



User manual

Version 3.0

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Specair in 3 minutes

Specair is a program for calculating emission or absorption spectra of air plasma radiation. It can calculate, display and save spectra based on a wide range of user input parameters.

The main user interface sections of Specair are indicated in Figure 1 below. To create a new spectrum the user specifies the input parameters for a new spectrum in the Calculation Options area to the left, and presses the “Calculate spectrum” button in the top left corner. The new spectrum will be displayed automatically in the Plot area in the center. Comments to individual spectra can be added in the Comments Area at the bottom, and the appearance of the spectrum can be changed in the Calculated Spectra area to the right or under the Plot menu. By selecting a spectrum at the top of this area, the user can see the used Calculation Options in the area to the bottom right.

In addition to calculating spectra, Specair can import experimental spectra in most of the commonly used file formats. Using Specair, the user can manipulate both imported and calculated spectra, by selecting the spectrum in the Calculated Spectra area and choosing among the options in the Data menu.

The data can be exported to other applications either by choosing “Export spectrum” in the File menu, or by selecting “Display Data” in the Data menu and the use Copy and Paste to, for example, MS Excel.

An actual plasma emission spectrum consists of many sharp lines, each broadened by several mechanisms including Doppler, collisional, natural or Stark broadening. In reality, however, the resolution of the collected data is determined by the instrumental broadening specific to each experimental setup. In Specair instrumental broadening is taken into account by convolving the plasma emission spectrum with a ‘Slit function’. The slit function represents the broadening caused by the spectrometer (slit width, pixel width, grating dispersion) and can be changed by selecting “Slit Function” from the Tools menu. The user can either use a trapezoidal slit function or import an experimental file. The imported file should be in a commonly used file format.

Specair has about 60 input parameters, all set in the Calculation options, which together determine the wavelength and intensity for each peak in the spectrum. The peaks, which correspond to various transitions between the internal energy states of atoms or molecules, are determined by the population of plasma species in the various energy levels, the energy differences and transitions rules between the excited states, and the radiative transition probabilities.

- 1. Temperatures**

The electronic, rotational, translational and vibrational temperatures, in Kelvin, define the respective Boltzmann population distributions of the internal energy levels.

- 2. Pressure**

The pressure can be set using several different units, and determine radiation intensity and the level of absorption.

- 3. Wavelength Range (nm)**

This specifies the wavelength range over which the spectrum will be computed.

4. Calculation Settings

The calculation settings allows the user to change certain aspects of the calculations, such as whether to include absorption, to generate Mole fractions automatically, or to convolve the spectrum with a slit function, to replicate experimental conditions. The Speed display option is recommended as it reduces lowers the resolution to match that of the slit function.

5. Mole Fractions

The relative amount of each species is indicated here. For plasma consisting of only one species the value should be 1, otherwise use fractional values. For example, use 0.5 for N₂ and 0.5 for CO, for two equal concentrations of these species. If the sum of the mole fractions of the species defined in your calculations exceeds unity, the program will still compute the spectrum, but a warning message will be given.

6. Radiative Transitions

Specair includes most of the common transitions for air plasmas, but also for plasmas containing carbon species. The naming of the transitions conforms to the standard spectroscopy conventions. The spectroscopic transitions to model are selected by entering a '1'. To exclude the transition, set the value to '0'. The numerical value is used as a multiplier to the Einstein emission coefficients and to the population in the upper state of the transition. Although calculations should normally be performed with these parameters set to one, any other numerical value can also be used. For example, choosing a value of 2 is a convenient way to multiply the population of the emitting level by a factor of 2. This could be useful to determine the extent of nonequilibrium in the population of excited states.

7. Room air absorbers to consider

This section lets the user specify experimental conditions, compensating for absorption in the air between the plasma and the spectrometer. Note that the absorbing species are considered to be at room temperature for this option. Set species to On to include them in the calculations, and specify the path length of air, in cm, and the relative mole fractions (0.21 for 21% oxygen in air etc.).

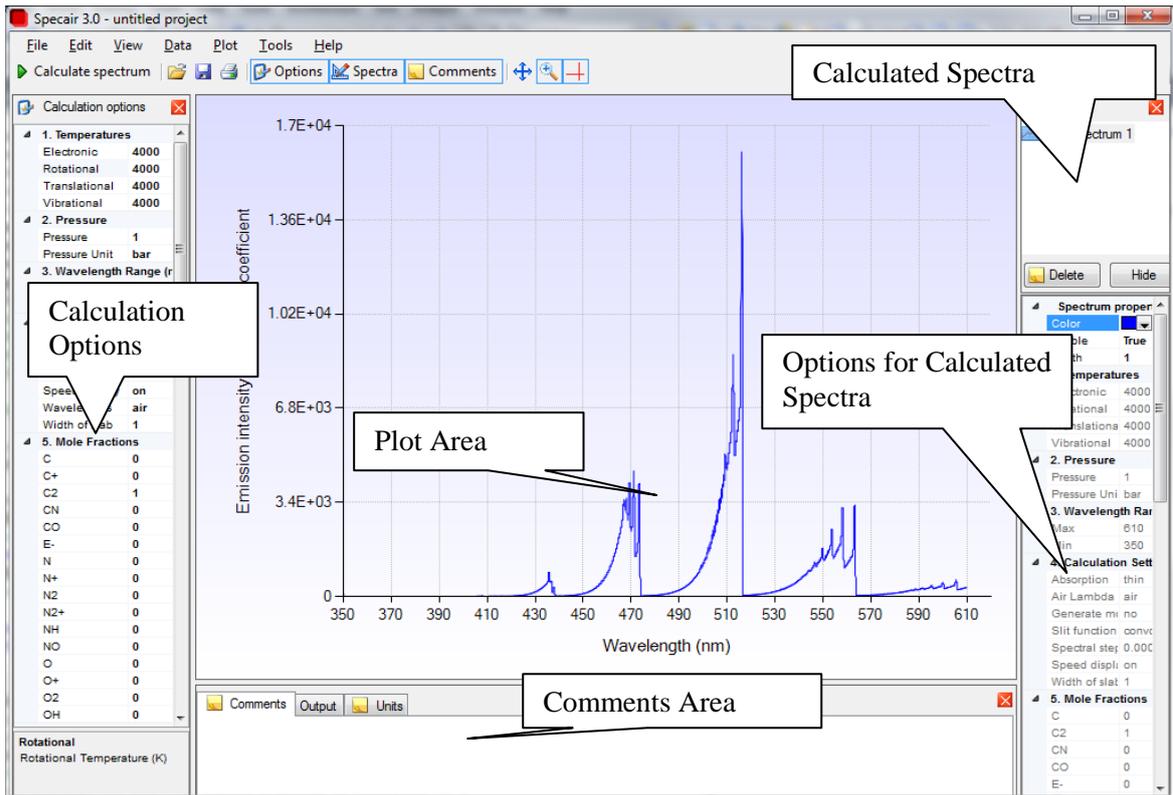


Figure 1. Screen shot of Specair.

1. Introduction to Specair

Specair is a computer program that models radiative spectra for plasmas. The areas of applications include analysis of plasma spectra and heat flux calculations, and it has been verified by numerous experiments.

The calculations in Specair are based on a quantum mechanical model that describes each energy level of the species included. The species are the most important radiating atoms, ions and diatomic molecules present in air plasmas, e.g. N_2 , O_2 , NO , N_2^+ , N , O , C , ... The spectra of diatomic molecules are computed as described in.

Laux, C.O., "Optical Diagnostics and Collisional-Radiative Models," VKI Course on Hypersonic Entry and Cruise Vehicles, Stanford University, June 30 – July 3, 2008.

The latest iteration of Specair combines a fast engine for calculations with an intuitive and versatile Windows-based user interface. The engine is written in Fortran, for maximal performance, and can calculate a high-resolution spectrum within a few seconds on a modern desktop computer. While spectra can be exported for advanced analysis or presentation purposes, the Specair interface provides many basic functions for immediate analysis.

2. The Specair User Interface

The Specair user interface, see Figure 2, offers many functions, which are detailed in the subsequent sections. After specifying the Calculation options for a spectrum, the user starts the calculation by pressing the Calculate spectrum button, by selecting Spectrum > Calculate Spectrum from the menu bar, or by pressing the F2 button. Once calculated, the spectrum will be displayed and ready to work with, using the functionalities described below.

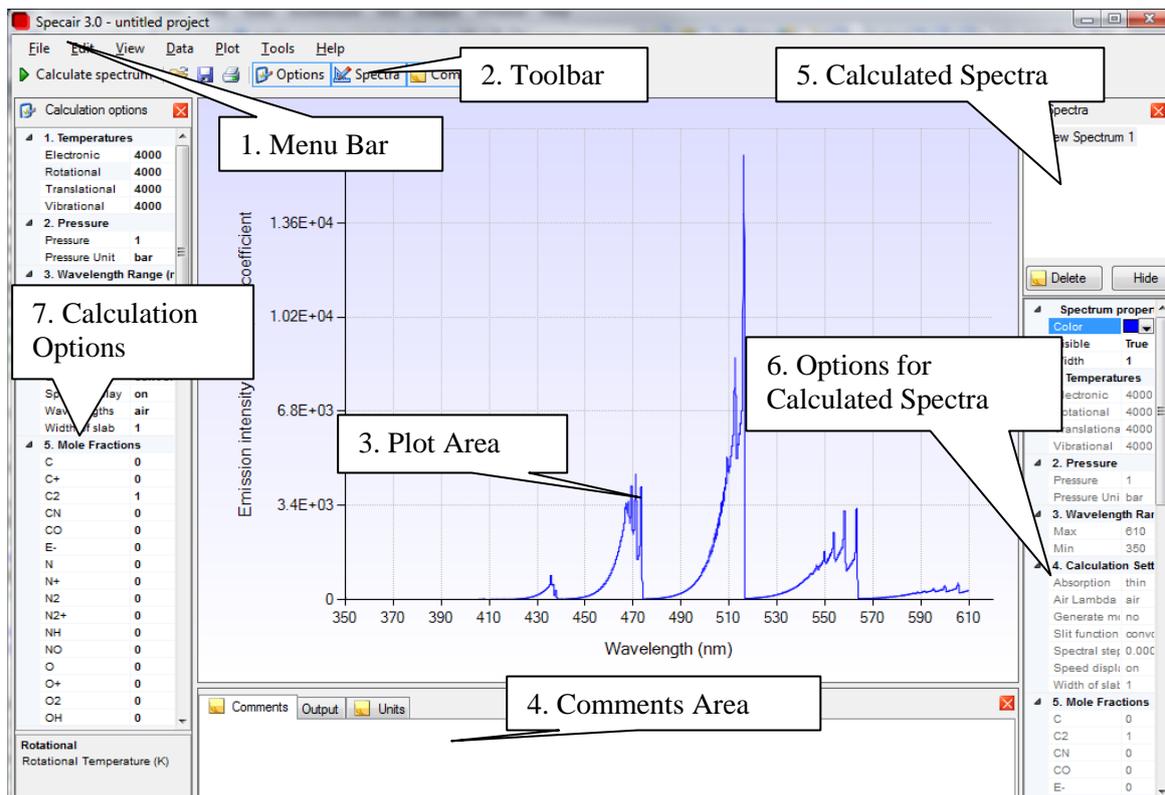
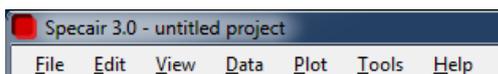
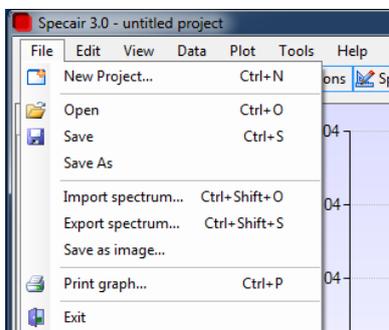


Figure 2. The Specair user interface.

2.1. Menu Bar



2.1.1. File menu



New Project... Ctrl+N

Create a new Specair project. This clears all the calculated spectra. The program will ask you if you want to save the current project, before closing it.

Open Ctrl+O

Open an existing Specair project. A Specair project contains all calculated spectra and the options used to calculate them, as well as any imported files.

Save Ctrl+S

Save the current project to a Specair data file.

Save As

Save the project as a new Specair data file.

Import spectrum...

Import a data file containing a spectrum. Most commonly use file formats are supported, such as Galactic .spc and JCamp-DX .jdx. For a text file the data should be listed in two columns, wavelength in nm and intensity, separated by spaces or tabs.

Export spectrum...

Export the spectrum selected in the Calculated Spectra area. For an ASCII text file output the file will contain two columns, wavelength in nm and intensity, separated by tabs. Specair also supports other commonly used file formats used in other applications.

Save as image...

Save the current view in the Graph Area to an image file. Several of the most popular image file formats are available (Bitmap, JPG, EMF, PNG, GIF, TIFF).

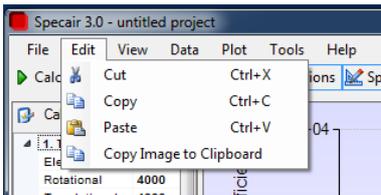
Print graph... Ctrl+P

Open a print dialog box for printing of the current view in the Graph Area.

Exit

Exit Specair.

2.1.2. Edit menu



Cut **Ctrl+X**

Cut the current field. Works with most text fields.

Copy **Ctrl+C**

Copy the current field. Works with most text fields.

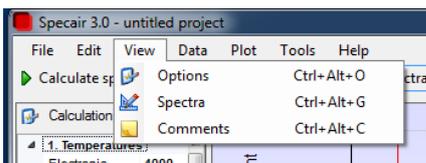
Paste **Ctrl+V**

Paste the clipboard content to a field.

Copy Image to Clipboard

Copy the current view in the Plot Area to the Clipboard. The image can be pasted into other programs, such as MS Office.

2.1.3. View menu



Options **Ctrl+Alt+O**

Show the Calculation Options.

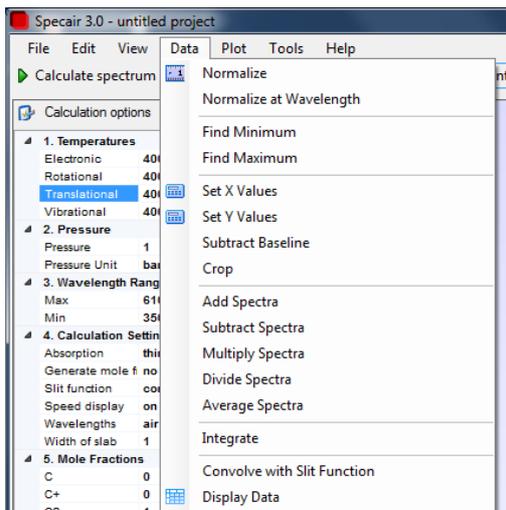
Spectra **Ctrl+Alt+G**

Show the Calculated Spectra.

Comments **Ctrl+Alt+C**

Show the Comments.

2.1.4. Data menu



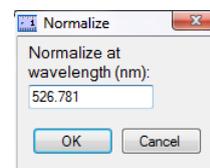
The data menu provides a number of operations that can be performed on both imported and calculated spectra. These functions are useful for correcting experimental spectra for drift, imperfect calibrations or different scaling. They also give the user a way to compare spectra, integrate them and to access the numerical data for further processing.

Normalize

Normalize all the selected spectra to a maximum value of 1.

Normalize at Wavelength

Open a dialog box for normalizing selected spectra at a given wavelength. The wavelength is initially set by the vertical marker but can be changed by the user. All spectra will be divided by the value the specified wavelength, determined by interpolation if necessary.



Find Minimum

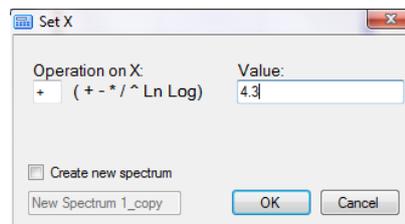
Find the minimum value among the data in the selected spectra. The cursor is placed at that point and the coordinates are displayed in the top right corner until the mouse enters the plot area.

Find Maximum

Finds the maximum point similarly to the Find Minimum above.

Set X Values

Open a dialog box to perform basic arithmetic on one or several selected spectra (see right figure). Select an operator in the first field and enter a value in the second. The operation will be performed on the X value (wavelength) for each point in the spectra, which will be replotted in the graph area. If “Create new spectrum” is selected a new spectrum will be created and displayed in the plot area, leaving the original spectrum intact.

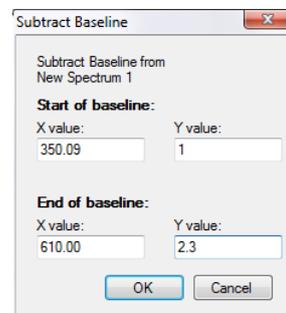


Set Y Values

Same as Set X Values above, except that the arithmetic operation will be performed on the Y value (emission intensity or absorption coefficient).

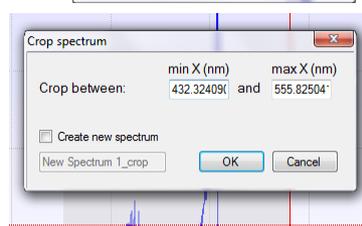
Subtract Baseline

Open a dialog box for subtracting a linear baseline from a selected spectrum (see right figure). This can be used, for example, to compensate for background noise in the experimental apparatus used to measure imported spectra. Press OK to subtract a segment defined by the start and end values.



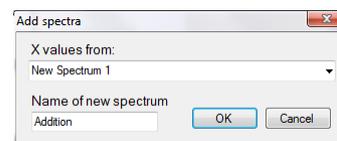
Crop

Open a dialog box for reducing the wavelength range of a spectrum. This can be useful, for example, to a small segment of an imported spectrum. The wavelength range is selected using the cursors in the plot area before selecting Crop, but can also be changed in the Crop window. If “Create new spectrum” is selected, a new, cropped copy will be generated, leaving the original spectrum intact.



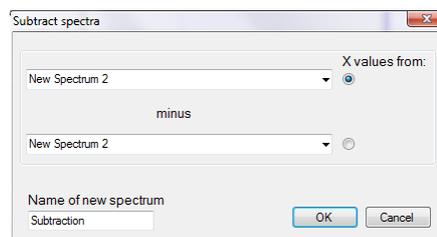
Add Spectra

Open a dialog box for adding two or more spectra. A new spectrum, with the name specified by the user, will be created with y-values at each wavelength being the sum of all corresponding points in the selected spectra. The wavelength (x) values are the same as one of the input spectra, as determined by the user. The y-values for the other spectra are interpolated values at the same wavelengths before the addition, allowing the user to quickly add spectra from different sources.



Subtract Spectra

Open a dialog box for subtracting one of two selected spectra from the other. A new spectrum, with the name specified by the user, will be created with y-values at each wavelength being the difference between the points in the top spectrum and the bottom spectrum, as determined by the user in the drop-down menus. The wavelength (x) values are the same as one of the input spectra, as determined by the “X values from” option. The y-values for the other spectrum are interpolated values at the same wavelengths, allowing the user to quickly subtract, for example, a calculated spectrum from an imported one to assess their agreements.



Multiply Spectra

Multiplies the points in selected spectra. Similar to “Add Spectra” above.

Divide Spectra

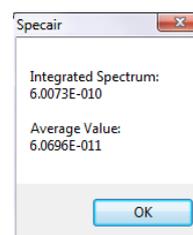
Divides the points in one selected spectrum by those in a second selected spectrum. Similar to “Subtract Spectra” above.

Average Spectra

Averages the y-values for two or more spectra and creates a new spectrum. This can be used, for example, to consolidate data from several experiments under identical conditions. This operation is equivalent to “Add spectra” above, followed by a division by the number of input spectra.

Integrate

Display the result of the numerical integration of the selected spectrum. A trapezoidal integration, using the wavelengths, is used, and the units are dependent on the input spectrum. The average y-value, equal to the area divided by the wavelength range, is also displayed.



Convolve with Slit Function

Convolve one or more selected spectra by the current slit function. Performing this operation on a non-convoluted spectrum is equivalent to selecting “convolution” for the “Slit function” option in the Calculation options. This menu option only works for spectra calculated in Specair.

Display Data

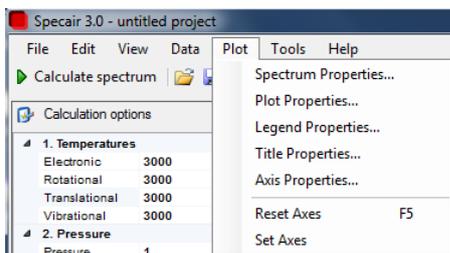
Open a window with data for the selected spectrum (see right figure). The data is represented as two columns, Wavelength (nm) and Intensity, and can be copied to other programs, such as MS Excel. Click in the top left corner to select all data.



Wavelength (nm)	Intensity
35.029979	13.978
35.030079	13.673
35.030179	13.38
35.030279	13.099
35.030379	12.833
35.030479	12.58
35.030579	12.338
35.030679	12.104
35.030779	11.876
35.030879	11.65
35.030979	11.426
35.031079	11.204
35.031179	10.982

Close

2.1.5. Plot menu



The plot menu contains all the options for modifying the plot area and the displayed spectra. This gives the user the option of creating professional-looking graphics, for presentation purposes, directly within Specair.

The options for changing the properties can also be accessed directly by clicking on elements in the plot, such as the axes or the spectrum traces.

Spectrum Properties

All the selected spectra will be changed when using this option, which allows the user to change the look of the traces. Each spectrum can be represented using lines, markers or both, or be hidden completely. Lines can have different widths, colors and styles whereas markers have options for marker type, size, color, border width and border color. Each spectrum can also have an associated legend text. This is shown if a legend is used (see Legend Properties below) and can be different from the spectrum name.



Plot Properties

The look of the background is changed using this option. The “Plot Area”, encompasses the region within the axes whereas the “Chart Area” includes those outside as well. Both areas can have backgrounds consisting of a single color or have gradient or hatch patterns where a Secondary Color has to be specified. The areas can be surrounded by borders with different widths, colors and dash styles, and the user can also add a shadow to the plot area, defined by an offset and a color.



Legend Properties

A legend can be added to the plot by selecting the “Show Legend” box on the top left. The legend has many options, as seen to the figure on the right. The legend style includes options for the text associated with each trace, such as font and color. The geometry of the legend is defined by its style (column or row) and its docking and alignment. The docking defines which side of the graph the legend is placed on and the alignment selects whether it is placed in the



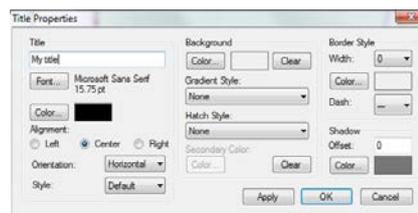
middle or a specific corner. The legend can be placed inside the “Plot Area”, i.e., within the axes.

The legend can have its own title, with options for font, color, background color and alignment. This means that the title is associated with its own area, separated from the rest of the legend by a separator, which can also be defined in terms of style and color.

The legend can have its own background, including gradients and hatch styles, just like the plot area (see above). Similarly it can have a border and a shadow.

Title Properties

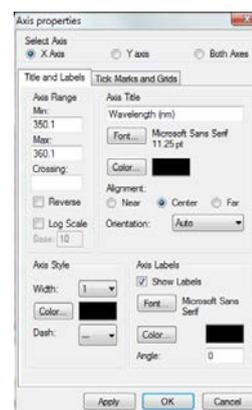
A title can be added to the plot. Like the legend and plot areas it can have background effects, a border and a shadow. The title can be aligned to the left, middle or center and the text orientation is variable. The title also has a few text styles, such as shadowing.



Axis Properties

The axis properties window can change one or both axes in the plot area. Each axis has an axis title which can be changed along with its font, alignment and orientation. The axis range can be defined manually as can the crossing, if the user prefers the other axis to be placed somewhere in the middle of the plot. The default setting is for the crossing to be at the minimum of the axis range. The *x*-axis can be reversed and both axes can use a log scale, provided that all values are greater than zero.

The width, color and dash style of the axes can be modulated. The labels can be removed and their font, color and orientation can be changed.

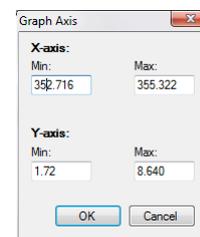


Reset Axes F5

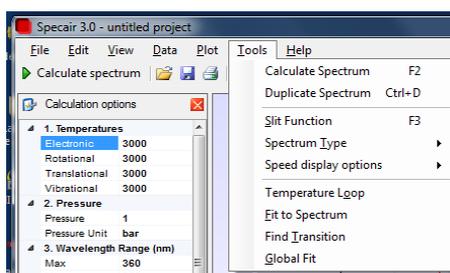
Set the axis range for both axes to encompass all visible spectra.

Set Axes

Set the axis ranges manually. This has the same effect as changing it under Axis Properties (see above) but the values can be preset using the plot markers.



2.1.6. Tools menu



Calculate Spectrum F2

Calculate and display a new spectrum based on the current settings in the Calculation options.

Duplicate Spectrum Ctrl+D

Create identical copies of all selected spectra. The new spectra have the suffix “_copy”.

Slit function F3

Open a dialog box for defining and selecting a slit function. For more details please read the Slit Function section below.

Spectrum type

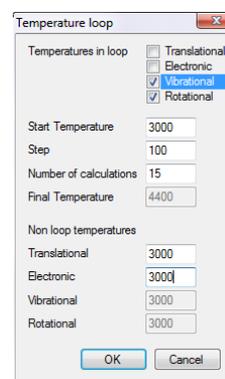
Specair can calculate both emission intensities and absorption coefficients. Both options use the same input parameters in the Calculation options. The spectrum types are displayed similarly in the plot area, but their units will differ.

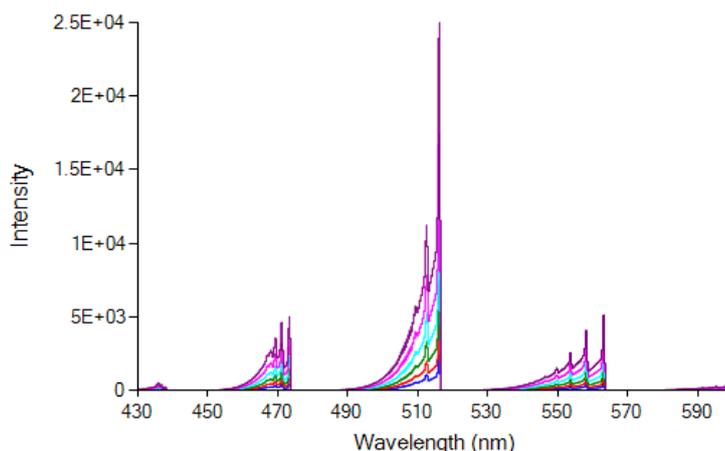
Speed display options

Specair automatically uses an optimal spectral resolution in its calculations. This resolution is usually far greater than that offered by the experimental equipment, as defined by the spectrometer’s slit function. By selecting the Speed display found in the Calculation options only a small subset of all points will be imported from the calculations, to speed up the subsequent manipulation of the calculated spectra. This option displays a certain number of points for each slit function full width half maximum (FWHM), as defined by this Speed display option. 10 or 20 points is often sufficient.

Temperature loop

The temperature loop allows the user to make many calculations in one batch, while varying one or more statistical temperatures. The user defines the Start Temperature, the Step, which is the incremental increase in temperature, and the number of spectra to calculate. The temperatures not selected at the top will be held constant at the values entered in the bottom text fields. An example of the temperature loop, for the C2 Swan transition, is shown in the figure below.



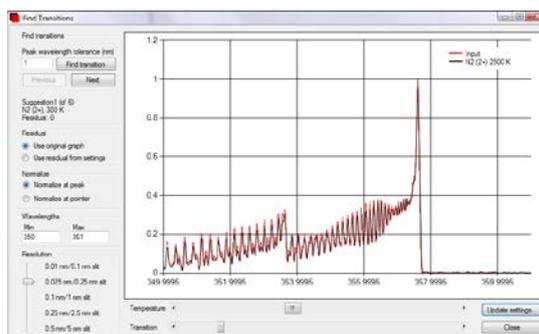


Fit to Spectrum

Specair can perform successive calculations to fit a selected experimental spectrum. The user can fit temperatures and mole fraction using several options. For more information see the section about curve fitting below.

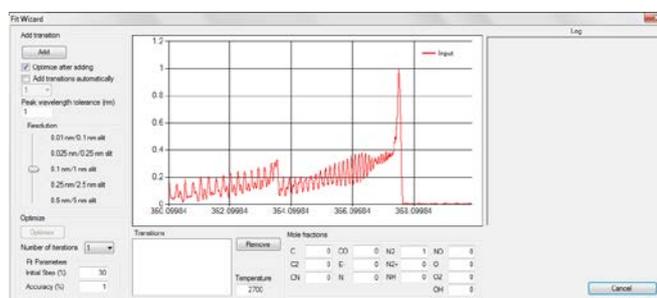
Find Transition

This option helps finding unknown transitions in a spectrum, either by automatically matching peaks or by manually scrolling through a number of precalculated spectra at various temperatures and resolutions. The user can use a selected spectrum as input, or the residual from subtracting a selected spectrum and one calculated from the current settings. The second option is useful for identifying smaller peaks under a spectrum that has already been fit. The resolution is changed to most closely match that of the selected slit function. The Find Transition function is intended only for finding starting points for further fitting and the absence of a hit does not mean that a transition is not present in the spectrum.

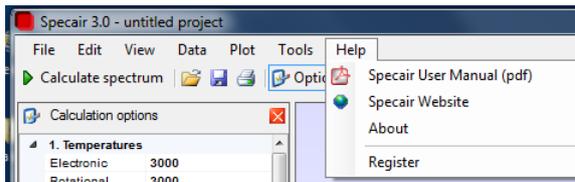


Global Fit

The Global Fit function, or fit wizard, can be used in some cases where the user wants to fit a complex spectrum with several species and transitions. The global fit incorporates both the Fit to Spectrum and Find Transition functionalities to successively add new species and transitions, and then fit both temperatures and mole fractions in an iterative manner. For more information see the section about curve fitting below.



2.1.7. Help menu



This menu contains resources for help and registration.

Specair User Manual (pdf)

Open the Specair User Manual (this document). An external pdf reader must be installed.

Specair Website

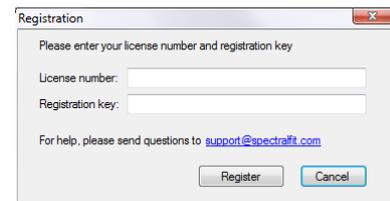
Open the Specair Website, www.spectralfit.com, in the default browser.

About

Display the current version and copyright information.

Register

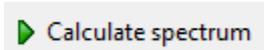
Specair is available in a shareware version with limited capabilities. The full version is enabled by entering the Licence number and Registration key obtained when purchasing a license. For more information about licenses, please visit the Specair website, www.spectralfit.com, or send an email to license@spectralfit.com.



2.2. Toolbar



The toolbar provides a quick way to access some of the most used functionalities, which are also found in the Menu Bar (see above).



Calculates and displays a new spectrum based on the current settings in the Calculation Options.



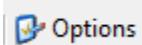
Open an existing Specair project.



Save the current Specair project.



Open a print dialog box for printing of the current view in the Graph Area.



Show/hide the Calculation Options.



Show/hide the Calculated Spectra.



Show/hide the Comments.



Reset the axes.



Zoom in when selecting an area in the plot



Enable the markers. The markers can be used to select an area without zooming, for use when cropping the spectrum, for example .



Zoom out. This button is only available when the user has zoomed into an area.

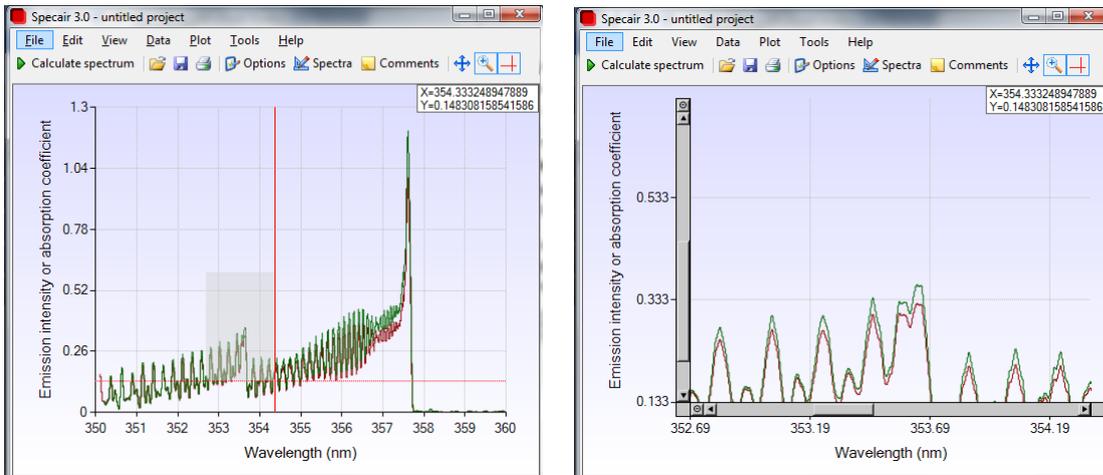
2.3. Plot Area

The Plot Area displays calculated and imported spectra as line charts. Wavelength in nm is displayed on the x -axis and intensity on the y -axis.

2.3.1. Zooming

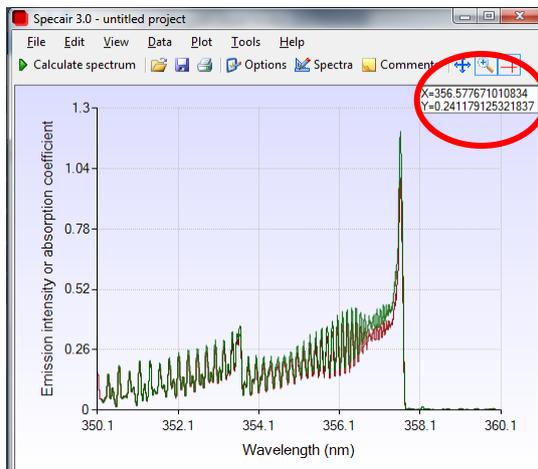
The user can zoom in on a region of interest by selecting that region with the mouse while pressing the left mouse button (see figure right below).

Scroll bars will appear along the two axes (see figure left below) allowing the user to move within the graph at the current magnification. Click on the round button at the left or top of the scrollbar to return to the previous magnification for the x - or y -axis respectively.



2.3.2. Tracking

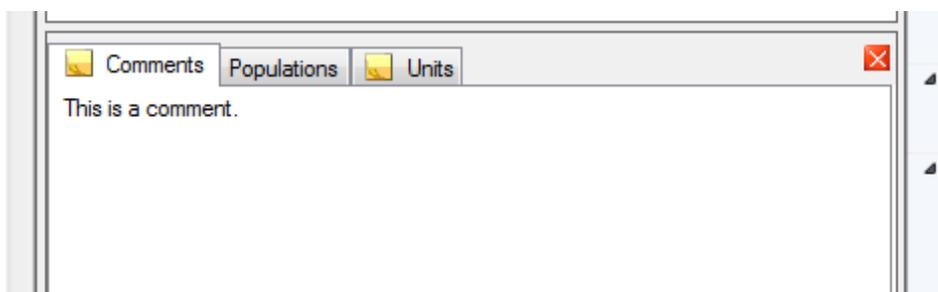
Specair automatically displays the coordinates of a data point when the mouse pointer is placed on top of it. The coordinates are displayed the top right corner of the Plot Area (see figure below) and the units are identical to the axis units (nm for x and intensity for y).



2.4. Comments Area

The Comments area consists of three tabs: Comments, Populations and Units.

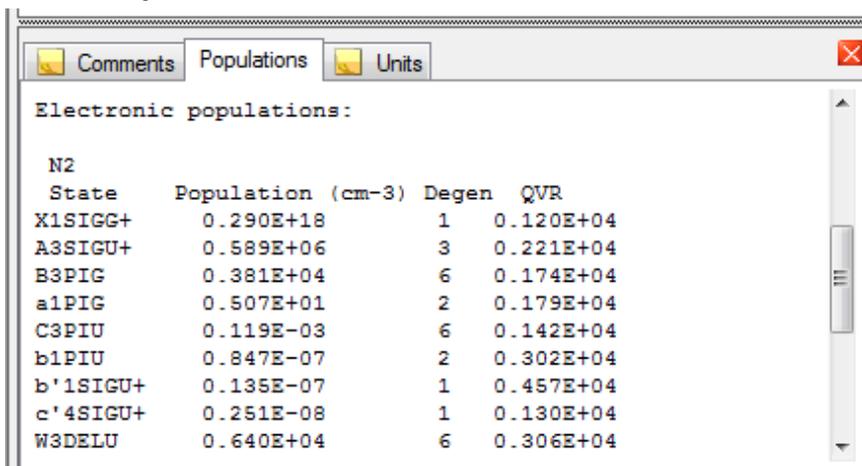
2.4.1. Comments



The Comments tab lets the user add comments to each spectrum in text format. The entered comments are associated with the currently selected spectrum in the Calculated Spectra area.

Analyzing an experimental spectrum might involve calculating many spectra in an iterative process. The comments section is there to help the user keep track of ideas or information above and beyond the Calculation Options, which are saved automatically.

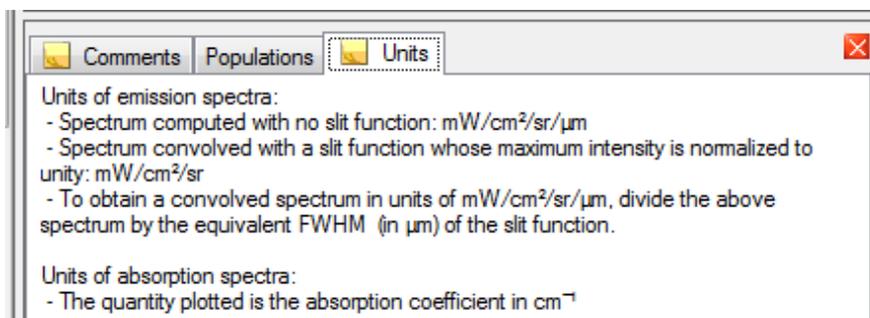
2.4.2. Populations

A screenshot of a software window with three tabs: 'Comments', 'Populations', and 'Units'. The 'Populations' tab is selected and active. The main area displays a table titled 'Electronic populations:' with columns for 'N2 State', 'Population (cm-3)', 'Degen', and 'QVR'.

N2 State	Population (cm-3)	Degen	QVR
X1SIGG+	0.290E+18	1	0.120E+04
A3SIGU+	0.589E+06	3	0.221E+04
B3PIG	0.381E+04	6	0.174E+04
a1PIG	0.507E+01	2	0.179E+04
C3PIU	0.119E-03	6	0.142E+04
b1PIU	0.847E-07	2	0.302E+04
b'1SIGU+	0.135E-07	1	0.457E+04
c'4SIGU+	0.251E-08	1	0.130E+04
W3DELU	0.640E+04	6	0.306E+04

The Populations tab displays, among other variables, the calculated electronic populations.

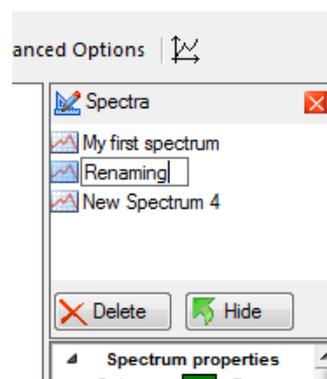
2.4.3. Units



The Units tab displays the different intensity units in Specair. The possibility of concurrently displaying many spectra of different origins, such as imported spectra and spectra calculated with or without convolving with a slit function, precludes a default intensity unit. Instead, the Unit tab provides a quick access to the Specair units and conversion factors.

2.5. Calculated Spectra

All spectra, calculated and imported, are listed in the Calculated Spectra area at the top right of the Specair window. New calculated spectra are automatically named 'New Spectrum' plus a number, and imported spectra also have "(imported)" added to their names. The user can manually enter a new name after clicking on an already selected spectrum.



Permanently delete all selected spectra from the current project.



Hide or show selected spectra in the Plot Area.

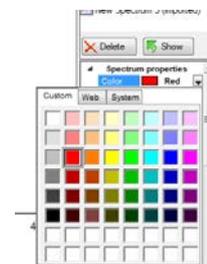
2.6. Options for Calculated Spectra

The Options for Calculated Spectra are located at the bottom right of the Specair window and display properties a selected spectrum in the Calculated Spectra area.

All spectra, both calculated and imported, have three properties that can be changed: Color, Visibility and Width.

Color

Spectra are automatically assigned a color, which is used when it is displayed in the Plot Area. This color can be manually changed by clicking on the drop-down menu (see figure to the right).



Visible

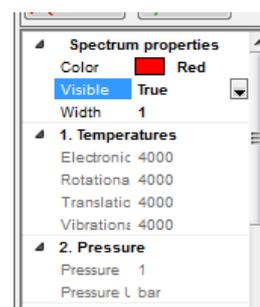
Set visibility of the spectrum in the Graph Area. Changing this property from True to False is identical to clicking the "Hide" button above.

Width

Change the line width, in pixels, for the spectrum in the Plot Area. The standard value is 1, but higher values are possible.

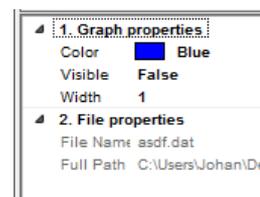
2.6.1. Calculated spectra

The remaining options for calculated spectra are a copy of the Calculation Options used for the calculation of that specific spectrum (see figure to the right). These entries cannot be changed manually, but serve as a quick reference.



2.6.2. Imported spectra

Imported spectra have no Calculation Options. Instead the name and path of the imported file is displayed (see figure to the right)



2.7. Calculation Options

The Calculation Options, found in the left of the Specair window, represent all the variable input parameters for spectrum calculations. There are about sixty independent variables in total, all displayed in a single list. Some variables, such as temperature, pressure and mole fractions, represent the physical conditions of the simulated plasma. Others let the user specify what to include in the calculations, over which range and with which resolution. The following sections explain each of these input parameters.

2.7.1. Temperatures

In Specair, the populations of molecules in specific energy states are assumed to follow Boltzmann's distributions at the electronic, vibrational, or rotational temperature. The levels of atomic species follow a Boltzmann distribution at the electronic temperature. The fourth temperature is the translational temperature, which together with the pressure, defines the total density of the plasma, as well as the line broadening coefficients (Specair includes in general Doppler, collisional, Stark and natural broadening). See the section below on the physical model for more information.

Electronic

The electronic temperature determines the populations of electronic levels (Boltzmann distribution at $T_{\text{electronic}}$).

Rotational

The rotational temperature determines the population of rotational levels (Boltzmann distribution at $T_{\text{rotational}}$).

Translational

The translational temperature is the classical thermodynamic temperature and determines, together with the pressure, the overall population of molecules in the plasma as well as the Doppler and collisional broadening widths.

Vibrational

The vibrational temperature determines the population of vibrational levels (Boltzmann distribution at $T_{\text{vibrational}}$).

2.7.2. Pressure

Pressure

The pressure determines, with the temperature, the number density of species, and therefore the absolute intensity of the spectrum.

Pressure Unit

This entry specifies the unit used for the number in the pressure entry. The most common units are available (Pa, bar, mbar, atm and torr).

2.7.3. Wavelength Range (nm)

Specair calculates spectra over a wide range of wavelengths, from the UV to the IR.

Max

The maximum wavelength of the calculated spectrum, in nm.

Min

The minimum wavelength of the calculated spectrum, in nm.

2.7.4. Calculation Settings

Generate mole fractions

Specair will automatically calculate mole fractions in air plasmas if this value is set to yes. The generated mole fractions, for air at 1 atm pressure with 300 ppm CO₂, are based on the temperatures. If this option is turned on the mole fractions entered manually in section “5. Mole Fractions” will not be considered. The calculated mole fractions are displayed in the Calculated Spectra section.

Self-absorption

When this option, relating to the radiative transport, is on Specair takes into account self-absorption of radiation within the length of the plasma slab (see entry on “width of slab” below). Turning it off means instead that all radiation produced will leave the plasma.

Slit function

With the Slit function option set to “no slit function”, Specair returns a spectrum with only Doppler, collisional, Stark and natural broadening. When set to “convolution” the spectrum will be convolved with the slit function specified in the Slit Function dialog box.

Speed display

With this option turned on the calculated spectra are returned with a resolution matching the Slit Function (see also Speed display options above). This significantly improves the speed and memory requirements without impacting the practical quality, and is the default option. The full resolution is returned with this option turned off, but this is not recommended as the program can quickly run out of memory.

Wavelengths

The returned wavelengths as observed in “air” or “vacuum”. The standard value is “air” as spectroscopic detectors are usually placed in room air.

Width of slab

Indicate the width of the plasma, in cm, along the line of sight of the spectrometer. The value determines the intensity of the calculated spectrum and is important when comparing absolute intensities with experimental data.

2.7.5. Mole Fractions

The relative amount of each species is indicated here. For plasma consisting of only one species the value should be 1, otherwise use fractional values. For example, use 0.5 for N₂ and 0.5 for CO, for two equal concentrations of these species. For a non-zero result, the Mole Fractions for

the species responsible for the selected transitions (see below) have to be greater than zero. The species are written without subscript, i.e., N2=N₂.

2.7.6. Radiative Transitions

The spectroscopic transitions to model are selected by entering a '1'. To exclude a transition, set its value to '0'. In the code, this numerical value is actually used as a multiplier to the Einstein emission coefficients or to the number density of the emitting state. Thus using a value of 2 would be equivalent to computing a spectrum with twice the population given by the Boltzmann distribution. This feature is left open such that the user can simulate a non-Boltzmann distribution for the emitting state of the selected transition.

Specair includes most of the common transitions for plasmas made of N, O and C compounds. The naming conforms to the standard spectroscopy literature.

2.7.7. Room air absorbers to consider

Specair can include the effects of room air absorption in the calculations. This is useful when analyzing experimental data collected with an air-filled gap between the plasma and the detector.

H2O

Set value to "on" to include IR absorption by water molecules in a humid air path. The default value is "off".

H2O Length

The optical path length, in cm, for the absorption by water molecules in the air gap. The path length refers to the total distance.

H2O Mole Fraction

The mole fraction for water in air. The standard value is 0.002, corresponding to 0.2%.

CO2

Set value to "on" to include IR absorption by carbon dioxide in the air gap. The default value is "off".

CO2 Length

The optical path length, in cm, for the absorption by carbon dioxide in the air. The path length refers to the total distance.

CO2 Mole Fraction

The mole fraction for carbon dioxide in air. The standard value is 0.00036, corresponding to 360 ppm.

O2

Set value to "on" to include VUV (i.e., below 200 nm) absorption by oxygen in the air gap. The default value is "off".

O2 Length

The optical path length, in cm, for the absorption by oxygen in the air. The path length refers to the total distance.

O2 Mole Fraction

The mole fraction for oxygen in the gap. The standard value in atmospheric air is 0.21, or 21%.

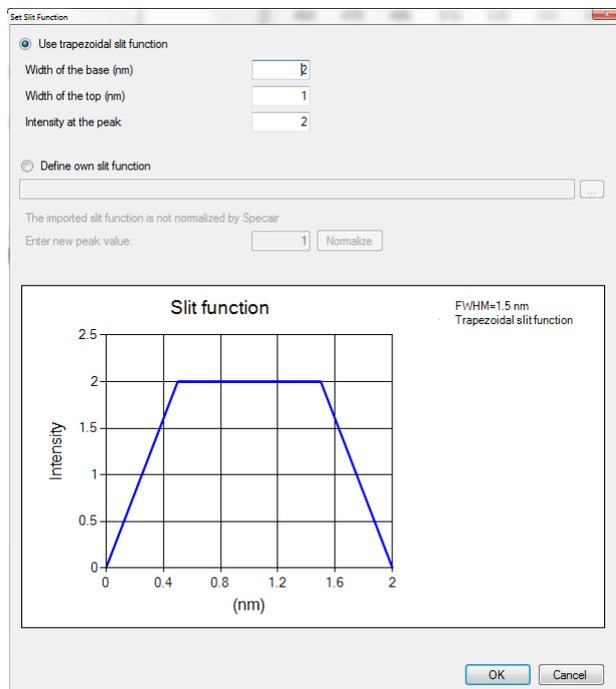
3. The Slit Function

The slit function is a measure of the broadening of spectral lines due to instrumental broadening. The slit function can be determined, for example by measuring a laser with a well defined wavelength (usually a HeNe at 632.8 nm). In Specair, the user can import such a measurement, and use it in calculations to simulate a real measured spectrum. A user defined trapezoidal slit function, the simplest approximation of a true slit function, can also be used. Note that a Gaussian slit function is well simulated by a triangular slit function (i.e. a trapezoid of top = 0)

To convolve a spectrum with the slit function, select “convolution” for the Slit function entry in the Calculation Options, and specify the slit function by selecting ‘Slit Function’ in the Spectrum menu, or by pressing F3, which opens the slit function window.

3.1. Trapezoidal Slit Function

In the absence of an experimental slit function, the user can specify a simplified one in the shape of a trapezoid. If the trapezoid is normalized to unity, i.e., the intensity is 1, the calculated spectrum will have the intensity given in $\text{mW}/\text{cm}^2/\text{sr}$. To obtain a spectrum in units of $\text{mW}/\text{cm}^2/\text{sr}/\mu\text{m}$, divide the above spectrum by the FWHM (in μm), which is indicated in the graph in the Slit function window (see figure below).



3.2. Imported Slit Function

An experimental Slit function can be imported in the Slit function window by selecting “Define own slit function” and then pressing the “...” button to open a file dialog box. The format of the

imported slit function should be a text file with two columns, wavelength in nm and intensity, separated by tabs or spaces.

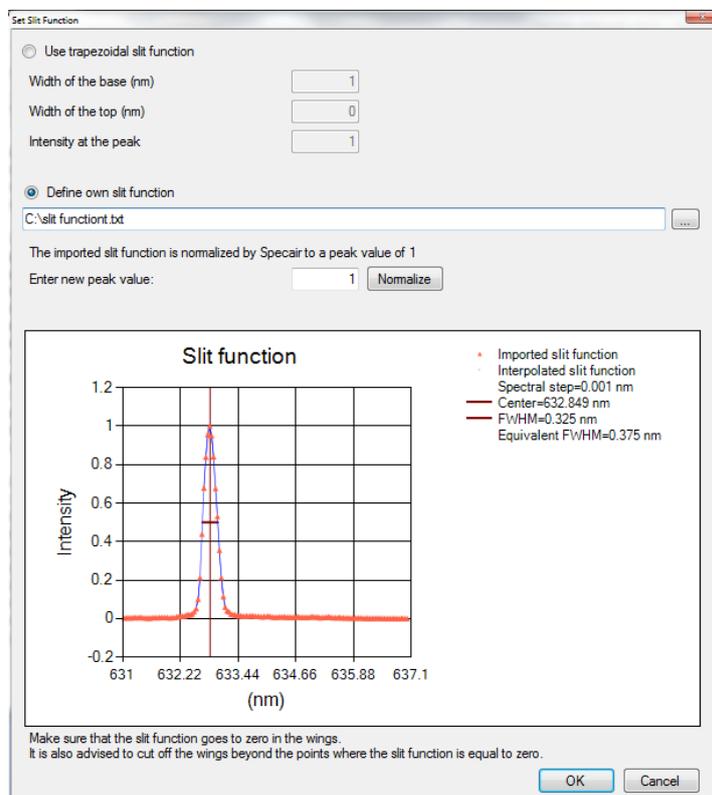
The imported slit function will be displayed in the graph below, in orange, together with a linear interpolation in blue. The interpolation uses the same spectral step as that defined by the user in the “Spectral step” box and Specair uses this version during the calculations.

IMPORTANT: It is strongly advised to cut off large wings of a slit function, such as those included in the example figure below, to avoid artifacts. Also, it is imperative to make sure the slit function does go to zero in the wings.

The center of the imported slit function will be detected automatically, based on center of the line indicating the FWHM, and it is advisable to verify that this is done correctly, since an error in this value produces shifts in the spectral peak wavelengths.

In addition, the FWHM is displayed, to aid in the calculation of absolute intensities. A spectrum calculated with an imported slit function will have intensities given in $\text{mW}/\text{cm}^2/\text{sr}$, if the slit function is normalized to unity. This normalization can be done directly in the slit function window by pressing the ‘Normalize’ button with a value of 1 for the ‘Enter new peak value’ entry. A different peak value can be used if desired. As in the case of a trapezoidal slit function, the above spectrum can be divided by the FWHM (in μm) to obtain units of $\text{mW}/\text{cm}^2/\text{sr}/\mu\text{m}$.

Specair calculates both the FWHM and the “equivalent” FWHM. The latter is defined as the integrated area under the slit function, divided by the peak value of the slit function. To obtain spectra in units of $\text{mW}/\text{cm}^2/\text{sr}/\text{mm}$, compute your spectrum with a slit function normalized to a maximum value of 1, and divide the obtained spectrum by the equivalent FWHM.

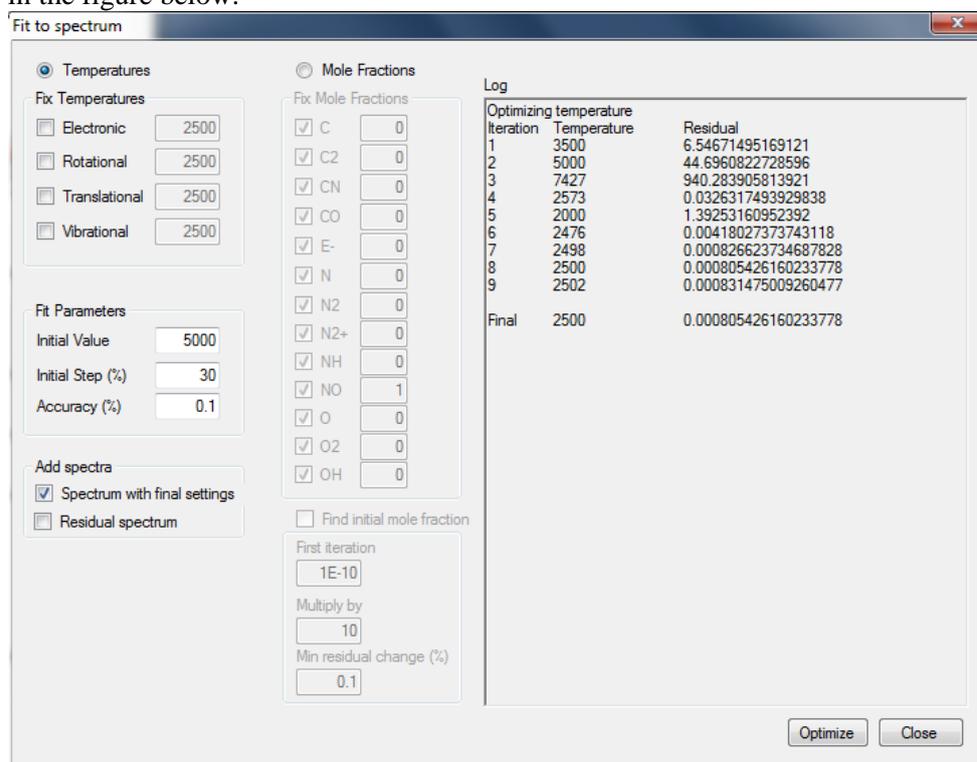


4. Spectral fitting

4.1. Basic fitting

4.1.1. Introduction to fitting

Fitting to experimental spectra is central to plasma spectroscopy. The conditions in which the plasma was generated can be understood by finding the parameters that replicate the measurements. This is a difficult and iterative process as a complex plasma is described by tens of variables. Specair provides a numerical fitting routine which can greatly speed up the process. The option can be accessed by selecting a spectrum to fit, hereafter called the experimental spectrum, and then selecting “Fit to Spectrum” in the tools menu. This opens the window shown in the figure below.



Specair implements Brent’s method to minimize a residual, the root-mean square of the difference between the experimental spectrum and the calculated spectrum. The spectra are calculated based on the current settings in the Calculation Options, including the slit function, which are held constant as either temperatures or mole fractions are varied until a minimum is found.

Please note that all experimental spectra are normalized in the process of fitting. This means it is advisable to make a copy within Specair of any imported spectra. It also means that, for a spectrum with a single electronic transition, the actual spectrum being fit is independent of the electronic temperature, which only changes the intensity. Similarly, the result will be independent of the mole fraction if only one species is present in the plasma.

The results from fitting are only as good as the starting point, the experimental spectrum. Specair automatically interpolates this spectrum before calculating the residual. It is advisable to

correct any drift or offset after an initial round of fitting, since a small offset in wavelength can lead to large residuals as sharp peaks no longer overlap.

4.1.2. Input parameters

The basic fitting routine normally minimizes the residual with respect to a single variable. A group of variables sharing the same value, such as all statistical temperatures under local thermal equilibrium (LTE), can also be used. The user manually selects “Temperatures” or “Mole Fractions”. All temperatures are fit simultaneously by default, but any combination of temperatures can be fixed while the others are varied. This is useful if the experimental plasma was not in LTE, such that vibrational and rotational temperatures, for example, have different values. The mole fractions, on the other hand, are fixed by default and the user selects the specific mole fraction(s) to vary by deselecting the check box. Several mole fractions can be fit together, but this is rarely useful in practice.

The minimization works by bracketing a minimum residual and narrow the range using inverse quadratic interpolation. There are three general parameters by which the user can specify the starting conditions and the end point, listed to the left below the temperatures. The first is the “Initial Value”, which is the temperature or mole fraction which will be used in the first calculation. The second parameter is the “Initial Step”, which specifies, in percent of the Initial Value, the second and third calculations. If the first residual is lower than the second and third, a minimum exists in the region around the initial value and the routine will proceed. If instead there is a trend toward the second or third value the routine will keep extending the region, by the Initial Step percentage, until a minimum has been bracketed. This means that a smaller Initial Step is preferable if the Initial Value is close to the final fit result, whereas a larger Initial Step is better if the final value could be within a large, unknown range. The third option is the “Accuracy”, which is the threshold for stopping further iterations. It is given as a percentage of the final value, such that 0.1% returns an answer within a 1-Kelvin range for a final temperature of 1000 K. Lower accuracy, such as 1% or 2%, requires fewer iterations and hence leads to faster fitting.

Unlike the temperatures, which are often between 300 and 12000 K, the mole fractions in a plasma can vary by many orders of magnitude. To quickly find a good starting point for fitting, the user can select “Find initial mole fraction”. This option starts by making a calculation at a very low mole fraction, specified under “First iteration”. Further calculations are then performed while increasing the mole fraction by an order of magnitude until a noticeable change in the residual is detected. The change in mole fraction between iterations is indicated under “Multiply by”, with 10 being the default, and the “Min residual change” is normally 0.1%. Once a sufficient change is detected the program proceeds to the regular fitting.

4.1.3. Outputs

For each iteration the iteration number, the value used in the calculation and the residual is displayed in the “Log” section to the right. This allows the user to directly observe the convergence and the improvement between successive fitting attempts. The magnitude of the residual will depend on both the overall magnitude of the spectra and the wavelength range, and is thus experiment specific.

Under the section “Add Spectra” the user can choose to calculate and display both the spectrum and the residual spectrum using the values found during fitting. The residual spectrum can be very informative when looking for underlying minor peaks or wavelength mismatches.

4.1.4. Fitting methodology

Due to the large number of parameters and the relatively long time for calculation, a brute force approach is often inadequate for spectral fitting. Any spectrum could, in principle, be fit by successively minimizing the residual for each parameter in an iterative manner, but in practice the number of calculations grow exponentially with the number of variables. So, if four different temperatures are used in combination with several species and transitions a guided approach is often superior.

For a simple spectrum the recommended order is to start with the dominant Radiative Transition. The experimenter should use previous knowledge about the conditions, if possible, or use Specair’s transition finder, which contains a database of spectra for individual transitions at a few temperatures. Once a candidate species and transition combination has been identified the mole fraction is set to a number between zero and one and the user selects the “Fit to spectrum” option in the Tools menu.

First the temperatures are fit together, unless the experimenter knows some of the temperatures, *a priori*. If the user believes that the selected transition accounts for the entire signal the next step is to fit each temperature separately. This is done by fitting primarily the vibrational and the rotational temperatures in an alternating fashion until both of them remain roughly constant between each round.

If more species are found in the spectrum the next step is instead to add the most prominent one, followed by the optimization of the corresponding mole fraction. Adding more species and transitions will change the optimal temperature, so the next step is to once more fit the temperatures and subsequently all the mole fractions, in order of importance. This cycle is repeated until a true global minimum is found. If necessary the various temperatures can also be optimized in a similar fashion. When the residual stops improving between successive alternation between temperatures and mole fractions the user can add even more species and transitions or declare victory. It is clear that each added variable increases the dimensionality of the minimization problem and it is often the case that repeated cycles are necessary until the method has fully converged. The Global fit function in Specair (see below) can automate these steps in many cases and is a recommended approach for complex spectra.

4.2. Finding transitions

Specair includes an automated method for finding underlying transitions in a spectrum. With a spectrum selected, The Find Transitions window (see figure below) is accessed under the Tools menu. The transition finder is intended to be a starting point for analysis, to be followed by further optimization, and it uses an extensive database of pre-calculated spectra at different temperatures and with slit functions of different widths.

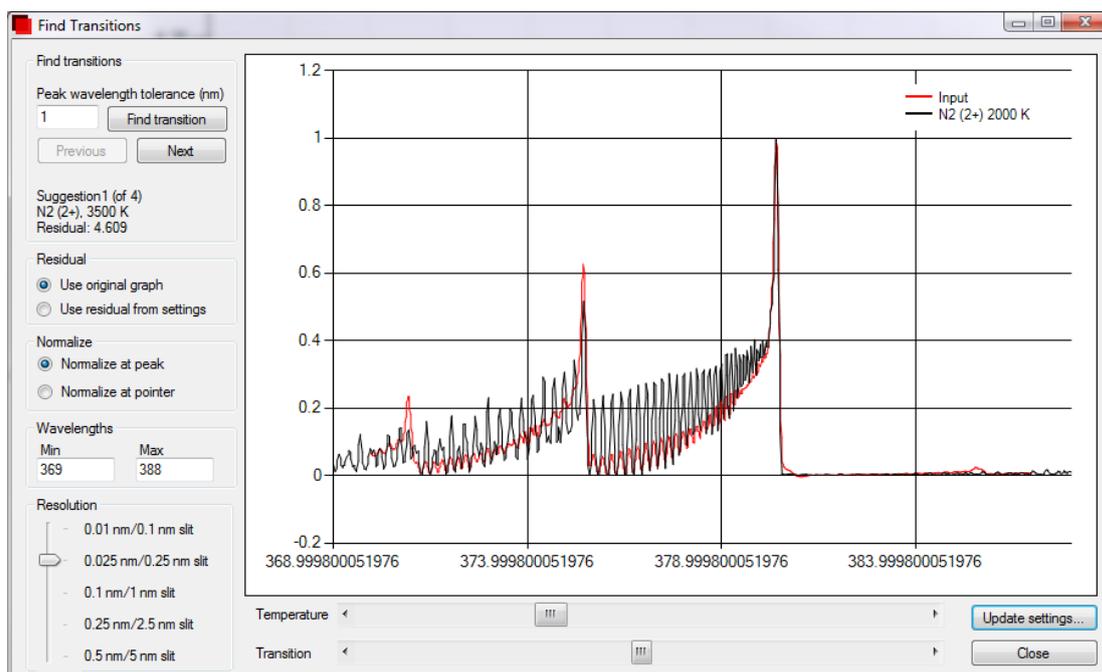
In the Find Transitions window the user can browse all available transitions and temperatures by sliding the horizontal scroll bars. This is an intuitive way of finding the right transition and

the proper temperature range that is much faster than calculating plenty of candidates from scratch.

The transition finder can also find the best candidates automatically, by searching the database for spectra that match the highest peak within the specified wavelength range. When pressing the Find transition button suggestions are returned in order of best fits. The Peak wavelength tolerance (nm) number indicates the small wavelength range around the main peak that will be considered. Increasing the range returns more hits, and can be useful if the experimental spectrum has an offset, but it also increases the number of false positives.

The default setting for the comparisons is to use the spectrum that was selected when opening the window. The user can also choose to “Use residual from settings”, where a calculated difference spectrum is used. A spectrum is calculated based on the current Calculation options and the difference between this spectrum and the selected, imported, spectrum is displayed, making it easier to find smaller peaks below larger ones that have already been fit.

To further refined the search, the user can limit the overall wavelength in which to search for a transition. The spectra can be normalized either at their main peaks or at a given wavelength, as indicated by a vertical pointer in the graph. Finally, the resolution, as defined by a spectral step/slit function width combination, can be changed using the slider in the bottom left corner. A triangular slit function is implemented here.



If a transition has been found the user can press the Update settings button to use the information for updating the calculation options or for fitting. This opens the Update settings window (see figure below).

The user can add the selected transition, or all the transitions associated with the found species. For example, if $N_2(1+)$ was identified the user can also add $N_2(2+)$ at the same time. This can be done while also Clearing existing transitions, i.e., setting all Radiative transitions to 0 in the Calculation options.

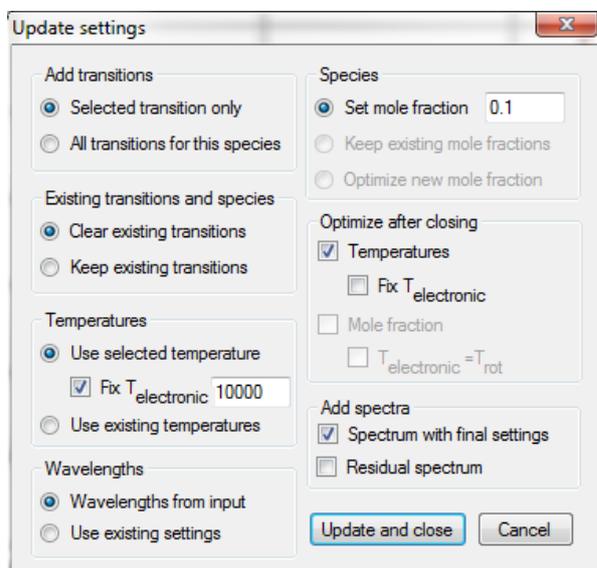
The temperatures can be updated to that selected in the transition finder. There is an option to Fix $T_{\text{electronic}}$, which is useful, for example, when studying plasmas from electric discharges. Even though the plasma is cold, the electronic temperature is high, which is needed to see a meaningful intensity.

The min and max wavelength in the calculation settings will be updated to those indicated in the transition finder unless the user chooses to Use existing settings. The wavelengths in the transition finder are those of the input spectrum by default, but can be changed by the user.

Under “Species” the user can specify the new value for the mole fraction associated with the selected transition. If Keep existing transitions is selected the user can choose to Keep existing mole fractions as well. There is also an option, Optimize new mole fraction, which automatically optimizes the mole fraction as described in the Basic fitting section above.

Once a mole fraction has been set, the temperatures and mole fractions can be further optimized. These selections are listed under “Optimize after closing”. The Fix $T_{\text{electronic}}$ option is similar to that above, intended to keep the electronic temperature high for reasonable intensities even if the other temperatures are low, as in the case of electric discharges. The other option, $T_{\text{electronic}} = T_{\text{rot}}$, sets the electronic temperature to be equal to the rotational temperature before fitting the mole fraction. This could be used if a fixed electronic temperature was used previously, while trying to optimized the rotational temperature at a high intensity.

The final options, under Add spectra, can be selected to automatically calculate both the final spectrum, after optimization for example, and the corresponding residual spectrum, i.e., the difference between the input spectrum and the calculated one.



4.3. Global fit

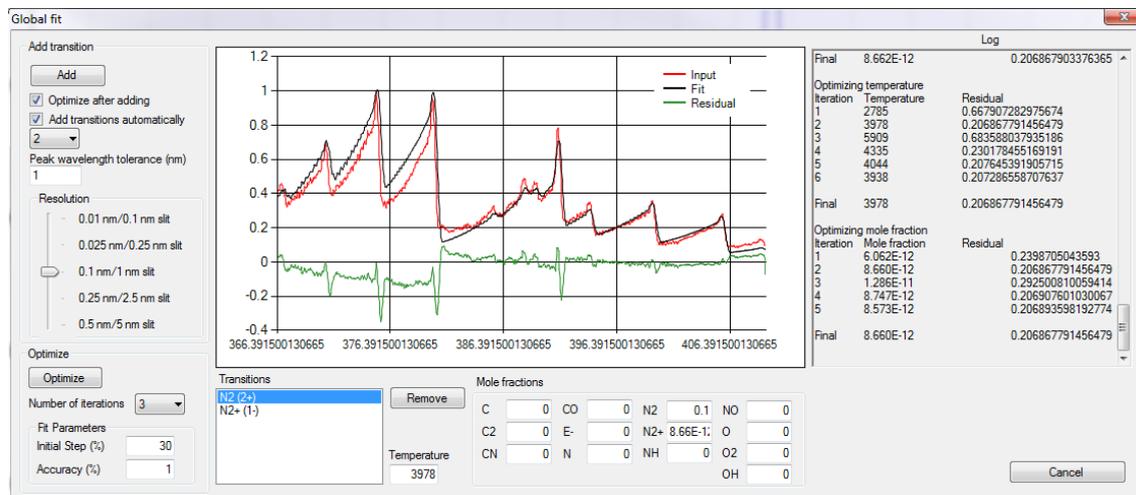
The Global fit window, accessed under the Tools menu and shown in the figure below, is an interface combining the basic fitting and the transition finder to streamline the fitting process. As described above, a general fitting procedure consists of adding transitions, one at a time, while optimizing all variables between each step. In the Global fit, both the addition of

transitions and the optimizations can be done automatically, significantly reducing the active time for the user.

The transitions are added by pressing the “Add” button, which launches the Find transition functionality described above. If the “Add transitions automatically” is selected the transition finder uses the first choice among its suggestions. Otherwise the user can verify that the right transition is chosen and also manually change the transition. The “Peak wavelength tolerance (nm)” and resolution selector are the same as in the transition finder. More than one transition can be added automatically, with the number selected in the drop-down menu. This will add transitions in order of prominence, if “Optimize after adding” is also selected.

The added transitions are listed below the graph window and they can be removed using the “Remove” button. After one or more transitions have been added the user can refine all parameters by pressing the “Optimize” button. The program will execute the basic fitting routine outlined above for all relevant variables, based on the last temperature used. The starting value for the mole fractions can be changed manually in the text boxes. Note that all plasmas have to be in Local Thermal Equilibrium ($T_{\text{electronic}}=T_{\text{translational}}=T_{\text{rotational}}=T_{\text{vibrational}}$) when using the Global fit. For different temperatures a manual fitting has to be done. To reach a global minimum many cycles, determined by the “Number of iterations”, should be performed.

The figure below shows an example where the peaks of $N_2(2+)$ and $N_2(1-)$ were identified and fit automatically. This particular spectrum was found to be out of Local Thermal Equilibrium.



5. The physical model for radiation used in Specair

5.1. Energy levels

Specair simulates emission intensities for a number of diatomic molecules. Emission occurs during molecule transitions from higher to lower energy levels. The energy of a level can be expressed as the sum of the electronic energy, the vibration energy and the rotational energy, $E_{e'v'J'} = hc(T_{e'} + G_{e'}(v') + F_{e'v'}(J') + st)$.

The term st is a small term due to lambda doubling and spin splitting which will be discussed later. The energy of the electronic levels $hcT_e = \varepsilon_e$ is often tabulated. Spectroscopy literature

frequently expresses the vibration energy as the polynomial expansion $hcG_e(v') = \varepsilon_{v'} = \omega_e \left(v' + \frac{1}{2} \right) - \omega_e x_e \left(v' + \frac{1}{2} \right)^2 + \omega_e y_e \left(v' + \frac{1}{2} \right)^3 + \omega_e z_e \left(v' + \frac{1}{2} \right)^4 \dots$

where the polynomial coefficients are tabulated. The energy of the rotational levels $F_{e'v'}(J')$ is calculated using a similar expression:

$$F_{e'v'}(J') = B_{v'}(J'(J'+1)) - D_{v'}(J'(J'+1))^2 + H_{v'}(J'(J'+1))^3 = \varepsilon_{J'}/hc.$$

The polynomial coefficients are normally tabulated.

However, for most transitions considered in Specair, the above expressions are not used. Instead, for the sake of accuracy, most energy states are computed in Specair by inverting Hamiltonian matrices. This method also allows the modeling of perturbations for several systems of importance in Specair (such as N₂ first and second positive, N₂⁺ first negative, NO alpha, beta, gamma, delta). More details about Specair can be found in the following publication:

Laux, C.O., "Optical Diagnostics and Collisional-Radiative Models," VKI Course on Hypersonic Entry and Cruise Vehicles, Stanford University, June 30 – July 3, 2008.

The general notation for an electronic level is $^{2S+1}\Lambda$. S is the quantum number associated with the total electron spin, and Λ is the quantum number associated with the absolute value of the projection of the orbital angular momentum along the internuclear axis. Λ takes the values 0, 1, 2, 3 associated with the Greek letters $\Sigma, \Pi, \Delta, \Phi$. The number $2S+1$ is called the spin multiplicity and the notation for each state is usually preceded by an identifying letter, often X for the ground state.

5.2. Spin

Each electronic level is split into $2S+1$ spin substates (spin-splitting) and for all $\Lambda \geq 1$, every spin substate is split in two Λ -substates (Λ -doubling). This gives us the degeneracy for each electronic level as $g_e = (2S+1)(2 - \delta_{0\Lambda})$, where $\delta_{0\Lambda}$ is the usual Kronecker delta. For diatomic molecules with nuclei of equal charges a u or a g is written to the right of the term $^{2S+1}\Lambda$. This indicates if the electronic wave function is symmetrical or not with respect to the operator \hat{i} , which inverts the coordinates of the nuclei and the electrons relative to the molecule's center of mass. The letter g indicates that the wave function is symmetric (gerade), and a u indicates that it is not.

For Σ -states a “+” or a “-“ is showed to the right of the term . This indicates if the electronic wave function is symmetric relative the operator σ_v which corresponds to a mirror reflection through a plane containing the internuclear axis.

To designate the spin substates the notation $^{2S+1}\Lambda_{\Omega}$ is often used. Ω is the quantum number associated with the projection of the total angular momentum \mathbf{J} along the internuclear axis. For diatomic molecules the total angular momentum exclusive of nuclear spin is the vector sum of orbital (\mathbf{L}), spin (\mathbf{S}) and rotational (\mathbf{R}) angular momenta, $\mathbf{J}=\mathbf{R}+\mathbf{L}+\mathbf{S}$. The projection of \mathbf{R} on the internuclear axis is zero, the projection of \mathbf{L} is units of momentum, the projection of \mathbf{S} is Σh and the total projection of \mathbf{J} is Ωh . For a $^2\Pi$ state ($\Lambda = \pm 1, \Sigma = \pm 1/2$), this gives us four possible values of Ω , 3/2, 1/2, -1/2, -3/2. A common notation is to just give the absolute value of Ω , and distinguish the positive values from the negative by their parity. We use (e,f) as parity notation and this gives the following notation for the four spin substates of the $^2\Pi$ state: $^2\Pi_{3/2,f}$, $^2\Pi_{3/2,e}$, $^2\Pi_{1/2,f}$ and $^2\Pi_{1/2,e}$.

For rotational levels, the notation $F_1, F_2 \dots F_{2S+1}$ is used to designate the $2S+1$ spin substates. The rotational energy is a function of the total angular momentum (rotational quantum number) J . As seen above Ω is the projection of J on the internuclei axis which gives that J can never be less than Ω .

5.3. Selection rules

For spontaneous transition between two states to occur, the transition has to fulfill the following conditions:

- $\Delta S = 0$
- $\Delta \Lambda = 0, \pm 1$
- $u \leftrightarrow g$
- $\Sigma^+ \leftrightarrow \Sigma^+$ or $\Sigma^- \leftrightarrow \Sigma^-$
- $\Delta J = \begin{cases} -1 & e \rightarrow e \text{ or } f \rightarrow f \\ 0 & e \rightarrow f \\ 1 & e \rightarrow e \text{ or } f \rightarrow f \end{cases}$

All other transitions are so rare that their emission has no significant importance for the detected radiation. As we can see, selection rules limit the possible transitions between different electronic states and rotational levels. There are no such limits for the transition between different vibration levels, between these levels everything goes.

5.4. Example

Figure 3 below, an image from Herzberg, p. 267, illustrates transitions between states. It represents the energy level diagram for a $^2\Pi - ^2\Sigma^+$ band where only the levels for J between 10.5 and 15.5 are included. K stands for the total angular momentum apart from spin. The broken-line branches are satellite branches and the dotted branches do not appear in a strict Hund's case (b). Δ -type doubling is present in the $^2\Pi$ state. Hund's cases distinguish different modes of coupling of the angular momenta.

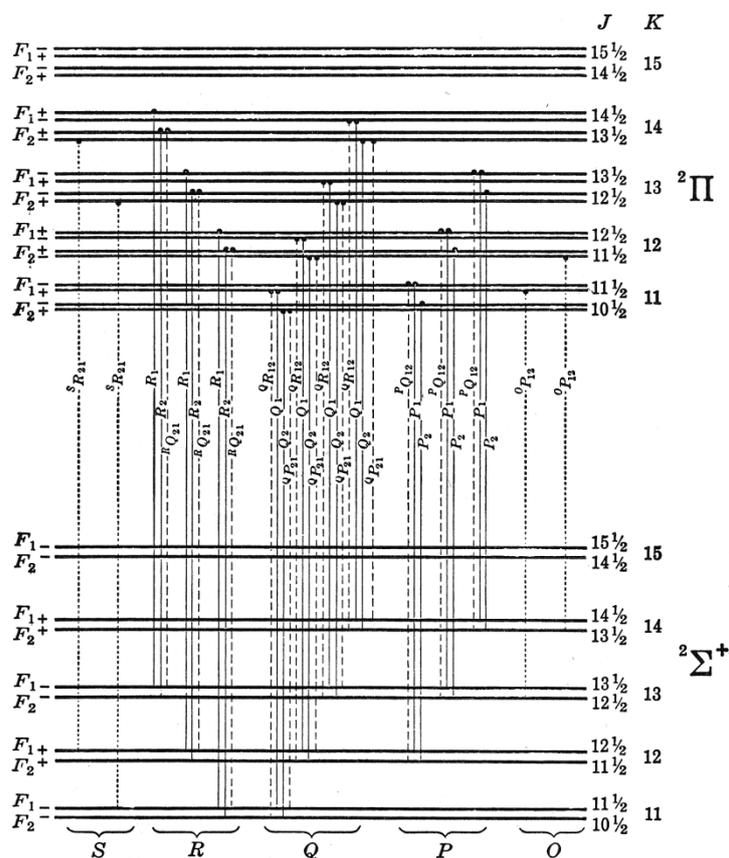


Figure 3 Energy level diagram from p.267, Herzberg, G., “Molecular Spectra and Molecular Structure, Volume I – Spectra of Diatomic Molecules”, Krieger Publishing Company.

5.5. Emission intensity

The emission intensity due to a transition from the upper energy level (e', v', J') to the lower energy level (e'', v'', J'') is expressed as :

$$I(\lambda) = n_{e'v'J'} \text{const} \sum (\text{Re}^{v''v'})^2 \frac{S_{J'J''}}{2S'+1} (E_{e'v'J'} - E_{e''v''J''}) \phi(\lambda - \lambda_0).$$

The expression gives the emission intensity as a product of, the number of molecules in the upper state (e', v', J''), the probability for spontaneous transmission from the upper state to the lower state and the energy difference between the two states. The probability constants, $\sum (\text{Re}^{v''v'})^2$ and $S_{J'J''}$ are both tabulated values and are not calculated by Specair. The population in the upper state is calculated with the expression

$$n_{e'v'J'} = N \frac{g_{e'} (2S'+1) e^{-\frac{\epsilon_{el'}}{kT_{el}} - \frac{\epsilon_{v'}}{kT_v} - \frac{\epsilon_{J'}}{kT_J}}}{\sum_{e'v'J'} g_{e'} (2S'+1) e^{-\frac{\epsilon_{el'}}{kT_{el}} - \frac{\epsilon_{v'}}{kT_v} - \frac{\epsilon_{J'}}{kT_J}}}$$

where N is the total number of molecules, g_e is the degeneracy of the electronic level e' , k is Boltzmann's constant, ϵ_{el} is the electronic energy, ϵ_v is the vibration energy and ϵ_J is the rotational energy for the state. T_{el} , T_v and T_J are the temperatures associated with the electronic, vibrational and the rotational levels respectively. Finally $\phi(\lambda - \lambda_0)$ is the line shape function.