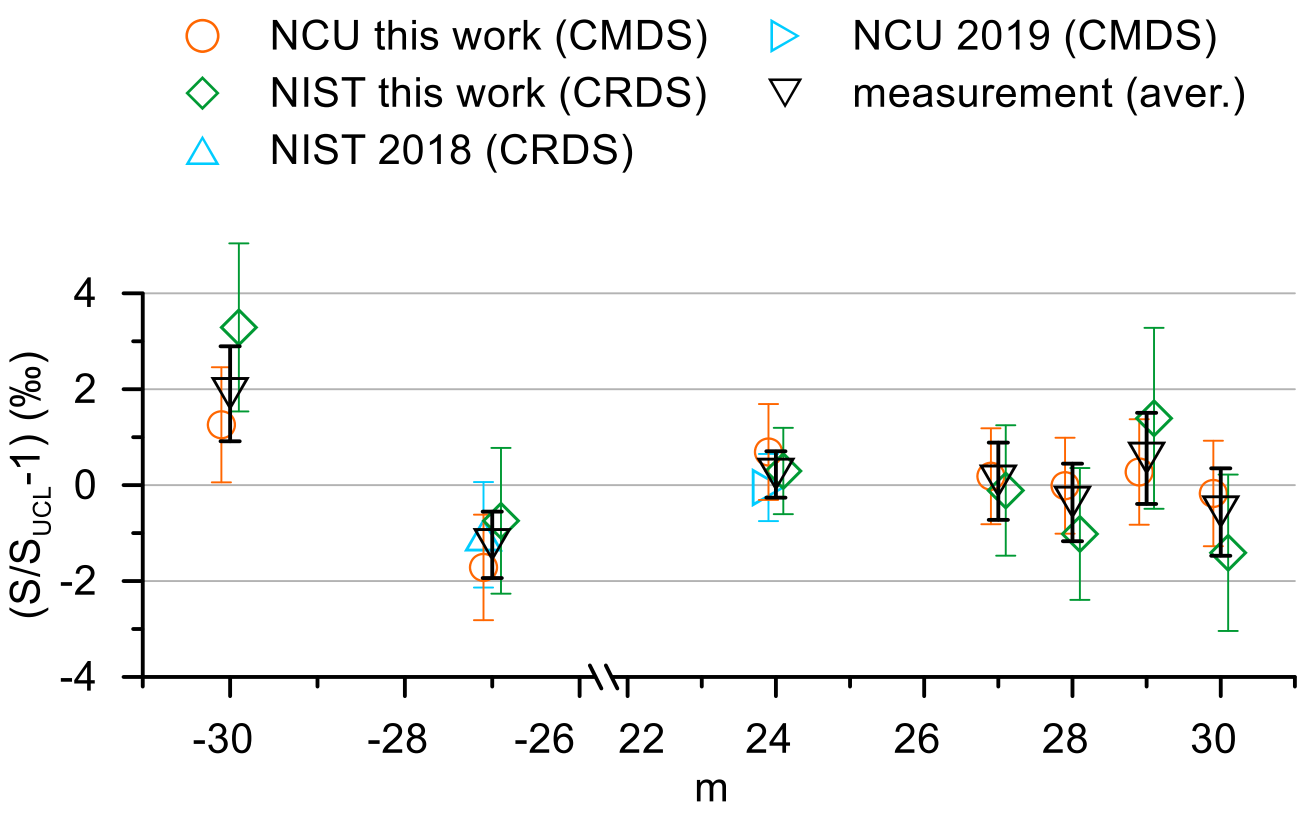
K. Bielska et al., Phys. Rev. Lett. 129, 043002 (2022), Supplemental Material

Experimental uncertainties & line profiles

	CRDS (NIST)	CMDS (NCU)	FTS (PTB)
line profile	HTP + LM	HTP + LM	SDVP + LM
Uncertainty sources			
pressure measurement	0.5‰ to 0.9‰	0.5‰	0.7‰
temperature measurement		0.3‰ to 0.7‰	0.01‰ to 0.2‰
spectrum modeling	0.2‰	0.6‰	1‰
sample isotopic composition	0.4‰	0.4‰	0.01‰
sample purity		0.03‰	0.0025‰
digitizer non-linearity	0.2‰		
path length			0.12‰
statistical uncertainty	0.6‰ to 1.4‰	0.5‰ to 0.5‰	0.1‰ to 0.5‰
Total uncertainty	**0.9‰ to 1.8‰**	**1.0‰ to 1.2‰**	**1.3‰**

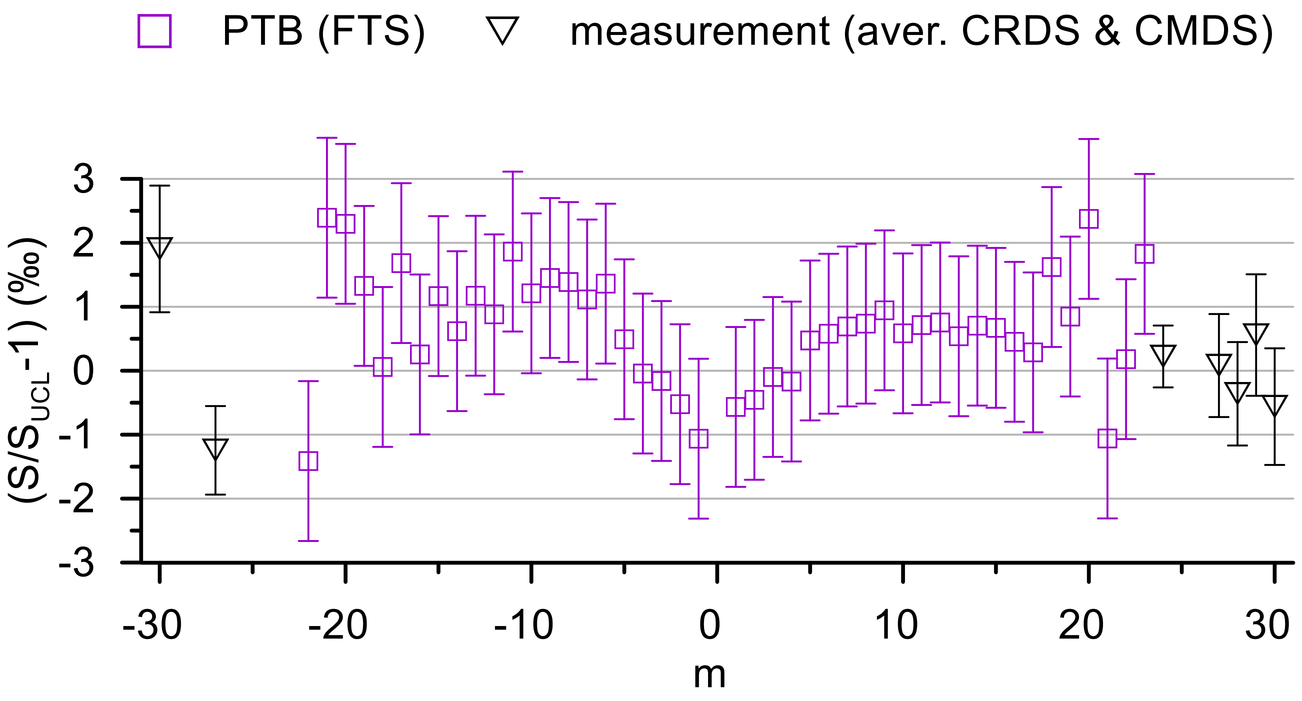
HTP - Hartmann-Tran profile (N. Ngo et al., J. Quant. Spectrosc. Radiat. Transf. 129, 89 (2013))
SDVP – speed-dependent Voigt profile (P.R. Berman, J. Quant. Spectrosc. Radiat. Transf. 12, 1331 (1972))
LM – line-mixing (R. Ciuryło, A. Pine, J. Quant. Spectrosc. Radiat. Transf. 67, 375 (2000))

Theory and experiment: intensities comparison



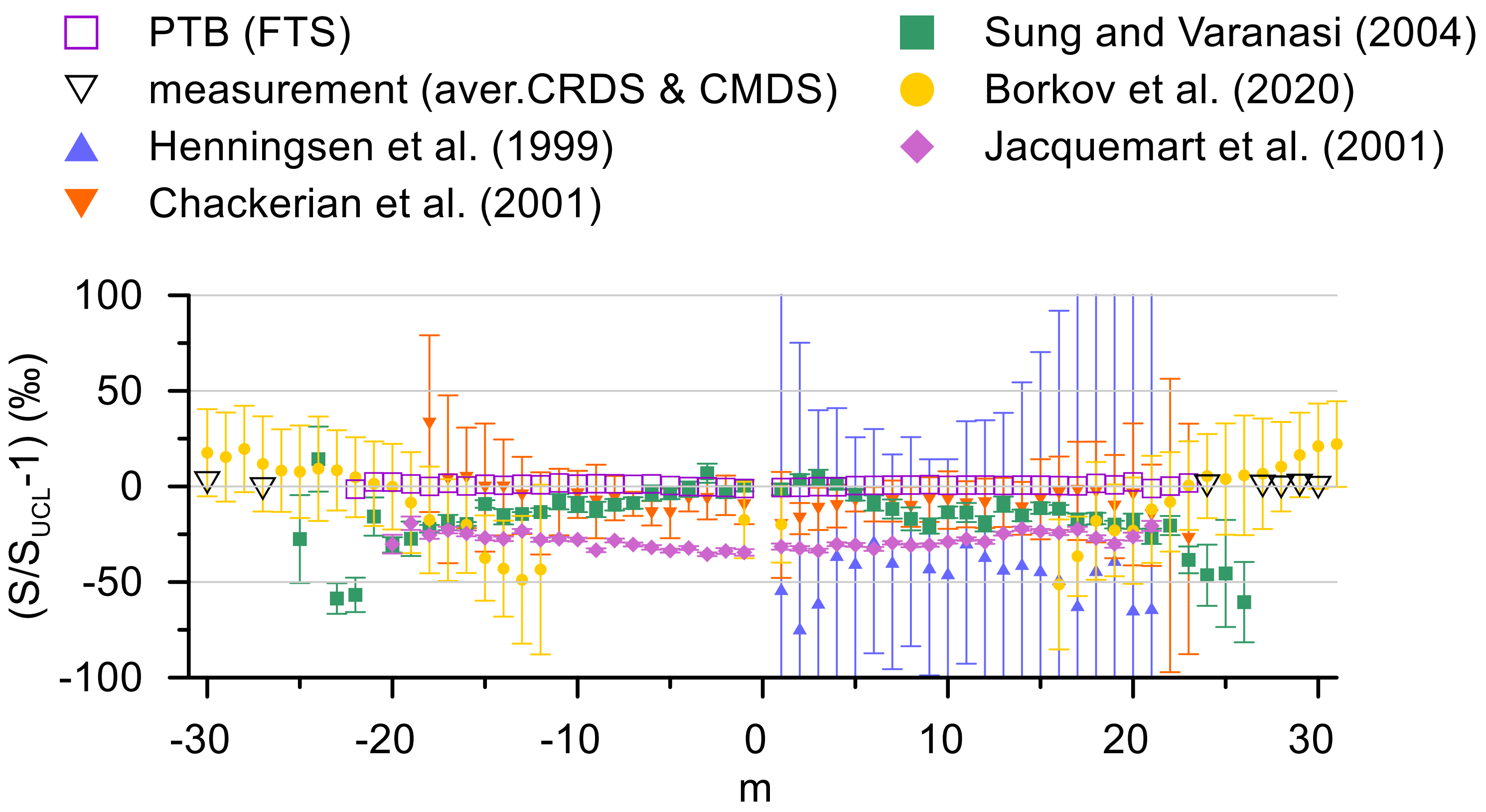
K. Bielska et al., Phys. Rev. Lett. 129, 043002 (2022)

Theory and experiment: intensities comparison



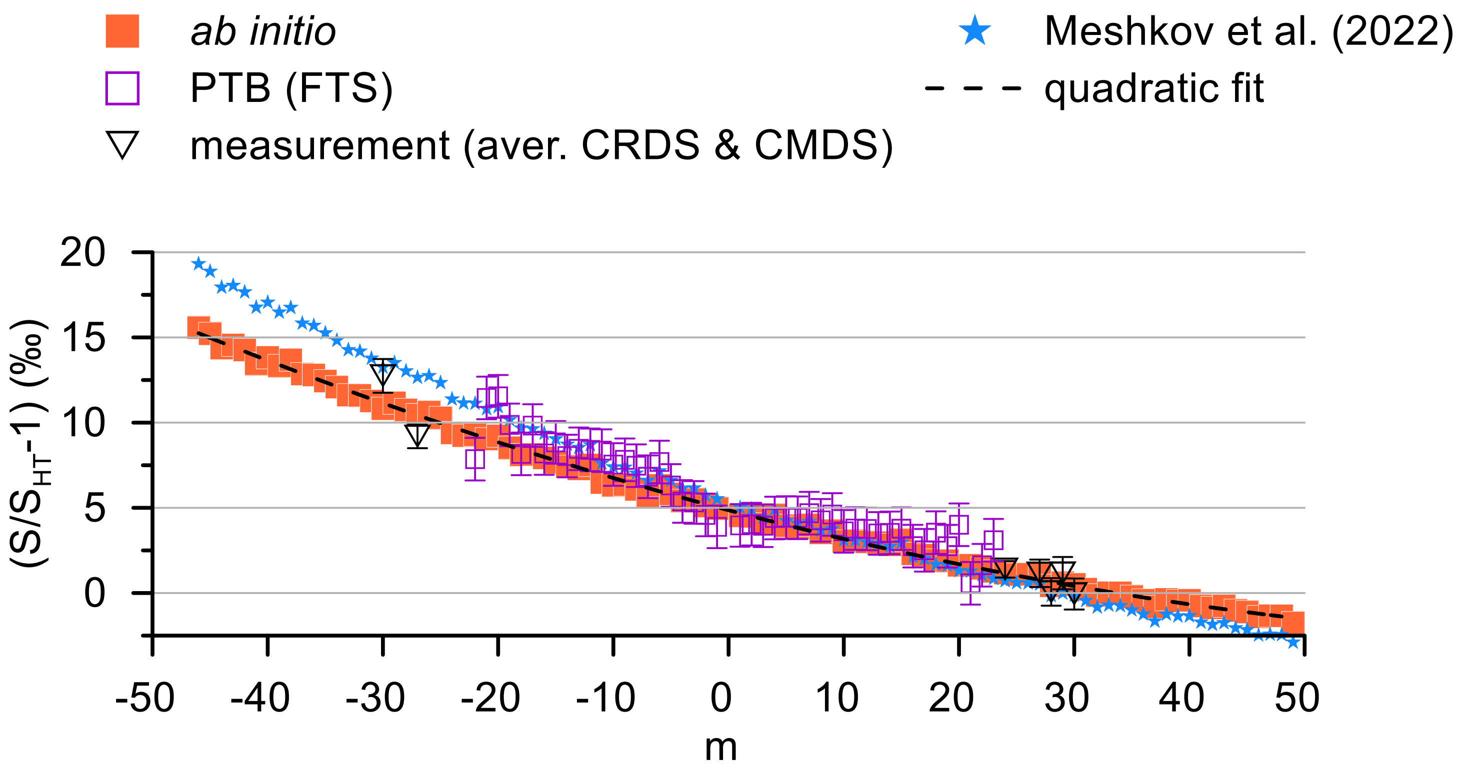
K. Bielska et al., Phys. Rev. Lett. 129, 043002 (2022)

Comparison with literature data



K. Bielska et al., Phys. Rev. Lett. 129, 043002 (2022)

Comparison with literature data: HITRAN 2020 and new global fit



K. Bielska et al., Phys. Rev. Lett. 129, 043002 (2022)

Conclusions and perspectives

- We obtained twenty-five fold reduction in uncertainty compared to literature data.
- Theoretical calculations provide CO line intensities also for bands (1-0), (2-0), and (4-0) that are expected to have similar accuracy.
- We recommend use of the presented theoretical approach for other molecules, followed by confirmation by independent, multi-laboratory measurements.
- New Task Group on Advanced Spectroscopy within Consultative Committee for Amount of Substance (CCQM) meeting at the International Bureau of Weights and Measures (BIPM) to bridge gas metrology and molecular spectroscopy.
- More coordinated, interactive comparisons are needed to provide accurate, spectroscopic reference data.

Thank you for your attention!