STRENGTH, WIDTH, AND PRESSURE SHIFT MEASUREMENTS OF 54 LINES IN THE OXYGEN A-BAND

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The absorption band of molecular oxygen, centered at 760nm and known as the oxygen A-band, is the atmospheric absorber for DIAL systems being developed to measure atmospheric temperature, pressure and density. To provide accurate line parameters for such systems, we have made a careful spectroscopic study of the A-band, with measurements of line strengths, widths, pressure-induced frequency shifts, and collisional narrowing effects. The width and shift parameters have been measured over a temperature range of -20°C to 100°C so that the temperature dependence of these parameters can also be determined.

To make accurate measurements of these line parameters, three separate experimental arrangements were used. In each, a cw narrow linewidth tunable dye laser was used to scan over the individual absorption lines. For strength and width measurements at ambient temperature, the laser was used in conjunction with a multi-pass absorption cell to make high resolution absorption spectra. To measure pressure induced frequency shifts at ambient temperature, a photo-acoustic (PA) cell was positioned between the laser and absorption cell, so that simultaneous scans could be made of both cells. This is basically the same technique used by Bösenberg (ref. 1) to measure water vapor shifts. Figure 1 is an example of one of these composite scans, showing simultaneous absorption and PA scans of the PP 15,15 line.

To measure widths and shifts as a function of temperature, we constructed an additional, temperature controllable, PA cell. This cell was used with the ambient temperature PA cell to produce simultaneous PA spectra at different temperatures and pressures.

To analyze the results from the above measurements, we wrote a least-squares fitting routine to fit standard line profiles to the observed profiles. We found that the Galatry collisionally narrowed profile (ref. 2) was better than the standard Voigt profile in fitting the observed profiles, so we used the Galatry function for the data analysis. The fitting

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process produced a set of line parameters for each scan of an individual line; these included: strength (absorption scans only), pressure broadened width, position (relative frequency only), and collisional narrowing parameter.

Using the strengths of the individual lines, we have determined the integrated band strength to be:

$$ S_B = 612 \text{ cm}^{-1} \text{ km}^{-1} \text{ amagat}^{-1} \quad (\text{std. dev.} = 1\%) $$

Width and shift results as a function of pressure are shown in figures 2 and 3 respectively. Widths and shifts were also measured in air. Line widths measured in air were found to be only about 3% greater than those measured in pure $\text{O}_2$. Pressure shifts however, were found to be 30% higher in air as compared to pure $\text{O}_2$. Results for pressure broadening coefficients and pressure shift coefficients for all the lines measured are shown graphically in figures 4 and 5 respectively.

We believe that these measurements, which include the first observations of pressure shifts and collisional narrowing in this band, will be an important contribution to lidar systems utilizing the A-band.

References
Figure 2.
Measurements of the self-broadened width vs. pressure for 7 P-branch lines. Each point was determined by fitting an observed profile (taken at the indicated pressure) with a Galatry profile. For clarity, widths for each successive line have been offset by 5 milli-Kaisers and 0.02 atm.

Figure 3.
Pressure induced frequency shifts of the PP 9,9 line. Each point corresponds to a scan similar to that shown in figure 1.
Figure 4.
Self-broadening coefficients of Oxygen A-Band lines.

Figure 5.
Pressure shift coefficients for both air-broadening and self-broadening of Oxygen A-Band lines.