Radiocarbon’s natural production, radiative decay, and isotopic rarity make it a unique tool to probe carbonaceous systems in the life and earth sciences. However, the difficulty of current radiocarbon ($^{14}$C) detection methods limits its scientific adoption. Here, two-color cavity ring-down spectroscopy detects $^{14}$CO$_2$ in room-temperature samples with an accuracy of 8% of the natural abundance in 3 minutes. The intra-cavity pump-probe measurement uses two cavity-enhanced lasers to cancel out cavity ring-down rate fluctuations and strong one-photon absorption interference (>10,000 1/s) from hot-band transitions of CO$_2$ isotopologues. Selective, room-temperature detection of small $^{14}$CO$_2$ absorption signals (<1 1/s) reduces the technical and operational burdens for cavity-enhanced measurements of radiocarbon, which can benefit a wide range of applications like biomedical research and field-detection of combusted fossil fuels.
The history of a measured sample can be revealed by the presence of trace species within its constituents. Species with more unique provenance, rare abundance, or association with a particular phenomenon offer more unambiguous distinctions with their detection. One of the most famous trace species is radiocarbon ($^{14}$C). It is a rare isotope of carbon (abundance $1.2 \times 10^{-12} ^{14}$C/c), which is produced in the atmosphere by the interaction of cosmogenic neutrons with nitrogen and radiatively decays with a half-life of ~5700 years. ($I$, $2$) These unique properties of radiocarbon can be leveraged for a wide variety of scientific applications (e.g., radiocarbon dating, isotope tracer studies, cosmogenic nuclide analysis, etc.), but the rarity of $^{14}$C makes measurements challenging. In the 1970s, nuclear physicist employed accelerator mass spectrometry (AMS) to increase the sensitivity of $^{14}$C detection. These room sized instruments utilized megavolt accelerators to separate $^{14}$C from its main interfering isobars ($^{14}$N and $^{13}$CH) and achieved unprecedented sensitivity (i.e., $10^{-16} ^{14}$C/c). ($3$, $4$)

While $^{14}$C detection with AMS was initially developed for radiocarbon dating, $^{14}$C’s isotopic rarity in concert with AMS’s sensitivity can track small quantities of $^{14}$C-labeled carbonaceous species through chemical systems. For example, the safety and efficacy of novel drugs can be tested in humans by administering $^{14}$C-labeled microdoses. These microdoses are small enough that they are not therapeutic, but $^{14}$C-tagged metabolites produced by the body can still be detected. ($5$)

The natural production and radiative decay properties of $^{14}$C provide opportunities to monitor the carbon cycle and fossil-fuel emissions. ($6$) Atmospheric CO$_2$ is in constant flux with terrestrial and marine ecosystems at rates 20 times greater than human emissions. This makes the attribution of atmospheric CO$_2$ measurements to emission point sources of combusted fossil fuels difficult and inaccurate. By measuring the dilution of atmospheric $^{14}$CO$_2$ with combusted fossil fuels depleted of $^{14}$C, anthropogenic emissions can be monitored and differentiated from natural CO$_2$ fluxes. ($7$, $8$) These atmospheric $^{14}$CO$_2$ tracer measurements can verify “bottom-
up” accounting estimates of fossil-fuel emissions and create a framework of accountability and trust for emission reduction agreements. (9–11) While scientists continue to find new applications using $^{14}$C, the size, cost, and complexity of AMS limit these endeavors, particularly for high-throughput and fieldwork measurements. (10–13) This has spurred the development of alternative and more accessible means of $^{14}$C detection.

Cavity ring-down (CRD) spectroscopy has emerged as a viable $^{14}$C detection technique. (14–20) It utilizes strong anti-symmetric-stretch band ($\nu_3$) transitions of $^{14}$CO$_2$ in the mid-IR and has demonstrated parts-per-quadrillion (ppq) precisions ($10^{-15}^{14}$C/c), which are well below the natural abundance (i.e., $1.2 \times 10^{-12}$ $^{14}$C/c). (16, 17) A high-finesse, optical cavity that is centimeters long can provide gas-laser interaction path lengths equivalent to kilometers. This cavity-enhanced path length increases the total gas absorption sensitivity, but this enhancement is not selective to the target analyte alone. Drifts in the cavity base loss and absorption interference from other species reduce the accuracy of traditional, cavity-enhanced techniques. Spurious reflections and external etalons coupled to the cavity cause frequency and time-dependent undulations in the cavity base loss. (21) Drifts in these unwanted signals compromise traditional CRD trace gas measurements. Near the $^{14}$CO$_2$ $\nu_3$ band in the Mid-IR, absorption interference is strong from CO$_2$-isotopologue hot-band transitions and other molecular species such as N$_2$O. Previous CRD measurements of $^{14}$CO$_2$ with accuracy below the natural abundance mitigated against this interference by cooling the test gas. (16–19) However, the most accurate measurements cooled with two-stage refrigeration units, dry-ice baths, or Stirling engines, which negated the reduced size and portability benefits of laser based techniques. Even after cooling, the extremely weak $^{14}$CO$_2$ signal had to be extracted from the dense interference (100 times smaller at natural abundance, 20 torr, and -20 °C). This required laser wavelength scans and spectroscopic line-shape fitting of multiple overlapping features. While CRD has demonstrated $^{14}$CO$_2$ sensitivities below the natural abundance which can be of service to mul-
tiple scientific fields, the difficulty of these measurements has largely confined them to laser spectroscopy laboratories.

Here, we present the first two-color, cavity ring-down spectroscopy (2C-CRDS) measurements of room-temperature $^{14}$CO$_2$ samples. This recently developed intra-cavity pump-probe technique uses an additional cavity-enhanced pump laser to selectively extract the signal of interest and cancel out instrument drift and unwanted background absorption interference. (22) Gas cooling and cavity-base-loss stability are no longer required for $^{14}$CO$_2$ sensitivity. The burden of signal extraction is transferred from spectroscopic analysis to an intrinsic 2C-CRDS capability, and because of its noise cancelation, experimental conditions that would have been prohibitively unstable are now a possibility (e.g., flow-through and field measurements). The unprocessed 2C-CRDS signal accurately detects $^{14}$CO$_2$ concentrations below one tenth of the natural abundance. This is achieved in three minutes, at room temperature, and without spectral-fitting compensation for interfering species or cavity-base-loss variations.

These results exceed requirements for most biological and biomedical $^{14}$C-tracer experiments. However, as is evident by the measurement precision demonstrated at 5‰ of the natural abundance, there is room for improving the 2C-CRDS measurement accuracy of $^{14}$CO$_2$. We determine precision from Allan deviation analysis that provides information about the stability of the 2C-CRDS signal during a single measurement. Accuracy is obtained from the mean absolute error of a linear fit to multiple sample types measured over a period of weeks. Factors that are contributing to the discrepancy between the demonstrated accuracy (91 ppq) and precision (6 ppq) are discussed, and spectroscopic strategies for overcoming this difference are presented. Improvements that bring the accuracy into line with the demonstrated precision would allow 2C-CRDS to address more demanding applications such as field measurements of fossil fuel emissions. This could transform existing “top-down” atmospheric CO$_2$ monitoring systems to constrain “bottom-up” estimates of fossil fuel emissions, provide stakeholders with
time and space resolved emissions data of both natural and fossil fuel derived CO₂, and create a platform of accountability and trust for national emission reduction commitments.

**Summary of technique**

Figure 1 shows a schematic with the primary components of our 2C-CRDS setup and a three level diagram of the $^{14}$CO₂ pump-probe scheme used in this paper. Two quantum cascade lasers (QCL) are injected into a high-finesse optical cavity in a counter propagating beam configuration. S- and p-polarization modes of the three-mirror, traveling-wave cavity share a common beam path but have different resonant cavity frequencies. (23) Using the Pound-Drever-Hall (PDH) technique, the pump laser is locked to a lower-finesse p mode ($\mathcal{F}_p = 5280$) close to the $^{14}$CO₂, $\nu_3$-band 1 – 0, P(14) transition. (24) The probe laser is locked to a high-finesse s mode ($\mathcal{F}_s = 67700$) near the $\nu_3$-band 2 – 1, R(13) transition. Ring-down measurements are initiated by

![Diagram of experimental setup](image-url)

Fig. 1. Summary of the experimental methods used for this study. A schematic of our 2C-CRDS experimental setup shown in panel (A), and the diagram of the ladder-type $^{14}$CO₂ P(14)-R(13) pump-probe scheme is presented in panel (B). Both the pump (blue) and probe (red) QCLs are locked to the high finesse optical cavity using 6 MHz modulation and PDH signals recorded at photo-detectors PD3 and PD4. The pump power is monitored with PD2 and ringdowns are recorded with PD1. Finally an additional reference QCL is locked to the $\nu_3$ 1 – 0, R(16) transition of $^{15}$N$^{14}$N$^{16}$O (modulation 1.7 MHz). The beatnote between this laser and the pump recorded at PD6 provides a frequency reference for the 2C-CRDS experiments. PBS and AOM stand for polarization beam splitter and acousto-optic modulator.
periodically interrupting the probe laser’s lock to the cavity. In between each ring-down event, the intra-cavity pump power is applied or removed by cycling the pump laser’s lock on and off. The difference between these “pump-on” and “pump-off” ring-downs provide a net, two-color signal sensitive to the pumped $\nu_3 = 1, J = 13$ population and compensated for instrument drift and one-color spectroscopic interference. Further details on the 2C-CRDS technique can be found in our previous paper on N$_2$O. (22)

Two-color, cavity ring-down spectroscopy of $^{14}$CO$_2$

The frequency spacing of the cavity resonant modes and the differences between the upper and lower transition frequencies influence the appearance of the intra-cavity two-color spectra. (22) The lasers are locked to a resonant mode of the cavity p- or s-polarization transmission “combs” and are simultaneously tuned when the cavity length is changed. Modes of a given polarization are separated by the cavity free spectral range ($FSR$), and for a three-mirror cavity, the s and p “combs” are interleaved with a spacing of approximately half the $FSR$. (23) These experimental constraints of the cavity discretize the frequency-separation selection between the pump and probe lasers and when combined with the transition frequencies of the analyte, dictate the appearance and position of the intra-cavity two-color spectroscopic features.

Because of the high, intra-cavity, pump-laser power (17 W) and the counter-propagating beam configuration, 2C-CRDS measurements can exhibit several qualitatively different spectroscopic features. For $^{14}$CO$_2$, coherent, step-wise, and Autler-Townes-splitting features are observed with this experimental setup. The coherent features occur when the sum of the pump and probe laser frequencies is equal to the sum of the upper and lower molecular transition frequencies. These peaks are effectively Doppler-free as the near-identical frequencies of the counter propagating beams cancel out Doppler shifts from longitudinal velocities. The step-wise peaks are Doppler broadened and, unlike the coherent features, populate the intermediate
\( \nu_3 = 1 \) level during a two-step absorption process. Regardless of the pump detuning, step-wise peaks always occur at near-zero probe detuning. Finally, for features where both the pump and probe are near resonance, an Autler-Townes-type splitting is observed. (25)

![Diagram showing 2C-CRDS spectra of \( ^{14}\text{CO}_2 \) from combusted glucose with 375 times the natural abundance of carbon-14. Measurements were taken at room temperature and 4 torr. Note that the spectra are plotted against pump detuning on the lower axis, and the shifted probe detunings are shown on the color-coded upper axes for each of the three pump-probe spacings. Features are annotated with the following symbols: coherent \( \dagger \), step-wise \( \ddagger \), Autler-Townes-type \(*\).]

Figure 2 shows 2C-CRDS spectra of the \( ^{14}\text{CO}_2 \) 1 – 0, P(14) and 2 – 1, R(13), intra-cavity, two-color transitions for a room-temperature, 4-torr, carbon-dioxide sample with 375 times the natural abundance of \( ^{14}\text{C} \). Three spectra from experiments where the pump and probe lasers were locked to different sets of cavity modes are plotted alongside simulations. The \( ^{14}\text{CO}_2 \), 2C-CRDS density matrix simulations are analogous to what was presented for our \( \text{N}_2\text{O} \) study. (22) Step-wise and coherent, two-color peaks were observed for experiments where the probe is locked to the mode on resonance with the \( ^{14}\text{CO}_2 \), 2 – 1, R(13) probe transition and the pump was locked to a cavity mode detuned by one \( FSR \) (443 MHz or ~7 times the Doppler half width) from the \( ^{14}\text{CO}_2 \), 1 – 0, P(14) pump transition center frequency. When combined with a high-resolution measurement of the 1 – 0, P(14) transition, (26) the Doppler-free, coherent
features provide an accurate quantification of the previously-unmeasured 2 – 1, R(13) transition wavenumber at 2213.9312(3) cm$^{-1}$ (accuracy limited by the beat-note frequency reference). This is 0.017 and 0.014 cm$^{-1}$ greater than \textit{ab initio} calculations for the 2 – 1, R(13) transition. (27, 28) For this experiment’s cavity geometry, the $^{14}$CO$_2$, 1 – 0, P(14) and 2 – 1, R(13), transition-pair frequencies are separated by nearly an exact odd integer multiple of the discretized p- and s-mode frequency spacing \((i.e., \sim 57 \times FSR/2)\). This allows the pump and probe lasers to be simultaneously tuned on resonance with their respective transitions. In this case with the lower pump level of the ladder-type system driven by a large effective Rabi frequency \((\sim 55 \text{MHz})\) and near identical pump and probe laser frequencies, the 2C-CRDS spectroscopic feature exhibits Autler-Townes-type splitting, which is well reproduced by the density matrix simulation. (29, 30)

**Measurements of $^{14}$C standards**

2C-CRDS’s $^{14}$C detection capabilities were characterized with CO$_2$ samples from commercial sources and combusted “$^{14}$C standards.” Spectra were taken at room temperature and 20 torr (Fig. 3A), and the $^{14}$C concentrations ranged from petrogenic (\(\sim\)zero $^{14}$C/c) to approximately double the contemporary abundance \((i.e., 1.2 \text{ parts per trillion (ppt) } ^{14}\text{C/c})\). At 20 torr, the spectroscopic feature complexity is greatly reduced with the step-wise resonances dominating and the Autler-Townes-type effect minimized as a result of collisional broadening. 2C-CRDS resolves $^{14}$CO$_2$ concentration differences that are fractions of the natural abundance in samples sourced from: petrogenic fuel (Petrogenic Cyl.), a 5240-year-old tree (TIRI Wood, Pinus sylvestris), 70 year old cellulose (IAEA C3), contemporary corn (Biogenic Cyl.), and $^{14}$C elevated leaves collected near a medical waste facility (EBIS Leaves). (31–35) To demonstrate the detection selectivity of the 2C-CRDS method, the unprocessed two-color signal with the probe on resonance is compared with duplicate sample analysis by AMS (Fig. 3B). Residuals from a
linear fit of this comparison have a mean absolute error of 91 ppq—an accuracy that is better than 8% of the contemporary $^{14}$C abundance. This level of precision requires 3 minutes of averaging, and further precision can be achieved for longer measurement times. However, for this set of samples, the limiting factor is uncompensated variations in the two-color signal, and in order to increase the accuracy for the P(14)-R(13) pair of $^{14}$CO$_2$ transitions, these variations must be compensated or removed.

Fig. 3. 2C-CRDS measurements of samples containing zero to two times the natural abundance of $^{14}$C. Panel (A) shows 2C-CRDS spectra averaged for a given sample type, and error bars represent the $2 - \sigma$ standard deviation of these groupings. Panel (B) shows the comparison of 2C-CRDS measurements to AMS. The error bars are the 95% confidence interval for a single two-color measurement with the probe on resonance. A linear fit of the comparison is used to infer equivalent carbon-14 concentrations (axes on right), and the slope is constrained by a combusted glucose sample which contains 30 times the natural abundance of carbon-14 (not shown). The net two-color signal for a sample containing the natural abundance of $^{14}$C is indicated by a dash-dot style line. Panel (C) displays the residuals of the fit. The legend in panel (B) is for all three panels.
Collisionally induced background

For the “14C-standard” samples measured here, the one-color spectra are dominated by absorption interference from hot-band transitions of CO2 isotopologues. 2C-CRDS reduces this one-color interference by 3 orders of magnitude (Fig. 4). However, additional two-color features are also present, which are contributing to the background at the 14CO2, 2 –1, R(13) probe frequency. At zero probe detuning, this background signal is similar in magnitude to the contemporary 14CO2 signal (Fig. 3A). Furthermore, off resonance (e.g., -300 MHz probe detuning) there are statistically significant differences between samples in the background signal.

Fig. 4. One- vs two-color background signals for the biogenic cylinder sample in the region surrounding the 2C-CRDS, 14CO2, 1 – 0 P(14), 2 – 1 R(13), two-color resonance. The net, two-color signal axis is on the left and the one-color signal axis is on the right. The grey rectangle surrounding some of two-color points delineates the area corresponding to the spectra shown for the “14C-standards” (Fig. 3A). While only probe detuning is indicated, the pump is scanned over an equivalent frequency range.

Like traditional pump-probe techniques, 2C-CRDS filters interfering transitions for species that are excited at both laser frequencies. This includes conventional quantum-state-linked transition pairs (e.g., 14CO2 1 – 0, P(14) and 2 – 1, R(13)) but also collisionally induced two-color signals. The intense intra-cavity pump power can excite species with relatively far detuned transitions to vibrationally excited states. Populations are then redistributed to other vibrational
and rotational states via collisions. For abundant species, even weak population transfer pathways from highly excited vibrational levels (~5000 cm\(^{-1}\) internal energy) can create signals significant to trace gas detection. Both positive and negative two-signals can occur depending on whether the pump-perturbed redistribution increases or decreases the probed state population. Inaccuracies from these unwanted two-color signals are exacerbated by their increased pump power dependence. Unlike the well saturated \(^{14}\)CO\(_2\) P(14) transition which has near zero pump detuning, the collisionally induced signals are likely pumped by relatively far detuned transitions and would be less saturated. Understanding the origin and variations of these background signals is important for maximizing the accuracy of 2C-CRDS detection, and we intend to conduct a more comprehensive study of the system dynamics.

2C-CRDS was designed to cancel out cavity ring-down base-loss variations and spectroscopic interference, but the effect of some experimental parameters on the two-color dynamic system needs further characterization. For example, Allan deviation analysis of vacuum 2C-CRDS measurements has optimal averaging and a resultant precision of \(10^{-3} \text{ [1/s]}\) in 2.78 hours (supplementary text). When CO\(_2\) is introduced into the cavity maximum averaging times are reduced to 10 minutes with a precision of \(2.3 \times 10^{-2} \text{ [1/s]}\) (6 ppq \(^{14}\)C/c). There is a clear correlation between the two-color signal and the intra-cavity pump power, and correcting for this variation with an empirically-determined, power-dependent model increases the time at which the minimum of the Allan deviation occurs. These pump power variation levels will not have an appreciable affect on the well saturated two-color \(^{14}\)CO\(_2\) signal (fig. S2), but they are likely causing significant variation in the two color background. The transmitted pump power drifted as the QCL thermally settled after power-up and with day-to-day changes in experimental conditions. Sample to sample pump power variation likely accounts for some of the two-color spread in Fig. 3 and the discrepancy between the accuracy (91 ppq) and precision (6 ppq).
Discussion

The selectivity of the uncompensated, room-temperature, two-color signal accurately detects a tenth of contemporary $^{14}$C abundance, which exceeds the requirements for nearly all $^{14}$C-tracer applications in biology and medicine. 2C-CRDS development was funded to detect $^{14}$C in biological samples separated by liquid chromatography (LC). Flow-through measurements have already been demonstrated in our earlier work. (22) This capability combined with its single frequency measurement selectivity should enable 2C-CRDS to make laser-based, in-line-flow-through measurements of $^{14}$C in LC effluent.

To push the limits of 2C-CRDS $^{14}$C detection, the small, two-color background variations must be addressed. While a model could be developed to compensate for variations in the P(14)-R(13) two-color background, there is likely another $^{14}$CO$_2$ two-color line pair with less interference. In contrast to one-color measurements of $^{14}$CO$_2$ that have a consensus transition ($\nu_3$ 1–0, P(20)) and rely on further mitigation of determined interference to increase sensitivity (test-gas cooling, spectroscopic line shape fitting and compensation, etc.), 2C-CRDS still has many unmeasured two-color $^{14}$CO$_2$ line pairs that could provide better opportunities for $^{14}$C detection. Within the tuning range of the QCL’s used in this study, P(14)-R(13) was the quantum-state-linked pair with the smallest two-color background, but collisionally induced signals can also be used for $^{14}$CO$_2$ detection. A preliminary investigation using the collisionally-assisted 1–0, P(20) and 2–1, R(13) pump-probe scheme yields a reduced two-color background, and the $^{14}$CO$_2$ signal is of similar strength to the linked two-color scheme used in this work due to facile rotational population relaxation within the $\nu_3 = 1$ manifold. The inclusion of collisionally-assisted pump-probe schemes significantly increases $^{14}$CO$_2$ two-color line-pair options and the likelihood of a set with reduced and stable background. After identifying the ideal line pair and constructing a model to compensate for any remaining two-color background signal, we are
confident the accuracy of 2C-CRDS $^{14}\text{CO}_2$ detection can be brought into line with the demonstrated precision.

While $^{14}\text{CO}_2$ is a particularly demanding case study, 2C-CRDS can be applied to other species for trace-gas detection and quantum-state-resolved molecular spectroscopy. High-energy transitions, similar to those causing the interfering two-color background, are of interest to astrophysical observations. 2C-CRDS’s Doppler-free coherent resonances can accurately determine high-energy transition frequencies which are difficult to measure through thermal excitation and can be used to investigate the atmospheric composition of exoplanets. (36–39)

2C-CRDS integrates the selectivity of pump-probe techniques with the sensitivity of cavity-enhanced detection. The resultant two-color spectrum focuses the sensitivity of the cavity on the species of interest and cancels out drift typical of cavity-enhanced instrumentation. These qualities are ideal for trace-gas measurement. Furthermore, the pump-probe line-pair selection of 2C-CRDS affords experimental flexibility. 2C-CRDS can be tailored to compensate for interfering species prevalent in a given application and designed to maximize noise cancelation for field work. Careful study of the $^{14}\text{CO}_2$ two-color line-pair options and associated background signals is needed to realize the full $^{14}\text{C}$ 2C-CRDS detection potential, but the demonstrated precision shows promise for atmospheric monitoring of anthropogenic $\text{CO}_2$ emissions. $^{14}\text{CO}_2$’s utility for tracking fossil fuel emissions has been demonstrated on scales ranging from individual point sources to continents, and can provide an objective metric for coalitions of nations and municipalities that have agreed to reduce green-house-gas emissions. (40, 41) 2C-CRDS’s unique combination of sensitivity and field ability offer a logistically feasible and affordable means of consistently monitoring combusted fossil-fuel emissions with $^{14}\text{CO}_2$.

References

1. W. F. Libby, *Physical Review* 69, 671 (1946).
2. R. R. Kinsey, C. L. Dunford, J. K. Tuli, T. W. Burrows, *9th International Symposium of Capture Gamma-Ray Spectroscopy and Related Topics* (1996). National Nuclear Data Center, information extracted from the NuDat 3.0 database (2021), https://www.nndc.bnl.gov/nudat3/.

3. D. E. Nelson, R. G. Korteling, W. R. Stott, *Science* **198**, 507 (1977).

4. C. L. Bennett, *et al.*, *Science* **198**, 508 (1977).

5. K. Turteltaub, J. Vogel, *Current Pharmaceutical Design* **6**, 991 (2000).

6. T. J. Heaton, *et al.*, *Science* **374** (2021).

7. I. Levin, B. Kromer, M. Schmidt, H. Sartorius, *Geophysical Research Letters* **30** (2003).

8. J. Turnbull, *et al.*, *Journal of Geophysical Research* **114**, D22302 (2009).

9. T. Lauvaux, *et al.*, *Environmental Science & Technology* **54**, 10237 (2020).

10. J. B. Miller, *et al.*, *Proceedings of the National Academy of Sciences* **117**, 26681 (2020).

11. K. R. Gurney, *et al.*, *Nature Communications* **12**, 553 (2021).

12. S. Dell’Orco, *et al.*, *Analytical Chemistry* **93**, 4351 (2021).

13. N. A. Kratochwil, *et al.*, *PLoS ONE* **13**, e0205435 (2018).

14. G. Genoud, M. Vainio, H. Phillips, J. Dean, M. Merimaa, *Optics Letters* **40**, 1342 (2015).

15. A. D. McCartt, T. Ognibene, G. Bench, K. Turteltaub, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **361**, 277 (2015).

16. I. Galli, *et al.*, *Physical Review Letters* **107**, 270802 (2011). PRL.
17. I. Galli, et al., *Optica* **3**, 385 (2016).

18. A. D. McCartt, T. J. Ognibene, G. Bench, K. W. Turteltaub, *Analytical Chemistry* **88**, 8714 (2016).

19. A. J. Fleisher, D. A. Long, Q. Liu, L. Gameson, J. T. Hodges, *The Journal of Physical Chemistry Letters* **8**, 4550 (2017).

20. V. Sonnenschein, et al., *Journal of Applied Physics* **124**, 033101 (2018).

21. H. Huang, K. K. Lehmann, *Applied Optics* **49**, 1378 (2010).

22. J. Jiang, A. D. McCartt, *The Journal of Chemical Physics* **155**, 104201 (2021).

23. S. Saraf, R. L. Byer, P. J. King, *Applied Optics* **46**, 3850 (2007).

24. R. W. P. Drever, et al., *Applied Physics B Photophysics and Laser Chemistry* **31**, 97 (1983).

25. S. H. Autler, C. H. Townes, *Physical Review* **100**, 703 (1955).

26. I. Galli, et al., *Molecular Physics* **109**, 2267 (2011). Molecular Physics.

27. E. J. Zak, et al., *Journal of Quantitative Spectroscopy and Radiative Transfer* **189**, 267 (2017).

28. X. Huang, D. W. Schwenke, R. S. Freedman, T. J. Lee, *Journal of Quantitative Spectroscopy and Radiative Transfer* **203**, 224 (2017).

29. R. Salomaa, S. Stenholm, *Journal of Physics B: Atomic and Molecular Physics* **9**, 1221 (1976).

30. H. Lee, Y. Rostovtsev, M. O. Scully, *Physical Review A* **62**, 063804 (2000).

31. E. M. Scott, *Radiocarbon* **45**, 293 (2003).
32. K. Rozanski, et al., *Radiocarbon* **34**, 506 (1992).

33. S. Trumbore, J. B. Gaudinski, P. J. Hanson, J. R. Southon, *Eos, Transactions American Geophysical Union* **83**, 265 (2002).

34. C. W. Swanston, et al., *Geoderma* **128**, 52 (2005).

35. P. J. Hanson, C. W. Swanston, C. T. Garten, D. E. Todd, S. E. Trumbore, *Soil Science Society of America Journal* **69**, 1492 (2005).

36. A. Foltynowicz, et al., *Physical Review Letters* **126**, 063001 (2021).

37. A. P. Showman, *Nature* **452**, 296 (2008).

38. G. Guilluy, et al., *Astronomy & Astrophysics* **625**, A107 (2019).

39. C.-L. Hu, et al., *The Journal of Physical Chemistry Letters* **11**, 7843 (2020).

40. K. R. Gurney, et al., *Environmental Science & Technology* **46**, 12194 (2012).

41. S. Basu, et al., *Proceedings of the National Academy of Sciences* **117**, 13300 (2020).

42. I. Gordon, et al., *Journal of Quantitative Spectroscopy and Radiative Transfer* **277**, 107949 (2022).

43. A. D. McCartt, T. J. Ognibene, G. Bench, K. W. Turteltaub, *Measurement Science and Technology* **25**, 095201 (2014).

44. D. Allan, *Proceedings of the IEEE* **54**, 221 (1966).

45. F. Czerwinski, A. C. Richardson, L. B. Oddershede, *Optics Express* **17**, 13255 (2009).
Acknowledgments

The authors would like to thank Professor Kevin K. Lehmann for his thoughtful comments on the manuscript, and Ted Ognibene, Kari Finstad, Kurt Haack, Alexandra Hedgpeth, Caroline Stitt, and Esther Ubick for their assistance with the various $^{14}$C samples.

**Funding:** Research reported in this publication was supported by the National Institute of General Medical Sciences of the National Institutes of Health (Award No. R01GM127573). The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health. This work was performed, in part, at the National User Resource for Biological Accelerator Mass Spectrometry, which is operated at the LLNL under the auspices of the U.S. Department of Energy (Contract No. DE-AC52-07NA27344). The user resource was supported by the National Institutes of Health, National Institute of General Medical Sciences (Grant No. R24GM137748).

**Competing interests:** ADM and JJ are employees of Lawrence Livermore National Laboratory, which is managed by Lawrence Livermore National Security (LLNS) LLC. LLNS has filed a patent application based on the 2C-CRDS technique, which is applied to $^{14}$CO$_2$ in this study.

**Data and materials availability:** All data are available in the main text or the supplementary materials.
Supplementary Materials for

Room-temperature quantification of $^{14}$CO$_2$ below the natural abundance with two-color cavity ring-down spectroscopy

A. Daniel McCartt and Jun Jiang
Correspondence to: mccartt1@lnl.gov

April 6, 2022

Materials and Methods

$^{14}$C Materials

The samples containing 30 and 375 times the natural abundance of $^{14}$C are from dilutions of a combusted glucose mixture (Sigma G-5020 and Mallinckrodt 4912). The “Petrogenic Cylinder” sample is instrument grade CO$_2$ sourced from petroleum feedstock (Praxair). The “Biogenic Cylinder” sample is also instrument grade CO$_2$ but sourced from ethanol-based production using contemporary corn (~2015) as the feedstock (Airgas). The “TIRI Wood” sample is “Belfast Pine, Sample B” from the Third International Radiocarbon Intercomparison with designator Q7780. (31) “IAEA C3” is cellulose produced in 1989 from ~40 year old trees and used in the “The IAEA $^{14}$C Intercomparison Exercise 1990”. (32) “EBIS Leaves” are from the “Enriched Background Isotope Study” and were collected near a medical waste facility that was emitting elevated levels of $^{14}$C. (33–35)
Sample Preparation

Duplicate samples containing up to 5 mg of carbon were aliquoted and dried under vacuum. These samples and approximately 150 mg of copper oxide were sealed in a quartz tubes using an acetylene torch. The tubes were then combusted at 900°C for 2 hours. Following combustion, AMS samples were graphitized and 2C-CRDS samples were transferred to the spectrometer front-end for purification. For 2C-CRDS sample purification, the quartz tubes were cracked under vacuum inside a bellows tube, and the sample gas was passed over an isopropanol/dry ice water trap. The gas was then exposed to a liquid nitrogen cold finger, and the gaseous species that remained were evacuated. The purified carbon dioxide was then introduced into the optical cavity.

Details of the 2C-CRDS Method

The three-mirror, traveling-wave cavity, with total nominal round trip length of 66 cm, consists of two plano mirrors and a plano-concave mirror with 1-m radius of curvature (LohnStar). The two plano mirrors are glued directly onto an invar cavity spacer. The concave mirror is housed in a piezoelectric-transducer (PZT) assembly which is attached to the invar spacer. The laser incidence angle at the PZT mirror is ~1.5°. The pump, probe, and reference lasers are continuous-wave (cw) distributed-feedback quantum cascade lasers (QCL) (Hamamatsu in high-heat-load packages). The pump (1000 mA maximum current) and probe (500 mA maximum current) lasers in the two-color, cavity ring-down experiments are each driven by a battery-powered QubeCL system from ppqSense, which provides low-noise electric current and temperature control. These lasers are modulated at 6 MHz. Light reflection off the cavity is measured with a HgCdTe (MCT) photodetector (Thorlabs PDAVJ8), and the MCT signal is demodulated with a frequency mixer (Mini-Circuit, ZRPD-1+). The resulting error signal is used as the input to the PID servo control loop (Vescent D2-125-PL) to achieve Pound-Drever-Hall laser frequency-
locking to the cavity. The reference QCL is driven by a current controller from Wavelength Electronics (QCL500 Laboratory Series). The temperature of the reference QCL is regulated with a PI servo control loop (PTC2.5K-CH, Wavelength Electronics). The reference laser was modulated at 1.7 MHz. After a double pass through an optical cell (10 cm, 4.5 torr N$_2$O) the transmitted intensity is recorded on an MCT photodetector (VIGO PVI-4TE-6/PIP-DC-20M) and the signal demodulated with a frequency mixer (Mini-Circuit, ZRPD-1+). Using wavelength modulation spectroscopy and the $\nu_3$ 1 – 0, R(16) transition of $^{15}$N$^{14}$N$^{16}$O at 2214.33886 ± 0.001 cm$^{-1}$, the reference laser is locked using a PI servo loop (New Focus LB1005). (42) The beatnote of the reference and pump lasers is recorded on an MCT detector (VIGO PVI-4TE-10.6/FIP-1k-1G) and provides frequency calibrations for the pump and probe lasers. The probe laser frequency is roughly measured using a wavemeter (Bristol 771) and then assigned a frequency using the beatnote and the cavity mode spacing. Timing for the experiment is provided with custom code implemented on a field programable gate array (NI PXIe-7976R, 5783). This system controls the AOMs (IntraAction Corp), provides corrections to the PDH servo integrators, and achieves ring-down rates greater than 2kHz.

For the “$^{14}$C standards” spectra, data acquisition was started with the cavity stabilized to zero probe detuning where ring downs were captured for 1000 seconds. To take the spectra, an additional 15 steps were measured for 100 seconds each. The cavity PZT was stepped using a feed-forward, pzt-creep-control profile in combination with closed-loop control from the frequency reference. (43)

Supplementary Text

Allan Deviation Analysis

In this paper, precision values represent the stability of the 2C-CRDS signal during the measurement of a single sample. Allan deviation analysis allows visualization and determination
of this parameter. (44, 45) Figure S1 shows the sliding Allan deviation plots for the 2C-CRDS signal when measuring an empty cavity under vacuum, the “14C standards”, and an elevated glucose sample containing 375 times the natural abundance of 14C. The fine grey lines are the Allan deviation analysis for each of the 14CO2 “standard” samples from Fig. 3. The black line is the average of these 14CO2 “standard” samples’ individual Allan deviations calculated from the square root of the mean of the sliding Allan variances. The orange line shows the Allan deviation of the elevated glucose sample. We used a sample with the largest 14CO2 content to maximize the potential drift in the 14CO2 2C-CRDS signal. Finally, the blue data points are the Allan deviation of an empty cavity under vacuum. This is a measure of the maximum obtainable precision of the system for a given averaging time.

Dips in the Allan deviation below the initial standard error of the mean trend (i.e., σ/√N) are likely non-physical representing a reversal of measurement drift and insufficient averaging time. For very stable measurements like the vacuum data, averaging times of sufficient length for the Allan deviation analysis would have been prohibitively long requiring days to weeks, and this additional data would have provided negligible additional information. For this reason, the dips seen in Fig. S1 are corrected by taking the value at the intercept of the initial standard error of the mean trend and the Allan deviation turn around. This is a small and conservative correction. For example, this changes the reported 14CO2 precision from 0.26% to 0.51% of the contemporary 14C abundance.

**Two-Color Signal Pump Power Dependance**

Figure S2 shows the pump-power dependance of the net two-color signal for a 20-torr carbon-dioxide sample with 375 times the natural abundance of 14C. The net-two color signal is plotted vs the pump intensity transmitted through the cavity. For this sample, the net two-color signal primarily originates from 14CO2 (>98%), and the signal is well saturated with half the applied
intra-cavity pump power only reducing the net two color signal by 12%.

References

31. E. M. Scott, *Radiocarbon* **45**, 293 (2003).

32. K. Rozanski, *et al.*, *Radiocarbon* **34**, 506 (1992).

33. S. Trumbore, J. B. Gaudinski, P. J. Hanson, J. R. Southon, *Eos, Transactions American Geophysical Union* **83**, 265 (2002).

34. C. W. Swanston, *et al.*, *Geoderma* **128**, 52 (2005).

35. P. J. Hanson, C. W. Swanston, C. T. Garten, D. E. Todd, S. E. Trumbore, *Soil Science Society of America Journal* **69**, 1492 (2005).

42. I. Gordon, *et al.*, *Journal of Quantitative Spectroscopy and Radiative Transfer* **277**, 107949 (2022).

43. A. D. McCartt, T. J. Ognibene, G. Bench, K. W. Turteltaub, *Measurement Science and Technology* **25**, 095201 (2014).

44. D. Allan, *Proceedings of the IEEE* **54**, 221 (1966).

45. F. Czerwinski, A. C. Richardson, L. B. Oddershede, *Optics Express* **17**, 13255 (2009).
Fig. S1. Comparison of averaging characteristics for vacuum (blue), $^{14}$C “standards” (grey and their average black), and a CO$_2$ sample with 375 times the natural $^{14}$C abundance (orange).
Fig. S2. Pump power dependence of the net two-color signal for a 20 torr, carbon dioxide sample with 375 time the natural abundance of $^{14}$C. The net two-color signal is plotted versus detector voltage for the transmitted cavity pump beam.