Quantitative Laser Spectroscopy for SI-Traceable Measurements of Greenhouse Gases

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Spectroscopic measurements of atmospheric gas concentration often require high precision, low uncertainty and traceability to primary gas standards. These methods have high selectivity and sensitivity by measuring photon absorption which occurs at known wavelengths for a given target molecule. In practice, field-based spectrometers are typically calibrated by measuring samples of primary gravimetric (or manometric) gas standards, whereas remote-sensing observations depend upon spectroscopic line parameter data and first-principles models of light-matter interaction in the atmosphere. However, given the relatively low concentrations involved even for the major isotopologues of atmospheric greenhouse gases, the realization of well-characterized gas standards can be challenging. This limitation is especially important in the case of rare isotopologues for which the absolute concentrations are reduced by orders of magnitude.

Here, we present recent advances in measurements and *ab initio* calculations of line intensities for greenhouse gases such as carbon dioxide, carbon monoxide and water vapor, where substantial reductions in uncertainties of line parameters have been achieved. Typically, line intensities are determined under laboratory conditions with high-resolution spectrometers that measure absorption spectra on samples of known concentration. Nevertheless, a number of experimental complications usually result in relative uncertainties of measured line areas which greatly exceed that of the calibration gas concentration. This situation usually precludes absolute, calibration-free spectroscopic measurements of line intensity and/or gas concentration. As shown in Fig. 1, we have substantially reduced the uncertainty in line intensities of near-infrared carbon dioxide transitions, demonstrating agreement between our spectroscopic measurements and *ab initio* calculations at the 0.3% level. This result highlights the potential for absolute, SI-traceable spectroscopic measurements of greenhouse gases, especially for minor isotopologues at natural abundance levels. We also discuss the potential of realizing quantum-noise-limited laser absorption measurements of radiocarbon in carbon dioxide using mid-infrared, cavity ring-down spectroscopy. This new approach is an attractive and economical alternative to conventional radiocarbon measurement techniques.

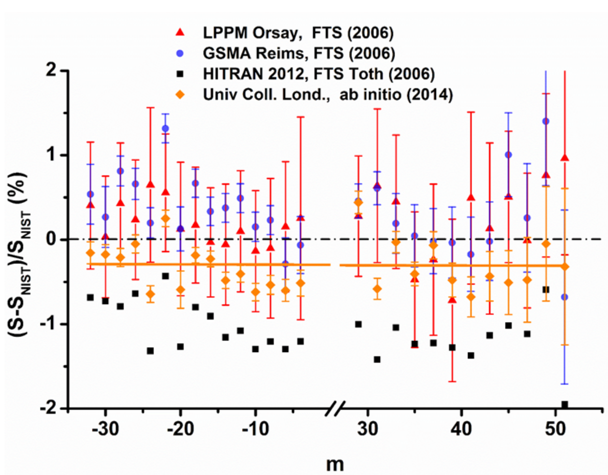

Figure 1. Reported line intensities for $^{12}C^{16}O_2$ transitions of rotational quantum number *m*, in the (30013)-(0001) vibrational band near 1600 nm. All values are relative to NIST spectroscopic measurements.