# SpecDis Manual

Version 1.63

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**System Requirements:**
Version 1.63 of SpecDis has been tested under Win 7 SP1 (32+64Bit), and Linux GTK2 64Bit (SLES 11.3). For Windows 7 it is important to install SpecDis on a partitioned drive other than C:\ to avoid administrator-right problems. Windows 8 has not been tested in detail but SpecDis should work under this OS, too. XP and Vista are not supported anymore.

**Capabilities (selection):**

- Automatic extraction of heats of formation and spectral data (excited states, IR/VCD, ORD) from output files
- Gaussian and Lorentzian curve generation
- Direct comparison of calculated spectra with experimental or calculated data
- Application of a "UV shift"
- Provide an enantiomeric ECD/VCD spectrum
- Arithmetic or Boltzmann weighted summation of spectra
- Plot results with Gnuplot in a "what you see is what you get" manner (up to 5 curves)
- Plot UV and CD traces of HPLC runs
- Generate spectral curves that can be processed in other software like Excel or Origin
- Read ORD values from Gaussian03 and Gaussian09 calculations and do a Boltzmann statistical weighting
- Read TD and/or MRCI results of Gaussian03+09, TURBOMOLE (escf,ricc2), ORCA, DALTON 2013, ADF, and NWChem
- Calculate similarity factors for matching of ECD/UV or VCD/IR curves
- Determination of a suited band width and/or shift/scaling factor using the similarity factor or a cross section algorithm

## Installation:

Copy SpecDis to a directory of your choice, on first start it will generate the *SpecDis.ini* in the same directory (your settings will be saved in this file).
To use the plotting routine within SpecDis you have to install Gnuplot on your system. Gnuplot is freely available under the following link:

www.gnuplot.info/
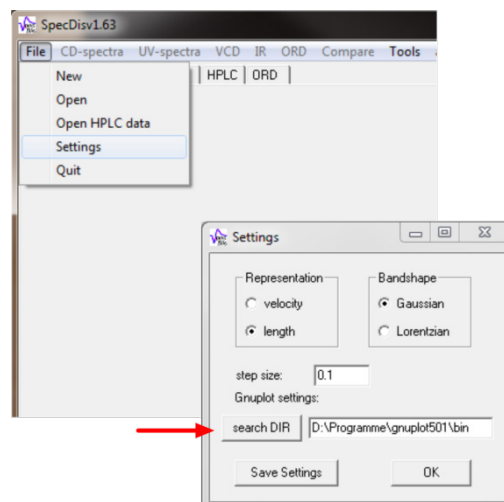
To get plots from gnuplot, SpecDis needs the directory of the file wgnuplot.exe (for Windows systems): Go to File → Settings and use the search button, normally the executable can be found in the \bin or the \binary directory of your gnuplot installation path.
For the linux version SpecDis need the path to the file 'gnuplot', usually this is /usr/bin. As Linux does not have default fonts you have to make sure that the Arial and symbol fonts are available on your system or you have to change the fonts in the new plotting settings in the ECD/UV or VCD/IR tab.

Since Version 1.60, gnuplot 4.6 is supported, plotting of png will only work with versions 4.6 and higher, as the new terminal pngcairo is used. If you use version 5.x check the corresponding checkbox in the settings, otherwise line thickness and color for eps do not fit.

**General Information:**
SpecDis is a software either to analyze excited-states calculations from Gaussian 03+09, Turbomole, ORCA and the DFT/MRCI software from Grimme, or to analyze and plot HPLC-UV and CD chromatograms with Gnuplot. For these purposes SpecDis can read several file formats but needs certain file extensions to recognize the different formats:

Calculated Data:
Gaussian03/09, Turbomole, ORCA, DALTON, ADF, NWChem:  *.out or *.log
DFT/MRCI:                                   *.cd and *.uv
SpecDis can use these files directly without any editing but it only reads excited states in the range of 100 to 4000 nm. VCD and IR data will be read from Gaussain09 files only (use the VCD keyword even if you only need IR, otherwise SpecDis cannot read the data) in the range from 0 to 4000 cm$^{-1}$, thus negative frequencies are ignored.

SpecDis has an own file format called *.bil. The first line is a comment line, followed by two columns with tab separated values. Which values are given is written in the comment line. This file format is needed for the Boltzmann statistical and the arithmetical summation of single ECD/UV, VCD/IR, or ORD spectra. Furthermore, it can be used to import spectra from other QM software by writing your own scripts that create the bil files from this unsupported software. To differentiate the bil files every method has its own file extension so that the extension is build up by a method token and the .bil extension (*.'token'.bil). The tokens are

cd for ECD (e.g. *.cd.bil), uv for UV, vc for VCD, ir for IR, and or for ORD. The same tokens are used for experimental spectra (see below).

Experimental Data:

SpecDis will read data from 100 nm to 4000 nm, only!

UV and CD spectra:
Spectra from JASCO Spectrometers:
SpecDis can directly read the Jasco ASCII fileformat, but you have to change the file-extension for UV or CD spectra to *.uv.exp.xy or *.cd.exp.xy, respectively.

ASCII Files:
These files should have the same extension as mentioned above (uv.exp.xy or cd.exp.xy)! SpecDis can read xy-files with tab spaced numbers (first nanometers, second strength values) and no empty line at the end of the file. In the case of UV spectra it can read *.csv files (semicolon separated files), too.

HPLC-UV or HPLC-CD:
SpecDis reads these files as pure xy-files, that means two numbers (first x, second y) which are tab separated (or semicolon separated). Use *.ccd or *.cuv as file-extensions, so that SpecDis recognizes them as CD or UV spectra, respectively. The range of the displayed chromatogram will be automatically selected from the file by SpecDis but you can also choose the retention time range (zoom) of interest in the corresponding edit box.

**Table 1.** File extensions for experimental data.

| Experimental Data | SpecDis file extension |
|---|---|
| ECD spectrum: JASCO ASCII-File (*.txt) | *cd.exp.xy |
| UV spectrum: JASCO ASCII-File (*.txt) | *uv.exp.xy |
| ECD spectrum, tab or semicolon separated (nm $\Delta\varepsilon$) | *cd.exp.xy |
| UV spectrum, tab or semicolon separated (nm;abs) | *uv.exp.xy |
| UV spectrum, *.csv (nm;abs) | *uv.exp.xy |
| VCD spectrum, tab or semicolon separated (cm$^{-1}$ $\Delta\varepsilon$) | *vc.exp.xy |
| IR spectrum, tab or semicolon separated (cm$^{-1}$; $\varepsilon$) | *ir.exp.xy |
| ORD spectrum, (nm;specific rotation) | *or.exp.xy |
| HPLC-UV chromatogram | *.cuv |
| HPLC-CD chromatogram | *.ccd |

**Settings:**
The most important settings are the choice of the bandshape (Lorentz or Gauss) and the representation of the calculated results that should be used in SpecDis. Keep in mind that ORCA provides ECD values only from the length formalism. SpecDis only reads data from ONE formalism, thus, if you change the representation you have to reload your calculated data!
The 'save settings' button save plot settings and the checkbox settings if you want to search in subfolders or in the same folder for extract heat/spectra, too.

## Theoretical Background:

Gauss Curves:

To get spectra from calculations that can be compared with the experiment you need to put gauss curves over the single oscillator and rotational strength values (calculations for ECD and UV are done in eV and subsequently converted to nm). The line-shape CD curves $\Delta\varepsilon(\lambda)$ were obtained from the 'bar-type' spectra by utilizing a Gauss distribution[1,5] according to:

$$\Delta\varepsilon(\lambda) = \frac{1}{22.96 \times 10^{-40}} \cdot \frac{1}{\sigma\sqrt{\pi}} \sum_k E_{0k} R_{0k} \exp\left[-\left\{\frac{(E - E_{0k})}{\sigma}\right\}^2\right],$$

where $\lambda_k$ and $R_{0k}$ are the wavelength and the rotatory strength of the $k^{th}$ electronic transition, respectively, and $\sigma$ is the exponential half-width, i.e., half the bandwidth of the CD band at $1/e$ peak height. The default $\sigma$-value in SpecDis is 0.16 eV which is in many cases a good alignment but other values in the range of 0.05 eV to 0.4 eV are usual, too. For the UV spectra a similar formula is used with the oscillator strength instead of the rotational strength.

Lorentz Curves:

The formula used to get Lorentz curves is the following:

$$\Delta\varepsilon(\lambda) = \frac{1}{22.96 \times 10^{-40}} \cdot \frac{1}{\sqrt{\pi}} \sum_k E_{0k} R_{0k} \frac{\gamma}{(E - E_{0k})^2 + \gamma^2}$$

where $\gamma$ is half the bandwith at half peak height, $\lambda_k$ and $R_{0k}$ are the wavelength and the rotatory strength of the $k^{th}$ electronic transition.

For UV spectra the constant is replaced by $2.870 \times 10^4$ and of course oscillator strength is used instead of rotational strength values.

For VCD and IR always the Lorentz curves are used with the following equations (calculations are done in wavenumbers):[2]

$$\text{VCD:} \quad \Delta\varepsilon(\upsilon) = \frac{1}{229600 \times 10^{-44}} \cdot \frac{1}{\pi} \sum_k \upsilon_{0k} R_{0k} \frac{\gamma}{(\upsilon - \upsilon_{0k})^2 + \gamma^2}$$

$$\text{IR:} \quad \varepsilon(\upsilon) = \frac{1}{91.48 \times 10^{-40}} \cdot \frac{1}{\pi} \sum_k \upsilon_{0k} D_{0k} \frac{\gamma}{(\upsilon - \upsilon_{0k})^2 + \gamma^2}$$

The constants are fitted to the units given from Gaussion09 (for VCD in $10^{-44}$ and for IR in $10^{-40}$ cgs units). Keep in mind that the absolute values from GaussView (version 5.09) are by a factor of $10^4$ higher as in SpecDis (most probably due to a missing conversion to the $10^{-44}$ units in Gaussview).

Boltzmann weighting:[3]

Experimental CD spectra are a summation of the CD spectra of every conformer of the structure measured. To get a better accordance of experiment and calculation you have to consider this behaviour. Therefore a PES scan has to be done, to find all conformers in a

certain range around the "global" minimum structure. From the thus obtained energies one can get weighting factors for every conformer using the following formula:

$$\frac{N_i}{N} = \frac{g_i e^{-E_i / k_B T}}{Z(T)}$$

with $N = \sum_i N_i$ and $Z(T) = \sum_i g_i e^{-E_i / k_B T}$

In this formula $i$ is the number of conformers found by the PES scan, $T$ is in SpecDis defined as 298 K and $g_i$ is assumed to be 1, as every conformer should be unique. Energies of the single conformers will be used as relative energies to the lowest lying structure found during the PES scan and $k_B$ is the Boltzmann constant. The intensities of the single spectra will be multiplied with this factor and after that added up to the overall spectrum, which can be compared with the experiment (energies for SpecDis have to be in kcal/mol!).

UV shift:
This is a pure empirical approach and safes much computational time. However, the shape of experimental and calculated UV spectra should be quite identical (same number of peaks, comparable relative intensities of the peaks), otherwise one should check if there are problems in the calculation or the measurements (e.g. choose better functionals/basis sets/methods).[3]

**Usage:**
The easiest way to use SpecDis is to drag a *.log* or *.out* file of Gaussian03+09 or ORCA and drop it to SpecDis. If this does not work use the menu File → Open.  The Spectra will then be drawn automatically. You can switch between the different pages to see the ECD/UV or VCD/IR spectra. It is possible to choose different wavelength ranges by editing the numbers on the upper right side, the range of the y-axis is automatically chosen. To Compare with other spectra you have to use the Compare menu, via Drag&Drop always a new session is started and old data will get lost.
Note that the change of the $\sigma/\gamma$-value for ECD/UV (or the $\gamma$-value for VCD/IR) in one tab is always automatically applied to the other tab as well. The same holds for the UV shift or the scaling factor.

**Multiplot:**
Normally SpecDis will display only two curves at once, thus the second one will get replaced automatically each time you add a spectrum. By checking the multiplot checkbox, SpecDis displays up to five spectra. Furthermore, you can choose at which position (curve2, 3, 4, or 5) the newly loaded spectrum will be placed.

**Autoscaling:**
As default SpecDis uses relative values to draw the spectra, the highest peak is set to 90% of the height of the diagram and all other values are scaled to fit this value. To get an impression of how the values of two spectra 'behave' in absolute units, you can switch off the 'auto scaling' checkbox. Keep in mind that this checkbox has no influence on the absolute values of the spectra, it just changes the presentation of the spectra in the images/plots. Saved curves still have the absolute values from the calculation or the measurement.

**Get an enantiomeric ECD/VCD spectrum:**
Just check 'enantiomeric CD' (or VCD) on the right side, the enantiomeric spectrum will be drawn now (the enantiomeric spectrum is a simply calculated by multiplication of the $\Delta\varepsilon$ values with (-1)). To save this spectrum be sure that 'normal CD' (or VCD) is unchecked and open 'CD-spectra' (or VCD) → 'Save cd.bil' (Save vc.bil) or 'Save xy'.


**Compare with experimental or calculated data:**
Once you have loaded a calculated spectrum you can compare it with other calculated or experimental spectra. Open Compare → … with CD/UV spectra if you want to compare a CD spectrum with a UV or CD spectrum or open Compare → …with UV spectrum if you want to compare a UV spectrum with another one.
**Note:** For a full comparison of calculated and experimental data, always read in the calculated spectra first, otherwise the UV shift and $\sigma$-value options will be disabled.
Compare more than two spectra: You have to check the 'multiplot' checkbox to compare more than two spectra, as long as 'multiplot' is unchecked SpecDis will only replace the second spectrum. With selected multiplet, you have to choose at which position (2-5) the new spectrum has to be loaded.

**Save images:**
To save a sketch from your spectra as a graphic file use 'Save Sketch' in the CD or UV menu. Choose a graphic format you like and save the file. These graphics are of a lower quality and are hard to process further. Most probably this option will be removed in one of the next versions! If you want an image for a publication, we strongly recommend to use the eps or png files from Gnuplot.


**Plot spectra with gnuplot:**
To get Gnuplot plots, SpecDis needs to know where the wgnuplot.exe is (have a look at the installation instructions above).
To get an eps file of the spectra shown in SpecDis, you have to use the 'Plot EPS' button (to get a png file use the 'Plot PNG' button). Choose a name for the plt-file in which all relevant input for gnuplot is saved. Then SpecDis automatically plots the spectra which are currently shown in the open tab. This works in a "What You See Is What You Get" manner for most of the spectra, only for HPLC-UV traces (here additionally a 3D plot is possible) and for VCD/IR spectra the gnuplot spectra look different (for VCD every spectrum has its own plot). All settings like the range and y-axis are taken as used before in SpecDis.
One important point here: while using "auto scaling", the y-range of the first ECD/UV spectrum is fitted to the range of the second one if it is an experimental curve and multiplot is deactivated. Otherwise all curves are adjusted to the one with the highest peaks (This is always done for VCD/IR). For ECD/UV it is recommend to read in the calculated spectrum first and the experimental one as second (if multiplot is not used). Just fool around with the ranges and the order of the spectra to get a feeling how to plot your spectra in the way you like it most.
**Important:** Keep in mind, that SpecDis normally does not know whether your values are in molar or relative units (in some cases it will detect this from the cd.exp.xy file). As a default it assumes that you use relative CD ($\Delta\varepsilon$) values in mdeg and labels the y-axis according to this.

**Note:** Do not use blanks or the underline character within your file name, the generation of the *.eps from the *.plt file with gnuplot might fail otherwise. SpecDis removes blanks and underlines automatically!

Since version 1.60, it is possible to choose several gnuplot settings directly within SpecDis. Have a look at the settings buttons in the CD or UV tabs. The settings are more or less self-explaining. Keep in mind that labels and so on have to be in gnuplot notation (see the gnuplot manual for details). You can also change the names of your curves here to avoid overwriting of curves with exactly the same name.

**Write data for Excel, Origin and so on:**
You can save the calculated gauss curve CD/UV spectra as xy ASCII files. These files can be easily imported into Excel or Origin and be further processed there. To save a CD spectrum as an xy-File Open CD-spectra → Save xy; to save a UV spectrum as an xy-File Open UV-spectra → Save xy. SpecDis saves the wavelength range that is visible in the tabs and the step size can be changed in the settings (default is 0.1 nm). For VCD/IR spectra the step size is hardcorded to 1 cm$^{-1}$.

**Extraction of energies/Generate Heat-files:**
Heat files contain one line with the energy in kcal/mol, these files are needed for the Boltzmann statistical weighting of spectra. The *.heat files can be generated from Gaussian or ORCA *.log or *.out files (use #p in the keyword line of Gaussian, otherwise it will not work properly!) with the heat extraction tool (Tools → extract heat). Just choose the directory in which the files (or the subdirectories) can be found.

SpecDis will look (if chosen only in every subdirectory) for *.log and *.out files. Mind that currently only PM3, AM1, SVWN, HF, BLYP, PBE and PBE1PBE, BHLYP, B3LYP, MPn and CCSD calculations are tested with Gaussian03 (Gaussian09 should work with all semiempiric, HF, all DFT methods and with MP2 calculations). ORCA and MOPAC2007/2009/2012 energies can be extracted for every method. All *.heat files will be written to a new 'heat' directory in the chosen directory.

Of course these heat-files can be created manually, if the energies were from other software packages or from other methods. Create a txt-file for example with the windows editor which contains one line: HEAT OF FORMATION = 0.0 kcal/mol where the number should contain the energy in kcal/mol. Save the file and edit the name so that it has the same name as the corresponding *.bil file with the file extension *.heat.

Since Version 1.63 SpecDis searches either in subfolders only or in the chosen directory only, use the checkbox.

**Extraction of spectra:**
Like in the case of the heat extraction every excited state calculation has to be in its own subdirectory. Open Tools → extract spectra and choose the directory in which all the files can be found. SpecDis searches for *.log or *.out files and writes the corresponding *.bil files in a new 'spectra' directory in the initially chosen main directory.

Since Version 1.63 SpecDis searches either in subfolders only or in the chosen directory only, use the checkbox.

**Summation of spectra:**
For the Boltzmann-weighted summation of spectra, you need a *.bil file and a *.heat file with the same name as the *.bil file in the same directory (From version 1.63 on it is possible to choose an additional directory for the heat files). To sum up spectra start the tool, choose the method and the files you want to sum up and click the ok button. After that a spectrum is generated, which can be saved via the corresponding menus in the CD-spectra or UV-spectra

menu. The used weighting factors are displayed in the text field (you can use copy&paste here).

**Similarity factors:**
This feature is in the tools menu and can be used to determine similarity factors as they are described by Bultinck *et al.* for IR and VCD spectra.[4,5] One can use this similarity factor or a cross section algorithm to automatically determine a suited bandwidth value and UV shift. For this you have to read in the calculated UV and CD spectra first and then add the experimental spectrum. SpecDis will check if parameters like wavelength region and intensities fit to each other (e.g. if the experimental UV is given in relative units, the calculated spectrum will be normalized to 1 or calculated intensities will be scaled if there is a large discrepancy) and will then run the algorithms for the given set of wavelength range, bandwidth values, and shifts. Users insight on the quality of measurements and calculations is indispensable here, otherwise, this algorithm might produce nonsense![5]

Formula used for the cross section algorithm:

$$\left| \int_{\lambda_1}^{\lambda_2} f(x)dx - \int_{\lambda_1}^{\lambda_2} g(x)dx \right|$$

With f(x) as the calculated curve and g(x) as the experimental curve. The cross sections of the curves are calculated for all possible combinations of the given parameters and the smallest ones are chosen as the best values.

Formulas used for the similarity factor:

UV similarity:
$$S = \frac{\int_{\lambda_1}^{\lambda_2} f(x)g(x)dx}{\sqrt{\int_{\lambda_1}^{\lambda_2} f^2(x)dx \int_{\lambda_1}^{\lambda_2} g^2(x)dx}}$$

CD similarity:
$$\Sigma_{fg} = \frac{\phi^{++}S^{++} + \phi^{--}S^{--}}{\phi^{++} + \phi^{-}}$$

Weighting factor for positive values (negative parts are calculated analogously):

$$\phi^{++} = \int_{f(x)>0} f(x)dx + \int_{g(x)>0} g(x)dx$$

Enantiomeric Similarity Index Δ:
$$\Delta = \left| \Sigma_{fg} - \Sigma_{fg_{Enantiomer}} \right|$$

For details see reference [5].

The similarity tool can also be used for VCD/IR using the cross section algorithm for IR or the similarity algorithm for IR and VCD as described by Bultinck et al.[4] SpecDis uses the results of the cross section algorithm (if IR is compared) to find the best $\gamma$ value and scaling factor. Like in the case for UV the similarity algorithm tends to too high $\gamma$ values.

## References:

1    (a) P.J. Stephens, N. Harada, *Chirality* **2010**, *22*, 229-233; (b) J. A. Schellman, *Chem. Rev.* **1975**, *75*, 323–331.
2    L. A. Nafie, in *Comprehensive Chiroptical Spectroscopy, Vol. 1* (Eds.: N. Berova, R. W. Woody, P. Polavarapu, K. Nakanishi), John Wiley & Sons, **2012**, p. 118.
3    (a) G. Bringmann, T. Bruhn, K. Maksimenka, Y. Hemberger, *Eur. J. Org. Chem.* **2009**, 2717-2727; (b) G. Bringmann, T. A. M. Gulder, M. Reichert, T. Gulder, *Chirality* **2008**, *20*, 628-642.
4    E. Debie, E. De Gussem, R. K. Dukor, W. Herrebout, L. A. Nafie, P. Bultinck, *ChemPhysChem* **2011**, *12*, 1542.
5    T. Bruhn, A. Schaumlöffel, Y. Hemberger, G. Bringmann, *Chirality* **2013**, *25*, 243-249.