High resolution laser absorption spectroscopy in the 10 micron window - from the lab to the atmosphere

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Abstract— We describe a narrow band tunable laser diode spectrometer in the 10 µm region, with step scanning Michelson interferometer control at a resolution of about 10⁻⁶. An Allan variance analysis shows that this allows to reaching a relative frequency stability of about 5 × 10⁻⁷ (1σ) over 1 hour. We present first absolute line-strengths of the ¹⁶O¹⁸O¹⁸O ozone isotopomer and discuss atmospheric implications.

I. INTRODUCTION

Current or future satellite missions for climate research, such as SWIFT, OCO-2 or ACCURATE, are extremely demanding in terms of the quality of molecular spectroscopic data. Very recent and future space missions are not any more limited by satellite instrument performance, but by the quality of spectroscopic data [1]. Most of the data available in spectroscopic databases [2,3] has been acquired by broadband FTIR instruments at an instrumental resolution of about 10⁻³ cm⁻¹ (or 10⁻⁶ relative at 10 µm), however.

II. SPECTROMETER PERFORMANCE AND APPLICATION

Here, we describe a narrow band (1–2 cm⁻¹) tunable IR laser diode spectrometer in the 10 µm (or 1000 cm⁻¹) region, which can reach a much higher spectral resolution. Diode laser emission is controlled by a step scanning Michelson interferometer, as first proposed in Ref. [4]. Using a new electronic interferometer control system based on a FPGA (Field Programmable Gate Array) in combination with acoustic vibration damping methods, we reach a resolution of the interferometer path difference of about 10⁻⁴ (< 2 nm / 1 m), which is close to the stability of the HeNe control laser. An Allan variance analysis shows that this phase emission control scheme allows to reach a relative frequency stability of about 5 × 10⁻⁶ (1σ) over 1 hour, which is a typical acquisition time for a molecular spectrum. This spectrometer is applied to the measurement of ozone samples enriched in the asymmetric ¹⁶O¹⁶O¹⁸O ozone isotopomer for the determination of absolute intensities, which yet suffer from large uncertainties [5].

Fig. 1. Spectrum of sample enriched in ¹⁶O¹⁸O¹⁸O ozone (668). The upper trace is the measured spectrum at p = ~ 3 hPa and T = 21°C. The lower trace shows an intensity stick plot from HITRAN 2012 [4], assuming a relative abundance of ¹⁶O¹⁸O¹⁸O of about 1.

Samples are produced from a liquid reaction using a dioxygenyl ion [6] and an example spectrum is shown in Fig. 1, demonstrating that amounts of ¹⁶O¹⁸O¹⁸O and ¹⁶O are about equal, allowing for a more precise determination of the absolute intensity of this ozone isotopomer.

REFERENCES