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First all optical measurements of carbon clumped isotopes using infrared laser absorption spectroscopy

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The isotope exchange between the doubly substituted $^{13}C^{16}O^{18}O$ molecule and the carbon dioxide isotopologue $^{12}C^{16}O_2$ has become an exciting new tool for geochemical, atmospheric and paleoclimatic research. Applications of this isotope proxy and thermometer range from stratospheric chemistry to carbonate-based geothermometry studies. Full exploitation of this new tool is nevertheless limited due to time consuming and costly analysis using mass spectrometric instrumentation. Laser spectroscopic measurement methods, on the contrary, might overcome many of these limitations, in particular the serious constraint of isobaric interferences. In this paper, we present a laser-based CO_2 isotopologue thermometer with capability for rapid analysis and simplified sample preparation and its application to temperature measurements of carbon dioxide samples from geothermal sources from the Upper Rhine Valley. An important advantage of the new instrument is that it can unambiguously measure all isotopologues of the $^{12}C^{16}O_2 + {}^{13}C^{16}O^{18}O \leftrightharpoons {}^{13}C^{16}O_2 + {}^{12}C^{16}O^{18}O$ exchange reaction. Its equilibrium constant and the corresponding temperature are therefore determined directly. The current measurement precision is better than 50 ppm within about 60 to 90 minutes. Unlike mass spectrometric Δ_{47} measurements, the laser approach is also independent of the isotope composition of the calibration gas. The use of an uncalibrated working reference is therefore sufficient and usage of international calibration standards is obsolete. This and the relatively low cost and size factors should help spreading this frontier science methodology to more laboratories and technological applications. Other isotopologues of carbon dioxide, such as $^{12}C^{18}O_2$, and further molecules can be accessed using the methodology. This opens up exciting new avenues in isotope research.