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# The Hydrogen and Helium Pressure Broadening at Planetary Temperatures of the 183 and 380 GHz Transitions of Water Vapor

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The pressure broadening of the $3_{1,3}$–$2_{2,0}$ and $4_{1,4}$–$3_{2,1}$ transitions of water at 183 and 380 GHz, respectively, has been obtained experimentally in the temperature region between 80 and 600 K using hydrogen ($H_2$) and helium (He) as broadening gases. This extends for the first time the study of condensable gases in general and water in particular into the temperature regime typical of the atmospheres of the outer planets. Above 250 K the measurements were taken in a conventional equilibrium cell. Low temperature measurements were taken in a collisionally cooled cell which can provide a laboratory environment very similar to that of the atmospheres of the outer planets. For the lines broadened by He, data were found to fit to the usual power law for the entire temperature range studied with resultant temperature exponent $n$ values of $0.49 \pm 0.02$ and $0.54 \pm 0.03$, respectively. For the H-broadened lines the data above 150 K were found to fit to the power law with resultant $n$ values of $0.95 \pm 0.07$ and $0.85 \pm 0.05$, respectively. Below 150 K the $H_2$ pressure broadening parameters were measured to have smaller values than predicted by the relation. The results are compared with earlier experimental and theoretical work. © 1993 Academic Press, Inc.

## INTRODUCTION

Remote sensing based on spectroscopic techniques has long provided information for our understanding of the transmission of radiation through planetary atmospheres and the development of theoretical models for atmospheric chemistry. The proper understanding and accurate interpretation of remote-sensing data requires laboratory measurements of basic molecular properties under controlled environmental conditions. There are two basic approaches. In the first the radiative properties of a chamber, containing the planetary mixture of atmospheric gases at appropriate temperature and pressure, are investigated in the laboratory. Interesting recent examples of such work are those of Joiner *et al.* (1989) and Steffes and Jenkins (1987), who have studied the lineshape of ammonia under conditions similar to those of regions of the Jovian atmosphere. In the second, measurements of spectroscopic parameters such as line frequencies, pressure broadening and shift parameters, and the temperature dependence of these parameters are made and used as the foundation for the development of theoretical methods. The resulting models make possible the calculation of the radiative properties of arbitrary combinations of gases over a wide range of environmental conditions. If only a few of the possible combinations of gas mixture, temperature, and pressure are important in the field data, the work involved in accumulating the spectroscopic data base and the theoretical methods for its interpretation is far greater than the work involved with the first method. However, in many circumstances the number of possible combinations is very large and the second method becomes of significant advantage.

Clearly, the optimal approach depends upon the physical and chemical complexity of the environments being studied and *the resolution, signal to noise, and spectral extent of the field data*. Over the years extensive attention has been paid to atmospheric transmission and remote sensing in the Earth's atmosphere and the study of the interstellar medium. As a result the resolution, signal to noise, and spectral extent of these field data are often very high. As a consequence, theoretical modeling has become the norm and several extensive data bases have been developed to serve these communities. These include catalogs developed by the Air Force Geophysics Laboratory (Rothman *et al.* 1987) and the Jet Propulsion Laboratory (Poynter and Pickett, 1985). Interestingly,

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these were initially developed to serve very different communities: those concerned with atmospheric transmission in the infrared and with microwave remote sensing of the interstellar medium. However, this modeling approach has allowed these efforts to complement each other and the two efforts have scientifically merged. For example, it is routine for the of parameters derived from microwave experiments to be used as inputs for simulations of infrared field measurements.

Helium and hydrogen are numerically the dominant species in the atmospheres of the outer planets and as such are the principal collision partners for spectroscopically active gases. However, the low vapor pressures of many of the important planetary species at the temperatures characteristic of the atmospheres of the outer planets preclude or make difficult the laboratory observation and measurement of the required parameters. Additionally, the existing data bases, which have largely been driven by fields other than planetary studies, concentrate largely on collisions with $N_2$ and $O_2$ near 300 K.

This paper describes the experimental methodology which has been developed and used in this laboratory to circumvent this low temperature difficulty. Specifically, we report the hydrogen ($H_2$) and helium (He) pressure-broadening coefficients of the $3_{1,3}$–$2_{2,0}$ and $4_{1,4}$–$3_{2,1}$ rotational lines of water at 183,310 and 380,197 MHz, respectively. Their temperature dependencies are reported over the range from 80 to 600 K. A simple power law is found to be sufficient in describing the temperature variation of the broadening coefficient for the $H_2O$–He system. However, there is a significant deviation from the standard power law at low temperatures for the $H_2O$–$H_2$ system.

## BASIC THEORY

We have recently discussed a number of the theoretical issues of importance to the characterization of pressure broadening in the regimes of interest to planetary science (De Lucia and Green 1988, Goyette *et al.* 1991), so we will be brief here. From the perspective of planetary science, the single most important fact is that there is not a well-founded theory which has been shown to make possible the calculation to reasonable accuracy of the pressure-broadened linewidths for the collision partners of interest (primarily $H_2$ and He). Furthermore, there is little experimental data suitable for the testing of such theories.

Much of the study of pressure broadening has been motivated either by considerations of the Earth's atmosphere or by studies of the interstellar medium. The former has led to studies of nitrogen ($N_2$) and oxygen ($O_2$) broadening at temperatures characteristic of the Earth's atmosphere and the latter to the study of collisions at very low temperatures.

For the temperatures of interest in this work, semiclassical Anderson, Tsao, and Curnutte (ATC)-like theories have ordinarily been used (Anderson 1949, Tsao and Curnutte 1961). In these, the interactions are described in terms of multipole expansions of the intermolecular potentials. As might be expected, those interactions describable by a single, long-range interaction have produced the best results. For example, in an earlier work Nerf (1975) showed that in the case of self-broadening of formaldehyde at room temperature these theories accurately accounted for the observed state-to-state variation, but that different choices among strategies for choosing a cut off yielded 30% variations in the calculated absolute cross sections.

Theoretical attempts to determine the temperature dependence of collision-broadened halfwidths are very limited. For a few $H_2O$ lines broadened by $N_2$ there are some theoretical results (Benedict and Kaplan 1959) based on standard ATC theory with classical trajectories and only dipole–quadrupole interactions considered. A recent theoretical work (Gamache and Rothman 1988) on temperature dependence of $N_2$broadened $H_2O$ lines predicted very accurately the temperature dependence of the $3_{1,3}$–$2_{2,0}$ line in the region above 200 K. However, none of these studies addresses $H_2$ and He broadening or the issue of low temperature.

## EXPERIMENTAL APPROACH

The block diagram illustrating the broadband millimeter and submillimeter (mm/submm) spectrometer used for this investigation is shown in Fig. 1. Briefly, the primary source of the radiation is a 10–15-GHz YIG oscillator. Its output is tripled and drives a 1-W 26–40-GHz traveling wave tube (TWT) amplifier, whose output is matched onto a harmonic multiplier (King and Gordy 1953, Helminger *et al.* 1983) for the generation of the required mm/submm power. The output of the harmonic multiplier is collimated by an electroformed copper horn and propagates quasi-optically via a series of Teflon lenses through the sample cell. Upon exiting the sample cell, the mm/submm waves are propagated into an InSb detector operating at 1.7 K (Helminger *et al.* 1970). Data are recorded in the "true lineshape" mode in which the frequency of the system is swept by the microprocessor-controlled synthesizer at a rate, relative to the bandwidth of the system, so that the lineshape is preserved.

For sample temperatures above 300 K, the measurements are performed in a quartz cell, 10 cm in diameter and 1 m long (Goyette and De Lucia 1990). In addition, we have developed several systems for pressure broadening measurements at temperatures far below those imposed by the usual vapor pressure limitations. In the first systems, macroscopic samples of spectroscopically active

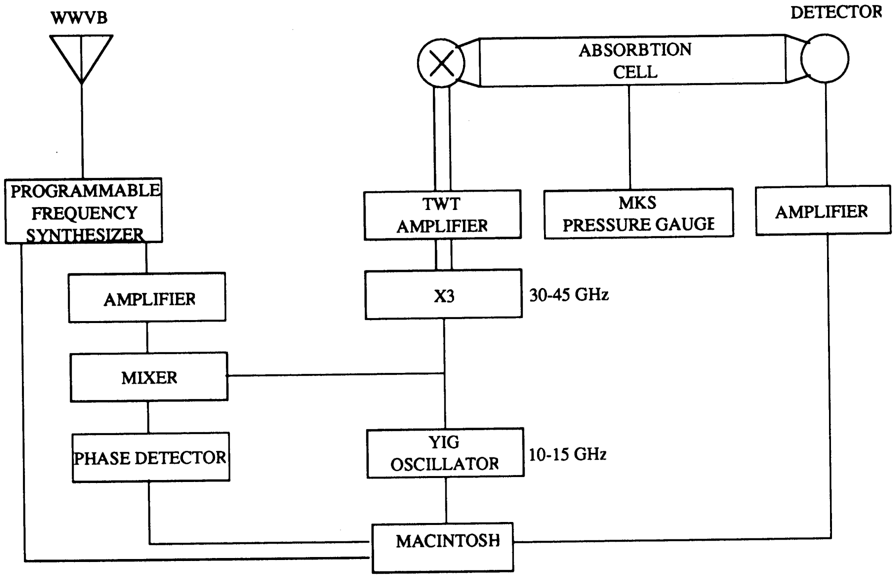

**FIG. 1.** Schematic diagram of the broadband spectrometer.

gas were cooled to a very low temperature (<4 K) using a newly developed collisional cooling technique and studied under essentially equilibrium conditions (Messer and De Lucia 1984, Willey *et al.* 1988). Compared to the well-developed method of free expansion jets, the collisional cooling technique is simpler to execute, and its geometry and molecular densities are more suitable for pressure-broadening experiments. With this method the collisions take place essentially in thermal equilibrium and the temperature of the system can be easily varied and measured.

The collisionally cooled cell used in this work is shown in Fig. 2. Its temperature is continuously variable from 80 to 300 K. The cell consists of a 4-inch-diameter copper pipe 1 foot in length with 2-inch-diameter end sections fitted with Mylar Brewster's windows. The cell is surrounded by a copper jacket which is 5 feet in length and cooled by flowing liquid nitrogen. Warm, spectroscopically active gas is introduced into the cell through a vacuum-insulated injector. The cell is filled with the static pressure of the broadening gas against which the sample gas cools, requiring fewer than 100 collisions to reach essentially thermal equilibrium. Because at 10 mtorr it takes about 20,000 collisions for a typical molecule to reach the wall where it condenses, the molecules observed are essentially in equilibrium at a known temperature with the broadening gas. Because molecular adsorptions are

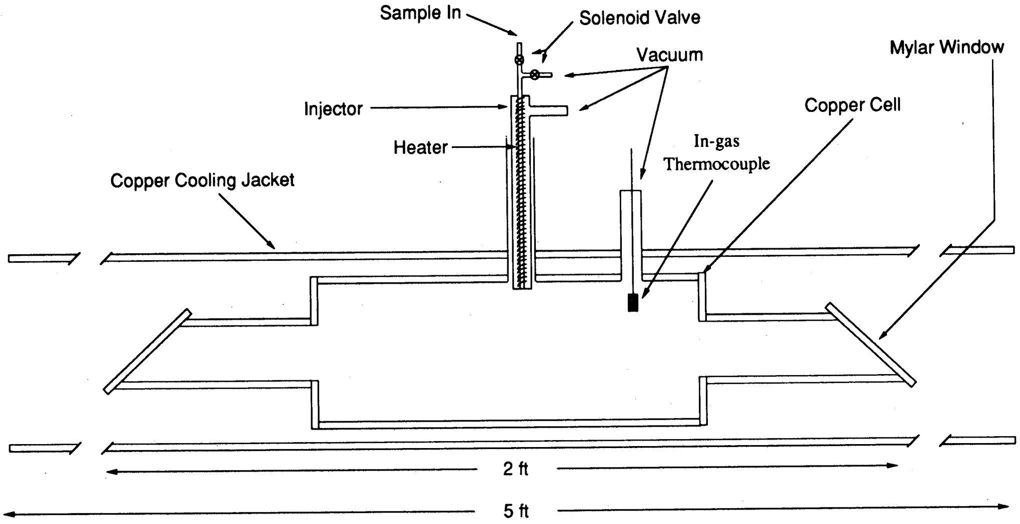

**FIG. 2.** The collisionally cooled cell used for the pressure broadening experiment.

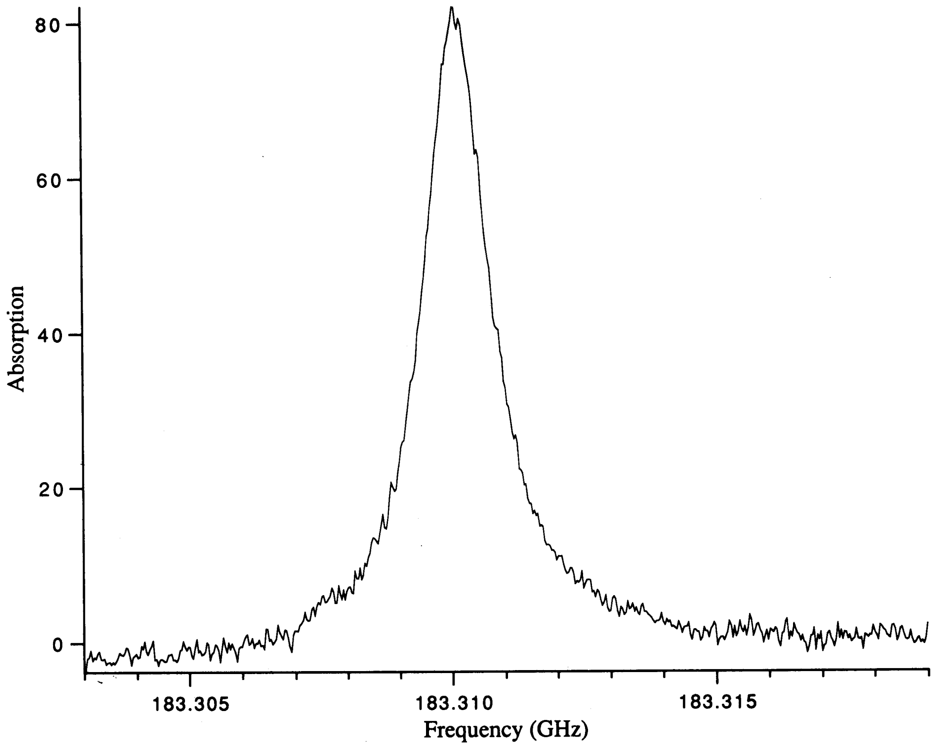

FIG. 4. Typical spectral line with injector modulation at ~10 Hz. The baseline reduction results from a subtraction in software of sweeps with and without molecules flowing into the cell.

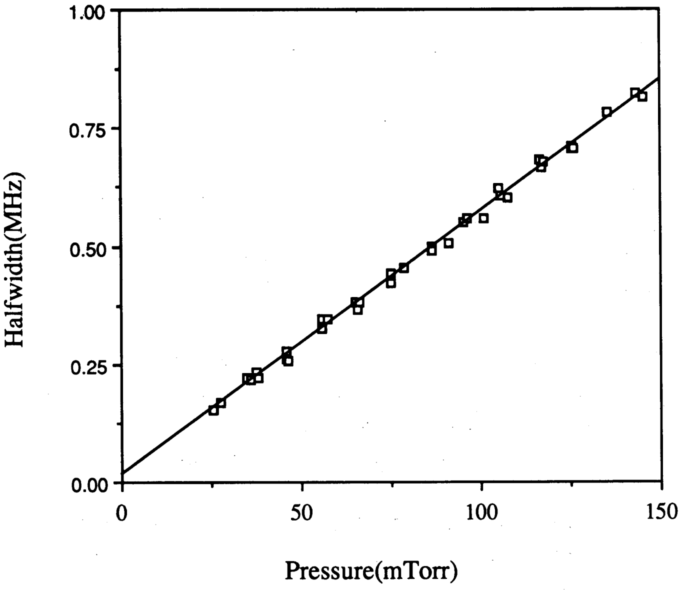

FIG. 5. A typical data set showing measured linewidths as a function of pressure. This particular example is for $H_2$ broadening of the 183-GHz line at 166 K.

**TABLE I**

**Measured Pressure Broadening Parameters for the $3_{1,3}$–$2_{2,0}$ Transition of Water[a]**

| Temperature (He) | $\gamma$ (He) | Temperature ($H_2$) | $\gamma$ ($H_2$) |
|---|---|---|---|
| 597 | 0.71 | 400 | 2.52 |
| 444 | 0.80 | 296 | 3.15 |
| 297 | 0.87 | 261 | 3.45 |
| 264 | 0.95 | 245 | 3.85 |
| 192 | 1.16 | 183 | 5.12 |
| 177 | 1.27 | 166 | 5.58 |
| 162 | 1.35 | 148 | 5.89 |
| 144 | 1.47 | 125 | 6.40 |
| 120 | 1.51 | 106 | 6.72 |
| 104 | 1.60 | 103 | 6.86 |
| 103 | 1.55 | | |
| 87 | 1.74 | | |
| 83 | 1.85 | | |

$\gamma_{He}(300\text{ K}) = 0.95 \pm .03$
$n = 0.49 \pm .02$

$\gamma_{H_2}(300\text{ K}) = 3.20 \pm .08$
$n = 0.95 \pm .07$

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[a] Temperature in degrees K; broadening parameters in MHz/Torr; absolute uncertainty estimated at ±5%.

TABLE II
Measured Pressure Broadening Parameters for the $4_{1,4}$–$3_{2,1}$ Transition of Water[a]

| Temperature (He) | $\gamma$ (He) | Temperature ($H_2$) | $\gamma$ ($H_2$) |
|---|---|---|---|
| 520 | 0.62 | 520 | 2.06 |
| 433 | 0.70 | 433 | 2.30 |
| 375 | 0.72 | 298 | 2.99 |
| 298 | 0.81 | 272 | 3.45 |
| 272 | 0.91 | 173 | 5.22 |
| 173 | 1.19 | 152 | 5.63 |
| 152 | 1.15 | 133 | 5.73 |
| 133 | 1.25 | 108 | 6.20 |
| 108 | 1.55 | | |
| $\gamma_{He}$(300 K) = 0.84 ± .01<br>$n$ = 0.54 ± .03 | | $\gamma_{H_2}$(300 K) = 3.19 ± .07<br>$n$ = 0.85 ± .05 | |

[a] Temperature in degrees K; broadening parameters in MHz/Torr; absolute uncertainty estimated at ±5%.

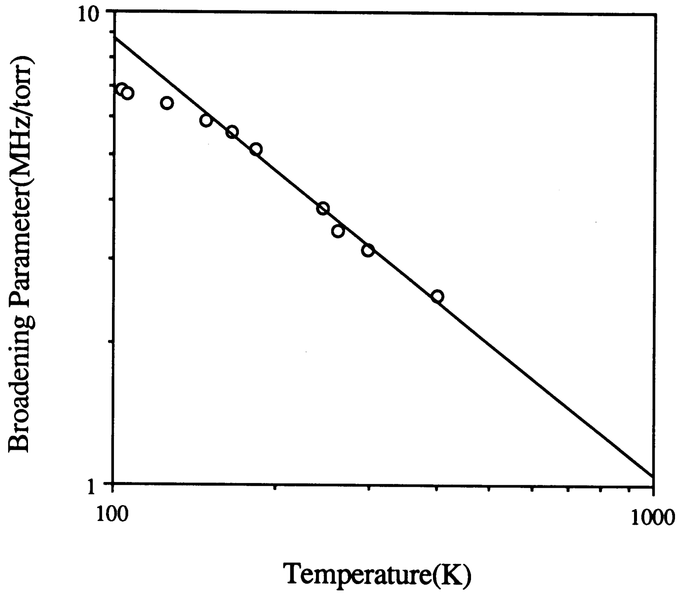

FIG. 7. Measured $H_2$ pressure broadening parameters for the $3_{1,3}$–$2_{2,0}$ rotational transition of $H_2O$ as a function of temperature. The straight line (on a log–log plot) drawn through the data points above 150 K represents a temperature coefficient of $n$ = 0.95 ± 0.07.

where $\sigma_0$ and $\gamma_0$ are the collisional cross-section and broadening parameter at the reference temperature $T_0$, respectively, and $n$ and $m$ are constants.

The temperature dependencies of the He and $H_2$ pressure-broadening parameters for the $3_{1,3}$–$2_{2,0}$ rotational transition in the ground vibrational state are shown in Figs. 6 and 7, respectively. Except for the lowest temperature measurements with $H_2$ as a collision partner, Eqs. (2) and (3) can be used to provide a good representation of the calculated cross sections and pressure broadening parameters. The constants which result from the fitting of the pressure broadening parameters shown in Table I to Eq. 2 are also shown in Table 1. The He data in Fig. 6 for the 183-GHz line show no significant deviation from a straight line with slope $n$ = 0.49 ± 0.02. This is consistent with other recent work of ours (Goyette *et al.* 1991) and is close to the $n$ = 0.5 predicted by hard sphere collision theory which sets $m$ = 0 in Eq. (3). Godon and Bauer (1988) studied $H_2O$–He line broadening between 300 and 390 K for the water vapor rotational line at 183 GHz. Although their measured values of $\gamma(300)$ = 0.862 MHz/Torr and $n$ = 0.39 ± 0.10 are generally consistent with the values reported in this work, the smaller temperature range made the calculation of the temperature dependence much more difficult. Significantly, the hydrogen data of Fig. 7 show a large deviation (which approaches 25% at low temperature) from the simple power law. However, above 150 K the relationship of Eq. (2) is valid with $n$ = 0.95 ± 0.07.

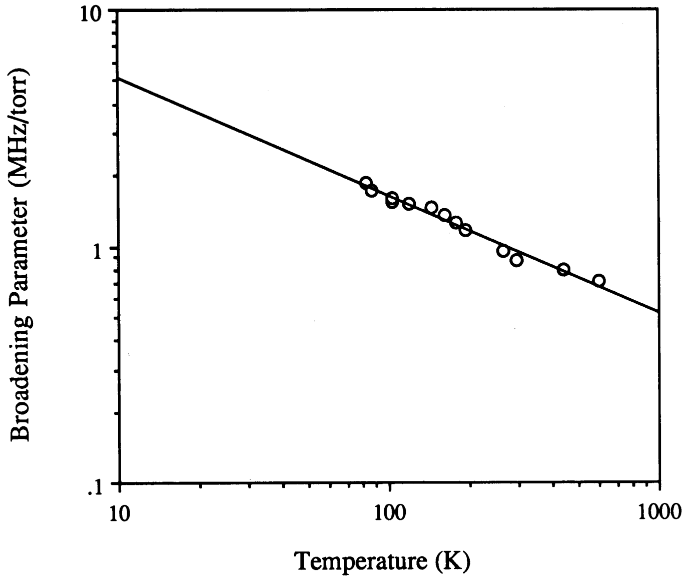

FIG. 6. Measured He pressure broadening parameters for the $3_{1,3}$–$2_{20}$ rotational transition of $H_2O$ as a function of temperature. The straight line (on a log–log plot) represents a temperature coefficient of $n$ = 0.49 ± 0.02.

The temperature dependencies of the He and $H_2$ pressure broadening parameters for the $4_{1,4}$–$3_{2,1}$ line are shown in Figs. 8 and 9, respectively. The experimentally determined broadening coefficients at the reference temperature $T_0$ = 300 K and temperature exponents $n$ are given in Table II. Again, except for the lowest temperature measurements (below 150 K) with $H_2$ as collision partner, Eqs. (2) and (3) provide an appropriate representation of the results. The He data in Fig. 8 show no significant deviation from the straight line with slope $n$ = 0.54 ± 0.03; which is again close to the $n$ = 0.5 predicted by the

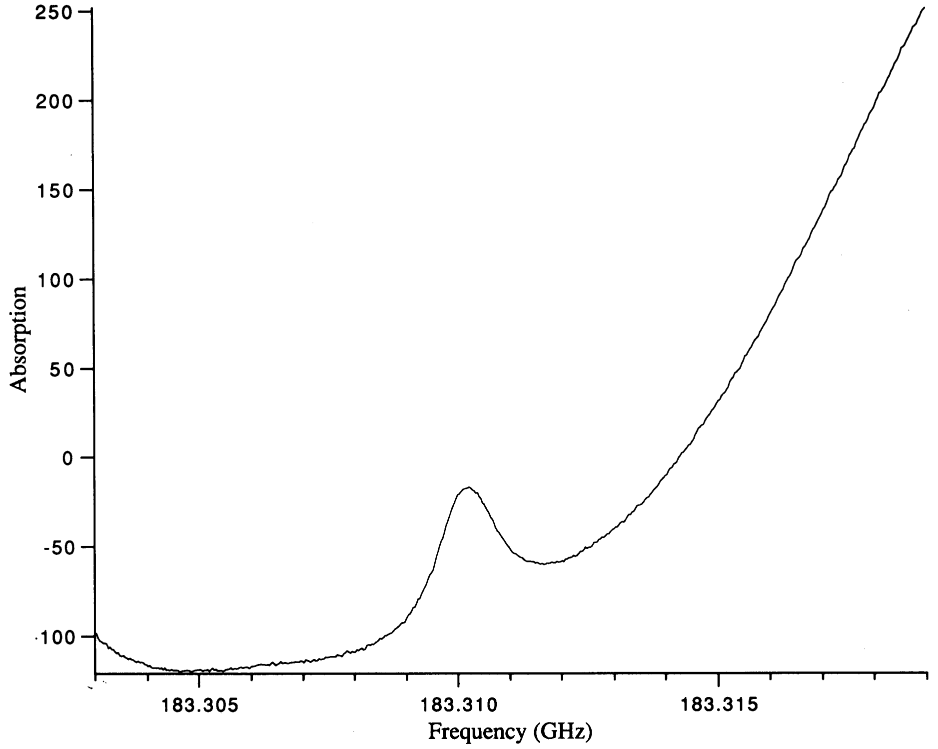

FIG. 3. Typical spectral line with baseline which results from the coherent microwave source.

very strong in the mm/submm region and because they become even stronger at low temperature (increasing as $\sim T^{-5/2}$), the amount of sample present as gas in the cell at anytime is so small that it has negligible influence on the temperature of the broadening gas. Pressure of the broadening gas is typically varied from 0.02 to 1.0 torr by a computer-controlled valve. Pressure measurements are made by an MKS capacitance manometer.

Multiple reflections within the cell due to the coherent nature of the mm/submm source radiation result in the undesirable side effect of baseline undulations. To circumvent this baseline problem, 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. Figures 3 and 4 show typical spectral lines before and after baseline subtraction.

## RESULTS

Helium and hydrogen pressure-broadening measurements were made on the $3_{1,3}$–$2_{2,0}$ and $4_{1,4}$–$3_{2,1}$ transitions of $H_2O$ between 80 and 600 K. At each temperature, linewidth measurements were made at about 25 different pressures between 0.05 and 1.0 Torr. Because at the lower pressures the Doppler width is not negligible compared with the collisional linewidth, a fit to a Voigt profile was used to extract the linewidth $\Delta\nu$. The pressure-broadening coefficient $\gamma$ for each temperature was obtained from a least-squares fit of the data to the relation

$$\Delta\nu = \gamma P + \Delta\nu_0, \tag{1}$$

where $P$ is the pressure and $\Delta\nu_0$ is a free parameter. The data points were weighted inversely with the pressure to allow for the more accurate measurements of the narrower lines. As expected, $\Delta\nu_0$ is ordinarily very small, indicating the effectiveness of the Voigt fitting procedure in eliminating contributions from Doppler broadening and the absence of unanticipated broadening mechanisms. A typical fit of the data to Eq. (1) is shown in Fig. 5 and the resultant pressure broadening coefficients are shown in Tables I and II.

The temperature dependence of pressure-broadening coefficients and pressure-broadening cross-sections are often described by

$$\gamma(T) = \gamma_0(T_0/T)^n \tag{2}$$

and

$$\sigma(T) = \sigma_0(T_0/T)^m, \tag{3}$$

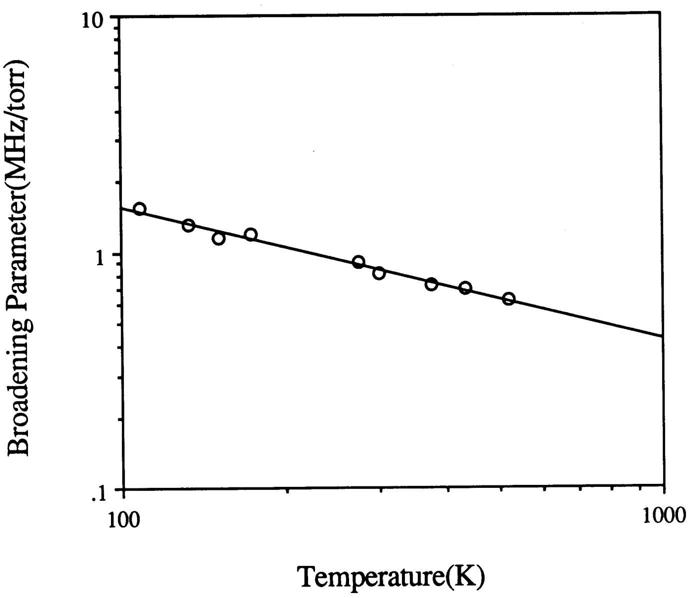

FIG. 8. Measured He pressure broadening parameters for the $4_{1,4}$–$3_{2,1}$ rotational transition of $H_2O$ as a function of temperature. The straight line (on a log–log plot) represents a temperature coefficient of $n = 0.54 \pm 0.03$.

hard sphere collision theory. Godon and Bauer (1988) have also studied the He broadening of this transition over the temperature range 300–373 K. Again, their observed pressure broadening parameters in this region are generally in agreement with ours, but their derived value of $n = 0.34 \pm 0.09$ is significantly different because of the relatively small temperature range observed.

## SUMMARY AND CONCLUSIONS

An experimental method, collisional cooling, has been developed which provides a new means for both measuring fundamental spectral properties of importance in planetary science as well as providing in a laboratory environment conditions similar to those of the planets themselves. It has made possible measurements of the $H_2$- and He-broadening parameters of the 183- and 380-GHz water vapor lines over a much wider range of temperatures than is possible via conventional techniques and demonstrated an approach that should be important for the development of spectral data base not only for microwave but also infrared planetary observations.

This work, as well as a number of other recent measurements on several transitions of HDO (Goyette *et al.* 1993), shows that above ~80 K helium as a collision partner behaves much as a classical hard sphere. This is shown both by the experimentally derived value of the temperature exponent $n$ ~0.50 and by the small state to state variation in the cross-sections. Although it would be premature to conclude for all collisions with He that $n = 0.5$, it would be surprising if it were not true to the accuracy required for most remote sensing applications in planetary science. Presumably, this is because helium has no internal degrees of freedom which can be excited in collisions and because it has a relatively large velocity which produces Fourier components in its collision spectra which extend to frequencies high enough to excite efficiently those collision-induced transitions which lead to broadening in ATC-like theories. Additionally, the collision energies are high enough so that quasi-bound states, which are dependent on the shallow attractive well between He and its collision partners, are not yet important (Green 1985, Willey *et al.* 1988).

In contrast, the behavior of hydrogen is significantly more complex. As illustrated in Figs. 7 and 9, the temperature dependence expected from Eq. 2 does not exist at the lower temperatures, and even at the higher temperatures where the variation broadly follows Eq. (2), $n$ is far from its hard sphere value of 0.50. The large deviation of low-temperature data from the straight line obtained from data above 150 K for hydrogen as shown in Figs. 7 and 9 cannot be attributed to the attractive well in the intermolecular potential which causes the quasi-bound state structure observed at very low temperature (Willey *et al.* 1989) both because the energies are still too high and because these phenomena lead to increased, rather than decreased, cross sections.

Because of the large concentrations of $H_2$ in the atmospheres of the outer planets and the low temperatures of those environments, it will be important to more carefully

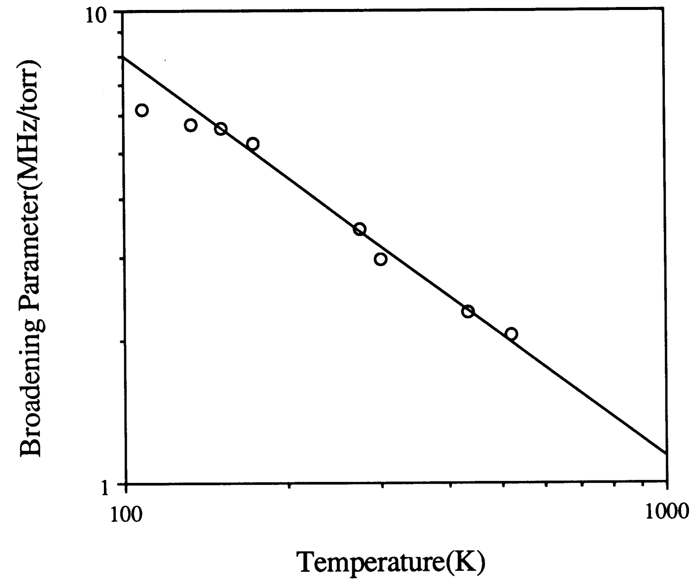

FIG. 9. Measured $H_2$ pressure broadening parameters for the $4_{1,4}$–$3_{2,1}$ rotational transition of $H_2O$ as a function of temperature. The straight line (on a log–log plot) drawn through the data points above 150 K represents a temperature coefficient of $n = 0.85 \pm 0.05$.

investigate the deviations from the usual power law that has ordinarily been used to describe the variation in collisional cross section with temperature. Specifically, it will be important to establish for other transitions and molecular species the critical temperature below which deviations from the power law occur. This will be a key step toward the goal of being able to build models of atmospheric processes which are based on the fundamental properties of the atomic and molecular species of the planetary atmospheres. The significant advantage of approaches based on fundamental molecular properties is their capability of describing atmospheric phenomena over the very large number of combinations of temperature, pressure, and gas mixture that can be encountered in modeling the contributions to the radiative transfer process from the layers of planetary atmospheres.

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