ELSEVIER

Journal of Quantitative Spectroscopy & Radiative Transfer 103 (2007) 558–564

Journal of Quantitative Spectroscopy & Radiative Transfer

www.elsevier.com/locate/jqsrt

Submillimeter measurements of N_2 and air broadening of hypochlorous acid

Brian J. Drouin

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099, USA

Received 4 October 2005; accepted 8 July 2006

Abstract

The pressure induced broadening of a several ${}^rQ_0$ pure rotational transitions of hypochlorous acid, HOCl, have been measured as a function of temperature. This set of rotational transitions is the dominant feature of the submillimeter spectrum in the 500 μm range where several remote sensing instruments currently operate. Additional features throughout the submillimeter spectrum have been recorded at the full-resolution of the room temperature Doppler linewidth using multiplier chains in the 110–500 μm wavelengths.

PACS: 33.70 Jg; 33.70 −w; 33.20 −t; 33.20 Bx

Keywords: Hypochlorous acid; Linewidths; Pressure broadening; Atmospheric spectra; Lineshape

1. Introduction

Recently there has been a surge of interest for radiometric sounding in the submillimeter wavelengths. A frequency range near 500 μm containing strong HOCl emission features is accessible from existing aircraft [1–3], balloon-borne [1], space-borne instruments [4,5] and planned space-borne instruments [6,7]. Stratospheric HOCl has been measured in shorter wavelengths by balloon-borne Fourier transform spectroscopy [8] and a variety of infrared techniques.

The rotational spectrum of HOCl has been investigated in numerous studies [9–13] in which the dipole moment and molecular rotation Hamiltonian are described in improving detail. Infrared studies [14,15] have contributed to the rotational analyses through spectral assignments that allow ground state combination differences to be independently determined. The previous and present work has incrementally improved the precision of predicted rotational transitions throughout the FIR where this light molecule has strong *b*-type transitions.

Accurate pressure and temperature dependent lineshape parameters are required for successful retrieval of concentration profiles from atmospheric limb sounding data. Only a single diode laser study [16] in the v_2 vibrational mode has investigated lineshape pressure dependence in this species. This work is an effort to

E-mail address: brian.j.drouin@jpl.nasa.gov.

0022-4073/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jqsrt.2006.07.007

characterize the pressure induced lineshape of an HOCl transition near 635 GHz that is a target of the Earth Observing Systems—Microwave Limb Sounder [5]. Several nearby transitions were also probed to characterize the precision of the measurements. During the course of measurement several new transition frequencies were measured and a revised Hamiltonian has been determined.

2. Experimental details, results and analysis

A series of multiplier chains, commercial, JPL built and hybrid, were utilized to record spectra across the submillimeter spectrum. Details of the spectrometer are given in Ref. [17]. Detector response, pressure and temperature are all recorded synchronously while the computer step sweeps the RF during the experiment.

This system utilized a double pass 5 cm diameter 1 m base length static/flow cell. Hypochlorous acid was generated by bubbling chlorine gas through a water solution containing yellow mercuric oxide. The resulting solution was attached to the vacuum system and pumped through the spectrometer free-space cell until strong, consistent signals were observable. Absorptions due to HOCl were found within ±5 MHz of all predicted transitions. Additional bands due to Cl_2O (including isotopes and excited bending modes) were also observed during the scanning.

For pressure-induced lineshape measurements, a static gas cell was utilized that allows buffer gas to be added sequentially to an existing gas parcel containing the absorber. This system differs from recent pressure-induced lineshape measurements [18,19] in this laboratory in that the spectral baseline is not recorded before and after each spectral sweep. The present technique requires little or no spectral baseline at all, such that scans can be compared with the convolution method while ignoring the distorting effects of a time-dependent baseline. Even with this constraint the available pressure range in which good signal to noise ratio was obtained, without a noticeable baseline, extended up to ≈ 1.5 Torr. Fig. 1 shows the $J = 1_{1,1} \leftarrow 0_{0,0}$ transition of $HO^{35}Cl$ recorded in the static cell as a reference scan to a pressure broadening run.

Pressure induced lineshape measurements indicated both a halfwidth and a lineshift with unprecedented precision for such measurements. Indeed, the signal to noise ratio was high, there were no apparent baseline effects and the temperature and pressure measurement equipment was fully calibrated. As a test the pressure broadening of the $J_{K_p,K_o} = 1_{1,1} \leftarrow 0_{0,0}$ and several other transitions in the same ${}^rQ_0$-branch was analyzed. As expected the weaker $J = 1 \leftarrow 0$ transition was a less precise measurement. Much more satisfying was the high precision of other Q-branch lineshape measurements. In fact, each of the ${}^rQ_0$ transitions measured in this study showed the same pressure dependent broadening and shifting of the line position.

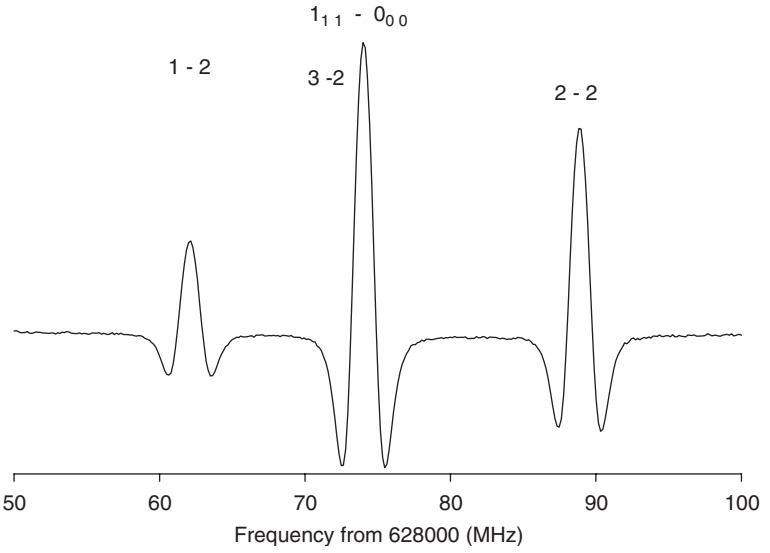

Fig. 1. The $J_{K_p,K_o} = 1_{1,1} \leftarrow 0_{0,0}$ transition of $HO^{35}Cl$ near 628 GHz. The Cl nuclear quadrupole splittings are not resolved in higher J transitions in the submillimeter region.