

## Pressure Broadening of the 2.5 THz H<sup>35</sup>Cl Rotational Line by N<sub>2</sub> and O<sub>2</sub>

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We report results from pressure broadening studies of the 2.5 THz (83.4 cm<sup>-1</sup>)  $J_{4-3}$  rotational line of H<sup>35</sup>Cl by N<sub>2</sub> and O<sub>2</sub>. Broadening coefficients have been measured in absorption at 296 and 201 K using a tunable far infrared spectrometer. At room temperature the N<sub>2</sub> pressure broadening coefficient is  $0.0669 \pm 0.0021$  cm<sup>-1</sup> atm<sup>-1</sup> ( $2\sigma$ ) with a temperature coefficient  $B$  of  $0.58 \pm 0.02$ , where  $B$  is defined by  $\alpha(T) = \alpha_0 T^{-B}$ . Oxygen broadening data are also reported. © 1991 Academic Press, Inc.

### INTRODUCTION

The remote sensing application of far infrared emission spectroscopy has been amply demonstrated over the past 10 years by a series of balloon flights, which carried limb-viewing interferometers; see Carli and Park (1), Chance *et al.* (2), and Traub *et al.* (3). The retrieval of concentration profiles of atmospheric trace molecules and free radicals requires high-precision spectroscopic parameters of these species. This need has driven systematic efforts to establish and improve the line parameter database for a number of these species. HCl is an important molecule in the atmospheric chlorine photochemistry involved in ozone depletion. We report here the pressure broadening coefficients of the 2.5 THz (or more precisely, 2.499 86 THz = 83.3865 cm<sup>-1</sup>) rotation line of H<sup>35</sup>Cl by N<sub>2</sub> and O<sub>2</sub>, for application to the analysis of far infrared spectra obtained in the stratosphere. Most previous pressure broadening measurements of HCl were done in the vibrational fundamental band. Recently, several line parameter measurements in the pure rotational band have been reported. They include position measurements by Nolt *et al.* (4) and width measurements by Sergent-Rozey *et al.* (5)

and Chance *et al.* (6). The present work is the outgrowth of the 1986 measurements reported by Chance *et al.* (6).

#### EXPERIMENTAL DETAILS

Rotational line parameters are measured in absorption using a tunable far infrared (TuFIR) radiation source obtained by either two- or three-wave mixing in a metal-insulator-metal (MIM) diode (Evenson *et al.* (7)). In two-wave mixing, a fixed frequency single-mode CO<sub>2</sub> laser output and a tunable CO<sub>2</sub> waveguide laser output are combined on the MIM diode. Figure 1 shows the arrangement. The tuning range of the waveguide laser, hence the tuning range of the spectrometer, is 145 MHz in the present experiments. In three-wave mixing, outputs from two fixed frequency CO<sub>2</sub> lasers and a microwave generator are combined on the MIM diode. The tuning range of this arrangement is  $\pm 20$  GHz. The advantage of broad tuning range, and the corresponding advantage in the baseline fit, are offset by generally lower power and less stable diode performance in the three-wave setup.

Our data set consists of measurement results from both the two-wave and three-wave arrangements. The TuFIR frequency is known to  $\pm 35$  kHz. Its spectral purity is approximately 10 kHz. For phase sensitive detection, the TuFIR beam is frequency modulated at 1-kHz rate with a modulation amplitude of 1 MHz. The transmitted radiation is detected with a phase sensitive detector as the first derivative (with respect to the frequency) of the lineshape. Digitized spectra are stored in a laboratory computer for later spectrum fitting analysis. A Pyrex absorption cell, 10 cm long and 2.5 cm in diameter, is fitted with 1.6-mm-thick polyethylene windows. For low-temperature

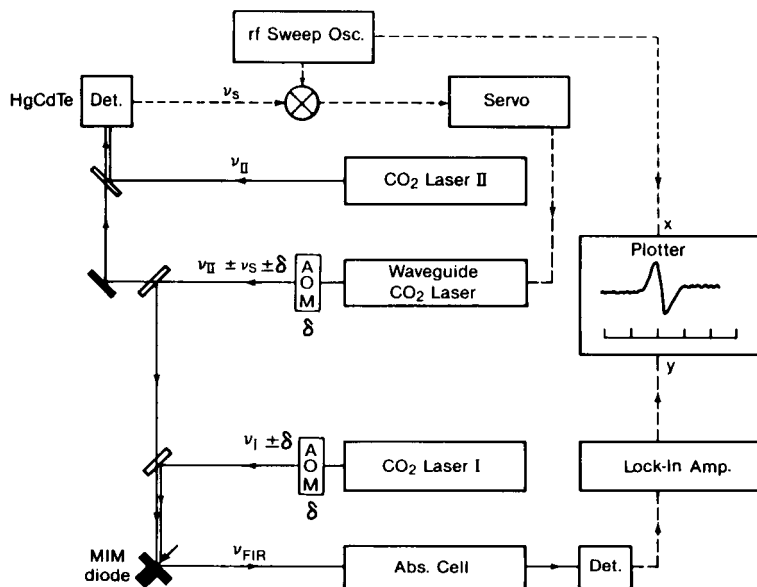


FIG. 1. Tunable far infrared spectrometer using a waveguide laser as the tuning element. The acousto-optic modulators (AOM) prevent feedback.

studies, the cell is immersed in a thermal bath filled with a mixture of dry ice and methanol. Three thermistors are taped to the cell wall to monitor the temperature. Zinc oxide based thermal compound is used between the thermilinear elements and the cell wall to ensure good thermal contact. The cell pressure is measured with an MKS 310 BHS-10 capacitance manometer at the middle of the cell. HCl has a well known tendency to adhere to surfaces causing pressure changes. To reduce this effect, partial evacuations and refilling processes were repeated until desired stability and acceptable peak absorption were obtained. Broadening measurements were made with gas pressures up to 10 Torr. Typically 6 to 10 spectra were taken for each broadening gas, pressure, and temperature. At regular intervals, power density spectra of the TuFIR source were recorded, and used for normalization of the spectra in the analysis.

#### DATA ANALYSIS AND DISCUSSION

The synthetic spectra are fitted to measured spectra using a nonlinear least-squares routine; see Fig. 2. The spectral synthesis consists of Lorentz widths, positions, intensities, and baseline corrections as fitting parameters. Fixed parameters include Doppler width, TuFIR power spectra, and integration time constants of the detection electronics. One-sigma errors of 0.7% due to temperature uncertainties and 0.5% due to pressure uncertainties are added in quadrature to the regression results, then the results are doubled to obtain the  $2\sigma$  errors cited in Table I.

Published values of these coefficients, except for those of Chance *et al.* (6), are reported in the literature with  $1\sigma$  uncertainties or overall estimation of systematic errors presumed to be at the  $1\sigma$  level. In comparing our data with others below, uncertainties are further annotated, where appropriate, whether they are  $1$  or  $2\sigma$  levels. Also, the units for broadening coefficients ( $\text{cm}^{-1} \text{atm}^{-1}$ ) are omitted throughout in the following discussion. Our room temperature broadening data can be compared directly with earlier results of Chance *et al.* (6), who reported coefficient values of  $0.068(\pm 0.007)$  and  $0.033(\pm 0.003)$  for nitrogen and oxygen, respectively. Thus, in the work reported here the  $2\sigma$  uncertainties have been reduced from 10% level to 3 and 5%, respectively. Our room temperature nitrogen broadening coefficient of  $0.0669(\pm 0.0011; 1\sigma)$  is also consistent with the value of  $0.0641(\pm 0.0035; 1\sigma)$  recently reported by Sergent-Rozey *et al.* (5).

Our results can be compared also with those of Houdeau *et al.* (8) and of Ballard *et al.* (9), who measured the linewidths in the  $1 \leftarrow 0$  vibrational transitions. These comparisons are sensible only if we assume that the vibration and the rotation are decoupled in the collisional broadening process. Under this assumption, the average of  $R(3)$  and  $P(4)$  rotation lines may be compared with our results. For the room-temperature nitrogen broadening, Houdeau *et al.* report 0.0684, while Ballard *et al.* report 0.0702. Our result, 0.0669, is consistent with both of these results at the  $1\sigma$  level. For the room-temperature oxygen broadening, Houdeau *et al.* report 0.0351. Our result, 0.0336, is again consistent at the  $1\sigma$  level. In fact, these agreements may be fortuitous, since the vibration-rotation coupling would be expected to introduce larger discrepancies than those observed in these comparisons. We note here that Houdeau *et al.* cite overall uncertainties of 5% (amounting to  $\pm 0.0034 \text{ cm}^{-1} \text{atm}^{-1}$  for room-temperature nitrogen), while Ballard *et al.* estimate overall uncertainties in

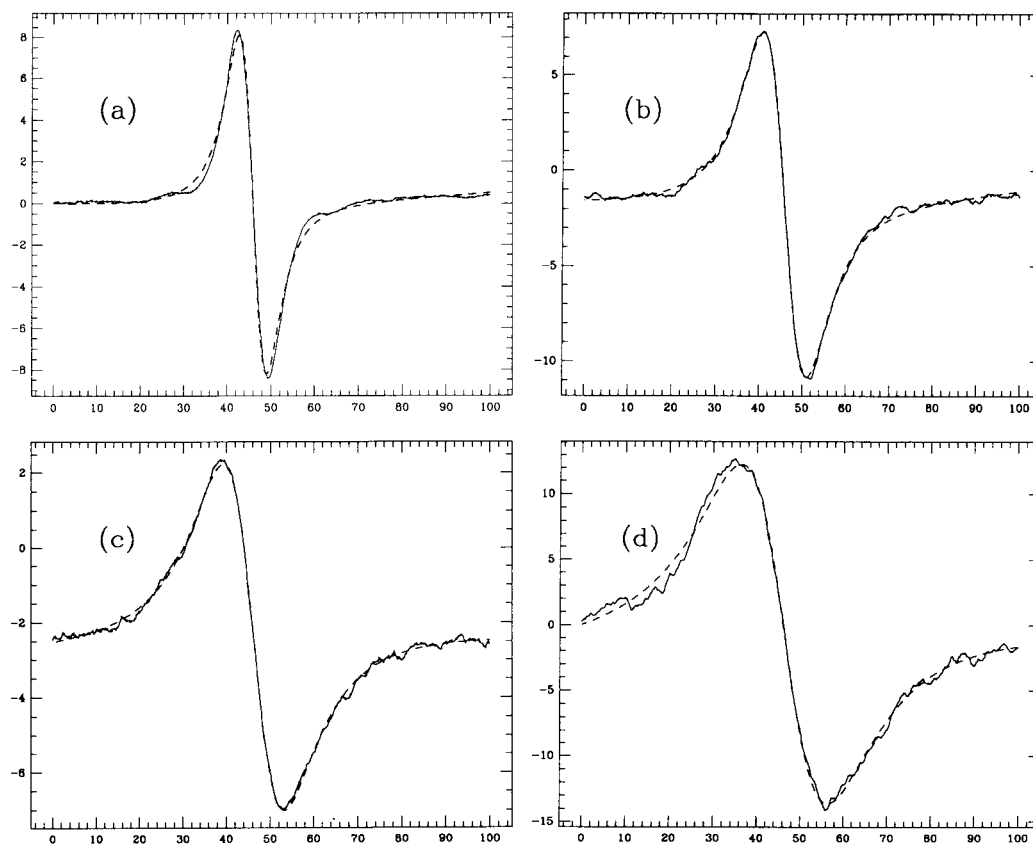


FIG. 2. Absorption measurements of HCl broadened by  $N_2$ . The synthetic spectra are shown in dashed lines. All spectra shown in the figure are taken at 296 K. The  $N_2$  pressures in torr cells are: (a) 1.09; (b) 2.62; (c) 3.98; (d) 6.07. The scan widths are the same for all spectra shown. Both the frequency and the intensity scales are marked in arbitrary units.

the measured widths of  $0.003 \text{ cm}^{-1}$ . We further note that Ballard *et al.* measured pressure broadening at total pressures of around 600 Torr. We presume that these are  $1\sigma$  errors.

Our room-temperature pressure induced frequency shift results can be compared with values reported by Houdeau *et al.* For nitrogen and oxygen, respectively, they report 0.0055 and 0.0095. We measure shifts of 0.0030 and 0.0019, respectively. Again, large discrepancies apparent here are expected in these comparisons between pure rotation and rotation-vibration transitions.

The low-temperature broadening data in Table I were obtained in a single run. The origin of the large error seen in the oxygen data is not understood. More measurements are needed to clarify this problem. There are no published results of low-temperature pressure broadening in pure rotation for direct comparison.

TABLE I

Pressure Broadening and Shift Coefficients for the 83.4-cm<sup>-1</sup> Lines of HCl (2 $\sigma$  Errors in Parentheses)

Broadening Gas	Temp = 296 K		Temp = 201 K
	Broadening (cm <sup>-1</sup> atm <sup>-1</sup> , HWHM)	Shift (cm <sup>-1</sup> atm <sup>-1</sup> )	Broadening (cm <sup>-1</sup> atm <sup>-1</sup> , HWHM)
N <sub>2</sub>	0.0669(21)	0.0030(8)	0.0836(22)
O <sub>2</sub>	0.0336(16)	0.0019(7)	0.0610(219)
Air*	0.0599(20)	0.0028(8)	0.0788(54)

\* Air is calculated as 0.21(O<sub>2</sub>) + 0.79(N<sub>2</sub>).

## CONCLUSIONS

We report here the pressure broadening coefficients and pressure shift coefficients of the 83.3865 cm<sup>-1</sup> pure rotation line of the HCl molecule. These coefficients are the most accurate values reported to date and will prove useful for the analysis of HCl in the Earth's stratosphere. We note that the low-temperature oxygen broadening may need to be studied further in order to obtain a more precise broadening coefficient.

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