VIS/UV Dual Comb Spectroscopy

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Motivation

- Ultraviolet (UV) spectral region underexplored → Dual-Comb (DC) Spectroscopy brings high resolution [1]
- Probe electronic transitions with complete state resolution
  - Photochemistry of atmospheric/astrophysical gases
  - Examples: CH_2O, CH_3I, NO_2, NH_3, SO_2, CO_2
- Challenges:
  - UV laser source with MHz repetition rate via nonlinear frequency up-conversion → short pulses required
  - Superposition and detection of UV radiation

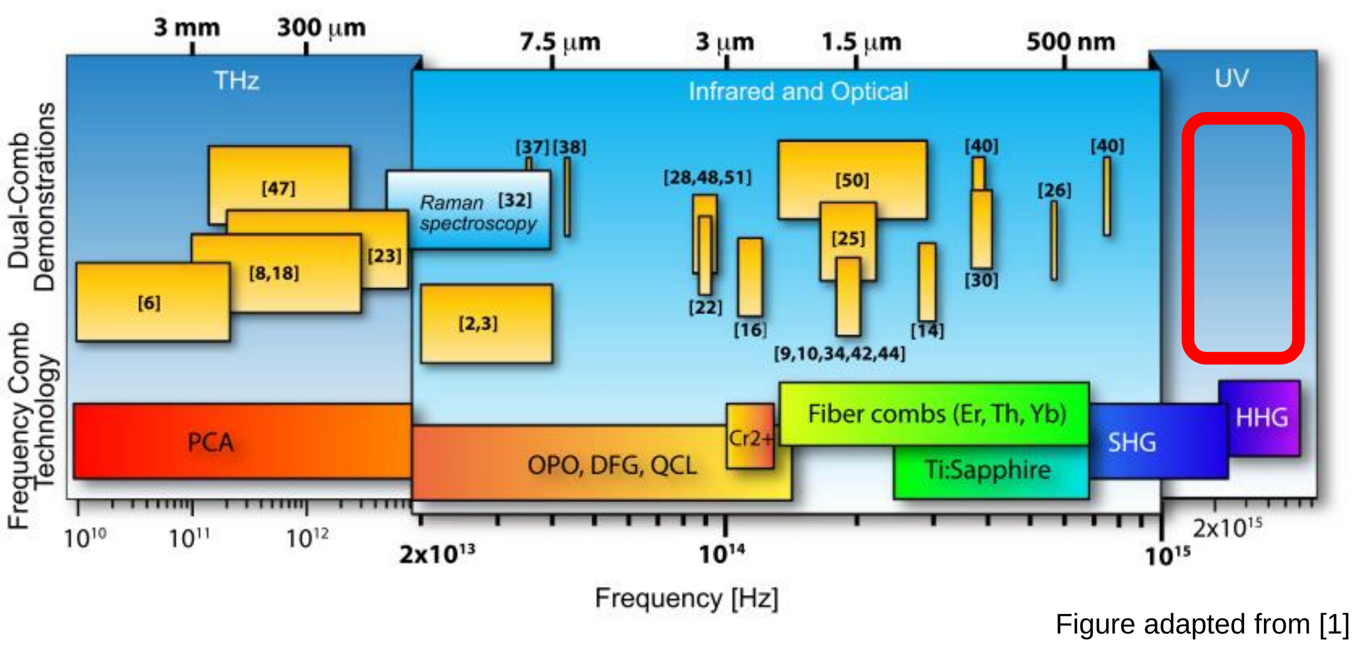


Figure adapted from [1]

Dual Comb Spectroscopy

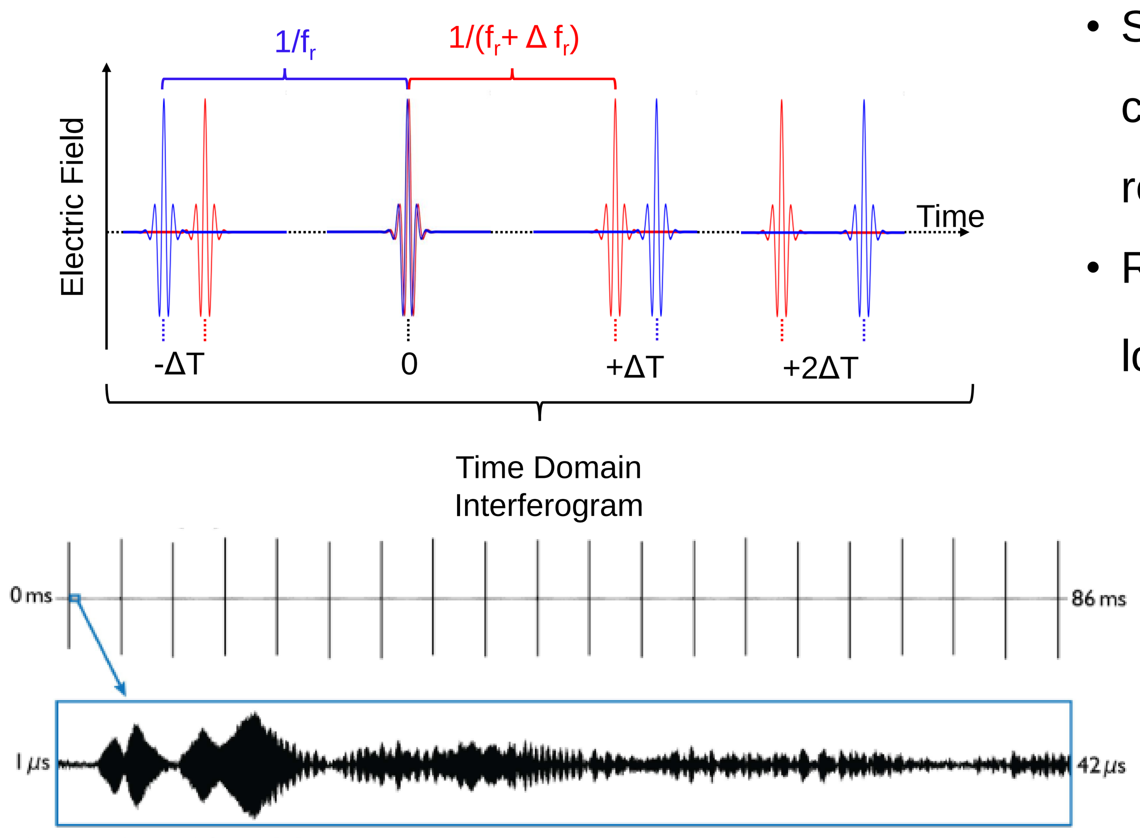


Figure adapted from [2]

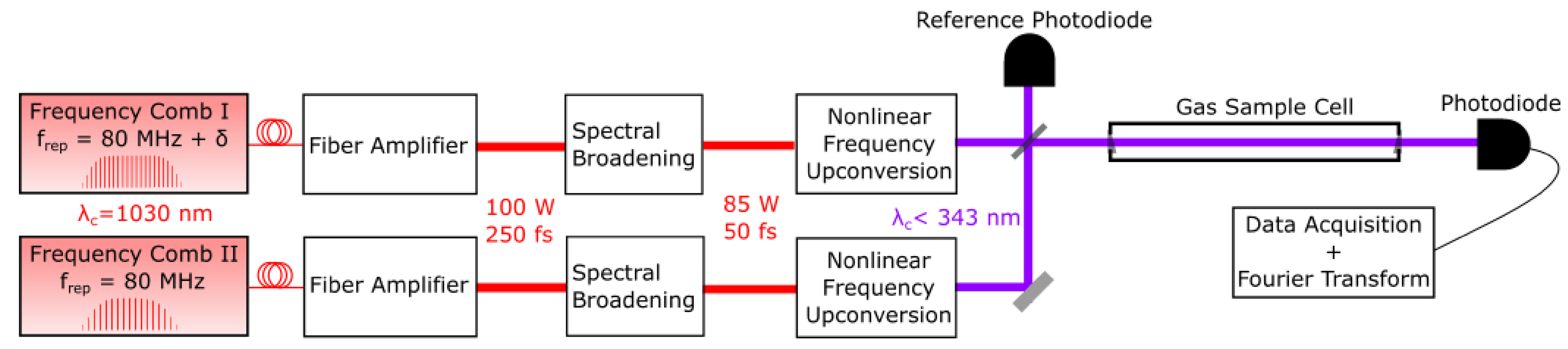
radio frequency spectrum

⇩

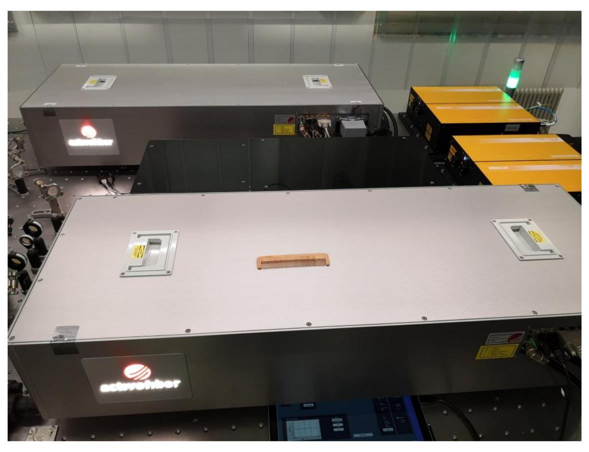
conversion to optical spectrum

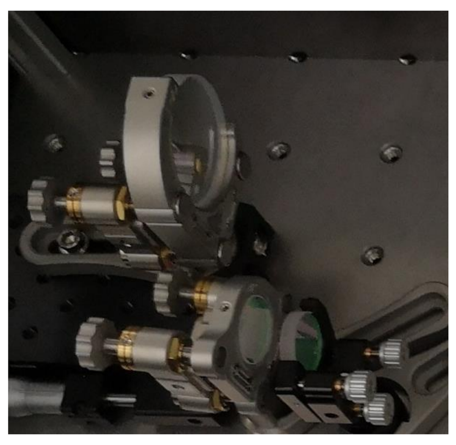
- Superposition of two frequency comb outputs with fixed repetition rates
- Repetition rate difference is locked to Δf_r
- Fast data acquisition with longer temporal delay than state-of-the-art spectrometers (higher spectral resolution, expect more than one order of magnitude improvement)

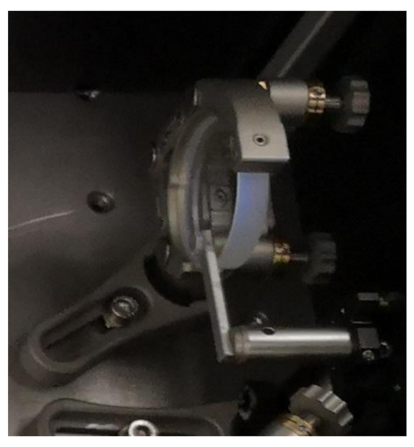
Setup



- Ytterbium oscillators seed pulse picking fiber amplifiers at 250kHz to 80 MHz repetition rate
- Pulse compression for efficient frequency up-conversion into the UV spectral region
- Gas sample cell with windows at Brewster's angle and fast photodiode for data acquisition







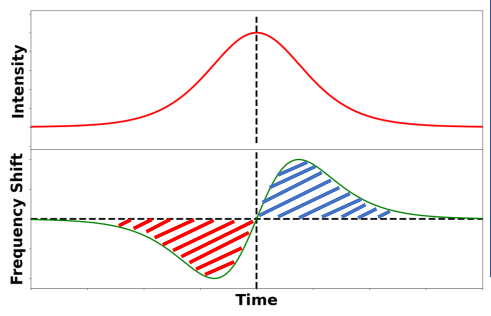
Spectral Broadening for Shorter Pulses

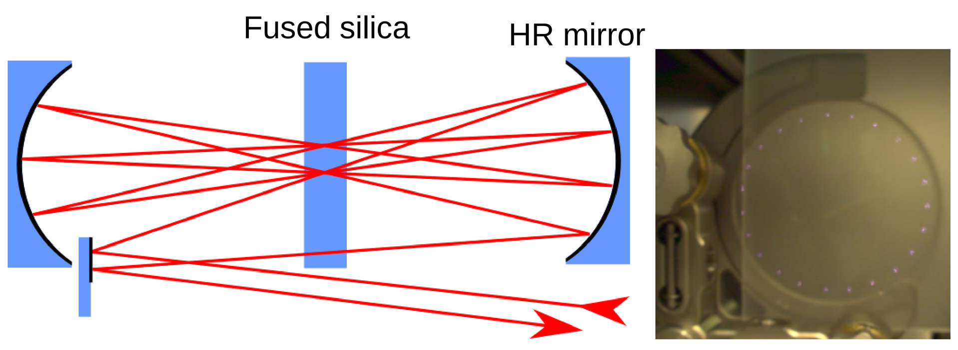
- At high intensities the refractive index of a medium, e.g. fused silica, becomes intensity dependent

$$n(t) = n_0 + n_2 \cdot I(t)$$

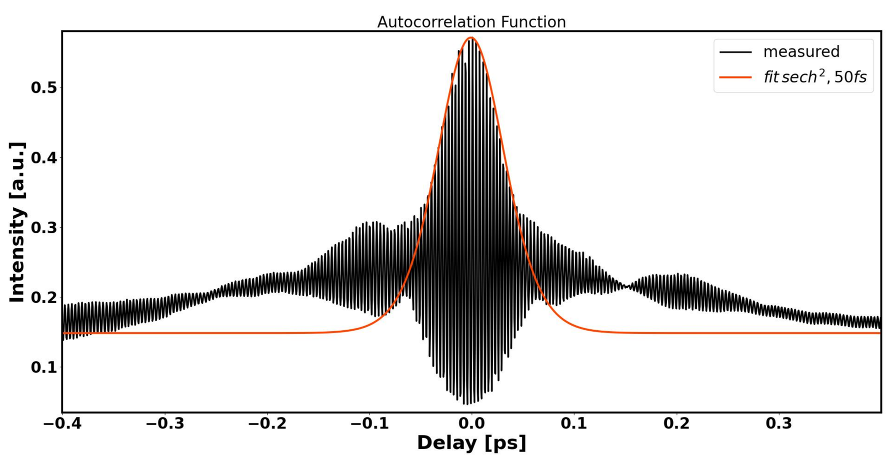
→ Instantaneous frequency shift dependent on slope of intensity profile (self-phase modulation)

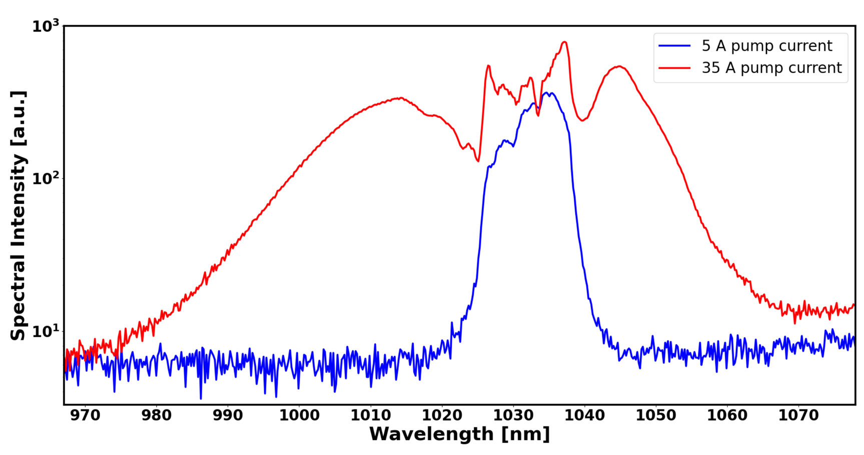
- Generation of new frequency components





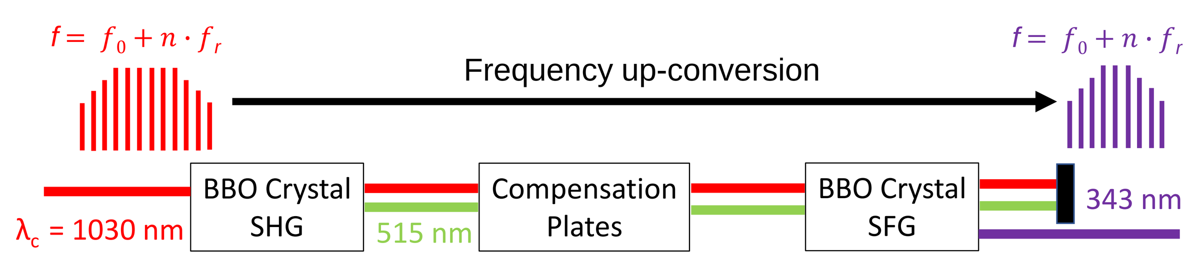
- Herriott-type multipass cell (MPC) setup
- 46 passes with focus between the two highly-reflective (HR) mirrors
- Mirrors operate in the negative dispersion regime to compensate group delay dispersion introduced by air and fused silica [3]





- Input beam: P_{avg} = 80 W with 250 fs pulse duration at 10 MHz repetition rate
- Spectrum after the MPC covers 997-1055 nm @ -10 dB level
- Autocorrelation measurement yields 50 fs pulse duration
- Power transmission T ~ 85 %

UV Frequency Comb Generation



- Two step nonlinear process in crystals
- Challenging tradeoff: bandwidth vs. efficiency

Atmospheric Gases

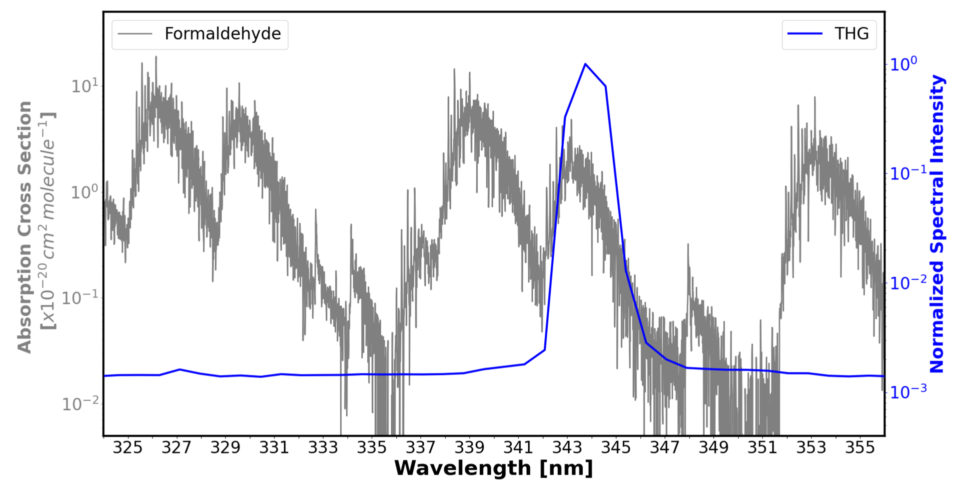
In collaboration with BOKU

- Absorbing solar UV light → trigger for photochemical reactions in the atmosphere
- Focus on gases, which contribute to global warming → every day relevance

Formaldehyde (CH_2O)

- Relevant gas for cities with smog issues, e.g. Mexico City [4]
- Essential input parameter for environmental simulations (e.g. indicator for isoprene [4])

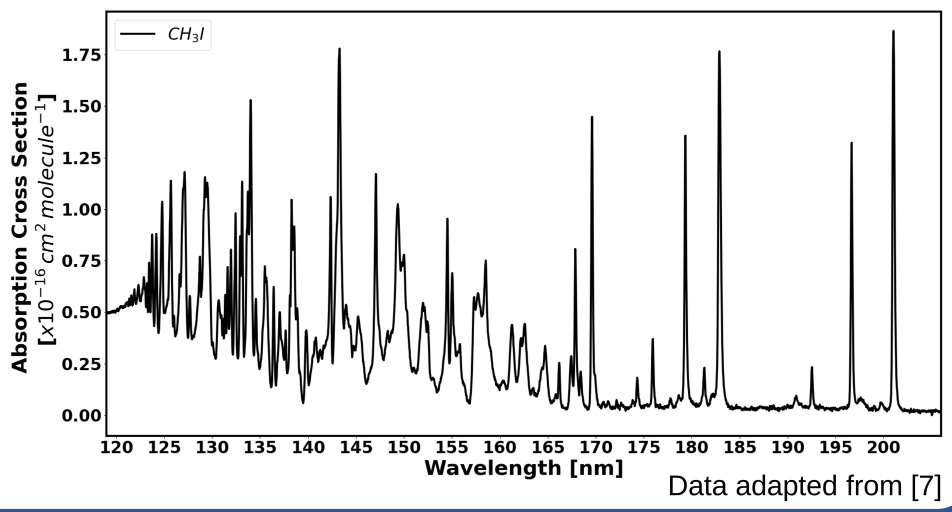
→ Determination of absolute absorption cross section



Data adapted from [5]

Iodomethane (CH_3I)

- Might enhance ozone destruction, e.g. emitted from algae in oceans [6]
- Absorption spectra and ionization energy needed for quantum mechanical simulations



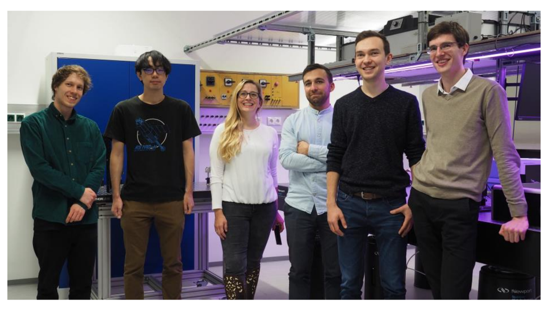
Data adapted from [7]

Outlook

- First realization of the near-UV DC spectrometer → investigate transition line widths & absolute absorption cross-section of formaldehyde with unprecedented spectral resolution
- Doppler-free two-photon excitation spectroscopy of benzene (interaction with ozone in the troposphere, noxious effects on human health [8])
- High harmonic generation for experiments deeper in the ultraviolet region (λ < 300 nm) → measure Rydberg series of iodomethane
- Pump-probe scheme for time-resolved studies with high temporal and spectral resolution

References

[1] Coddington, Ian, Nathan Newbury, and William Swann. "Dual-comb spectroscopy." *Optica* 3.4 (2016): 414-426.
[2] Birgitta Bernhardt. "Dual Comb Spectroscopy". PhD thesis. Ludwig-Maximilians-Universität, 2011
[3] Gröbmeyer, Sebastian, et al. "Self-compression at 1 µm wavelength in all-bulk multi-pass geometry." *Applied Physics B* 126.10 (2020): 1-6.
[4] Tatum Ernest, Cheryl, Dieter Bauer, and Anthony J. Hynes. "High-Resolution Absorption Cross Sections of Formaldehyde in the 30285–32890 cm^{-1} (304–330 nm) Spectral Region. " *The Journal of Physical Chemistry A* 116.24 (2012): 5910-5922.
[5] Cantrell, Chris A., et al. "Temperature-dependent formaldehyde cross sections in the near-ultraviolet spectral region." *Journal of Physical Chemistry* 94.10 (1990): 3902-3908.
[6] Tegtmeier, Susann, et al. "The contribution of oceanic methyl iodide to stratospheric iodine." *Atmospheric Chemistry and Physics* 13.23 (2013): 11869-11886.
[7] Locht, Robert, et al. "Medium and high resolution vacuum UV photoabsorption spectroscopy of methyl iodide (CH_3I) and its deuterated isotopomers CD_3I and CH_2DI. A Rydberg series analysis." *Chemical Physics* 365.3 (2009): 109-128.
[8] Fally, Sophie, Michel Carleer, and Ann C. Vandaele. "UV Fourier transform absorption cross sections of benzene, toluene, meta-, ortho-, and para-xylene." *Journal of Quantitative Spectroscopy and Radiative Transfer* 110.9-10 (2009): 766-782.



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