

Temperature-Dependence of Air-Broadened Line Widths and Shifts in the ν_3 Band of Ozone

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Abstract

The 9.6- μm bands of O_3 are used by many remote-sensing experiments for retrievals of terrestrial atmospheric ozone concentration profiles. Line parameter errors can contribute significantly to the total errors in these retrievals, particularly for nadir-viewing. The McMath-Pierce Fourier transform spectrometer at the National Solar Observatory on Kitt Peak was used to record numerous high-resolution infrared absorption spectra of O_3 broadened by various gases at temperatures between 160 and 300 K. Over 30 spectra were analyzed simultaneously using a multispectrum nonlinear least squares fitting technique to determine Lorentz air-broadening and pressure-induced shift coefficients along with their temperature dependences for selected transitions in the ν_3 fundamental band of $^{16}\text{O}_3$. We compare the present results with other measurements reported in the literature and with the ozone parameters on the 2000 and 2004 editions of the HITRAN database.

1. Introduction

Since 1978 NASA has been continuously measuring global ozone levels from a variety of satellites. Instruments monitoring ozone use the UV, IR, and microwave spectral regions. IR measurements often use the strong ν_3 band at 9.6 μm . While earlier remote sensing efforts focused on measuring total column abundances of atmospheric ozone or on determining stratospheric ozone distributions, more recent sensors such as the Tropospheric Emission Spectrometer (TES) on the AURA satellite are designed to monitor the distribution of ozone in the troposphere. Tropospheric ozone is of concern to environmental scientists because it is produced primarily from photochemical reactions in polluted air, it is toxic to plants and animals (including humans), and it acts as a greenhouse gas in the upper troposphere. Since atmospheric pressures in the troposphere are larger than in the stratosphere, uncertainties in the knowledge of ozone air-broadening and shift parameters will have a greater contribution to errors in retrievals of tropospheric ozone concentrations [1,2]. Also, since atmospheric temperatures range from about 300 K near the ground to 195 K or lower at the tropopause, quantitative knowledge of the temperature-dependence of ozone air-broadening and shift parameters is important.

Previous measurements of the temperature-dependence of air-broadening parameters for O₃ [3-5] focused on the ν_1 , ν_2 and rotational bands. Low-temperature studies in the ν_3 band [6-8] measured N₂-broadening and O₂-broadening separately. Determining the n value for air-broadening from these separate measurements of N₂- and O₂-broadening results in values that include the uncertainties of both sets of measurements. Therefore it is more desirable to measure air-broadening and shift parameters directly. We have recorded a number of high-resolution air-broadened O₃ spectra covering the ν_3 band at temperatures from 160 to 300 K. In the present work we report broadening and shift parameters and their temperature dependences for 41 selected transitions in the P branch of this band.

2. Experimental Details

All 31 spectra used in this study were recorded using the McMath-Pierce 1-meter Fourier transform spectrometer (FTS) with the KCl beam splitter, 8 mm aperture, and He-cooled As:Si detectors. Optical filters were used to limit the band pass to either 500 – 1400 cm⁻¹ or 800 – 1400 cm⁻¹. Four of the spectra, each with 0.3 to 0.5 torr of nearly-pure ozone in a 10 cm cell at room temperature were used in our previously-published intensity study [9]. These spectra and four additional room-temperature air-broadened spectra ($p = 76$ to 204 torr, VMR $\sim 4\%$) using the 10-cm cell were all recorded at 0.0027 cm⁻¹ resolution with the FTS set up in double-passing mode. Two sets of low-temperature spectra were included in the analysis; both of these sets were recorded at 0.005 cm⁻¹ resolution. A set of 15 air-broadened spectra were recorded using the NASA Langley 50-cm coolable sample cell at temperatures from 213 to 298 K, pressures from 86 to 220 torr, and volume mixing ratios from 0.3 to 0.6%; one low-pressure spectrum of nearly-pure O₃ at 1.3 torr was also recorded with this cell. A 9.5-cm coolable cell, graciously loaned to us by Dr. Charles Chackerian of NASA Ames Research Center, was used to record one spectrum of nearly pure O₃ at 2.2 torr and 170 K, plus five spectra of air-broadened ozone at temperatures from 160 to 186 K and pressures between 94 and 203 torr. Unfortunately the loss of one detector and other technical difficulties resulted in these lowest-temperature spectra having much poorer signal-to-noise ratios than the others. Nevertheless, these spectra were included in the analysis but given much lower weights.

3. Analysis

The multispectrum technique developed by Benner et al. [11] was used to analyze small intervals of the 31 spectra simultaneously. The strategy for the multispectrum fitting of this diverse set of spectra was as follows:

- 1) Four low-pressure spectra for which concentrations were determined by UV absorption at 254 nm (see Ref. [9]) were fit together first to obtain absolute line intensities.
- 2) Intensities were fixed to these retrieved values for subsequent fitting of the air-broadened spectra.
- 3) Room-temperature air-broadened spectra were added to the fit first, followed by the lower-temperature spectra down to 213 K.
- 4) Noisy spectra from 186 to 160K were added to the fit with low weights due to relatively poor signal-to-noise ratio.

In addition to the line intensities determined from fitting the four low-pressure spectra, air-broadened widths, pressure-induced shifts, and the temperature dependences of the widths and shifts were determined for 41 v_3 P-branch transitions in the spectral region between 1016 and 1025 cm^{-1} . The lower state quantum number ranges of these transitions were $J'' = 15 - 26$ and $K_a'' = 0 - 11$.

4. Results and Discussion

In Figures 1 and 2 below, the v_3 air-broadening coefficients and temperature dependence exponents determined in this study are plotted as functions of J'' along with the corresponding N_2 -broadening values measured by Spencer et al. [6] and the values from the 2000 and 2004 editions of the HITRAN database [12,13].

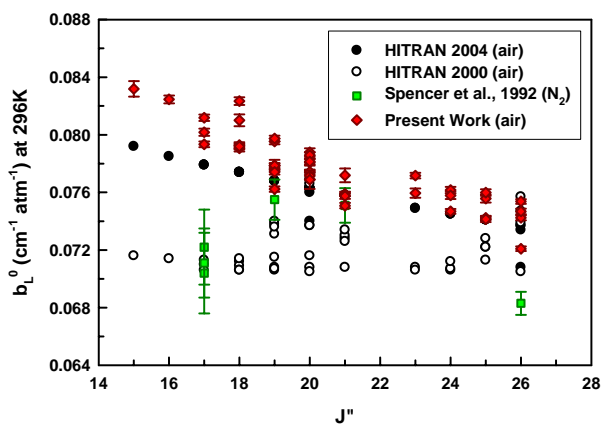


Figure 1. Air-broadening coefficients.

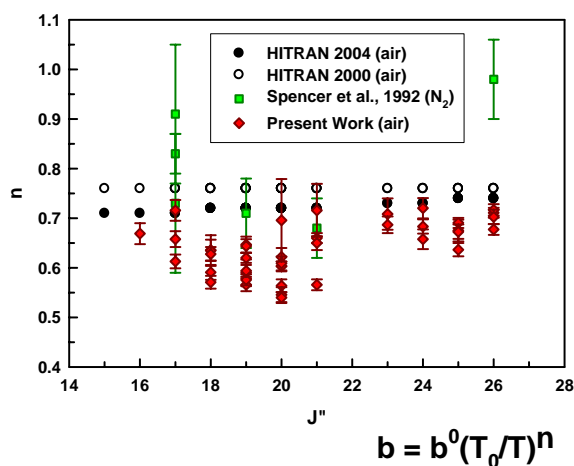


Figure 2. Air-broadening temperature dependence exponents.

There are no other direct measurements of air-broadening or air-induced line shifts in the A-type v_3 band available for comparison. However, comparison with results for transitions with the same lower-state quantum numbers in the B-type bands [3-5] indicates that air-broadened widths in the rotational band and the three vibration-rotation fundamental bands are in agreement within the absolute uncertainties of the measurements (typically 5% or better). Air-induced shifts are also consistent between the three fundamental bands. Comparison of the present v_3 widths and shifts with our previous results in the A-type $3v_3$ band [14] indicates that there is no discernable vibrational dependence of the widths, but the vibrational dependence of the shifts is quite apparent (Fig. 3).

Regarding the temperature dependence exponents for air-broadening the results of comparisons are less clear. The temperature dependence exponents we have determined for v_3 air-broadening are 5 to 25% smaller than the corresponding HITRAN 2004 values [13]. The v_3 measured values generally decrease with J'' , while the HITRAN 2004 values increase with J'' . There is also some indication that the measured n values in the v_1 , v_2 and rotational bands [3-5] also tend to decrease as J'' increases. Since the present study only involves 41 P-branch lines, a final resolution of

these issues awaits completion of analysis for a larger number of spectral lines in the ν_3 and other bands.

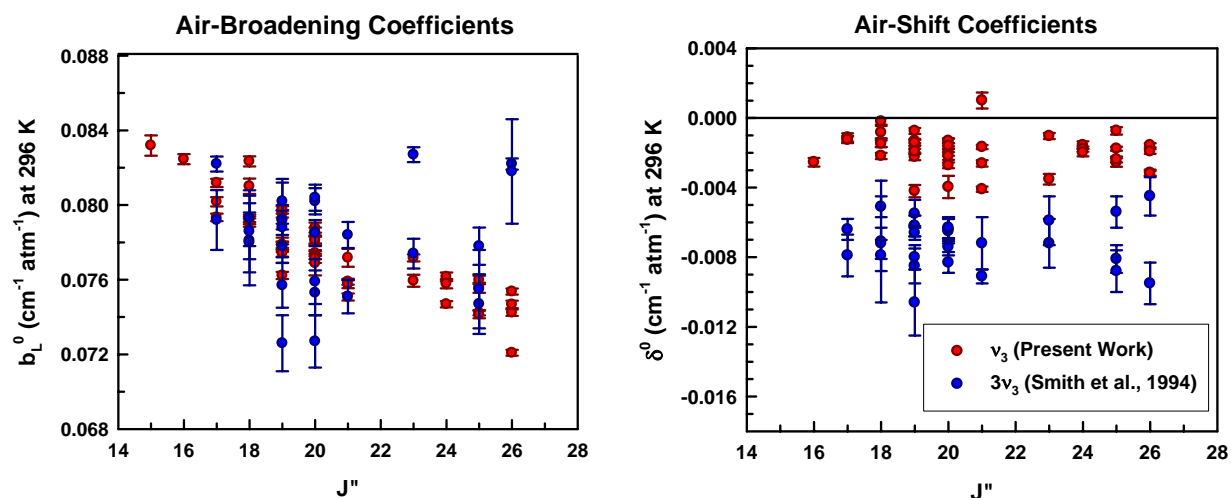


Figure 3. Comparison of air-broadening and shift coefficients measured in the ν_3 and $3\nu_3$ bands.

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