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Pressure broadening of oxygen by water

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ABSTRACT

A need for precise air-mass retrievals utilizing the near-infrared O_2 A-band has motivated measurements of the water-broadening in oxygen. Experimental challenges have resulted in very little water broadened oxygen data. Existing water broadening data for the O_2 A-band is of insufficient precision for application to the atmospheric data. Line shape theory suggests that approximate O_2 pressure broadening parameters for one spectral region, such as the A-band, may be obtained from comparable spectral regions such as the O_2 60 GHz *Q*-branch, which is also used prominently in remote sensing. We have measured precise O_2–H_2O broadening for the 60 GHz *Q*-branch and the pure-rotational transitions at room temperature with a Zeeman-modulated absorption cell using a frequency-multiplier spectrometer. Intercomparisons of these data and other O_2 pressure broadening data sets confirm the expectation of only minor band-to-band scaling of pressure broadening. The measurement provides a basis for fundamental parameterization of retrieval codes for the long-wavelength atmospheric measured values. Finally, we demonstrate the use of these measurements for retrievals of air-mass via remote sensing of the oxygen A-band.

1. Introduction

Oxygen is a well-mixed gas in Earth's atmosphere, with a mixing ratio that is extremely well known, allowing oxygen absorption features to be utilized in remote sensing applications for the retrieval of other atmospheric quantities. The O_2 60 GHz *Q*-branch has long been used for the retrieval of atmospheric temperature from satellites (e.g. [1]), aircraft (e.g. [2]) and from the ground [3,4]. The pure rotational transitions in the Terahertz region may be useful for retrievals of stratospheric temperatures or air-mass, but the opacity of the water continuum reduces their utility below the tropopause. The O_2 A-band at 0.76 μm has been used extensively in ground-based [5], airborne [6] and satellite [7–10] remote sensing to provide the information on atmospheric path lengths necessary to characterize cloud and aerosol abundances, to retrieve surface pressure and to retrieve column abundances of other trace gases, such as CO_2 and CH_4, using coincident near-infrared measurements. Current and planned spaceborne missions utilizing the O_2 A-band for the purposes of greenhouse gas retrievals include the TANSO-FTS on the Japanese Greenhouse Gases Observing satellite (GOSAT) [11], the NASA Orbiting Carbon Observatory re-flight (OCO-2) [12] and the Chinese TanSat satellite instrument [13].

The accuracy of the remotely sensed quantities depends directly on the accuracy of the spectroscopic input (line positions, line intensities and lineshape) used in the forward models within the retrieval algorithms (e.g. [14–16]). The parameterization of the lineshape includes pressure broadening and may also include additional physics such as shifts, mixing, narrowing and speed-dependence. For current and future remote-sensing measurements to be used to their full potential, it is necessary

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to continue to characterize and reduce uncertainties in the spectroscopic input to the models, particularly those uncertainties that could lead to spatially or seasonally dependent biases in the retrieval products. Pressure broadening by water vapor can make an additional contribution to the observed width of the lines, which in turn affects the retrieval of the target quantity. Since atmospheric water vapor is highly variable in space and time, the reduction of spectroscopic uncertainties associated with water vapor is important in order to avoid the introduction of spatially and/or temporally dependent biases in the retrieved products.

Due to the experimental challenges involved, few previous studies have been performed to measure the pressure broadening of oxygen by water vapor. Here, we report new, precise measurements of O_2–H_2O broadening for the 60 GHz *Q*-branch and the pure-rotational transitions. As a linear molecule with no electric dipole moment, oxygen pressure broadening is expected to show little electronic or vibrational dependence, and so we assume that the measured values can also be applied to the O_2 A-band at 0.76 μm. In Section 2, we describe results from previous studies of O_2–H_2O broadening in order to provide context for this new work. Section 3 contains a description of the experimental setup for the new measurements. In Section 4, we detail the approach taken to determine the O_2–H_2O broadening parameters from the new measurements, compare with results from previous studies and explore some of the implications for remote sensing by showing the impact on forward model calculations in the 60 GHz and 0.76 μm regions. A concise summary of the work is provided in Section 5.

2. Previous studies of O_2–H_2O broadening

The new measurements described in this work have enabled the determination of precise O_2–H_2O broadening parameters for lines in the 60 GHz *Q*-branch (spanning frequencies from 47 to 119 GHz) and for pure rotational transitions between 424 and 1850 GHz. Since we are assuming that oxygen pressure broadening has little electronic or vibrational dependence, we should consider these new measurements not only in the context of previous measurements in this spectral region, but also in the context of measurements of O_2–H_2O broadening at other frequencies.

Previous high quality measurements of spectroscopic parameters for the 60 GHz *Q*-branch include air and self-broadening [17,18], line-mixing [18,19], and pressure broadening temperature dependence [19,20]. However, only two transitions in the 60 GHz *Q*-branch have published water-broadening values [21–23]. While self- and air-broadening parameters for the pure rotational (*S*-branch) transitions have been reported by [24–26], we are not aware of previous measurements of O_2–H_2O broadening for these transitions.

Fanjoux et al. [27] performed high temperature (between 446 and 990 K) measurements of O_2–H_2O broadening for the Raman *Q*-branch at 1553.3 cm^{-1}, with the goal of contributing to understanding of combustion in rocket engines. While the temperature range of this study is obviously very different from the range of ambient atmospheric temperature, Fanjoux et al. had extrapolated their data to compare with the measurement from [21] and had concluded that their results were relatively consistent with this datapoint for this single line, providing some support for the assumption of vibrational independence of the pressure broadening.

In the O_2 A-band at 0.76 μm, state-of-the-art spectroscopic techniques have produced very high quality (self and air) broadening and shift parameters for the oxygen A-band [28,29]. Other studies have obtained the temperature dependence of the pressure broadening and shift parameters [30] as well as line-mixing/collision-induced absorption [31]. O_2–H_2O room temperature pressure broadening was measured for six lines in the A-band by Vess et al. [32]. The water-broadened widths inferred by [32] were over 50% larger than the values implied by the earlier work [21–23,27] in other spectral regions. Due to physical constraints such as the low vapor pressure of water and the large Doppler widths of transitions in the A-band, the data of Vess et al. was not very sensitive to the water-broadening itself, and the error bars are large.

In summary, the previous data for O_2–H_2O broadening consists of measurements of only two transitions in the 60 GHz complex [21–23], a comprehensive study of the Raman *Q*-branch at 1553.3 cm^{-1} at temperatures outside the range of interest for remote sensing of ambient atmospheric conditions [27], and a study of six lines in the 0.76 μm A-band [32], with large error bars, that was not consistent with the results of the other two studies. The single-line limitations of the millimeter region studies of [21–23] and the discrepancy between the parameters derived from [27] and the direct measurements of [32] provided a strong motivation for additional measurements.

3. Experimental setup

A room temperature apparatus designed for static gas containment was fitted with a variable temperature cold finger and was filled with a fixed amount of oxygen and water vapor. Temperature control of the cold-finger was accomplished through setting the voltage of thermoelectric (TE) coolers attached to an aluminum block encircling the cold finger. By controlling the finger temperature in the 242–280 K range the vapor pressure of water in the static gas cell was maintained at fixed values during each spectroscopic measurement. The area of the gas cell probed by the spectrometer was maintained at room temperature which fluctuated between 294 and 298 K. The spectrometer described in Drouin et al. [33], with an additional source described in Gupta et al. [34], was utilized to record the lineshapes of dozens of oxygen transitions, each as a function of water vapor pressure. In order to remove spectral features due to standing waves and water vapor absorption, Zeeman modulation was employed through application of an axial magnetic field. As in the previous work on O_2 [26] the convolution method described by Pickett [35] was utilized to facilitate treatment of instrument and magnetic field effects on the lineshape. A single transition (9^- at 58323.876 GHz) was measured as a function of oxygen pressure to check consistency with the