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Temperature dependent pressure-induced lineshape of the HCl $J = 1 \leftarrow 0$ rotational transition in nitrogen and oxygen

Brian J. Drouin*

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

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Abstract

The pressure-induced broadening and shift of the lowest rotational transition of hydrogen chloride have been measured in both nitrogen and oxygen as a function of temperature. This work improves the accuracy of the broadening parameter and provides the first experimental parameterization of the pressure shift. The HCl air broadened half-width is determined to $< 4.1\%$ across the temperature range of the stratosphere and upper troposphere.

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1. Introduction

Measurements of hydrogen chloride (HCl) are necessary for closure of the stratospheric chlorine budget. HCl acts as a reservoir for chlorine in the stratosphere, effectively regulating the active forms of chlorine. Monitoring the behavior of HCl in extreme environments such as the arctic and antarctic polar vortices will help to constrain models of winter/summer ozone loss in these regions. Using microwave limb sounding techniques simultaneous measurements of HCl, O₃, HNO₃, and ClO are possible, even in dense aerosol or polar stratospheric cloud regions [1].

Precision and accuracy of laboratory measurements for the pressure broadening of the HCl $J = 1 \leftarrow 0$ transition will directly affect the precision and accuracy of the atmospheric concentration profiles determined from the Earth Observing System Microwave Limb Sounder (EOS-MLS) [2]. Tabulation in the HITRAN [3] database has drawn on the excellent infrared data from Pine and Looney [4].

* Fax: +1-818-354-8460.

E-mail address: bdrouin@mail2.jpl.nasa.gov (B.J. Drouin).

However, this data has not directly agreed with any rotational study. Furthermore, the current data available for the rotational transition do not include any temperature dependencies in the major atmospheric gases. Therefore, the required data for thorough analysis of the expected MLS profiles is incomplete.

Previous measurements of the $J = 1 \leftarrow 0$ rotational transition pressure-induced lineshape have been made in nitrogen using both tunable far-infrared (TuFIR) [5,6] and Fourier transform (FT) [7] techniques, with the latter TuFIR study [6] including measurements in oxygen. Pine and Looney [4] have measured the pressure broadening parameters in nitrogen and air of the infrared $v = 1 \leftarrow 0$ ro-vibrational transitions, including the $J = 1 \leftarrow 0$ and $0 \leftarrow 1$ transitions. Unfortunately, as is often the case in comparisons of pressure broadening parameters, the independent measurements are not in excellent agreement with each other. The FT study [7] agrees well with the IR study of Pine and Looney [4] but only barely overlaps the quoted uncertainty of the first TuFIR measurement [5]. This early TuFIR measurement comes 15–20% above the two FT techniques, and the more recent value falls considerably lower by 8%. The precisions quoted in the rotational half-width parameters vary from 0.8% to 10%, a result typically derived from the quality of the data fit. However, accuracy is often estimated closer to 5% in such studies due to measurement difficulties. The infrared study [4] also claims high precision (1%), and because the P and R branch values are in close agreement, they are expected to be very close to those of the pure rotational transitions. It is possible to reach high precision for half-width parameters in the infrared, if the instrumental lineshape is well understood, and careful control of experimental variables are addressed. This IR study, in which measurements were done at 202 and 295 K, is also the only previous temperature dependent study in N_2 . Pine and Looney also examined the pressure broadening coefficients of HCl in dry air, which can be compared directly to a values calculated from individual N_2 and O_2 values.

2. Experimental

The entire experimental design is shown in Fig. 1. Measurements were carried out with two similar free-space flow cells; $L = 1.0$ and 0.7 m, both with a 7.3 cm diameter, each enclosed within temperature controlled jackets. For temperatures below room temperature methanol, passively cooled by $N_{2(l)}$, was flowed through the jacket, whereas a resistively heated ethylene glycol/water mixture was used for elevated temperature measurements. Teflon or poly-propylene windows in the ‘top-hat’ shape were fitted into opposite ends of the cell for direct contact of the inner window surface within the temperature controlled region, at reduced temperatures, secondary teflon or styrofoam windows were used to keep moisture from condensing upon the outer surface of the windows. Two separate multiplier chains ($\times 36$ or $\times 42$) were implemented to obtain 625 GHz radiation. The chains consisted of a Hewlett Packard sweep synthesizer operating at 17.385–17.387, or 14.901–14.903 GHz followed by an active sextupler (Agilent or Millitech) that pumps a JPL-built antiparallel planar Schottky diode multiplier ($\times 6$ or $\times 7$) [8]. For efficient generation of the even harmonic the Schottky diode pair was biased to +0.200 V. The submillimeter radiation passed twice through the cell using a polarizing grid and a rooftop reflector. A liquid-helium cooled InSb bolometer followed by a lock-in-amplifier was used for detection of the frequency modulated source. The implementation of a multiplier chain provides an easily tunable, stable, synthesized radiation source for doing broadband spectroscopy and lineshape measurements.

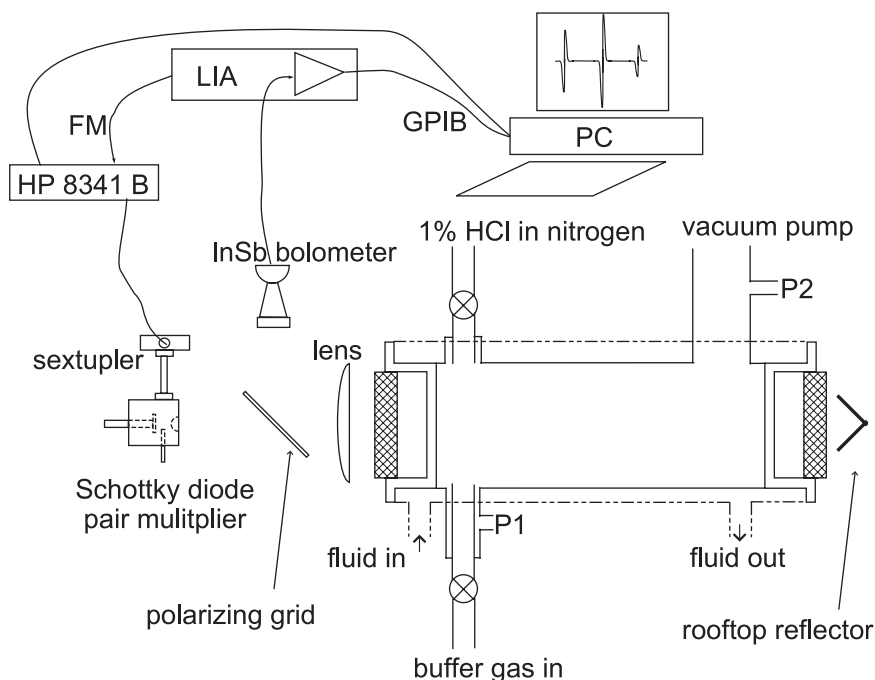


Fig. 1. Experimental setup for measurement of HCl $J = 1 \leftarrow 0$ lineshape.

The HCl spectra analyzed are the H^{35}Cl , $J = 1 \leftarrow 0$ and H^{37}Cl $J = 1 \leftarrow 0$, pure rotational transitions at 625.9 and 624.9 GHz, respectively. At all measured pressures and modulation frequencies used the characteristic hyperfine pattern due to the $I = 3/2$ Cl nucleus is observable. Frequency modulated scans of the H^{35}Cl isotopomer spanned 90 MHz, allowing enough frequency space to accommodate extended wings of the heavily pressure broadened transitions (up to 10 MHz FWHM). For application of the convolution method [9] to the spectra it is imperative that all reference and test spectra are completely enclosed within the given scan range. Reasonable sensitivity combined with a large dipole moment allowed measurements with S/N ratio > 500 for this transition even at small concentrations. Consequently, a small modulation depth (< 2 MHz) was sufficient for producing acceptable first derivative spectra. Degradation of the S/N at higher pressures of broadening gas sets a limit for the dynamic range of measurements available for a given partial pressure/modulation depth. No scans with $S/N < 20$ were included in the analyses. If the partial pressure of HCl was chosen for maximum signal at 100 mTorr ($S/N = 500$), then the maximum pressure was typically reached at 1000 mTorr. However, beginning a run at 500 mTorr, with a larger partial pressure of HCl, allows a larger pressure range for the broadened scans, often up to 2500 mTorr. A run consists of a series of scans, at a single temperature, taken at a set of different broadening gas pressures, typically 100–250 mTorr apart with pressure either increasing *or* decreasing incrementally through the run.

During a given run every care was taken to ensure that the only variable of the experiment is the partial pressure of the broadening gas. The invariance of baseline, absorber partial pressure, source power, bath temperature and modulation amplitude are each addressed as important prerequisites of the experimental design. For a reliable baseline subtraction, each scan is preceded and followed by

a scan of the cell with no absorber present. The absorber partial pressure is adjusted with a Teflon needle valve which withstands the corrosive nature of the hydrogen chloride gas. To obtain the stable low partial pressures necessary (< 1 mTorr), a 1% HCl in nitrogen (Air Products) mixture was flowed through the spectrometer cell at pressures ranging from 1 to 20 mTorr.

The gases entering the cell thermally equilibrate rapidly and pass through the cell towards a rotary-vane vacuum pump with a maximum pumping speed of ~ 24 l/s. Maximum flow speeds were found to give more consistent results, no pressure gradient was observed across the 1 m flow cell. The total pressure is monitored at both ends of the 1 m cell (only one end for the 0.7 m cell) using calibrated capacitance manometers. The pressure gauges for the 1 m cell showed deviations of less than 1% from actual pressure in a comparison to a standard. These pressures were then adjusted with a polynomial to give an actual pressure to much better than 1%. The pressure gauge used for the 0.7 m cell showed deviations of less than 0.25% in comparison to standard and the reading was used directly as the actual pressure. The difference pressure between two compared scans was used as the pressure ordinate in subsequent data analysis. The temperature is monitored using a pair of ‘T’ type thermocouples, one embedded in the coolant sleeve and the other resting in an ice bath. The coolant temperature was regulated to within 2° of the desired temperature down to 195 K and up to 353 K.

The only variable within a given run was the partial pressure of broadening gas, which was flowed in through a port opposite to the mixture inlet for the 1 m cell or in through a $1/2''$ glass ‘T’ in combination with the HCl mixture for the 0.7 m cell. Broadening gas pressures ranging from 100 to 2600 mTorr were used in both systems with 1% HCl in N_2 mixtures of 1–25 mTorr fixed for a given run. No systematic differences in the pressure and/or temperature dependence were discernable between the two experimental designs.

3. Analysis

A $H^{35}Cl$ run at 210 K in oxygen broadening gas is depicted as a series of superimposed graphs in Fig. 2. The individual differences (if any) of the pressure broadening coefficients for these hyperfine components have been ignored in the analysis. With the convolution method described below all features in the baseline subtracted spectrum are treated equally. All attempts to fit the individual components with separate broadening coefficients have shown insignificant differences.

Frequency modulated scans of the HCl rotational transitions result in a first derivative lineshape that is a combination of the Doppler and the Lorentz components. The complication of overlapping hyperfine patterns makes an ab initio representation of the lineshape difficult. Instead, the convolution method of Pickett [9] was used. Pickett has shown that pressure broadening due to a foreign gas may be determined by a convolution method which does not require precise knowledge of the instrumental lineshape or of the concentration of the broadened molecule. The experimental spectrum $S(v, p)$ at the pressure p is given by

$$\begin{aligned} S(v, p) &= \int_{-\infty}^{\infty} S_r(v', p') L(v - v', p - p') dv' \\ &= S_r(v', p') L(v - v', p - p') \end{aligned} \quad (1)$$

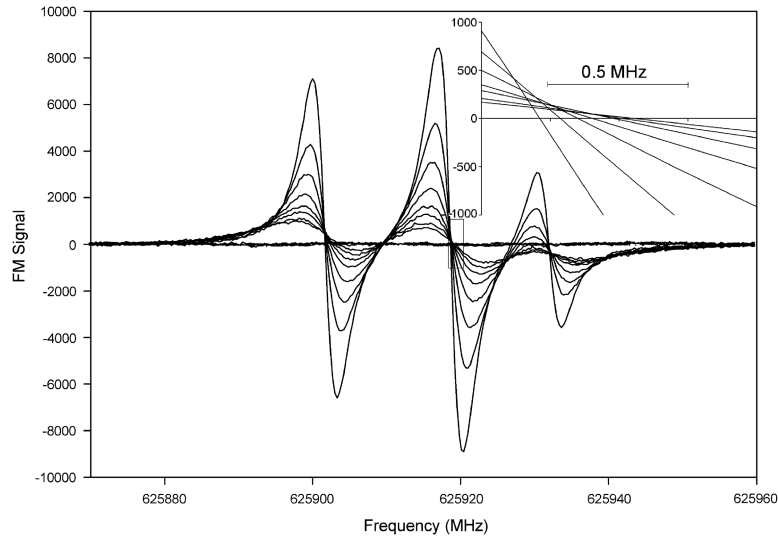


Fig. 2. A 210 K run of 20 mTorr 1% HCl in Nitrogen and 760–2520 mTorr Oxygen. The traces decrease in amplitude for higher pressures measured at 250 mTorr increments. The inset shows the lineshift to higher frequency for higher pressures.

$$L(v - v', p - p') = \frac{I \Delta v_{\Gamma}^2}{\Delta v_{\Gamma}^2 + (v - v' + \Delta v_{\delta})^2}, \quad (2)$$

where $S_r(v', p')$ is a reference spectrum taken at a lower pressure p' with half-width $\Gamma(p')$ and shift $\delta(p')$. $L(v - v', p - p')$ is a Lorentzian function the half-width (Δv_{Γ}) and shift (Δv_{δ}) of which are dependent only upon the change in pressure due to additional broadening gas, see Eqs. (3) and (4). The intensity factor, I , contains the Fourier constant and scales the spectra by peak height.

$$\Delta v_{\Gamma} = \Gamma(p) - \Gamma(p'), \quad (3)$$

$$\Delta v_{\delta} = \delta(p) - \delta(p'). \quad (4)$$

The advantage of the method is that the information regarding instrumental effects, Doppler broadening, and all sources of pressure broadening common to both the low- and high-pressure samples is contained in the reference spectrum. The convolution method allows the additional pressure broadening to be readily determined in the regime where it is comparable to other contributions to the half-width. For example, if $S_r(v, p')$ is a Gaussian, $S(v, p)$ will be a Voigt profile. The requirements for the method to be valid are that the absolute pressure of the broadened molecule remain constant as the foreign gas is varied, that the absorption of the reference spectrum be linear at the line center and that the power and instrument function be constant over the broadened line profile.

The parameters of this Lorentzian are varied within a non-linear least-squares-fit routine (Lab Windows) until the convoluted spectrum matches the test spectrum.

Fig. 2 includes the residuals from the fits of the 1020–2520 mT test spectra with the 760 mT spectrum as a reference. The graph inset in Fig. 2 highlights the shift of the transition center frequency, which is near the maximum for this range of temperatures and broadening gases. The absence of

any systematic residuals indicates that there are no problems due to baseline shifts, no evidence for line-mixing and no need for including hyperfine dependence of the lineshape parameters. Not shown in Fig. 2 are the residuals of convolution fits with the other scans as reference spectra, generally all available data points in a given run were used in determination of a broadening coefficient, N pressure measurements in a given run gives $N(N - 1)/2$ data points. From seven to twelve pressure measurements were made in any given run. The final data set used contains data from 29 N_2 runs and 25 O_2 runs at eight different temperatures (358, 343, 300, 273, 250, 230, 210 and 195 K).

Parameters determined from the Lorentzian convolution fits represent a *difference* between the reference and test spectra. As expected, the broadening parameters are linearly dependent upon the broadening gas pressure at a given temperature. The Lorentzian peak height was inversely proportional to the difference pressure, an indication of an under-modulated spectrum. Systematic line shifts were determinable from the data sets. For determination of lineshape parameters the half-widths and lineshifts are assumed to have a linear pressure and power-law temperature dependence as shown in Eqs. (5) and (6):

$$\Delta v_{\Gamma} = \gamma_o \Delta p \left(\frac{296}{T} \right)^n, \quad (5)$$

$$\Delta v_{\delta} = \delta_o \Delta p \left(\frac{296}{T} \right)^s. \quad (6)$$

Values for the Δv parameters determined in the convolution fitting are necessarily positive for the broadening coefficients (Δv_{Γ}). Line shifts (Δv_{δ}) can be positive or negative. Values of the dependent variables Δv_{δ} or Δv_{Γ} are used to determine the coefficients of Eqs. (5) and (6) based on a parametric fit to all temperature and differential pressure data. The removal of Doppler and instrumental contributions to the lineshape in the spectral comparison also removes the need to fit an intercept, therefore reducing the number of co-dependent variables in the analysis. The parametric fit also provides the correlation coefficient between the linear pressure dependence and the exponential temperature dependence. Correlation coefficients, reported as $\chi_{\Gamma,n}$ and $\chi_{\delta,s}$ for correlation between γ_o and n or δ_o and s , respectively, of ~ 0.4 are obtained. Without the elevated temperature data the correlation coefficients were 20–30% larger.

Projections of the data sets onto 296 K are shown in Figs. 3 and 4 for reference to the data scatter about the linear portion of the fit. The graphs contain 1194 data points for N_2 (black) and 1080 for O_2 (grey). Temperature dependencies of the shift and broadening parameters per Torr broadening gas are shown in Fig. 5. The symbols in Fig. 5, N (black) and O (grey), refer to individual pressure dependencies determined for each run and plotted *vs.* the average temperature during that run. These points were not used in the analyses but are depicted graphically to show the day-to-day scatter of the experimental data. The individual 2σ precisions, based on the linear fit of each run, are much smaller than the symbol size on the graph (typically $< 2\%$), and therefore omitted. Clearly many runs within the same temperature ranges show very little overlap within this precision, indicating that the overall accuracy is worse than the precision. Solid lines shown in Fig. 5 are calculated from the parameters in Table 1 using Eqs. (5) and (6). The parametric fit determines a broadening/shift coefficient and the corresponding temperature exponent based on each comparative data point within every run thus obtaining an un-weighted parameter set based on the experimental accuracy. Traditional methods of determination of the exponent from a log–log plot of the results of each run inherently weight

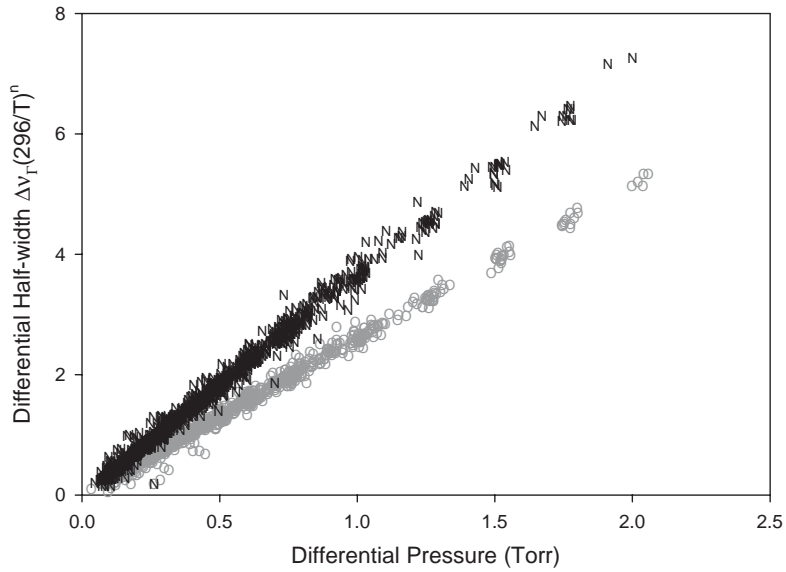


Fig. 3. Pressure broadening of HCl projected to 296 K in N_2 (black) and O_2 (grey).

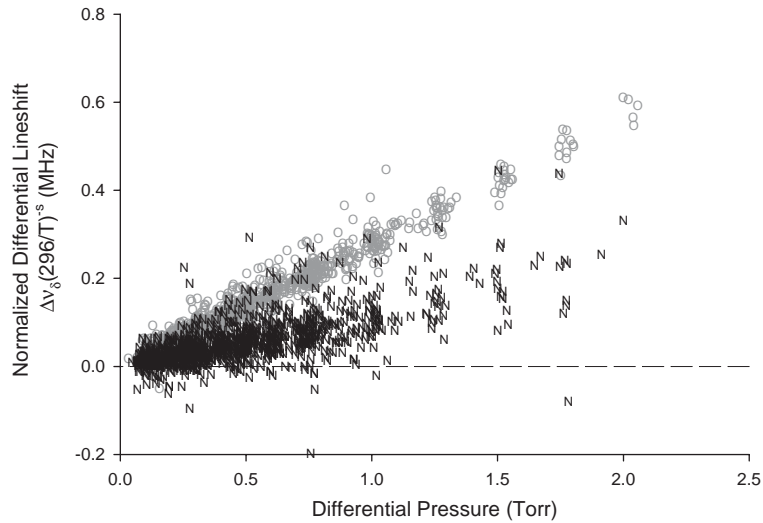


Fig. 4. Pressure shift of HCl projected to 296 K in N_2 (black) and O_2 (grey).

the runs equally, where some runs may contain more data than others, or the data quality may be different. Calculation of the error in the half-width or lineshift using the errors listed in Table 1 and measurement uncertainties is outlined by Drouin et al. [10].

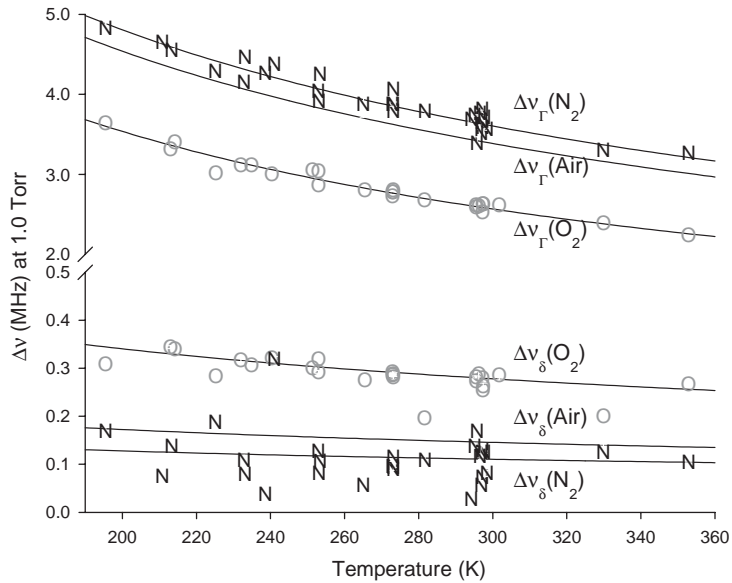


Fig. 5. Pressure broadening and pressure shift coefficients of individual runs N₂ (N, black), O₂ (O, grey) in MHz/Torr. Solid lines are curves based on the parametric fits at 1.0 Torr plotted vs. temperature.

Table 1
Half-width and lineshift parameters^a for H³⁵Cl

	Nitrogen	Oxygen	Air ^b
<i>Half-width parameters</i>			
γ_o (MHz/Torr)	3.639(7)	2.595(5)	3.420(7)
n	0.71(3)	0.79(1)	0.73(3)
$\chi_{\Gamma,n}$	0.4010	0.4425	0.4097
2σ (180 K)	4.3%	2.4%	3.9%
<i>Lineshift parameters</i>			
δ_o (MHz/Torr)	0.111(3)	0.280(1)	0.146(3)
s	0.36(19)	0.50(3)	0.4047
$\chi_{\delta,s}$	0.3687	0.4047	0.3763
2σ (180 K)	22.1%	4.2%	17.8%

^aParameters are defined in Eqs. (5) and (6). The units of γ and δ are MHz/Torr.

^bThese values are determined from a fit to the calculated function $\sum_i c_i \gamma_{0,i} (296/T)^{n_i}$, where $c_{N_2} = 0.79$, $c_{O_2} = 0.21$, errors are propagated linearly.

4. Discussion

The possible experimental sources of error were previously described, but some discussion of potential errors in the data analysis will now be given. Proper application of the convolution method

requires attention to a few key spectroscopic issues. These spectroscopic requirements are low tolerance to fluctuations in power and spectral dispersion as well as weak absorption. Weak absorption was obtainable consistently with the 1% HCl mixture (but not with a pure HCl lecture bottle). Fluctuating power and dispersion have been minimized to contribute to less than 1% of systematic error in the line broadening parameters and less than 3% systematic error in the line shift parameters.

During most FM experiments the power was not monitored as a function of frequency, so a systematic check of this potential source of error was done. Through reconfiguration of the system, measurements of the power deviations throughout the scan could be quantified. On a pair of scans where the power fluctuated as much as 10% within each scan, but retained the deviation in both scans, it was found that the determinable half-width difference did not change outside the experimental scatter when the spectrum was normalized to the power. However, the shift parameter determined from the normalized spectra was observed to change a few percent in the direction of *decreasing* power. Such a fluctuation is manifested in the comparison of two pressure broadened scans because, although the actual transition is symmetrically broadened, a deficit of power on one side of the line produces a slightly smaller detection response to the absorption. The reconfiguration necessary to monitor power fluctuations is experimentally demanding, and would result in poor reproducibility over the course of an extended run, therefore power was monitored only during initial alignment. Power induced apparent shifts should fluctuate randomly with the day-to-day re-alignment of the submillimeter optics and is likely to be the major source of scatter in the lineshift data points in Figs. 4 and 5.

Assessing potential contributions to systematic error due to frequency dependent dispersion fluctuations over the scan is somewhat more difficult. Dispersion in the direct absorption lineshapes at high absorption and low pressure was directly observable through (first-derivative type) deviations from pure Gaussian lineshape in the Doppler profile. However, at the lower absorption and higher pressures of the measurements for pressure broadening these affects were not obvious. Furthermore, the changes in dispersion were not large enough to cause systematic residuals in the convolution analysis. Quantification of the experimental spectral dispersion was not done, but simulations of spectra containing small (1%) and larger (10%) degrees of spectral dispersion fluctuation were made in order to test the sensitivity of the analysis to such errors. The simulations with 10% dispersion fluctuation were visibly worse than the experimental data in both lineshape symmetry and in the fitted residuals, thus indicating that this level of dispersion fluctuation is not present in the data set. Simulations with 1% dispersion did not have such obvious indications of the problem, and the algorithm exhibited results in compliance with the simulated lineshape to within 1%. Since the affects due to large amounts of dispersion were not observed in the data set it is assumed that the experimental spectral dispersion is less than 1% and does not contribute to any systematic error.

The concurrent analysis of the weaker isotopomer H^{37}Cl transition is another, independent, check of these potential problems since the instrumental parameters are necessarily different at this frequency. No differences in derived broadening parameters could be discerned for the two isotopomers. The line shift parameters are $\sim 10\%$ higher. However, this parameter is difficult to measure for the H^{35}Cl isotopomer and the value for the weaker isotopomer is less precise.

With these tests it is reasonable to believe that significant systematic errors contributing to the reported pressure broadening parameters have been addressed. The difficulty in measuring a small lineshift parameter is outlined. Considering these difficulties, the precision of the nitrogen and oxygen lineshift parameters ($1\sigma \leq 3 \text{ kHz/Torr}$), given from the data fits are quite striking, and deemed

Table 2

Half-width parameters (MHz/Torr) for HCl in N₂ and air from this and other studies

Ref.	$\Gamma(\text{N}_2)$	$\Gamma(\text{air})$	Temp. (K)	Method	ν'
Ref. [5]	4.10(10)		298	TuFIR	0
Ref. [7]	3.83(3)		296	FTIR	0
Ref. [6]	3.41(2)	3.29(3)	298	TuFIR	0
This work ^a	3.64(4)	3.42(4)	296	Multiplier	0
Ref. [4] ^b	3.78(4)	3.52(4)	296	FTIR	1
This work ^a	4.77(15)	4.51(13)	202	Multiplier	0
Ref. [4] ^b	4.75(28)	4.58(26)	202	FTIR	1

^a $\Gamma(T) = \gamma_o(296/T)^n$, $\Delta\Gamma(T)$ see Ref. [10].

^bThese values represent the average of the $R(0)$ and $P(1)$ values reported in Ref. [4].

optimistic. Since the error analyses indicate that the shift parameters are more susceptible to systematic errors it is recommended that 3σ error bars be used on these values (27% for air at 180 K).

A comparison of the present and pertinent previous results on nitrogen and air broadening of $J = 1 \leftarrow 0$ HCl are given in Table 2. The N₂ broadening parameter is in best agreement with the $J = 0 \leftarrow 1$ and $1 \leftarrow 0$ transitions of the fundamental vibrational transition. At room temperature the error bars for both N₂ and air overlap at the 2σ level, at 202 K the agreement is within 1σ . The discrepancies between the submillimeter studies (TuFIR, FTIR and present) reflect a gradual improvement of the technology available for studying this spectral region and the importance of simple and comprehensive treatment of the data. The original TuFIR study, which reports results 6.5–15% higher for individual hyperfine components, obtained significantly different results (at the 1σ level) for each component, a result not supported by the present analysis. Furthermore, these TuFIR 1σ error bars (of the individual components) are an order of magnitude larger than the present work. The more recent TuFIR analysis also treats each line independently, however, the error bar for the reported average value is much smaller than the previous TuFIR work, indicating better agreement with the present assumption that the lines broaden equivalently. The broadening parameter from this study is significantly different than this work, requiring 4σ for each parameter to overlap. The 1σ error bar of 0.6% in this study seems optimistic, and is likely to reflect the precision of the experiment, and not necessarily the accuracy. The FIR-FTIR study incorporates infrared techniques for data reduction, and the results are 5% higher than the present N₂ broadening parameter, the present result and this study overlap at the 3σ level. In this study the analysis required fixing the self-broadening coefficient, a potential source for systematic error in the reported foreign gas broadening parameter. All previous studies require the use of an instrument function that incorporates the affect of modulation/apodization on the lineshape. One of the strengths of the convolution method is the removal of these potential error sources from the analysis model.

5. Conclusion

This paper has presented a comprehensive analysis of the N₂ and O₂ pressure-induced lineshapes of HCl for the $J = 1 \leftarrow 0$ submillimeter rotational transition. The improved accuracy will facilitate

the study of HCl in the Earth's stratosphere and upper troposphere. The work allows computation of air broadening parameters accurate to $< 4.1\%$ at the 2σ level. This work provides indication of a pressure shift, a shift that is well pronounced in O_2 , and still important in N_2 and air. Consistent values for the lineshape parameters were obtained for the nearby transition at 624,950 MHz of the $H^{37}Cl$ isotopomer.

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