Spectroscopic Detection of Radiocarbon Dioxide at Parts-per-quadrillion Sensitivity

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Abstract: A compact and simple laser spectroscopy apparatus at 4.5 μm, based on saturated-absorption cavity ring-down (SCAR), has approached the ultimate sensitivity of accelerator mass spectrometry, measuring radiocarbon dioxide concentration down to few parts per quadrillion.

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1. Introduction
A few years ago, the first optical detection of a radiocarbon-containing species was demonstrated by our group [1–3] with a proof-of-principle experiment based on the newly developed SCAR spectroscopic technique [4–6]. Here, we show that radiocarbon dioxide concentration can be measured down to few ppq by using an improved SCAR setup which is more performing, despite being much simplified and less expensive.

2. Experimental setup
With respect to the experimental apparatus presented in our previous works [1–3,5] (named SCAR1 in the following), the new setup [7] (named SCAR2) relies on significant changes aimed, on one hand, to improve the performance in terms of sensitivity, acquisition time and amount of carbon sample needed, and, on the other hand, to drastically reduce costs, power consumption and size of the final instrument, thus envisaging a future portability.

Compared with the SCAR1 cavity, the cooling temperature of the SCAR2 ring-down cavity has been reduced by 25 K (down to 170 K), its volume has been reduced by about one order of magnitude (down to 6 mg), the effective interaction path has been increased by 40% (up to 5.2 km) and the acquisition rate has been more than doubled (up to 2500 decays/s).

The laser system has been completely changed with respect to SCAR1. SCAR2 employs two QCLs, both emitting in the range 2208 – 2212 cm−1, with output powers as large as 100 mW. QCL1 is used as probe laser for the SCAR spectroscopy of the (00'1 − 00'0) P(20) transition of 14C16O2. QCL2, used as absolute frequency reference, is frequency-locked to the (02'1 − 02'0) R(16)e transition of N2O at 2209.0854 cm−1.

3. Measurement procedure and results
A LabVIEW program controls all the experimental parameters and the acquisition routine, that has been optimized as the best trade-off between speed and sensitivity. A single acquisition consists of three back-and-forth stepwise scans of the QCL1 frequency across the target transition. For each frequency step, 3350 SCAR signals are acquired and averaged. A typical back-and-forth scan spans 600 MHz, with 61 points spaced by 10 MHz, and takes about 3.5 minutes.

The acquired SCAR decays for each scanned frequency are analyzed with the effective saturation parameter, a procedure thoroughly described in Ref. [6]. As a result, the gas-induced cavity decay rate, γg, is determined for each scanned frequency. The six γg values belonging to the single sweeps (three back and three forth) are further averaged together. Left Fig. 1 shows the SCAR spectrum for a modern CO2 sample averaged over a single measurement run made of three scans.
In order to analyze the repeatability and precision of the measured spectral areas, which is proportional to the radiocarbon dioxide concentration, we have recorded several 11-minutes-long runs by resetting for each run the experimental conditions, and by measuring the P(20) spectral area for each recording following the procedure described above. The result is shown in right Fig. 1 for ten consecutive runs. A repeatability comparable to the single run uncertainty allows a further precision improvement for the area determination, achieving a value of about 0.4% by weighted averaging over ten runs, acquired in about 2 hours. This uncertainty corresponds to about 5 ppq radiocarbon dioxide concentration.

4. Conclusions

Radiocarbon dioxide is a key molecule for dating objects of biological origin or to discriminate between combustion of fossil fuels (totally depleted of $^{14}\text{C}$) and bio-fuels. It hence represents a marker for monitoring and discriminating carbon dioxide released in the atmosphere, with direct implications on climate change studies. Furthermore, the SCAR technique can be applied to any molecule having sufficiently strong transitions to be saturable by available laser sources. This widens a lot the range of applicability of our technique, encompassing fields as security, biomedicine, environment, that can undergo a paradigmatic change from proper exploitation of SCAR spectroscopy, that has pushed trace gas sensing much beyond the state of the art.

References