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High-temperature carbon isotope spectroscopy for chemical kinetic studies of fuel blends
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As chemical kinetic mechanisms for the combustion of multi-component fuel blends increase in complexity, additional experimental data are needed to differentiate key kinetic pathways and constrain reaction models. Fuel components possessing different structures in a mixture are known to have different effects on overall ignition behavior[1]; however, several reaction pathways for these mechanisms remain unidentified or ambiguous. Since many fuels and fuel components decompose into similar intermediates, improving understanding of competition of these common intermediates for oxidation pathways has broad importance to petroleum-derived fuel combustion. In this project, we introduce a coupled approach of isotopic labeling of mixtures of fuel intermediates with multi-isotopologue time-resolved detection via laser absorption during shock tube kinetics studies.

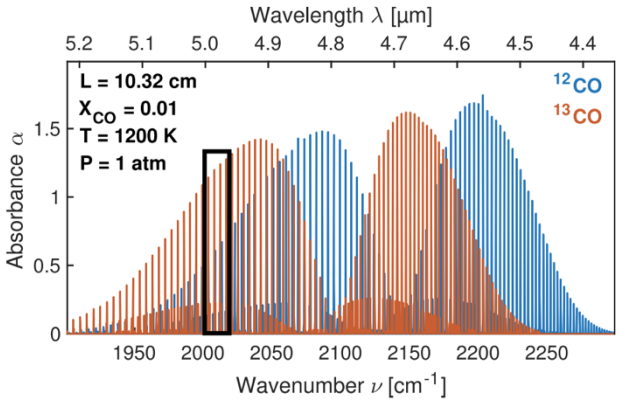

Figure 1 Simulated spectra of $^{12}C^{16}O$ and $^{13}C^{16}O$ calculated at conditions relevant to combustion. Targeted spectral region outlined in black. Spectral line parameters taken from HITEMP database.

A laser absorption diagnostic technique, probing the mid-infrared vibrational bands of $^{12}C^{16}O$ and $^{13}C^{16}O$ near 4.9 μm, was developed for sensitive multi-isotopologue temperature and concentration measurements in high-temperature gaseous systems. Transitions in each of the P-branches of the fundamental bands of $^{12}C^{16}O$ and $^{13}C^{16}O$ were chosen based on absorption linestrength, relative spectral isolation, and temperature sensitivity. For an isotopologue, changes in nuclear mass of a molecule changes its fundamental vibrational frequency[2], as shown in Fig. 1. A close inspection of the P-branches within 1900–2100 cm^{-1} reveals several isolated absorption features near 2008 cm^{-1} as attractive targets. Five total rovibrational transitions are spectrally-resolved over a ~1.2 cm^{-1} domain using a 50 kHz triangle scan function with a distributed-feedback quantum cascade laser, yielding a 100 kHz effective measurement rate of both isotopologues and respective temperatures, independent of mixture composition. The measured spectra, shown in Fig. 2, comprises two rovibrational transitions for $^{12}C^{16}O$ and three for $^{13}C^{16}O$, allowing for multiple two-line thermometry options. In addition, relevant broadening parameters for the P(0,22) transition of $^{13}C^{16}O$ near 2007.8767 cm^{-1} were measured to enable higher time resolution (>1 MHz) measurements using fixed-wavelength methods. Time-resolved multi-isotopologue thermometry performance was validated in a shock tube over a range of temperatures (1100–2400 K) relevant to combustion kinetics investigations.

In order to demonstrate the ability of the technique to discern competitive oxidation between different components of a fuel mixture, two fuels with distinctly different structure (and hence, ignition behavior), methane (CH_4) and ethylene (C_2H_4), were chosen for inclusion in reactive mixtures for the initial competitive oxidation tests. Shock tube oxidation experiments were performed with different mixtures of $^{13}CH_4$, $^{12}C_2H_4$, O_2, and Ar to validate the sensor's ability to measure both species during a reaction. Representative results with different initial reactant temperatures are shown in Fig. 3. Evidence of $^{12}C_2H_4$ undergoing earlier oxidation than $^{13}CH_4$ is clearly discernable at lower temperatures. To the authors' knowledge, these are the first simultaneous time-resolved measurements of multiple CO isotopologues originating from intentionally

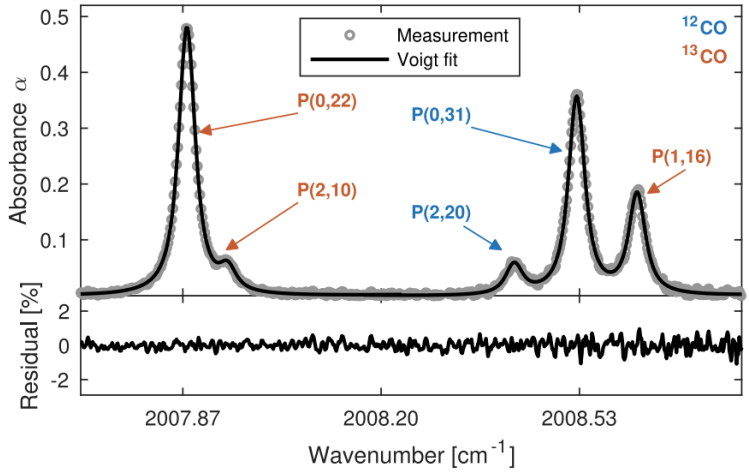

Figure 2 Example scanned-wavelength Voigt fitting of data in a high enthalpy shock tube experiment.

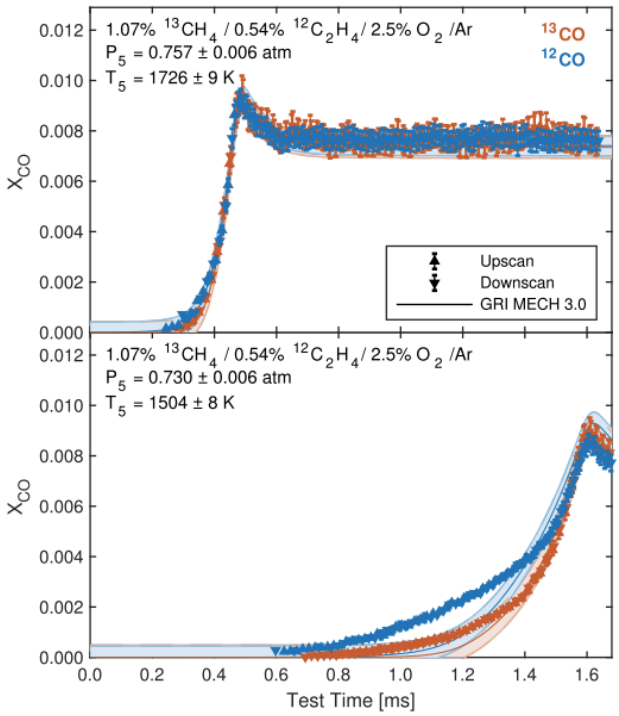

Figure 3 Measured CO mole fraction during ignition of fuel/O_2 mixture diluted in Ar at 1726 K (top) and at 1504 K (bottom) alongside chemical kinetic predictions. Shaded regions indicate uncertainties in kinetic model due to uncertainty in mixture composition.

isotopically-labeled fuels in a reacting mixture. Using the method, we provide experimental evidence revealing distinct competitive oxidation in a relevant fuel mixture.

This award from ACS PRF has enabled a new avenue of combustion kinetics research by facilitating the development of multi-isotopologue laser absorption spectroscopy for high-temperature gases. The coupled isotopic labeling and detection technique shows potential to improve understanding of competitive oxidation in multi-component fuel mixtures to distinguish reaction pathways and respective rates by unambiguously identifying the parent fuels of intermediate species. Additionally, the award has helped support a postdoctoral scholar, strengthening and broadening the PI's capability in chemical kinetics modeling and providing supplemental leadership and mentoring of graduate students in the laboratory. Several isotopically-labeled predictive reaction models have been created as part of this effort (one of which shown in Fig. 3), and their development and refinement—informed by experimental data—are the subject of forthcoming investigations. This ongoing work has been presented at a national conference and published in a leading journal[3] in the field of combustion, eliciting engagement and feedback from the combustion kinetics community and initiating new research ideas that may stem from this work.

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2. Hanson, R. K., Spearrin, R. M. & Goldenstein, C. S. *Spectroscopy and Optical Diagnostics for Gases*. (Springer, 2016). doi:10.1007/978-3-319-23252-2
3. Pineda, D. I., Bendana, F. A., Schwarm, K. K. & Spearrin, R. M. Multi-isotopologue laser absorption spectroscopy of carbon monoxide for high-temperature chemical kinetic studies of fuel mixtures. *Combust. Flame* **207**, 379–390 (2019).