An Interband Cascade Laser Sensor Dedicated To Monitor Gaseous Ethanol Above Sparkling Wines

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Introduction

Figure 1: Gaseous species invade the headspace above glasses, thus modyfing the chemical space perceived by consumers.

Under standard wine tasting conditions, conveyed by evaporation through the wine surface and by bursting bubbles in case of sparkling wines, gaseous species progressively invade the headspace above glasses (including ethanol, many other volatile organic compounds, and even gas-phase CO_2 in sparkling wine glasses) [1]. In recent years, a spectrometer based on tunable diode laser absorption spectroscopy (TDLAS) (the so-called CO_2-DLS), was developed to monitor gas-phase CO_2 in the headspace of champagne glasses [2-4]. Moreover, because ethanol is known to have a strong impact on the wine bouquet [5], micro-gas chromatography was used in the past to monitor gaseous ethanol in the headspace of champagne glasses, but with a relatively poor temporal resolution leading to a one-minute data sampling interval [1].

Here, the idea of monitoring gas-phase ethanol with a high temporal resolution led to an update of the CO_2-DLS. Ethanol molecule is highly active in the 1000 cm^{-1} and 3000 cm^{-1} region with strong ro-vibrational transition. Nevertheless, standard soda-lime-silica tasting glasses absorb mid-infrared light below 2200 cm^{-1}. Thus, the glass restricts light sources to the absorption in the 3000 cm^{-1} region. In this spectral area, diode laser and quantum cascade laser (QCL) are less suitable [6]. Therefore, a new technology laser source were used: Interband Cascade Laser (ICL), to scan few cm^{-1}, centered at 2989 cm^{-1} peak, of the ethanol broadband spectrum. The CO_2-DLS setup was thus adapted to include the ICL in order to quantify ethanol by straightforward absorption spectroscopy.

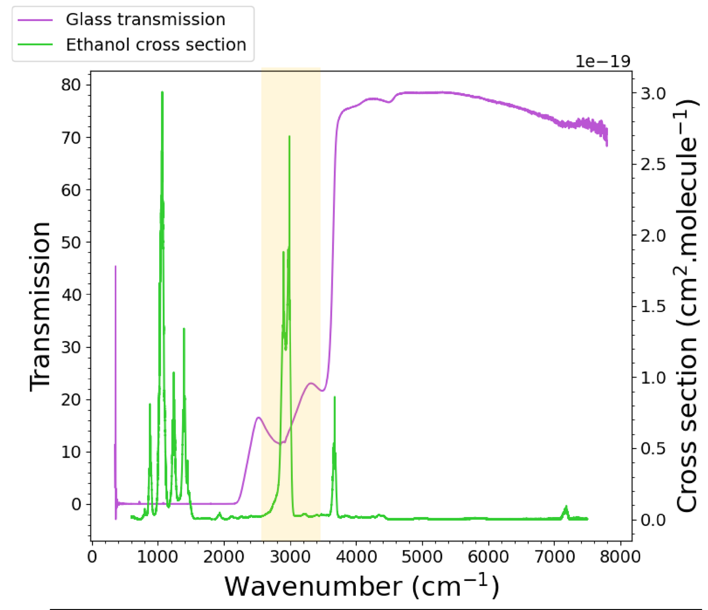


Figure 2: Light transmission through an INAO glass (FTIR) overlapped with the ethanol cross-section (Hitran database).

Experimental Setup & Data Processing

ICL DFB laser (nanoplus):

	Hardware	Value
Temperature	Thorlabs TED 8040	44.5°C
Current	Thorlabs LDC 8010	20 mA
Sawtooth signal	NI PXI-7852R	20 – 75 mA | 42 Hz

Table 1: The nanoplus DFB ICL parameters and the hardware used to scan the ethanol absorption peak centered at 2989.5 cm^{-1}. All the hardwares are interfaced by a LabVIEW software.

Beer-Lambert law:

$$T = \exp(-\rho N L \sigma_{eff})$$

- T: Transmission
- ρ: Molecule mixing ratio
- N: Molecule density
- L: Optical path
- σ_{eff}: Cross section (DB)

HITRANonline

Non-linear fit :

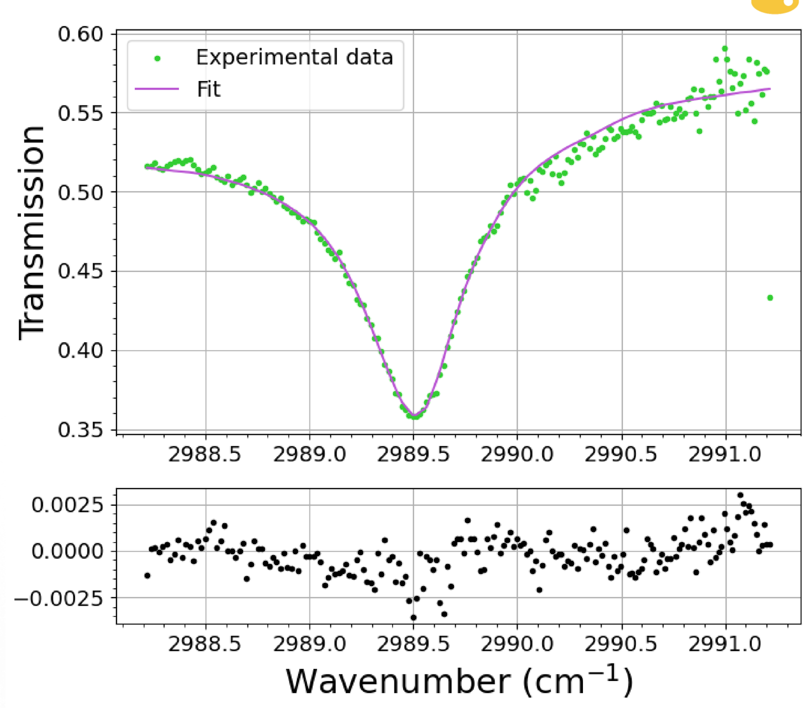


Figure 4: The fit (in purple) of an experimental transmission spectrum (in green) recorded by the ICL. The light went through a gas cell filled with 1000 ppm of ethanol broadened with nitrogen along an optical path of 150 cm under atmospheric pressure and ambient temperature. The black line is the difference between the experimental data and the fit.

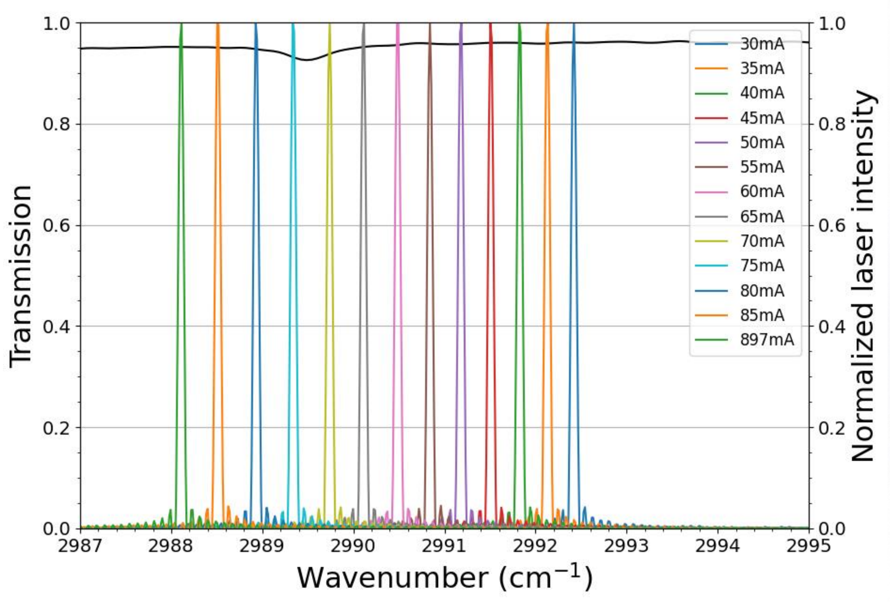
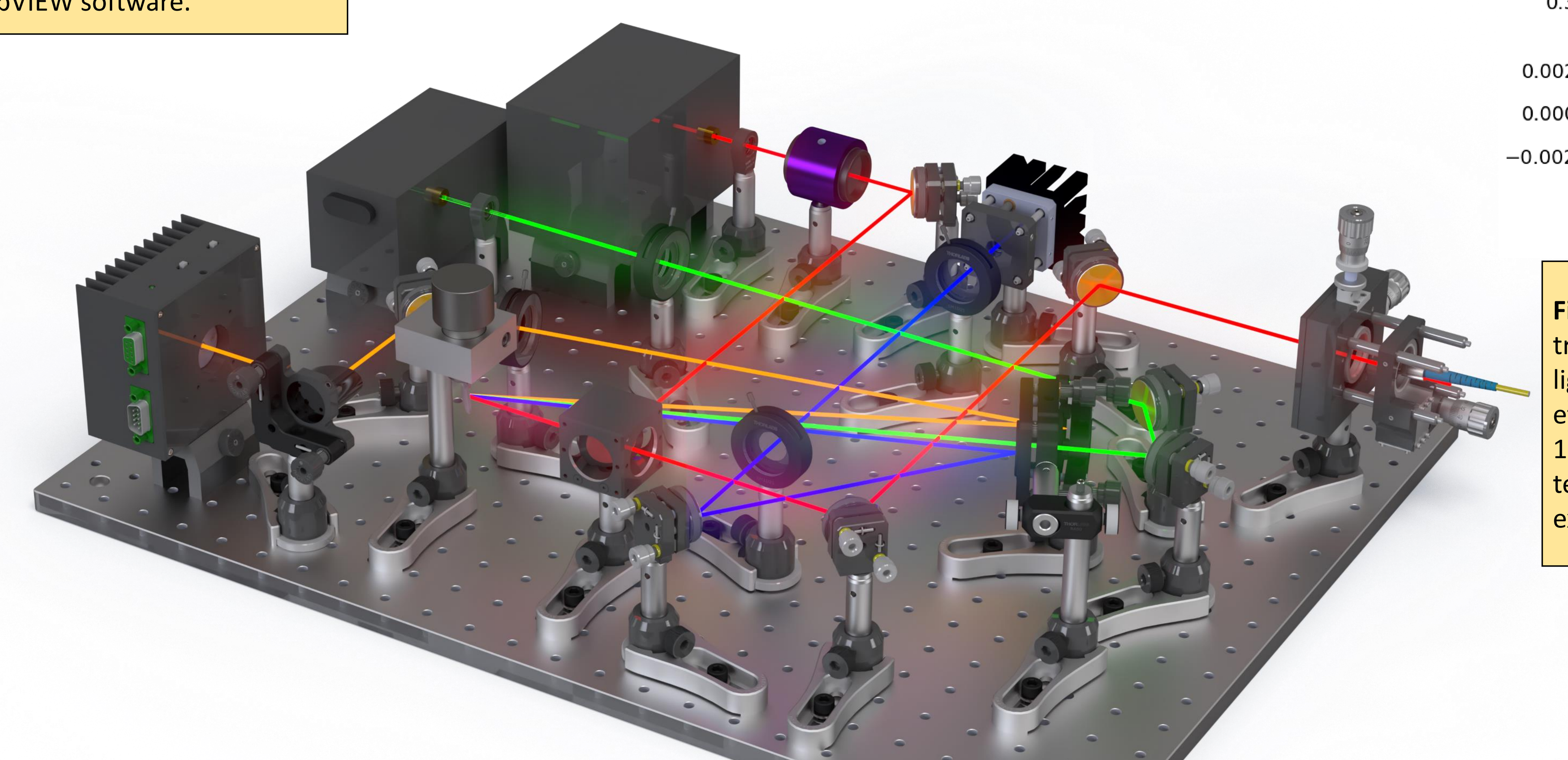


Figure 3: Overlapping of the different laser emissions over a FTIR ethanol spectrum. The laser emissions obtained by a FTIR are normalized. The laser temperature was fixed at 44.5 °C and the current was adjusted from 30 mA to 89.7 mA. The ethanol transmission spectrum was recorded with a FTIR from a gas sample with 0.5% of ethanol in a 17 cm cell under 296 K and 1 atm.



Spectrometer features :

- 3 Infrared lasers selected by a galvanometric mirror
- Single fibered output beam
- Germanium crystal Fabry-Perot → FSR = 0.045 cm^{-1}
- InAs photodiode detector

Figure 5: 3D view of the spectrometer involving three lasers, two for the monitoring of gas-phase CO_2 (shown with the orange and green beam), and one for the monitoring of gas-phase ethanol (shown with the blue beam). The red beam is the common pathfollowed by the three lasers.

Technical Validation

Gas bottle	Concentration (ppm)
1	200 ± 10
2	995 ± 50
3	1978 ± 99

Table 2: Three manufactured gas-phase ethanol concentrations in ppm broadened by nitrogen and their errors.

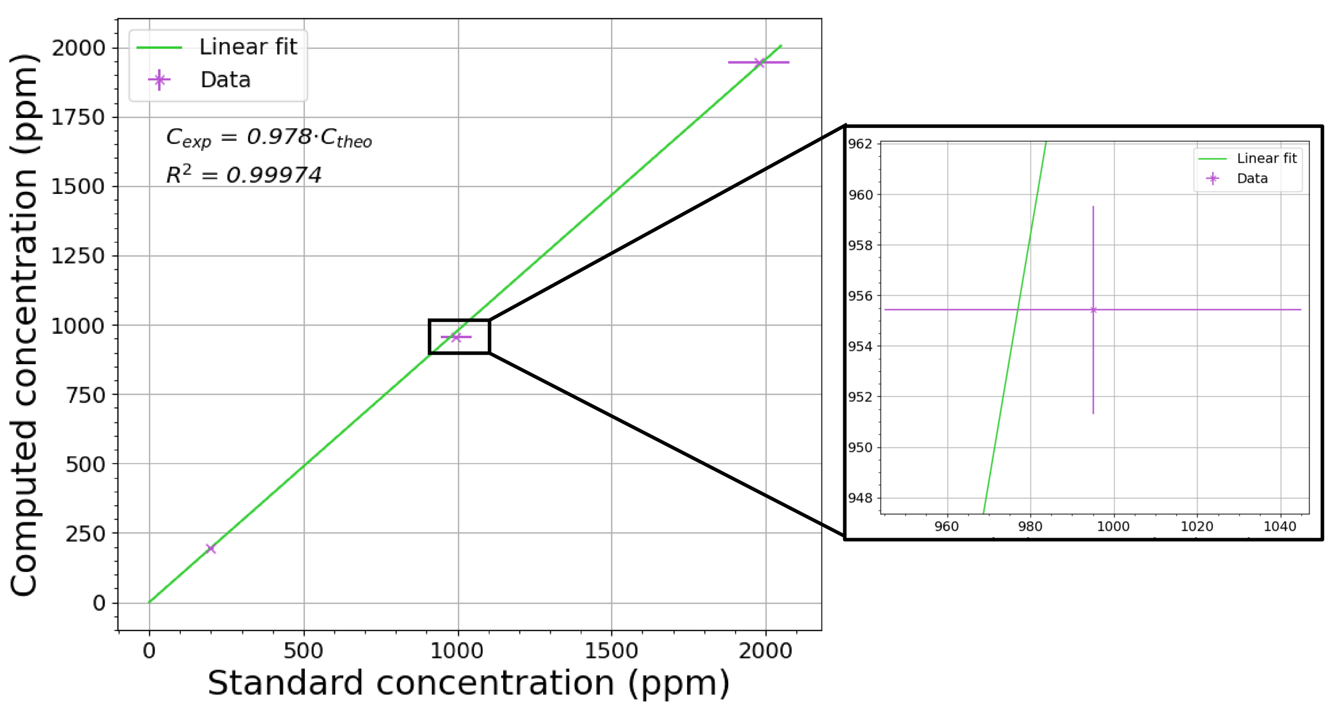


Figure 7: Computed concentration of gas-phase ethanol as a function the manufactured concentration. Each data point is the arithmetical mean of a thousand of spectra. A zoom close to 1000 ppm is shown to illustrate the low standard deviation of the measurement along the thousand spectra.

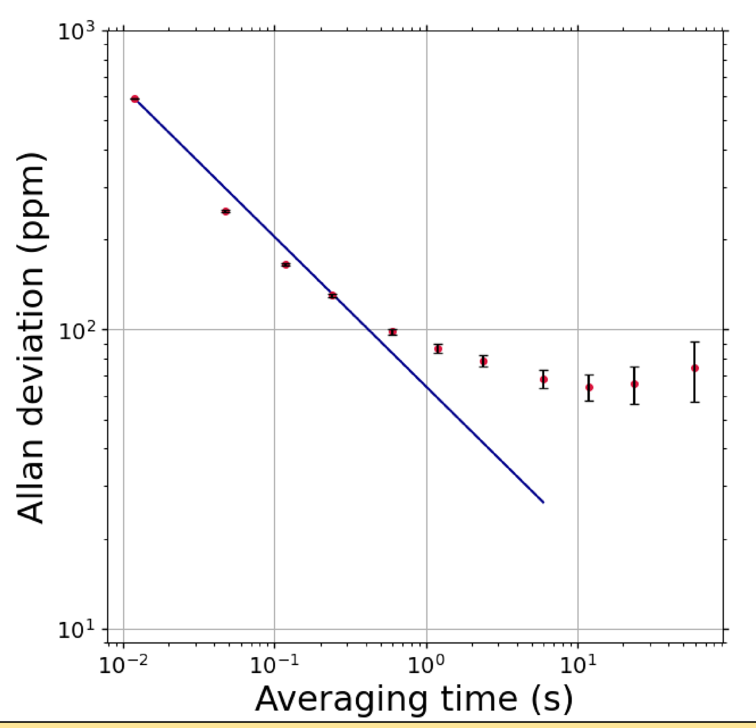


Figure 8: Standard Allan deviation of the spectrometer trough a glass of wine with an optical path of 5.6 cm. With an integration of one second, the limit of detection of the ICL spectrometer is 1000 ppm.

Conclusion & Perspective

In the headspace of wine glasses, the accurate monitoring of gaseous ethanol is crucial to get a full picture of the wine bouquet. With this aim, an infrared laser spectrometer was developed to quantify ethanol by straightforward absorption spectroscopy. Applications in the field of wine science are planned in a near future.

References:

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