Physikalisch-Technische Bundesanstalt
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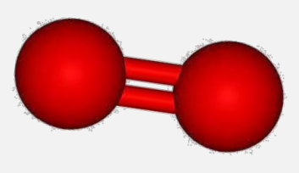
PRISPECTEMP PROJECT IN PROGRESS: NEW MEASUREMENTS OF A-BAND OF OXYGEN IN PURE GAS AND MIXTURES WITH NITROGEN

INTRODUCTION

This work is a part of European Partnership project 22IEM03 "Primary Spectroscopic Thermometry for Gases" (**PriSpecTemp**) [1]. The project aims to improve primary gas temperature measurements with a target uncertainty of 25 mK using existing spectroscopy capabilities.

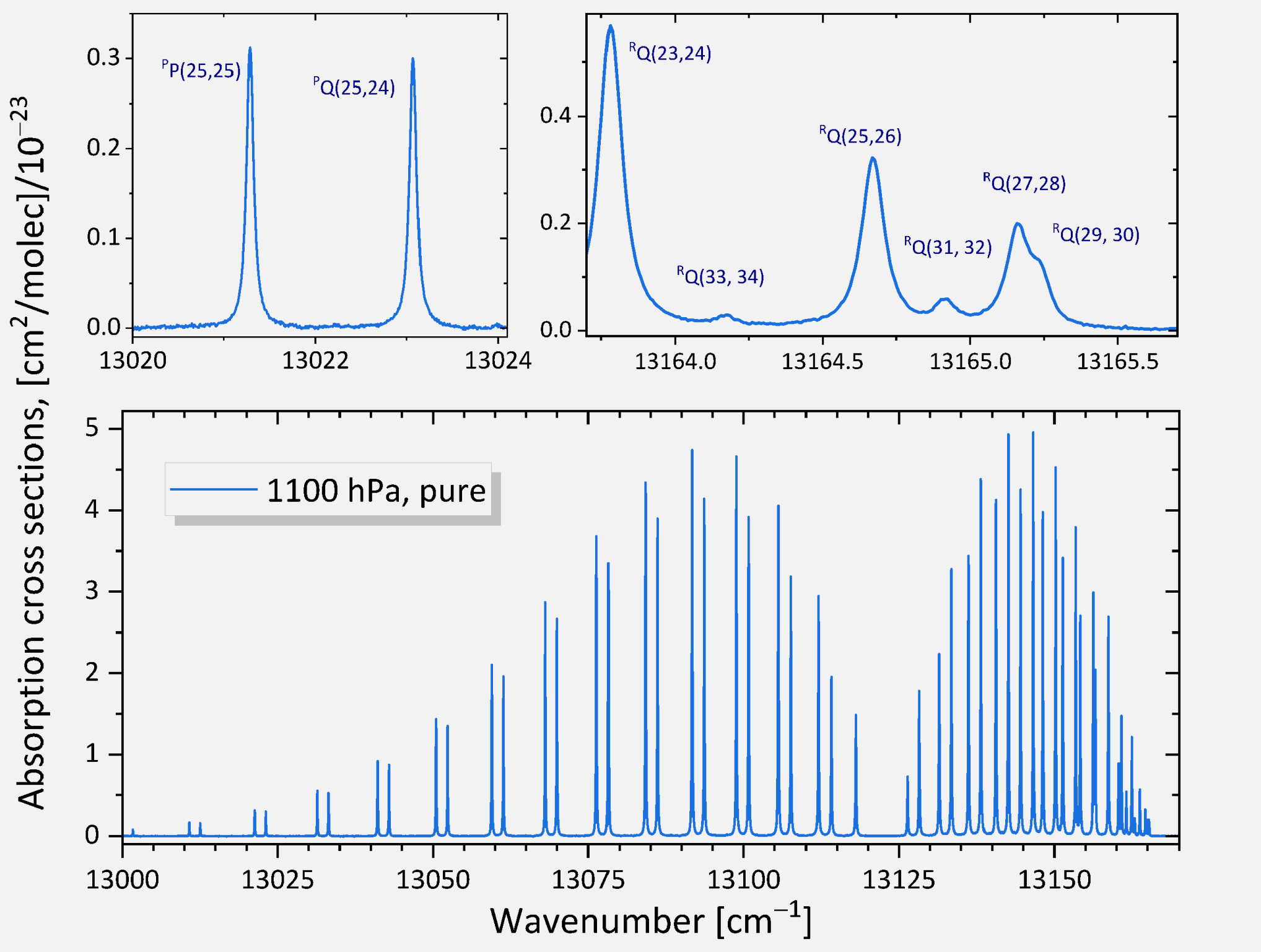
The main idea is to determine the optimal transitions for a number of 'sensor' molecules, such as O_2, CO and CO_2, for Rotational-Vibrational Spectroscopic Gas Thermometry method (RVSGT). The interval from 200 to 400 K is targeted. A cross-validation against other non-contact technique, such as Doppler broadening thermometry and two-line laser thermometry, is also planned.



Oxygen is one of the target molecules for this since it mixes uniformly in the atmosphere and it is used to calibrate intensities of spectra retrieved by satellites and ground-based instruments [2].

SPECTRUM OF A-BAND

The A-band of molecular oxygen arises from the $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ electronic transition. This transition is electric dipole and spin forbidden, and appears due to the magnetic dipole.



The A-band is particularly important because:

- Does not saturate over long pathlengths [3];
- Free from absorption of other atmospheric molecules.

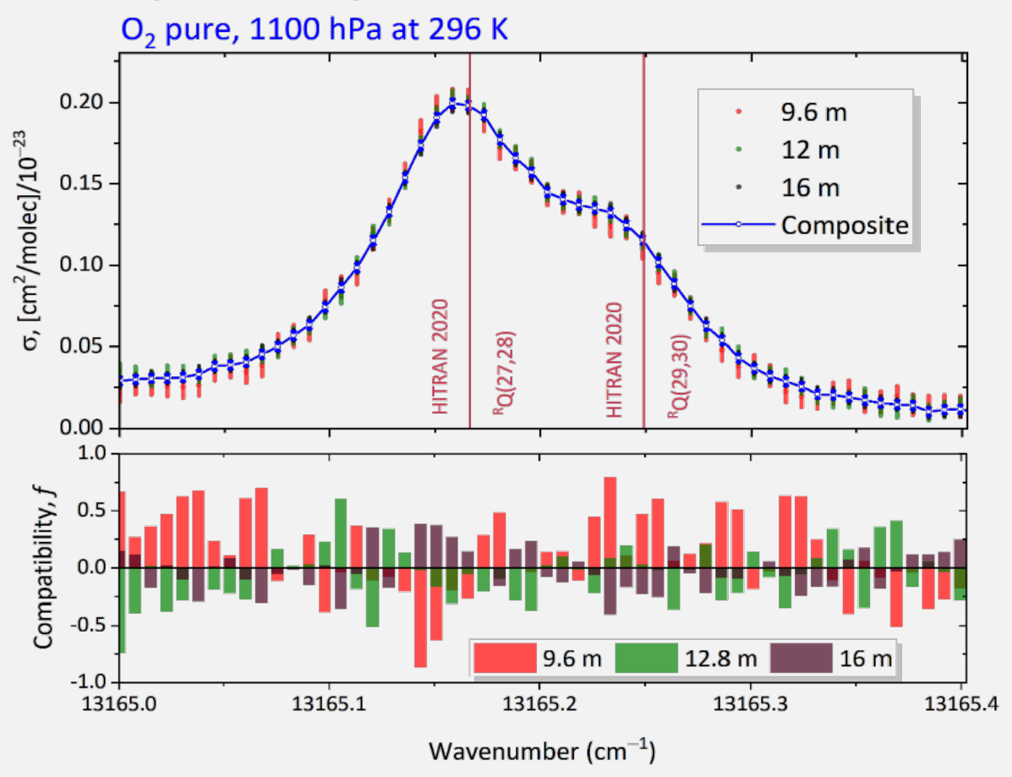
EXPERIMENT

- All measurements were performed using Bruker IFS-125;
- spectra of pure O_2 and mixtures with nitrogen were recorded.

Parameter	Description
Resolution / apodization	0.016 cm^{-1} / Boxcar
Detector	RT-Si diode
Source	Tungsten lamp
Beamsplitter	Quartz VIS
Optical filter	Bandpass CW 776nm, FW 24
Commercial multi-pass cell with changeable path	KBr windows Base length: 0.8 m Varied 3.2 – 32 m
Temperature (secondary calibration)	4 Pt-100 sensors along the cell
Pressure (primary calibration)	1300 hPa INFICON
Thermostate	JULABO HighTech FP-89 (water)
Gas mixer (NPL calibrated)	Sonimix 2106-512 (www.lni-swissgas.eu)
Gases (from Linde)	O_2 (5.0), N_2 (7.0) Synthetic air: 20.0(2) cmol/mol O_2

COMPOSITE SPECTRUM

Several samples were recorded at various path lengths to obtain composite spectra (see our recent articles [11,12]).



Validity of averaging:

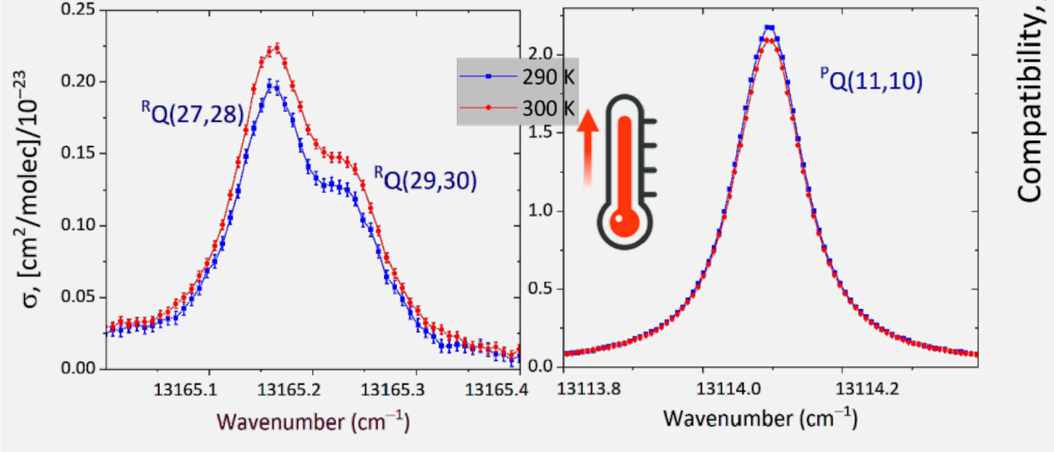
$$f = \frac{1}{\sqrt{2}} \cdot \frac{|\sigma_i - \sigma_j|}{\sqrt{\Delta\sigma_i{}^2 + \Delta\sigma_j{}^2}},$$

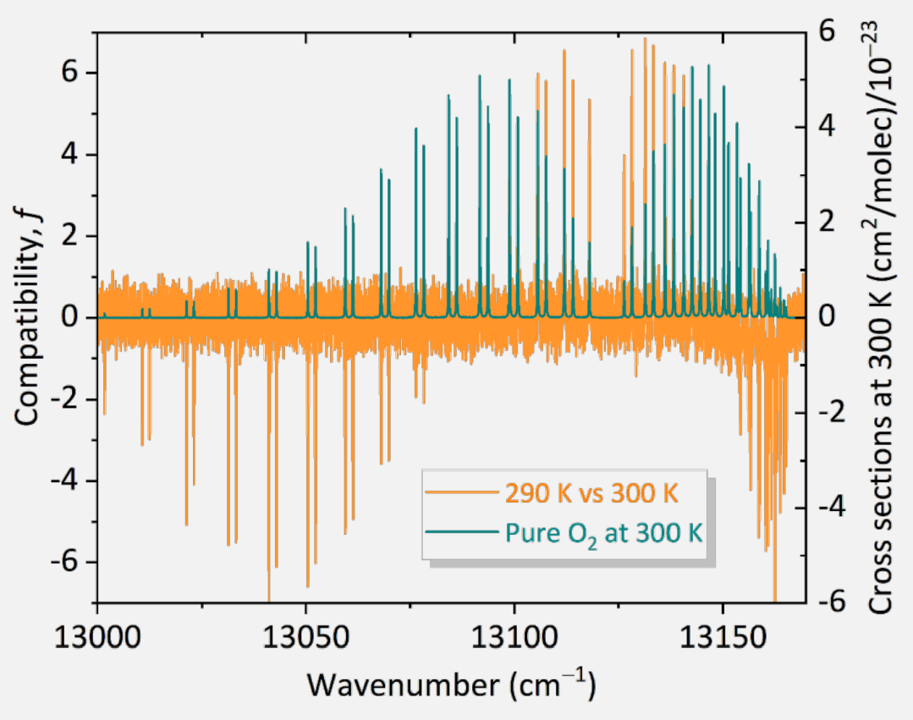
metrological compatibility, where $\Delta\sigma_x$ are the uncertainties of σ_x.

$f \in [-1, 1]$ → **comparable.**

EFFECT OF TEMPERATURE

A few spectra were recorded in the range of 290 – 300 K.





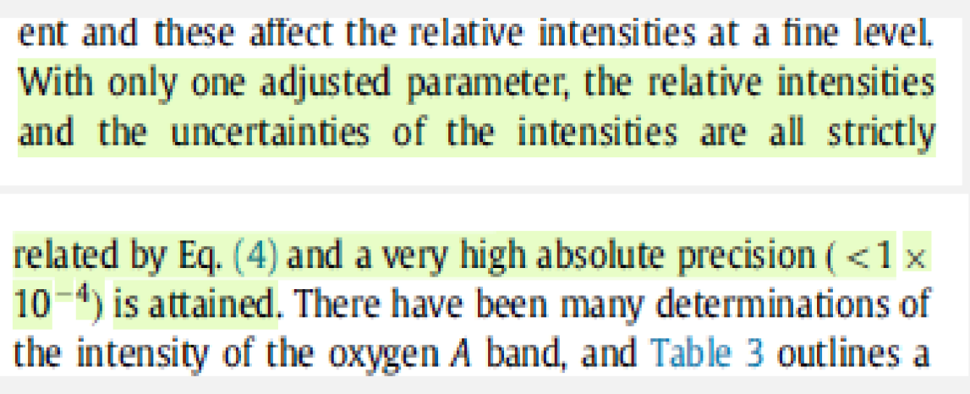
Low *J*-lines gain, and high *J* loose the intensity upon cooling.

PURE OXYGEN

Pure O_2: weighted average 2.25(3) ·10^{-22} cm/molec (1.3 %, $k = 2$), similar uncertainties as in later studies.

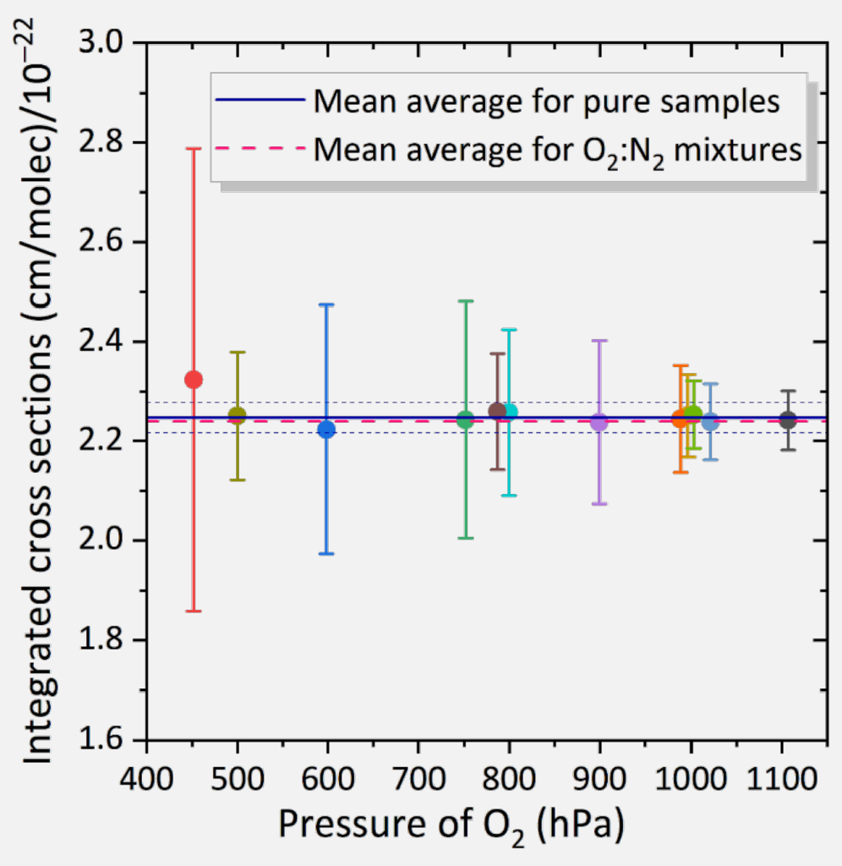
The data from Ref. [2] stands out, being the most precise, namely (2.2547(2) ·10^{-22} cm/molec).

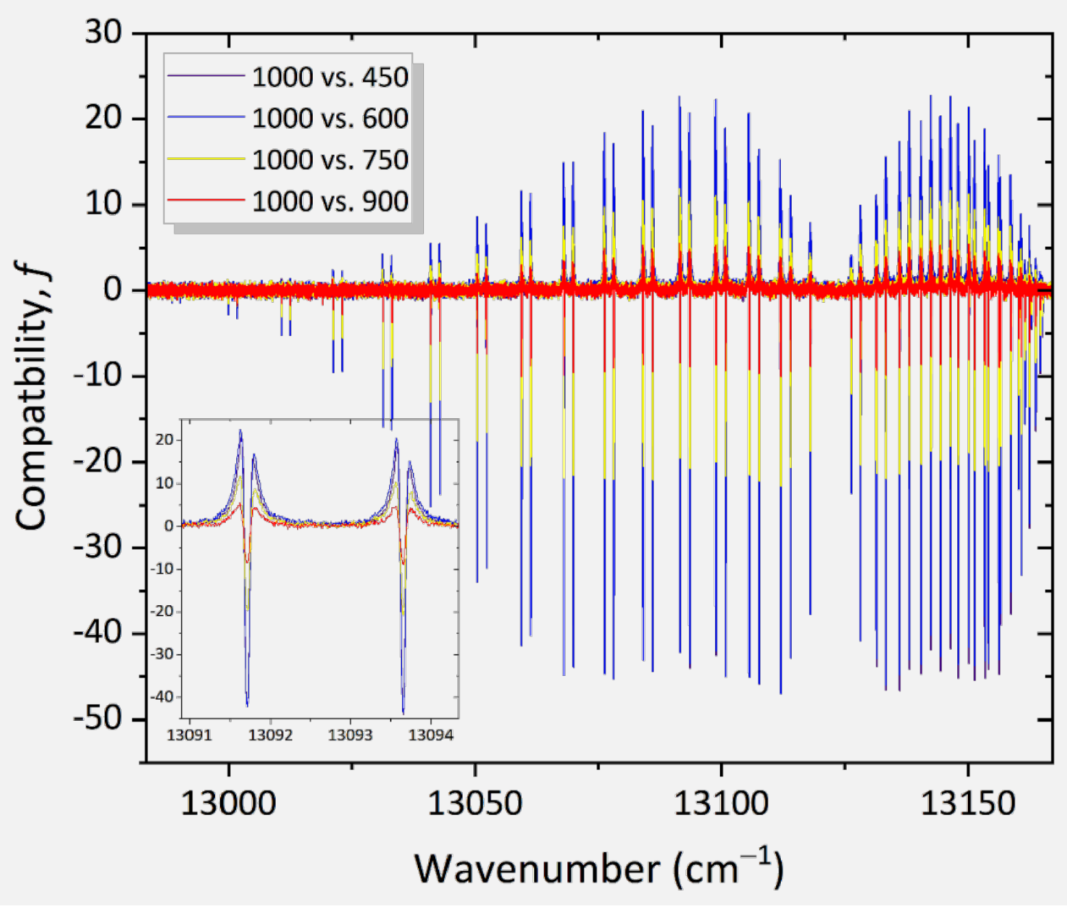
Quote:



ent and these affect the relative intensities at a fine level. With only one adjusted parameter, the relative intensities and the uncertainties of the intensities are all strictly

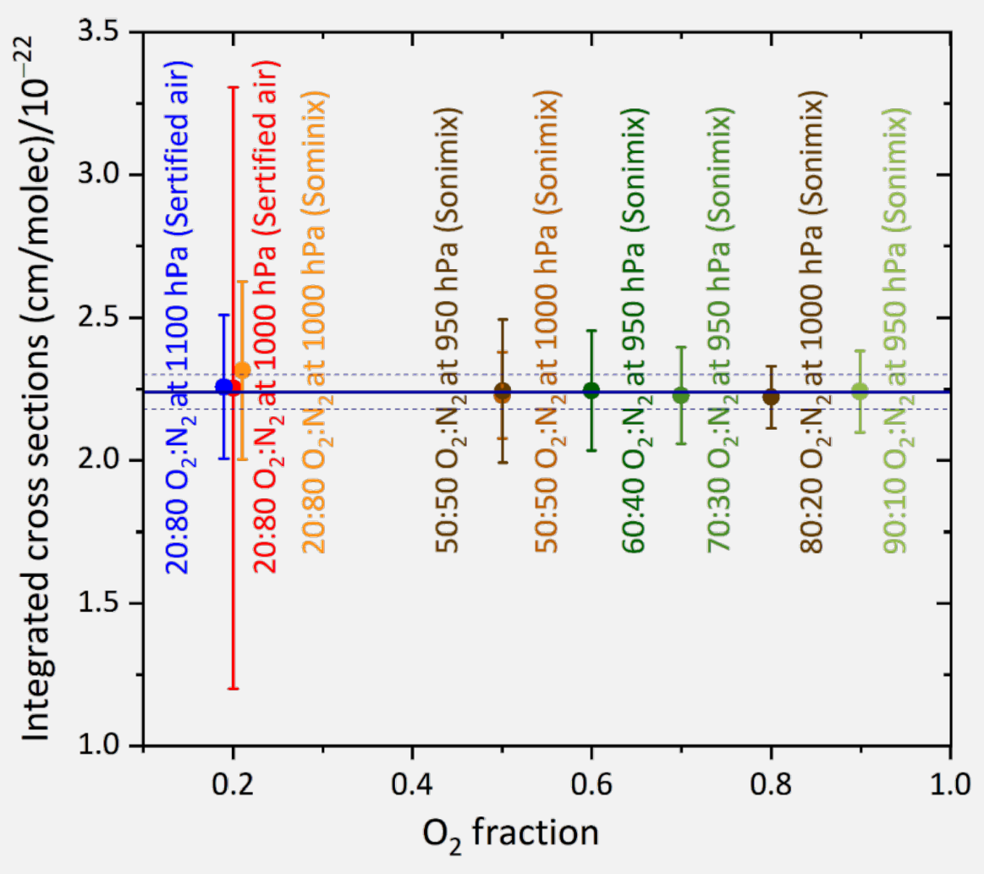
related by Eq. (4) and a very high absolute precision ($<1 \times 10^{-4}$) is attained. There have been many determinations of the intensity of the oxygen *A* band, and Table 3 outlines a





Strong dependence on sample pressure → reliable determination of broadening and shifting coefficients for N_2 and O_2. Line shifts are bathochromic (red shift).

MIXTURES WITH NITROGEN

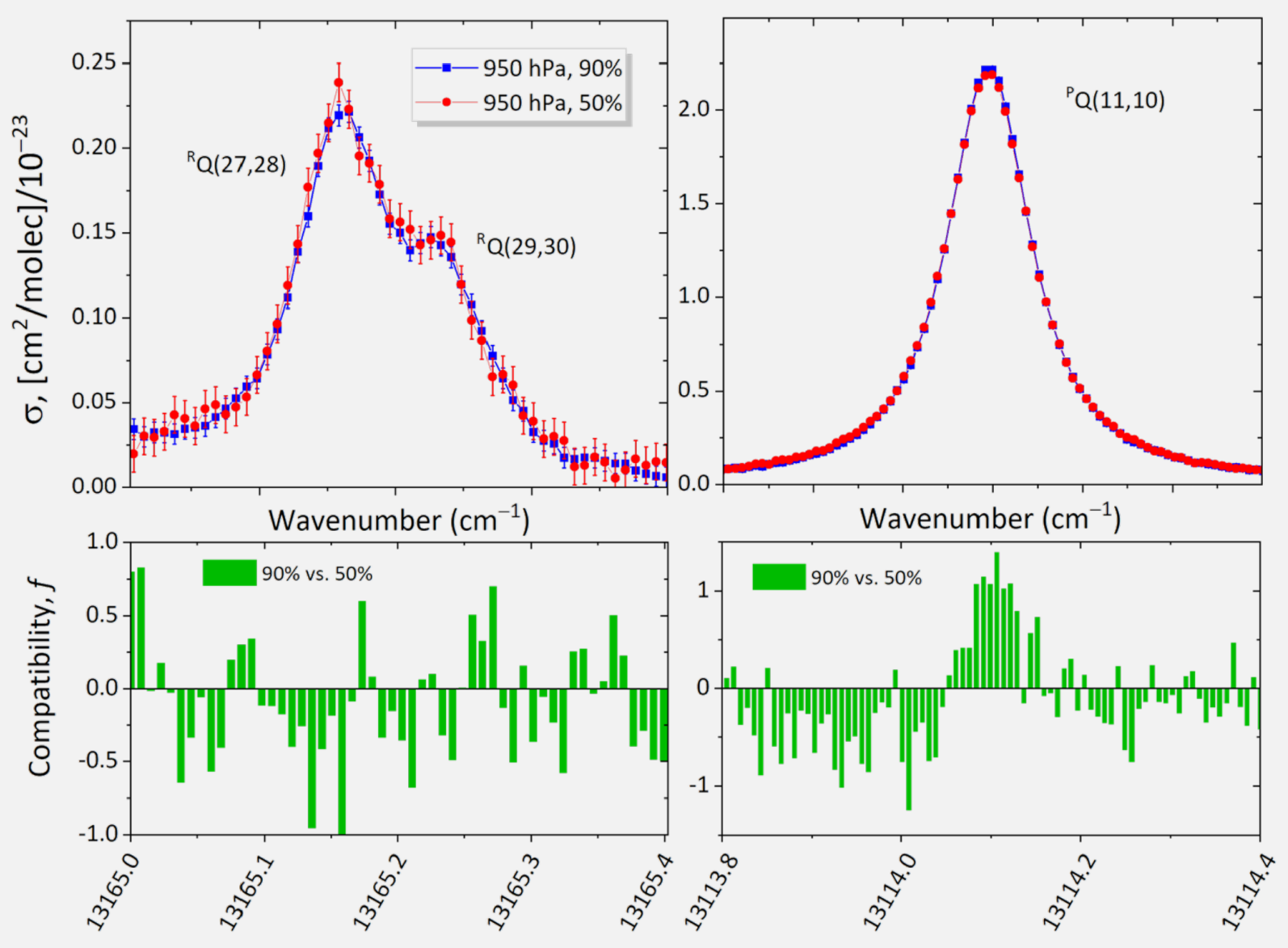


Samples:

- certified air from Linde;
- mixtures were prepared by Sonimix.

Integrated intensities over the whole band agree for all recorded spectra.

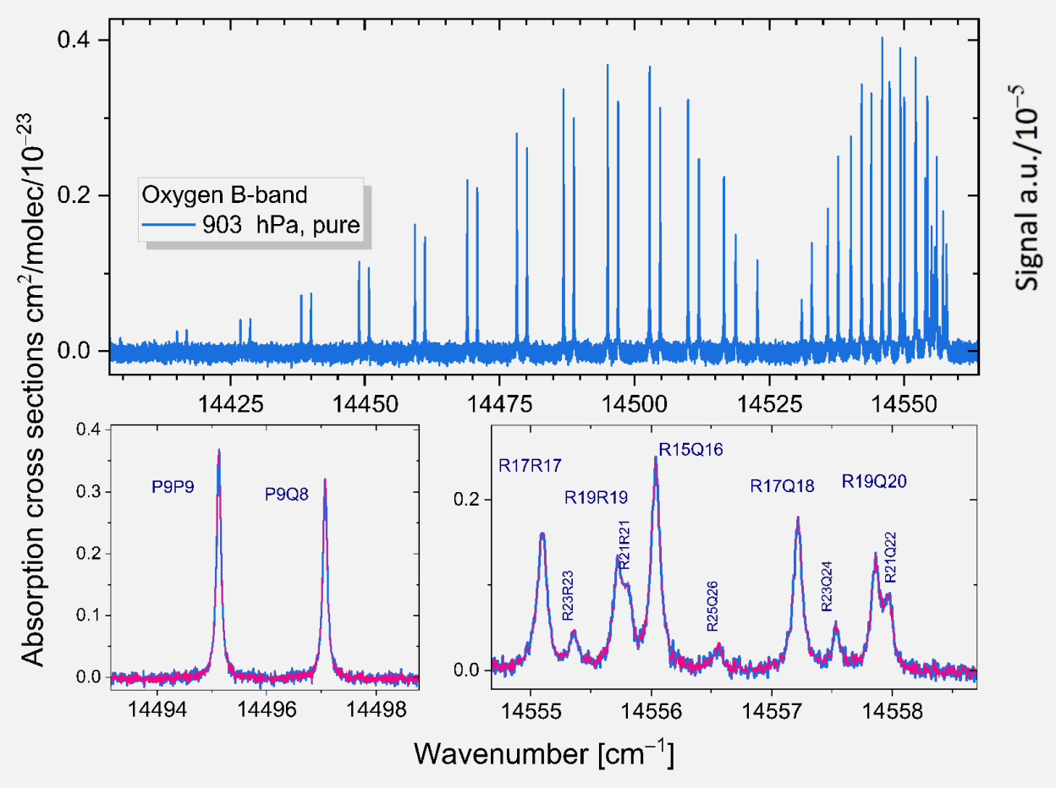
O_2 in mixtures with nitrogen: 2.24(6) ·10^{-22} cm/molec (2.7 %, $k = 2$)

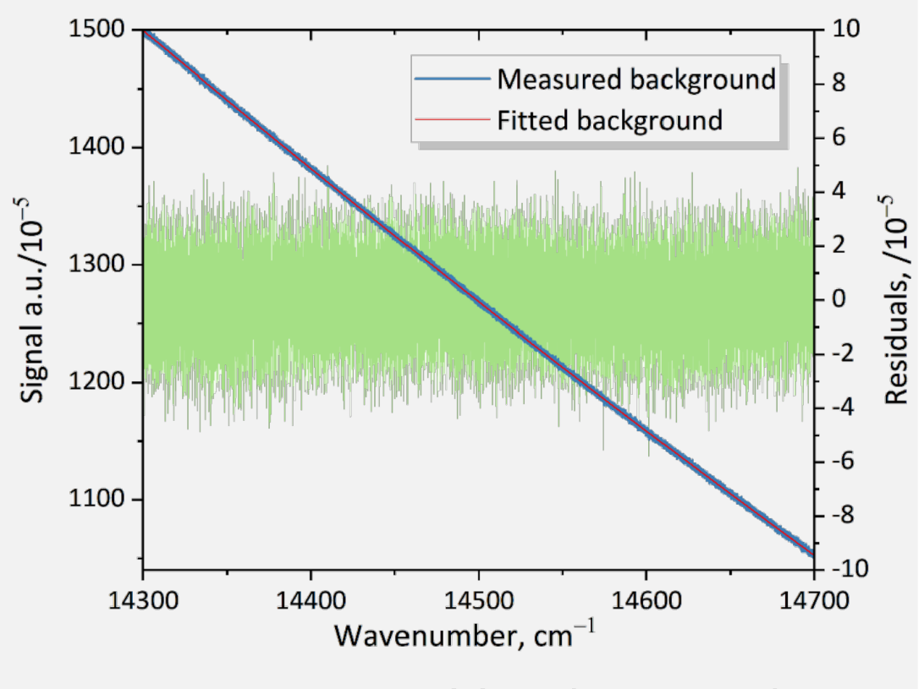


Line profiles show only a weak dependence on the mixture composition → broadening and shifts for N_2 and O_2 are very similar.

SIDE PRODUCT: B-BAND

Integral: 1.07·10^{-23} cm/molec

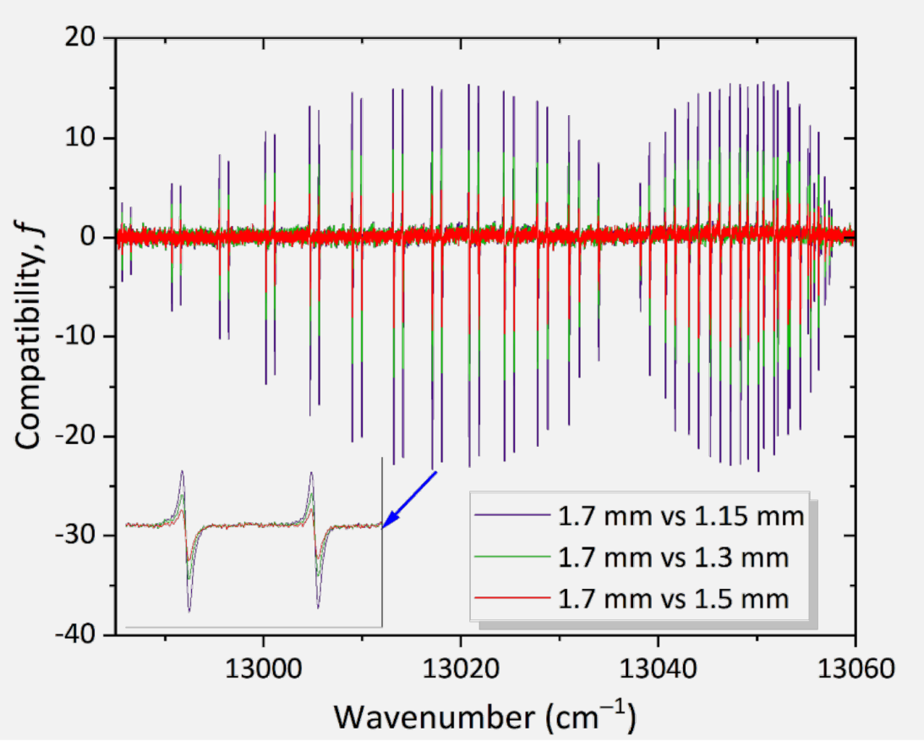


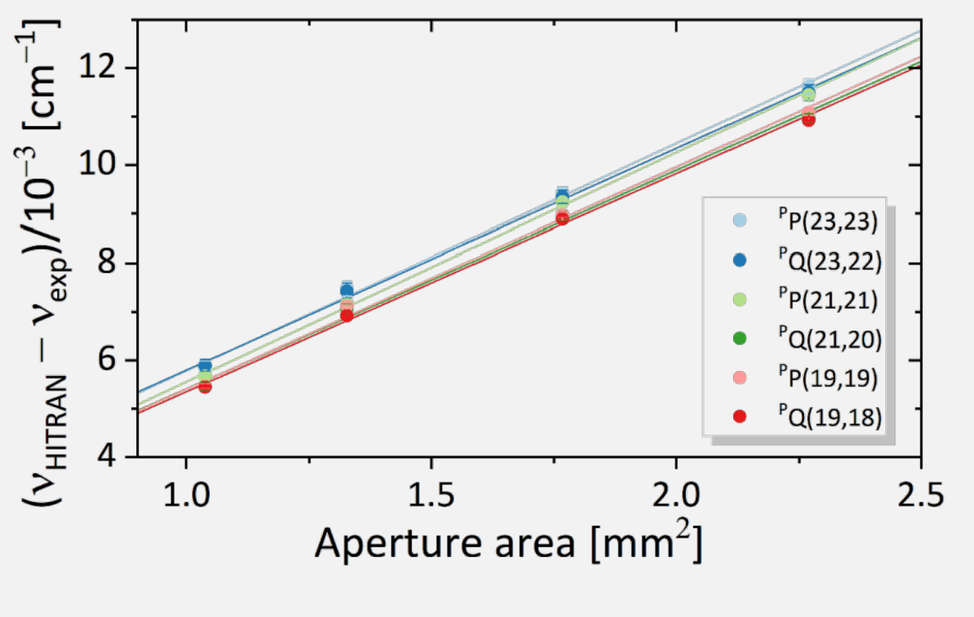


Experimental background was fitted with a polynom.

TECHNICALITIES: APERTURE

- Resolution: 0.032 cm^{-1}
- Pressure: 1100 hPa, pure gas

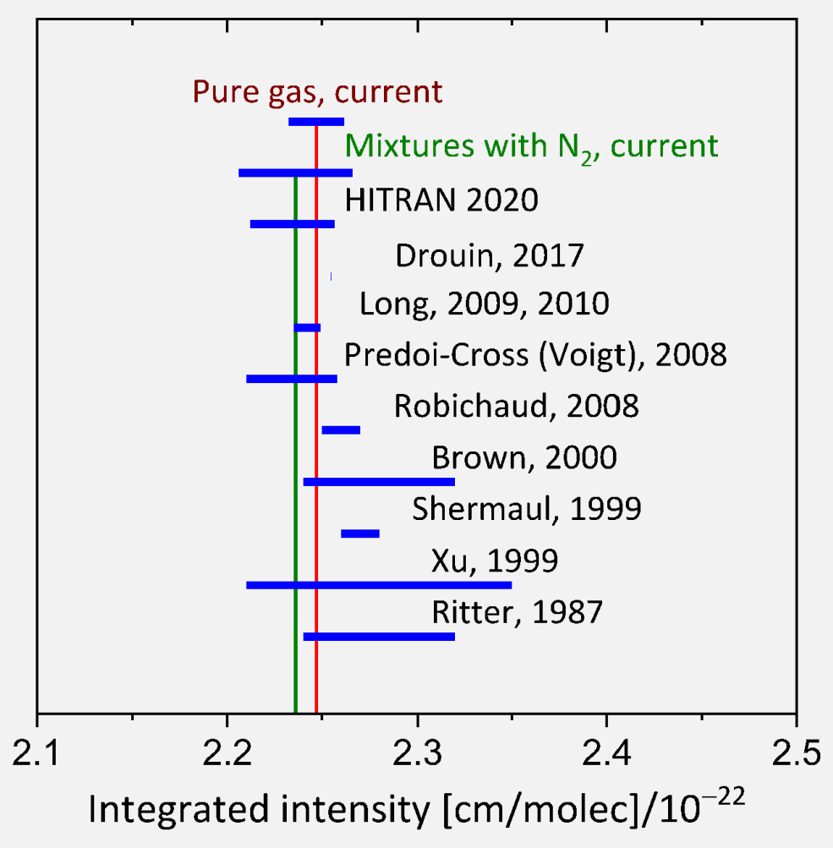




- Decreasing aperture shifts the lines to higher wavenumbers.

CONCLUSIONS AND OUTLOOK

- Spectra of O_2 and its mixtures with nitrogen are recorded primarily at 296 K, but a few at slightly different temperatures;
- Uncertainties for every wavenumber are evaluated;



← Overall agreement of averaged values with literature sources.

NB: most of the literature values are a sum over intensities of fitted lines, whereas ours are a direct integration. Integration has a larger uncertainty.

PriSpecTemp further development:

- Line-by-line analysis in progress (in collaboration with Dr. Ha Tran and Dr. Le Cong Tuong).
- Potential yields are pressure broadening and line shift coefficients together with the rotationless magnetic dipole moment and Hermann-Wallis factors.
- CO_2 measurements are ongoing.

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Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or EURAMET. Neither the European Union nor the granting authority can be held responsible for them.

The project has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.

EUROPEAN PARTNERSHIP
Co-funded by the European Union
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