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AIR- AND OXYGEN-BROADENING COEFFICIENTS FOR THE O_2 ROTATIONAL LINE AT 60.46 CM^{-1}

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Abstract. Using an NBS laser-based tunable far infrared spectrometer, we have measured the air- and oxygen-broadening coefficients for the $J = 10 \leftarrow 10$, $N = 11 \leftarrow 9$ O_2 rotational transition at 60.46 cm^{-1} (1.812 THz). The air-broadening coefficient is $5.04 \pm 0.38 \times 10^{-7}$ $cm^{-1}Pa^{-1}$ (0.0511 ± 0.0039 $cm^{-1}atm^{-1}$) (HWHM) at 245 ± 6 K; the oxygen-broadening coefficient is $4.92 \pm 0.47 \times 10^{-7}$ $cm^{-1}Pa^{-1}$ (0.0499 ± 0.0048 $cm^{-1}atm^{-1}$)(HWHM) at 259 ± 2 K. These direct experimental measurements of the air-broadening coefficient should improve the accuracy of retrieval calculations for far infrared stratospheric balloon experiments which use O_2 rotational lines to calibrate the viewing geometry.

Introduction

The rotational spectrum of O_2 provides lines from a species of known concentration in the far infrared stratospheric emission spectrum [Bussoletti and Baluteau, 1974; Abbas et al., 1984]. These lines have been used to determine balloon gondola altitude and instrument pointing geometry when other sources of calibration are not available. For example, the analysis of balloon data obtained in the 1982 Balloon Intercomparison Campaign uses modeling of the O_2 spectrum in the 30 to 70 cm^{-1} range to establish limb-viewing angles for the Istituto di Ricerca sulle Onde Elettromagnetiche experiment [Abbas et al., 1987]; (J. Park, private communication, 1987).

The use of O_2 emission features to determine or verify experimental geometries requires accurate parameters for the rotational lines. The lines seen in the stratospheric far infrared emission spectrum are saturated; they are pressure-broadened lines with ratios of strength to linewidth that place them, by several orders of magnitude, within the square root regime of the Lorentzian curve of growth. Thus, error in determination of line-of-sight abundances, from which viewing angles or altitudes may be derived, is directly proportional to error in both the line strengths and the pressure-broadening coefficients. The line strengths are accurately known for the O_2 rotational transitions since the lines are magnetic dipole transitions. To our knowledge, however, no experimental determinations of pressure-broadening coefficients for any rotational lines above 425 GH (14.17 cm^{-1}) [Pickett et al., 1981] have previously been made. Values for the pressure broadening of these lines can only be inferred, with low accuracy, from values for lines at much lower energy. In order to improve the accuracy for this and similar analyses, we have obtained and analyzed fully resolved line measurements to determine the air-broadening coefficient for one of the calibrating O_2 lines at a temperature and a range of pressures close to conditions found in the mid-stratosphere. The pure oxygen-broadening coefficient, which may be of interest for line-broadening theory calculations, was determined as well.

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Experimental

Apparatus. We generated tunable far infrared radiation (TuFIR) by means of CO_2 laser difference frequency in a metal-insulator-metal (MIM) diode [Evenson et al., 1984]. This NBS-developed technique has been demonstrated to be an excellent source of coherent radiation for spectroscopy. As summarized by Evenson et al. [1984], the technique has been used to measure highly accurate far infrared frequencies of stable molecules to serve as frequency and wavelength calibration standards and to measure frequencies of transient species for astronomical searches. The complete TuFIR spectrometer is described elsewhere [Evenson et al., 1984; Evenson et al., 1985; Evenson et al., 1986]. Its general features are summarized here. Radiation from two CO_2 lasers is combined on a beam splitter and then focussed on a MIM diode, where the difference frequency (far infrared) radiation is generated. One laser is a CO_2 waveguide laser, frequency-offset locked to a saturated fluorescence stabilized CO_2 laser. The second laser is a saturated fluorescence stabilized CO_2 laser and is frequency modulated. The FIR radiation is thus also frequency modulated. Phase sensitive detection is used to measure the modulation-broadened first derivative of the absorption. The waveguide CO_2 laser provides a tunability of about ±120 MHz. Acousto-optic modulators operating at 90 MHz are used to isolate the lasers from the MIM diode and to provide an additional 180 MHz of tunability. By changing pairs of CO_2 laser lines, we can cover about 80% of the spectrum between 0.3 and 6 THz. The FIR

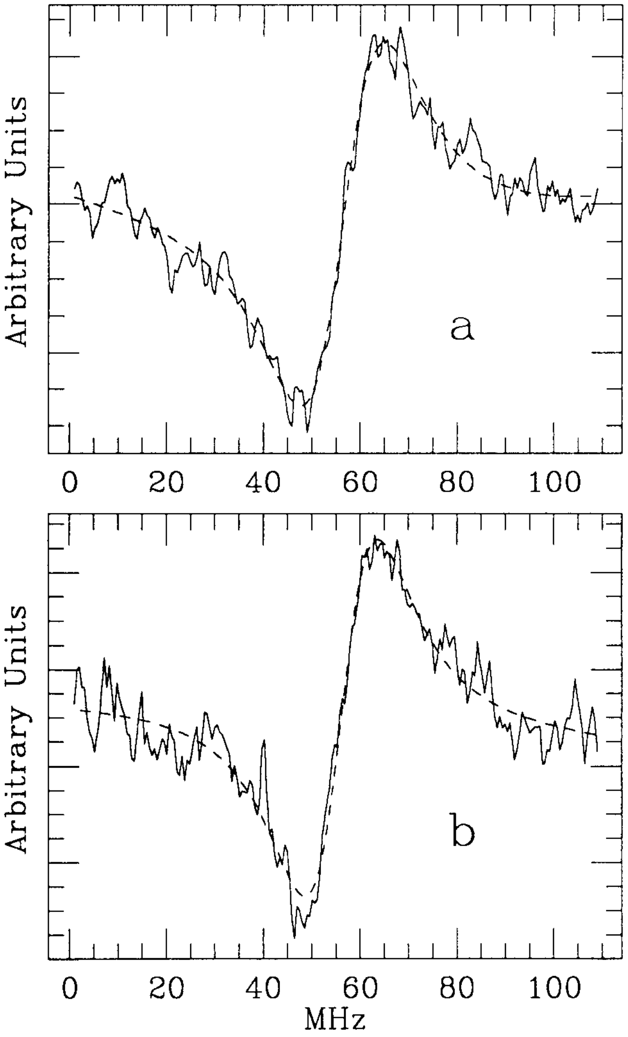

Fig. 1. Air- and oxygen-broadened derivative spectra of the 60.46 cm^{-1} $J = 10 \leftarrow 10$, $N = 11 \leftarrow 9$ O_2 rotational transition. Spectrum (a) is from 705 Pa (5.30 torr) of a mixture of 22.5% O_2 and 77.5% N_2 at 244 K. Spectrum (b) is from 665 Pa (5.00 torr) of pure oxygen at 260 K. The horizontal scale is in MHz, showing the range of frequency swept by the TuFIR spectrometer. The vertical scale is the derivative of the absorption, in arbitrary units. The nonlinear least-squares fits to the spectra are shown as dashed lines.

frequency is known to ± kHz and has a spectral purity of ~10 kHz. Thus, this source is capable of providing fully resolved measurements at the Doppler width of the O_2 transition, 1.2×10^{-4} cm^{-1} (3.6 MHz) FWHM.

The rotational transitions of O_2 are weak, since they are magnetic dipole transitions. In the atmosphere, the large column density of O_2 offsets the weakness of the lines. In the laboratory, a number of system improvements were necessary to conduct these measurements. First, the absorption cell was lengthened to 4 m to provide a longer absorption path. In the Lorentzian limit, the central absorption of the 60.46 cm^{-1} O_2 line in this cell is 4.3% for pure oxygen at 259 K and 0.96% for air at 245 K. The cell consisted of a copper tube with inside diameter of 1.4 cm. To provide for cooling, the cell was surrounded by loosely fitting foamed plastic insulation with provision to add liquid nitrogen to the annular space. Cooling was not applied to the last 20 cm of the cell ends in order to avoid window condensation. Precise temperature control was not possible. We estimate that the high thermal conductivity of the thick-walled copper tube held temperature variations to less than ±5 K. Cell temperature was read from a thermistor sensor located at the center of the cell. The insertion of roughly equal quantities of liquid nitrogen at six locations along the length provided a 20 to 30 minute period of cooling. The cell was shielded from stray and earth magnetic fields by the iron laser table and a soft iron cover (magnetic fields can produce Zeeman broadening of the oxygen lines).

Second, we had to make a number of improvements to reduce the residual standing wave in the spectral transmission of the system. For the longer cell, the free spectral range is 35 MHz, which produces overlapping structure with the line absorption. To reduce the amplitude of the reflected power in the cell, we used 80 micrometer thick polypropylene windows which have very small measured reflectance at 60 cm^{-1}. We identified another component of the standing wave response with the reflections between the MIM diode and the detector. To reduce this, we installed a rotating polyethylene wedge in the beam directly in front of the detector. This serves to modulate the optical path by several wavelengths and varies the phasing of the standing wave pattern within the integration time of a spectral point reading.

Finally, the detector sensitivity was improved by a reduction in the cold-filtered spectral response. While the ^4He-pumped composite Ge bolometer is well optimized for the 1 kHz modulation of the phase sensitive detection, its performance is essentially photon-noise limited in wide bandwidth operation. The spectral response bandwidth and resultant photon noise for the bolometer was reduced with a cold filter having a low pass cut-off at 90 cm^{-1} to achieve the necessary sensitivity for these measurements.

Spectra and Analysis. To obtain spectra, the FIR frequency was stepped sequentially by computer control of the waveguide laser to sample 214 frequency values spanning 110 MHz centered on the O_2 line. The frequency modulation amplitude is either 2.5 or 5.0 MHz. Scans were alternated in frequency direction and the signals averaged. In some cases, baseline scans with an empty cell were made and subtracted from the data in order to correct for the signal component caused by the gain roll-off or power variation of the waveguide as it was swept in frequency. Figure 1 illustrates the results obtained for an air-broadened line and for an oxygen-broadened line.

For the air-broadened studies, scans were obtained using either laboratory air or mixtures of N_2 and O_2 containing 22.5 - 24% O_2. A total of five spectra, at pressures up to 1010 Pa (7.6 torr), are in the data set for air broadening.

Table I. Air- and Oxygen-Broadening of the 60.46 cm^{-1} O_2 Rotational Line

	Pressure Pa (torr)	Lorentz Width[a] 10^{-4} cm^{-1}
Air	165 (1.24)	1.56 ± 0.13
	205 (1.54)	1.83 ± 0.29
	705 (5.30)	4.34 ± 0.18
	998 (7.50)	5.39 ± 0.55
	1010 (7.60)	6.19 ± 0.73
O_2	162 (1.22)	1.50 ± 0.08
	665 (5.00)	3.90 ± 0.21
	1010 (7.60)	5.92 ± 0.46

[a] Half width at half-maximum. Uncertainties are the 2σ uncertainties from least-squares fitting of the spectra. Uncertainties due to temperature and pressure measurement are added in quadrature to the uncertainties in pressure-broadening coefficients obtained by weighted linear regression.

The air broadening results were not corrected for this slight variation in composition, since the correction is insignificantly small. For pure oxygen studies (99.6% pure) three spectra, at pressures up to 1010 (7.6 torr), are in the data set.

The individual spectra are interactively fitted using an iterative least-squares program based upon the algorithm of Marquardt [1963]. Derivative spectra are calculated using a complete radiative transfer model, including the effects of line saturation, by subtraction of two separate spectra spaced apart by the effective modulation width (2/π x the modulation amplitude). Voigt line profiles are calculated using fixed Doppler widths. The Lorentz width, the line position, the absorber amount, baseline offset, tilt, and quadrature are varied in the fitting procedure. The fitted spectra are included in the examples shown in Figure 1. Results from the least-squares fitting of the spectra are given in Table I.

Results and Discussion

Pressure-broadening coefficients for air- and oxygen-broadening are obtained from the linewidths in Table I using weighted linear regressions. Constant terms are included in the regressions to account for spurious line-broadening effects, but their values were not significantly high. The air-broadening coefficient is $5.04 \pm 0.38 \times 10^{-7}$ $cm^{-1}Pa^{-1}$ (0.0511 ± 0.0039 $cm^{-1}atm^{-1}$) (HWHM) at 245 ± 6 K; the oxygen-broadening coefficient is $4.92 \pm 0.47 \times 10^{-7}$ $cm^{-1}Pa^{-1}$ (0.0499 ± 0.0048 $cm^{-1}atm^{-1}$) (HWHM) at 259 ± 2 K. Uncertainties are 2σ, and include the effects of temperature and pressure uncertainties, added in quadrature to the results from linear regression.

Current values of air-broadening coefficients in the AFGL line parameter listing [Rothman et al., 1983] are derived by theoretical extrapolation from microwave measurements, rather than by direct measurement. The listing gives 3.95×10^{-7} $cm^{-1}Pa^{-1}$ (0.0400 $cm^{-1}atm^{-1}$) as the value for the O_2 line at 296 K. Temperature scaling of the AFGL value using temperature coefficients of -0.7 to -2.0 [Pickett et al., 1981] gives values at 245 K of between 4.5×10^{-7} and 5.7×10^{-7} $cm^{-1}Pa^{-1}$ (0.046 and 0.058 $cm^{-1}atm^{-1}$). Thus the major uncertainty in O_2 pressure broadening for temperatures other than 245 K is the limited knowledge of the temperature dependence.

In the only other study of air-broadening of O_2 lines in the submillimeter/far infrared that we are aware of, Pickett et al. [1981] find values for the air-broadening coefficients of lines at same temperature. The Pickett et al. [1981] study also finds temperature dependences that vary significantly. Since determination of line-of-site abundances, from which viewing geometries are inferred, depends directly on the pressure-broadening for these saturated lines, extreme caution should be exercised when using pressure-broadening values, or their temperature dependences, that have not been directly measured for the same spectral lines used in calibration.

The present direct experimental measurement of one of the lines used to calibrate stratospheric emission spectra should improve the viewing geometry retrieval calculations, and substantially decrease the uncertainties, in analyses of far infrared stratospheric balloon experiments. The results reported here are part of a larger comprehensive study of the nitrogen- and self-broadening of molecular oxygen that is currently under way. We report the results obtained to date in order to support current balloon data analyses which require spectral fitting of the O_2 spectrum to verify viewing angles and gondola altitudes.

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Correction to "Air- and Oxygen-Broadening Coefficients for the O_2 Rotational Line at 60.46 cm^{-1}", by D. A. Jennings et al., Geophysical Research Letters, 14 (7), 722-725, 1987.

In the paper cited above, a line of text was inadvertently omitted from the first sentence of the third paragraph of the Results and Discussions section (p. 724). This sentence should read:

In the only other study of air-broadening of O_2 lines in the submillimeter/far infrared that we are aware of, Pickett et al. [1981] find values for the air-broadening coefficients of lines at 3.96 and 14.17 cm^{-1} that are respectively 9% and 45% larger than the AFGL values at the same temperature.

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