ROOM-TEMPERATURE QUANTIFICATION OF $^{14}CO_2$ BELOW THE NATURAL ABUNDANCE WITH TWO-COLOR, CAVITY RINGDOWN SPECTROSCOPY

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In this talk, we report the first room-temperature optical detection of radiocarbon dioxide ($^{14}CO_2$) samples at concentrations below the natural abundance level (1.2 parts per trillion, $^{14}C/C$), using the recently-developed two-color, mid-IR, pump-probe, cavity ringdown (CRD) technique. With 3 minutes of averaging, our two-color CRD method successfully differentiates, with an accuracy of 8% of the ^{14}C natural abundance, five combusted ^{14}C standards with $^{14}CO_2$ concentrations ranging from petrogenic (zero $^{14}C/C$) to approximately double the contemporary abundance. Room-temperature quantification of $^{14}CO_2$ is not possible with any existing one-photon cavity-enhanced techniques at our demonstrated ^{14}C concentration levels, due to severe spectral overlap between the very weak target $^{14}CO_2$ ν_3-band transitions ($\sim$5/s ringdown rate at natural abundance) and the strong hot-band transitions of CO_2 isotopologues ($>$10000/s). All previous CRD-based, one-photon $^{14}CO_2$ measurements at the sub-natural-abundance level required cooling of the test gas (-20 to -100°C) to mitigate the strong background absorption.

Our unprecedented high-sensitivity, high-selectivity detection of $^{14}CO_2$ at room temperature is made possible by the dual-background compensation capabilities of the two-color CRD technique. The two-color measurement utilizes two cavity-enhanced pump and probe lasers to excite, respectively, the $\nu_3 = 1 \leftarrow 0$, P(14) and $\nu_3 = 2 \leftarrow 1$, R(13) rovibrational transitions of $^{14}CO_2$. With the pump radiation switched off during every other probe ringdown events ($>$2 kHz rate), the CRD rate fluctuations and strong one-photon absorption interference are effectively cancelled out during the two-color measurements. Highly-selective, room-temperature detection of weak $^{14}CO_2$ absorption signals reduces the technical and operational burdens for cavity-enhanced measurements of radiocarbon. This is a crucial achievement that will enable laser-based radiocarbon quantification outside a laser laboratory setting, and benefit a wide range of scientific applications, such as ^{14}C-labeling analysis of biomedical samples and field monitoring of fossil fuel emission.