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High sensitivity CRDS of the $a^1\Delta_g - X^3\Sigma_g^-$ band of oxygen near 1.27 μm: Extended observations, quadrupole transitions, hot bands and minor isotopologues

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ABSTRACT

The CW-Cavity Ring Down Spectroscopy (CW-CRDS) technique has been used to record the high sensitivity absorption spectrum of the $a^1\Delta_g$–$X\ ^3\Sigma_g^-$ band of oxygen near 1.27 μm. The spectra were obtained between 7640 and 7917 cm^{-1} with "natural" oxygen and with a sample highly enriched in ^{18}O. The absolute intensities of 376 and 643 oxygen transitions were measured in the two spectra. They include the $a^1\Delta_g - X\ ^3\Sigma_g^-$ (0–0) bands of $^{16}O_2$, $^{16}O^{18}O$, $^{16}O^{17}O$, $^{17}O^{18}O$ and $^{18}O_2$. The (0–0) bands of $^{16}O_2$ and $^{18}O_2$ show weak quadrupole transitions with line intensities ranging from 1×10^{-30} to 1.9×10^{-28} cm/molecule. They are accompanied by the $a^1\Delta_g - X\ ^3\Sigma_g^-$ (1–1) hot bands, which are reported for the first time. The line profiles of the transitions of the $^{16}O^{17}O$ and $^{17}O^{18}O$ isotopologues were observed to be broadened due to an unresolved magnetic hyperfine structure. Accurate spectroscopic parameters of the different energy levels involved in the observed bands were derived from a global fit of the observed line positions, combined with microwave and Raman measurements available in the literature.

1. Introduction

The knowledge of accurate spectroscopic parameters for lines in the $a^1\Delta_g - X\ ^3\Sigma_g^-$ band of oxygen is very important in the field of remote sensing in relation to high-accuracy measurements of atmospheric greenhouse gases such as CO_2 and CH_4. One reason is that due to the uniform mixing of oxygen, the oxygen lines are often used as a benchmark for intensity calibration of atmospheric spectra taken by satellite instruments. Another reason is that taking the ratio of the column abundance of CO_2 or CH_4 to that of O_2 cancels many common systematic errors, especially the ones that are instrument-related [1].

Due to their importance, magnetic dipole transitions in this band were tabulated in the HITRAN database [2] since its inception [3]. Since then these parameters have been continuously updated as HITRAN was evolving. The intensities of the $a^1\Delta_g - X\ ^3\Sigma_g^-$ (0–0) band for $^{16}O_2$ in HITRAN (which were derived using formalism described in Ref. [4] and modified for HITRAN2000 using experimental parameters from Lafferty et al. [5]), however, were found to be inadequate for atmospheric retrievals such as the ones in Ref. [1]. The new list of $^{16}O_2$ intensities recently adopted for HITRAN was derived by Orr-Ewing based on experimental results from Newman et al. [6]. These intensities have proven to be more accurate in application to atmospheric retrievals [1]. In order to further improve the

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quality of retrievals, Washenfelder et al. [1] applied an empirical scaling to HITRAN2008 intensities of $^{16}O^{18}O$ that originated from Ref. [4]. These intensity improvements have served as a basis for an interim update of the HITRAN oxygen file that was placed on the HITRAN website (http://www.cfa.harvard.edu/hitran/updates.html) in November 2009. Despite recent updates, there is still significant room for improvement of spectral parameters of the $a^1\Delta_g - X\ ^3\Sigma_g^-$ band of molecular oxygen. For instance, recently Gordon et al. [7] have shown the necessity of including electric quadrupole lines in this region to the HITRAN line list in order to improve the residuals of the solar absorption spectrum. Furthermore, the intensities of $^{16}O^{18}O$ lines in the updated 2009 HITRAN file, while being better than those in the official release of HITRAN2008, are still in need of further improvements.

In the derivation of the current $a^1\Delta_g - X\ ^3\Sigma_g^-$ line positions of $^{16}O_2$ in HITRAN, the $X\ ^3\Sigma_g^-$ spectroscopic constants from Rouillé et al. [8] and $a^1\Delta_g$ rotational constants determined from the microwave spectrum by Hillig et al. [9] were used. Gamache et al. [4] state that the term energy of $a^1\Delta_g$ was taken from Krupenie [10]. However, although none of the subsequent HITRAN papers have elaborated on this, the term values of Krupenie were adjusted in HITRAN to match unpublished FTS spectrum measured by Brault [11]. The effective term values were 7883.75639 cm^{-1} for $v=0$ and 9367.20879 cm^{-1} for $v=1$. In HITRAN2008, the line positions of $^{16}O^{18}O$ were calculated using ground state constants of Mizushima and Yamomoto [12] and excited-state rotational constants reported by Herzberg and Herzberg [13]. Just like for the principal isotopologue, the term values of Krupenie [10] were adjusted to match unpublished FTS spectrum [11] (the effective value was 7885.06858 cm^{-1}).

Although the resulting HITRAN line positions have not received criticism from the users and the quality of the input constants (especially for $^{16}O_2$) is quite reasonable, it seems that direct measurements of the $a^1\Delta_g - X\ ^3\Sigma_g^-$ band may provide a means of obtaining a more consistent set of line positions. Moreover, line positions reported in the most recent measurements by Cheah et al. [14] differ from those in HITRAN by more than 0.01 cm^{-1}. Cheah et al. [14] stated that their line positions were superior to the corresponding ones in HITRAN. This disagreement between data also calls for additional experimental studies.

In order to attend the problems listed above and extend the observations, spectra of the $a^1\Delta_g - X\ ^3\Sigma_g^-$ electronic transitions have been recorded by CW-Cavity Ring Down Spectroscopy (CW-CRDS) in this work. Using two oxygen samples, new spectroscopic information was obtained for five isotopologues, including $^{16}O^{17}O$ for which the $a^1\Delta_g - X\ ^3\Sigma_g^-$ band is not currently listed in HITRAN, and the $^{17}O^{18}O$ species for which no spectroscopic data in the $a^1\Delta_g$ state was previously available.

2. Experimental details and sample composition

The high sensitivity CW-CRDS absorption spectra of O_2 isotopologues were recorded in the 7640–7917 cm^{-1} region. Two samples were used: the first one contained oxygen with an isotopic composition near natural abundance (hereafter referred to as ^{16}O sample) and the second one (hereafter referred as ^{18}O sample) was a sample highly enriched in ^{18}O (Cambridge Isotope laboratories, $>95\%$ of $^{18}O_2$). The pressure value of the recordings was fixed to 50.0 Torr. Additional spectra of the ^{18}O sample were recorded at 5.0 Torr in the 7876–7900 cm^{-1} region corresponding to the strongest lines, since some of them were saturated at 50.0 Torr.

The fibered distributed feedback (DFB) laser CW-CRDS spectrometer used for these recordings has been described in Refs. [15–17]. Each DFB laser diode has a typical tuning range of about 40 cm^{-1} by temperature tuning from −5 to 60 °C. For the present experiment, nine DFB laser diodes were needed to cover the 7640–7917 cm^{-1} region of interest.

The electro-polished stainless steel ringdown cell (l=1.42 m, inner diameter Φ=11 mm) was fitted with a pair of super-mirrors. The reflectivity of these mirrors (about 99.997%) corresponds to empty cell ring down times of about τ=200 μs. About one-hundred ringdown events were averaged for each spectral data point; the complete temperature scan of one DFB laser (15,000 spectral points) required about 70 min. The achieved noise equivalent absorption was about $\alpha_{min}=4\times10^{-11}$ cm^{-1} over the whole spectrum. The pressure measured by a capacitance gauge (MKS 100 Torr full range with 0.1% accuracy) and the ringdown cell temperature were monitored during the spectrum recording. Fig. 1 shows the overview of the two spectra recorded at a pressure of 50.0 Torr and a temperature of 300.2 K. The spectrum does not cover the high energy part of the $a^1\Delta_g - X\ ^3\Sigma_g^-$ band above 7917 cm^{-1} as no fibered DFB laser could be purchased for this spectral region.

Each 40 cm^{-1} wide spectrum recorded with one DFB laser was calibrated independently on the basis of the wavelength values provided by a Michelson-type wavemeter (Burleigh WA-1650, 60 MHz resolution and 100 MHz accuracy). The calibration was further refined

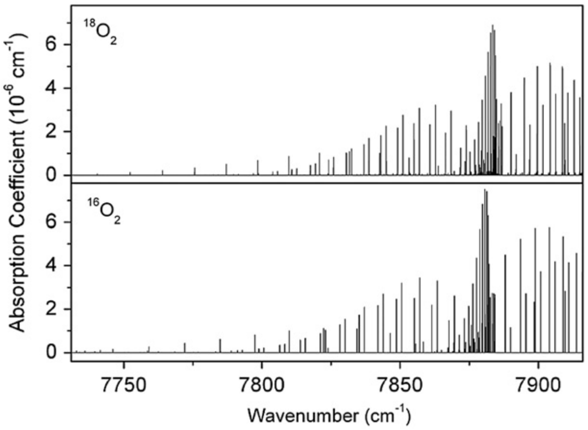

Fig. 1. Overview of the $a^1\Delta_g - X\ ^3\Sigma_g^-$ band of oxygen recorded by CW-CRDS (P=50.0 Torr, T=300.2 K). The upper and lower panels correspond to O_2 with an isotopic composition near natural abundance sample and a highly ^{18}O-enriched sample, respectively.