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# The Pressure Broadening of the $3_{1,3}$–$2_{2,0}$ Transition of Water between 80 and 600 K

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The pressure broadening of the $3_{1,3}$–$2_{2,0}$ transition of water has been measured over the 80 to 600 K temperature region for $O_2$, $N_2$, and He collision partners. Above 250 K the measurements were made in a conventional equilibrium cell. At lower temperatures a newly developed cell which uses collisional cooling to circumvent the temperature limits ordinarily imposed by vapor pressure was used. For helium broadening and for broadening due to $O_2$ and $N_2$ above 140 K, the results could be fit to the usual exponential temperature dependence with $n = 0.49(2)$, 0.85(3), and 0.74(3), respectively. However, below 140 K the $O_2$ and $N_2$ experimental results are smaller than predicted by this simple exponential relation. © 1990 Academic Press, Inc.

## I. INTRODUCTION

The study of water vapor has occupied several generations of microwave and infrared spectroscopists and will undoubtedly occupy several more. This work has been inspired by a diverse set of motivations which range from a basic desire to unravel the spectra of this prototype light asymmetric rotor to a need to understand its role in atmospheric transmission, remote sensing, and heat balance. A remarkable knowledge of the energy level structure of water over a very wide range of states has resulted. However, because of well-known experimental and theoretical difficulties, the characterization of its collisional properties in general and its pressure-broadening parameters in particular is at a much less advanced state.

Nevertheless, because of its central importance a number of pressure-broadening measurements have now been made and compared with a variety of calculations. These have been summarized recently in a particularly interesting paper of Gamache and Rothman (*1*). This paper calculates the temperature variation of pressure-broadening parameters for a number of transitions of water and notes the general absence of experimental data which can serve as a testing ground for theoretical development.

In the past, pressure-broadening studies have ordinarily been limited by the vapor pressure of the species under study. In order to circumvent this limitation, we have been developing over the past several years a simple method, collisional cooling, for use in a variety of spectroscopic applications, including studies of pressure broadening (*2*). Most of our work to date has been at very low temperatures, below 5 K, and has focused on a variety of new phenomena which occur primarily at these very low energies (*3–6*). More recently we reported a liquid nitrogen implementation of this technique (*7*). In this paper we describe a modification of this system appropriate for pressure broadening studies at temperatures above 77 K. It is fortunate that the atmospherically abundant oxygen and nitrogen have significant vapor pressures at 77

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K because the critical requirement of the collisional cooling technique is that the collision partner have at least a few mTorr of vapor pressure at the temperature of the observation.

We have selected the $3_{1,3}$–$2_{2,0}$ transition of water near 183 GHz for initial study because of its importance in the millimeter-wave atmospheric spectrum and because some prior work on it exists which can serve as a bench mark for these new measurements. Bauer *et al.* (*8*) have measured the self- and air-broadening parameters of this line at four temperatures in the 299–251 K region. More recently, Bauer *et al.* (*9*) have reported additional pressure-broadening measurements of this line by $O_2$, $N_2$, and Ar in the 300–390 K range. In this paper we report the measurement of the pressure-broadening parameters of this line for collisions with $O_2$, $N_2$, and He between 80 K and 600 K and compare and contrast the results of these studies with each other as well as with the results of theoretical studies. The most significant results of these observations are that the coefficients which determine the variation of the pressure-broadening parameters with temperature are best determined by measurements over a very wide temperature range and that at low temperature the experimental results show a variation from the simple power law theory.

## II. EXPERIMENTAL DETAILS

Two different cells were used in these studies; the first a quartz equilibrium cell for use at higher temperatures and the second a low-temperature collisional cooling system. Figure 1 shows the equilibrium cell. It consists of a 2-in.-diameter tube of fused quartz 2 ft in length, with fused quartz windows. The quartz cell is enclosed in a 4-ft long copper jacket to which copper cooling coils are attached and around which a resistance heater is wrapped. The cell and jacket are enclosed in a 6-ft-long jacket of fiberglass insulation. The cell temperature can be varied between ~80 and 600 K by resistance heating and liquid nitrogen cooling through the copper coils. For pressure-broadening measurements the usable lower temperature limit is set by the vapor pressure of the spectroscopic gas. Temperature measurements are made by a thermocouple attached to the cell. In operation, approximately 0.02 Torr of $H_2O$ is admitted to the cell and the pressure of the broadening gas is increased incrementally from 0.1 to 1.0 Torr through a computer controlled valve.

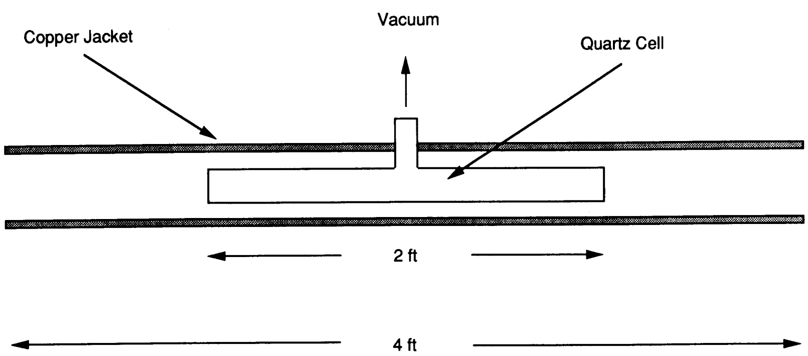


FIG. 1. The equilibrium cell used for measurements at temperatures for which the sample gas has sufficient vapor pressure.

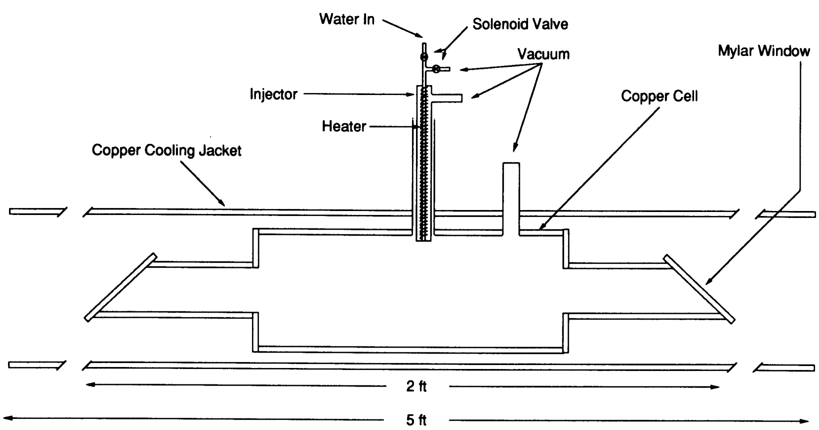


FIG. 2. The collisionally cooled cell used for the low-temperature pressure-broadening experiments.

Figure 2 shows the collisionally cooled cell used for the low-temperature measurements. Its temperature is continuously variable from ~80 to 300 K, with the usable upper limit set by the trapping point of the spectroscopic gas. The cell consists of a 5-in.-diameter copper pipe 1 ft in length with 2-in.-diameter end sections with Brewster's angle flanges. Indium sealed 0.005-in. Mylar windows are attached to the flanges. The cell is surrounded by a copper jacket 5 ft in length with cooling coils attached, and a 7-ft fiberglass jacket.

Spectroscopically active gas, which would have a vanishingly small vapor pressure at low temperature, flows into the system via the injector shown in the middle of the cell. The injector consists of a heated 0.04-in. diameter copper tube in a vacuum region separated from the cell by a 0.005-in. stainless steel diaphragm. The cell is filled with a static pressure of broadening gas against which the injected gas cools. The injected gas cools very rapidly, requiring fewer than 100 collisions to closely approach the temperature of the broadening gas; in contrast to the many thousands of collisions for it to reach the cold walls where it traps. The pressure of the broadening gas was varied from 0.02 to 0.3 Torr by a computer-controlled valve.

For the experiments described, we have used a broadband implementation of the millimeter/submillimeter techniques which we have previously described (*10, 11*). Briefly, a computer-controlled 10–15 GHz YIG oscillator is tripled to drive a 1-W, 26–40 GHz TWT amplifier. The output of this amplifier is multiplied into the millimeter/submillimeter by a crossed waveguide harmonic generator, propagated quasioptically through the cells described above, and detected in a 1.5 K InSb detector. Pressure measurements were made by an MKS capacitance manometer. Thermal transpiration caused by the temperature difference between the cell and gauge was corrected using the method of Takaishi and Sensui (*12*). For the temperatures and pressures used in these experiments the corrections are small, typically less than three percent.

Data were recorded in the "true lineshape" mode in which the microwave frequency was swept rapidly through the absorption line, thereby placing all of its Fourier components within the bandwidth of the detection system. An undesirable side effect of this system is that many of the Fourier components of the baseline undulations (the so called 'reflections') also are preserved and the deconvolution of the spectral lineshape can be difficult. This is especially true for the broader lineshapes characteristic of pressure-broadening measurements.

To circumvent this limitation a reliable baseline subtraction method has been developed for use with the collisionally cooled cell. A modulation ($\leqslant 10$ Hz) of the molecules injected into the cell is produced by a computer controlled valve placed immediately ahead of the injector. Alternate frequency sweeps are taken with the sample molecules in and out of the cell. Sweeps with no molecules in the cell are averaged and subtracted from the sweeps with molecules. The result is a fast, reliable subtraction of baseline which is unaffected by changes in baseline. Figures 3 and 4 show a typical observed spectrum before and after baseline subtraction.

Because the data were taken in the regime in which the contribution of the Doppler broadening to the observed linewidth was small, and because the large number of data would have made fitting a Voigt profile time consuming, the digitized data were fit to a Lorentzian lineshape with provision for both linear and quadratic terms in the baseline. A small correction for the contribution of the Doppler broadening was subtracted via (*13*)

$$\Delta\nu_o^2 = \Delta\nu_p^2 + \Delta\nu_d^2, \qquad (1)$$

where $\Delta\nu_p$ is the pressure-broadened linewidth, $\Delta\nu_o$ is the observed linewidth, and $\Delta\nu_d$ is the Doppler linewidth. For each temperature, data were recorded for about 25 different pressures. The corresponding pressure-broadening coefficient was obtained from a least-squares fit to these data with the points weighted inversely as the square of the pressure. Figures 5 and 6 show examples of the better and poorer of these fits.

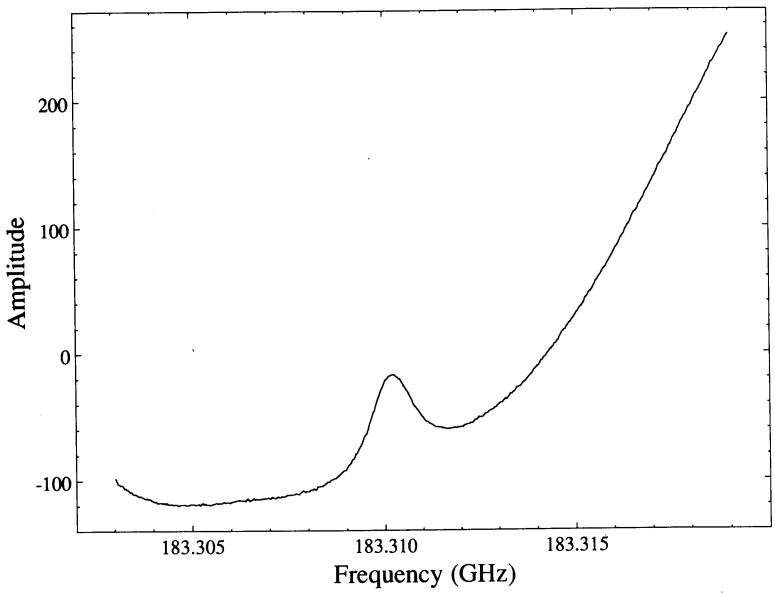


FIG. 3. Typical spectral line with baseline which results from the coherent microwave source.

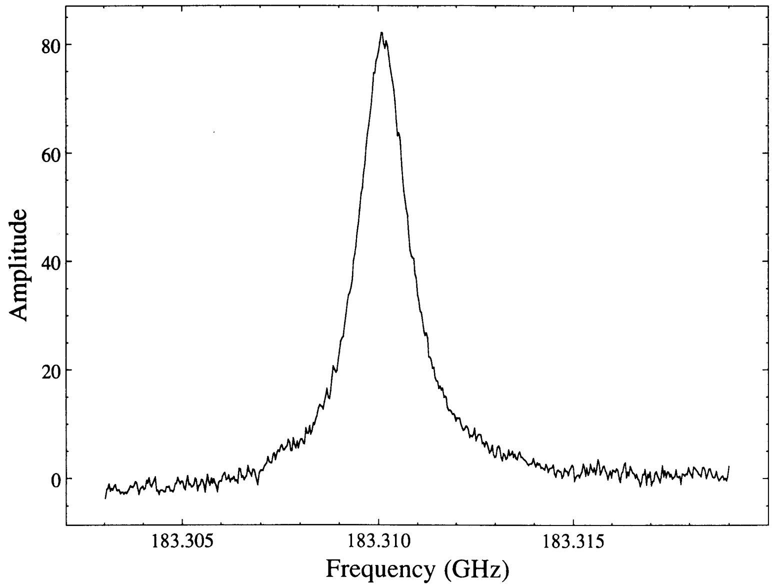


FIG. 4. Typical spectral line with injector modulation at ~10 Hz. The baseline reduction results from a subtraction in software of sweeps with and without molecules flowing into the cell.

To avoid problems which might result from the warming of the background gas and to minimize the effect of $H_2O$ self-broadening, the flow rate of the sample gas into the cell was kept low. Typical flow rates used were approximately $1 \times 10^{18}$ molecules/sec. At a cooling gas pressure of 150 mTorr, the partial pressure of the spectroscopic gas is ~0.2 mTorr, as determined both by absorption coefficient measurements and by the numerical simulation of spectroscopic gas transport through the cell. Although this is still a low pressure, the inherent sensitivity of mm/submm spec-

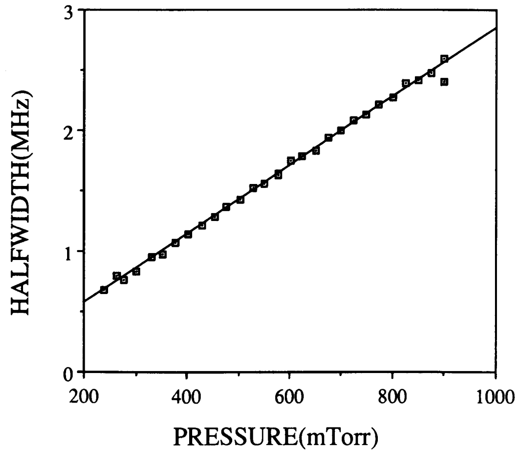


FIG. 5. Measured linewidths as a function of pressure typical of the better data sets.

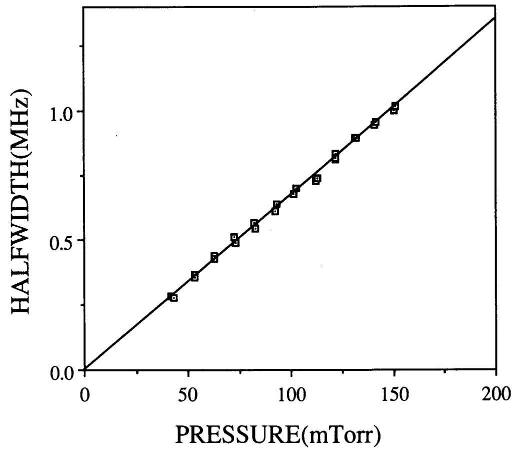


FIG. 6. Measured linewidths as a function of pressure typical of the poorer data sets.

troscopic techniques and the increase in absorption coefficient at low temperature provided good signals for these experiments.

The principal reason that our experimental knowledge of pressure-broadening parameters is orders of magnitude smaller than our knowledge of line frequencies is simply that the measurements are very time consuming. Many measurements must be made at each temperature, and if temperature coefficients are desired, a number of different temperatures must be considered. In addition, a range of collision partners adds yet another dimension to the measurement matrix. Finally, since lineshapes rather than just line centers must be recovered, more stringent requirements are placed on spectral resolution and baselines. As a specific example, the results presented in this paper for a single transition required the measurement and analysis of ~750 lineshapes. Clearly modern data analysis and computational techniques have helped to mitigate these problems. However, in the microwave region where spectral resolution is very high, Doppler broadening low, and pressure-broadening measurements advantageous; the separation of baseline effects from the spectral lineshape is a significant limitation on both the automation of experimental systems and the analysis of data. We have found that the injector modulation technique discussed above has led to at least an order of magnitude increase in the data acquisition efficiency. It thus becomes an important element of studies of this nature.

## III. RESULTS

Pressure-broadening measurements were made on the $3_{1,3}$–$2_{2,0}$ transition of $H_2O$ at 183 310.117 MHz. Results for broadening by $O_2$, $N_2$, and He at a number of temperatures in the range 80–600 K are shown in Table I. Measurements above 264 K were done in the equilibrium cell, while at temperatures below 200 K, measurements were made in the collisionally cooled cell. Figures 7–9 show the results for $O_2$, $N_2$ and He. Open squares represent data collected in the equilibrium cell, while solid squares represent data collected in the collisionally cooled cell.

TABLE I

Measured Pressure Broadening Parameters

| Nitrogen | | Oxygen | | Helium | |
|---|---|---|---|---|---|
| Temperature (K) | $\gamma^a$ (MHz/Torr) | Temperature (K) | $\gamma^a$ (MHz/Torr) | Temperature (K) | $\gamma^a$ (MHz/Torr) |
| 597 | 2.45 | 597 | 1.54 | 597 | 0.71 |
| 444 | 2.99 | 444 | 2.01 | 444 | 0.80 |
| 297 | 4.40 | 297 | 2.70 | 297 | 0.87 |
| 264 | 4.81 | 264 | 2.84 | 264 | 0.95 |
| 192 | 5.76 | 192 | 3.99 | 192 | 1.16 |
| 177 | 6.10 | 177 | 4.40 | 177 | 1.27 |
| 162 | 6.59 | 167 | 4.39 | 162 | 1.35 |
| 144 | 6.84 | 157 | 4.92 | 144 | 1.47 |
| 120 | 7.35 | 135 | 5.37 | 120 | 1.51 |
| 104 | 8.53 | 122 | 5.54 | 104 | 1.60 |
| 103 | 8.23 | 108 | 5.89 | 103 | 1.55 |
| 87 | 9.12 | 95 | 6.69 | 87 | 1.74 |
| 83 | 9.46 | 83 | 7.03 | 83 | 1.85 |
| $\gamma_{N_2}(T_0) = 4.19(15)$ | | $\gamma_{O_2}(T_0) = 2.77(10)$ | | $\gamma_{He}(T_0) = 0.95(3)$ | |
| n = 0.74(3) | | n = 0.85(3) | | n = 0.49(2) | |

[a]Absolute uncertainty estimated at ± 10%, relative uncertainty at ± 5%.

Figures 10–12 show the same data plotted using a logarithmic axis. Except for the lowest-temperature measurements with $O_2$ and $N_2$ as collision partners, the relation

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

where $\gamma(T_0)$ is the pressure-broadening parameter at the reference temperature $T_0$ (300 K) and $n$ is the temperature constant, can be used to provide an appropriate fit to the data. This expression is commonly used to characterize the temperature variation of the pressure-broadening coefficients, although not ordinarily to the lowest temper-

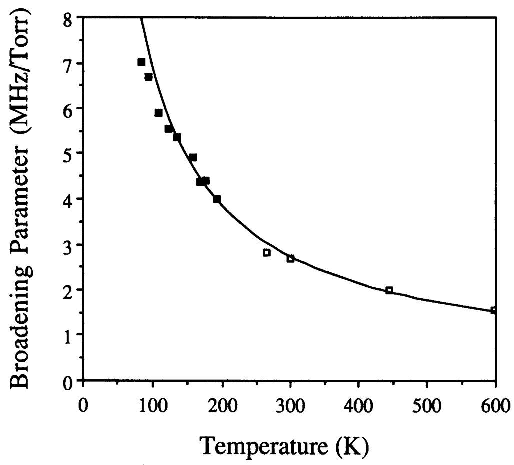


FIG. 7. Measured $O_2$ pressure-broadening parameters for the $3_{1,3}$–$2_{2,0}$ transition of $H_2O$ as a function of temperature. (□) Equilibrium cell; (■) collisionally cooled cell.

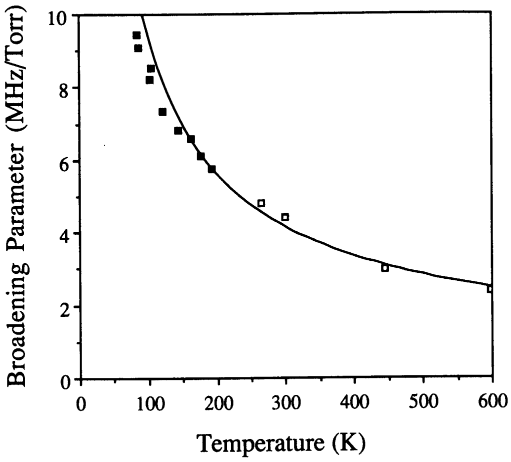


FIG. 8. Measured $N_2$ pressure-broadening parameters for the $3_{1,3}$–$2_{2,0}$ transition of $H_2O$ as a function of temperature. (□) Equilibrium cell; (■) collisionally cooled cell.

atures of the experiments reported here (*14*). The best fits for $O_2$ and $N_2$ were obtained when the eight highest temperature points were used. Since all fits to the He data set were equally good, all points were included. The results of these fits are shown in both the linear and logarithmic plots as the solid line. The He data in Fig. 12 show no significant deviation from a straight line with slope $n = 0.49(2)$. This result is close to the $n = 0.5$ predicted by hard sphere collision theory. The $O_2$ data in Fig. 10 show a small drop from the straight line of slope $n = 0.85(3)$ at the lowest temperatures. Although this difference is not large, we believe it to be real. The $N_2$ data of Fig. 11 show a larger and more significant deviation from the line of slope $n = 0.74(3)$ at the lowest temperatures.

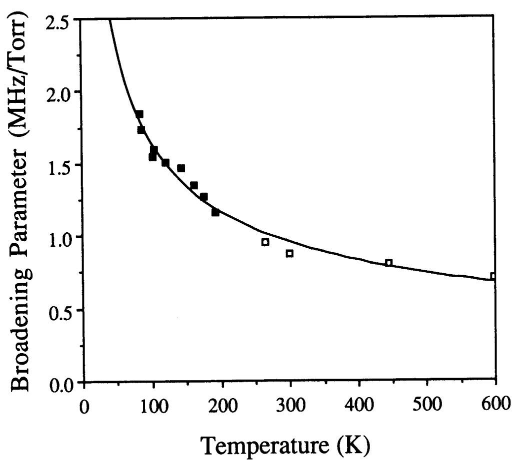


FIG. 9. Measured-He pressure-broadening parameters for the $3_{1,3}$–$2_{2,0}$ transition of $H_2O$ as a function of temperature. (□) Equilibrium cell; (■) collisionally cooled cell.

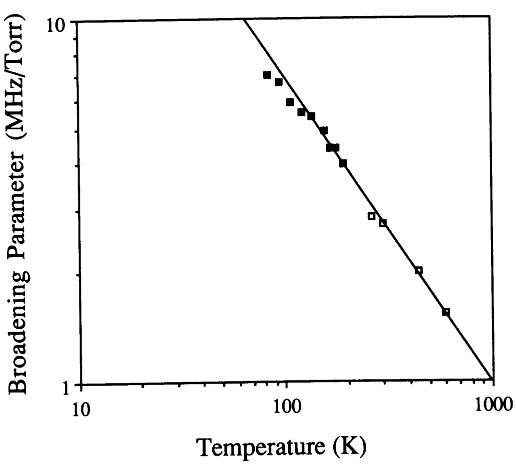


FIG. 10. Measured $O_2$ pressure-broadening parameters for the $3_{1,3}$–$2_{2,0}$ transition of $H_2O$ as a function of temperature. The straight line plotted through the eight highest-temperature data points represents a temperature coefficient of n = 0.85. (□) Equilibrium cell; (■) collisionally cooled cell.

## IV. DISCUSSION

Because these are the first pressure-broadening measurements which we have made with the liquid nitrogen collisional cooling system, we have made a number of observations, calculations, and experimental modifications to ensure that the measured linewidths are representative of collisions between the spectroscopic gas and the cooling gas and that the energies of the collisions are determined by the temperature of the walls of the cell. Experimentally, the earlier system of Ref. (7) was modified so that the volume occupied by the cooled spectroscopic gas was more isolated from the window regions. In addition, the entire cell was enclosed in a long isothermal envi-

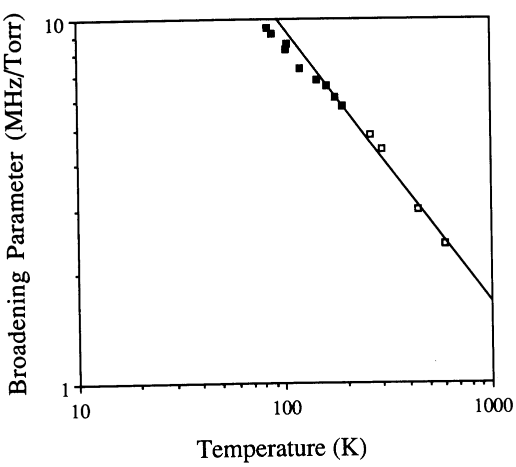


FIG. 11. Measured $N_2$ pressure-broadening parameters for the $3_{1,3}$–$2_{2,0}$ transition of $H_2O$ as a function of temperature. The straight line plotted through the eight-highest temperature data points represents a temperature coefficient of n = 0.74. (□) Equilibrium cell; (■) collisionally cooled cell.

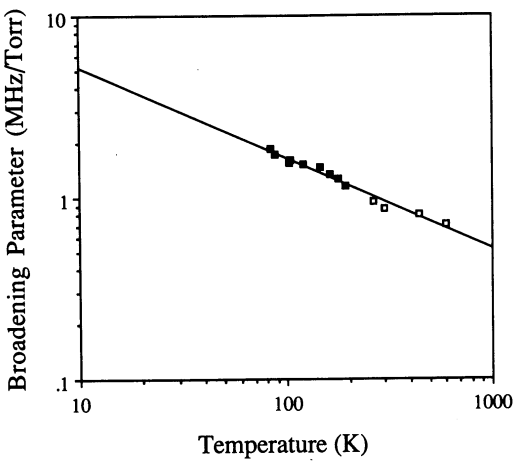


FIG. 12. Measured He pressure-broadening parameters for the $3_{1,3}$–$2_{2,0}$ transition of $H_2O$ as a function of temperature. The straight line represents a temperature coefficient of n = 0.49. (□) Equilibrium cell; (■) collisionally cooled cell.

ronment with insulating Teflon windows which separated the cooled region from the outside. The dilution ratio of the spectroscopic gas in the cooling gas, typically $10^{-3}$, was determined both from calculations based on the observed spectral absorption and by measurements of sample flow rate coupled with numerical simulations of the diffusion of the spectroscopic gas through the cell. This dilution ratio is sufficiently large that self-broadening contributions to the observed linewidths are significantly less than 1%.

As in our earlier experiments at helium temperatures, we have measured the pressure-broadening parameters as a function of the flow rate of the spectroscopic gas. Figure 13 shows the result at a cell temperature of 87 K. This provides an experimental check for self-broadening, for heating of the cooling gas by the warm spectroscopic gas, or

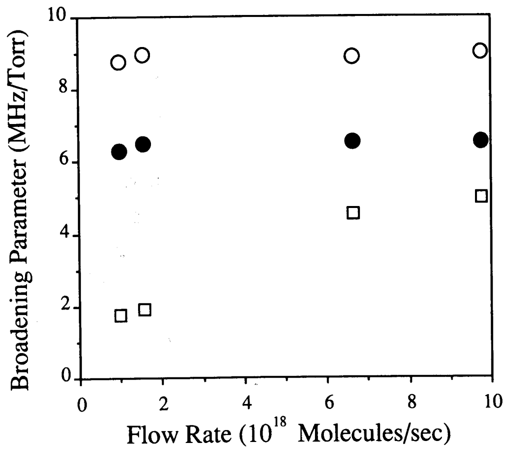


FIG. 13. Measured pressure-broadening parameters at 87 K as a function of flow rate. (□) He; (●) $O_2$; (○) $N_2$.

for some other unanticipated effect. For collisions with $O_2$ and $N_2$ no effects were observed up to the limit on flow rate placed by the vapor pressure of the water and the throughput of our injector. For helium, the higher flow rates caused a noticeable increase in the measured pressure-broadening parameter as well as a marked nonlinearity in the linewidth–pressure graph. The numerical simulation of the dynamics of the cell shows that at constant flow rate the fraction of water in the helium buffer gas is larger than in experiments with oxygen or nitrogen, due partially to the higher pressures the experiment can be run at (because of the smaller pressure-broadening coefficient of helium) and partially to the larger fraction of water that does not trap out in the near vicinity of the injector. The increased linewidth in the helium experiments can be attributed semiquantitatively to the resulting self broadening although we do not rule out the existence of other contributions. For all of the experiments reported here typical flow rates were about an order of magnitude below the maximum rates shown in Fig. 13.

Figure 14 shows a plot of the measured air-broadening parameters of Ref. (*8*) (open boxes) and Ref. (*9*)(open circles). It can be seen that the individual pressure broadening measurements of the earlier work generally fall within 10% of those (solid line) calculated from our data. However, the two experiments taken individually lead to rather different results. The scatter in the lower temperature set was such that no temperature variation was calculated, whereas for the higher temperature data the smoother variation with temperature led to the value of $n = 0.64(10)$, somewhat lower than the 0.76(3) calculated from the $O_2$ and $N_2$ results obtained in the current work.

It is also interesting to compare these results with those obtained from theory. Gamache and Rothman have calculated the temperature variation for a number of transitions of waver vapor, broadened by collisions with nitrogen, and obtained values that ranged from $n = 0.75$ to $n = 0.58$. For the $3_{1,3}$–$2_{2,0}$ transition considered here they obtained $n = 0.73$ as the exponential temperature coefficient. This value is in excellent agreement with the results of this study. In Ref. (*9*) Bauer *et al.* obtained a similar value of $n = 0.70$ for the $3_{1,3}$–$2_{2,0}$ transition. In addition, they obtained values of $n$ which ranged from $n = 0.17$ to $n = 0.71$ for a different set of transitions than those considered by Gamache and Rothman. Clearly it is important to develop a reliable body of experimental data for the temperature coefficient of the pressure-broadening parameter for a variety of molecular species. This will provide the experimental and theoretical cross checks which are necessary for a healthy development of the field.

An interesting feature of these results is the decrease below the empirical power law at the lower temperatures for collisions with $N_2$ and to a lesser extent for collisions with $O_2$. Gamache and Rothman used the $3_{1,3}$–$2_{2,0}$ transition as a test of the consistency of their theory with the exponential power law of Eq. (1) and found excellent agreement over the range 200 to 1000 K. Within this range our experimental data also show good agreement. However, below about 150 K our results start to show observable deviation. This should not be an unexpected result. In this case, both detailed numerical calculations (*15*) and Anderson-theory-like concepts show that as the collision energy is reduced the broadening efficiency of a collision is also reduced, largely due to the unavailability of Fourier components from the collision to induce rotational transitions. In addition, simple considerations show that this reduction will occur first for heavy

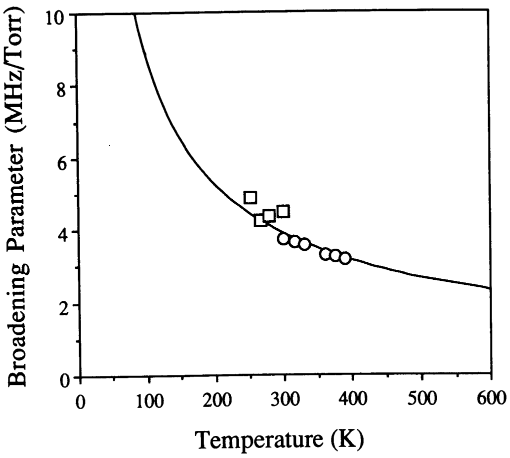


FIG. 14. A comparison of the experimental results of Bauer *et al.*, Refs. (*8*) (□) and (*9*)(○), with the results calculated from this work (solid line).

species with long-range interactions. Thus, the progression of the largest effect for $N_2$ with its relatively large quadrupole moment, a smaller but observable effect for the equally heavy, but small quadrupole moment $O_2$, to no observable effect for the light (and fast) He atom is consistent with this picture.

## V. SUMMARY AND CONCLUSIONS

In this study we have measured the temperature variation of the pressure broadening of the $3_{1,3}$–$2_{2,0}$ transition of water over almost a decade. This was made possible by the use of a heated cell at the elevated temperatures and a new collisionally cooled cell for measurements at temperatures at which water has a vanishingly small vapor pressure. Except for collisions with $N_2$ and $O_2$ below 150 K, the temperature dependence of the observed pressure broadening parameters can be described by the usual empirical power law. The values $n = 0.85(3)$, $n = 0.74(3)$, and $n = 0.49(2)$ were obtained for broadening by $O_2$, $N_2$, and He, respectively. The deviations of the experimental results from the power law theory at low temperature are qualitatively in agreement with simple theoretical ideas.

## VI. ACKNOWLEDGMENTS

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