

Collisional Broadening of HCl Rotational Transitions Using Tunable Far-Infrared Radiation

K. V. Chance¹, I. G. Nolt², L. Zink³, D. A. Jennings³,
K. M. Evenson³, M. D. Vanek³, and J. V. Radostitz²

¹Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138

²Chemical Physics Institute, University of Oregon, Eugene, OR 97403

³National Bureau of Standards, Boulder, CO 80303

Abstract

Using tunable far-infrared radiation, we have measured pressure broadening coefficients and pressure-induced lineshifts for several rotational transitions of HCl. Results are presented here for the 83.39 cm^{-1} R_3 line of H^{35}Cl , broadened and shifted by N_2 and O_2 .

INTRODUCTION

Far-infrared emission spectroscopy of the atmospheric limb from balloon platforms has proved to be a very useful means for measuring photochemically important trace gases, including HCl, in the stratosphere (1,2). For the analysis of the spectra obtained in the stratosphere, it is necessary to have accurate values of the molecular parameters for the molecules under consideration. Many molecules, including HCl, have spectral lines that are saturated in stratospheric spectra, so that the pressure broadening coefficients are as important as the line intensities in determining concentration profiles. Several recent studies have been made of collisional broadening of HCl by nitrogen and oxygen in the infrared fundamental band (3,4,5), but no previous broadening studies exist for the pure rotational transitions. We report our preliminary results for the room temperature broadening coefficients and shifts for one of the rotational transitions of HCl that is useful in stratospheric concentration derivations.

EXPERIMENTAL AND RESULTS

The TuFIR method for producing far-infrared radiation of high spectral purity was first described by Evenson et al. (6) (*c.f.* Fig. 1 in Nolt et al., this conference). Derivative spectra were obtained using a $2.5 \times 50 \text{ cm}$ pyrex absorption cell with high-density polyethylene windows. Pressures were measured to better than 1% with a precision capacitance manometer. The results presented here are for ambient temperature measurements. The cell has since been fitted with precision thermistors for future studies of the temperature dependence of line parameters. Examples of spectra are shown in Figure 1.

The technique used for these measurements has the advantage of being able to fully resolve the spectral lines for far-infrared transitions. This is of particular importance for studies of molecules where the precise concentration of absorber is difficult to determine and to maintain constant (such as HCl and OH), since the determination of linewidth and lineshift parameters is almost fully independent of absorber amount as long as the system is dilute in absorber.

The spectra are interactively fitted using an iterative least-squares program (SPECFIT) based upon the algorithm of Marquardt (7). Derivative spectra are calculated using a complete radiative transfer model, including the effects of line saturation, by subtraction of two separate spectra spaced apart by the effective modulation width.

Voigt line profiles are calculated using fixed Doppler widths, with line intensities calculated from the dipole moment and quadrupole structure of HCl. The Lorentz width, the line position, and the absorber amount are varied in the fitting procedure. For the HCl R₃ line, there are two major quadrupole components within the Doppler envelope. The relative position and the Lorentz width of these two components were locked together, and the spectra fitted to determine the average Lorentz width and lineshift for each spectrum. Baseline offset, tilt, and quadrature are also varied in the least-squares procedure. Minor quadrupole components were not included in the fitting.

A total of 11 spectra were included in the final data set for N₂ broadening of the HCl line, with N₂ pressures up to 6 torr. For O₂ broadening, 6 spectra were included in the data set, with O₂ pressures up to 8 torr. The values presented here include substantially larger error limits than should be present in the final results. The values for the pressure broadening coefficients, α_L , and pressure shift coefficients, β , are:

Broadening gas	$\alpha_L(\text{cm}^{-1} \text{ atm}^{-1})$	$\beta (\text{cm}^{-1} \text{ atm}^{-1})$
N ₂	0.068(7)	$3.0(0.6) \times 10^{-3}$
O ₂	0.033(3)	$2.0(0.4) \times 10^{-3}$

Acknowledgments

This research involved a collaboration of three institutions. The construction of the Tu-FIR spectrometer at NBS was made possible by the Chemical Manufacturers Association (FC84-533 A/B) and NASA (W-15, 047). Research at the University of Oregon was partially supported by NASA (NAGW-222). Research at the Smithsonian Astrophysical Observatory was supported by the Chemical Manufacturers Association (FC85-544).

REFERENCES

1. B. Carli, F. Mencaraglia, and A. Bonetti, Fourier spectroscopy of the stratospheric emission, *Int. J. IR and MM Waves*, **1**, 263, 1980.
2. W. A. Traub and K. V. Chance, Stratospheric HF and HCl observations, *Geophys. Res. Lett.* **8**, 1075, 1981.
3. J. Ballard, W. B. Johnston, P. H. Moffat, and D. T. Llewellyn-Jones, Experimental determination of the temperature dependence of nitrogen-broadened line widths in the 1-0 band of HCl, *J. Quant. Spectrosc. Radiat. Transfer* **33**, 365, 1985.
4. J. P. Houdeau, M. Larvor et C. Haeusler, Etude à basse température des largeurs et des déplacements des raies rovibrationnelles de la bande fondamentale de H³⁵Cl comprimé par N₂, O₂, D₂ et H₂, *Can. J. Phys.* **58**, 318, 1980.

5. A. S. Pine and J. P. Looney, N_2 and air broadening in the fundamental bands of HF and HCl, *41st Symposium on Molecular Structure and Spectroscopy*, Columbus, Ohio, 1986.

6. K. M. Evenson, D. A. Jennings, and F. R. Petersen, Tunable far-infrared spectroscopy, *Appl. Phys. Lett.* *44*, 576, 1984.

7. Marquardt, D. L., An Algorithm for Least-squares Estimation of Non-linear Parameters, *J. Soc. Indust. Appl. Math.*, *2*, 431-441, 1963.

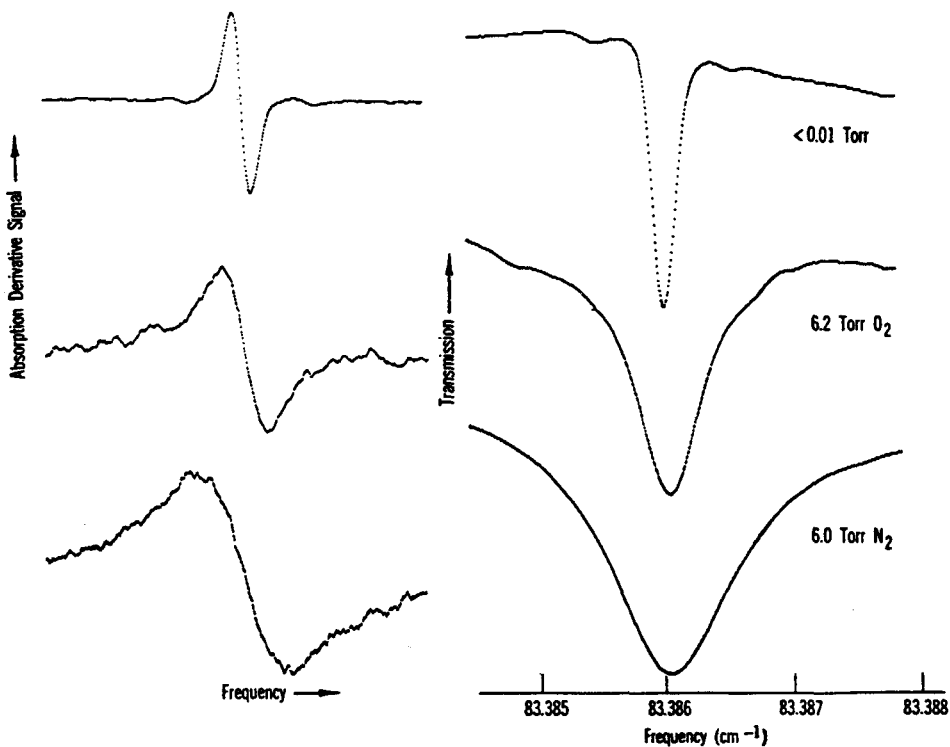


Figure 1. This figure shows the absorption derivative signals and transmission curves (obtained by numerical integration of the derivative curves) of the HCl R_3 line for (a) the unbroadened Doppler case and (b,c) the same transition as broadened by oxygen and nitrogen at pressures roughly equivalent to the stratospheric pressure at an altitude of 32 km. For (a) the central absorption of the line is 7%. Note the quadrupole structure of the transition, evident as two small satellite lines in (a).