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VARIABLE TEMPERATURE PRESSURE BROADENING OF HNO_3 IN THE MILLIMETER WAVE SPECTRAL REGION

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Abstract—The O_2 and N_2 pressure-broadening parameters of the $18_{0,18}$–$17_{0,17}$, $22_{7,15}$–$21_{7,14}$, and $29_{0,29}$–$28_{0,28}$ transitions in the ground vibrational state of HNO_3 have been measured in the temperature range between 100 and 380 K. Above 190 K the measurements were made in an equilibrium cell. Below 190 K, a cell with collisional cooling to circumvent the temperature limits imposed by the vapor pressure of the sample gas was used. The data were fit to the usual exponential temperature dependence with resultant n values ranging from 0.67(5) to 0.84(10) for O_2 and from 0.62(3) to 0.74(9) for N_2.

INTRODUCTION

HNO_3 plays an important role in the chemistry of the upper atmosphere and therefore its line frequencies have been extensively studied in the microwave and infrared (i.r.).[1] However, there have been relatively few data on the pressure-broadening parameters, particularly at temperatures other than room temperature.[2–5] This is understandable since HNO_3 decomposes rapidly at temperatures above 400 K and since low-temperature measurements are ordinarily limited by its vapor pressure, which becomes very small even at 200 K. To circumvent the limitations imposed by the vapor pressure of the sample gas, we have developed a method, known as collisional cooling, for the study of gas-phase samples at temperatures far below the point at which the samples freeze.[6–8] We have also developed 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 recently used these techniques to study the O_2, N_2, and He pressure-broadening of H_2O in the 80–600 K temperature range.[9]

In this paper we present the O_2 and N_2 pressure-broadening coefficients for the $18_{0,18}$–$17_{0,17}$, $22_{7,15}$–$21_{7,14}$, and $29_{0,29}$–$28_{0,28}$ transitions in the ground vibrational state of HNO_3 in the temperature range from 100 to 380 K. The results are compared with the previous air-broadening study of May and Webster[5] and with the previous Anderson theory calculations of Tejwani and Yeung.[10] We find that a simple power-law equation is sufficient to describe the temperature variation of the pressure-broadening parameters even to the lowest temperatures reported here, in contrast to a drop off below the power law at low temperatures which was seen in our previous study of H_2O. These results, along with our previous room-temperature study of HNO_3 over a wide range of quantum states,[2] should be applicable to the calculation of pressure-broadening parameters in the i.r.

EXPERIMENTAL DETAILS

We have discussed the experimental details of our variable temperature pressure-broadening techniques in a recent paper.[9] Briefly, for temperatures above 190 K, which is a rough lower limit on the usable vapor pressure of HNO_3, a conventional equilibrium cell was used. The cell consists of a quartz tube in an oven with a 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 190 K, is shown in Fig. 1.

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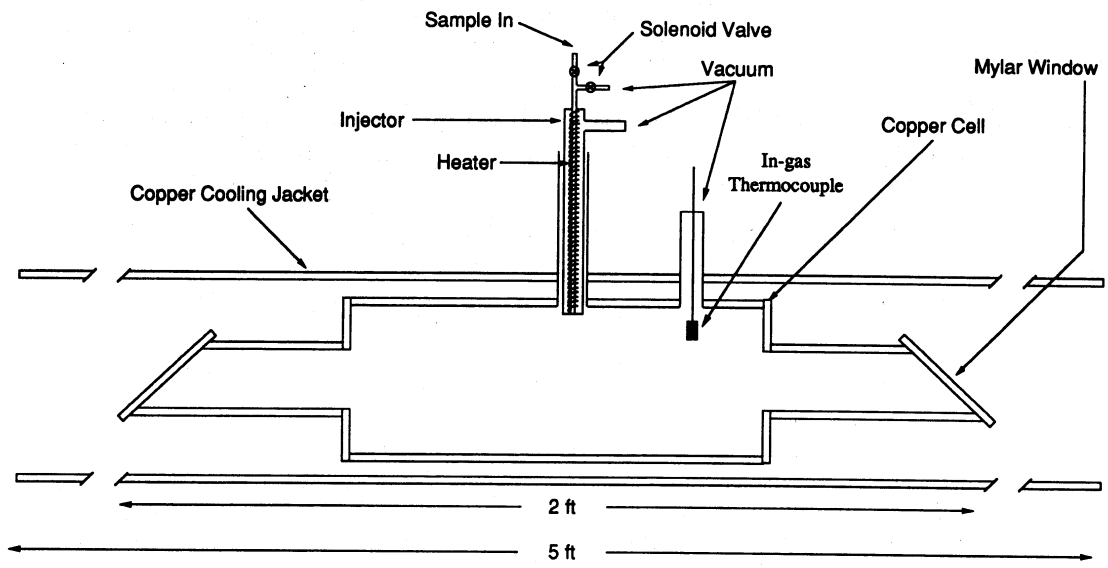

Fig. 1. The collisionally cooled cell and injector assembly used for low temperature experiments.

This cell has been slightly modified from our previous work to provide 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.

Spectroscopically-active gas, which would have a very low 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. 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.[11,12] 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 quasioptically 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.[13] 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 the baseline undulations (reflections) which make deconvolution of spectral lineshape difficult. We have therefore used the baseline subtraction technique described in Ref. 9 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 a fitting a Voigt profile time consuming, the digitized data were fit 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 as the square of 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,[14]

$$\Delta\nu_o^2 = \Delta\nu_p^2 + \Delta\nu_d^2 \tag{1}$$

Table 1. Measured pressure-broadening parameters.†, ‡, §

$18_{0,18} - 17_{0,17}$			$22_{7,15} - 21_{7,14}$			$29_{0,29} - 28_{0,28}$		
Temperature	$\gamma(O_2)$	$\gamma(N_2)$	Temperature	$\gamma(O_2)$	$\gamma(N_2)$	Temperature	$\gamma(O_2)$	$\gamma(N_2)$
104	6.04	9.11	193	4.46	6.29	113	5.47	7.93
114	5.63	8.41	216	4.25	5.64	130	4.89	7.02
132	5.09	7.80	243	3.87	5.31	193	4.04	5.72
193	4.05	6.12	251	3.51	5.17	216	3.80	5.23
216	4.11	5.88	284	3.24	4.77	243	3.38	5.02
239	3.57	5.58	298	3.25	4.62	251	3.24	4.66
251	3.41	5.18	324	2.96	4.21	284	2.94	4.47
284	3.22	5.10				298	3.19	4.03
298	2.97	4.57				324	2.52	3.72
327	3.03	4.20						
337	2.76	4.76						
354	2.71	4.11						
380	2.28	3.95						

† Temperature in degrees K.

‡ Broadening parameters in MHz/Torr.

§ Absolute uncertainty estimated at ± 10%, relative uncertainty at ± 5%.

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 HNO_3 molecules into the cell was kept low. A flow rate analysis, similar to that done in Ref. 9, was done on HNO_3. No observed effects were seen in the measured linewidth with increased flow rate.

RESULTS AND DISCUSSION

Pressure-broadening measurements were made on the $18_{0,18}$–$17_{0,17}$, $22_{7,15}$–$21_{7,14}$, and $29_{0,29}$–$28_{0,28}$ transitions of HNO_3 at the frequencies 231,627.279 MHz, 369,487.272 MHz, and 369,257.890 MHz respectively. Results for broadening by O_2 and N_2 are shown in Table 1. Figures 2, 3 and 4 show the results from Table 1 plotted on linear axis where open squares represent N_2 broadening coefficients and open circles represent O_2 broadening coefficients.

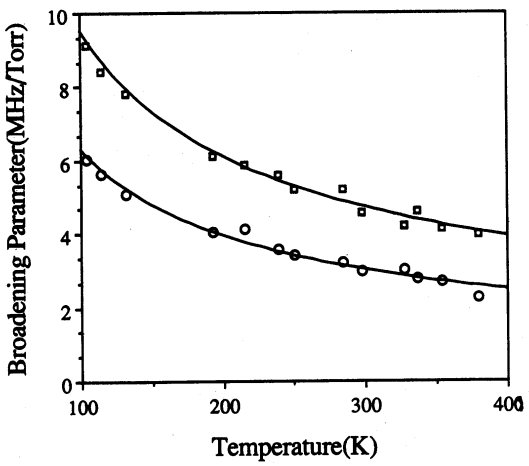

Fig. 2. Measured pressure-broadening parameters of the $18_{0,18}$–$17_{0,17}$ transition of HNO_3 broadened by O_2 (○) and N_2 (□). The solid lines are the result of a least-squares fit to Eq. (2).

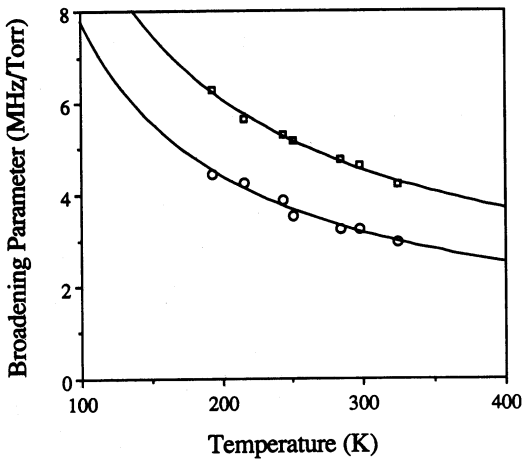

Fig. 3. Measured pressure-broadening parameters of the $22_{7,15}$–$21_{7,14}$ transition of HNO_3 broadened by O_2 (○) and N_2 (□). The solid lines are the result of a least-squares fit to Eq. (2).

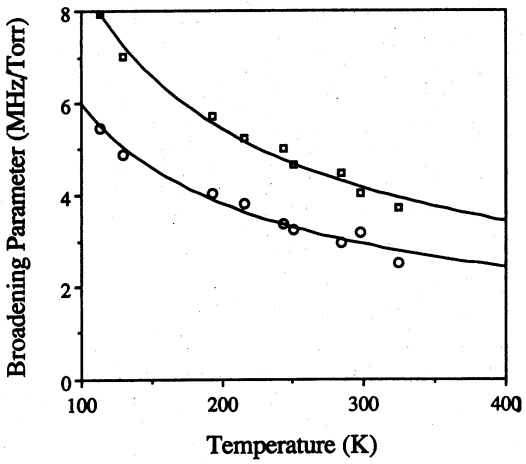

Fig. 4. Measured pressure-broadening parameters of the $29_{0,29}$–$28_{0,28}$ transition of HNO_3 broadened by O_2 (○) and N_2 (□). The solid lines are the result of a least-squares fit to Eq. (2).

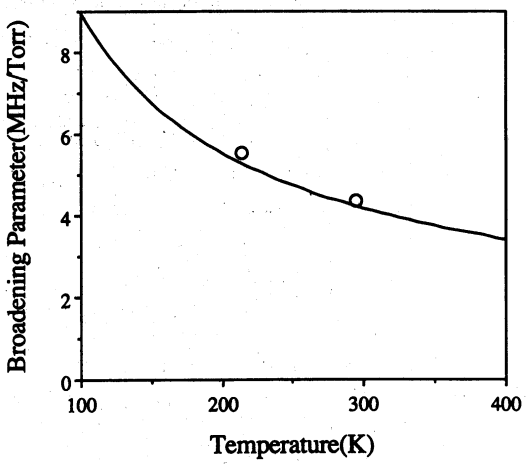

Fig. 5. Average temperature variation of air-broadening parameter. (———) Results of this work; (○) data from Ref. 5.

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

$$\gamma(T) = \gamma(T_0)[T_0/T]^n, \tag{2}$$

where $\gamma(T_0)$ is the pressure-broadening parameter at reference temperature T_0(300 K) and n is a constant exponent of the temperature ratio. This expression is commonly used to characterize the temperature variation of pressure-broadening parameters.[15] The results for the best-fit parameters are given in Table 2 along with their statistical uncertainties. The results are also plotted as the solid lines in Figs. 2, 3 and 4. The results for temperature coefficients give values from $n = 0.84$ to 0.62. As can be seen from the figures, the previous power law equation adequately describes the variation in the experimental results even down to the lower temperatures.

May and Webster[5] have recently studied the ν_3 and ν_4 vibrational bands of HNO_3 in the i.r. They have made air-broadening measurements at temperatures of 295 and 214 K and have determined a single average pressure-broadening parameter for all of the lines in the vibrational band. Combining our O_2 and N_2 data to obtain air-broadening coefficients and averaging over the three transitions that were studied here, we obtain an average-air broadening parameter of $\gamma(T_0) = 4.16$ MHz/torr (where $T_0 = 300$ K) and $n = 0.70$. The resulting curve is shown in Fig. 5, along with the results from Ref. 5.

As can be seen, there is good agreement between the i.r. data and the microwave results, with the i.r. data falling within 5% of our calculated line. Therefore, the results reported here should be directly applicable in the i.r. and should give a reasonable estimate of the air-broadening parameter of HNO_3 at the temperature and pressure ranges encountered in the upper atmosphere.

Tejwani and Yeung have calculated theoretical air-broadening parameters using Anderson theory.[10] The results of these calculations for the transitions studied here are listed in Table 3 along with the results from this work, where the data from Table 2 and Eq. (2) have been used to calculate

Table 2. Best fit 300 K broadening parameters and n values.†, ‡

	$18_{0,18}$ - $17_{0,17}$		$22_{7,15}$ - $21_{7,14}$		$29_{0,29}$ - $28_{0,28}$	
	O_2	N_2	O_2	N_2	O_2	N_2
γ(300K)	3.01(4)	4.71(7)	3.17(8)	4.51(11)	2.91(7)	4.20(9)
n	0.69(3)	0.64(3)	0.84(10)	0.74(9)	0.67(5)	0.67(4)

† Broadening parameters in MHz/Torr.

‡ Uncertainties are one standard deviation taken from the least squares fit.

Table 3. Air-broadening parameters experiment (this work) vs theory (Ref. 10).†

	$18_{0,18} - 17_{0,17}$		$22_{7,15} - 21_{7,14}$		$29_{0,29} - 28_{0,28}$	
	This work	Ref. 10	This work	Ref. 10	This work	Ref. 10
γ(300K)	4.34	4.60	4.22	4.38	3.91	4.30
γ(200K)	5.64	6.37	5.73	5.72	5.14	5.40

† Broadening parameters in MHz/Torr.

the air-broadening data at 200 and 300 K from the experimental data. As can be seen from the data in Table 3, the variation between theory and experiment range from less than 1% to as large as 13%.

SUMMARY

In this study, we have measured the temperature variation of the pressure-broadening of HNO_3 for the $18_{0,18}$–$17_{0,17}$, $22_{7,15}$–$21_{7,14}$, and $29_{0,29}$–$28_{0,28}$ transitions in the ground vibrational state. Measurements were made for both O_2 and N_2 broadening in the 100–380 K temperature range by the use of a heated equilibrium cell for elevated temperatures and the use of a collisionally cooled cell at the lower temperatures where HNO_3 has a small vapor pressure. The observed pressure-broadening data can be fit to the usual empirical power law, giving n values between 0.62(3) and 0.84(10). Good agreement is seen between the data and previous experimental data obtained in the i.r.

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