HIGH PRECISION MEASUREMENTS OF LINE MIXING AND COLLISIONAL INDUCED ABSORPTION IN THE O_2 A-BAND

ERIN M. ADKINS, MÉLANIE GHYSELS, DAVID A. LONG, JOSEPH T. HODGES, *Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD, USA*.

Molecular oxygen (O_2) has a well-known and uniform molar fraction within the Earth's atmosphere. Consequently, the O_2 A-band is commonly used in satellite and remote sensing measurements (GOSAT, OCO-2, TCCON) to determine the surface pressure-pathlength product for transmittance measurements that involve light propagation through the atmospheric column. For these missions, physics-based spectroscopic models and experimentally determined line-by-line parameters are used to predict the temperature- and pressure-dependence of the absorption cross-section as a function of wave number, pressure, temperature and water vapor concentration. At present, there remain airmass-dependent biases in retrievals of CO_2 which are linked to limitations in existing models of line mixing (LM) and collisional induced absorption (CIA) [a]. In order to better quantify these effects, we measured O_2 A-band spectra with a frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) system. Because of the high molar fraction of O_2 in air samples, line cores and near wings of the dominant absorption transitions are heavily saturated, which makes it impossible to obtain continuous FS-CRDS spectra over the entire range of optical depth. Here, we focused on LM and CIA effects which dominate the valleys between strongly absorbing transitions. To this end, the FS-CRDS system employs a thresholding mechanism that avoids the optically thick regions and scans over the entire O_2 A-band and beyond the band head region. This approach provides high signal-to-noise ratio spectra that can be fit to yield LM and CIA parameters. These results are intended to provide strong constraints on multispectrum fits of continuous and broadband Fourier-transform-spectroscopy based O_2 A-band spectra.

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[a] Long D.A and J.T. Hodges, *J. Geophys. Res.* 2012, 117: p. D12309.