PRACTICAL WORK N° 1

Smoothing spectra by least-squares fits

Smoothing is used to improve the experimentally obtained curves via elimination of the "background" noise introduced by the measurement errors or by the instrument itself. This approach allows determining the parameters of a function going through the experimental points or, at least, near them.

From the general point of view, it means replacing a "cloud" of N points $\{x_i, y_i\}$ by a function $f(\{a_k\}, x)$, where $\{a_k\}$ denote a set of parameters. The least squares method consists of determining these parameters by minimizing the sum of the squared deviations

$$E(\{a_k\}) = \sum_{i=1}^{N} W_i \quad \left(f(\{a_k\}, \quad x_i) - y_i\right)^2$$

with a given weight function W. In the particular case where we can choose

$$f(\{a_k\}, \quad x) = \sum_k a_k f_k(x) \quad ,$$

this method leads to solve a system of linear equations for $\{a_k\}$, the set of functions $f_k(x)$ is supposed to be known. In particular, the polynomial regression consists to take as $f_k(x)$ a polynomial of a given power of x.

1. Application to determination of spectral line shapes

Frequently, the shape of spectral lines corresponds to a Lorentz function: the intensity $F(\omega)$ at the wavenumber ω is given by

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

where $S = \int_{-\infty}^{+\infty} d\omega\, F(\omega)$ is the integral intensity of the spectral line, ω_m is the wavenumber of the maximum and γ is the half-width at half-height.

For the present Practical Work, 5 files containing data for the same spectral line recorded at various gas pressures (1, 3, 6, 10 and 15 atmospheres) are provided. Each file contains solely one column with the experimental values $F^{\exp}(\omega)$ corresponding to a grid on ω starting from 2280 cm^{-1} and going to higher values with a constant step equal to 0.01 cm^{-1} (number of lines is to be evaluated by yourself).

The aim is to determine, for each given pressure, the characteristics of the spectral line (the parameters S, γ and ω_m) using the least-squares method. We can also note that for the case of a Lorentzian spectral line the calculation can be reduced to a system of linear equations is we adjust $F^{-1}(\omega)$ instead of $F(\omega)$. In fact, the problem is reduced to a simple parabolic regression. For these calculations the weight function is to be taken as constant ($W_i = 1$).

2. Improving the numerical approach

The numerical difficulty appearing in this problem is due to the fact that the experimental data are noisy and with the use of $F^{-1}(\omega)$ instead of $F(\omega)$ we give too much importance to the points where $F(\omega)$ is small (in the spectral wings). We can believe therefore that the use of the experimental values $\left(F^{\exp}(\omega)\right)^2$ as the weight function should greatly improve the determination of the parameters of the Lorentzian line.

It is advised to plot on the same figure (at least, for the first spectrum at 1 atm) the experimental intensities and the theoretical ones (calculated with the parameters S, γ and ω_m) corresponding to both the constant weight function $W_i = 1$ and the improved weight function $W_i = \left(F_i^{\exp}\right)^2$, as it is done on Fig. 1 below. For the other pressures, it will be sufficient to put on the figures only the experimental points and the improved theoretical curve.

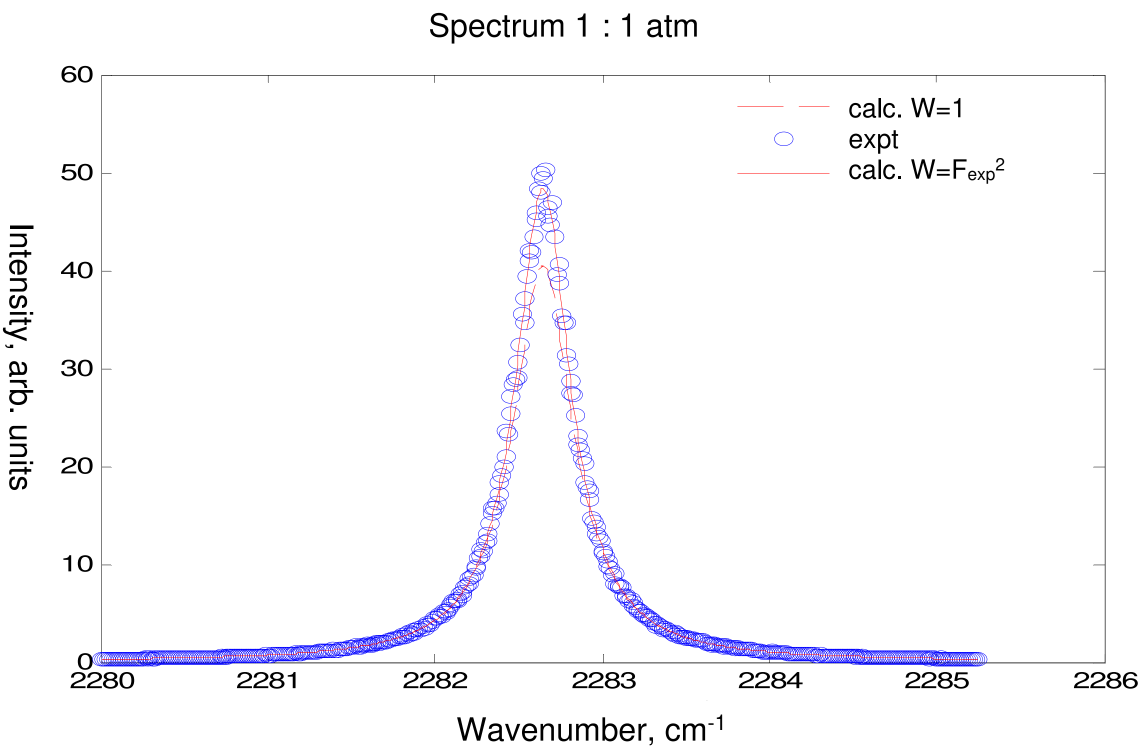

Figure 1. Comparison of smoothed line intensities obtained with two different weight functions W_i=1 and $W_i = \left(F_i^{\exp}\right)^2$ with the experimental intensities used for fits.

3. Dependence of line shape on pressure

It is well known that the position of the maximum and the line width are characterized by a linear dependence on pressure:

$$\omega_m = \omega_0 + p\,\Delta\omega \quad \text{and} \quad \gamma = p\,\gamma_1 \; .$$

Therefore, performing a linear regression of the maximum positions plotted in function of pressure we can obtain the position corresponding to the zero pressure ω_0 (wavenumber corresponding to the transition in the isolated molecule) and the shift coefficient $\Delta\omega$. Similarly, the linear regression of the line widths plotted in function of pressure allows getting the broadening coefficient γ_1 (please note that, as it should be, the width is zero at zero pressure).