

THERMO NO-LIF
Publish Version 1.0
user guide

Kae Ken Foo

July 21, 2020

© 2020 Kae Ken Foo

All rights reserved

Univ. Lille, CNRS, UMR 8522 - PC2A - Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France.

First edition:	12 May 2020
Second edition:	29 June 2020
Third edition	16 July 2020

Introduction

Laser-induced fluorescence (LIF) is a laser based technique generally applied to probe the relative populations of individual quantum states of species within isothermal or reacting flows. The principle of LIF is rather simple. It requires a tunable laser which has access to the wavelengths required to excite the target species. When the spectral envelope of the laser overlaps with one of the many absorption lines of the species, the molecules or atoms will go into excitation states and subsequently emit fluorescence. Recording the fluorescence intensity as a function of wavelength, so called "excitation spectrum", reflects the relative populations of different states, which are temperature dependent as given by a Boltzmann distribution. If we assume the probed species has a relatively constant concentration, the LIF signal can be assumed, to a good approximation, a function of temperature only.

The Boltzmann plot method is widely used to extract temperature information from LIF excitation spectra. The following is a description of the principle of the Boltzmann plot method, directly quoting Ohno et al. [2006]:

Let us consider two energy levels, E_i (lower level) and E_j (upper level), of two different line intensities with respective atomic densities of N_i and N_j . Under the thermal equilibrium condition, the relation between N_i and N_j can be established using the Boltzmann distribution:

$$\frac{N_j}{N_i} = \frac{g_j}{g_i} \cdot \exp \left[-\frac{E_j - E_i}{k_B \cdot T} \right], \quad (1)$$

where g_i and g_j are the statistical weights of the respective states, k_B is the Boltzmann constant, and T is the temperature in K. If the total population density is N_0 , the Boltzmann relation applicable to the population distribution over a certain state is given by

$$\frac{N_j}{N_i} = \frac{g_j}{Z(T)} \cdot \exp \left[-\frac{E_j - E_i}{k_B \cdot T} \right], \quad (2)$$

where $Z(T)$ is the sum of the weighted Boltzmann function of all the discrete energy levels, which is called the partition function:

$$Z(T) = \sum_m g_m \cdot \exp \left[-\frac{E_m}{k_B \cdot T} \right]. \quad (3)$$

Now, when the excited species is de-excited from the upper energy level E_j to lower energy level E_i , the emission coefficient of the spectral line can be expressed by:

$$\epsilon_{ji} = \frac{h \cdot c_0}{4 \cdot \pi \cdot \lambda_{ji}} \cdot A_{ji} \cdot N_j, \quad (4)$$

where λ_{ji} is the wavelength of the emitted fluorescence, h is the Planck's constant, c_0 is the light speed in vacuum, and A_{ji} is the transition probability (the probability of a particle in excited state j spontaneously emits light in a random direction and is de-excited to state i per second). Putting Eq.4 in Eq.2 and rearranging them gives

$$\frac{\epsilon_{ji} \cdot \lambda_{ji}}{A_{ji} \cdot g_j} = \frac{h \cdot c_0 \cdot N_0}{4 \cdot \pi \cdot Z(T)} \cdot \exp \left[-\frac{E_j}{k_B \cdot T} \right]. \quad (5)$$

Taking the logarithm in both sides of Eq.5 gives

$$\ln \frac{\epsilon_{ji} \cdot \lambda_{ji}}{A_{ji} \cdot g_j} = -\frac{E_j}{k_B \cdot T} + C, \quad (6)$$

where C is a constant. Now, plotting Eq.6 with E_j in the x-axis and $\ln(\epsilon_{ji} \cdot \lambda_{ji} / (A_{ji} \cdot g_j))$ in the y-axis will result in a straight line, and the temperature can be determined from the slope. A Boltzmann plot is straightforward and insightful as any deviations from the linear slope can be easily spotted. However, the deviations are usually the results of uncertainties arise from the determination of fluorescence intensities.

In case where the required accuracy of temperature measurements is higher than the Boltzmann plot method can offer, temperature determination can be achieved through fitting the LIF excitation spectrum. Rensberger et al. [1989] compare the experimental spectrum to a synthesised spectrum and varying the fit parameters (temperature and Gaussian linewidth) to minimise the sum of the squares of the residuals. Bessler et al. [2003] created LIFSim, a software tool that allows to simulate absorption and LIF spectra (excitation and emission) for NO and O₂, to fit experimental spectra. **Thermo NO-LIF** was developed using MATLAB R2019a App Designer. The purpose of the software is similar to that of LIFSim, to synthesise NO-LIF excitation spectra and determine temperature through a direct fitting algorithm and the Boltzmann plot method. The following sections describes each function in details and an user guide.

Tab: File conversion

Thermo NO-LIF processes LIF excitation spectra in wavenumber (cm^{-1}). The file conversion function allows user to convert their experimental spectra into a format suitable for **Thermo NO-LIF**. The input LIF excitation spectrum files can be in either wavelength (nm) or wavenumber (cm^{-1}). User is to select the column numbers of **wavelength/wavenumber**, **LIF signal** and **laser fluctuation** in their files. The last one is optional, it is requested to reduce the jitter in the **LIF signal** caused by shot-to-shot variations in the laser energy. The process also allows users to shift the entire spectrum accordingly, to better match the theoretical line positions. Users can specify the prefix and suffix for the output files. The file conversion can process files in batch through multi-select.

Figure 1 presents a screenshot of the file conversion tab in **Thermo NO-LIF**. To convert the file, users are advised to follow the procedures:

1. Select “File conversion” tab.
2. Press “Input file(s)” and select the file(s) needed to convert.
3. Select the spectral unit used in the input file(s).
4. Specify the column numbers correspond to the wavelength/wavenumber, LIF signal and laser energy (optional; enter 0 if no such information).
5. Enter a value to adjust the experimental spectrum so that it matches better with its theoretical counterpart.
6. Enter a prefix or/and a suffix to distinguish the input and output file(s).
7. Select a directory where the output file(s) would be saved.
8. Press “Execute” to begin the process. The button will change to “Done” when the conversion is complete.

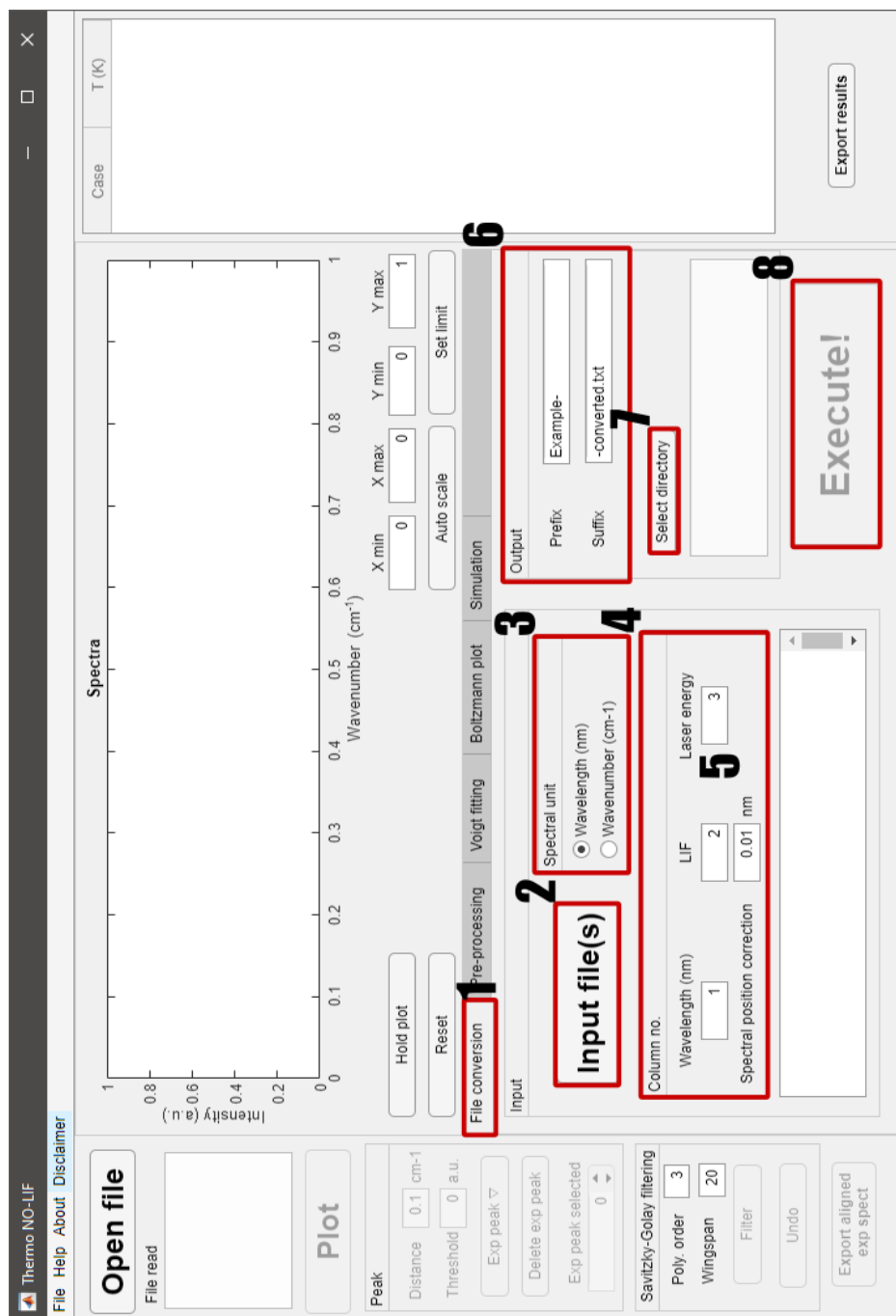


Figure 1: Screenshot of the file conversion tab in Thermo NO-LIF.

Tab: Pre-processing

It is well documented that the experimental spectrum as it is obtained is not linear in wavelength Rensberger et al. [1989], Bessler and Schulz [2004]. It is evident when comparing the experimental spectrum with its synthesised counterpart. The spectral positions of experimental LIF peaks do not align with the known line positions. This misalignment is caused by the stepping motor rotating a grating sine bar to drive the laser tuning system. Here, users can adjust the spectral position of the experimental LIF peaks, so that they are as close to the theoretical line positions as possible. Users are required to select the peaks using a MATLAB function, `peakseek.m` by Peter O'Connor. The function searches all the peaks within an array. Users are required to specify the minimum peak separation (in data points) and a threshold for peak height. Users can also delete peaks that are misidentified. However, users cannot add peak manually.

Selected experimental LIF peaks are compared to peaks identified in a synthesised spectrum, that has all the aspects as close to the experimental spectrum as possible. To generate the synthesised spectrum, users are required to specify either the `instrumental linewidth`, `temperature`, `pressure` and `collisional coefficient` or the `Voigt linewidth`, `Lorentzian factor` and `temperature`. Once users have selected the same amount of experimental and synthesised peaks, **Thermo NO-LIF** adjusts the experimental spectrum according to the synthesised peaks.

Figures 2 and 3 show the before and after screenshot of aligning an experimental spectrum against its synthesised counterpart. The procedure can be broken down into several steps:

1. Select “Pre-processing” tab.
2. Press “Open file” and select the experimental spectrum for input.
3. Plot the experimental spectrum by pressing “Plot”.
4. Enter appropriate values for “Distance” and “Threshold”, which represents the minimum distance between two peaks and the minimum intensity to be considered as peaks.
5. Press “Exp peak ∇ ”.
6. Extra peaks can be deleted using “Exp peak selected” and “Delete exp peak”.
7. Enter the best guess of spectral parameters. Select either “Temperature/Pressure” or “Linewidth/Lorentzian”.

8. Start and finish wavenumbers are pre-filled when users plot the experimental spectrum. However, due to the uncertainty in the laser tuning system, users might want to adjust the “Start” and “Finish” wavenumber to match the experimental spectrum.
9. Plot the synthesised spectrum by pressing “Simulation plot”.
10. Users can hide or show the synthesised plot using the slide.
11. Enter appropriate values for “Distance” and “Threshold”.
12. Press “Sim peak Δ ”.
13. Extra peaks can be deleted using “Sim peak selected” and “Delete sim peak”.
14. Once user has the same amount of peaks in the experimental and synthesised spectra, press “Align”.
15. Confirm the experimental spectrum matches the synthesised spectrum. Press “Export aligned exp spect” to save the realigned experimental spectrum.

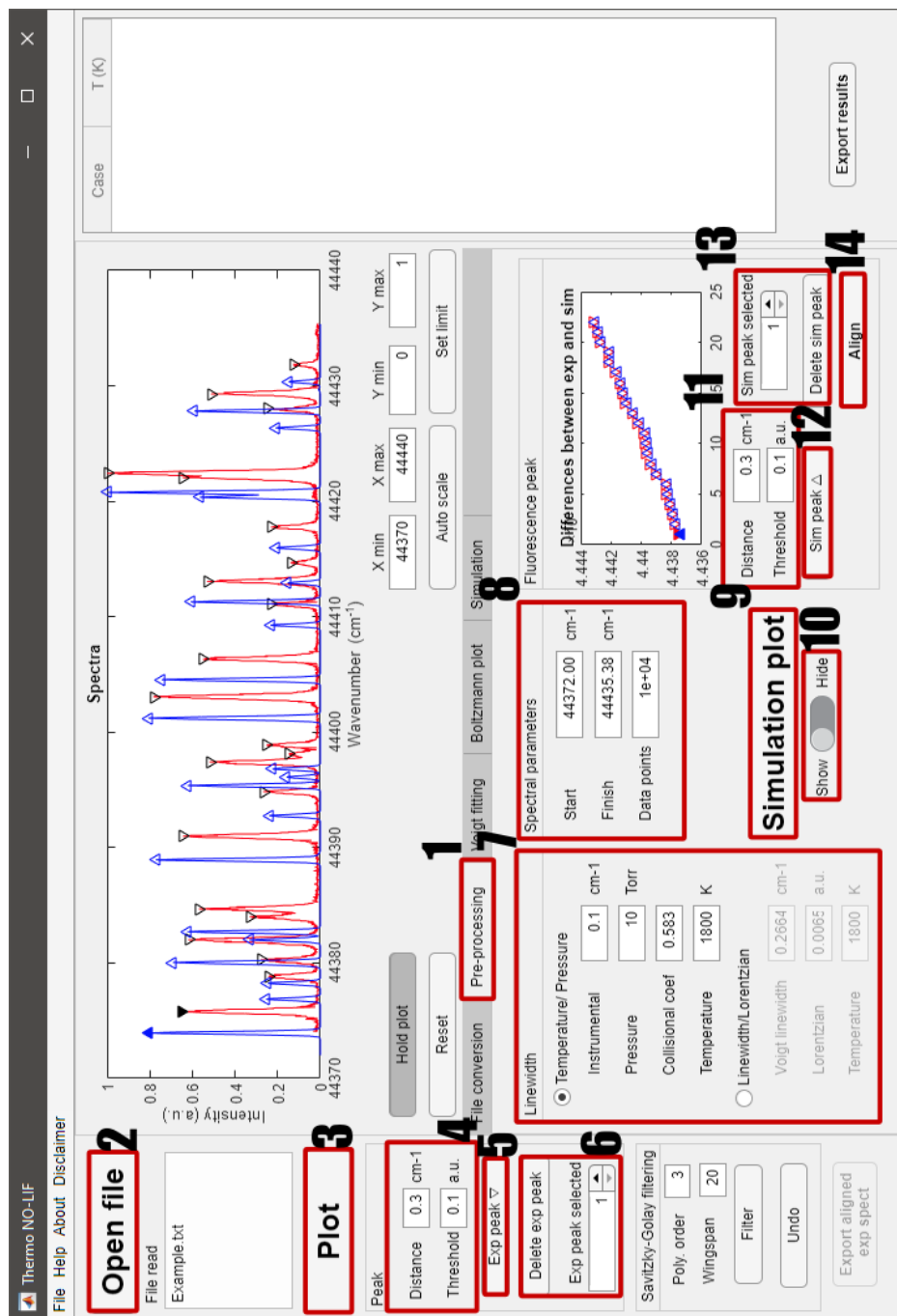


Figure 2: Screenshot of the pre-processing tab in **Thermo NO-LIF**. Blue is experimental spectrum; red is synthesised spectrum. Before the alignment.

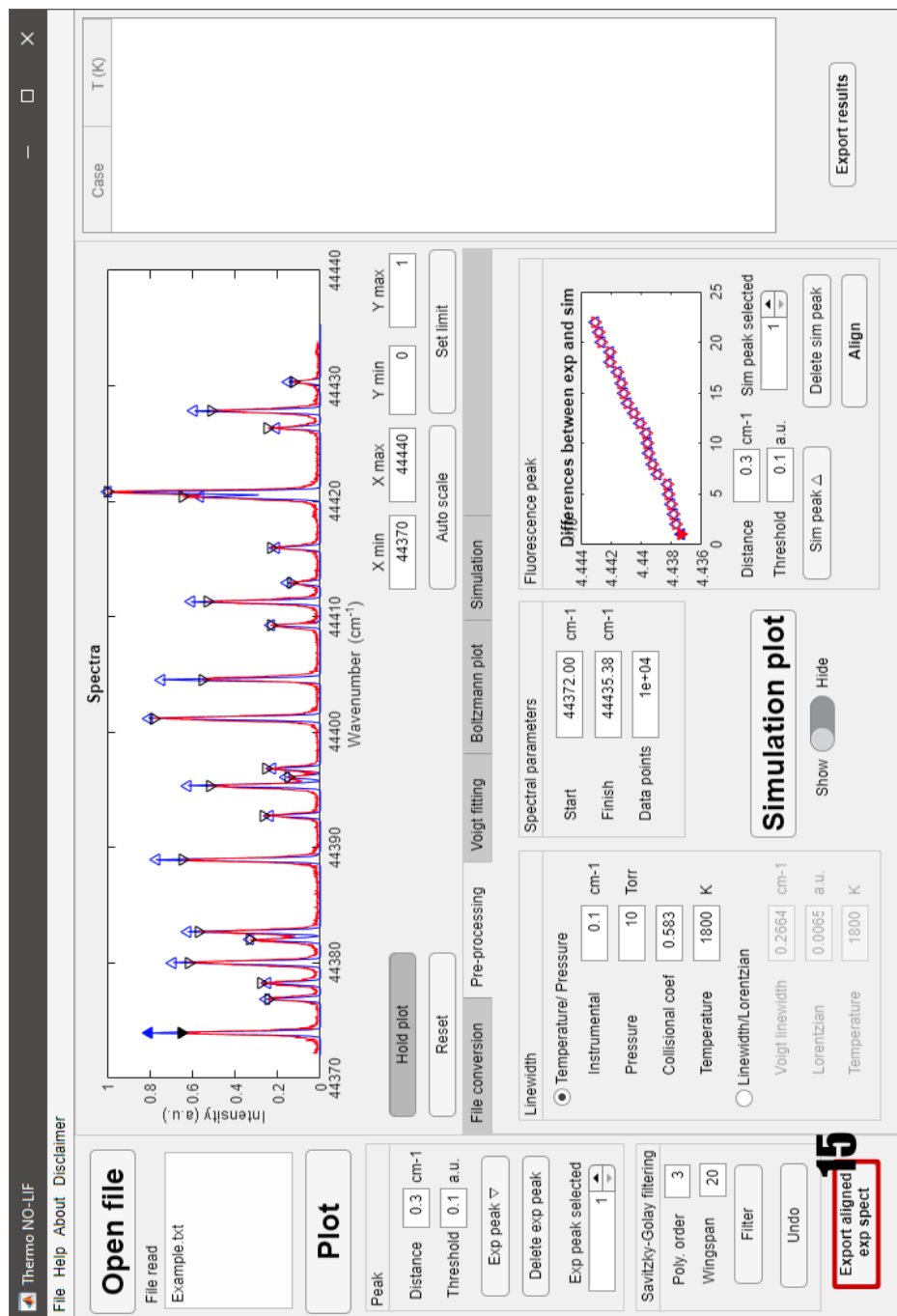


Figure 3: Screenshot of the pre-processing tab in **Thermo NO-LIF**. Blue is experimental spectrum; red is synthesised spectrum. After the alignment.

Tab: Voigt fitting

This is the procedure where temperature information is derived from an experimental LIF spectrum. It automatically fits the experimental LIF spectrum to an equation that describes the LIF intensity together with the convolution of the instrumental lineshape and the absorption lineshape. However, because the experimental LIF spectrum is introduced in normalised form, the equation must be divided by a normalise term so that the fluorescence intensities of both experimental and estimated LIF spectra are in the same order of magnitude. To circumvent the issue, **Thermo NO-LIF** constructs a library of synthesised LIF spectra, extracts the maximum intensity within the spectral range at each temperature and fit the maximum intensity as a function of temperature to a Fourier series with eight terms.

To construct the library of synthesised LIF spectra, **Thermo NO-LIF** fits an experimental spectrum to a pseudo-Voigt lineshape function (linear combination of Gaussian and Lorentzian function) without considering the spectroscopic parameters:

$$V(\nu, \Gamma) = \cdot G(\nu, \Gamma) \otimes L(\nu, \Gamma), \quad (7)$$

$G(\nu, \Gamma)$ is the Gaussian function

$$G(\nu, \Gamma) = \exp \left[-4 \cdot \ln 2 \cdot \left(\frac{\nu - \hat{\nu}}{\Gamma} \right)^2 \right] \quad (8)$$

and $L(\nu, \Gamma)$ is the Lorentzian function

$$L(\nu, \Gamma) = \left[1 + 4 \cdot \left(\frac{\nu - \hat{\nu}}{\Gamma} \right)^2 \right]^{-1}. \quad (9)$$

Here, ν is wavenumber in unit $[\text{cm}^{-1}]$, $\hat{\nu}$ is the spectral position of the peak intensity obtained from LIFBASE (Luque and Crosley [1999]), Γ is the full-width at half maximum (FWHM).

Substituting Eqs. 8 and 9 into Eq. 7 gives

$$V_p(\nu, \Gamma) = (1 - \eta) \cdot \exp \left[-4 \cdot \ln 2 \cdot \left(\frac{\nu - \hat{\nu}}{\Gamma} \right)^2 \right] + \eta \cdot \left[1 + 4 \cdot \left(\frac{\nu - \hat{\nu}}{\Gamma} \right)^2 \right]^{-1}, \quad (10)$$

This provides an approximation accurate to $\sim 1\%$.

After constructing a library of synthesised spectra, **Thermo NO-LIF** identifies the maximum peak in the experimental spectrum which is used to trace

the evolution of the theoretical fluorescence peak within the same spectral range from 200 to 3000 K. This step is essential because, theoretically, the maximum fluorescence peak within a certain range is not always the same transition at every temperature. With this information, **Thermo NO-LIF** fit the experimental spectrum again, considering the spectroscopic parameters normalised by the temperature-dependent maximum fluorescence peak it just acquired.

The LIF intensity, I_i , of the i^{th} transition can be characterised as follows:

$$I_i \propto N_0 \cdot I_L \cdot g_\nu \cdot B_i \cdot f_{Bi} \cdot \frac{A_i}{\sum_i A_i + k_p + k_q} \quad (11)$$

where I_L is the incident laser intensity, N_0 is the total number density, f_{Bi} is the Boltzmann fraction of the initial level, B_i is the Einstein absorption coefficient obtained from LIFBASE (Luque and Crosley [1999]) and g_ν represents the spectral overlap of the laser profile and the absorption line. The last term is to describe the fluorescence quantum yield which depends on the Einstein emission coefficient A_i divided by the sum of A_i over all vibrational states plus predissociation rate k_p and quenching rate k_q . This equation is only valid if the I_L is maintained in the linear LIF regime.

A few modifications are required to simplify Eq 11. Firstly, N_0 is omitted in the following equations because the total number density of NO within the measured volume is assumed to be constant throughout the measurement. Secondly, the fluorescence quantum yield of NO is neglected since it is independent of the rotational number. Lastly, f_{Bi} can be expressed as a function of T :

$$f_{Bi} = \frac{(2J_i + 1)}{Q_{vib} \cdot Q_{rot} \cdot Q_{elec}} \cdot e^{-\frac{E_i}{k_B \cdot T}} \quad (12)$$

where $(2J_i + 1)$ is the degeneracy of the rotational state and J_i is the rotational quantum number of lower state of i^{th} transition. The energy of the rotational state, E_i is calculated following the equations and molecular constants given by Gillette and Eyster [1939]. Q_{vib} , Q_{rot} and Q_{elec} are the vibrational, rotational and electronic partitions calculated numerically. As a result, Eq. (11) can be reduced to

$$I_i \propto I_L \cdot g_\nu \cdot B_i \cdot \frac{(2J_i + 1)}{Q_{vib} \cdot Q_{rot} \cdot Q_{elec}} \cdot e^{-\frac{E_i}{k_B \cdot T}}. \quad (13)$$

Here, I_L can be normalised through dividing the LIF excitation spectrum using the temporal energy profile of the incident laser.

By combining Eqs. (13) and (10) with a constant background c , the synthesised spectrum $S(\nu)$ can be expressed as:

$$S(\nu) = c + \sum_i B_i \cdot \frac{(2J_i + 1)}{Q_{vib} \cdot Q_{rot} \cdot Q_{elec}} \cdot e^{-\frac{E_i}{k_B \cdot T}} \cdot \left((1 - \eta) \cdot \exp \left[-4 \cdot \ln 2 \cdot \left(\frac{\nu - \hat{\nu}}{\Gamma} \right)^2 \right] + \eta \cdot \left[1 + 4 \cdot \left(\frac{\nu - \hat{\nu}}{\Gamma} \right)^2 \right]^{-1} \right). \quad (14)$$

Here, B_i , J_i , E_i , Q_{vib} , Q_{rot} and Q_{elec} are spectroscopic properties, which are available in the literature for NO. As a result, the fitting parameters are T , η , Γ , $\hat{\nu}$ and c . It is necessary to fit $\hat{\nu}$ because, as aforementioned, the spectral positions of experimental and simulated transitions do not match. **Thermo NO-LIF** allows a tolerance of $\pm 0.2 \text{ cm}^{-1}$ for $\hat{\nu}$.

Both the experimental spectrum and Eq. (14) must be normalised to unity to perform the fitting process. The conventional way to normalise a spectrum is to divide the total spectrum with the maximum intensity. However, it is impossible to obtain the maximum intensity without constructing the whole spectrum. Hence, Eq. (14) is required to be divided with a temperature-dependent normalisation term. One of the approaches is to construct a library of simulated spectra that has the same spectral range as the examined experimental spectrum. Then, it extracts the maximum theoretical fluorescence intensity, corresponding to the experimental ones, as a function of temperature. The non-linear function is fitted with a Fourier series.

To use the Voigt fitting function is quite simple:

1. Select “Voigt fitting” tab.
2. Press “Open file” and select the pre-processed experimental spectrum for input.
3. Plot the experimental spectrum by pressing “Plot”.
4. Input the fitting parameters, initial guesses and criteria.
5. Press “Voigt fitting” and wait....
6. The results are shown in this box with **Temperature** at the very bottom.

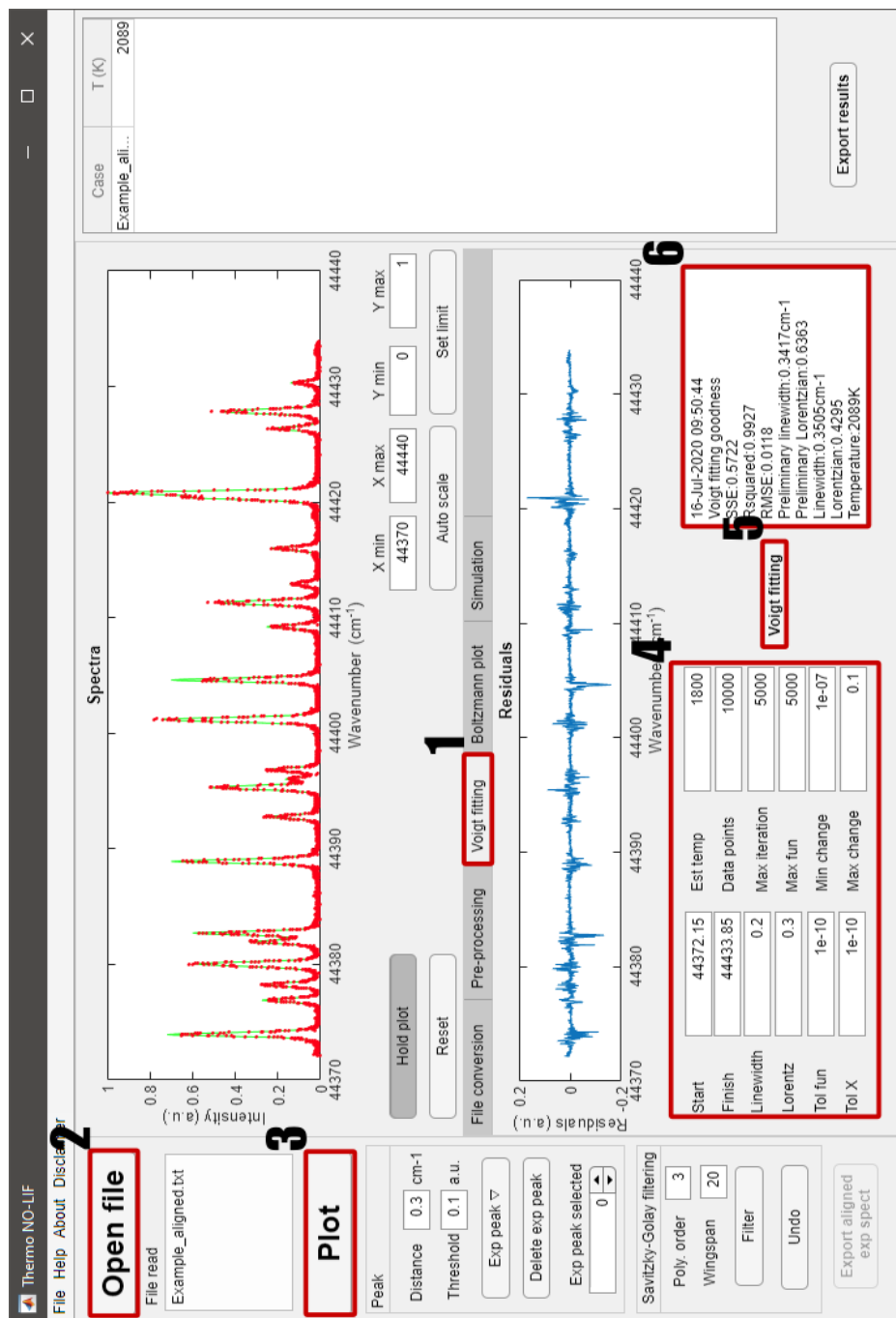


Figure 4: Screenshot of the Voigt fitting tab in **Thermo NO-LIF**. Blue is experimental spectrum; green is the best-fitted spectrum.

Tab: Boltzmann

The principle of the Boltzmann's plot method is described in Chapter . A simple walk-through is given below:

1. Select "File", "Work directory" to specify where the experimental spectra are stored.
2. Select "File", "Output directory" to specify where the results will be saved. The default directory is C:/Users/Public/Documents.
3. Select "Boltzmann plot" tab.
4. Press "Open file" and select the pre-processed experimental spectrum for input.
5. Plot the experimental spectrum by pressing "Plot".
6. Select the peaks. This step is essential.
7. Press "Line identification".
8. The transitions identified within the experimental spectrum are shown. BEWARE: **Thermo NO-LIF** only identifies the lines which are visible in the experimental spectrum.
ATTENTION: The degeneracy ($2J+1$) only takes into account the significant transition.
OR: Avoid doublet or triplet lines that have different degeneracies.
9. The lines are shown in this box. Users can select the line(s) and the corresponding peak(s) will be highlighted in the main plot. The selection also used to construct the Boltzmann's plot.
10. Press "Boltzmann".
11. OPTIONAL: The outlier helps user to identify any deviation from the linear plot.
12. The Boltzmann's plot is shown. The red dash-lines represent the \pm outlier threshold.
13. The **Temperature** is shown here.
14. The table is editable. User can customise the name of each case. Press "Export results" to export the results.

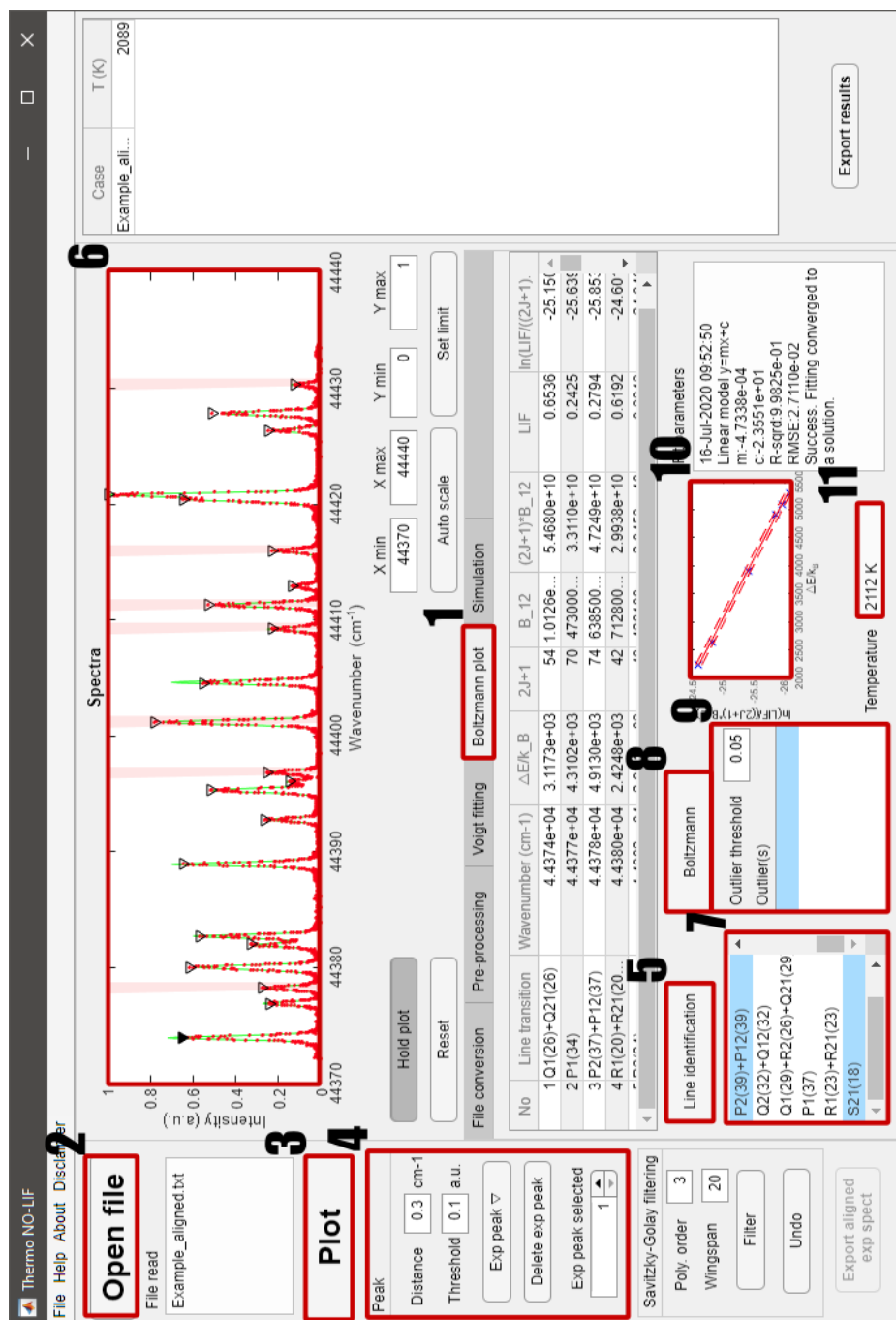


Figure 5: Screenshot of the Boltzmann tab in Thermo NO-LIF.

Simulation

Thermo NO-LIF can generate a library of synthesised LIF excitation spectra of NO A-X(0,0) band at any pressure and temperature. Or the user can specify the FWHM and Lorentzian factor. Please follow the following step to construct the library:

1. Select “Simulation” tab.
2. Select the desired spectral range.
3. Select the desired temperature range.
4. Select the desired temperature and pressure condition.
OR: Select the desired FWHM and Lorentzian factor.
5. Select the output folder and file name. Press “Generate”.

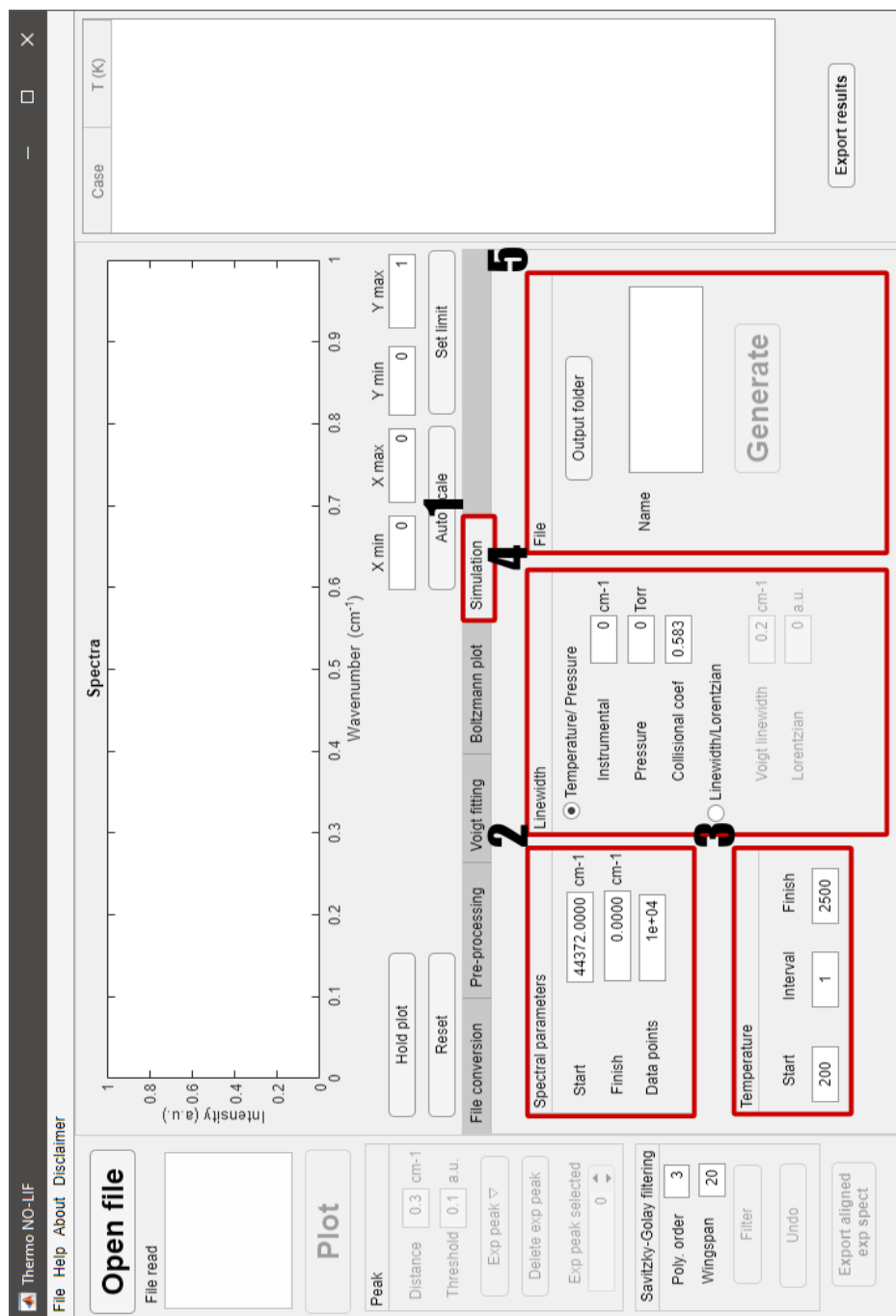


Figure 6: Screenshot of the Simulation tab in Thermo NO-LIF.

Bibliography

- W. Bessler and C. Schulz. Quantitative multi-line NO-LIF temperature imaging. *Applied Physics B*, 78:519–533, 2004.
- W. Bessler, C. Schulz, V. Sick, and J. Daily. A versatile modeling tool for nitric oxide LIF spectra. *Proceedings of the Third Joint Meeting of the U.S. Sections of The Combustion Institute*, 2003.
- R. Gillette and E. H. Eyster. The fundamental rotation-vibration band of nitric oxide. *Physical Review*, 56:1113–1119, 1939.
- J. Luque and D. R. Crosley. Lifbase: Database and spectral simulation program (version 1.5). *SRI international report MP*, 99(009), 1999.
- N. Ohno, M. A. Razzak, H. Ukai, S. Takamura, and Y. Uesugi. Validity of electron temperature measurement by using Boltzmann plot method in radio frequency inductive discharge in the atmospheric pressure range. *Plasma and Fusion Research: Regular Articles*, 1:028, 2006.
- K. J. Rensberger, J. B. Jeffries, R. A. Copeland, K. Kohse-Höinghaus, M. L. Wise, and D. R. Crosley. Laser-induced fluorescence determination of temperatures in low pressure flames. *Applied Optics*, 28:3556–3566, 1989.