PLEfit2D

Fitting 2D Fluorescence-Excitation Spectra of Single-Walled Carbon Nanotubes

User's Guide

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Contents

1 Introduction

Due to the one-to-one correspondence between the chiral structure of a single-wall carbon nanotube (SWCNT) and its optically excited states, two-dimensional (2D) fluorescence-excitation (PLE) spectroscopy is a powerful tool for the analysis of SWCNT samples. Changes in the optical properties of SWCNTs often reveal themselves in PLE maps as shifts in peak positions, peak widening, amplitude changes, etc. These changes can only be consistently and meaningfully quantified by fitting a physically accurate model to the data. This 2D fitting model, as proposed in reference [1], is implemented in a graphical user interface (GUI), named PLEfit2D. This GUI allows for the flexible and accurate fitting of PLE maps of SWCNT samples. Quantitative information about the lineshape and intensity of every chirality present in the sample can also be extracted. The GUI greatly aides the usage of this model, *e.g.* comparison between slices of experimental data and fit can be monitored throughout the fitting process, residual plots can be made and the fit parameters can be extracted and saved in multiple formats.

This document is intended to guide the user through the necessary steps to efficiently fit 2D PLE spectra of CNTs with PLEfit2D. First we describe how PLEfit2D needs to be installed and thereafter a short introduction on the empirical fitting model is provided. The other parts of the manual are dedicated to a thorough description of all functionalities of PLEfit2D. If you would like to use PLEfit2D with minimal background feel free to skip to the quick start tutorial provided at the end of this manual.

2 Installation

The GUI is developed in MATLAB®, but does not require a MATLAB® license to use it. To be able to install the GUI on your computer a Windows PC is required since PLEfit2D does not yet support Mac OS. Please follow the following steps:

- Download the PLEfit2D installer from ... [1]. You have the option to choose between a self-contained installer and a web-based version which is much smaller and hence more portable but requires a stable internet connection.
- Run the installer. This will open a MATLAB® based installation interface with fairly straightforward instructions. In most cases, the installer will first need to install MATLAB® Runtime. This is a standalone set of shared libraries that enables the execution of compiled MATLAB® applications or components without installing MATLAB® itself. Be advised that this installation of MATLAB® Runtime can take some time and requires several gigabytes of free storage space.
- Finish the setup and start PLEfit2D. The first time the application is run a prompt will open, asking the user to select a directory to store temporary files, such as application

states or "snapshots" of the GUI. Be aware that you must have full reading and writing access to the selected folder. The path to the chosen directory can be changed at any time under File > Settings (see Section 10).

- A quick-start tutorial can be found in Section 11.

3 The Empirical Fitting Model

To obtain an accurate fit of the 2D PLE maps, we have developed an empirical fitting model that can nicely reproduce the emission and excitation spectra and as such create a 2D fit function for each chiral structure present in the sample. The fitting model consists of a set of 2D basis functions ($F_i, i \equiv (n,m)$) as described in [1]. The total fitting model is then a linear combination of these individual chirality-dependent contributions:

$$\mathbb{F}\left(E_{\text{em}}, E_{\text{ex}}\right) = \sum_{i}^{N} A_i F_i\left(E_{\text{em}}, E_{\text{ex}}\right) \tag{1}$$

with N the number of chiralities i, E_{em}, E_{ex} the ranges of the PLE map expressed in eV and A_i the chirality-dependent amplitudes. These amplitudes give a relative measure of the chiral abundancies in the sample, though modulated by their PL quantum efficiencies. Additionally, basis functions that correspond to a constant or bilinear background can also be included in the model, see Section 10.

The chirality-dependent 2D basis functions, $F_i(E_{\text{em}}, E_{\text{ex}})$ are obtained from a direct product of an emission lineshape, $M_i(E_{\text{em}})$, and an excitation lineshape $X_i(E_{\text{ex}})$, which are then combined through a direct product to obtain the 2D fit function:

$$F_i\left(E_{\text{em}}, E_{\text{ex}}\right) = M_i(E_{\text{em}}) \otimes X_i(E_{\text{ex}}). \tag{2}$$

In the following sections, the emission and excitation profiles are briefly discussed, while more details can be found in reference [1].

The emission profile

The emission is modeled by a superposition of a main excitonic contribution and (optional) phonon side bands (PSBs). The exciton peak is described by a Voigt lineshape with peak position E_{11}, full-width-at-half-maximum (FWHM) linewidth ϕ_{11} and shape parameter η_{11}. The shape parameter defines the contribution of the Lorentzian (ϕ_{L}) and Gaussian (ϕ_{G}) FWHMs to that of the Voigt lineshape (ϕ_{V}) and is given by $\phi_{\text{L}}/\phi_{11}$. Hence, it takes a value in the interval $[0, 1]$, where 0 corresponds to a fully Gaussian lineshape and 1 to a fully Lorentzian one. In the GUI, you can choose to fit with a Gaussian, Lorentzian or

Voigt lineshape (see Section 8). The FWHM of the Voigt is approximated by the following analytical expression derived by Olivero *et al.* [2],

$$\phi_{\mathrm{V}} = 0.5346\phi_{\mathrm{L}} + \sqrt{0.216598\phi_{\mathrm{L}}^2 + \phi_{\mathrm{G}}^2}. \tag{3}$$

The Voigt profile is implemented through the Faddeeva function by use of the open source C++ code by Steven G. Johnson (with slight modification) with wrapper for MATLAB® [3].

Thus, the excitonic emission lineshape involves **three fit parameters** (E_{11}, ϕ_{11} and η_{11}) **for each chirality**.

Additionally, if observed, optional PSB contributions can also be added to the emission profile. The most important PSBs observed in the emission spectra of individual SWCNTs are the D-band PSB of the K-momentum dark exciton [4], and the radial breathing mode (RBM) PSB [5]. Therefore, we included these PSBs as optional in the emission profile of the SWCNTs. However, when including these for each chiral structure separately, the number of fit parameters would increase drastically (i.e. position, linewidth and amplitude for two different PSBs for each chiral structure). In addition, most of these PSB features are strongly overlapping with excitonic peaks from other chiralities and thus the model easily becomes over-parameterized. To reduce the number of additional fit parameters we make the following assumptions and constraints:

- The linewidth ϕ_{11} (and shape parameter η_{11}) of the PSBs is assumed to be the same as that of the excitonic peak.
- The frequency (ω) of the RBM, and hence the relative position of the corresponding PSB with respect to the excitonic emission of the SWCNTs, can be easily determined by using the empirical equation from Bachilo *et al.* modified for empty sodium deoxycholate (DOC)-coated SWCNTs. [6, 7]

  $$\omega_{\mathrm{RBM}} = \frac{221.8\,\mathrm{cm}^{-1}\,\mathrm{nm}}{d} + 11.2\,\mathrm{cm}^{-1} \tag{4}$$

  with d the diameter of the SWCNT in nm. A good estimation of this diameter can be directly extracted from the PLE maps, by inverting the continuous extension of the empirical relations for the emission and excitation peak positions of empty DOC-coated SWCNTs (see further, Equation 8, Supporting Information of [8] and Reference [1]).
- The PSB in emission related to the D-band optical phonon of the K-momentum dark exciton is positioned at ~ 170 meV of the K-momentum dark exciton and ~ 140 meV below the bright exciton. The K-momentum dark exciton has higher energy than the bright exciton and the energy separation between both is in theory chirality-dependent [4, 9]. To simplify, we use a fixed, chirality-independent energy separation between

the dark and bright excitonic states, which is reasonable as the energy differences are relatively small with respect to the D-band optical phonon itself. The amplitude of the PSB relative to the excitonic emission peak is determined by the exciton-phonon coupling which is known to highly depend on the diameter of the SWCNTs [10]. We therefore included a diameter-dependence of the amplitude of these PSBs (d^β) instead of fitting separate amplitudes for each chirality.

The total emission profile is then composed of a sum of these individual components:

$$\begin{aligned} M_i(E_{\mathrm{em}}) =& V(E_{\mathrm{em}}; E_{11}, \phi_{11}, \eta_{11}) + A_{\mathrm{K},11} \cdot d^\beta \cdot V(E_{\mathrm{em}}; E_{11} - E_{\mathrm{K},11}, \phi_{11}, \eta_{11}) + \\ & A_{\mathrm{RBM}} \cdot d^\beta \cdot V(E_{\mathrm{em}}; E_{11} - E_{\mathrm{RBM}}, \phi_{11}, \eta_{11}) \end{aligned} \tag{5}$$

$A_{\mathrm{K},11}$ and A_{RBM} are respectively the amplitudes of the D-band PSB of the K-momentum dark exciton and the RBM PSB relative to the excitonic emission peak. $E_{\mathrm{K},11}$ is a parameter to determine the position of the D-band PSB compared to the emission peak and will be calculated based on $E_{\mathrm{K},22}$, see further. E_{RBM} is the position of the RBM PSB given by Equation 4 and d is the diameter corresponding with the selected peak position. Each contribution to $M_i(\lambda_{\mathrm{em}})$ is shown in Figure 1a. The full emission profile, then consists of $3N$ fit parameters, with N the number of chiralities. The optional PSBs then add an additional three more parameters, *i.e.* $A_{\mathrm{K},11}$, A_{RBM} and β. See Table 1 for a comprehensive overview of all parameters mentioned above.

The excitation profile

The excitation profile is composed of excitonic, as well as band-to-band transitions (BTBs) and one optional phonon side band. The excitonic excitation profile is modelled by a Voigt lineshape with peak position E_{22}, FWHM linewidth ϕ_{22} and a shape parameter η_{22}. The BTB B_{22} is modeled as a convolution of $1/\sqrt{(|E - E_{22}|)}$ with a Gaussian profile. B_{11} is calculated as $1/\sqrt{(|E - E_{11}|)}$, without convolution because E_{11} is supposed to be located far enough from the region of interest. If this is not the case, PLEfit2D has the option to introduce a fitmask (see Section 6) such that wavelength-ranges not described by the fitting model can be removed, for example the excitation light, (PSBs of) the E_{11} transition or the higher E_{33}, E_{44} transitions.

The D-band PSB of the K-momentum dark exciton in excitation results from the absorption of the incident photon into the nonzero angular momentum dark exciton state by emission of a K-point TO phonon. In excitation, the phonon is located $\sim 170\,\mathrm{meV}$ above this dark exciton and its position can be used to directly obtain the position of the D-band PSB $E_{\mathrm{K},11}$ in the emission spectrum (see Equation 7). The linewidth (and lineshape) is assumed to be the same as that of the excitonic peak and similar as in emission a diameter-dependence of the amplitude of the PSB (d^β) is included.

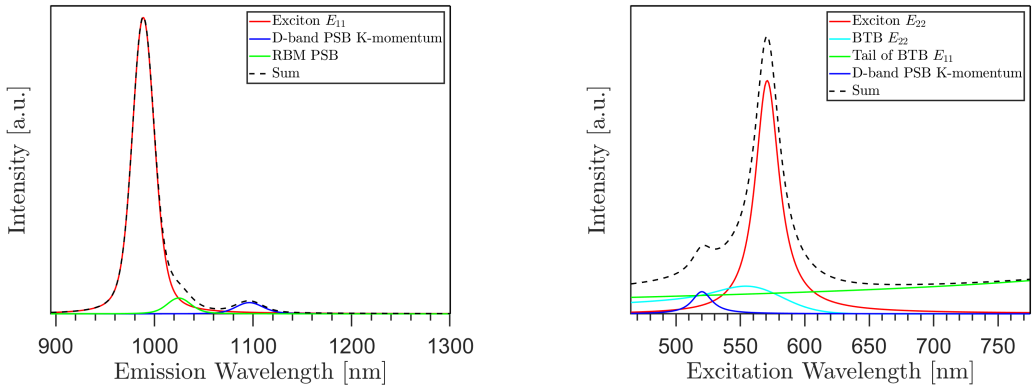

Figure 1: *(a) Emission and (b) excitation spectrum for a (6,5) SWCNT showing all the different contributions.*

The total excitation profile is a sum of these individual components:

$$\begin{aligned} X_i(\lambda_{\mathrm{ex}}) =& V(E_{\mathrm{ex}}; E_{22}, \phi_{22}, \eta_{22}) + A_{22} \cdot B_{22}(E_{\mathrm{ex}}) + A_{11} \cdot B_{11}(E_{\mathrm{ex}}) + \\ & A_{\mathrm{K},22} \cdot d^{\beta} \cdot V(E_{\mathrm{ex}}; E_{22} + E_{\mathrm{K},22}, \phi_{22}, \eta_{22}) \end{aligned} \tag{6}$$

A_{22}, A_{11} and $A_{\mathrm{K},22}$ are the amplitudes of the BTBs and D-band PSB of the K-momentum dark exciton relative to the excitonic excitation peak and $E_{\mathrm{K},22}$ determines the position of the D-band PSB compared to the excitation peak. The position of the D-band PSB $E_{\mathrm{K},11}$ will be determined based on the position of the D-band PSB in excitation $E_{\mathrm{K},22}$. To first approximation the D-band PSBs of the K-momentum dark exciton are symmetric with one optical transition. If the same difference in energy between the dark and bright exciton is considered, then for each SWCNT transition we find [11]:

$$E_{\mathrm{K},11} = 2 \cdot h\nu - E_{\mathrm{K},22} = 2 \cdot 1350\,\mathrm{cm}^{-1} \cdot hc - E_{\mathrm{K},22} \tag{7}$$

with $h\nu$ [eV] the energy of the D-band phonon. The excitation profile can thus be fitted with $3N + 2$ fit parameters, where the optional PSB adds two more fit parameters, *i.e.* $A_{\mathrm{K},22}$ and $E_{\mathrm{K},22}$. All these parameters and a short description can be found in Table 1.

Emission Profile	Description	Excitation Profile	Description
E_{11}	Peak position of the Voigt lineshape for the first optical transition (emission)	E_{22}	Peak position of the Voigt lineshape for the second optical transition (excitation)
ϕ_{11}	FWHM of the Voigt lineshape	ϕ_{22}	FWHM of the Voigt lineshape
η_{11}	Shape parameter of the Voigt lineshape $\phi_{\mathrm{L},11}/\phi_{11}$	η_{22}	Shape parameter of the Voigt lineshape $\phi_{\mathrm{L},22}/\phi_{22}$
A_{RBM}	Amplitude of the RBM PSB	A_{22}	Amplitude of the BTB B_{22} of the second optical transition
E_{RBM}	Position of the RBM PSB, calculated by Equation 4	A_{11}	Amplitude of the BTB B_{11} of the first optical transition
$A_{\mathrm{K},11}$	Amplitude of the D-band PSB of the K-momentum dark exciton	$A_{\mathrm{K},22}$	Amplitude of the D-band PSB of the K-momentum dark exciton
$E_{\mathrm{K},11}$	Position of the D-band PSB, calculated from $E_{\mathrm{K},22}$ (see Equation 7)	$E_{\mathrm{K},22}$	Position of the D-band PSB

Shared Parameters	Description
β	Diameter-dependence of PSB amplitudes

Table 1: *Table containing all model parameters for the emission and excitation profiles. The parameters indicated in blue are calculated internally instead of fitted. Amplitudes in emission and excitation are always relative to the corresponding main exciton peak.*

4 Calibration of the PLE data

Before using the fit program it is important to make sure that the input data is well calibrated. This is of course highly dependent on the experimental setup used to record PLE spectra. Make sure that:

- variations in excitation power at each wavelength are corrected for;
- the spectrum is corrected for spectral efficiency of the detector and spectrograph over the emission range;
- the data is calibrated for any filter or other optics used in the excitation or emission path;
- the spectrum is corrected for possible re-absorption in the sample cell.

5 Overview of the Interface

When starting the program you will see a window as presented in Figure 2, which is divided into four panels and a toolbar:

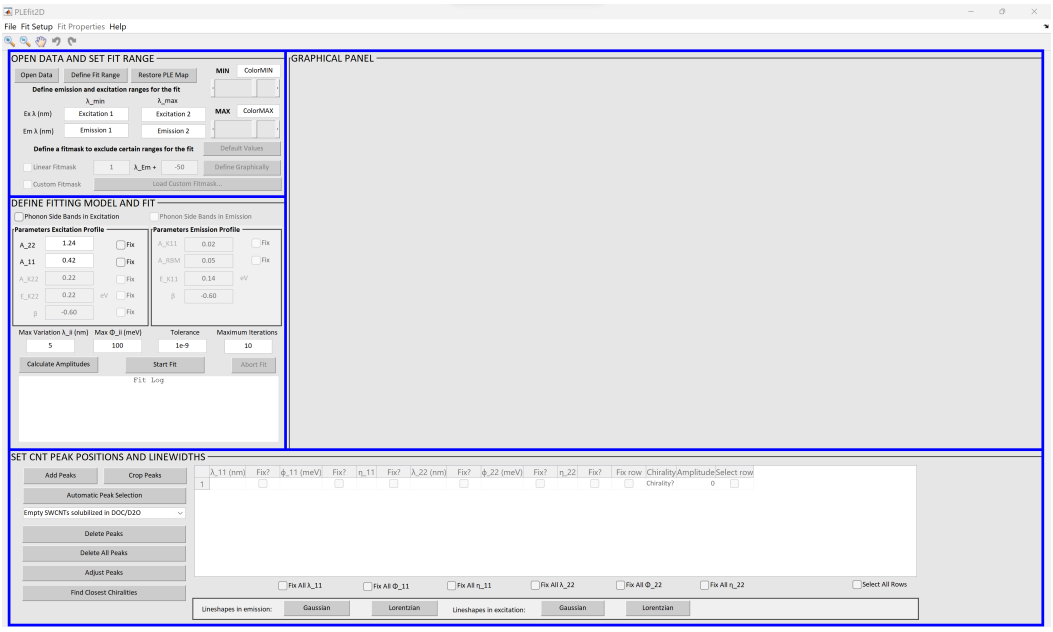

Figure 2: *Overview of the PLEfit2D interface. The interface is divided into four main panels (outlined in blue) plus a toolbar.*

- **Open Data and Set Fit Range**: To load the PLE data and set the range of interest for the fit. Also the fitmask can be controlled in this panel.
- **Define Fitting Model and Fit**: To set and select the fit parameters common for all chiralities.
- **Set CNT Peak Positions and Linewidths**: All the peak positions and the linewidths for the individual SWCNT chiralities can be modified here and optimized values will be returned after fitting. Also predefined peak positions can be loaded here and the specific lineshape (Voigt, Lorentz or Gauss) can be selected.
- **Graphical Panel**: The output of the 2D fit program is visualized and compared with the original data. Slices from the experimental data and fit can be shown.
- **Toolbar**: To load and save the workspace, parameters and figures, as well as to select the fitting algorithm for the amplitudes, a proper background and to enable fitmasks.

Each of these panels will be described in detail in the following sections.

6 Open Data and Set Fit Range

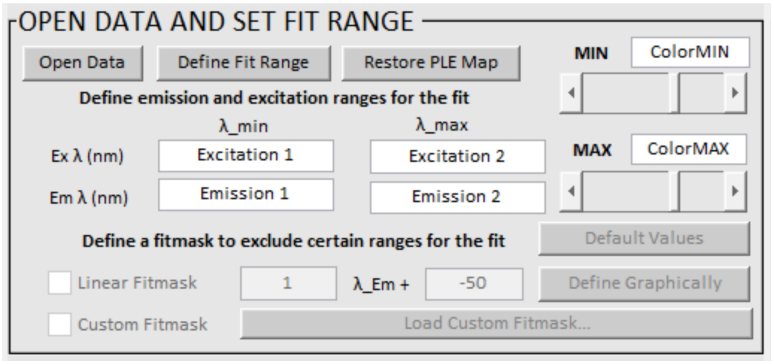

Figure 3: *The 'Open Data and Set Fit Range' panel.*

To start fitting, load a 2D PLE spectrum by pressing the **Open Data** button. Similarly, data can also be opened through the toolbar menu. The program is able to read three different data formats, being .mat, .xlsx and .csv files. All these formats require a specific data structure. It is important that your data is expressed as a function of wavelength and not energy. The fit will occur in energy, but an internal conversion with the appropriate Jacobian transformation is being performed automatically, hence it is important to give the data as measured in wavelength.

- **.mat** The native file format commonly used in MATLAB®. This file should contain three variables named `X`, `Y` and `Z`. `Z` is a matrix of the 2D PLE data with the PL intensities. `X` and `Y` are a row and a column vector containing the emission and excitation wavelengths in nm. Make sure that the variables `X` and `Y` match the length of the rows and the columns of the matrix `Z` respectively.

- **.xlsx** The first sheet (name does not matter) of the Excel file should have the format as shown in Figure 4a. The first column and first row of the data contain the emission and excitation wavelengths, respectively. The `Z` matrix containing the PLE intensities should start at the second row, second column and span the same number of rows and columns as the emission and excitation ranges, respectively. The Excel sheet cannot contain any other information except for the data.

- **.csv** The layout of the data needs to be the same as the Excel file except that the values are separated by commas, see Figure 4b.

	A	B	C	D	E	F	G	H
1	Em\Ex	460	465	470	475	480	485	490
2	797.0844	190.6256	-716.539	839.3211	-24.8594	-330.365	-129.779	-333.069
3	798.0889	-130.034	-676.157	560.7233	963.0489	59.8804	163.8662	-166.427
4	799.0934	99.121	204.3979	539.4513	731.9089	386.8279	80.86646	828.1138
5	800.0977	-24.7521	-34.9734	-53.0995	-72.2556	-790.776	139.209	-252.924
6	801.1019	-1191.88	-594.662	-373.251	-444.703	-159.472	245.9856	-312.053
7	802.1061	177.5084	-442.021	667.8311	-311.063	506.6882	611.4375	13.97074
8	803.1102	-311.602	3.179786	-52.4162	-832.135	72.75328	10.88765	108.3713
9	804.1142	254.0641	-308.452	-446.478	187.1076	-820.24	-35.5697	512.8024
10	805.1181	664.5577	33.65288	27.86974	300.2318	-768.603	-360.088	-340.774
11	806.122	-11.5154	-264.399	346.0512	-61.1283	172.1633	228.9136	-408.167
12	807.1257	-579.731	-96.4018	-120.952	61.28235	202.2693	148.5367	-186.158
13	808.1294	172.2104	-121.77	-416.513	610.8729	84.14144	-431.32	43.04818
14	809.133	-518.261	266.7125	-3.55995	-87.129	223.3545	300.8971	453.6429

(a)

```
Em\Ex,460,465,470,475,480,485,490,495,500,505,510,515,520,525,
797.0844318,190.6255802,-716.5387434,839.3210886,-24.85944604,
798.0889344,-130.0336622,-676.1566715,560.7232979,963.0488866,
799.0933536,99.12099947,204.397929,539.4513383,731.9088892,386
800.0976894,-24.75208671,-34.9734268,-53.0994975,-72.25563511,
801.1019418,-1191.881428,-594.6622796,-373.251278,-444.7029874
802.1061108,177.5084317,-442.020822,667.8310881,-311.0625533,5
803.1101965,-311.6022829,3.179785673,-52.41621097,-832.1348772
804.1141987,254.064134,-308.4519644,-446.4782196,187.1076021,-
805.1181176,664.5576701,33.65287611,27.86974373,300.2317696,-7
806.121953,-11.51543992,-264.3992806,346.05117,-61.12830753,17
807.1257051,-579.7310581,-96.40181318,-120.9522284,61.28234512
808.1293738,172.2103822,-121.7698768,-416.5133335,610.8729104,
809.1329591,-518.2606351,266.7124674,-3.559951941,-87.12899781
810.136461,217.1653588,-310.7051303,714.522333,-37.37534528,42
811.1398795,59.55115086,-232.110762,206.0061595,4.593337041,-6
812.1432146,108.892768,-122.7957702,-87.86498407,269.1726434,-
```

(b)

Figure 4: *Examples of input in the (a) .xlsx format and in the (b) .csv format. The PL intensities are highlighted in blue.*

Once the data has been loaded, a 2D PLE map will be shown in the top left figure of the graphical panel.

The **Define Fit Range** button enables the user to define the rectangular excitation-emission wavelength range of interest over which the fit will be performed. If this button is pressed, a cross will appear when you slide the cursor over the experimental PLE map. Then two opposite corners of the desired rectangular area can be selected by left-clicking. After the first selection, two crossing white lines will appear, indicating the first corner. Then the second corner can be chosen and the data will be adjusted. Clicking outside the PLE range will make the selected point snap to the closest data point. Note that the text boxes in the panel can also be used to adjust the fit range manually. By pressing enter or clicking elsewhere on the interface the data will be cropped. The program always remembers its initial full data.

The **Restore PLE map** button can be used to restore the full data range and plot it again.

The color of the data will be mapped between the values provided in the ColorMIN and the ColorMAX edit boxes. To adjust the minimum and the maximum of the colorscale use the sliders or manually set a value in the edit boxes. If a fit was made, both the experimental data and the fit will be scaled simultaneously. Note that the slider and edit box will only become available if data is loaded.

Fitmask

The GUI allows to define a fitmask to mask certain regions of the PLE data and exclude them from the fit. This can be useful for example to exclude stray light from the excitation lamp, background peaks that can't be attributed to CNTs, (the PSBs of) the E_{11} transition or the higher energy E_{33}, E_{44} transitions in excitation. The GUI provides three options to implement such a fitmask:

1. **The automatic fitmask** is made from all the NaN values initially included in your data file and is automatically used as a fitmask. In this manner, you can exclude specific ranges from your experimental data, directly when you load the PLE data.
2. **The linear fitmask** is defined by the function $a \cdot \lambda_{\mathrm{em}} + b$ and all PLE data above this line will be excluded from the fit. This mask is typically used to exclude overlapping excitation light and can be enabled by checking the corresponding box in the 'Open Data and Set Fit Range' panel. Doing so also enables the buttons **Define Graphically** and **Default Values**. Clicking the former allows to draw a line on the experimental PLE map by left-clicking to select two points. Clicking the latter restores a and b to their default values, 1 and -50, respectively.
3. **The custom fitmask** can similarly be enabled by checking the corresponding box in the 'Open Data and Set Fit Range' panel. This activates the 'Load Custom Fitmask' button, which allows to load a user-made mask. The file containing this fitsmask *must* be of the same format and size as the experimental PLE data (see Figure 4) and must consist of zeros and ones, to exclude and include data points, respectively. If the mask is successfully loaded its filename will be shown in the panel.

If desired, a total fitmask equal to the product of the automatic fitmask, the linear fitmask and the custom fitmask can be saved under File > Save Fitmask. This is useful if the same fitmask needs to be applied to other data with the same dimensions.

7 Define Fitting Model and Fit

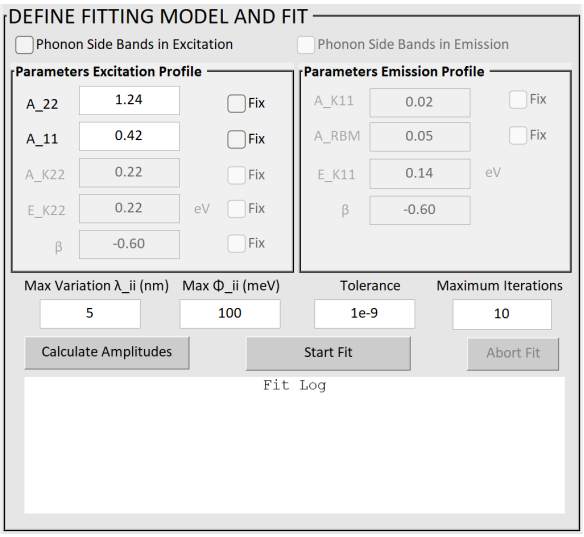

Figure 5: *The 'Define Fitting Model and Fit' panel.*

The chirality-independent fit parameters are defined here. By default the first two edit boxes of the parameters of the excitation profile are enabled. These are the amplitudes of the BTBs A_{22} and A_{11}. In every fit these parameters are automatically taken into consideration. The checkboxes **Phonon Side Bands in Excitation** and **Phonon Side Bands in Emission** enable PSBs and once selected the corresponding additional fit parameters will become available. PSBs in emission can only be included when also those in excitation are included. The boxes in this panel all correspond to parameters explained in Section 3.

If the "PSBs in excitation" box is checked three additional edit boxes will be enabled. These are the amplitude $A_{\mathrm{K},22}$ of the D-band PSB relative to the excitation peak E_{22}, the position of the D-band PSB $E_{\mathrm{K},22}$ compared to the excitation peak and the diameter-dependence of the PSB amplitudes β. If both boxes are checked also the amplitudes of the D-band PSB $A_{\mathrm{K},11}$ and RBM PSB A_{RBM} relative to the emission peak E_{11} will become available. The position of the PSB $E_{\mathrm{K},11}$ will be determined based on the position of the PSB in excitation $E_{\mathrm{K},22}$ (see Equation 7).

In the same panel the per-iteration bounds for the variation $\Delta_{\lambda,\mathrm{max}}$ of the wavelengths can be set; *i.e.* between iterations the wavelengths can extremally become $\lambda_{ii} \pm \Delta_{\lambda,\mathrm{max}}$ nm. Similarly, the maximum value ϕ_{max} for the linewidths can also be adjusted here; *i.e.* in each iteration the linewidths are bounded by $\phi \in]1, \phi_{\mathrm{max}}]$. Additionally, this panel allows for the convergence tolerance and the maximum number of iterations to be changed, the former of which requires some further explanation.

In general, convergence in the least-squares algorithm can be defined in terms of the change in the fit parameters or the change in the residual. In MATLAB® the tolerance values that govern these are called `TolX` and `TolFun`, respectively. In the current implementation of PLEfit2D, both tolerances are set to the same value, namely the one in this panel. A decent value based on the estimated noise level of the data and the number of fitted peaks is given by the program whenever data is loaded, the fitting range is changed or the number of peaks is altered. However, this should be interpreted as a first order-of-magnitude suggestion. Tweaking of this value may be needed. In fact, in some cases it is more useful to start with a less restrictive value (*i.e.* a larger value, such as 10^{-4}) to more superficially explore the parameter space and manually keep some volatile parameters in check until a decent fit is achieved, then decrease the tolerance value to fully converge the fit.

The amplitudes A_i (see Equation 1) can be calculated by pressing the **Calculate Amplitudes** button and the current parameters are used to generate the 2D basis functions F_i. This is useful to have a first indication of the degree of optimization or ill-conditioning of peak positions.

Once you are satisfied with the fit setup and have added all the chirality-dependent fit parameters (see Section 8) the **Start Fit** button can be pressed. After each iteration the `Fit Log` displays some useful information to track progress: the iteration number, the number of function evaluations (`Fnc-count`), the norm of the last iteration step and the 2-norm of the squared residuals (`2-norm Res. Squared`). The fitting can terminate for any of the reasons listed below and this reason is then also shown on the `Fit Log`.

- Change in the fit parameters (norm of step) was less than the specified tolerance, corresponding to `TolX`.
- Change in the residual was less than the specified tolerance, corresponding to `TolFun`.
- Number of iterations exceeded the maximum set in this panel.
- Fitting aborted by the user. If you are not satisfied with the current fitting progress, the procedure can be aborted with the **Abort Fit** button. You will be given the option to output the parameters of the current iteration. This can be quite practical if lengthy calculations need to be aborted and the progress needs to be saved.

Be aware that only in the first two cases convergence is reached and a reliable fit can be expected, up to the accuracy that the tolerance value allows. Note that checkboxes to fix each parameter are provided, such that those parameters are not optimized in the fit procedure. For a fully and correctly converged fit, all parameters must be allowed to vary during the final fitting.

Parameter shuffling In some extreme cases the solver might get stuck in parameter space. PLEfit2D can recognize when this occurs and will randomize the linewidths and shape parameters within a reasonable range to push the solver away from such fixpoints.

8 Set CNT Peak Positions and Linewidths

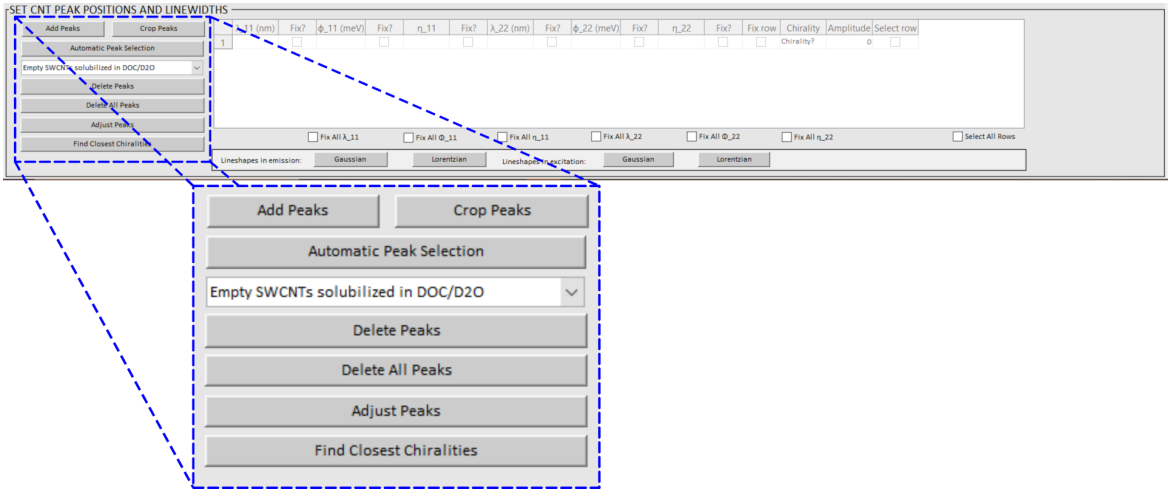

Figure 6: *The 'Set CNT Peak Positions and Linewidths' panel.*

To initialize a fitting procedure the SWCNT peaks that you want to include in your fit need to be selected. This can be done either manually or by using empirical relations from literature as starting values, for which several examples are included in the program. For each peak the parameters λ_{11}, ϕ_{11}, η_{11}, λ_{22}, ϕ_{22}, η_{22} are defined. Be careful, the peak positions λ_{ii} should be expressed in nm, while the linewidths ϕ_{ii} are expressed in meV. Even though the fit itself is performed in energy, we opted to keep the positions in wavelengths as this relates back to the actual experimental data.

By pressing the button **Add Peaks** a crossed cursor will appear while moving over the 2D experimental data plot. Multiple positions can be selected by left clicking and deleted again by right clicking. Save all these peaks simultaneously by pressing ENTER. Press ESCAPE to abort selecting peaks. The initial values for the emission and excitation linewidths (ϕ_{11} and ϕ_{22}) are set to 25 meV and 35 meV, respectively, and to 0.5 for the shape parameters η_{11} and η_{22}.

The program can also use empirical relations from literature to set initial peak positions.

- Select the desired relations from the dropdown menu
- Press the button **Automatic Peak Selection** to load the peaks.

Only peaks with positions within the current fit range will be included and shown. It is the responsibility of the user to further reduce the number of peaks to those that are actually detectable in the experimental data (see further, **Delete Peaks**). The first and second optical transition frequencies (wavenumbers v_{11} and v_{22}) of SWCNTs can be expressed as a function of the SWCNT diameter d (in nm) and chiral angle α in a general empirical relation [12, 13]:

$$\tilde{v}_{ii} = \frac{10^7\,\mathrm{cm}^{-1}}{B_1^i + B_2^i\,d} + \frac{A_\mu^i \cos(3\alpha)}{d^2}\,\mathrm{cm}^{-1}. \tag{8}$$

Here $\tilde{v}_{ii}$ are the transition frequencies (in cm^{-1}) for the first ($i = 1$) and second ($i = 2$) optical transitions respectively. The empirical equations which can be chosen from are given in Table 2. These relations are a recent refinement [13] of the relations reported earlier in reference [8] (based on more extensive data).

Transition	B_1^i [unitless]	B_2^i [nm^{-1}]	$A_{\mu=1}^i$ [nm^2]	$A_{\mu=2}^i$ [nm^2]
	Empty SWCNTs solubilized in DOC/D_2O [13]			
$\tilde{v}_{11}$	147.67	1097.40	-636.12	318.35
$\tilde{v}_{22}$	145.60	581.37	1114.73	-1397.35
	Water-filled SWCNTs solubilized in DOC/D_2O [13]			
$\tilde{v}_{11}$	123.37	1129.97	-662.63	289.68
$\tilde{v}_{22}$	135.28	594.46	1177.93	-1472.02
	Triacontane-filled SWCNTs solubilized in DOC/D_2O [13]			
$\tilde{v}_{11}$	129.98	1119.53	-562.17	280.06
$\tilde{v}_{22}$	139.65	588.46	956.80	-1442.14
	Mixture of empty and filled SWCNTs solubilized in SDS/D_2O [12]			
$\tilde{v}_{11}$	157.5	1066.9	-710	369
$\tilde{v}_{22}$	145.6	575.7	1375	-1475

Table 2: *Parameters in the general empirical relation (see Equation 8) for the first and second optical transition frequencies (in wavenumbers). The diameter of the SWCNT is given by* $d = \frac{\sqrt{3}a}{\pi}\sqrt{n^2 + nm + m^2}$, *with* $a = 0.142\,\mathrm{nm}$ *in the case of the updated relations from reference [13] or* $a = 0.144\,\mathrm{nm}$ *in the case of the original empirical relations from Bachilo et al. [12] (mixture of empty and filled). The parameter* μ *relates to the modulus,* $\mu := (n - m) \bmod 3 = 1, 2$.

Load custom peak positions

If this option is selected in the pop-up menu a window will open when the button **Automatic Peak Selection** is pressed. A list of custom peak positions expressed in nm can now be loaded. PLEfit2D supports three different data formats:

- **.mat** This file should contain two column vectors named PeakX and PeakY with the emission and excitation wavelengths respectively.
- **.xlsx** The first sheet of the Excel file should contain the emission and excitation wavelengths in the first and second column, respectively. The actual values need to start at the second row allowing for comments in the first row.
- **.csv** The layout needs to be the same as the Excel file but the values are separated by commas.

During the fitting procedure all peaks on the 2D PLE data map will be taken into account and adjusted. Multiple peaks can be defined on the full data range and if the fitting range is adjusted, PLEfit2D will give a red color to the peaks that are located outside the current fit range (in the table). By pressing **Crop Peaks** those red colored peaks, being the ones outside the selected data range, will be deleted or they can be kept to fit the tails of possible background peaks from outside the fitting range.

Peaks can be deleted, either graphically or by selecting rows in the peaks table, by pressing **Delete Peaks**. If any rows in the table are currently selected, using the check box in the last column, these will be deleted. If no peak is selected, a crossed cursor will appear while moving over the 2D experimental data. Peaks can then be deleted in the same manner as adding them. First select which peaks you want to remove by left-clicking. They will be marked by a red circle. This selection of red circles can also be adjusted by left (select) and right (deselect) clicking. Pressing enter will delete the selected peaks. To delete all peaks press **Delete All Peaks**.

Peak positions can also be changed in three different ways:

- Manually, by editing the numbers in the table. This method can also be used to change other fit parameters.
- Semi-graphically, by first selecting a single peak in the table and pressing **Adjust Peaks**. The selected peak will be indicated with a red colored circle. Moving over the 2D experimental data and left-clicking with the crossed cursor will allow you to define the new peak position.

- Graphically, if no single peak was selected in the table while pressing the button **Adjust Peaks** PLEfit2D will allow you to select a peak graphically by moving over the 2D experimental data and selecting it by left clicking with the crossed cursor then proceed in the same way as the semi-graphical way.

To make a crude automatic assignment of the current peak positions to chiralities press **Find Closest Chiralities**. The program will then take the currently selected empirical relations from the pop-up menu and compare them with the peak positions in the table. The closest chirality for each peak will then be assigned and added to the table. Note that these assignments are only based on the approximate empirical relations and it is important to realize that these may be wrong. Peak positions can shift for each sample depending on the external and internal environment, in particular for near-zigzag SWCNTs the automatic assignments are not that good. It is the user's responsibility to double-check the assignments (*e.g.* check for duplicate assignments).

The shape parameters η_{11} and η_{22} can be set to Gaussian or Lorentzian lineshapes by pressing the appropriate buttons under the table. For each peak the value will be set to 0 or 1 respectively while their values are set to be fixed while fitting.

9 Graphical Panel

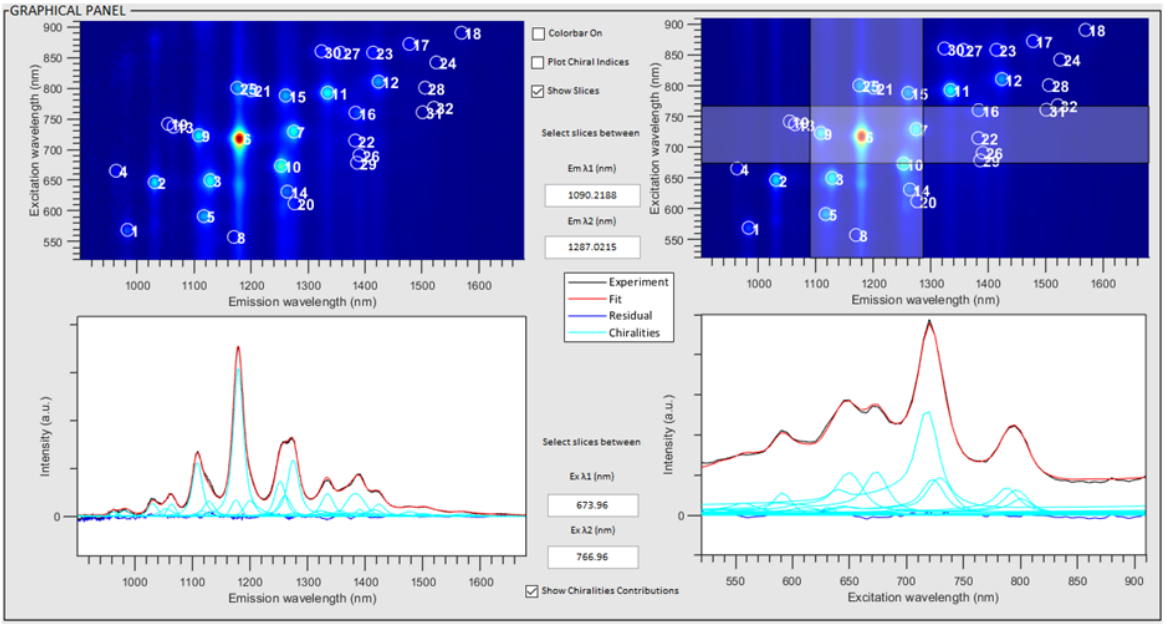

Figure 7: *The 'Graphical Panel' showing the converged fit of a PLE map from a HiPco SWCNT sample solubilized in DOC/D_2O.*

Once the data has been loaded and all parameters are initialized the fitting procedure can be started or amplitudes can be calculated. After a fit or amplitude calculation, the program will update all the parameters and show the 2D PLE fit in the upper right subplot of the graphical panel (see Figure 7). The fit can be compared with the experimental data in more detail by comparing slices through the data. Two plots of cross sections are shown in the bottom two panels, showing an experimental curve averaged over a certain range (light gray bars in the 2D PLE fit), the corresponding fitted curve (averaged over the same range) and the residual defined as the difference between the experimental and fitted curve (exp-fit). If the checkbox **Show Chiralities Contributions** is selected also the separate contributions for each chirality (light blue) are shown in the bottom panels. The light gray bars in the 2D PLE fit can be adjusted in width by clicking and dragging at the edges or can be moved by clicking and dragging their central part. The values of the edges in excitation and emission are shown in the small textboxes and can also be adjusted there.

In the graphical panel there are three additional checkboxes. The first one turns on the colorbar scale for the experimental PLE map and if a fit is available also for the fit. The second one shows the chiral indices of the currently selected empirical relation in the pop-up menu of the bottom panel on the experimental 2D PLE data. The final one turns of the light gray bars in the fit.

10 Toolbar

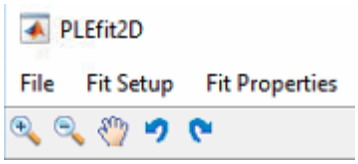

Figure 8: *The toolbar of PLEfit2D.*

The toolbar consists of three menus: **File**, **Fit Setup** and **Fit Properties**. The latter of these will only become available after a fit or an amplitude calculation has been done or when a saved workspace is loaded. A workspace contains the full state of the program, including all parameters as well as the full data and corresponding fit, and can be saved or loaded from the first menu item.

File

Standard operations, such as loading and saving of data or exiting the program can be performed from this menu. The menu items for each operation are detailed below.

Open Data Load data the same way as the **Open Data** button under the 'Open Data and Set Fit Range' panel.

Load Workspace Load a previously saved workspace in its entirety.

Load Parameters Load only the fit parameters from a previously saved workspace.

Save Workspace Save the current state of the program (data, setup and parameters) as a workspace in an Excel document (.xlsx) or a CSV file. Note that a workspace can be saved only after a fit has been performed or amplitudes have been calculated. The layout of a saved file is separated in five parts (sheets in the case of Excel):

1. **Fitparameters**: contains all the parameters used in the fit and their errors. Moreover it also shows which parameters were fitted and which ones were fixed. If a parameter was fixed, the corresponding errors are put to zero.
2. **Data**: contains the full experimental data on which the fit was performed.
3. **Fit**: contains the actual fit, which doesn't necessarily have the same dimensions as the full data, as it may represent a reduced fit range. Once a workspace is loaded the full data will be adjusted to this fit range but can always be restored by pressing the **Restore PLE map** button.
4. **FitMask**: To be able to efficiently save the three different fitmasks in PLEfit2D we use reverse binary conversion to reduce these three fitmasks to one fitmask. The values in this composite fitmask range from 0-7 (see Figure 9). The values for the three constituent fitmasks can then be constructed easily by converting these values to binary again. Each layer (see Figure 9) corresponds to one of the three fitmasks of PLEfit2D, being the custom (2^2), the automatic (2^1) and the linear fitmask (2^0).

   For example $5 \overset{\text{bin}}{\equiv} 101$ indicates a value of 1 in the custom fitmask, a value of 0 in the automatic fitmask and a value of 1 in the linear fitmask.
5. **File Information**: contains the date of saving and the path to the PLE data file. If a saved workspace was loaded or only its parameters then the path to this particular file will also be mentioned here.

Please do not adjust the structure of saved workspaces. This is important to be able to load them later.

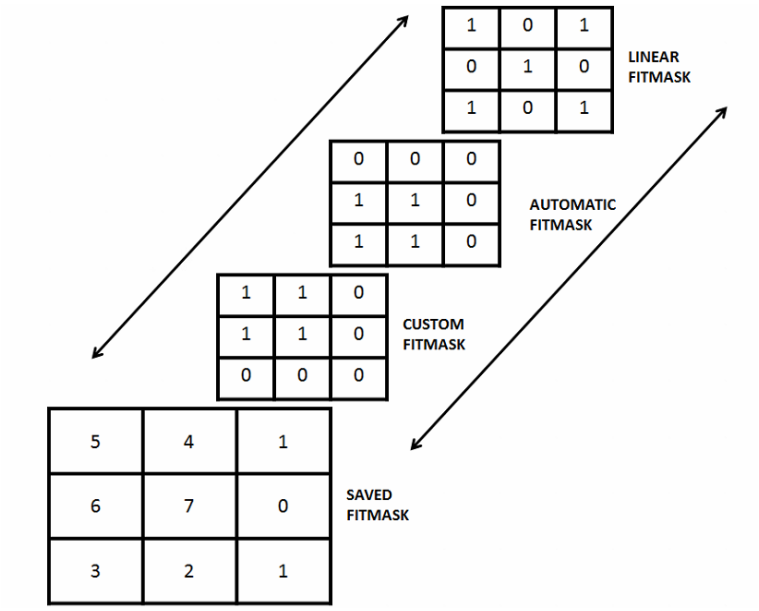

Figure 9: *Graphical structure of how the three fitmasks are saved into one composite fitmask. The three different fitmasks can be reconstructed again from the general fitmask by binary conversion.*

Save Figures Tweak and save the figures from the Graphical Panel. A separate window with each of the four figures will appear, left to right and top to bottom: the 2D experimental PLE map, the 2D fitted PLE map, slices of the emission spectrum and slices of the excitation spectrum.

The toolbar of this window provides several options:

- **Show labels:** toggle on/off the markers and labels at the fitted peak positions on both the experimental and the fitted 2D PLE map. [default: on]
- **Slice normalisation:** toggle between two normalization methods for the slices, either w.r.t. the maximum value of the full fitting range [default] or w.r.t. that of the slice itself.
- **Set slices intervals:** set excitation wavelength intervals for the emission slices and emission wavelength intervals for the excitation slices. These are shown in a separate window, where both the number of slices and the interval for each slice can be adjusted and then applied. These intervals are tracked internally, so closing the Save Figures window does not result in losing them. This also makes it possible to load new data and immediately view the same slices for comparison. By default, four equal slices are made across the excitation and emission ranges.

- **Show slices intervals:** toggle on/off the visualization of the slices intervals on the 2D maps. The excitation wavelength intervals are shown on the experimental map and the emission wavelength intervals on the fitted map, corresponding with the slices plots below. [default: off]

Finally, in the middle of the Save Figures window are two sliders which can be used to set the color scale of the 2D maps and a button to save the plots when you are satisfied with them. This can be done either as a single image containing all four plots, or as four separate images. Figure 10 shows an example of the single image option.

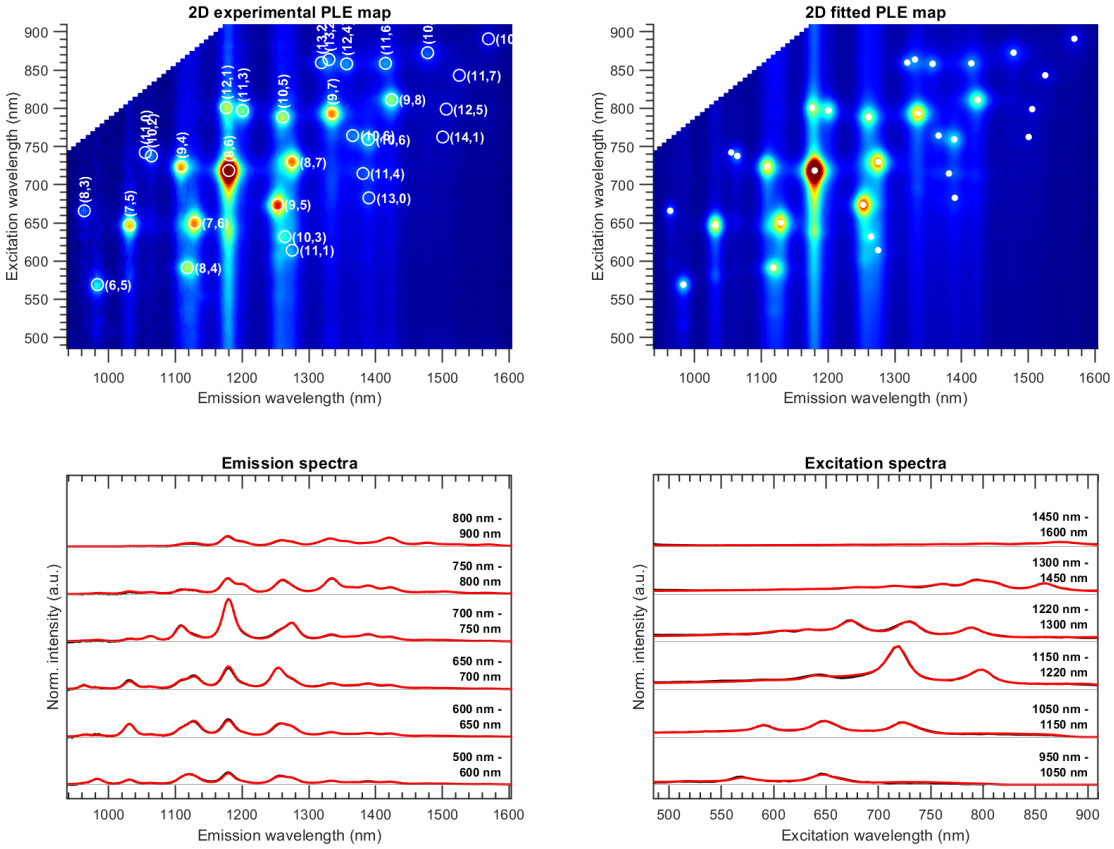

Figure 10: *Converged fit of a PLE map of HiPco SWCNTs in DOC/D_2O saved together in one panel and showing 6 slices in both excitation and emission, normalised w.r.t. the full fitting range.*

Save Fitmask Save the currently active fitmask to a separate file in one of the following formats: a MATLAB® datafile (.mat), an Excel document (.xlsx) or a CSV file (.csv). This fitmask can then later be loaded for other experimental data with the same

dimensions, via the **Load Custom Fitmask...** button in the 'Open Data and Set Fit Range' panel of the GUI. This is a particularly useful option in case the same unwanted feature appears in a large number of data measured over the same range, such as a line from the excitation light.

Settings Open the Settings window, where the path to the temporary file directory for PLEfit2D can be changed.

Exit Exit the program.

Fit Setup

This tab in the toolbar menu includes the choice of the algorithm to determine the chirality-dependent amplitudes, the choice of the background in the fitting model and the settings for the fitmask. It also allows to store the current fit setup, retrieve a previously stored setup or to revert to the factory setup.

Amplitudes Fitting According to Equation 1, the SWCNT peak amplitudes can be obtained through a simple linear regression, using MATLAB®'s built-in function `mldivide`. This is used when the submenu option **Standard Linear Regression** is checked.

In some circumstances however, *e.g.* when peak positions are not yet optimized or ill-conditioned, this can result in negative PLE amplitudes for some of the peaks which is, of course, not physically possible. Therefore, a constrained least-squares algorithm could instead be used to ensure non-negative amplitudes, such as MATLAB®'s built-in function `lsqnonneg`. Using such an algorithm comes at a price, though, since it sacrifices the robustness of the standard linear regression and it is much slower. Since amplitudes need to be calculated in each iteration, this leads to a significant increase in the total computational time. Therefore, the GUI provides an adapted version of the standard linear regression scheme instead, which is used when the option **Adapted Linear Regression** is checked.

The adapted linear regression scheme works as follows. The amplitudes are first calculated using standard linear regression and then checked for negative values. If none exist, the scheme ends and is hence identical to standard linear regression. If negative amplitudes were obtained, however, the basis functions those correspond to are temporarily excluded from the fit function and standard linear regression is performed again using the remaining basis functions. This process is repeated until linear regression no longer yields any negative amplitudes. The negative-amplitude basis functions that were identified throughout this process are assigned an amplitude of zero in the final output. This means that, when using this scheme, an amplitude of zero in the table from the 'Set CNT Peak Positions and Linewidths' panel signifies a problematic

peak that may warrant close inspection. It may have drifted away from any sensible position and/or be fitting the background.

Background Model Select the basis function(s) used to fit the background, for which three options are available:

- **No background**.
- **Constant background**. This is implemented by adding unity as an additional basis function in Equation 1, *i.e.* $F_{N+1}(E_{\mathrm{em}}, E_{\mathrm{ex}}) = 1$. Thus the amplitude of this basis function yields the magnitude of a constant background signal. This amplitude is ignored by the Adapted Linear Regression scheme, meaning negative constant backgrounds are possible. For PLE maps that are well-corrected this is the best fitting option.
- **Constant and Bilinear Background**. This is implemented by adding four additional basis functions in Equation 1 proportional to a constant (similarly as above), a linear function in excitation, a linear function in emission and a bilinear function in both excitation and emission:

$$F_{N+1}(E_{\mathrm{em}}, E_{\mathrm{ex}}) = 1 \tag{9}$$
$$F_{N+2}(E_{\mathrm{em}}, E_{\mathrm{ex}}) = E_{\mathrm{ex}} \tag{10}$$
$$F_{N+3}(E_{\mathrm{em}}, E_{\mathrm{ex}}) = E_{\mathrm{em}} \tag{11}$$
$$F_{N+4}(E_{\mathrm{em}}, E_{\mathrm{ex}}) = E_{\mathrm{em}} E_{\mathrm{ex}} \tag{12}$$

  Again, the amplitudes of these background functions are ignored by the Adapted Linear Regression scheme, meaning negative constant contributions and negative slope linear contributions to the background fit are possible.

Save Settings... Store the current fit setup as a JSON file, letting the user set up their fitting environment in an identical way quickly and easily in the future, by selecting the 'Load Settings' menu item.

Load Settings... Load a previously saved fit setup.

Save Default Settings... Store the current fit setup as the default setup, *i.e.* the setup which is in effect when the PLEfit2D program is loaded.

Load Default Settings... Load the default fit setup.

Load Factory Settings... Restore the fitting environment to its factory-default setup.

Fit Properties

This part of the toolbar will only become available if a fit has been done or if a full workspace has been loaded. The following menu items are available:

Residual PLE Map (DATA-FIT) Plot a 2D map of residuals from the difference between the experimental data and the fit.

Set Previous Fit Range If the fit range has been changed, this option returns it to what it was for the most recent fit.

Plot Peak Positions + Error Bars Open an errorbar plot of the PLE peak positions in a separate window.

Last Fit Log Open the full log from the most recent fit. Note that this is not saved across sessions, i.e. the log will be empty after loading a full workspace.

Error Bars on Fit Parameters Open a table of the uncertainties on the fit parameters in a separate window. This contains the chirality-dependent parameters and amplitudes as well as the global, chirality-independent parameters that govern the PSBs in excitation and emission.

Show Lorentzian and Gaussian Linewidths Equation 3 is used to convert the linewidth and shape parameter for each Voigtian peak into the linewidths of its constituent Lorentzian and Gaussian lineshapes.

Histogram of Amplitudes on CNT Grid Open a new window showing the fitted PL intensities (amplitudes) as colorized histogram bars on a 3D hexagon grid (see Figure 11). These bars represent the relative intensities, *i.e.* the percentual contribution of each chirality to the total PL intensity. The grid can also be viewed top-down to reduce the plot to a 2D version.

To make this figure, each peak must be assigned a chirality, which can be done automatically or manually. Be aware that the automatic assignment is merely a crude classification based on the distance of each peak position to the known positions for the particular set of data selected in the Automatic Peak Selection dropdown menu. In case multiple peaks end up getting assigned the same chirality, the generated plot shows the sum of their relative amplitudes.

It should be stressed that this plot does not directly show the relative abundances of the chiral species in the sample, since those must be calculated from the PL intensities using the chirality-dependent PL quantum efficiencies.

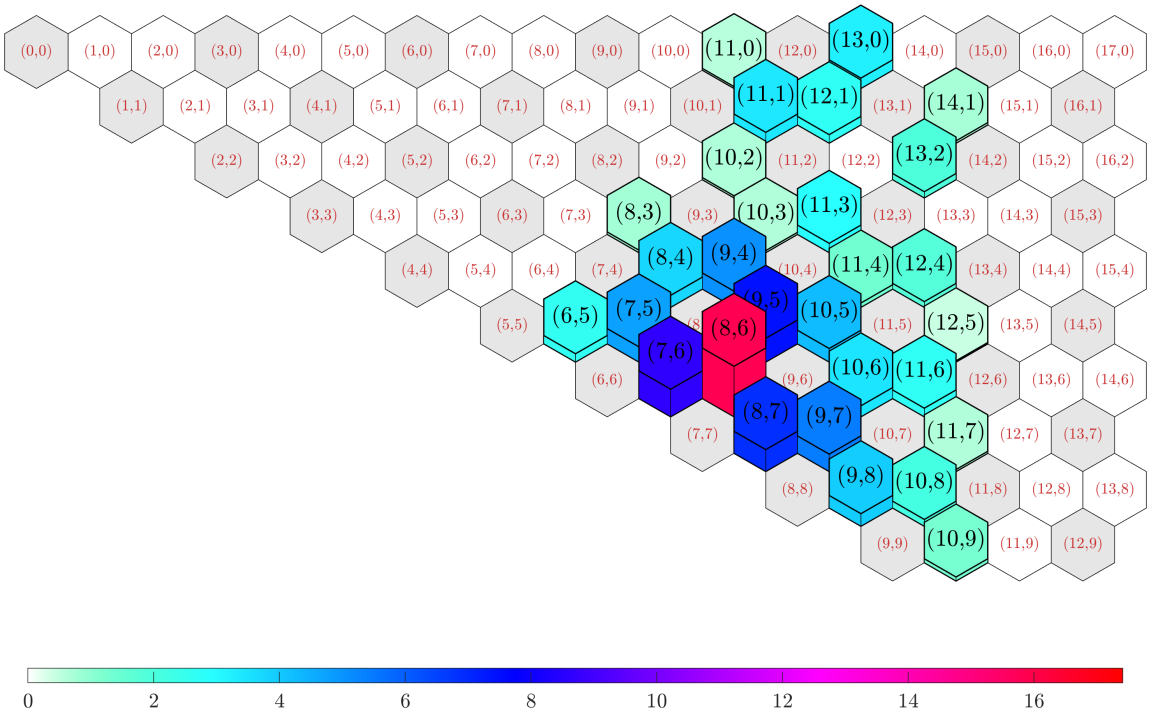

Figure 11: *Fitted relative PL intensities A_i of Figure 10 plotted on a hexagonal grid. Smaller (red) labels denote chiralities which are not included in the fit and hence not fitted. Metallic chiralities are marked by gray hexagons.*

11 Quick Start Tutorial

Miguel has a SWCNT sample he wishes to characterise using PLE data he's measured. Here are the steps he takes to do so using PLEfit2D.

1. Miguel makes sure he has corrected his data for

   a) variations in excitation power at each wavelength,

   b) the spectral efficiency of the detector and spectrograph over the emission range,

   c) any filters or other optics used in the excitation or emission path,

   d) re-absorption in the sample cell.

   This has already been done for the example data available for download from [INSERT URL].

2. Miguel then formats his PLE data as explained in section 6. This has also already been done for the example data available for download from [INSERT URL].

3. Confident he's ready to rock 'n' roll, Miguel now starts up PLEfit2D. Since it's the first time he's done so, the program asks him where he would like it to store its metadata. Miguel simply leaves this as the suggested default and clicks OK.

4. Miguel opens his data by clicking the **Open Data** button from the OPEN DATA AND SET FITTING RANGE panel and selecting his correctly formatted file from the pop-up selection window. The data is immediately plotted in the GRAPHICAL PANEL.

Follow this short tutorial to quickly start working with PLEfit2D.

1. To load an experimental PLE map, assuming the data has a correct data format compatible with PLEfit2D, press the **Open Data** button in the 'Open Data and Set Fit Range' panel. Once successfully loaded, the data will be shown in the 'Graphical Panel'.

2. Press **Add Peaks** in the 'Set CNT Peak Positions and Linewidths' panel and use the crossed cursor to select peak positions on the experimental data by left-clicking and confirming by pressing enter.

3. If phonon side bands are present select the check boxes for phonon side bands in the 'Define Fitting Model and Fit' panel.

4. Press **Start Fit** in the same panel to start the fitting procedure.

5. Once terminated, all parameters will be updated and the fit will be shown below the experimental PLE map in the 'Graphical Panel'.

6. Select the check box Show Slices in the 'Graphical Panel' to compare the experimental data with the fit.

7. Check if convergence was reached, if this is not the case then it is a good idea to start a new fitting procedure. Maybe changing the number of maximum iterations or other parameters in the 'Define Fitting Model and Fit' panel.

8. Saving the fit can be done in the toolbar under the tab File $\rightarrow$ Save Workspace and can be loaded again under File $>$ Load Workspace.

Best Practices

Fitting the data can best be approached by following these steps:

- Start with simply calculating the amplitudes by pressing **Calculate Amplitudes**
- As it is important to have good starting conditions, you can then change parameters, if needed, and see if you need additional chiralities or that some of the peaks need to be removed.
- Set 10 iterations and start a fit. Maybe using the Least Squares fitting algorithm for the amplitudes to speed up the process. After 10 iterations, most peaks should be starting to go to their actual value. You can then again check if you need to add a peak somewhere, or if a peak became too broad (*e.g.* bumping against the max ϕ value). You can readjust and restart a short iteration.
- Once close to a good visual fit, increase the number of iterations, choose the Non-negative Least Squares algorithm and start your final fit.

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License and Copyright Information

The functions `findjobj` and `findjobj_fast` used in the code for PLEfit2D are subject to the following licensing information.