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A novel method of carbon dioxide clumped isotope analysis with tunable infra-red laser direct absorption spectroscopy

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Precise clumped isotopes analysis of carbon dioxide opens up new horizons of atmospheric and biogeochemical research. Recent advances in laser and spectroscopic techniques provides us necessary instrumentation to access extremely low sub-permill variations of multiply-substituted isotopologues.

We present an advanced analysis method of carbon dioxide clumped isotopes using direct absorption spectroscopy. Our assessments predict the ultimate precision of the new method on the sub-permill level comparable to state of the art mass spectrometry. Among the most auspicious intrinsic properties of this method we highlight genuine $\Delta_{^{16}O^{13}C^{18}O}$ and $\Delta_{^{16}O^{13}C^{18}O}$ measurements without isobaric interference, measurement cycle duration of several minutes versus hours for mass spectrometric analysis, reduced sample size of $\sim$ 10 μmol and high flexibility, allowing us to perform *in-situ* measurements.

The pilot version of the instrument is being developed in an international collaboration framework between Heidelberg University, Germany and Pierre and Marie Curie University, Paris, France. It employs two continuous interband quantum cascade lasers tuned at $4.439\ \mu m$ and $4.329\ \mu m$ to measure doubly ($^{16}O^{13}C^{18}O$, $^{16}O^{13}C^{17}O$) and singly ($^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{16}O^{12}C^{17}O$, $^{16}O^{12}C^{18}O$) substituted isotopologues, respectively.

Two identical Herriot cells are filled with dry pure CO_2 sample and reference gas at working pressure of $1 - 10\ mbar$. Cells provide optical path lengths of $\sim 17\ m$ for the laser tuned at doubly substituted isotopologues lines and use a single pass for the laser tuned at the stronger lines of singly substituted isotopologues. Light outside of the gas cells is coupled into optical fiber to avoid absorption by ambient air CO_2. Simulations predict sub-permill precision at working pressure of $1\ mbar$ and room temperature stabilised at the $\pm 10\ mK$ level.

Our prime target is to apply the proposed method for continuous *in-situ* analysis of CO_2. We are foreseeing potential applications to the following environmental issues: assessments of distinct sources of atmospheric CO_2, temperature reconstructions from terrestrial and marine archives, extra-terrestrial atmosphere studies, etc.