ROOM TEMPERATURE OPTICAL DETECTION OF $^{14}CO_2$ AT PARTS-PER-QUADRILLION LEVEL ACCURACY WITH TWO-COLOR CAVITY RINGDOWN SPECTROSCOPY

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In this talk, we report room-temperature optical detection of radiocarbon dioxide ($^{14}CO_2$) with better than 10 parts-per-quadrillion (10^{15}, ppq) (^{14}C/C) measurement accuracy with the two-color cavity ringdown (2C-CRD) technique. The current sub-10-ppq measurement accuracy of $^{14}CO_2$ is 10X better than our previous work [McCartt, A. D., & Jiang, J. (2022). $ACS\ Sensors$, 7(11), 3258-3264], which demonstrated the first-ever room temperature detection of $^{14}CO_2$ at concentrations below the natural abundance ($\sim$1200 ppq ^{14}C/C). This significantly enhanced measurement capability of our 2C-CRD technique, achieved with under 2 minutes of averaging, is made possible by a combination of 30X improvement in the signal-to-noise ratio in our detection system and nearly 10X reduction in the magnitude of the collisionally-induced background 2C signal. As in our previous work, cavity-enhanced pump and probe laser beams are used to excite a pair of ν_3=1-0 and ν_3=2-1 rovibrational transition of $^{14}CO_2$. With the pump radiation switched off during every other probe ringdown events, the net 2C signals from the difference between the pump-on and pump-off decay rates is immune to drifts of the CRD rates and spectral overlaps from one-photon molecular transitions. The 10-ppq level detection capability of our 2C-CRD technique has been reproducibly demonstrated with several rounds of measurements of combusted ^{14}C standard samples (with close to contemporary ^{14}C concentrations) and low ^{14}C content biofuel samples (10-80 ppq ^{14}C/C). Room temperature optical detection of $^{14}CO_2$ at our demonstrated sensitivity and accuracy is not possible with other existing one-photon detection methods, because of severe spectral overlap between the very weak $^{14}CO_2$ ν_3-band transitions ($\sim$4/s RD rate at natural abundance) and the strong hot-band transitions of other CO_2 isotopologues ($\sim$10000/s). In addition to its use for ultra-trace analysis, our cavity-enhanced 2C technique is well-suited for rovibrational-state-resolved measurements in chemical dynamics and high-resolution spectroscopic studies, which we will discuss at the end of the talk.