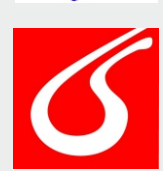


ASSIGNING THE VIBRATION-ROTATION SPECTRA USING THE LOOMIS-WOOD FOR WINDOWS PROGRAM PACKAGE



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Web page of the LWW project : <http://www.lww.amu.edu.pl/>

Preparing a new LWW project - creating the internal peak list and energy files from external sources

The LWW (Loomis-Wood for Windows) program package has been used since its early development [W. Łodyga et al., J.Mol.Spectrosc. 243 (2007) 182-188] for several dozens of spectroscopic studies. Although it was originally designed to be used together with the SIMFIT program [P. Pracna et al., J.Mol.Spectrosc. 184 (1997) 93-105] for simultaneous fitting of vib-rot and rotational spectra of symmetric-top molecules (LWW - 2005), it has been step-by-step adapted also to the cases of asymmetric-top molecules (LWWa - 2006) and certain types of molecules with large amplitude motions (hydrazine, methylamine, LWWI - 2006-2008). The main focus of this poster is to explain the initial steps necessary for creating a new LWW project and discuss the strategies for starting the first assignments of vib-rot spectra. The minimum requirement for a new LWW project to be created is to supply it with the **peak list file** and the **file of energies**. The spectrum can be simply generated from the peak list by a built-in LWW program utility, but it is preferable to use the real experimental spectrum as the third input file during creating a new project.

For using the LWW program package with different source of data, a big attention has been paid to making the import of these three files as simple and flexible as possible. This is accomplished by providing user defined input format templates for all the three mentioned input file types in order to support a large variety of input file formats.

For details of individual steps of creating a new project, please consult the Help file which exists either as a part of the LWW program package or which can be run as a stand-alone program (compiled html file supplied with the installation package) section Starting Project.

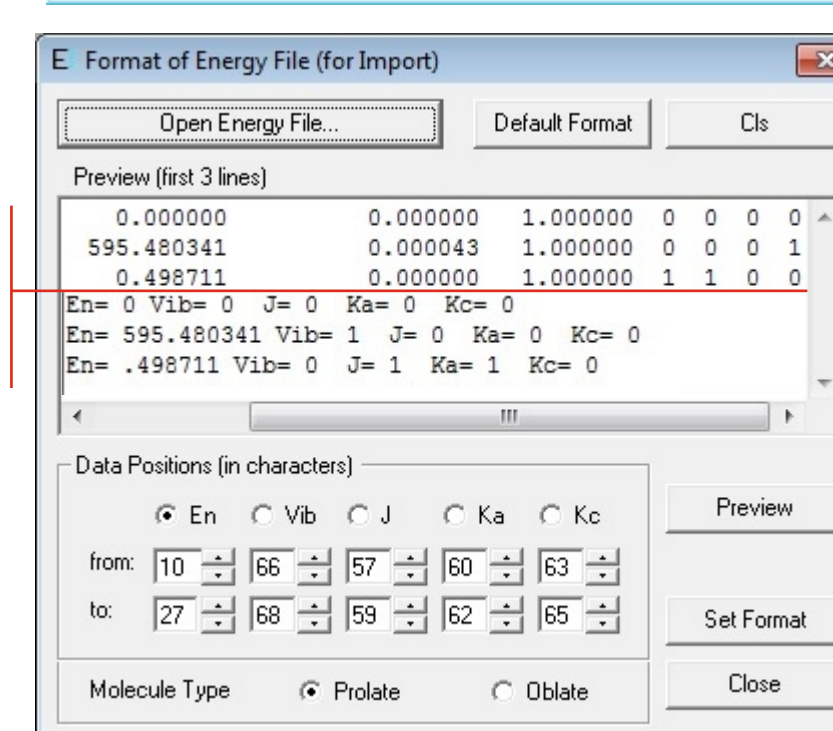
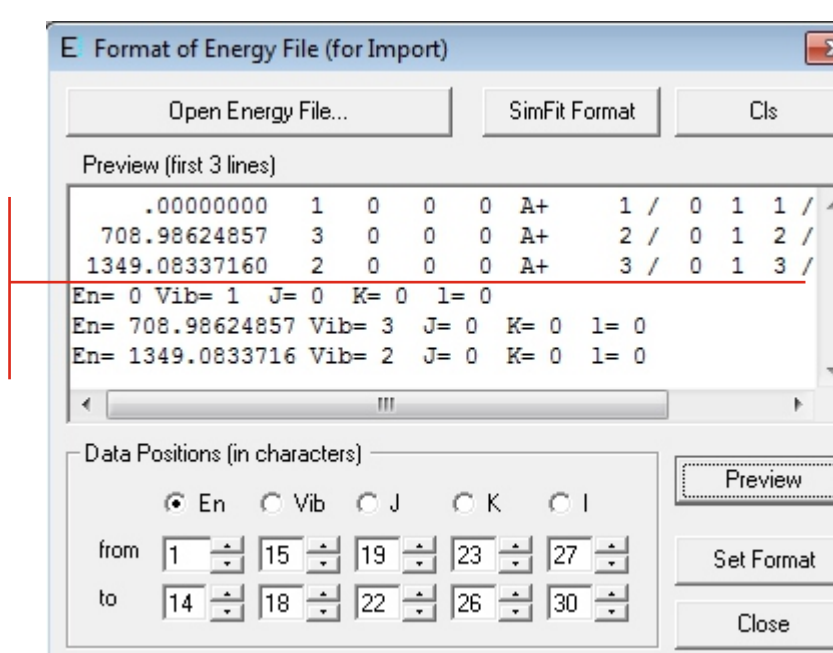
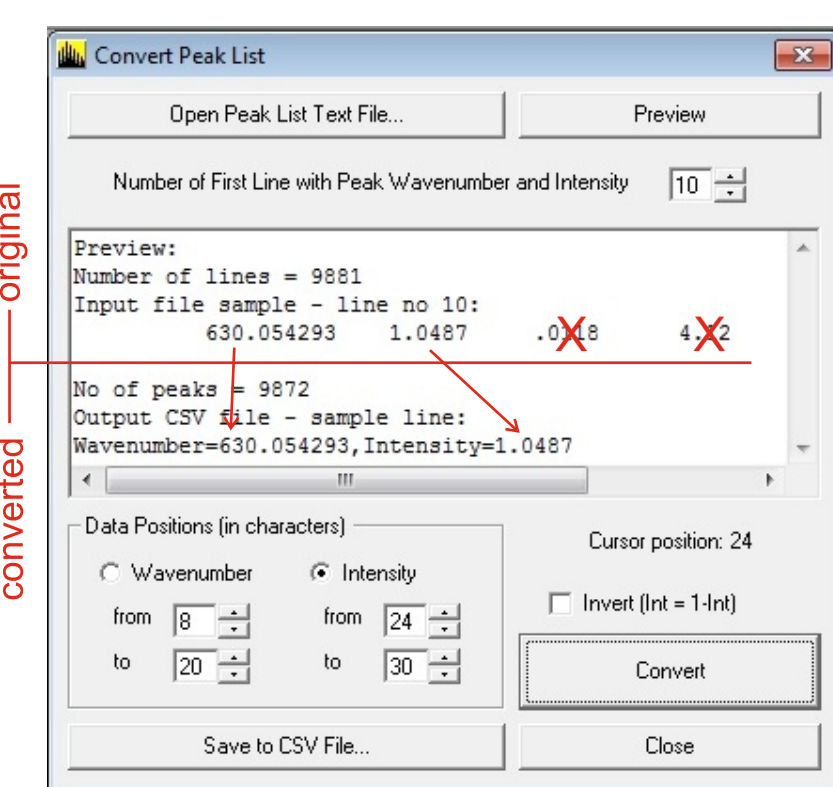
The peak list file

It is assumed to be an ASCII file with at least two entries for each peak position (in cm⁻¹ units) and the peak maximum (in absorbance or transmittance units, i.e. in the range between 0 and 1). For input files with more entries for each peak, the two necessary input items can be filtered out by the input utility (Help > Tools > Conversion of the Peak List). For internal use in the program, the peak list is stored in a CSV format for which the user is asked to supply a file name during the setup procedures. This file name is saved, together with all other program settings, into the project file (.lww extension by default) which is used for opening a project in exactly the same state in which it has been saved (see Help > Saving and loading a project).

Energy file

For the two fitting programs most frequent to the authors, the SIMFIT (symmetric-top case) and Pickett (asymmetric-top case), the corresponding format templates are predefined in the LWW and LWWa programs, respectively, so that the energy files generated by these programs can be read on input directly, with no format adjustments. Quite obviously, it is assumed that each line of the energy file contains one energy (in cm⁻¹ units) with the corresponding quantum numbers [vib, J, K, l] for the symmetric top case, [vib, J, Ka, Kc] for the asymmetric top case and [vib, J, K, sym] for LAM case. For all other formats of energy files, each version of the program is equipped by a tool for a user-defined input format of the energy file. It allows for any ordering and lengths of the individual input entries and can be set up interactively using the on-screen utility (see Help > Import and export of data). We were led to keeping the energy file separated from being calculated inside the LWW program from spectroscopic constants by the idea of making the program package compatible with any program for fitting the assigned spectra that can generate a file of energies. The approach of using a general energy file also allows for a 'generalized' lower-state combination difference (LSCD) checking described further.

For the case of symmetric-top molecules (nondegenerate vibrational levels and fundamental level of degenerate vibrations), where the energies can be represented by analytical polynomial formulas, we provide with the installation package also simple Excel spreadsheets that can be used for an easy start with calculation of the energy file. Several files with rotational energies in individual vibrational states can be merged into one input energy file either by a tool of the LWW program (see Help > Tools > Merge Energy Files) or an external text editor. In all other cases, the exact rovibrational energies are calculated rather diagonalization of the rovibrational Hamiltonian matrices and thus the use of their external calculation is preferable.



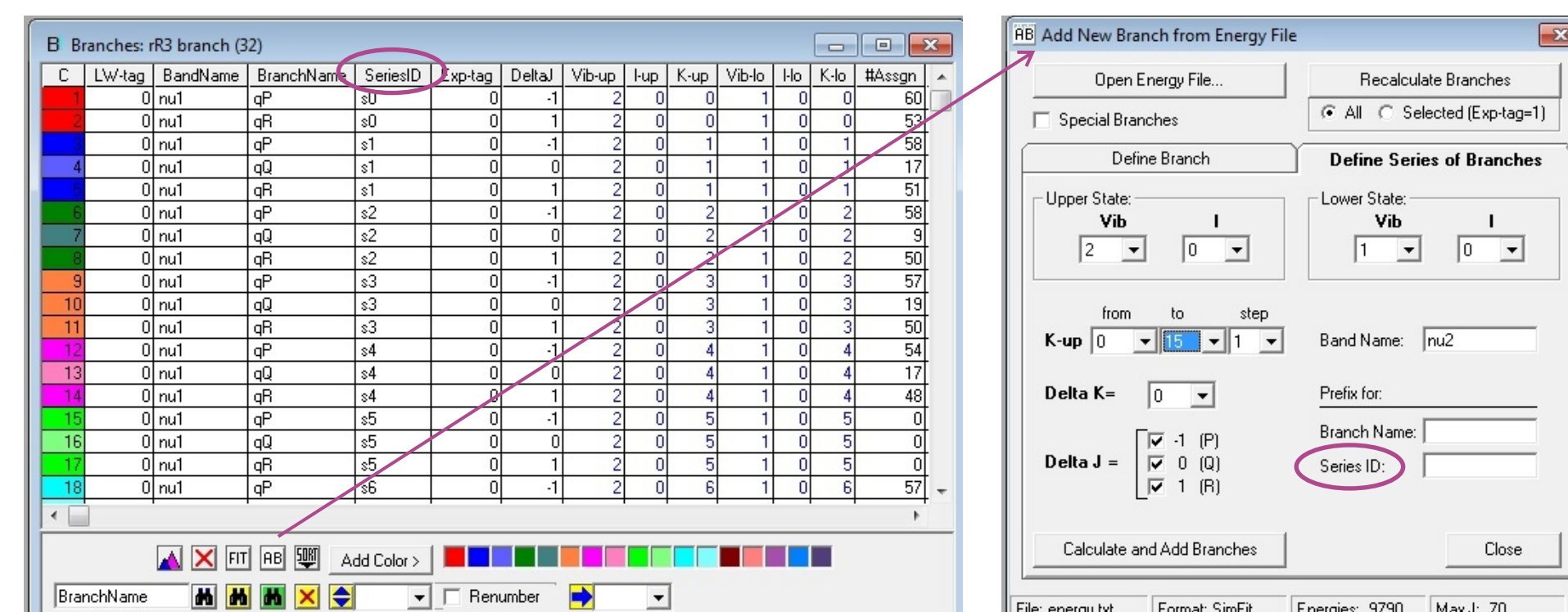
original
converted

SimFit energy file
(symmetric top)

Pickett energy file
(asymmetric top)

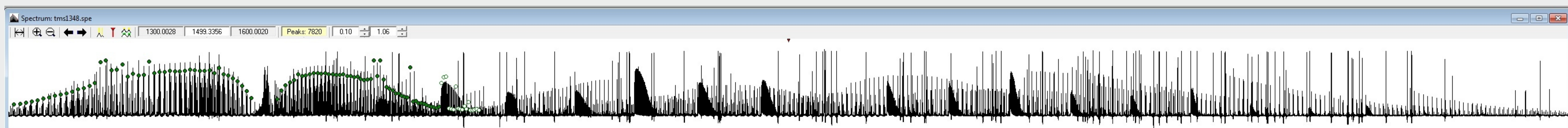
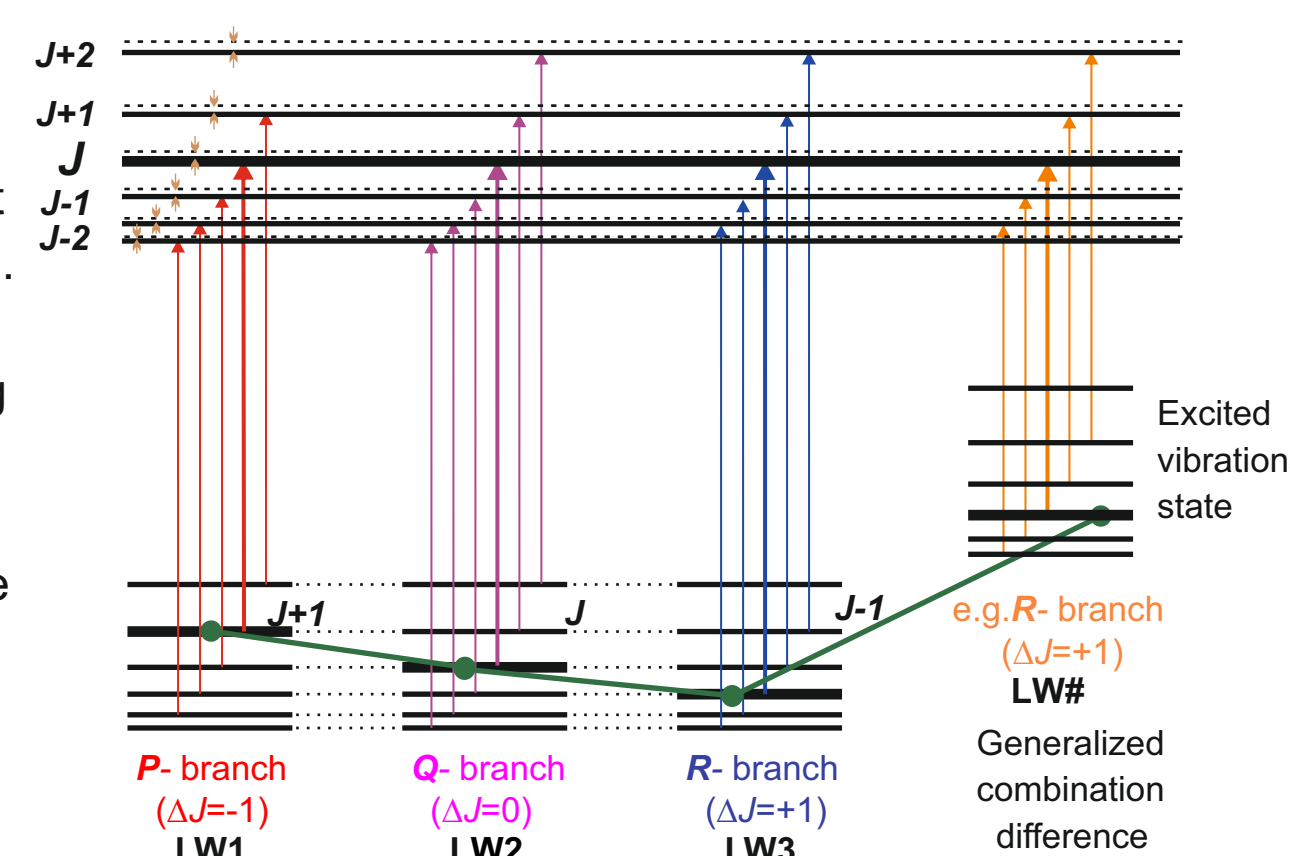
Loomis-Wood diagrams combined with LSCD checking

The central concept of the LWW program, that lies in the background of its key features, is the concept of **spectral branches**, by which we mean a series of transitions that share the same set quantum numbers except J, which in turn is the only running variable in it. The table of branches organized in the **Branches window**, which is the central control point of the LWW program, has to be filled with the appropriate branches before the assignment procedures are started. The flexibility of the selection of branches that can be combined in the LSCD checking described below require that they are generated from a file of energies. The branches can be in principle defined one by one (Define Branch tab), but is clearly more convenient to use the option of batch branch generation (Define Series of Branches tab).



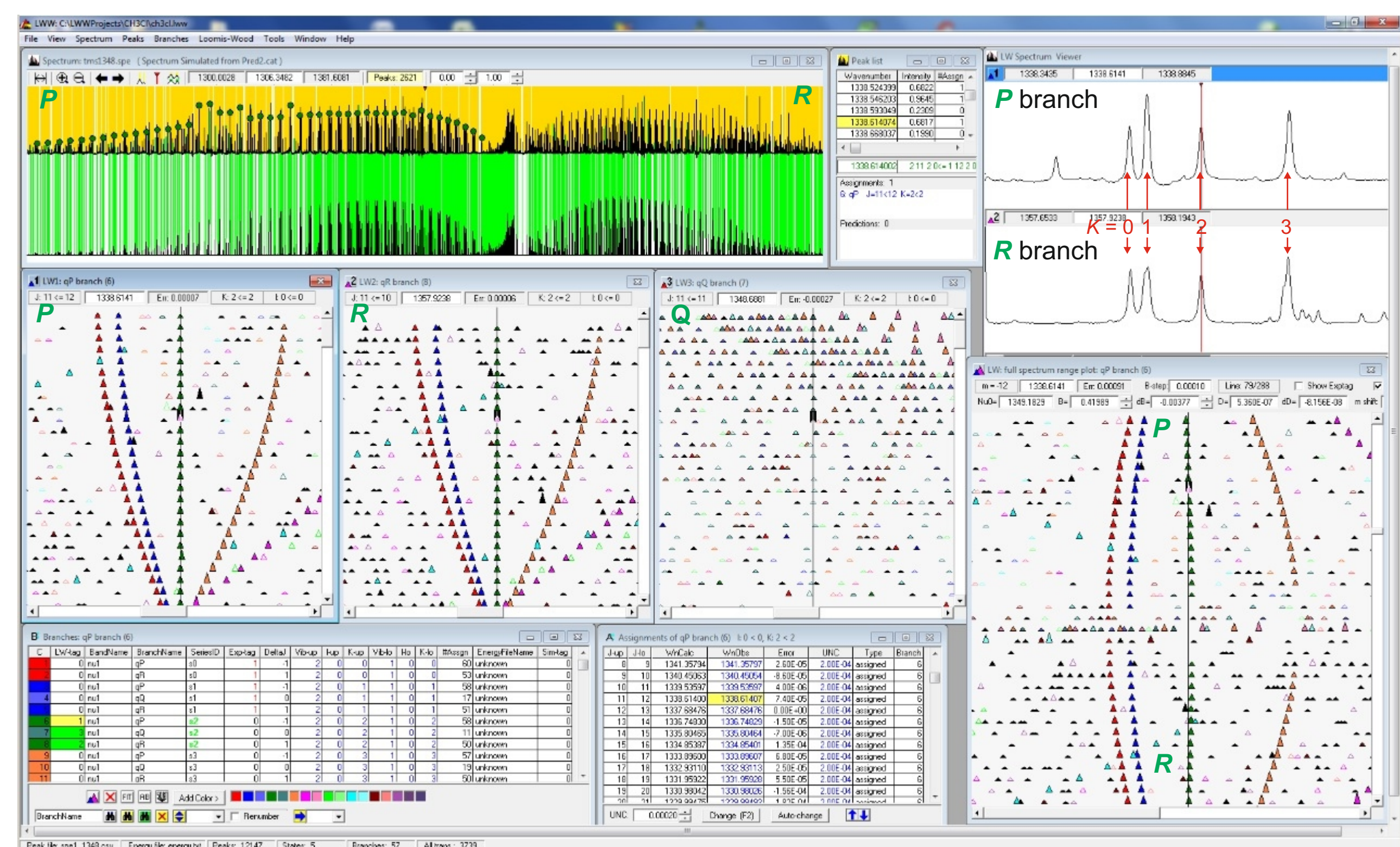
In comparison with the Giessen-Cologne LW program [B.P. Winnewisser et al., J.Mol. Spectrosc. 136 (1989) 12] which works with the P and R branches, the LWW program integrates also the Q branches into the LSCD checking. There can be always three Loomis-Wood diagrams open at the same time. These do not have to be, however, bound to the rotational levels in the ground vibrational state. Any of the LW diagrams can be linked to another vibrational state. This may be useful e.g. in cases of assigning overtone or combination bands where sometimes only one of the **PIQIR** branches has significant intensities. In such cases, the branches missing in the overtone/combination band can be substituted for LSCD checking by the branches from the hot band, provided this has been quantitatively analyzed. The only requirement for binding several branches in the LSCD checking is they share the same upper levels and that they have the same **SeriesID** identification.

The manipulation with branches is made easy in case of incorrect assignments detected by LSCDs. Whole branches can be given another K-assignment by moving them as one object. This may be also followed by shifting their J-assignments up or down by the utilities in the Branches window.



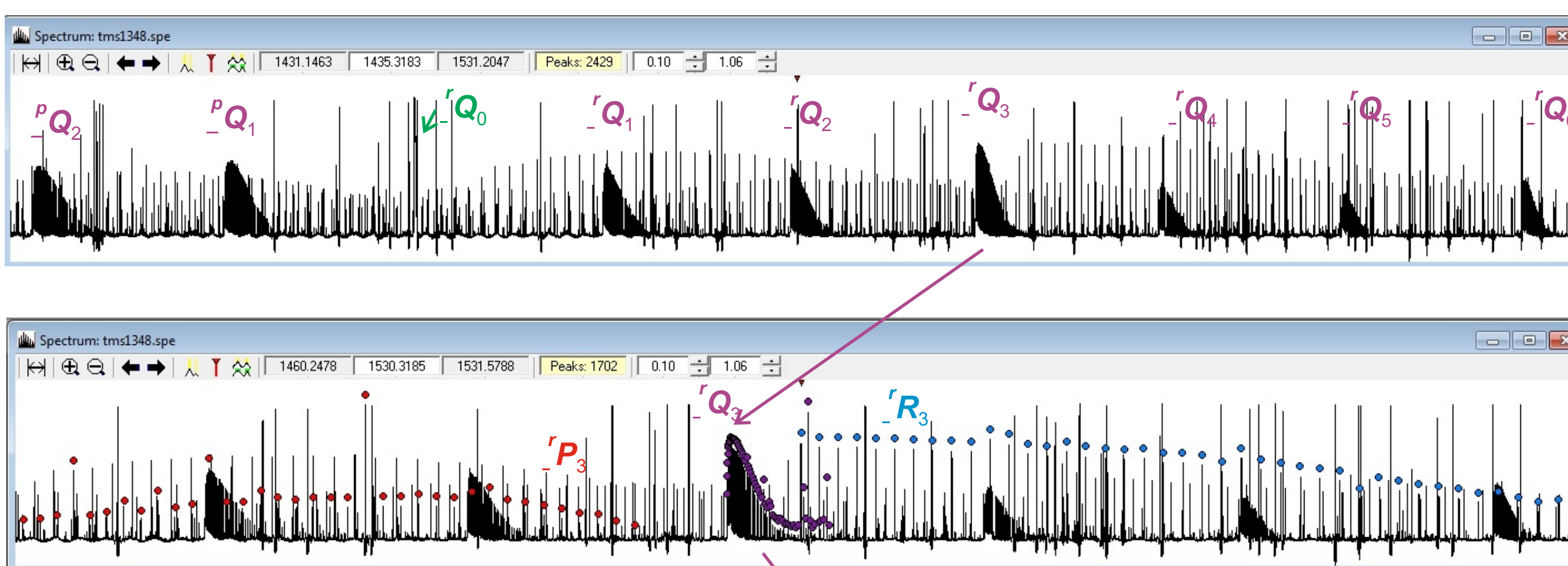
Starting assignments in a parallel band of a symmetric top molecule (¹³CH₃Cl)

Assignments in a parallel v₂ band (CH₃ symmetric bending) can be done in a really straightforward manner by following the typical **K-clusters** in the **P** and **R** branches and could be accomplished even without LSCD checking. Using the LWW program, however, accelerates the assignments tremendously by assigning whole branches **by practically one click**.

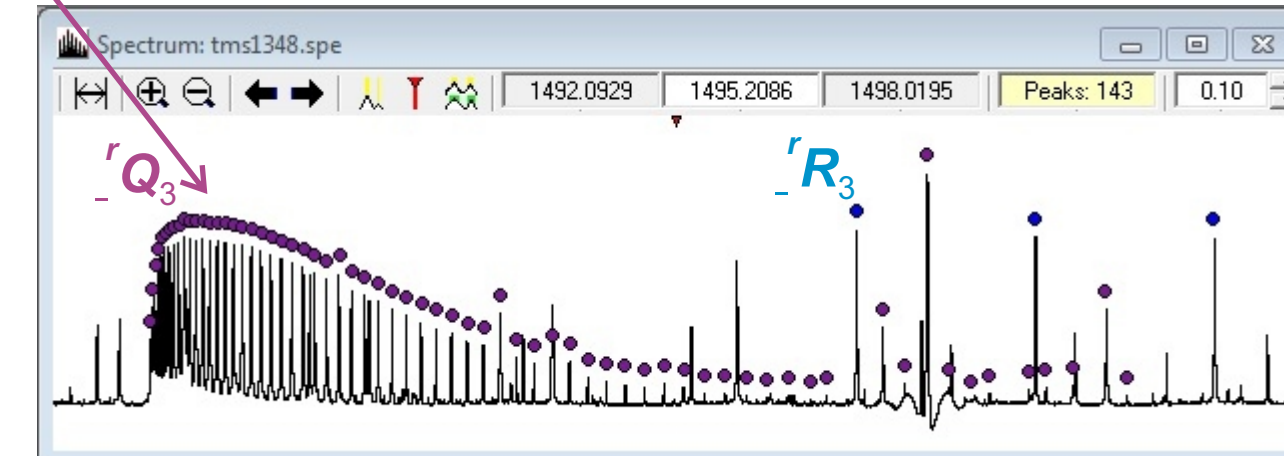


Starting assignments in a perpendicular band of a prolate symmetric top molecule (¹³CH₃Cl)

The perpendicular v₅ band (CH₃ degenerate asymmetric bending) does not have such compact K-clusters in the **P** and **R** branches and these cannot be discerned in the spectrum so easily. In this case of the strongly prolate symmetric top molecule (A ~ 5.2 cm⁻¹, B ~ 0.43 cm⁻¹) the prominent **Q branches** are usually used instead as an entry point to the assignments. Their K-assignment can be counted from the seemingly missing (but in fact very sharp) '**Q**'₀ branch. We chose the K=3 '**P**'₁'**Q**'₁'**R**' branches as an example here.

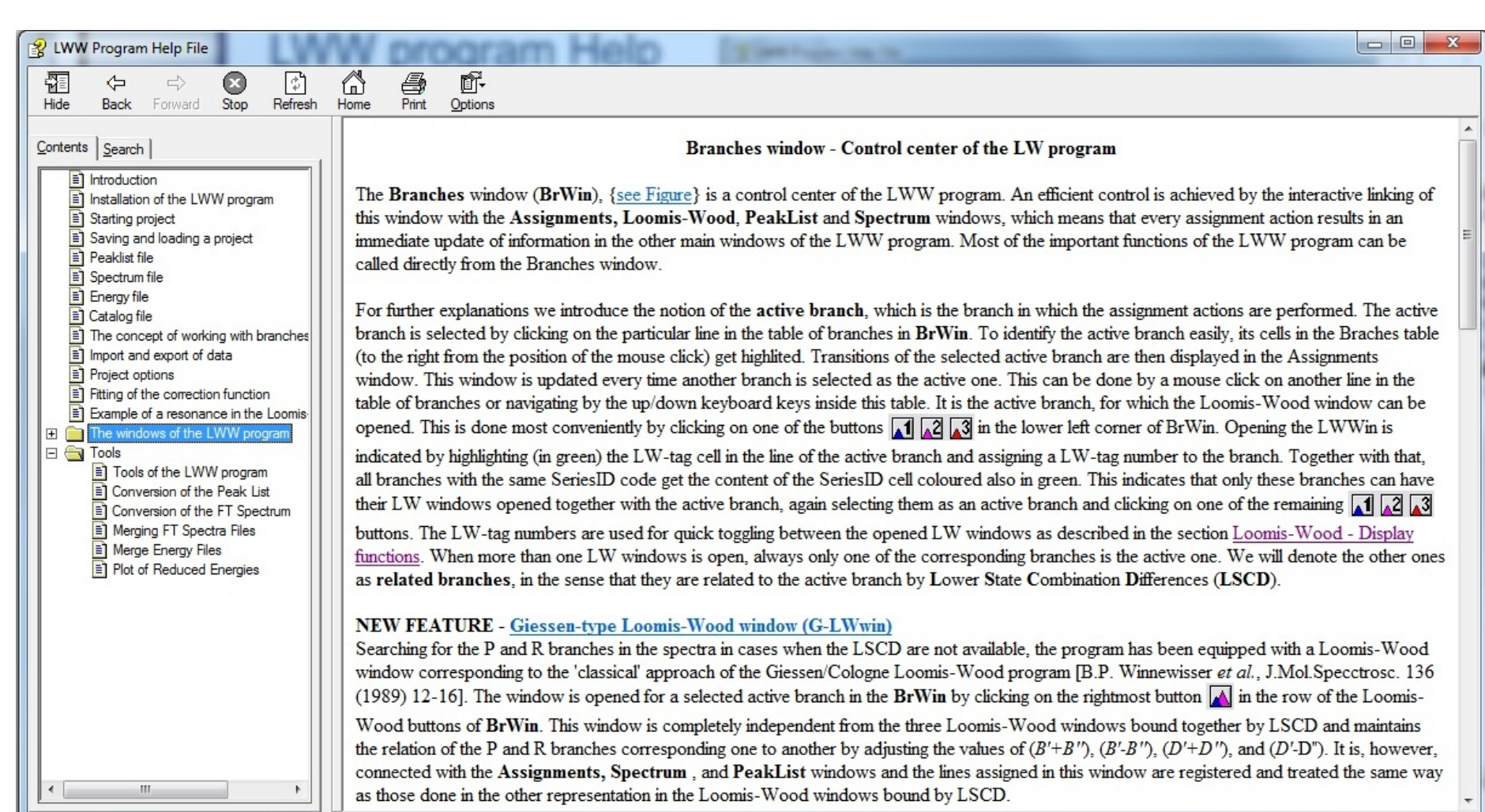


After locating the '**Q**'₃ branch, in which the J-assignments need not be clear in the beginning, we combine it with the strong '**R**'₃ branch and subject these two to mutual LSCD checking. The considerably weaker '**P**'₃ branch can be finally used for another independent LSCD checking and **verifying the assignment correctness unambiguously**.



LWW program Help

The LWW can be opened either directly from the LWW program or independently in a web browser as a compiled HTML file.



The LWW diagrams display visually discernible series which are guiding the assignments effectively. Their similar shape is due to the LSCD binding of the three diagrams. After fitting the correction function, all three series should be aligned along the central vertical lines of the LW diagrams. When this alignment does not occur, the K-assignments are obviously **incorrect** !

