

Towards trace gases detection in the UV range by coupling Dual Comb Spectroscopy and Integrated Path Lidar

Abel Feuvrier, Huu Dat Nguyen, Jérôme Morville, Patrick Rairoux, Sandrine Galtier

Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, UMR5306

F-69100 Villeurbanne, France

Lead Author e-mail address: abel.feuvrier@univ-lyon1.fr

Abstract: Detecting reactive trace gases in the atmosphere requires fast acquisition time and in-situ probing without air sampling. Several trace gases present a maximum absorption cross-section in the ultraviolet (UV) range, which call for a spectrally-resolved spectroscopy technique with a fast acquisition rate in this range to detect them. The Dual Comb Spectroscopy (DCS) technique meets these requirements. We present a DCS setup using a homemade bidirectional Ti:Sa laser cavity in the infrared (IR) range and use Second Harmonic Generation (SHG) to extend it to the UV range. We use O₂ detection to quantitatively characterize the setup in the IR range and show preliminary UV-DCS interferograms.

1. Introduction

Reactive trace gases in the atmosphere, such as NO_x, BrO or HO and Aromatics have a major influence over air quality [1,2] and consequently on climate [3] and present a maximum absorption cross-section in the UV range. To detect these reactive species in the atmosphere, the development of measurements without air sampling is required. In this context, coupling UV-Lidar techniques with absorption spectroscopy is an undeniable technique [8]. It should be noted that radicals detection requires a spectroscopic technique with high spectral resolution (to be able to assess several species simultaneously or to avoid interfering species) and fast acquisition time (to overcome intensity and phase fluctuations of the light source due to atmospheric turbulence). Since these gases are reactive and their concentration in the atmosphere is very low (ppt), achieving sufficient SNR for their optical detection requires the use of an integrated optical path technique (IP-LIDAR) [6, 7]. Coupling UV Lidar and spectroscopy on long path absorption exists since the 90's on SO₂, NO₂, O₃, OH, BrO, HONO [17-21].

Recent works demonstrate Dual Comb Spectroscopy (DCS) LIDAR in the NIR as a novel methodology for atmospheric remote-sensing of green-house gases, agricultural gases or urban pollution (see the review of Cossel *et al* [22]). Some laboratory demonstrations have been recently reported in the UV [9-11].

Based on our feasibility study for long-path absorption UV-DCS [5], we are developing a dedicated experiment, toward atmospheric trace gases detection. Our approach is based on a bidirectional ring Titanium-Sapphire (BD-TiSa) laser and proof-of-principle resolved spectral molecular lines has been reported [12]. We present in this paper recent achievements of IR-DCS using a BD-TiSa and the first results in the UV spectral range using this laser cavity arrangement.

DCS spectroscopy principle is reported in detail in [4, 13]. From a spectral point of view, DCS uses the coherent beating between two optical frequency combs (OFCs) with different repetition rates $f_{rep,1/2}$. This beating results in a radiofrequency (RF) comb (comb of spectral lines separated by $\Delta f_{rep} = f_{rep,1} - f_{rep,2}$) whose frequencies can be mapped to the optical frequencies (as illustrated in Figure 1). Thus, any spectroscopic information in the optical range is imprinted on the RF comb. In the temporal domain, OFCs are coherent trains of pulses (a train of fs pulses generated by a mode-locked laser for example). DCS in the temporal domain corresponds to the beating between the two trains of pulses. The Fourier transform of the resulting interferogram reveals the spectral signature of the absorbing medium (see Figure 2). The absence of moving mechanical pieces like in conventional Fourier-transform spectroscopy allows interferogram acquisition rate up to several kHz, at which most atmospheric turbulence effects are frozen out.

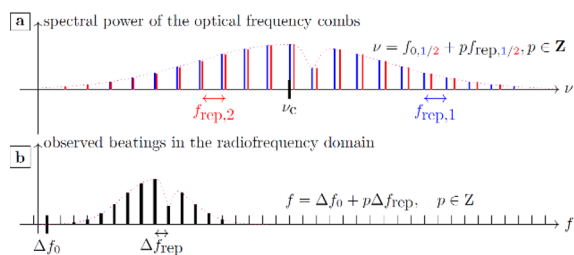


Figure 1. Principle of DCS in the spectral domain. The two combs (in blue and red) have a slight repetition rate difference Δf_{rep} . Thus, their beating creates a RF frequency combs. f_0 , offset frequency with $\Delta f_0 = f_{0,1} - f_{0,2}$.

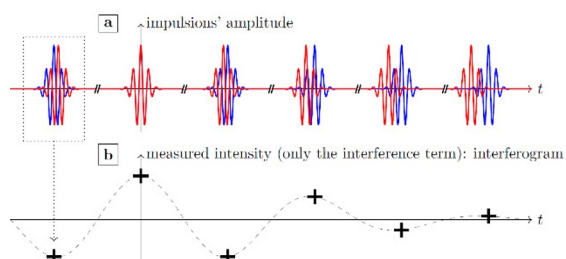


Figure 2. Principle of DCS from a temporal point of view. The two trains of pulses (in blue and red) have a slight repetition rate difference. Thus, one direction “walks through” the other, pulse pair after pulse pair. The integrated interference term gives, on a larger scale (each pair of pulse produces one point) an interferogram, whose Fourier transform contains information about the pulses and the absorption medium.

2. Experimental setup

Since DCS relies on the beating between two frequency combs, one needs to ensure a high degree of mutual coherence between the two combs. In our case, a homemade bidirectional cavity has been built: since the two combs share the same gain medium (Ti:Sa crystal) and cavity, they have a high degree of mutual coherence without any need for feedback loop [12,14]. A schema of the cavity is presented in Figure 3.

The choice of Ti:Sa was made to ensure high enough output power (up to 300 mW average output power in each direction in the IR), along with low intensity noise, which makes this setup suitable for long-path absorption spectroscopy in the IR and UV range. The cavity produces around 100 fs-long pulses with a repetition rate of about 118 MHz, whose carrier wavelength can vary from 760 to 810 nm.

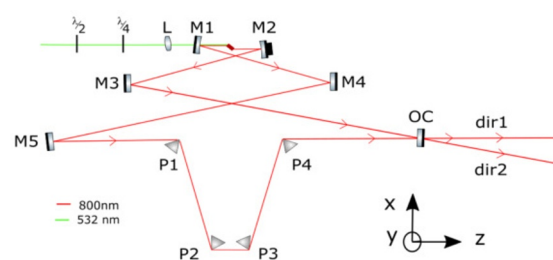


Figure 3. Schema of the bidirectional cavity [15]. A 532 nm pump laser is focused in a Ti:Sa crystal, creating two counterpropagating beams that are emitted in different directions through the output coupler mirror. A prisms compressor is used to compensate for dispersion, enabling the solitary wave to propagate inside the cavity.

3. Requirements for gas detection

To estimate the mutual coherence between the two combs, the detection of the A-band of ambient O_2 centered at 760 nm, was carried out with our laser setup (see figure 4). The resulting spectrum, shown in Figure 5, gives an upper bound of 1.5 GHz for the spectral resolution of our experiment, which corresponds to the pressure-broadened linewidth of O_2 under ambient atmospheric conditions (1 atmosphere, 296°K). The close-up on the P branch shows Fano-like asymmetric line-shape, the origin of which has not yet been identified in our setup. Such asymmetric line-shapes were reported in other DCS spectra [16].

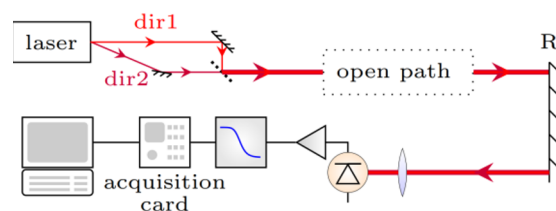


Figure 4. Setup for the O_2 detection experiment. After propagations through the open path (7 meters), the beams are superimposed and focused on a photodiode. The output current is amplified through a transimpedance amplifier, filtered-out with a low-pass filter with 50 MHz cut frequency to avoid aliasing. The signal is digitized with a 12 bit acquisition card.

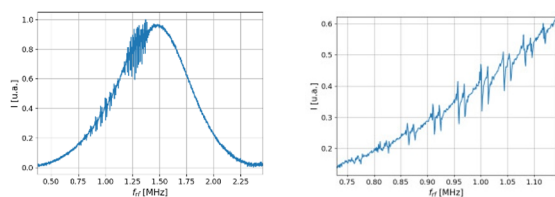


Figure 5. The Fourier-transform of a 5ms temporal windows of the IGM. The x-scale corresponds to the Fourier frequencies. (left) Envelop of the light pulses in which is imprinted the absorption spectrum signature of O₂ (P and R branches of the A band), obtained with the DCS setup and averaged over 10 spectra. (right) a close-up shows Fano-like line shapes.

4. DCS the UV range

The extension into the UV range, is achieved by frequency-doubling through a 1-mm long BBO crystal, creating UV output power up to 40 mW in average for each OFC. This output power is sufficient to achieve UV-DCS on a km-long open path [5]. The UV generated beams are then combined to obtain interferograms such as the one presented in Figure 6. The spectral envelop of the Fourier transform of the UV interferogram agrees in width and shape with the one measured using a conventional grating spectrometer (GS) within the uncertainty of the GS measurement (see figure 7).

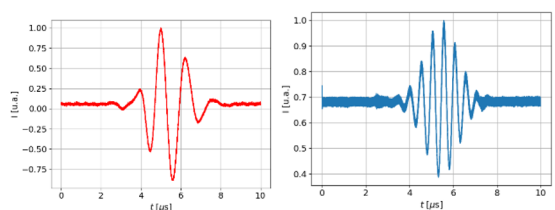


Figure 6: Interferograms obtained at the same time in the IR range (left) and in the UV range (right) with a contrast up to 70% and a noise ratio of about 20 in the UV range for a single-shot measurement. $\Delta f_{\text{rep}}=4,3$ Hz and $f_{\text{rep}} = 118$ MHz.

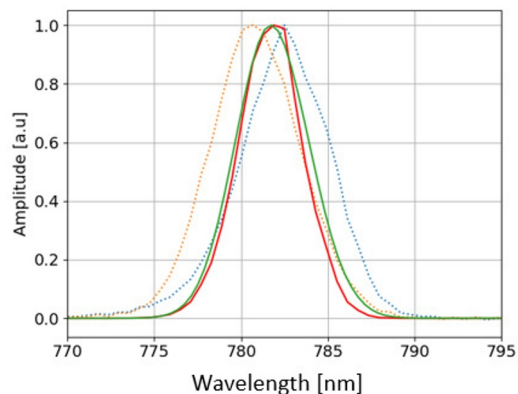


Figure 7: Comparison of retrieved spectra using UV-DCS and a grating-based spectrometer (GS). (blue dotted line) GS spectrum of the light radiation of direction 1. (Orange dotted line) GS spectrum of direction 1. (red plain line) Calculated combined spectra of direction 1 and direction 2. (green plain line) retrieved envelop spectra using the UV-DCS setup. The absolute position of the spectra has been adjusted on each other.

Proof-of-concept UV-DCS using this setup using will be first made on atomic Cesium for methodology validation, then on a gas cell of NO₂ as a first step towards an open-path implementation of UV-DCS.

4. References

- [1] Yang, X., Wang, H., Lu, K. *et al.* Reactive aldehyde chemistry explains the missing source of hydroxyl radicals. *Nat Commun* **15**, 1648 (2024).
- [2] Saiz Lopez, A., Borge, R., Notario, A. *et al.* Unexpected increase in the oxidation capacity of the urban atmosphere of Madrid, Spain. *Sci Rep* **7**, 45956 (2017).
- [3] Daniel J. Jacob, Darrell A. Winner, Effect of climate change on air quality, *Atmospheric Environment*, Volume 43, Issue 1, 2009, Pages 51-63
- [4] Newbury, N.R.; Coddington, I.; Swann, W. Sensitivity of coherent dual-comb spectroscopy. *Opt. Express*, 2010, 18, 7929–7945.
- [5] Galtier *et al*, Towards DCS in the UV Spectral Range for Remote Sensing of Atmospheric Trace Gases, *Remote sensing vol. 12*, 2020
- [6] Nicolas Cézard and Jean-Michel Melkonian, "Long-wave infrared multi-wavelength IPDA lidar for standoff detection of chemical warfare agents: theoretical study," *Appl. Opt.* **59**, 11167-11179 (2020).
- [7] Ehret, G *et al.* MERLIN: A French-German Space Lidar Mission Dedicated to Atmospheric Methane. *Remote Sens.* 2017, 9, 1052.

- [8] Platt, U.; Stutz, J. *Differential Optical Absorption Spectroscopy: Principles and Applications*; Springer: Berlin/Heidelberg, Germany, 2008
- [9] Chang et. al., Multi-harmonic near-infrared-ultraviolet Dual Comb spectrometer, *Optics letters*, 2024, 7
- [10] Xu et. al., Near-ultraviolet photon-counting Dual Comb Spectroscopy, 2023, arXiv.2307.12869
- [11] Fuerst et. al., Broadband ultraviolet dual comb spectroscopy, 2023, arXiv.2312.07038
- [12] Galtier et. al., High-resolution dual comb spectroscopy using a free-running, bidirectional ring titanium sapphire laser, *Optics Express* 2022.
- [13] Picqué and Hänsch, Frequency Comb Spectroscopy, *Nature Photonics*, 2019, 13
- [14] Ideguchi et. al., Kerr-lens mode-locked bidirectional dual-comb ring laser for broadband dual-comb spectroscopy, *Optica*, 2016, 3
- [15] Pivard, Development of a dual comb laser source toward atmospheric radical OH monitoring, PhD thesis, Université de Lyon, 2021
- [16] Guay et. al., Addressing asymmetric Fano profiles on molecular lines in dual-comb spectroscopy, *Optics letters*, 2022, 47
- [17] M. Hausmann, U. Brandenburger, T. Brauers, and H.P. Dorn. Detection of tropospheric OH radicals by long-path differential optical-absorption spectroscopy: Experimental setup, accuracy, and precision. *Journal of Geophysical Research: Atmospheres*, 102(D13):16011–16022, 1997.
- [18] H. Fuchs et al, Comparison of OH concentration measurements by DOAS and LIF during sapphire chamber experiments at high OH reactivity and low NO concentration. *Atmospheric Measurement Techniques*, 5 (7), 1611-1626, 2012.
- [19] K. Hebestreit et al. DOAS measurements of tropospheric bromine oxide in mid-latitudes. *Science*, 283 (5398) 55-57, 1999
- [20] G. Hönninger, H. Leser, O. Sebastián, and U. Platt. Ground-based measurements of halogen oxides at the Hudson Bay by active longpath DOAS and passive MAX-DOAS. *Geophysical Research Letters*, 31 (4) 2004
- [21] J. Stutz, et al. Simultaneous DOAS and chamber measurements of HONO in Houston, TX. *Atmospheric Environment*, 44(33):4090-4098, 2010.
- [22] K. C. Cossel et al. 2 - remote sensing using open-path dual-comb spectroscopy, in *Advances in Spectroscopic Monitoring of the Atmosphere*, W. Chen, D. S. Venables, and M. W. Sigrist, eds. (Elsevier, 2021), pp. 27–93.