JOURNAL OF MOLECULAR SPECTROSCOPY **164**, 233–238 (1994)

Temperature Dependence of Self-Induced Pressure Broadening and Shift of the 6_{43}–5_{50} Line of the Water Molecule

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Experimental results on the collisional self-shift and self-broadening of the 6_{43}–5_{50} rotational water line at 439 GHz are presented in the temperature range 250–390 K. The (T_0/T) exponent for the shift and broadening are $\alpha = 2.59(20)$ and $\beta = 0.62(9)$, respectively. A method for the remote measurement of gas temperature, based on spectral collisional shift and broadening, is proposed.

INTRODUCTION

Although water vapor is a minor part of the terrestrial atmosphere, it influences the transmission of electromagnetic radiation and the heat balance of the lower atmosphere (*1*). Precise knowledge of broadenings and shifts of H_2O spectral lines and their variation with temperature are required for the calculation of the windows of water vapor absorption and for determination of water concentration in the earth's atmosphere (*2–5*).

The present paper is the continuation of investigations of pressure lineshift and line broadening performed earlier at the Institute of Applied Physics, Academy of Sciences of the USSR, Nizhny Novgorod (formerly Gorky) (*6–8*).

EXPERIMENTAL DETAILS

The present investigation of the temperature dependence of self-shift and self-broadening of water vapor for the 6_{43}–5_{50} line in the ground state was carried out using a radioacoustic submillimeter spectrometer RAD (*9*). The method of investigating lineshift and line broadening by the RAD has been described, for instance, in Ref. (*10*). A copper radioacoustic cell was cooled in a thermostat by means of liquid nitrogen vapor. Pressure in the cell was controlled during the investigation with a sensitive membrane-type manometer with an accuracy better than 5%. The temperature of the cell wall was measured using two platinum thermometers with an accuracy 0.01 K. The gradient and variation in the cell wall temperature during the frequency measurements were less than 0.3 K.

EXPERIMENTAL RESULTS

The self-shift and self-broadening of the 6_{43}–5_{50} H_2O line were measured in the pressure and temperature range 0.1–0.9 Torr and 250–390 K, respectively. The pressure dependence of the center frequency and half-width of this line are displayed in Figs. 1 and 2, and the values of shift and broadening parameters are presented in Tables I and II. The center frequency is equal to $\nu_0 = 439150.791(10)$ MHz, without pressure shift. This value agrees well with the measurement in Ref. (*11*) of $\nu = 439150.812(50)$ MHz, within experimental error. The small numerical difference between our datum

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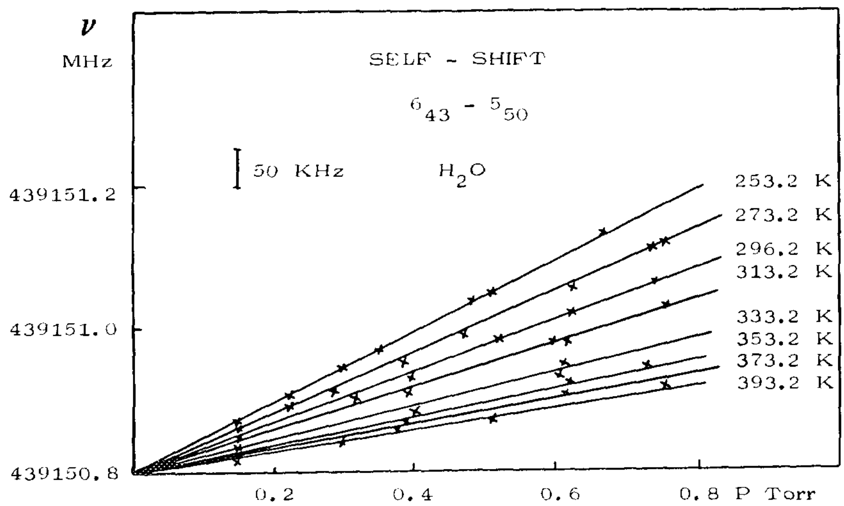

FIG. 1. The linecenter frequency variation of the 6_{43}–5_{50} H_2O line on pressure for different temperatures.

and the datum from Ref. (*11*), about 20 KHz, is probably a consequence of the pressure shift, which was not taken into consideration in Ref. (*11*).

The temperature dependence of shift and broadening parameters was approximated by using the power law (*12, 13*) for the shift

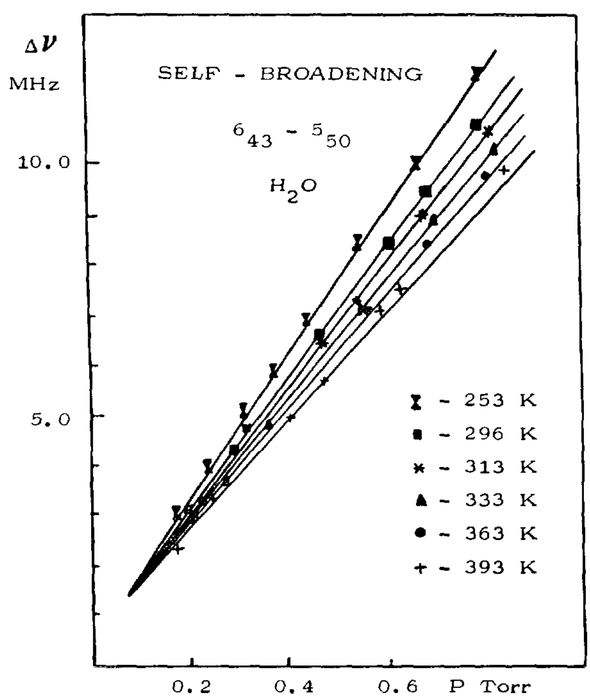

FIG. 2. The half-width variation of the 6_{43}–5_{50} spectral H_2O line on pressure for different temperatures.

TABLE I

Pressure Self-Shift Parameter of the 6_{43}–5_{50} H_2O Line for Different Temperatures

T K	253.2(2)	273.2(2)	293.2(2)	296.2(2)	313.2(2)
$\Delta\nu_{sh}$ KHz/Torr	500(25)	431(20)	360(20)	366(20)	317(25)
T K	333.2(2)	353.3(2)	373.2(2)	386.2(3)	393.2(3)
$\Delta\nu_{sh}$ kHz/Torr	236(25)	199(30)	183(25)	176(30)	148(40)

$$\Delta\nu_{sh}(T) = \Delta\nu_{sh}(T_0)[T_0/T]^{\alpha} \tag{1}$$

and for the broadening

$$\Delta\nu_{br}(T) = \Delta\nu_{br}(T_0)[T_0/T]^{\beta}. \tag{2}$$

T_0 was chosen to be 296 K in accordance with the value used in the GEISA (*14*) and HITRAN data banks (*15*). The fit of experimental values is presented in Figs. 3 and 4. Within experimental error, for the shift parameter

$$\Delta\nu_{sh}(T) = 346(10)[296/T]^{2.59(20)}\ \text{kHz/Torr},$$

and for the broadening parameter

$$\Delta\nu_{br}(T) = 13.06(25)[296/T]^{0.62(9)}\ \text{MHz/Torr}.$$

CONCLUSION

It is interesting that the value of the (T_0/T) exponent of the shift and the broadening differ considerably among spectral lines (*12, 13*). In Ref. (*16*), the exponent, β, for self-broadening of the water vapor line between 13 550 and 13 950 cm^{-1} was found to be J-dependent with an average value of 0.75, and the average exponent, α, for self-shifting was measured to be 1.57. In our case the discrepancy of temperature-dependence exponents of the self-shift and self-broadening of the 6_{43}–5_{50} water line is bigger, $\alpha - \beta = 1.9(4)$

In the binary collision approximation, for a majority of atmospheric gases up to atmospheric pressure, the shift and broadening of spectral lines are linearly dependent on pressure. The function of the ratio of the broadening parameter to the shift parameter

TABLE II

Pressure Self-Broadening Parameter of the 6_{43}–5_{50} H_2O Line for Different Temperatures

T K	253.2(2)	296.2(2)	313.2(2)	333.2(3)	363.2(3)	393.2(3)
$\Delta\nu_{br}$ MHz/Torr	14.45(50)	12.98(40)	12.72(35)	12.06(40)	11.43(30)	11.01(30)

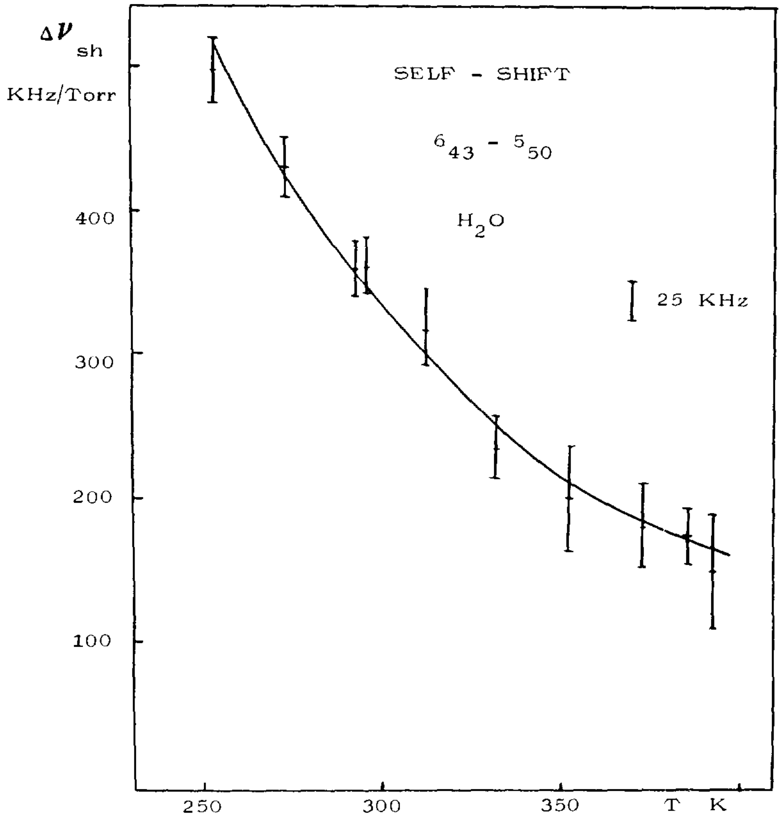

FIG. 3. The dependence of the pressure lineshift parameter on temperature: $\Delta\nu_{sh}(T) \sim T^{-2.56(20)}$.

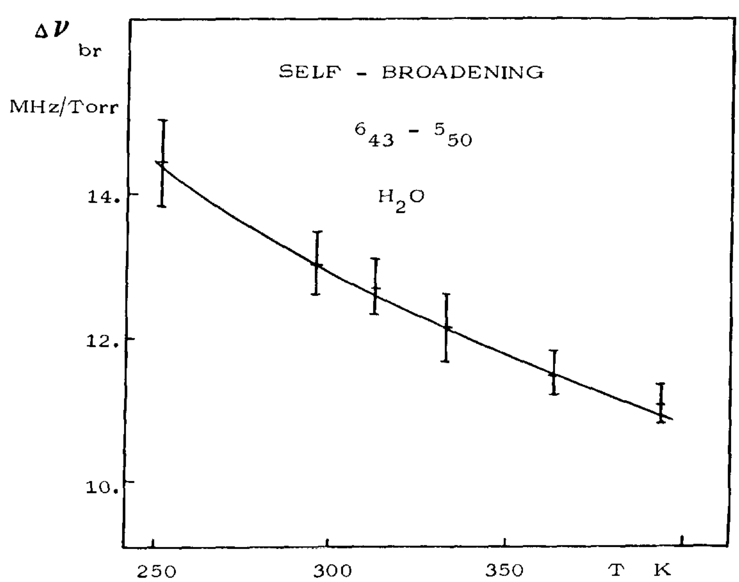

FIG. 4. The dependence of the pressure line-broadening parameter on temperature: $\Delta\nu_{br}(T) \sim T^{-0.62(9)}$.

$$F(T) = \frac{\Delta\nu_{br}(T)}{\Delta\nu_{sh}(T)} \quad (3)$$

depends only on the transition, the temperature, and the composition of the gas. In the laboratory, we can measure this function $F(T)$ for a chosen reference spectral line and then use it for remote determination of the temperature of that gas. It is enough to measure exactly the ratio between the half-width and the shift of the reference line. (The function determined using the 6_{43}–5_{50} water molecule in the case of water vapor depends roughly quadratically on the temperature (Fig. 5).)

The method does not require measurements of the gas pressure or linestrength, but needs only accurate frequency measurements of spectral line parameters. If Eqs. (1) and (2) are valid for the temperature dependence of the pressure shift and line broadening, the value of gas temperature will be

$$T = T_0\left(\frac{\Delta\nu_{sh}(T_0)}{\Delta\nu_{br}(T_0)}F(T)\right)^{1/(\alpha-\beta)}.$$

It should be noted that the accuracy of remote measurement of the gas temperature depends essentially on the accuracy of the measurements of the shift and broadening parameters of a reference line, and on the discrepancy between their temperature-dependence exponents (i.e., $\alpha - \beta$). Therefore, the problem of the search for proper reference lines and their theoretical prediction needs to be tackled soon.

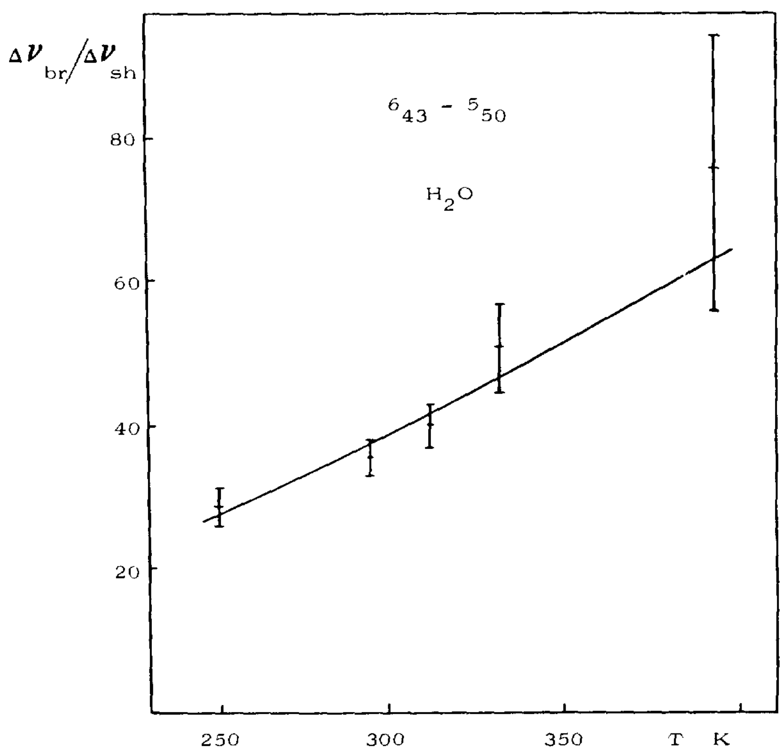

FIG. 5. Ratio of the line-broadening parameter to the lineshift parameter as a function of temperature: $F(T) \sim T^{1.9(4)}$.

ACKNOWLEDGMENTS

The author thanks Prof. A. F. Krupnov for his encouragement and interest in this work and for helpful criticism of various points in an earlier draft, Prof. F. C. De Lucia for helpful discussion, Dr. G. Fraser for help in preparing the manuscript, and especially Dr. A. S. Pine for reading the manuscript and suggesting improvements and for constructive comments and criticism.

RECEIVED: August 31, 1992

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