

Traceable spectral reference data of atmospheric species at the PTB FTIR central facility

Motivation

WMO GAW stations

- WMO GAW program [1] requires accurate knowledge of traceable spectral line parameters [2] for remote sensing products.
- CCQM new Task Group Advanced Spectroscopy aims to harmonize the primary spectroscopic methods for amount of substance.[3]
- Accurate line intensity has other important applications such as absolute isotopic composition [4], spectroscopic temperature determination [5].

FTIR infrastructure

Measured spectrum of the CO 3-0 band

Spectral fitting (CO)

Parameter	Value
Line shape function	IUPAC recommended [8]
Line mixing model	Rosenkranz
Signal-to-noise ratio	Up to 5100
Instrumental function	LINEFIT program
Doppler width	Calculated

Uncertainty budget (CO)

Line intensity (S) uncertainty contribution ($k=1$)

- Path length
- Line area
- Apparatus function
- Pressure
- Temperature effect
- Isotopic and purity

Combined uncertainty = 1.38%

International comparison (CO)

Four methods [9, 10]

Literature data (FTIR) compared to UCL(AB initio), see Refs. [11,12]

Line intensity data at PTB

Molecule	Method	Bands (μm)	Best uncertainty ($k=1$)
CO [9]	FTIR	1.57	0.14%
N ₂ O [7]	FTIR	2.25	0.15%
CO ₂	FTIR / TDLAS	2.01, 2.72	0.37% 0.5%
H ₂ O	TDLAS / FTIR*	1.37, 1.39, 2.55, 2.71	0.5%
NH ₃ [13]	TDLAS / FTIR*	1.53	0.5%

* In plan

Isotopic ratio using line intensity

Isotope ratios from peak areas of CO₂ isotopologues [16]

CCQM-P204 [17]: PTB IRMS vs. PTB OIRS

Conclusion and outlook

- Line intensities of the P(22) to R(22) lines of the CO 3-0 band are reported at permille level accuracy and compared to CMDS/CRDS measurements and *ab initio* calculation [9].
- The present work of CO is the foundation for CCQM Task Group on Advanced Spectroscopy to promote the development, realization and harmonization of primary spectroscopic methods for amount of substance through rigorous intercomparison experiments.
- We propose the accurate (3-0) CO line intensities to be used as intrinsic spectroscopic references.
- For NH₃, independent amount fraction measurements show that our line intensities measured by TDLAS give more accurate results than the current data in HITRAN. We plan to do further measurements of NH₃ line intensity using FTIR.
- Optical isotopic ratio method using line intensity ratios [4,16,17] is a novel alternative compared to mass spectroscopy, offering field deployable size and continuous measurement mode.

References

- Global Atmosphere Watch Programme (GAW). <https://community.wmo.int/activity-areas/gaw>
- Report of the 27th meeting of the CCQM. BIPM report.
- I.E. Gordon et al., JQSRT 277, 107949 (2022)
- A. J. Fleisher, et al., Nat. Phys. 17, 889 (2021)
- SRT-s14 Primary spectrometric thermometry for gases. <http://www.metpart.eu/iem-call-2022>
- V Ebert. Spectral reference data for atmospheric monitoring.
- V Werwein, et al., Appl. Opt. 56, E99 (2017)
- J. Tennyson et al., Pure Appl. Chem. 86(12): 1931–1943 (2014)
- K. Bielska et al., Phys. Rev. Lett. 129, 043002 (2022)
- K. Bielska et al., BIPM-WMO workshop, presentation T1-A6 (2022)
- G. Li et al., Astrophys. J. Suppl. Ser., 216, 15 (2015)
- Y. G. Borkov, et al., JQSRT 253, 107064 (2020)
- A. Pogany et al. JQSRT 276, 107884 (2021)
- K. Sung et al. JQSRT 113:1066–83 (2012)
- P. A. Coles et al., Mon. Not. R. Astron. Soc. 490:4638–47 (2019)
- R. van Geldern et al. Anal. Chem 86, 12191–12198 (2014)
- J. Viallon et al., CCQM-P204 report (in preparation)

Acknowledgement

The authors acknowledge collaboration in the European Metrology Research Programme (EMRP) projects Spectral reference data for atmospheric monitoring (ENV06). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

Physikalisch-Technische Bundesanstalt
National Metrology Institute

Bundesallee 100
38116 Braunschweig, Germany
www.ptb.de

Gang Li
Working Group 3.42
Spectral Gas Analysis and Reference Data
phone: +49 531 592-3235
e-mail: gang.li@ptb.de

Volker Ebert
Department 3.4
Analytical Chemistry in Gas Phase
phone: +49 531 592-3400
e-mail: volker.ebert@ptb.de