

VARIABLE TEMPERATURE PRESSURE BROADENING OF THE $4_{1,4}-3_{2,1}$ TRANSITION OF H_2O BY O_2 and N_2

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Abstract—The O_2 and N_2 pressure-broadening parameters of the $4_{1,4}-3_{2,1}$ rotational transition in the ground vibrational state of H_2O have been measured in the temperature range between 100 and 520 K. Above 250 K the measurements were made in an equilibrium cell. Below 250 K a cell, which uses collisional cooling to circumvent the temperature limits imposed by the vapor pressure of the sample gas, was used. The data were fitted to an exponential temperature-dependence for data above 150 K with resultant n values of 0.81(3) for O_2 and 0.70(3) for N_2 , where the entries in parentheses represent the error in the last significant figure of the parameter. Below 150 K the measured pressure-broadening parameters are smaller than those calculated using these values of n .

INTRODUCTION

Water is an important constituent of the Earth's atmosphere. It is important to understand its role in atmospheric transmission, remote sensing and heat balance. Although the energy level structure of water has been the subject of a number of investigations, relatively few experimental data exist on its pressure-broadening parameters over a very wide temperature range. This is understandable since the vapor pressure of water is very small at temperatures below 260 K. To circumvent the limitations imposed by the low vapor pressure of the sample gas, we have used collisional cooling to study gas phase samples at temperatures far below the point at which the sample gas freezes.¹⁻³ In addition to the collisional cooling cell, we have employed a variable temperature equilibrium cell for use at temperatures which permit a large vapor pressure of the sample gas to be sustained in the cell. We have employed this technique previously to study O_2 , N_2 and He pressure-broadening of H_2O and HNO_3 in the 80–600 K temperature range.^{4,5}

In this paper we present the O_2 and N_2 pressure-broadening coefficients of the $4_{1,4}-3_{2,1}$ transition in the ground vibrational state of H_2O in the temperature range from 100 to 520 K. The results are compared with the previous experimental and theoretical pressure-broadening study by Bauer et al.^{6,7} We find that a simple power-law equation is sufficient to describe the temperature variation of the pressure-broadening parameters above 150 K. At temperatures below 150 K the pressure-broadening parameters of N_2 drop off below the line predicted by the power law.

EXPERIMENTAL DETAILS

We have discussed the experimental details of our variable temperature pressure-broadening techniques in Ref. 4. Briefly, for temperatures above 250 K, which is an approximate lower limit on the usable vapor pressure of H_2O , a conventional equilibrium cell was used. The cell consists of a quartz tube in an oven with temperature variable between 80 and 600 K. The oven extends beyond the cell to ensure that the windows are maintained at the same temperature as the cell.

The collisional cooling cell, used at temperatures below 250 K, is shown in Fig. 1. This cell has an in-gas thermocouple for direct gas temperature measurements. The cell temperature can be varied between 80 and 300 K. The upper temperature limit for data collection is set by the freezing point of the sample gas.

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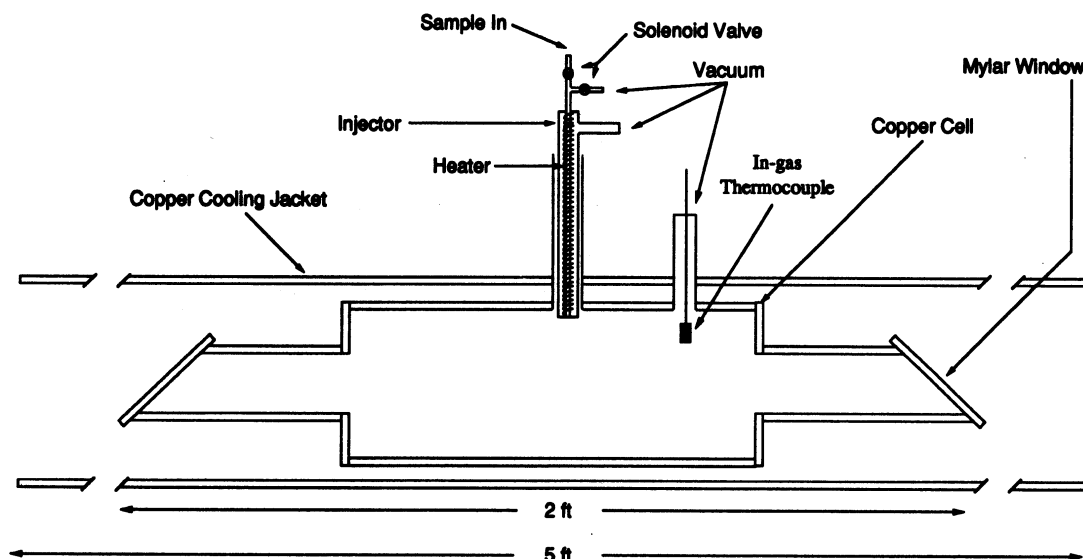


Fig. 1. The collisionally cooled cell and injector assembly used for low temperature experiments.

Spectroscopically active gas, which would have a vanishingly small vapor pressure at low temperature, flows into the cell via the injector shown in the center of the cell in Fig. 1. The injector consists of a heated 0.035-in. dia stainless steel tube in a vacuum region separated from the cell by a 0.01-in. thick stainless steel diaphragm. The cell is filled with a static pressure of broadening gas against which the sample gas cools. The sample gas cools rapidly, requiring fewer than 100 collisions to approach the broadening gas temperature, in contrast to the many thousands of collisions required to reach the cell walls where it traps. The pressure of the broadening gas is controlled through a computer controlled valve and was varied between 0.02 and 0.3 torr.

We have previously described the broadband spectrometer and millimeter/submillimeter techniques used in this experiment.^{8,9} The output from a computer-controlled 10–15 GHz YIG oscillator is tripled to drive a 1-W, 26–40 GHz TWT amplifier. The output of the TWT is multiplied into the millimeter/submillimeter by a crossed waveguide harmonic generator and propagated quasi-optimally through the cells described above. The microwaves are then sent into a 1.5 K InSb detector. Pressure measurements are made by an MKS capacitance manometer. Thermal transpiration caused by the temperature difference between the cell and gauge is corrected using the method of Takaishi and Sensui.¹⁰ Pressure corrections in this study were small, typically less than 3%.

The microwave power was swept rapidly in frequency through the absorption line. The bandwidth of the digitizer and detector was large enough to preserve all significant Fourier components. This also preserves baseline undulations (reflections) and makes deconvolution of spectral lineshape difficult. Consequently, we have used the injector modulation baseline subtraction technique described in Ref. 4 to reduce this effect in the collisional cooling cell.

For each pressure-broadening parameter, data were recorded at about 30 different pressures. Since the large amount of data would have made fitting a Voigt profile time consuming, the digitized data were fitted to a Lorentzian lineshape with a linear and quadratic term in the baseline. The broadening coefficients were obtained from a least-squares fit to these data with points weighted inversely with the pressure. The measurements were confined to the region where the Doppler contribution was small. The correction for Doppler broadening was subtracted off via the equation,¹¹

$$\Delta\nu_o^2 = \Delta\nu_p^2 + \Delta\nu_D^2 \quad (1)$$

where $\Delta\nu_p$ is the pressure-broadened line width, $\Delta\nu_o$ is the observed linewidth, and $\Delta\nu_D$ is the Doppler width.

To avoid possible problems with warming of the background gas in the collisional cooling cell, the flow rate of H_2O molecules into the cell was kept low. A flow rate of 1×10^{18} molecules/sec, which is similar to that used in Ref. 4, was used here.

Table 1. Measured pressure-broadening parameters. Absolute uncertainty is estimated at $\pm 5\%$.

T(K)	γ_{O_2} (MHz/Torr)	γ_{N_2} (MHz/Torr)
520	1.60	2.79
433	1.76	3.20
375	1.91	3.54
298	2.42	4.18
272	2.70	4.60
173	3.76	5.97
152	4.29	6.33
133	4.99	6.70
108	5.70	7.01

RESULTS AND DISCUSSION

Pressure-broadening measurements were made on the $4_{1,4}-3_{2,1}$ rotational transition of H₂O at 380,197.327 MHz. Results for broadening by O₂ and N₂ are shown in Table 1. Figures 2 and 3 show the results from Table 1 for O₂ and N₂ respectively plotted on a linear scale. Also shown in these figures are the previous pressure-broadening results from Ref. 6. In these figures circles represent the results from this work and boxes represent the previous study of Ref. 6. It is clear from these figures that the data sets from both studies agree to within experimental accuracy but taken individually lead to somewhat different results. This demonstrates the need to study as wide a temperature range as possible.

The data of Table 1 were fit to the power law formula

$$\gamma(T) = \gamma(T_0)[T_0/T]^n \quad (2)$$

where $\gamma(T_0)$ is the pressure-broadening parameter at reference temperature $T_0(300)$ and n is a constant exponent of the temperature. This expression is commonly used to characterize the temperature variation of pressure-broadening parameters.¹² The results for the best fit parameters above 150 K are given in Table 2 along with their statistical uncertainties. Also listed in Table 2 are the results of theoretical calculations from Ref. 7 and the previous experimental results from Ref. 6. The data from Table 1 and best fit curves are plotted in Figs. 4 and 5 for N₂ and O₂ respectively, where the axes are logarithmic so the calculated lines will appear as straight lines of slope $-n$. The results for temperature coefficients give values of $n = 0.70$ and 0.81 for O₂ and N₂ respectively. As can be seen from the figures, the power law equation adequately describes the variation in the experimental results down to 150 K. Below 150 K the N₂ broadening parameters begin to fall off below the line predicted by the power law equation.

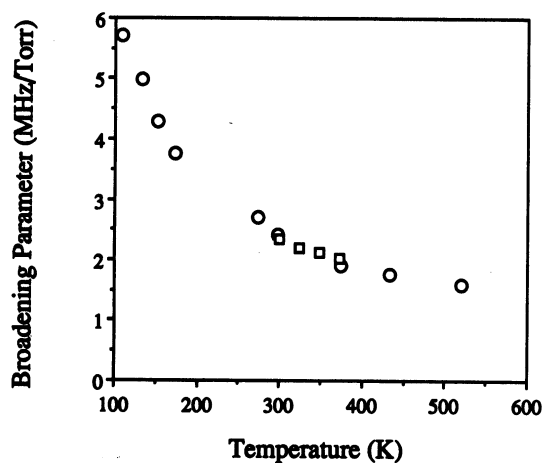


Fig. 2. Measured O₂ pressure-broadening parameters of the $4_{1,4}-3_{2,1}$ transition of H₂O. (○) Data from this work; (□) Data from Ref. 6.

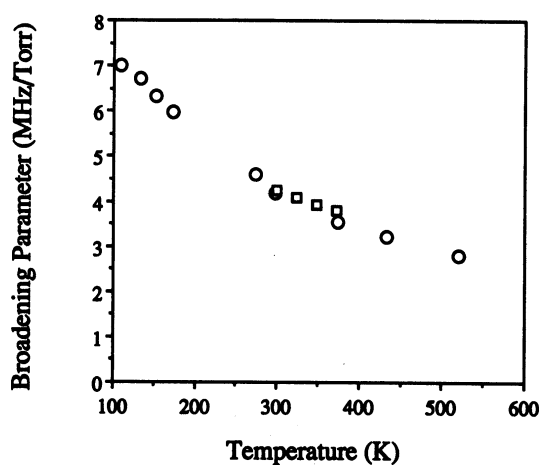


Fig. 3. Measured N₂ pressure-broadening parameters of the $4_{1,4}-3_{2,1}$ transition of H₂O. (○) Data from this work; (□) Data from Ref. 6.

Table 2. Best fit of 300 K broadening parameters γ (MHz/torr) and n values. Uncertainties are one standard deviation taken from the least-squares fit.

	This work		Ref. 7 (calc)		Ref. 6 (exp)	
	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂
γ (300K)	4.16(4)	2.44(3)	4.11	2.63	4.23	2.33
n	0.70(3)	0.81(3)	0.69	0.70	0.52(14)	0.64(14)

It can be seen from Table 2 that the results reported here are in agreement with the experimental results of Ref. 6 but the wider range in temperature leads to much smaller error bars on the best fit parameters. This is to be expected since the data from Ref. 6 only include the temperature range from 300 to 375 K. Over this narrow temperature range the pressure-broadening parameter changes only about 14% making it very difficult to make an accurate measure of the difference. However, the experimental data set reported here varies about 270% over the temperature range from 150 to 520 K which allows for a more accurate measurement. It is also interesting to note that for N₂ the results of this work are in excellent agreement with the theoretical prediction of Ref. 7 for both the 300 K pressure-broadening parameter and the temperature coefficient n . Both values fall within 1 SD of the best fit parameters of the predicted values. The results for O₂ show relatively good agreement with those predicted in Ref. 7 but in general not as good as the N₂ data set. This may be due to the increased difficulty of calculations for systems not dominated by a single large multipole term.

We have previously reported the results for a similar study of the $3_{1,3}-2_{2,0}$ transition of water at 183,310.117 MHz. The results for N₂ and O₂ were 4.19(15) and 2.77(10) MHz/torr respectively for the broadening parameter at 300 K and 0.74(3) and 0.85(3) respectively for n . A comparison with Table 2 shows that the values of n for both the $4_{1,4}-3_{2,1}$ and $3_{1,3}-2_{2,0}$ transitions for both O₂ and N₂ are nearly identical. The 300 K pressure-broadening parameters are also very close for both transitions with the largest difference occurring as a 13% decrease in pressure-broadening coefficient from the lower J transition to the higher J transition.

SUMMARY

In this study we have measured the temperature variation of the N₂ and O₂ pressure-broadening parameters of the $4_{1,4}-3_{2,1}$ transition in the ground vibrational state of H₂O. Measurements were made in the temperature range between 100 and 520 K by the use of a heated equilibrium cell for elevated temperatures and the use of a collisionally cooled cell at the lower temperatures where

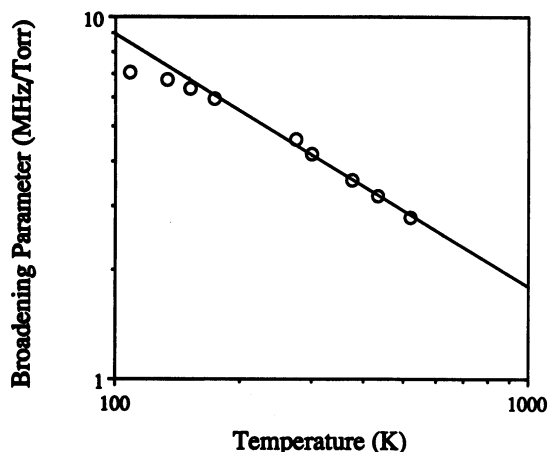


Fig. 4. Measured N₂ pressure-broadening parameters of the $4_{1,4}-3_{2,1}$ transition of H₂O (logarithmic scale). (○) Data from this work. The solid lines are the result of a least-squares fit to Eq. (2).

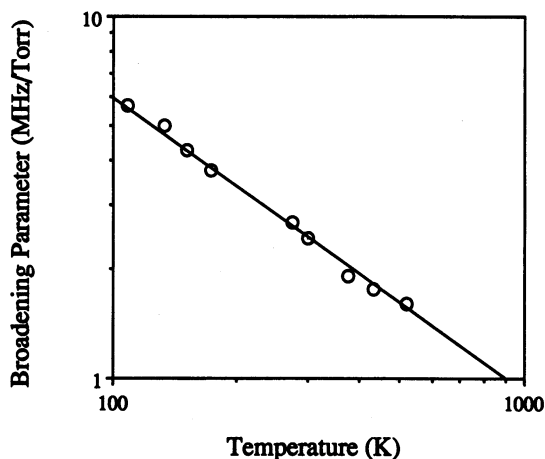


Fig. 5. Measured O₂ pressure-broadening parameters of the $4_{1,4}-3_{2,1}$ transition of H₂O (logarithmic scale). (○) Data from this work. The solid lines are the result of a least-squares fit to Eq. (2).

H₂O has a vanishingly small vapor pressure. Above 150 K the observed pressure-broadening data can be fitted to the usual empirical power law, giving n values of 0.81(3) and 0.70(3) for O₂ and N₂ respectively. Good agreement is seen between this data set and previous experimental and theoretical work.

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