`starkfit` User Manual

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Class organization

The `starkfit` GUI requires 4 class definition files which contain all of the functionality to process and fit the spectra:

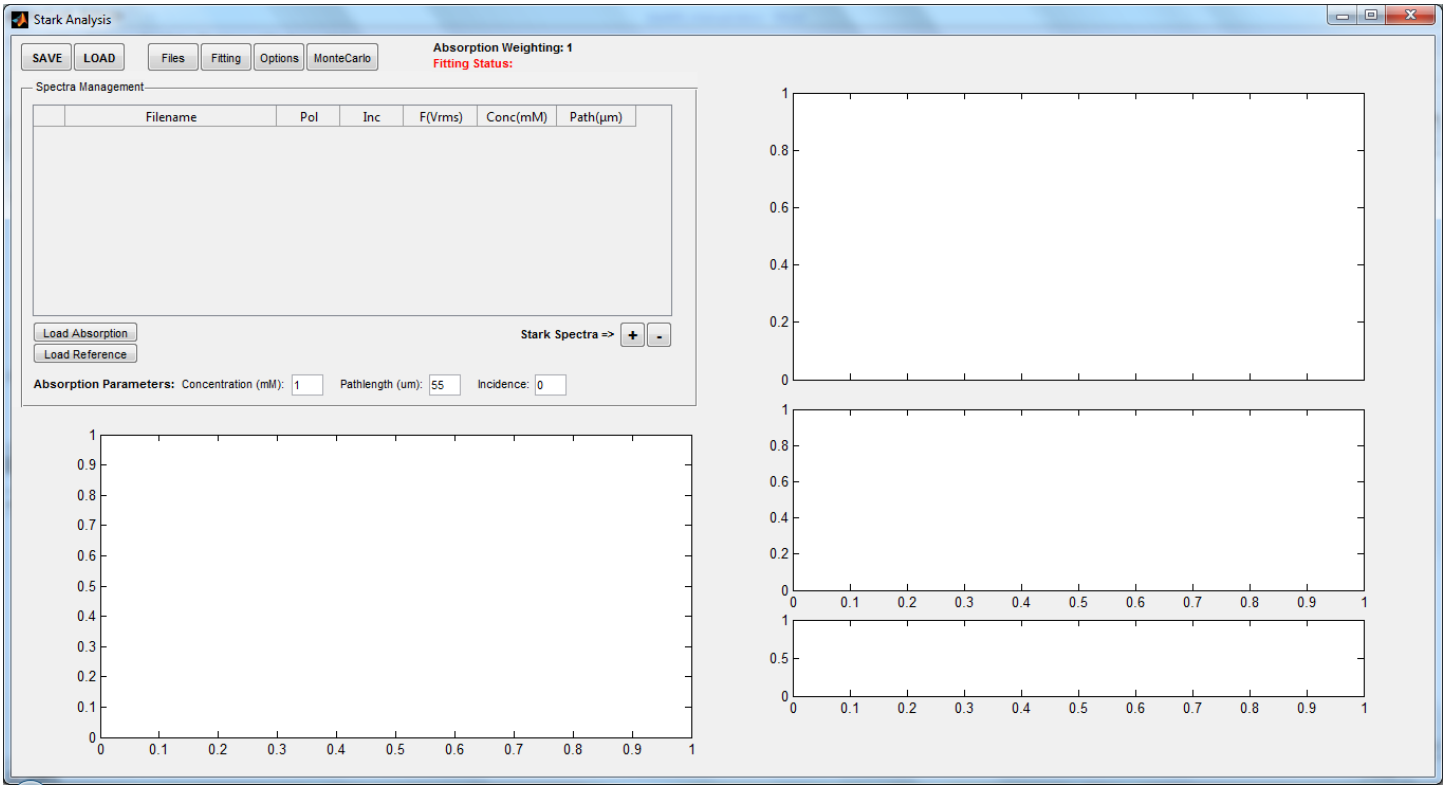
- `SpecObj` – superclass that contains methods for baseline correction, conversion from absorption to extinction, and all of the properties common to both LT absorption and Stark spectra
- `stkSpecObj` – inherits `SpecObj` and extends properties specific to Stark spectra and includes methods to load spectrum files, normalize spectra to a single field value (currently 1 MV/cm) and calculate the value of χ from polarization and incidence angles
- `ltaSpecObj` – inherits `SpecObj` and includes methods to load spectrum files
- `stkFitObj` – properties include all of the fitting parameters and Monte Carlo results, `aobj` is a `ltaSpecObj` instance and `sobj` is a vector of `stkSpecObj` instances, one for each spectrum loaded.

When `starkfit` is called from the command line, the GUI is built and then the main loop creates a `stkFitObj` named `obj`. This instance is what is saved in a `.mat` file from the GUI and can be re-loaded for later use and re-fitting.

All code was written using MATLAB R2011b and validated on a Toshiba laptop running Windows 7.

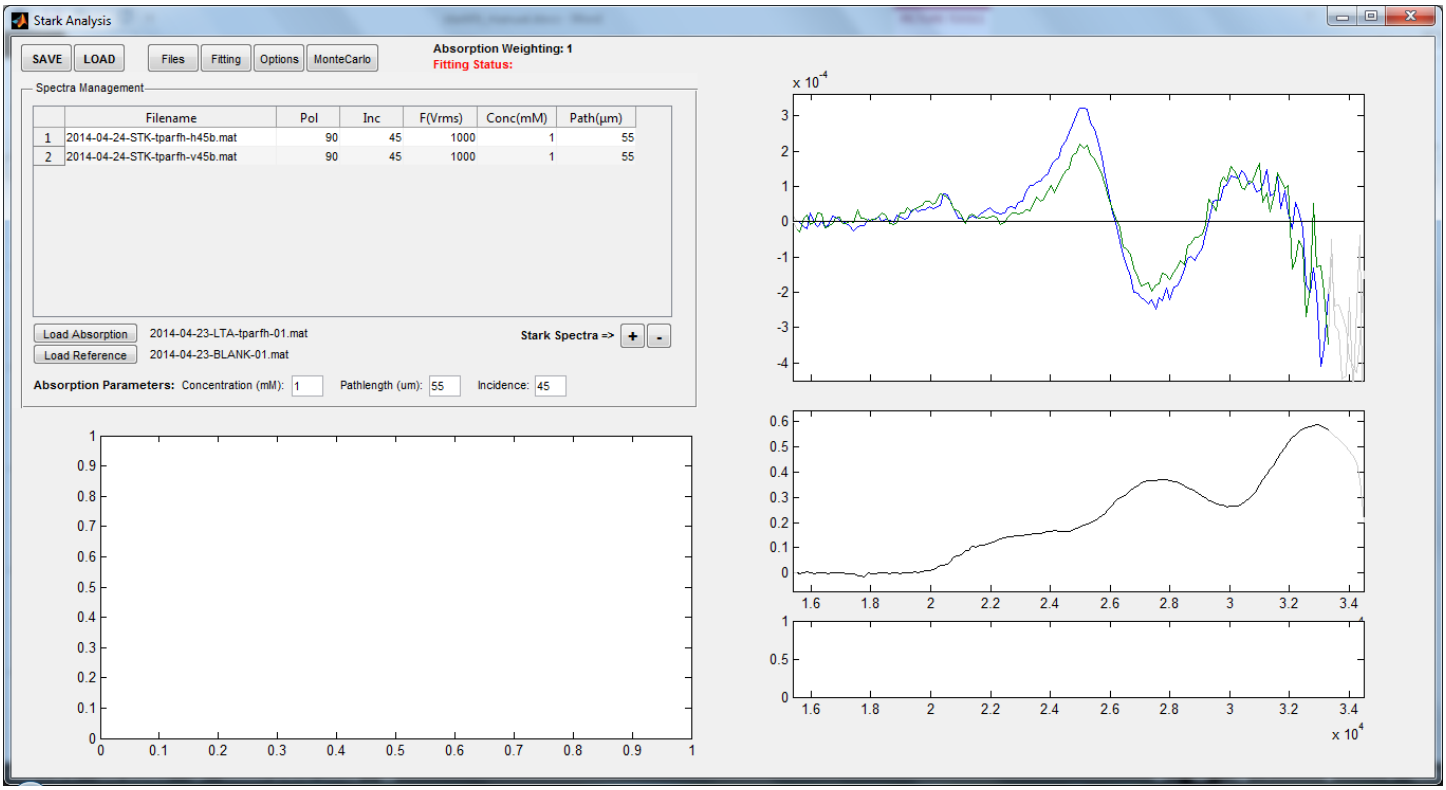
General workflow

In the command line, type `starkfit` to load the GUI.

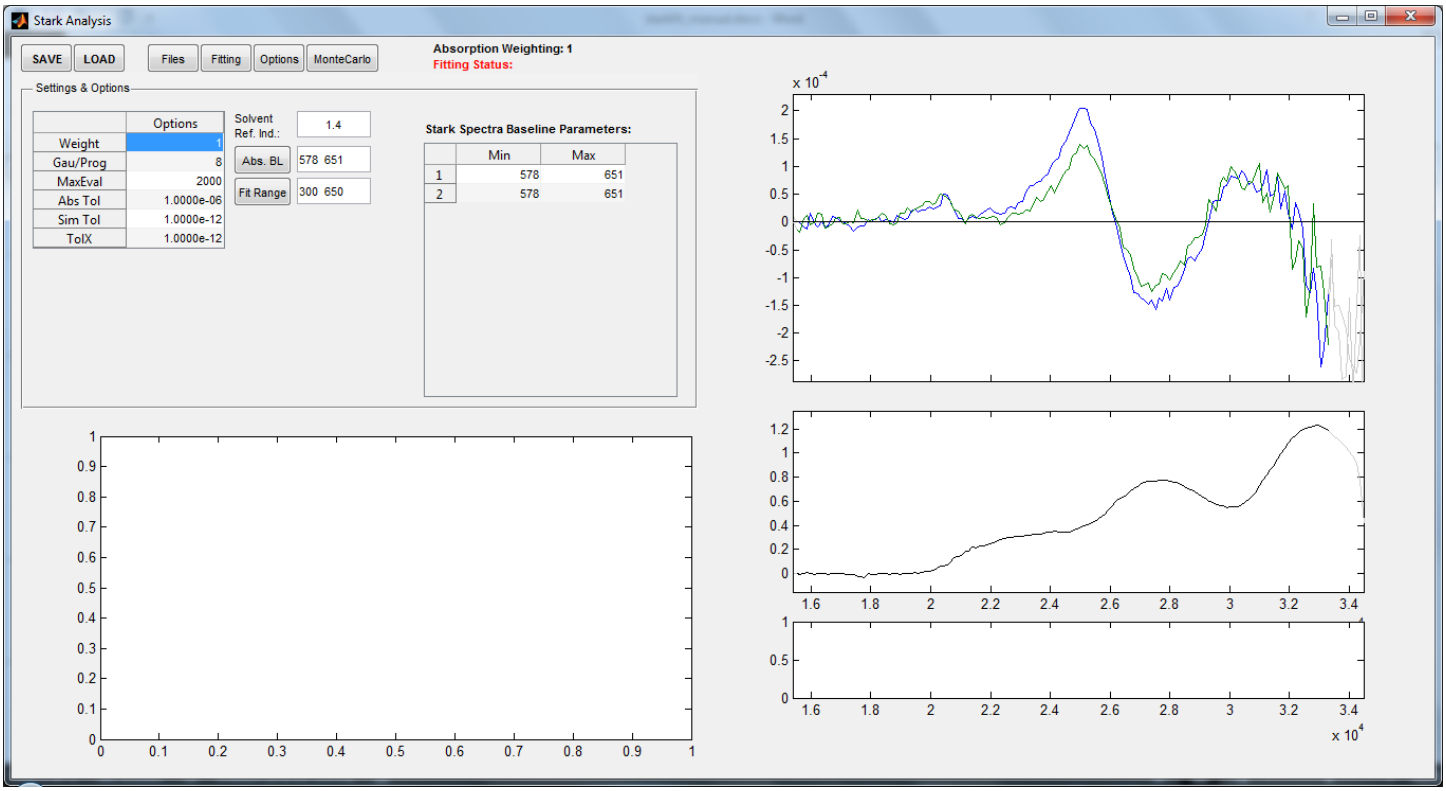


The ‘SAVE’ and ‘LOAD’ buttons can be used to save the current project as a .mat file for later use or load a previously saved project. ‘LOAD’ will be able to open any `.mat` file that contains a `stkFitObj` named `obj`, even if this was created manually from the command line.

The ‘+’ and ‘–‘ buttons are used to add or remove Stark spectrum files from the project. Once loaded, the files will appear in the table, which you can use to adjust the experimental parameters for each spectrum: Polarization (°), angle of incidence (°, 0° is when the probe beam is normal to the plane of the cuvette), applied field (V_{rms}), sample concentration (mM), and pathlength (μm).

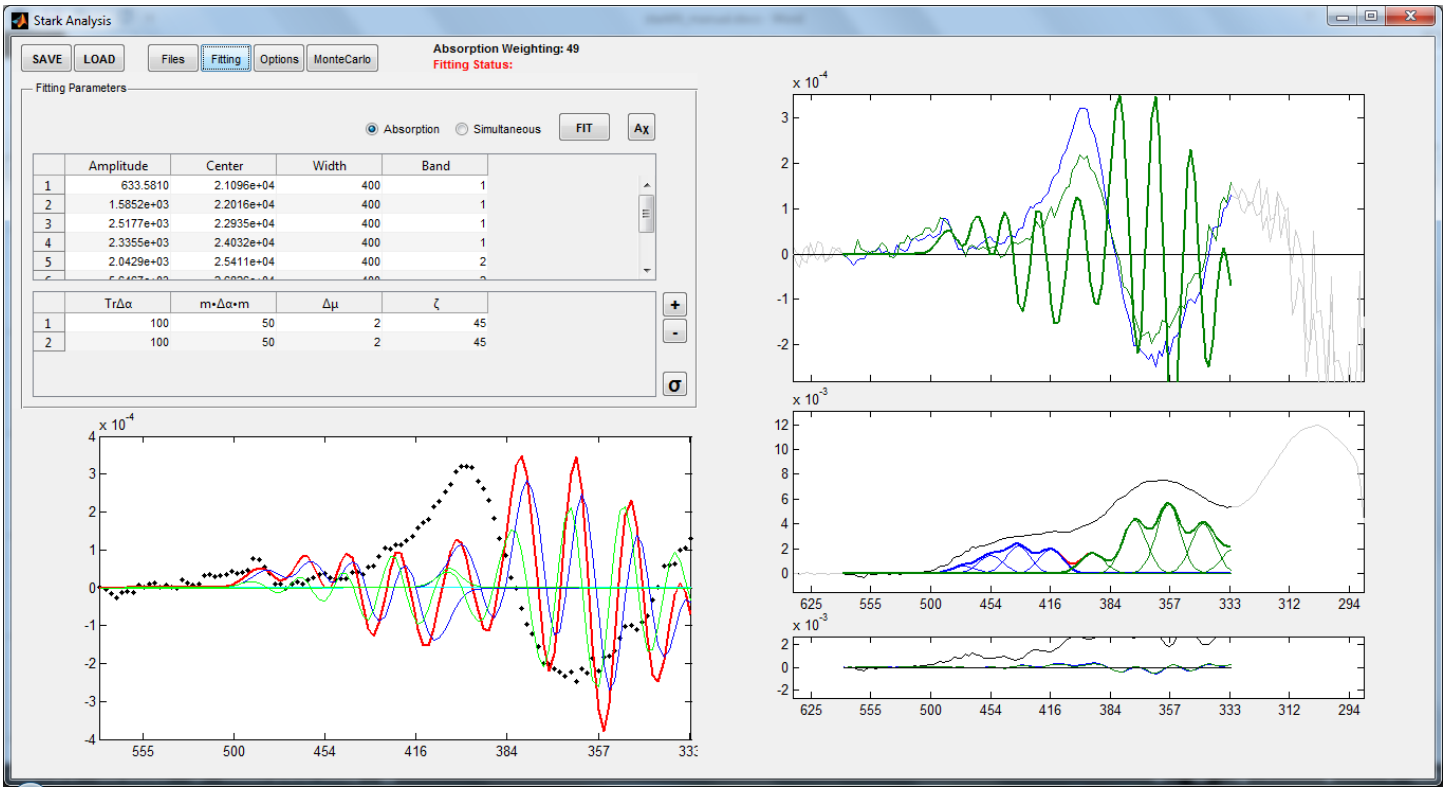


The ‘Load Absorption’ and ‘Load Reference’ buttons highlighted in red above are used to load in the two files necessary to create the low temperature absorption spectrum. The experimental properties can be adjusted with the text boxes at the bottom of the panel.



Once all of the files have been loaded, click on the 'Options' button to adjust the settings for baseline correction and options for the nonlinear fit. In the Options table to the left, generally the only value that needs to be set is 'Weight'; a higher value will fit the Stark spectra better than the absorption spectrum. Usually I start with a high value, ≥ 1.0, to get a good initial fit. Afterwards I cycle between a high and low (~0.1) value. If the fit is robust, the fitted parameters should not change much with the weighting factor. The `Gau/Prog` option doesn't do anything, it's left over from when I tried to fit with vibronic progressions.

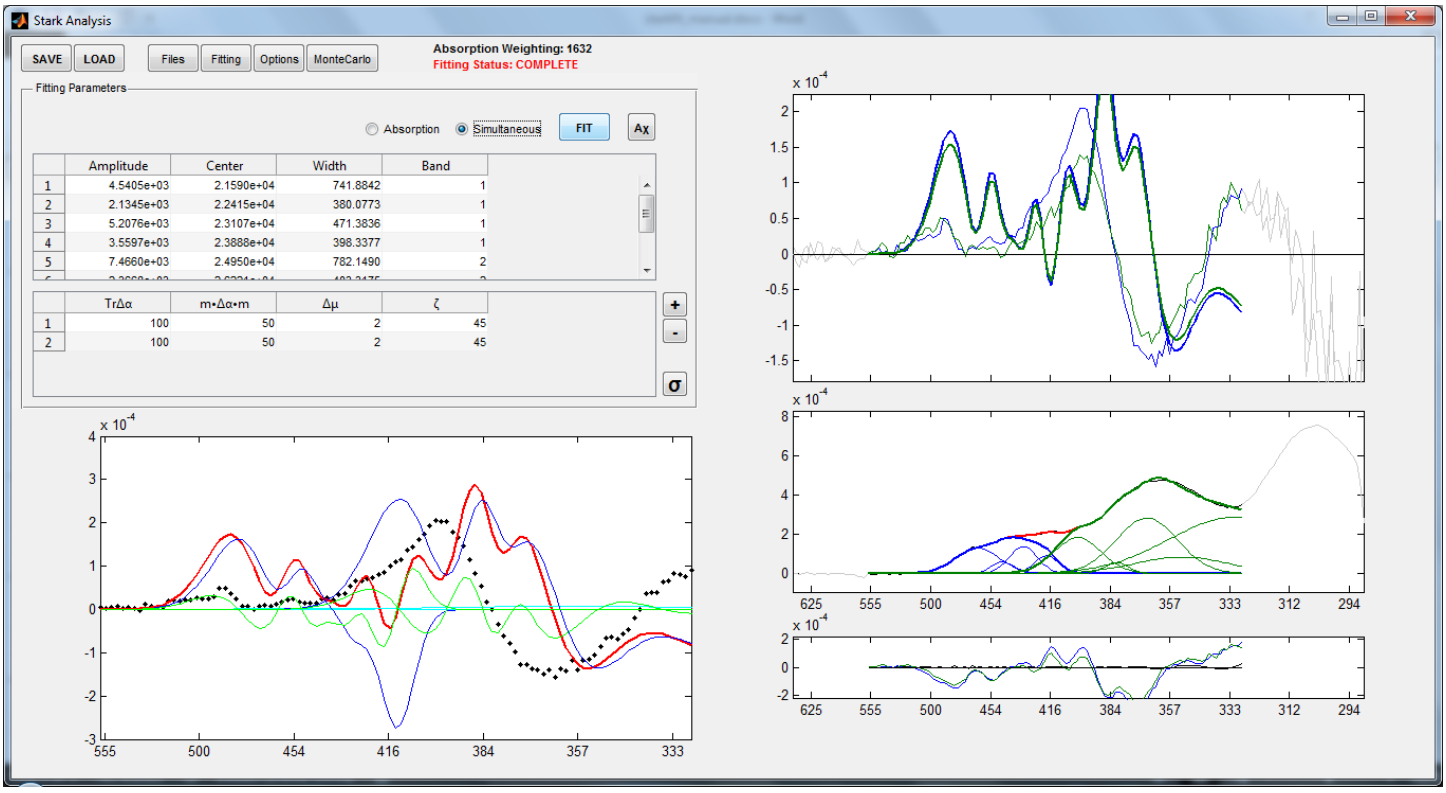
Click on the 'Abs BL' button to graphically select the baseline region for the LT absorption spectrum; alternatively you can enter the values directly in the text box next to this button. You can do the same with the 'Fit Range' button and text box to select the region of the spectra that will be fitted. You can enter the values for the baseline range of each Stark spectrum in the table to the right. To streamline this process, whenever the `loadSpec()` method of a `stkSpecObj` or `ltaSpecObj` instance is called, the last (reddest) 10% of the data points are selected as the baseline region as a first guess. If you've collected enough baseline in the scans, this generally works well, and the values do not have to be adjusted.



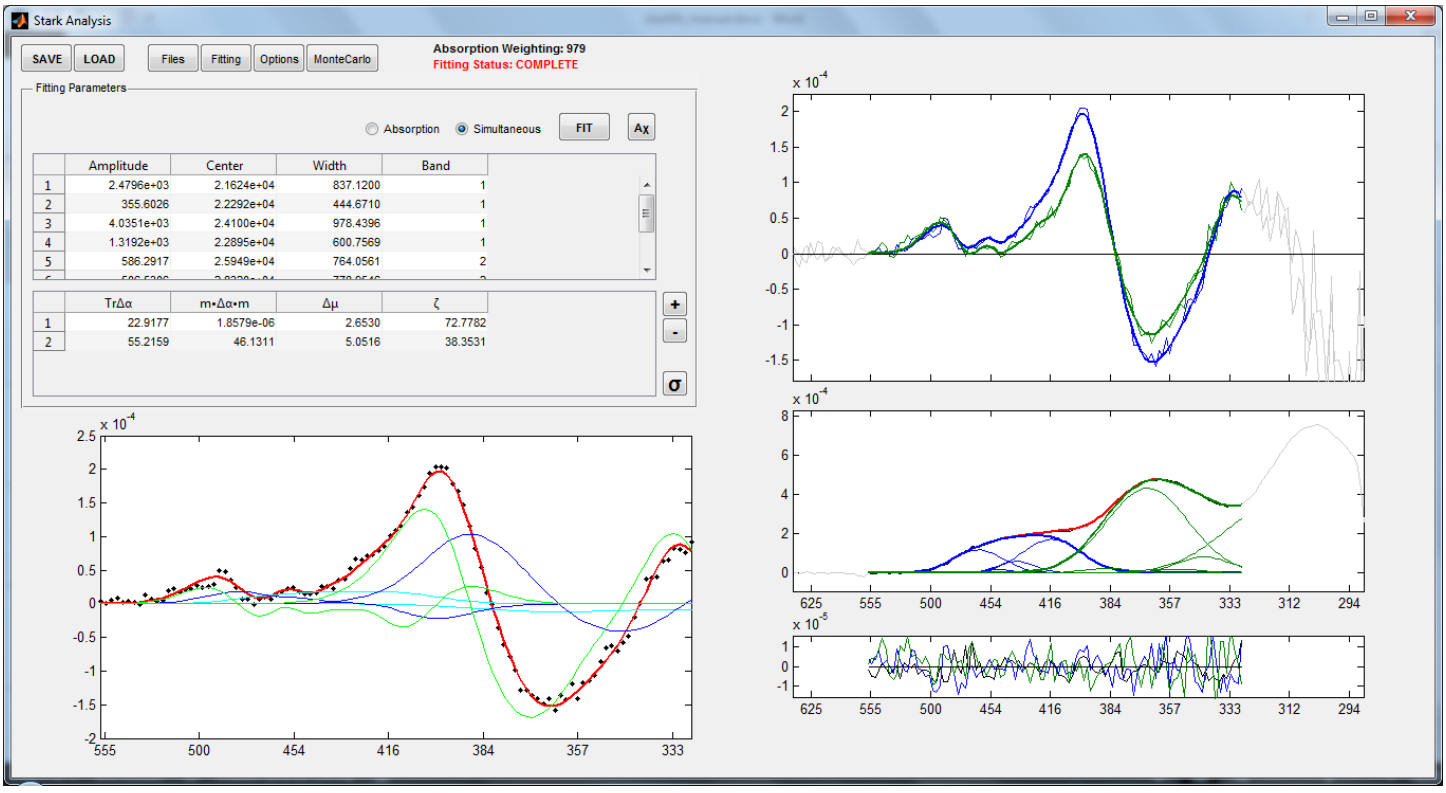
Click on the 'Fitting' button at the top of the screen. To add a transition, click the '+' button and use the crosshairs to select the positions of the gaussians on the LT absorption spectrum; hit Enter when you're done. The gaussian parameters (amplitude in M^{-1} cm^{-1}, center in cm^{-1}, and width in cm^{-1}) will appear in the top table and can be adjusted manually. The band column indicates which absorption band the gaussian belongs to. The bottom table will be populated with default values for $Tr\,\Delta\vec{\alpha}$, $\vec{m}\cdot\Delta\vec{\alpha}\cdot\vec{m}$, $\Delta\vec{\mu}$, and ζ; adjust these manually. The A_χ coefficients can be viewed and edited by toggling the 'Aχ' button at the upper right corner of the panel.

Make sure the 'Absorption' option is selected and click the 'Fit' button. The nonlinear least squares routine to fit the LT absorption spectrum will run. When the fitting is completed, the red status label at the top of the window will say 'COMPLETE'.

The fitted spectra are plotted as bold lines in the top two axes on the right side of the window. The bottom plot shows the residuals for all of the spectra. The left plot shows the derivative components for the fit of the first Stark spectrum loaded into the project. Experimental data is plotted as black circles, the total fit as a bold red line, the A_χ components in cyan, the B_χ components in blue, and the C_χ components in green. The y-axes in all plots are in units of M^{-1} (extinction/wavenumber) and also divided by the weighting factor for the absorption spectrum.



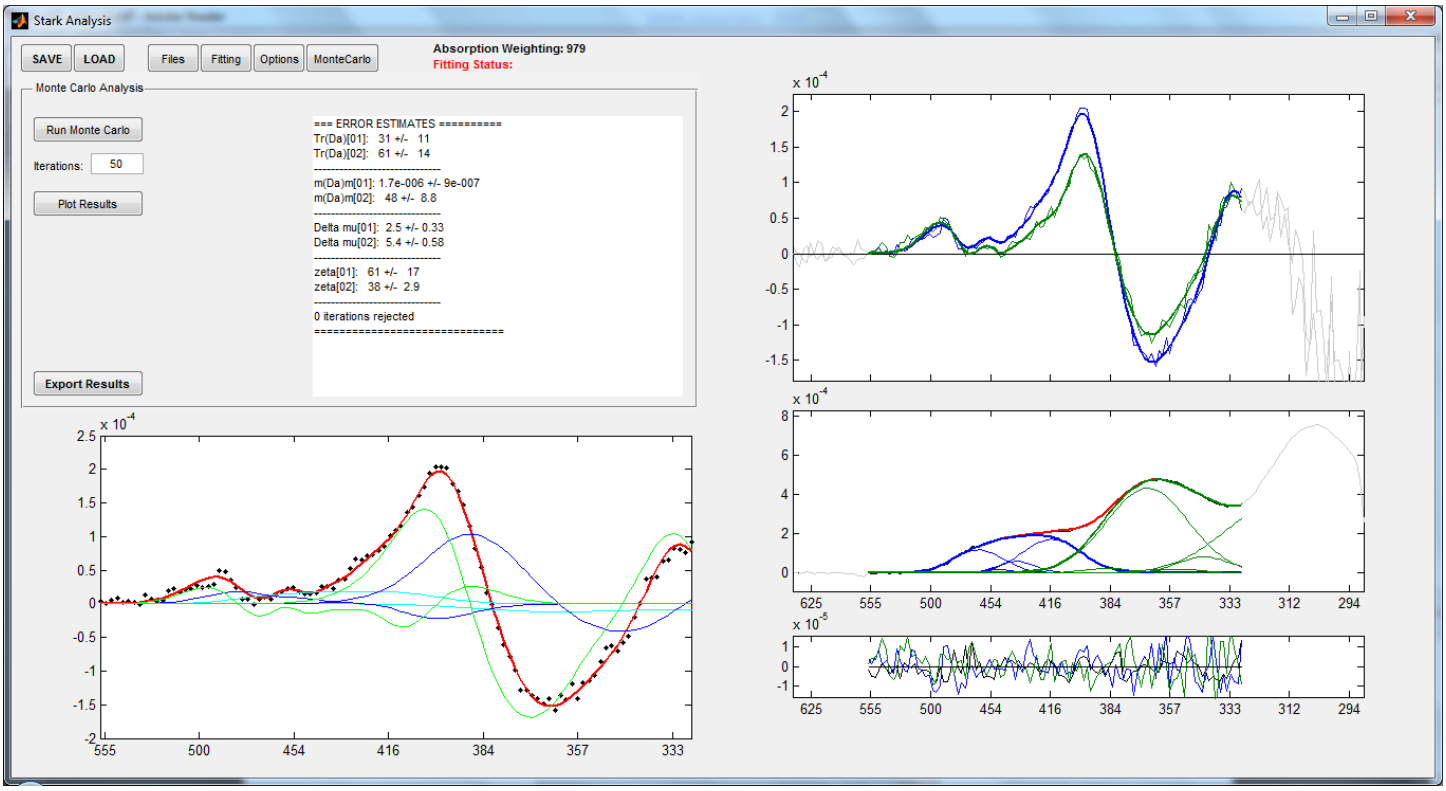
Now select the 'Simultaneous' option, and click 'FIT' again. The nonlinear least squares minimization will run using the gaussian components of the LT absorption spectrum to fit all of the Stark spectra. After each fit the parameters table is updated with the fitted results.



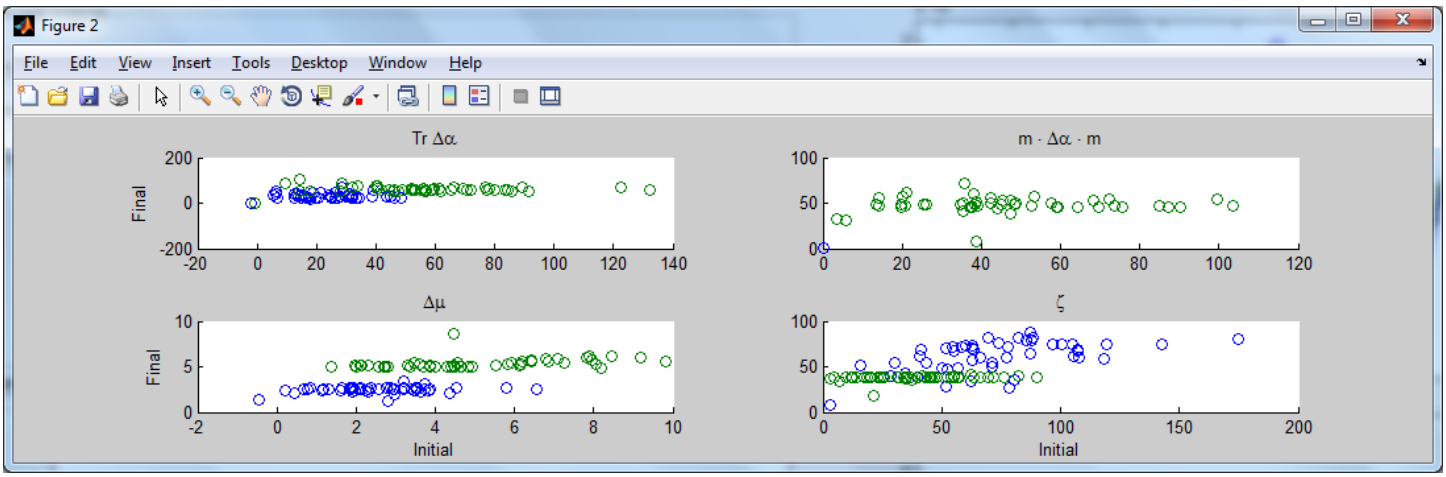
The 'σ' button will run a nonlinear regression fitting ONLY the Stark spectra and parameters, the gaussian parameters will stay the same. The results of this fit will be printed out to the command line as `beta` and `ci`. `beta` is a vector of the

fitted parameters in the form $[\times n\, Tr\Delta\vec{\vec{\alpha}}\,; \times n\, \vec{m}\cdot\Delta\vec{\vec{\alpha}}\cdot\vec{m}\,; \times n\, \Delta\vec{\mu}; \times n\, \zeta]$ where $\times n$ represents the number of absorption bands. `ci` is an array of confidence intervals for each of the corresponding parameters in beta. This data is not stored in the object, and the Monte Carlo method seems to be a more robust process to estimate parameter error.

Click on the 'MonteCarlo' button at the top of the window. Enter the number of iterations you would like to run in the text box, the default is 50, and click 'Run Monte Carlo'. The progress of the simulation will be shown in the white box to the right of the buttons. When the simulation is complete, the results and error estimates will be shown in the same place.

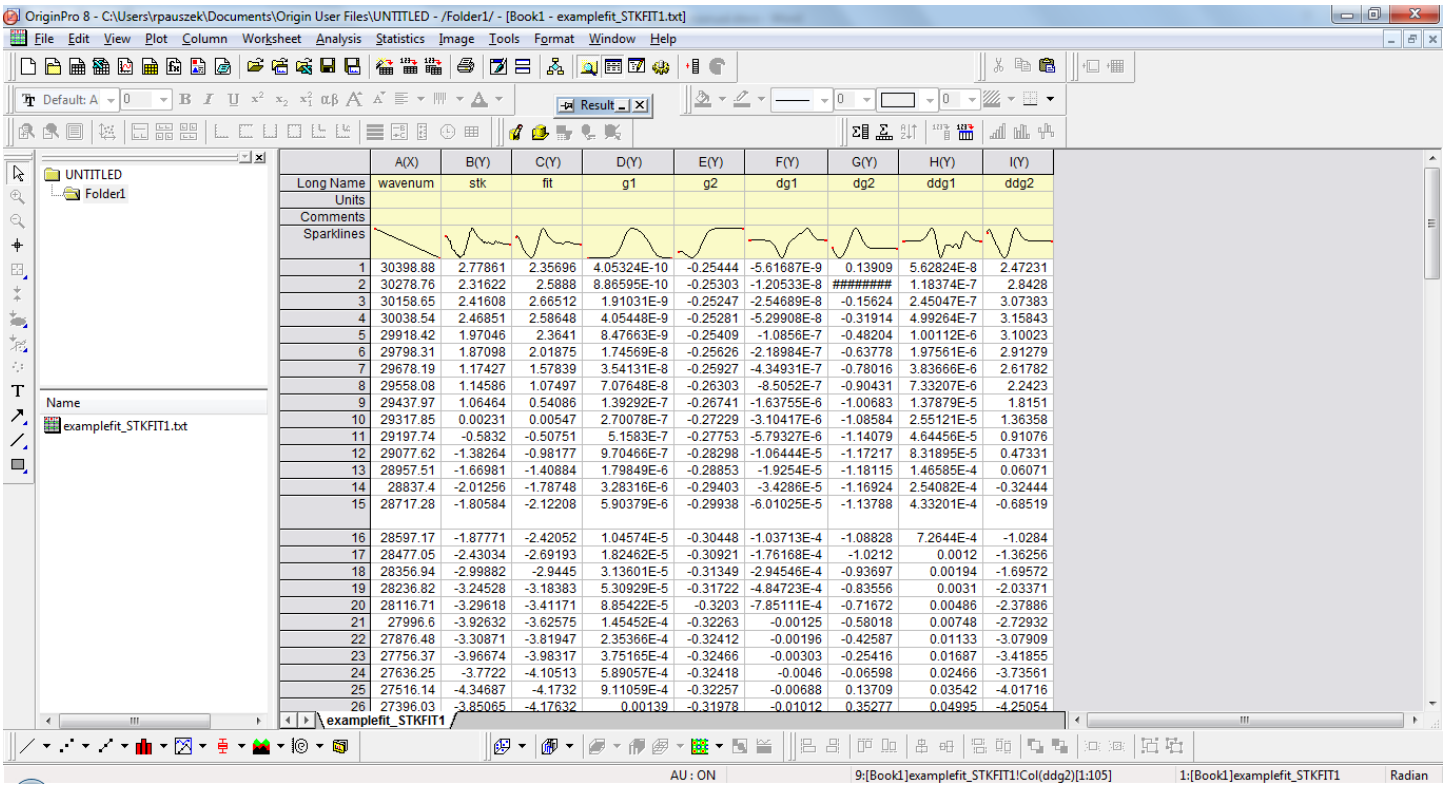


Click the 'Plot Results' button to show a graph of the initial and final parameters used in the Monte Carlo simulation. A 'good' run is indicated by the values elongated along the x-axis (a wide spread of initial values) but little variation along the y-axis (the parameters converged to a common value). The parameters for each transition are colored differently.



Finally click the 'Export Results' button. This will generate `.txt` files containing the data and fits that can be imported directly in Origin for plotting. The files are saved as "pathname/projectname_ABSFIT.txt" for the LT absorptions fit and

"pathname/projectname_STKFIT#.txt" where # is the number of the Stark spectrum in the order they were loaded into the project. If the project has not been saved yet, you will be prompted to do so before the `.txt` files are written.



	A(X)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	H(Y)	I(Y)
Long Name	wavenum	stk	fit	g1	g2	dg1	dg2	ddg1	ddg2
Units									
Comments									
Sparklines									
1	30398.88	2.77861	2.35696	4.05324E-10	-0.25444	-5.61687E-9	0.13909	5.62824E-8	2.47231
2	30278.76	2.31622	2.5888	8.86595E-10	-0.25303	-1.20533E-8	########	1.18374E-7	2.8428
3	30158.65	2.41608	2.66512	1.91031E-9	-0.25247	-2.54689E-8	-0.15624	2.45047E-7	3.07383
4	30038.54	2.46851	2.58648	4.05448E-9	-0.25281	-5.29908E-8	-0.31914	4.99264E-7	3.15843
5	29918.42	1.97046	2.3641	8.47663E-9	-0.25409	-1.0856E-7	-0.48204	1.00112E-6	3.10023
6	29798.31	1.87098	2.01875	1.74569E-8	-0.25626	-2.18984E-7	-0.63778	1.97561E-6	2.91279
7	29678.19	1.17427	1.57839	3.54131E-8	-0.25927	-4.34931E-7	-0.78016	3.83666E-6	2.61782
8	29558.08	1.14586	1.07497	7.07648E-8	-0.26303	-8.5052E-7	-0.90431	7.33207E-6	2.2423
9	29437.97	1.06464	0.54086	1.39292E-7	-0.26741	-1.63755E-6	-1.00683	1.37879E-5	1.8151
10	29317.85	0.00231	0.00547	2.70078E-7	-0.27229	-3.10417E-6	-1.08584	2.55121E-5	1.36358
11	29197.74	-0.5832	-0.50751	5.1583E-7	-0.27753	-5.79327E-6	-1.14079	4.64456E-5	0.91076
12	29077.62	-1.38264	-0.98177	9.70466E-7	-0.28298	-1.06444E-5	-1.17217	8.31895E-5	0.47331
13	28957.51	-1.66981	-1.40884	1.79849E-6	-0.28853	-1.9254E-5	-1.18115	1.46585E-4	0.06071
14	28837.4	-2.01256	-1.78748	3.28316E-6	-0.29403	-3.4286E-5	-1.16924	2.54082E-4	-0.32444
15	28717.28	-1.80584	-2.12208	5.90379E-6	-0.29938	-6.01025E-5	-1.13788	4.33201E-4	-0.68519
16	28597.17	-1.87771	-2.42052	1.04574E-5	-0.30448	-1.03713E-4	-1.08828	7.2644E-4	-1.0284
17	28477.05	-2.43034	-2.69193	1.82462E-5	-0.30921	-1.76168E-4	-1.0212	0.0012	-1.36256
18	28356.94	-2.99882	-2.9445	3.13601E-5	-0.31349	-2.94546E-4	-0.93697	0.00194	-1.69572
19	28236.82	-3.24528	-3.18383	5.30929E-5	-0.31722	-4.84723E-4	-0.83556	0.0031	-2.03371
20	28116.71	-3.29618	-3.41171	8.85422E-5	-0.3203	-7.85111E-4	-0.71672	0.00486	-2.37886
21	27996.6	-3.92632	-3.62575	1.45452E-4	-0.32263	-0.00125	-0.58018	0.00748	-2.72932
22	27876.48	-3.30871	-3.81947	2.35366E-4	-0.32412	-0.00196	-0.42587	0.01133	-3.07909
23	27756.37	-3.96674	-3.98317	3.75165E-4	-0.32466	-0.00303	-0.25416	0.01687	-3.41855
24	27636.25	-3.7722	-4.10513	5.89057E-4	-0.32418	-0.0046	-0.06598	0.02466	-3.73561
25	27516.14	-4.34687	-4.1732	9.11059E-4	-0.32257	-0.00688	0.13709	0.03542	-4.01716
26	27396.03	-3.85065	-4.17632	0.00139	-0.31978	-0.01012	0.35277	0.04995	-4.25054

In the `ABSFIT` files all y-data values are in M^{-1} cm^{-1}; the columns are:

- `wavenum` – x data in wavenumbers
- `abs` – experimental absorption spectrum
- `fit` – the fitted spectrum
- `band`n – the sum of the gaussians that make up the nth absorption band
- `b`n`gau`j – the jth gaussian of the nth absorption band

In the `STKFIT` files all y-data values are in M^{-1} cm^{-1} and normalized to 1 MV/cm; the columns are:

- `wavenum` – x data in wavenumbers
- `stk` – experimental Stark spectrum
- `fit` – the fitted spectrum
- `g`n – the A_χ term of the nth absorption band
- `dg`n – the B_χ term of the nth absorption band
- `ddg`n – the C_χ term of the nth absorption band