Measurements of Line Strength and Line Shape Parameters of the HCl R3 (0-2) 5739.263 cm$^{-1}$ and the HF R1 (0-2) 7823.820 cm$^{-1}$ Transitions

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Abstract. Line strengths and line shape parameters have been measured for a single absorption transition of both hydrogen chloride and hydrogen fluoride gases. These parameters were determined from spectral absorbance measurements over a range of temperatures and pressures using single-mode laser diodes as the laser sources. The measured parameters are compared to values reported in scientific literature. Significant differences are observed that will impact spectroscopic measurements of species concentrations, temperature, and pressure.

1. Introduction

Laser diode absorption spectroscopy is a powerful nonintrusive diagnostic technique for gas phase systems. It is often used to measure species concentrations, temperatures, and velocities in high-temperature, harsh, or otherwise inaccessible environments [1-4]. In order to minimize the uncertainties in the measured quantities, accurate line shape parameters are required. For this paper, the interest is in measuring concentrations of hydrogen chloride (HCl) and hydrogen fluoride (HF). This paper presents a methodology to determine the line shape parameters for these two molecular species.

Single-mode laser diodes typically have a spectral line width that is several orders of magnitude smaller than the width of a measured absorption line. Hence, the measured absorption profile is an accurate representation of the actual line shape with no need to deconvolve the laser line width from the spectral line shape. The line shapes are modeled as Voigt profiles. Voigt profiles contain both Doppler (temperature) and Lorentzian (pressure) broadening effects. The absorption model assumes that the line strength and pressure broadening parameters are well known. These parameters are available in the HITRAN database [5]. However, the uncertainties of the tabulated parameters are usually not well known.

This paper describes the research efforts to validate the HITRAN parameters for single absorption transitions of HCl [R3 (0-2), 5739.263 cm$^{-1}$] and HF [R1 (0-2), 7823.820 cm$^{-1}$] and presents the results of the measured values of line strength and pressure broadened line shape parameters. Low concentration HCl and HF gas, on the order of parts per million (ppm), was introduced into a temperature and pressure controlled absorption cell and interrogated using collimated laser diode beams. The resulting absorption profiles were collected and analyzed to determine the targeted line shape parameters. The measured line shape parameters were then compared to the values listed in the HITRAN database.
2. Laser absorption diagnostics

The fundamental equation for absorption spectroscopy is the Beer-Lambert Law [6]. The Beer-Lambert relation gives the transmitted radiation intensity, \( I(\omega) \), of a collimated beam of light after passing through some homogeneous absorptive medium as

\[
I(\omega) = I_0(\omega) \cdot e^{-\kappa(\omega,P,T,\chi)},
\]

where \( I_0(\omega) \) is the incident radiation intensity, \( \kappa(\omega,P,T,\chi) \) is the spectral absorbance, \( \omega \) is the optical frequency, \( P \) is the pressure, \( T \) is the temperature, and \( \chi \) is the mole fraction of the absorbing species. Rearranging equation (1), the spectral absorbance is expressed as:

\[
\kappa(\omega,P,T,\chi) = -\ln \left( \frac{I(\omega)}{I_0(\omega)} \right).
\]

Figure 1 (a) shows a notional absorption profile, Eq. (1), and (b) an absorbance profile, Eq. (2).

For a single molecular transition, the absorbance can be expressed as

\[
\kappa(\omega,P,T,\chi) = S^0(T) \chi N(T,P) L \Phi(T,P),
\]

where \( S^0(T) \) is the line strength, \( N(T,P) \) is the total number density, \( L \) is the optical path length, and \( \Phi(T,P) \) is the line shape function. A Voigt profile is used as the line shape function in this work. The Voigt profile is the convolution of a Doppler-broadened line shape and a pressure (or Lorentz)-broadened line shape and is given as

\[
\Phi(T,P) = \frac{a \sqrt{\ln 2}}{\pi^{3/2} \gamma_D} \int_{-\infty}^{\infty} \frac{e^{-y^2}}{a^2 + (x-y)^2} dy,
\]
where

\[
a = \frac{\gamma_L}{\gamma_D} \sqrt{\ln 2} \quad \text{and} \quad x = \frac{\omega - \omega_0}{\gamma_D} \sqrt{\ln 2}.
\]

Here, \(\gamma_D\) is the Doppler-broadened line half-width at half maximum (HWHM), \(\gamma_L\) is the Lorentz-broadened line HWHM, and \(\omega_0\) is the optical frequency at the absorption line center or peak. The Doppler HWHM is given as

\[
\gamma_D(T) = \frac{\omega_0}{c} \sqrt{\frac{2kT}{m}} = 3.58 \times 10^{-7} \omega_0 \sqrt{\frac{T}{M}},
\]

where \(c\) is the speed of light, \(k\) is the Boltzmann constant, \(m\) is the molecular mass, and \(M\) is the molecular weight.

The Lorentz HWHM is an empirical value given by

\[
\gamma_L(P, T, \chi) = \gamma_{\text{air}}(T_0) \left(\frac{T_0}{T}\right)^\eta P(1 - \chi) + \gamma_{\text{self}}(T_0) \left(\frac{T_0}{T}\right)^\eta P \chi,
\]

where \(\gamma_{\text{air}}(T_0)\) is the air-broadened HWHM in cm\(^{-1}/\)atm. at the reference temperature \(T_0\) and \(\gamma_{\text{self}}(T_0)\) is the self-broadened HWHM cm\(^{-1}/\)atm. at the reference temperature \(T_0\). \(\gamma_{\text{air}}, \gamma_{\text{self}}, \) and \(\eta\) are constants and are available in the HITRAN database. The reference temperature used for the HITRAN database is 296 K. For this work, \(\chi\) is on the order of parts per million and equation (5) is approximated as

\[
\gamma_L(P, T) \approx \gamma_{\text{air}}(T_0) \left(\frac{T_0}{T}\right)^\eta P.
\]

For analysis purposes, it is convenient to calculate the integrated absorbance \((A)\) using equation (3)

\[
A = \int_{-\infty}^{\infty} \kappa(\omega, P, T, \chi) d\nu = S^0(T) \chi N(T, P)L
\]

since by definition the integrated Voigt profile is equal to unity.

Equation (7) can also be written as

\[
A = S^0(T) \Theta(T, P),
\]

where \(\Theta(T, P)\) is referred to as the column density. The line strength is a function of temperature only and can be expressed as

\[
S^0(T) = S^0(T_0) f(T),
\]

where the constant \(S^0(T_0)\) is the line strength at the reference temperature \(T_0\). The temperature correction factor is given by
\[ f(T) = \frac{Q(T_0)}{Q(T)} \frac{1 - \exp \left( -\frac{hc \omega_0}{kT} \right)}{1 - \exp \left( -\frac{hc \omega_0}{kT_0} \right)} \exp \left( -\frac{hc}{k} \left( \frac{1}{T} - \frac{1}{T_0} \right) E'' \right), \]

where \( E'' \) is the lower energy state, \( Q(T) \) is the molecular partition function at temperature \( T \), and \( h \) is the Planck constant. Combining Eqs. (8) and (9) yields

\[ A = S^0(T_0)f(T)\Theta(T, P). \quad (10) \]

3. Experimental approach

The quantities tabulated in the HITRAN database that are measured during this effort are as follows:

- \( S^0(T_0) \), the line strength at \( T_0 \);
- \( \gamma_{\text{air}}^0(T_0) \), the air-broadened HWHM at one atmosphere pressure and \( T_0 \);
- \( \eta \), the coefficient of temperature dependence of the air-broadened HWHM.

Line strength is determined from the integrated absorbance, equation (10). \( \gamma_{\text{air}}^0(T_0) \) and \( \eta \) are determined from a linearized version of equation (6). A detailed description of the analysis process is given in Section 4.

Examination of equations (6) and (10) reveals that absorption data are needed over a range of temperatures and pressures in order to accurately determine these three parameters. An absorption cell was constructed that allowed independent control over the temperature and pressure. A schematic of the equipment setup is shown in Figure 2.

[Figure 2. Schematic of the experimental arrangement.]
The calibration gases were introduced into a temperature-controlled absorption cell. A vacuum pump and a needle valve on the downstream side of the absorption cell were used to control the flow rate of the calibration gas. A needle valve on the upstream side of the absorption cell was used to control the pressure by creating a critical orifice and choking the flow. The absorption cell consisted of a stainless-steel tube sealed with windows on both ends. The fiber-coupled beam from the laser diode was routed to the absorption cell and directed through the calibration gas sample using a collimator. A pair of mirrors was used to create a multipass optical arrangement. The laser beam was then coupled into a second optical fiber and directed to a photodiode. The photodiode output signal was recorded on the computer hard disk along with the temperature and pressure of the calibration gas measured inside the calibration cell.

At each temperature set point, the pressure was adjusted to the desired value and the flow rate was minimized to increase the calibration gas dwell time in the absorption cell. Each data point was recorded when the temperature of the calibration gas inside the absorption cell had stabilized.

4. Data analysis and results

Absorption data were acquired at various concentrations, path lengths, temperatures, and pressures for both HCl and HF. The spectral data were curve fit with the Voigt profile and a polynomial background for \( I_0(\omega) \) to obtain the integrated absorbance, the Lorentz HWHM, and the column density.

4.1. Line strength determination

From Equation (10), the integrated absorbance results can be expressed as

\[
A_i = S^0(T_0) f(T_i) \Theta(T_i, P_i)
\]

where the subscript \( i \) indicates each unique temperature, pressure, and mole fraction data point in the test matrix. When \( A_i \) is plotted against \( f(T_i) \Theta(T_i, P_i) \) the resulting slope is equal to the reference line strength \( S^0(T_0) \).

Figure 3 shows a plot of Equation (11) for the HF data acquired during this effort along with the linear fit to the data. The line resulting from the line strength in the HITRAN 2012 database is also shown for comparison. The line strength value from our measurements is \( 6.79 \times 10^{-20} \) as compared to the HITRAN value of \( 7.62 \times 10^{-20} \). The measured value is 10% lower than the HITRAN value.

![Figure 3. Plot of HF integrated absorbance vs. \( f(T)\Theta(T, P) \).](image-url)
4.2. Lorentz HWHM scaling parameters determination

From Equation (6), the Lorentz HWHM can be expressed as

\[ \gamma_i(P_i, T_i) = \gamma_{air}^0 \left( \frac{T_0}{T_i} \right)^\eta P_i. \quad (12) \]

Taking the logarithm of equation (12) yields

\[ \log(\gamma_i) - \log(P_i) = \log(\gamma_{air}^0) + \eta \log\left( \frac{T_0}{T_i} \right), \quad (13) \]

which is a linear equation where \( \eta \) is the slope and \( \ln(\gamma_{air}^0) \) is the intercept.

Figure 4 shows a plot of equation (13) for the HF data acquired during this effort and the resulting straight line fit. The inferred Lorentz line parameters are shown in Figures 5 and 6. Figure 5 shows the HF temperature-corrected Lorentz HWHM from equation (12) plotted as a function of pressure. Also shown in Figure 5 is the temperature-corrected Lorentz HWHM predicted using HITRAN tabulated values for \( \eta \) and \( \gamma_{air}^0 \). The measured value of \( \gamma_{air}^0 \) is 0.098 compared to the HITRAN value of 0.085. The measured value is 15% higher than the HITRAN value.

Figure 6 shows the pressure-corrected Lorentz HWHM vs. temperature ratio. Also shown in Figure 6 is the predicted value using HITRAN parameters. The measured value for \( \eta \) is 0.65. The HITRAN value is 0.50. The measured value is 30% higher than the HITRAN value.

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**Figure 4.** Plot of equation (13) for the HF absorption data analyzed during this effort.
4.3. Results summary

This analysis process was repeated for HCl with similar results. A summary of the results for both gases is shown in Table 1. The differences between our measured values and the values retrieved from the HITRAN database varies from 10 to 45%. These difference have a significant impact on the measured mole fractions and on the properties inferred from line shape, such as temperature and pressure.
Table 1. Comparison of measure line shape parameters and values listed in the HITRAN database.

| Species | Parameter | Units                  | Measured Value | HITRAN Value | Difference |
|---------|-----------|------------------------|----------------|--------------|------------|
| HF      | $S^0(T_0)$ | molecules·cm⁻¹·cm⁻²    | 6.81x10⁻²⁰     | 7.62x10⁻²⁰   | 11%        |
| HF      | $\gamma^0_{air}(T_0)$ | cm⁻¹·atm | 0.098         | 0.085        | 15%        |
| HF      | $\eta$    | –                      | 0.65           | 0.5          | 30%        |
| HCl     | $S^0(T_0)$ | molecules·cm⁻¹·cm⁻²    | 1.37x10⁻²⁰     | 1.25x10⁻²⁰   | 10%        |
| HCl     | $\gamma^0_{air}(T_0)$ | cm⁻¹·atm | 0.0833        | 0.0574       | 45%        |
| HCl     | $\eta$    | –                      | 0.622          | 0.566        | 10%        |

5. Summary and conclusion
HF and HCl line strengths and line shape parameters have been experimentally measured over a range of temperatures and pressures. Significant differences between the measured parameters and the parameters listed in the HITRAN database have been noted. The differences between our measured values and the values retrieved from the HITRAN database vary from 10 to 45%. These differences have a significant impact on the measured mole fractions and on the properties inferred from line shapes, such as temperature and pressure.

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Distribution A: Approved for public release; distribution is unlimited.

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