

Towards new laser based UV absorption cross sections for traceable atmospheric remote sensing of ozone

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Need for new traceable ozone data

Why accurate ozone measurements are needed

In the context of global warming and atmospheric composition changes ozone (O₃) is a key molecule as it impacts the thermal structure of the atmosphere, has unique UV shielding capacity and plays a key role in atmospheric oxidation. It is also the third anthropogenic greenhouse forcer with a radiative forcing of ~0.40 Wm⁻² (1). In turn, O₃ levels are affected by long-term shifts in atmospheric composition and temperature (2,3), impacting air quality, agriculture, and health.

Amount of ozone measurements

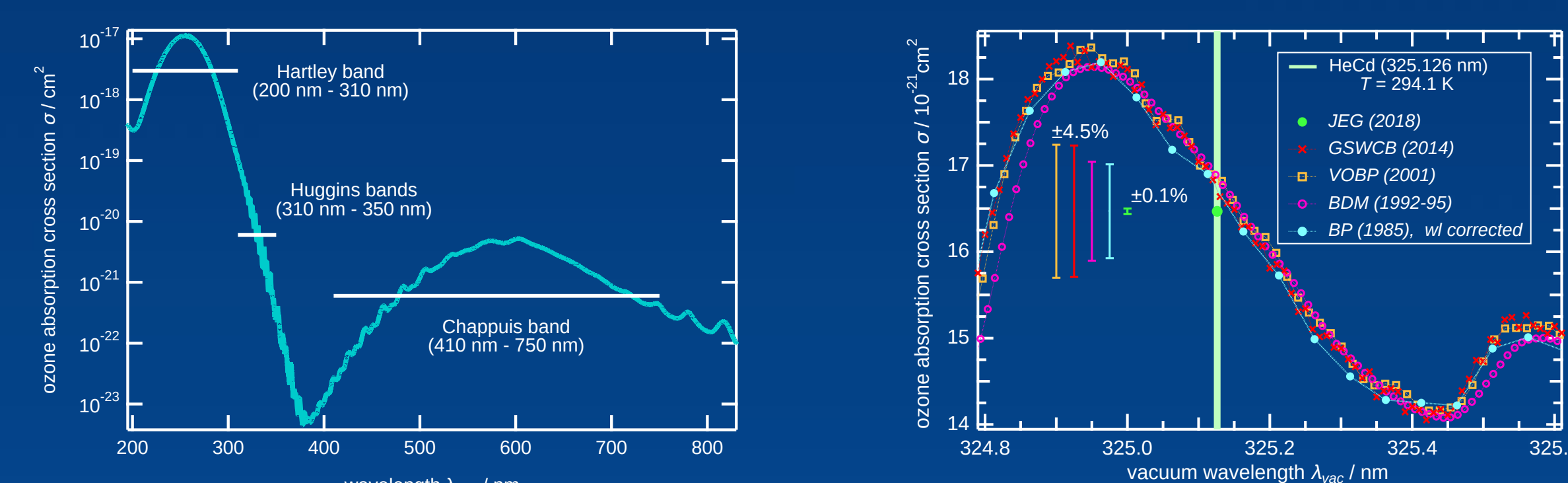
$$I/I_0 = \exp(-\sigma \cdot n_{O_3}(p, T, y) \cdot l)$$

It relates the fraction of the transmitted light (I/I_0) to the absorption length l , the ozone number density n_{O_3} and the absorption cross section σ .

UV/VIS absorption data for ozone remote sensing have recently been reviewed by the ACSO Expert Group (4) on behalf of IO3C (5), WMO (6) and the IGACO-O3/UV Action (7).

UV/VIS broadband absorption cross section in the UV/VIS and at 253.65

The evaluation indicated that the recommended cross-section at 253.65 nm (8) needed to be revised, leading to the establishment of a dedicated CCQM/GAWG (9) working group. The ozone cross section is an integral part of the metrological traceability chain, where standard reference photometers operating at 253.65 nm are used as primary standards for ozone measurements. There is now good agreement between the newly recommended ACSO broadband cross sections ((4), figure below) and the revised value at 253.65 nm (10). Given the very large dynamic range of the ozone absorption cross section, biases in other wavelength ranges, introduced by the use of dispersive instruments prone to the presence of stray light, cannot be excluded. Indeed, there is evidence that room temperature biases of about 2% might exist in the Huggins bands ((11), figure below). Given the uncertainty of the available measurements, uncertainties and biases of up to 6% are expected at the lowest atmospheric temperatures. This urgently calls for new temperature dependent measurements in regions where atmospheric observing platforms such as LIDARS, UV satellites, as well as Brewer, Dobson and SAOZ spectrophotometers operate.



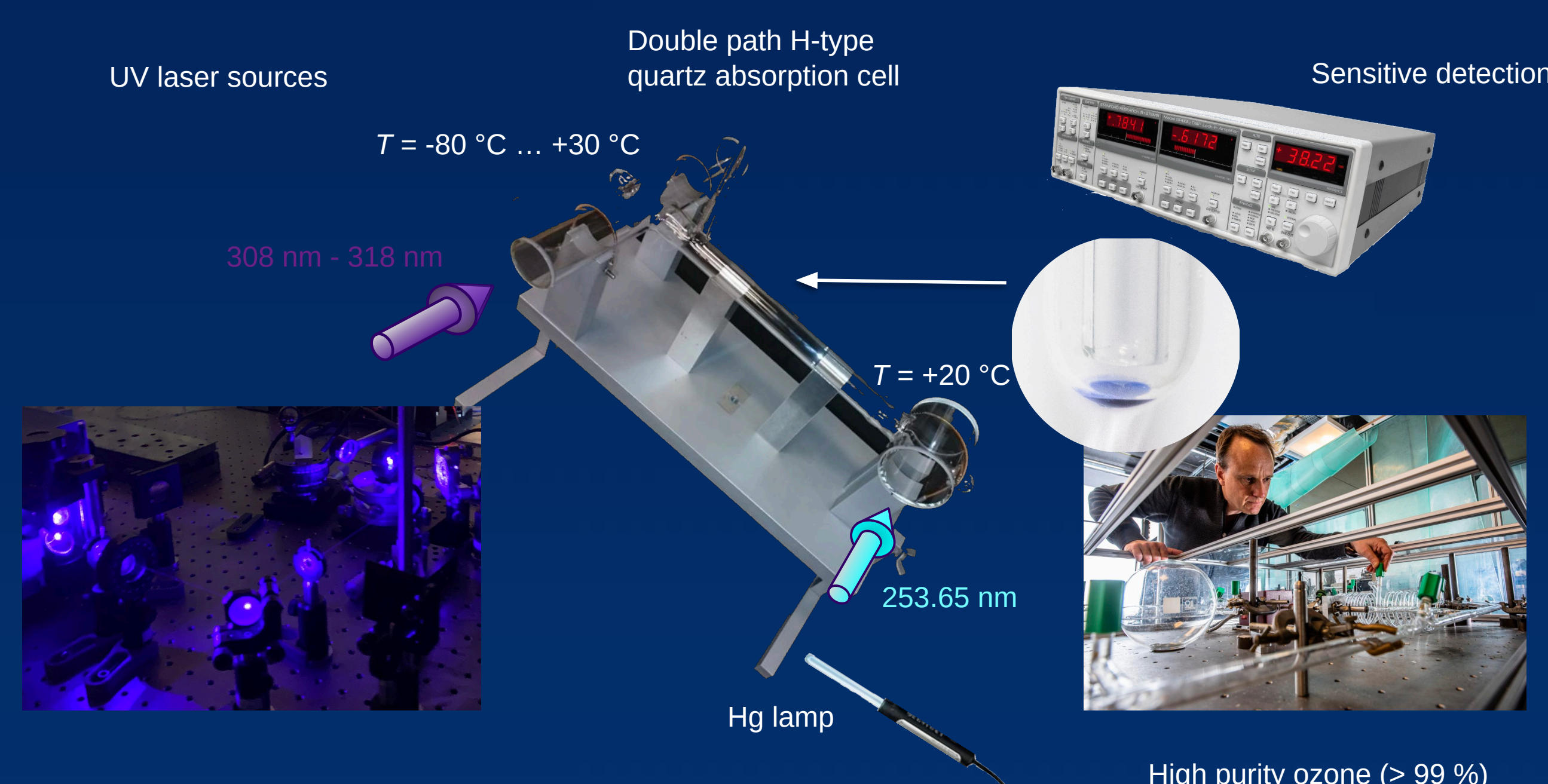
Ozone absorption cross section in the UV and VIS ranges, including spectral regions used for remote sensing (left). Shown curve corresponds to one of the data sets (BDM) recommended by ACSO. On the right, different measurements are compared to a recent laser study ((11), JEG (2018) with vertical bars representing typical standard uncertainties. The comparison indicates a possible bias in the recommended data.

Immediate project goals

- ➔ Develop new, innovative UV sources for extended laser-based cross section measurements between 308 nm and 318 nm
- ➔ Provide traceable ozone absorption cross section data with better than 1% relative uncertainty for the temperature range between -80 °C and +30 °C.
- ➔ Employ and validate the new data using stratospheric LIDAR and Brewer instruments.

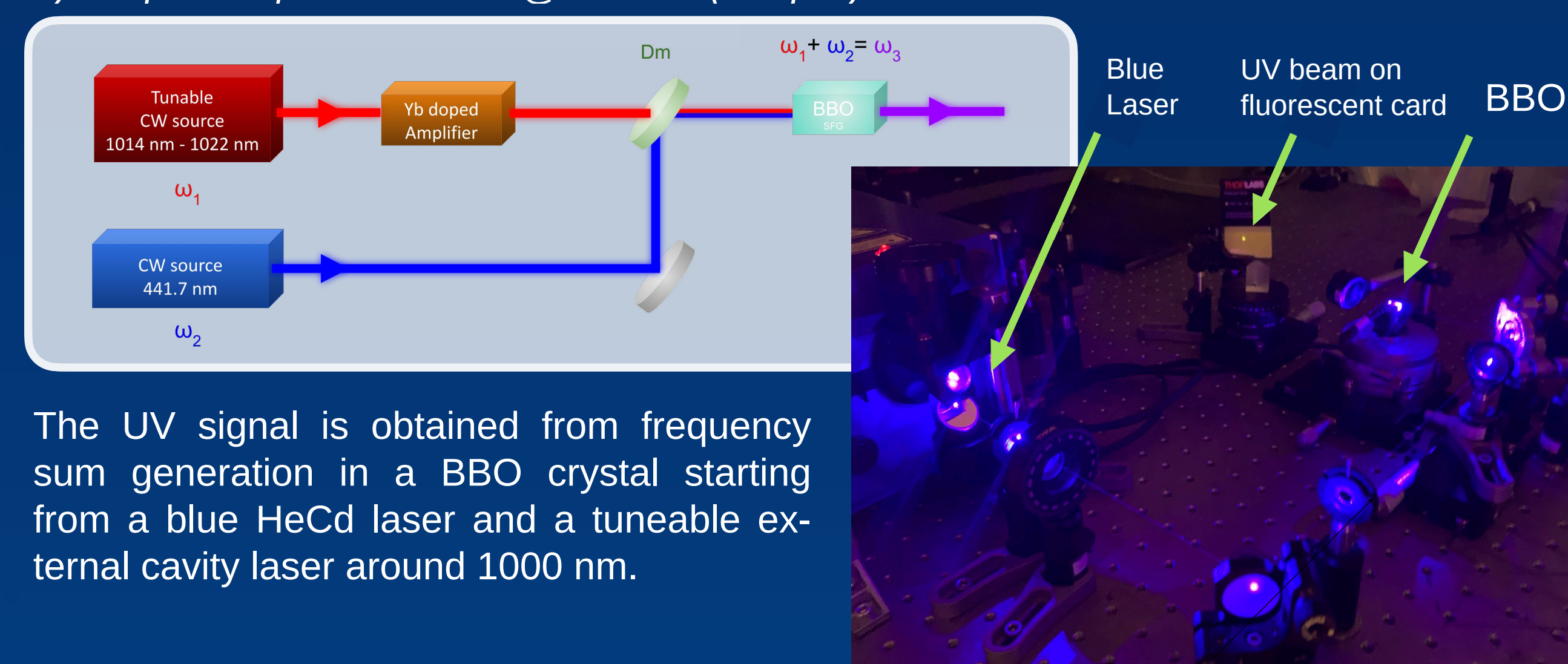
New laser based approach

General Setup



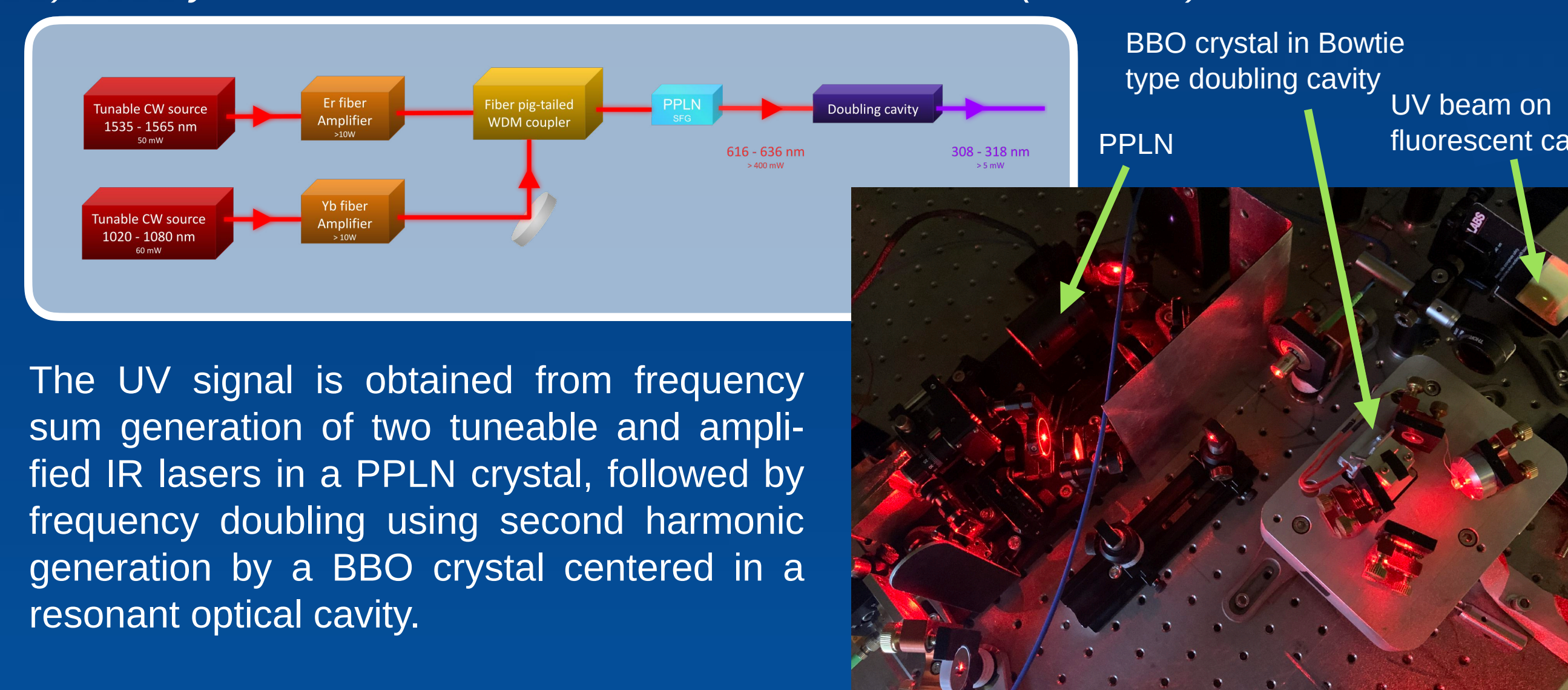
Two new high-resolution UV laser sources

1) Simple low power source @ 308 nm (~ 5 μW)



The UV signal is obtained from frequency sum generation in a BBO crystal starting from a blue HeCd laser and a tuneable external cavity laser around 1000 nm.

2) Broadly tuneable source between 308 nm and 318 nm (~ 10 mW)



The UV signal is obtained from frequency sum generation of two tuneable and amplified IR lasers in a PPLN crystal, followed by frequency doubling using second harmonic generation by a BBO crystal centered in a resonant optical cavity.

System performances & traceability

The installation of the experimental setup is still in progress and some uncertainties still need to be confirmed. All quantities involved in the cross section determination have relative uncertainties less than the relative uncertainty of 3.1 10⁻³ for the absorption cross section at 253.65 nm (10). Note that wavelength resolution and uncertainty are one to two orders of magnitude better than comparable numbers for dispersive measurement methods.

	Range	standard uncertainty / stability	Rel. standard uncertainty u_r	Note / Traceability
Pressure / hPa	0 - 130		2 10 ⁻³	Calibration by LNE
Temperature / °C	-80 ... +30	0.5	< 2.5 10 ⁻³	Pt100 sensor calibration using calibrated SRPT
Temperature / °C	20	0.1	3 10 ⁻⁴	Pt100 sensor calibration using calibrated SRPT
Ozone purity / %	≥ 99.8	0.06	0.06	(12)
UV Source 1 / nm	307.8 ... 308.2	3 10 ⁻⁴	10 ⁻⁶	Calibrated wavelength metre
UV Source 2 / nm	308 ... 318	3 10 ⁻⁴	10 ⁻⁶	Calibrated wavelength metre
Absorption length / mm	600	0.2	3 10 ⁻⁴	Vernier caliper with gauge block calibration
Reference cell length / mm	10.002	0.003	3 10 ⁻⁴	Interferometric measurement (13)

Bold values indicate validated performances, whereas italic numbers signify expected performances.

Summary and expected impact

Conclusion

- ➔ Installation of an experiment for SI traceable measurement of the UV ozone absorption cross sections in the Huggins bands is in progress.
- ➔ Two high-resolution UV laser systems for the 308 nm - 318 nm wavelength range have been installed.
- ➔ The characterisation of the laser systems is ongoing
- ➔ The construction of a metal-free absorption cell, which allows a direct reference to the recommended absorption cross section at 253.65 nm, is underway.
- ➔ Traceable ozone absorption cross section data with better than 1% relative uncertainty for the temperature range between -80 °C and +30 °C should be obtained

Impact of new cross section data

- ➔ Provide fiducial spectroscopic data to the ozone research community
- ➔ Reduce systematic uncertainties (14) of stratospheric LIDAR measurements, enabling stratospheric LIDAR to become a reference method for ozone profile measurement.
- ➔ Improve radiative forcing of ozone through more accurate measurements in the critical upper troposphere/lower stratosphere region.
- ➔ Resolve or reduce the discrepancy observed in opposite trends of the global tropospheric ozone burden derived from satellite instruments (15) (e.g. OMI or TROPOMI operating in the UV versus IASI in the IR).

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