# A Study of the Intensity of the Self-Broadened Fundamental Band of Hydrogen Chloride*

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## Abstract

The variation with pressure of the contour of the fundamental vibration-rotation band of hydrogen chloride has been examined spectroscopically. A very short path length absorption cell has been designed and built to facilitate this investigation.

The intensity of this band has been calculated for pressures of the absorbing gas from 20 to 50 atm. The present work indicates that the band intensity for polar molecules is definitely an increasing function of pressure. The lower limiting value of $154$ $cm^{-2}$ $atmos^{-1}$ extrapolated from the present data is consistent with the $160 \pm 30$ $cm^{-2}$ $atmos^{-1}$ value measured by Penner and Weber.

The band intensity ($cm^{-2}$ $amagat^{-1}$) is expressed as a function of density (amagat), and is found to be inversely proportional to the gas density. Evidently, a failure of Beer's law is occurring at the large densities of gas used in this study.

Index Headings: Absorption, Atmospheric Optics;
Infrared; Spectra

A relatively simple experimental technique has been developed to measure directly the intensity as a function of pressure, of the fundamental band of hydrogen chloride. The integrated absorption coefficients that have been measured by this technique are believed to be fairly accurate, because

1) The absorption coefficients could be measured precisely at any frequency over the band and for a considerable range of pressures. This precision was made possible by limiting the cell length to 0.047 cm and thereby the maximum measured absorption to about 80 per cent at 51.0 atm.

2) The instrumental slit width of the grating instrument used was much smaller than the band width. When the rotational fine structure was smoothed out by pressure broadening, the necessity for correcting or compensating for instrumental distortion of the band shape was eliminated.

Under these conditions, a true absorption coefficient could be calculated for each frequency and also the band intensity or integrated absorption coefficient, which is the integral of the absorption coefficient taken over the spectral width of the band. No foreign-gas broadening is necessary. No extrapolation of the band absorption area to the limit of zero path length is performed as in the Wilson-Wells method.[1] Nor is it necessary to assume pressure independence of the band intensity.

The spectrometer in this study was a Perkin-Elmer model 337 double beam grating spectrophotometer with a thermocouple detector used in the region from 2.7 to $4\mu$.

The absorption cell was machined from stainless steel. The gaskets were teflon O-rings and the windows were 25 mm diameter sapphire 6 mm in thickness. When completely assembled, the distance between the inside surfaces of the windows was the thickness of a 0.47 mm monel spacer. The cell withstood hydrogen fluoride and hydrogen chloride gases and was tested to a maximum pressure of 136.1 atm.

Several procedures for pressurizing hydrogen chloride in the cell were investigated. One of the greatest problems encountered was what appeared to be polymer formation or perhaps adsorption of hydrogen chloride on the walls of the cell and tubing. This problem was reflected in the time dependence of some of the data runs. If a charge of gas was left in the cell and analyzed at successive intervals, a noticeable drop of intensity of the absorption band was observed. The following procedure for pressurization was used for this reason. With the rest of the system evacuated, the cell and the line to the cell was filled with hydrogen chloride at a low pressure. High pressure argon was then admitted to this line and acted as a piston to put the pure hydrogen chloride in the cell at the desired pressure. The assumption is made here that little mixing will occur between the noble and corrosive gases over a few hours in a tube of small cross section. Furthermore, the region of possible mixing was always a considerable distance from the absorption cell.

After the cell had been filled in the manner outlined above, spectrometer runs were made at pressures of 1, 6.8, 13.6, 23.8, 24.0, 40.8, 44.2, 47.6, 51.0, 54.4, 61.2, 74.9, and 102 atm. The runs at less than 23.8 atm. were not of interest in this study except for calibration. It was evident that the area under the absorption curve continued to increase for pressures above 51.0 atm. However, in the range from 51 atm to 102 atm the absorption across the peak of the curve was so great that no accurate estimate of the absorption coefficient could be made. For example, the runs at 102 atm were completely absorbing at the peak of the absorption curve for a distance of some 35 wave numbers. The rotational fine structure was sufficiently blurred at 23.8 atm. that the recorder pen easily followed the band contour. The rotational fine structure disappeared completely by 51 atm.

The spectrograms chosen for computer analysis in this study were run with procedures set up to minimize the effects of the time dependence. These procedures included a consistent method of filling the cell, the selection of a consistent time for making the run, and the selection of only those runs which fitted into a continuous rotational smoothing sequence.

A continuous rotational smoothing sequence is one in which the rotational fine structure blurs out smoothly with increasing pressure. Figure 1 illustrates such a sequence. The area under the absorption coefficient curve, the band intensity, and the integrated absorption coefficient (the band intensity divided by the pressure in atmospheres) are tabulated in Table I for all pressures run. Each entry represents the average of several runs at a particular pressure. All data were collected at room temperature, $297 \pm 5^{\circ}K$. All major calculations

performed in this study were carried out on the IBM 7040 Computer at the University
of Tennessee Computing Center.

The integrated absorption coefficient is plotted as a function of the pressure
in Figure 2. With the exception of the value 186.62 cm$^{-2}$ atmos$^{-1}$ at 44.2 atm, and
the value, 193.52 cm$^{-2}$ atmos$^{-1}$ at 47.6 atm, the points more or less cluster around
the straight line that has been drawn. Using the criterion of continuous rotational
smoothing, mentioned above, for selecting runs to be analyzed, the points at 44.2
and 47.6 atm are the least accurate of all the points plotted.

Of interest here is the very evident pressure dependence of the integrated
absorption coefficient. The value measured by Penner and Weber[2] of $160 \pm 30$ cm$^{-2}$
atmos$^{-1}$ for this coefficient is close to the value of 154 cm$^{-2}$ atmos$^{-1}$ extrapolated
from the present data.

The pressure measurements were converted into number density values
using the relationship between density, in amagat, and pressure, in atmospheres,
reported by Beaume and Coulon.[3] The integrated absorption coefficient versus
density is plotted in Figure 3. Within experimental error, the integrated ab-
sorption coefficient is inversely proportional to the density. This implies a
failure of Beer's law at the large densities of gas used in this study.

## Figure Captions

1. Fig. 1. A continuous rotational smoothing sequence  a) 51.0 atm  b) 34.0 psi

   c) 23.8 atm

2. Fig. 2. The intensity of the fundamental band of HCl as a function of pressure.

3. Fig. 3. The intensity of the fundamental band of HCl as a function of density.

## Footnotes

1. E. B. Wilson and A. J. Wells, J. Chem. Phys., 14, 578 (1946).

2. S. S. Penner and D. Weber, J. Chem. Phys., 21, 649 (1953).

3. R. Beaume and R. Coulon, Compt. Rend., 266, series B, 1024 (1968).

TABLE I

The Band Intensity and Integrated Absorption

Coefficient as a Function of Pressure

| Pressure (atm) | Band Intensity ($cm^{-2}$) | Integrated Absorption Coefficient ($cm^{-2}$ atmos$^{-1}$) |
|---|---|---|
| 23.8 | 3904.190 | 163.97 |
| 34.0 | 6391.520 | 187.91 |
| 34.0 | 6277.290 | 184.55 |
| 40.8 | 8234.122 | 201.73 |
| 40.8 | 8308.062 | 203.54 |
| 44.2 | 8656.797 | 195.77 |
| 44.2 | 8251.917 | 186.62 |
| 47.6 | 8739.469 | 193.52 |
| 51.0 | 11022.430 | 216.04 |