Program for Analyzing IR Spectra Based on Loomis-Wood Diagrams and Lower State Combination Difference Checking

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Motivation

Creation of a flexible and open application program for easy and efficient assignment and preliminary analysis of vibration-rotation IR spectra

Previous programs

Š. Urban, J. Behrend, P. Pracna: A Computer Assisted Procedure of Assignments of Vibration-Rotation Bands of Asymmetric and Symmetric Top Molecules, J.Mol.Struct. 690 (2004) 105-114.

- \+ Program working with a semigraphical representation of **branches** by Loomis-Wood diagrams linked together by **LSCD** (Lower State Combination Difference) relations.
- \+ Lower/upper states given by a table of energies, not by an internal polynomial representation.
- \- IR spectrum only simulated from a peaklist, no graphical representation of the real IR spectrum
- \- Difficult export/import of data for linking to external fitting

R. Brotherus: INFIA - Program for Rotational Analysis of Linear Molecule Spectra, J.Comp.Chem. 20, (1999) 610-622.

- \+ Very good graphical interface
- \+ Display of the IR spectrum with interactive assignment features
- \- Simple polynomial representation of energy levels and fitting
- \- Limited application to different type of molecules than linear

Present and planned developments

Combining the good features of the previous prototypes, making the program flexible and user-friendly.
The first version is designed for symmetric top molecules, further extension to asymmetric top molecule and molecules with large amplitude motions / splittings is under development.

Basic ideas

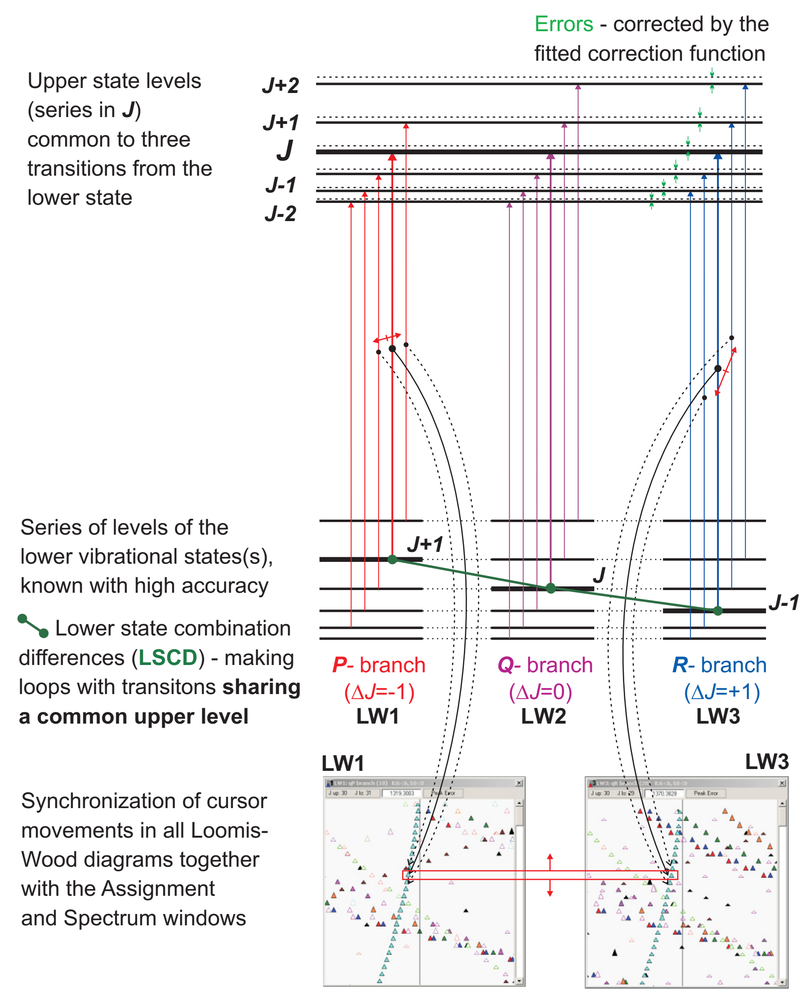
The idea of **interactive checking of assignments** is based on the assumption that one of the vibrational levels pertaining to the analyzed band, usually the lower one, is known with accuracy comparable to the wavenumber accuracy of the IR spectrum, so that the **combination difference principle** can be used.

The basic logical units, which are handled by the current program, are **spectral branches**, i.e. series of transitions with ***J*** being the only rotational quantum number changing along the series and all other quantum numbers in the lower and upper states fixed to values corresponding to the selection rules.

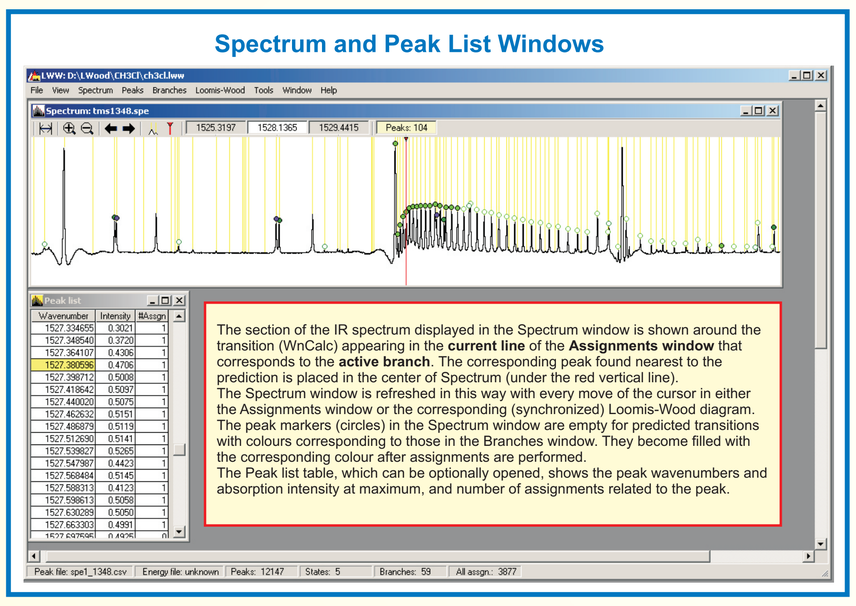
Branches sharing the same set of fixed quantum numbers of the upper vibrational level can be checked simultaneously by Lower State Combination Differences. This is simplified by displaying simultaneously the Loomis-Wood diagrams corresponding to the selected branches and allowing to perform assignment actions directly in these diagrams.

In the beginning of the assignment, the rotational structure of the yet unknown vibrational level can be given only approximately. Assigning together branches with the same set of fixed quantum numbers of the upper vibrational level allows to correct the upper state energies by a **simple polynomial correction function** with only one variable, the rotational quantum number ***J***. Coefficients of this function are fitted interactively to minimize the differences between observed (WnObs, assigned) and calculated (WnCalc, predicted from the table of energies) wavenumbers.

Branches in Loomis-Wood diagrams and their linking by combination differences



Spectrum and Peak List Windows

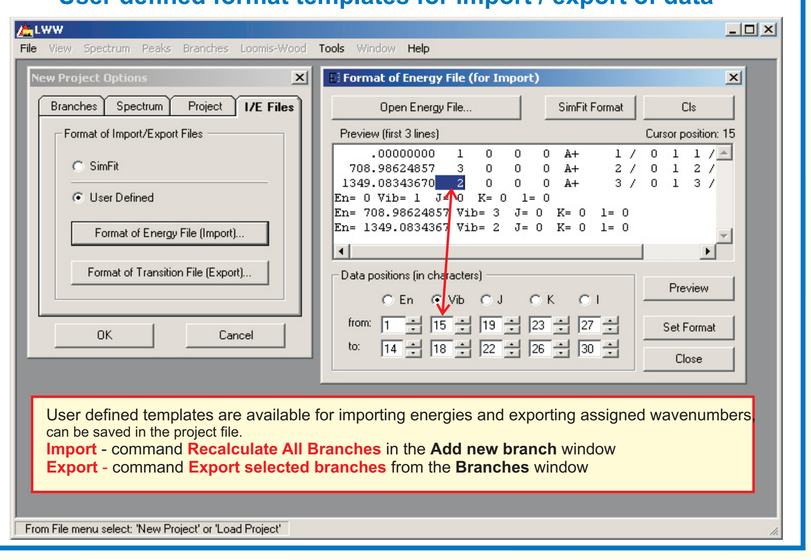


The section of the IR spectrum displayed in the Spectrum window is shown around the transition (WnCalc) appearing in the **current line** of the **Assignments window** that corresponds to the **active branch**. The corresponding peak found nearest to the prediction is placed in the center of Spectrum (under the red vertical line).
The Spectrum window is refreshed in this way with every move of the cursor in either the Assignments window or the corresponding (synchronized) Loomis-Wood diagram.
The peak markers (circles) in the Spectrum window are empty for predicted transitions with colours corresponding to those in the Branches window. They become filled with the corresponding colour after assignments are performed.
The Peak list table, which can be optionally opened, shows the peak wavenumbers and absorption intensity at maximum, and number of assignments related to the peak.

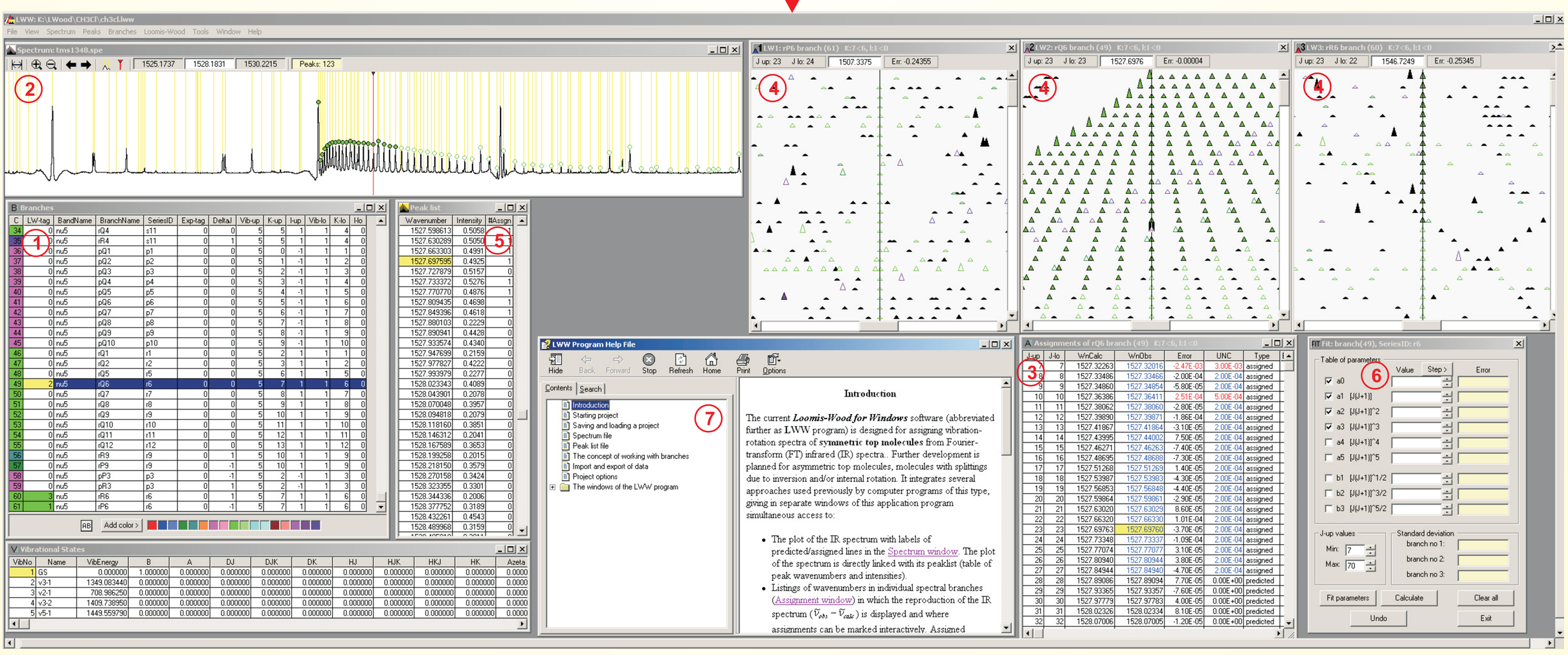
Main windows of the Loomis-Wood program

1. Branches window
2. Spectrum window
3. Assignments window (active branch)
4. Loomis-Wood windows (LW diagrams)
5. Peak list windows
6. Fit window
7. On-line Help window

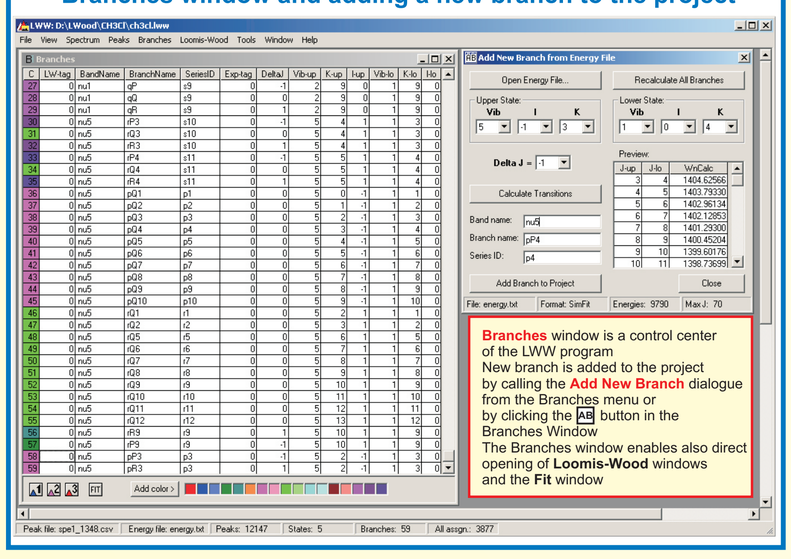
User defined format templates for import / export of data



User defined templates are available for importing energies and exporting assigned wavenumbers can be saved in the project file.
Import - command **Recalculate All Branches** in the **Add new branch** window
Export - command **Export selected branches** from the **Branches** window

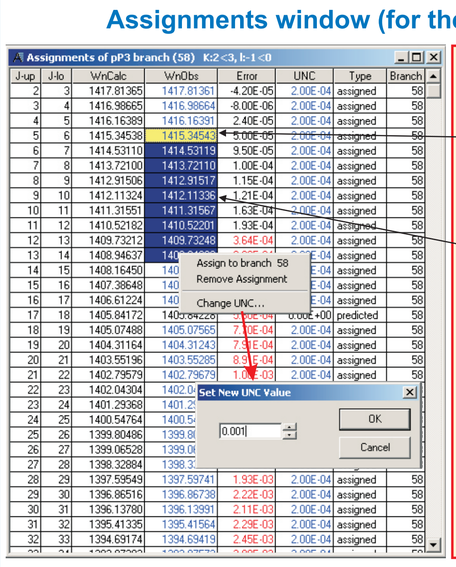


Branches window and adding a new branch to the project



Branches window is a control center of the LWW program
New branch is added to the project by calling the **Add New Branch** dialogue from the Branches menu or by clicking the button in the Branches Window
The Branches window enables also direct opening of **Loomis-Wood** windows and the **Fit** window

Assignments window (for the active branch)



The **Assignments** window is fully synchronized with the Loomis-Wood windows in assignment functions

The **current line** in the table of assignments corresponds to the highlighted symbol in the related Loomis-Wood diagram

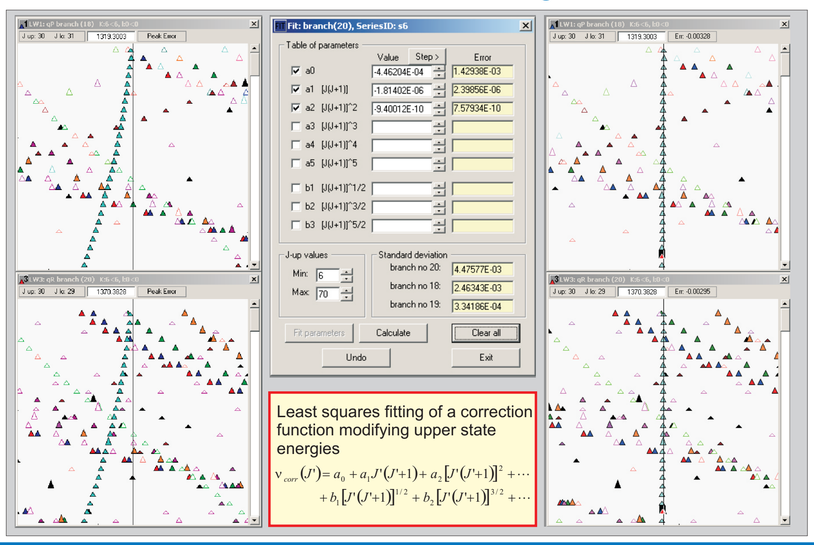
Assignments can be performed on whole groups of transitions

Assigned transitions appear in **blue** colour, predicted in **black**

Error = WnObs-WnCalc
Errors > estimated accuracy of wavenuber of isolated lines **WnObs** appears in **red**, in **blue** colour otherwise

Transitons with larger errors (usuallly overlapped) can be assigned with lower accuracy (lower weight for fitting) in the **Set New UNC** dialogue. Such UNCertainties appear in **red**, while correctly reproduced transitions have UNC in **blue** colour

Loomis-Wood windows before and after fitting of correction function



Least squares fitting of a correction function modifying upper state energies

$$\nu_{corr}(J') = a_0 + a_1 J'(J'+1) + a_2 [J'(J'+1)]^2 + \cdots + b_1 [J'(J'+1)]^{1/2} + b_2 [J'(J'+1)]^{3/2} + \cdots$$