Technical Project 1-Numerical Methods

Technical report submitted to

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from

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1 Introduction

In this project, we used smoothing method to improve the experimentally obtained curves by eliminating background noises. This helps to determine the various factors associated with the data and the overall improvement of the data. Here we use the least square fit to smoothen the experimental values by modeling them to a lorentz function. The least squares method is a mathematical technique used to find the best-fitting curve or function that minimizes the sum of squared differences between observed data points and the predicted values from the model.

The least squares method involves minimizing the sum of the squares of the vertical deviations (residuals) between the observed data points (y_i) and the corresponding values predicted by the model ($f(x_i)$), given by the formula $\sum_{i=1}^{n}(y_i - f(x_i))^2$. Here, n represents the number of data points, y_i denotes the observed values, x_i represents the independent variable values, and $f(x_i)$ is the model's prediction at each x_i. The goal is to determine the parameters of the model that best describe the relationship between the variables by minimizing this sum of squared differences.Here, the squared error is the difference between the intensity of the data point at a given frequency and the intensity of the Lorentz function at the same frequency.

2 Theoritical Description

The spectral lines are modeled by Lorentz Function. The choice of the Lorentzian function for modeling spectral lines finds its foundation in its ability to accurately represent physical phenomena associated with the spectral lines. Spectral lines often exhibit broadened shapes due to natural broadening mechanisms. The Lorentzian function elegantly captures this broadening effect. Its mathematical form, characterized by a symmetric, bell-shaped curve, closely resembles many experimental spectral lines, facilitating analytical calculations and fitting procedures. Moreover, the Lorentzian function's parameters, like peak position, width, and amplitude, directly correspond to pertinent physical properties, offering insights into the underlying processes generating the observed spectral lines. Consequently, due to its alignment with natural broadening, resonance behaviors, mathematical symmetry, and interpretability, the Lorentzian function stands as a favored choice for modeling and interpreting spectral lines. The intensity $F(\omega)$ at the wavenumber ω is given by:

$$F(\omega) = \frac{S}{\pi} \cdot \frac{\gamma}{(\omega - \omega_m)^2 + \gamma^2}$$

where γ is the half-width at half-height, ω_m is the wavenumber of the maximum intensity, and $S = \int_{-\infty}^{\infty} F(\omega)\, d\omega$ represents the integral intensity of the spectral line over all wavenumbers. The equation describes the profile of the spectral line, with ω_m indicating the peak position and γ governing the width of the spectral line, exhibiting a Lorentzian-like shape.

We will deal with 5 different data files recorded for the same spectral line at various pressures. The file contains the experimental value of the lorentz function, $F^{exp}(\omega)$ corresponding to the $\omega = 2280cm^{-1}$ and going up $0.01cm^{-1}$. The aim was to determine the characteristic parameters of the spectral line (S, γ, ω_m) using the least square's method. We notice that the problem reduces to a simple parabolic regression if we use the inverse of the function instead of the function($F^{-1}(\omega)$). The inverse of the function is:

$$F^{-1}(\omega) = \frac{\pi}{S\gamma}\omega^2 - \frac{2\pi\omega_m}{S\gamma}\omega + \frac{\pi(\omega_m^2 + \gamma^2)}{S\gamma}$$

Now, instead of using the ω values directly, we use the reduced parameter x, as the original values are very large.

$$x = \frac{\omega - \bar{\omega}}{\sigma}$$

Where

$\bar{\omega}$ = mean of the wavenumbers

σ = standard deviation of the wavenumbers

So, the new equation with the reduced varaible becomes:

$$F^{-1}(x) = \frac{\pi\sigma^2}{S\gamma}x^2 + \frac{2\pi\sigma}{S\gamma}(\omega - \omega_m) + \frac{\pi}{S\gamma}\{\gamma^2 + (\bar{\omega} - \omega_m^2)\}$$

Now, to minimize the coeffiecients, we use

$$E(a_0, a_1, a_2) = \sum_{i=1}^{N} W_i(a_2x_i^2 + a_1x_i + a_0 - y_i)^2$$

$$\begin{pmatrix} \sum W_i & \sum W_i \cdot x_i & \sum W_i \cdot x_i^2 \\ \sum W_i \cdot x_i & \sum W_i \cdot x_i^2 & \sum \cdot W_i \cdot x_i^3 \\ \sum W_i \cdot x_i^2 & \sum W_i \cdot x_i^3 & \sum W_i \cdot x_i^4 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} \sum W_i \cdot y_i \\ \sum W_i \cdot y_i \cdot x_i \\ \sum W_i \cdot y_i \cdot x_i^2 \end{pmatrix}$$

Now, we can obtain the values of a_0, a_1, and a_2 by solving this matrix equation. Using these values, we can calculate:

$$\omega_m = \overline{\omega} - \frac{\sigma \cdot a_1}{2 \cdot a_2} \quad (9)$$

$$\gamma = \sigma \cdot \sqrt{\frac{a_0}{a_2} - \frac{a_1^2}{4a_2^2}} \quad (10)$$

$$S = \frac{\pi \cdot \sigma}{\sqrt{a_0a_2 - \frac{a_1^2}{4}}}1$$

We will calculate both the weighted and unweighted theoretical functions from the calculated values and then plot them against to the experimental values. The weight function used throughout the project is $W_i = (F_i^{exp})^2$

We will also plot the various peak frequencies obtained for different pressures as well as the line widths(γ).

$$\omega_m = \omega_0 + p\Delta\omega \text{ and } \gamma = p\gamma_1$$

From these equations we will find the position corresponding to zero pressure (ω_0), shift coefficient($\Delta\omega$) and the broadning coefficient(γ_1).

3 Computational Results

TABLE 1: S, γ and ω_m values for all pressures

	Unweighted			Weighted		
Pressure	S	γ	ω_m	S	γ	ω_m
1 atm	27.892	0.219	2282.645	30.436	0.200	2282.645
3 atm	30.464	0.597	2282.943	30.602	0.600	2282.945
6 atm	30.423	1.196	2283.378	30.681	1.207	2283.381
10 atm	30.450	2.005	2283.958	30.867	2.023	2283.965
15 atm	30.468	3.011	2284.692	31.044	3.060	2284.704

The table 1 contains the value of the parameters for both weighted and the unweighted functions.These values of the characteristics of the spectral line.

Plots obtained for various pressure values for the modeling of the spectra with the Lorentz function.

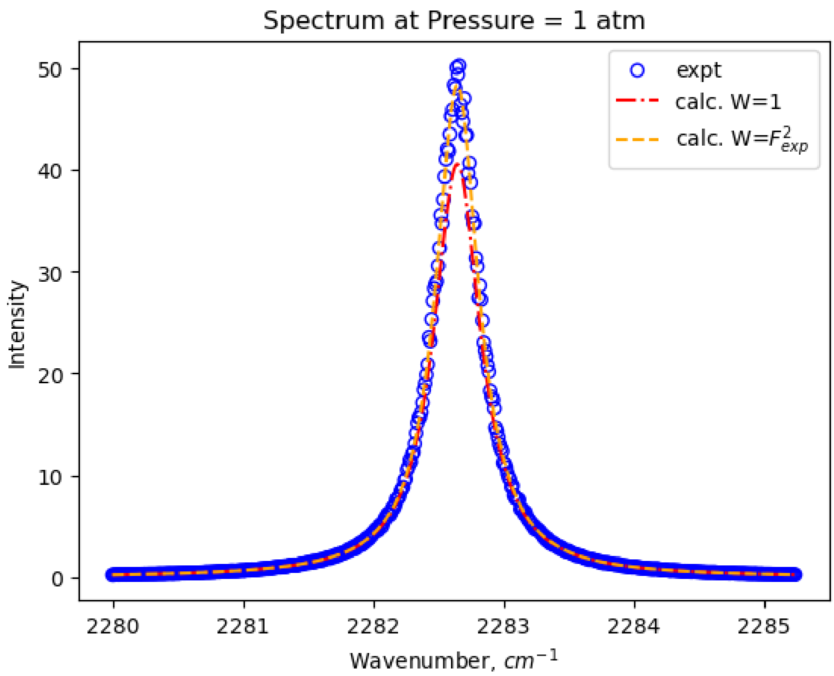

FIGURE 1: Comparison of smoothed line intensities obtained with two different weight functions $W_i = 1$ and $W_i = (F_i^{exp})^2$ with the experimental intensities for $P = 1atm$.

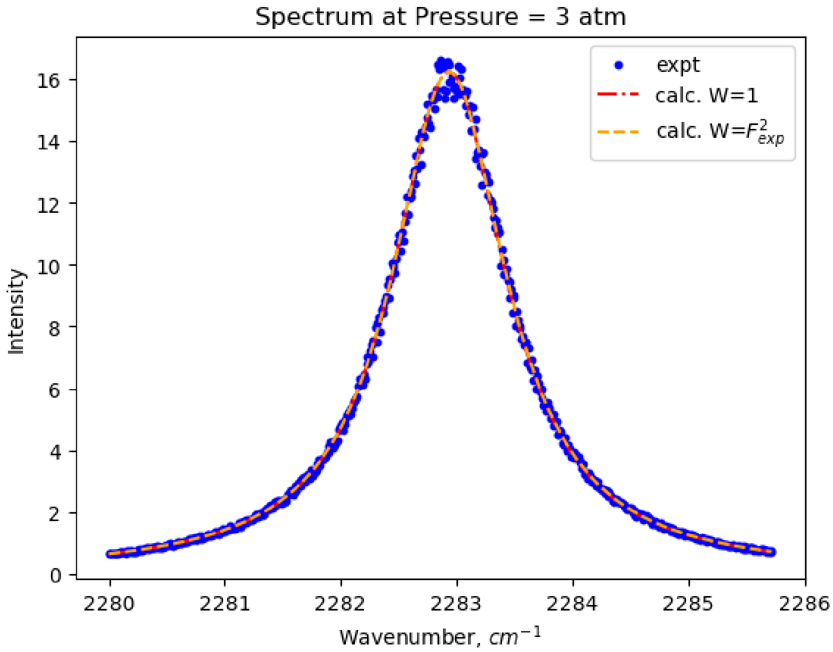

FIGURE 2: Comparison of smoothed line intensities obtained with two different weight functions $W_i = 1$ and $W_i = (F_i^{exp})^2$ with the experimental intensities for $P = 3atm$.

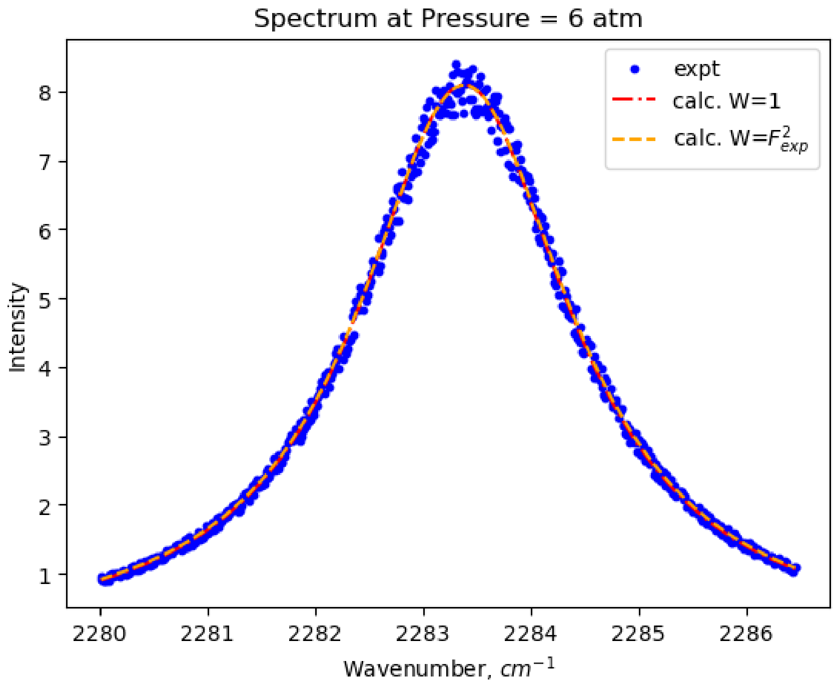

FIGURE 3: Comparison of smoothed line intensities obtained with two different weight functions $W_i = 1$ and $W_i = (F_i^{exp})^2$ with the experimental intensities for $P = 6atm$.

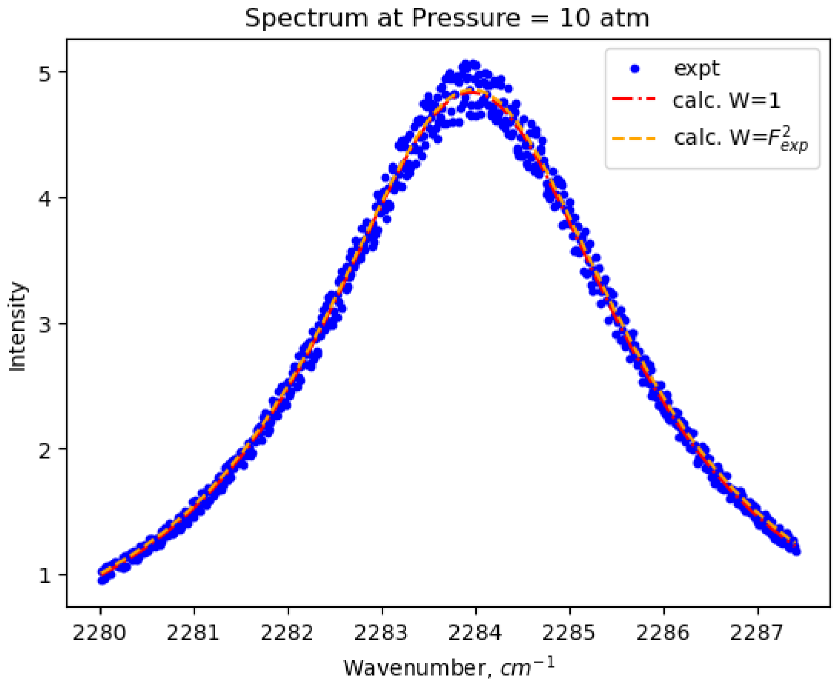

FIGURE 4: Comparison of smoothed line intensities obtained with two different weight functions $W_i = 1$ and $W_i = (F_i^{exp})^2$ with the experimental intensities for $P = 10atm$.

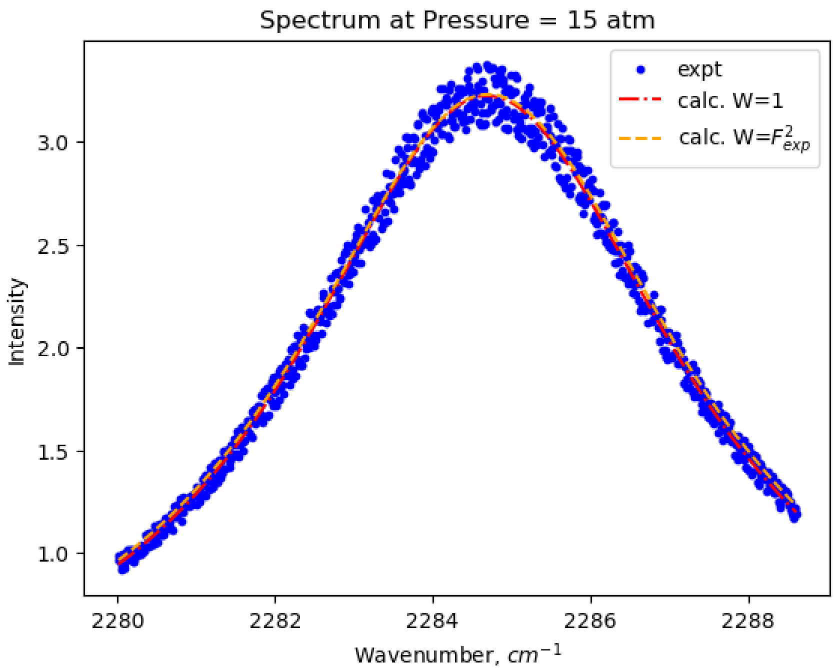

FIGURE 5: Comparison of smoothed line intensities obtained with two different weight functions $W_i = 1$ and $W_i = (F_i^{exp})^2$ with the experimental intensities for $P = 15atm$.

After plotting the intensities, we perform linear regression to the find the values of the position corresponding to zero pressure (ω_0), shift coefficient($\Delta\omega$) and the broadening coefficient(γ_1).

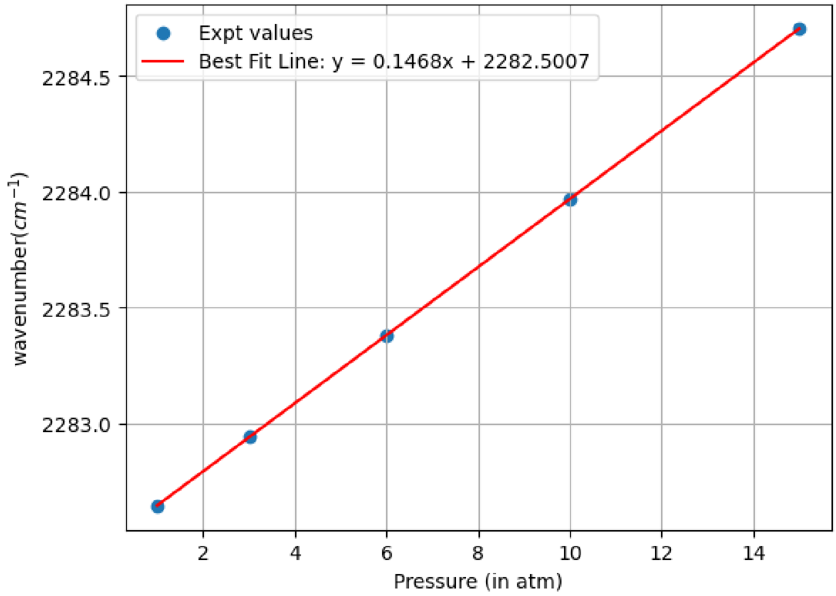

FIGURE 6: Variation of peak wavenumber ω_m with pressure P

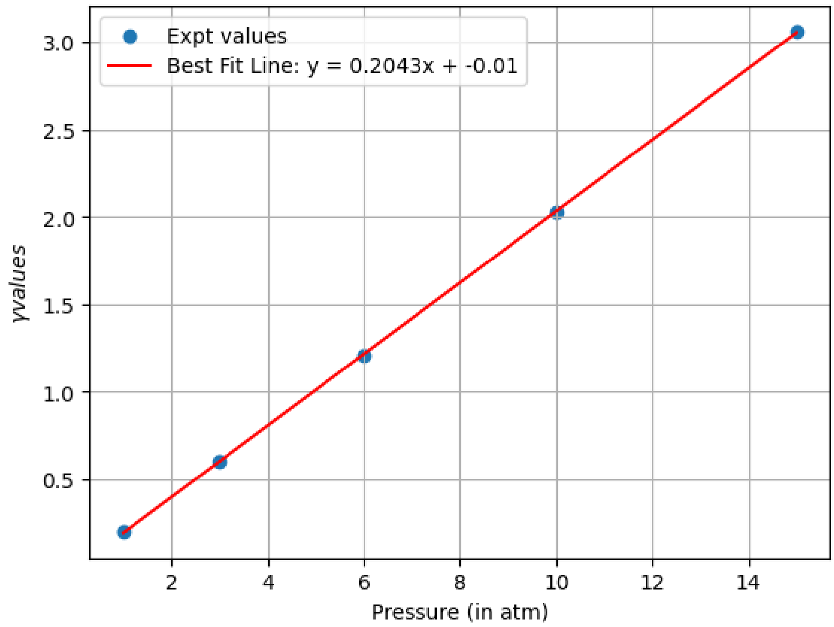

FIGURE 7: Variation of broadening coefficient γ_1 with pressure P

From the figures given above, it can be seen that $\omega_0 = 2282.500$ and $\Delta\omega = 0.1468$. Again, it is evident from the linear fit of the curve that the value of the broadening coefficient $\gamma_1 = 0.2043$.

4 Conclusion

In the project, we used the least square method to model a lorentz function onto the experimental data of the spectral line recorded at various pressures and found the values for the half width, broadening coefficient and the maximal wavenumber. These are the characteristics of a spectral line and can help us in understanding the underlying physical processes giving the observed spectra. To acheive our goals, we used the files provided to us containing the experimental values of the Intensities and then calculated both unweighted and weighted theoritical value of the intensity using the lorentz function and finally plotted them together to visualize all the results and calculate the various parameters.