Saturated-Absorption Cavity Ring-Down Spectroscopy

P. Cancio Pastor, I. Galli, G. Giusfredi, D. Mazzotti, P. De Natale
Istituto Nazionale di Ottica - CNR, Largo Fermi 6, 50125 Firenze FI, Italy
European Laboratory for Non-linear Spectroscopy, Via Carrara 1, 50019 Sesto Fiorentino FI, Italy
pablo.canciopastor@ino.it

Abstract: A novel approach to cavity ring-down spectroscopy with the sample gas in saturated-absorption regime allows to decouple and simultaneously retrieve empty-cavity background and absorption signal, improving both measurement sensitivity and resolution.

OCIS codes: 300.6340 Spectroscopy, infrared; 300.6390 Spectroscopy, molecular; 300.6460 Spectroscopy, saturation

The availability of a molecular-spectroscopy technique, able to combine the ultimate performance in terms of sensitivity, resolution and frequency accuracy, can be crucial in many fundamental physical measurements. Indeed, profiting from the strength and ease of saturation of many mid-IR ro-vibrational transitions, this technique could provide new insights in elusive quantum-mechanical effects encoded in molecules. Such a technique could also represent a major step forward in trace-gas sensing. Cavity ring-down (CRD) spectroscopy has already proven to be a good technique to directly provide a sensitive and quantitative measurement of gas absorption coefficient with a simple experimental set-up. In principle, it is not limited by amplitude noise of the laser source, but only by detection shot noise. However, variations of the empty-cavity decay rate always prevent to achieve this ultimate limit and to average measurements over long times. Other techniques (e.g. CRD heterodyne spectroscopy and NICE-OHMS) are even more sensitive than standard CRD, but they are more complex (frequency modulations and/or lockings are needed), less quantitative (calibration procedures are needed) and require fast and sensitive detectors, generally unavailable in the mid IR.

We present a new spectroscopic technique, namely saturated-absorption cavity ring-down (SCaR), that improves the CRD sensitivity [1]. We show that the progressive decrease of the saturation level during each SCaR event makes our technique very effective in identifying and decoupling any variation of the empty-cavity decay rate. Saturated absorption induces a deviation of the SCaR signal from the perfectly exponential behavior, making a detailed treatment of non-linear effects needed to fit experimental data to the underlying physics of matter-radiation interaction. We developed and tested a new model which is very effective in exploiting the SCaR spectroscopic technique. The experimental set-up [2] is based on a difference-frequency-generated CW coherent source widely tunable in the mid IR, with the near-IR pump/signal lasers phase-locked one another through a fs Ti:sapphire optical frequency comb (OFC). The 1-m-long cavity is formed by 2 high-reflectivity mirrors with 6-m radius of curvature and optical losses of 440 ppm around 2340 cm$^{-1}$. With this set-up we performed several spectroscopic measurements to test both sensitivity and resolution using the newly developed model.

Fig. 1: Comparison between experimental data and theoretical model. Experimental data points for saturation level $G_0=50$, the fit curve (in red) and the residuals are plotted with left scale (in black). Saturated decay functions $f(t)$, simulated for different values of $G_0$ (labeling curves), are plotted with right scale (in blue).
In Fig. 1 SCaR measurements are compared with the model we have developed. The experimental data in this figure are the average of 3072 decay signals measured at a fixed frequency near the absorption peak of the transition of Fig. 2 over a 4-s time interval. The discrete noise values in the tail of the SCaR signal are due to the resolution of the 18-bit digitizing oscilloscope (with 10 MS/s sampling rate). Almost flat residuals witness the validity of the theoretical model.

Fig. 2 shows a low-pressure, Doppler-limited absorption spectrum of a ro-vibrational transition of \(^{12}\text{C}^{16}\text{O}_2\) recorded with SCaR. The non-zero background absorption is due to Lorentzian wings of nearby transitions. This spectrum was recorded in about 12 minutes by separately averaging the \(\gamma_g\) (gas decay rate) and \(\gamma_c\) (empty cavity decay rate) values resulting from the SCaR fitting routine. Since the IR frequency was scanned forward and backward in 10-MHz steps, no sub-Doppler features are visible at line center. The measured peak absorption rate is consistent with the value calculated from the line-strength reported by the HITRAN database [3], within the uncertainties. A minimum detectable absorption coefficient \(\alpha_{\text{min}}=1.1\cdot10^{-9}\) cm\(^{-1}\) can be derived. When comparing Gaussian fit residuals of \(\gamma_c\) in Fig. 2 with the measured \(\gamma_g\), it is evident that our technique effectively makes the measured gas absorption almost unaffected by any variations of the empty-cavity decay rate. Indeed, the fluctuations of the former curve are about a factor of 20 lower than the latter one and only a slight residual correlation is observed. This factor also quantifies the sensitivity improvement over standard CRD, that can only measure an overall decay rate \(\gamma=\gamma_g+\gamma_c\) and is inevitably limited by any background fluctuation contained in \(\gamma_c\). As mentioned above, this key point would enable a further gain of sensitivity with measurements averaged over longer times.

In conclusion, we have found that the saturation regime has proven to be generally useful for background reduction, whereas it also provides detection of sub-Doppler spectroscopic features, when higher resolution is needed. Finally, we have shown that frequency-comb-assisted SCaR spectroscopy can provide absolute frequency measurements of molecular transitions.

References

[1] G. Giusfredi, S. Bartalini, S. Borri, P. Cancio, I. Galli, D. Mazzotti, and P. De Natale, “Saturated-absorption cavity ring-down spectroscopy”, Phys. Rev. Lett. 104, 110801 (2010).
[2] I. Galli, S. Bartalini, P. Cancio, G. Giusfredi, D. Mazzotti, and P. De Natale, “Ultra-stable, widely tunable and absolutely linked mid-IR coherent source”, Opt. Express 17, 9582-9587 (2009).
[3] Harvard-Smithsonian Center for Astrophysics, http://www.cfa.harvard.edu/hitran.