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BRIEF COMMUNICATION

PRESSURE BROADENING OF THE 118.455 cm^{-1} ROTATIONAL LINES OF OH BY N_2, O_2, H_2, AND He

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Abstract—We measured the pressure broadening of the 118.455 cm^{-1} (3.551 Thz) rotational lines of OH by H_2, He, N_2 and O_2. From these measurements, we calculated the pressure broadening of this line by air. The broadening coefficients are 6.06(16) and $10.13(25) \times 10^{-7}$ cm^{-1} Pa^{-1} at 296 and 194 K. We also measured the position of the manifold of lines, with results that are in excellent agreement with a previous accurate determination. The frequency of the strongest component of the transition ($F = 4 \leftarrow 3$), and its 2σ uncertainty is 3 551 185.42(3) MHz.

The spectroscopic determination of OH concentration profiles in the Earth's stratosphere requires accurate line parameters, including pressure broadening coefficients. The manifolds of OH lines at 83.869 and 118.455 cm^{-1} are particularly important for quantitative measurements of OH.[1] We have previously measured the pressure broadening coefficients for both of these manifolds of lines.[2,3] Table 1 compares existing N_2 broadening coefficients with calculated values of Buffa et al.[4] The measured values are given with 2σ uncertainties. The calculated values are good to 10–20%. The measured temperature dependence for the 118.455 cm^{-1} line contrasts with the rest of the temperature dependences in the table. For this reason, we have remeasured them with the improved spectrometer that was used recently for the 83.869 cm^{-1} measurements.

The present line parameters are measured in absorption using a tunable far-infrared (TuFIR) radiation source. A detailed description of this radiation source, the spectrometer arrangement, the OH source chemistry, and the data analysis procedure is contained in Ref. 2. Briefly, the TuFIR frequency is known with an accuracy and spectral purity of ~ 10 kHz. The wall of the absorption cell (50 cm long and 2.5 cm in diameter) is coated with halocarbon wax; the entire cell is cooled to a set of selected bath temperatures. The total pressure is measured with a capacitance manometer with a 0.15% uncertainty. Individual gas flow rates are measured by mass flow meters with a 0.8% uncertainty. Because of the source chemistry, we measure the pressure broadening by H_2 and He as well as the broadening by N_2 and O_2.

The OH transition at 118.455 cm^{-1} ($F_1, 7/2^+ \leftarrow F_1, 5/2^-$) is split by the proton hyperfine interaction into three lines. These three lines, in order of increasing frequency, correspond to $F = 4 \leftarrow 3$, $F = 3 \leftarrow 3$ and $F = 3 \leftarrow 2$. Their relative intensities should be 27 : 1 : 20, based on angular momentum coupling.[5] From an analysis of microwave resonance data,[6] we obtain frequency separations for the two higher transitions of 19.04 and 0.70 MHz above the lowest transition. In the present analysis the positions, widths and intensities of the two smaller hyperfine components are referenced to those of the lowest frequency transition.

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Table 1. Existing N_2 broadening coefficients (10^{-7} cm^{-1} Pa^{-1}, HWHM)

	Measured[2]		Calculated[4]	
OH118	296 K	210 K	300 K	200 K
	9.00(27)	9.05(27)	9.7	12.0
OH83	296 K	192 K	300 K	200 K
	9.58(30)	14.84(56)	11.1	14.8

Table 2. Pressure broadening coefficients (10^{-7} cm^{-1} Pa^{-1}, HWHM) for the 118.455 cm^{-1} lines of OH†

	Temperature	
Broadening gas	296(3) K	194(3) K
H_2	8.81(30)	10.62(23)
He	1.47(04)	1.90(06)
N_2	6.75(20)	11.06(31)
O_2	3.47(15)	6.65(31)
Air‡	6.06(16)	10.13(25)

†2σ uncertainties shown. One atmosphere $= 1.01325 \times 10^5$Pa.
‡$\gamma_{air} = 0.79\gamma_{N_2} + 0.21\gamma_{O_2}$.

The results of our measurements are summarized in Table 2. Air broadening is calculated as $\gamma_{air} = 0.79\gamma_{N_2} + 0.21\gamma_{O_2}$. The $F = 4 \leftarrow 3$ line position at the lowest pressure for He broadening (and thus the lowest total line width) is 3 551 185.42(3) MHz at 296 K. The uncertainty is 2σ.

The pressure-broadening coefficients for N_2 and O_2 here differ substantially from the previously published results by Chance, et al.[2] The remeasured temperature dependence is now consistent with the observed dependence for the 83.869 cm^{-1} line of OH.[3] The remeasured results agree well with the calculated values of the N_2 broadening by Buffa et al[4] (they calculate 9.7 and 12.0×10^{-7} cm^{-1} Pa^{-1} at 300 and 200 K while we measure 6.75 and 11.06×10^{-7} cm^{-1} Pa^{-1} at 296 and 194 K).

Our spectrometer system has undergone an important evolution during the six year interval between measurement sets. The TuFIR spectrometer now operates with three-wave mixing, the waveguide laser is now fixed in frequency, and a tunable microwave source is used to generate two tunable sidebands. The amplitude stability has improved as a result. In addition, the spectrometer scan width has been increased substantially, all but eliminating the baseline curvature. The detector performance has improved steadily. With the overall signal-to-noise ratio improvement, we have been able to increase the pressure range for the broadening gases, which has made the regression procedure very robust. We have improved the error propagation analysis in the derivation of partial pressures from the flow meter readings. These improvements have yielded a more accurate set of broadening coefficients in comparison to our earlier work.

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