

Advanced graphical software for assignments of transitions in rovibrational spectra

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Abstract

We have developed advanced graphical software for significantly accelerated and verified assignments of rotationally resolved rovibrational molecular spectra. The program combines the traditional approach of Loomis–Wood diagrams, which are used to visualize spectral branches and facilitate their identification, with the power of interactive combination difference checking, which provides an immediate verification of correct assignments of quantum numbers to spectral lines. Assignment procedures and other tools of the program are designed in a fully graphical Windows environment to accelerate the usually tedious assignment work and make the use of the program highly intuitive. The use of an appropriate rovibrational Hamiltonian for fitting the assigned transitions is made easy by the flexible, user-programmed interfaces for exporting assigned data directly in the needed format and importing rovibrational energies back to the assignment program. The program is designed for the MS Windows operating systems and is available upon request with a full documentation on <http://www.lww.amu.edu.pl>.

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1. Introduction

The development of experimental techniques, which produce large amounts of spectroscopic data and, on the other hand, a boom of computing power of personal computers with programming environments that enable creation of interactive application programs lead to development of various interactive programs, which facilitate the tedious procedures of assigning rotational and rovibrational molecular spectra [1–7]. Most of these programs are based on the original idea of the Loomis–Wood algorithm [8], which makes use of periodically recurring patterns of lines in the spectrum and organizes them in such a way that this periodicity is translated into emerging, visually recognizable continuous patterns in the so-called

Loomis–Wood diagrams. This facilitates enormously the identification of series of transitions belonging to individual spectral branches. This advantage is further enhanced by a typically interactive manner of assignment procedures in these computer programs. Assignments of quantum numbers to the identified branches are, however, only tentative in this step and have to be verified for overall consistency with other branches by fitting of parameters of the effective rovibrational Hamiltonian. When this calculation is done internally in the computer program, it is usually only approximate. Exact calculations are usually performed only in external fitting programs, from which the energy levels are imported. The latter approach is used in programs described in Refs. [3,5,6], where the first is designed for analyzing rovibrational spectra and includes also interactive combination difference (CD) checking. It can in principle work with any file of energies, but supplying it with levels from external calculations is done in a

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rather complicated way. The second and third programs are used typically with the asymmetric top programs SPFIT [9] or ASFIT [6].

The CD checking of rovibrational assignments is based on the assumption that either the lower or the upper vibrational state pertaining to the studied band has already been analyzed within the experimental accuracy and provides accurate information about the spacings of its rotational levels. The most common case is checking by lower state combination differences (LSCD), where the lower state is usually the vibrational ground state. But the algorithm works equally well for upper state CD checking. In further text we will assume, with no loss of generality, that CD checking is based on the knowledge of the rotational structure of the lower vibrational level.

The power of LSCD checking lies in the fact, that the correctness of assignment checking is independent of the accuracy of description of rovibrational levels of the upper state and thus can be also checked interactively. The CD approach has been used in the two mentioned programs [2,3], but each of them suffered from some inconveniences. The INFIA program [2] provides a very good graphical user interface, but its use is restricted to linear molecules and with certain limitations to symmetric top molecules. The other program with implemented CD checking [3] is general for any symmetric/asymmetric top molecule, but has only a semi-graphical representation of the Loomis–Wood diagrams. It displays only small sections of the infrared spectrum and does not provide facilities for displaying the whole spectrum.

The current program package has been inspired, as for the plot of the analyzed spectrum, by that of the INFIA program [2], but internally follows the general approach of Ref. [3], having both the lower and upper levels of the spectral branches represented by a table of energies with full sets of quantum numbers. These energies are not calculated on an approximate level, but can be imported from any external general fitting program through reading files generated by such programs. This is achieved by the built-in intuitive and flexible user-programmed import interface. Similar procedures are used also for exporting assigned data to external fitting.

The present version of our program is limited to the class of symmetric top molecules, but the described general representation of energy levels, together with a modular design of the program, makes the generalization towards other types of molecules easy and straightforward. The development to the case of asymmetric top molecules is under way and further extensions to molecules with large-amplitude or hyperfine splittings are planned.

2. Spectroscopic background of the algorithm

The purpose of representing the spectrum in the form of a Loomis–Wood (LW) diagram consists in facilitating the visual identification of smooth and continuous patterns in complicated spectra, e.g. with overlapping bands

and/or high density of lines. Such patterns correspond to individual spectral branches, by which we understand series of transitions with only the J quantum number of the total angular momentum changing along the series and all remaining quantum numbers of the lower and upper states fixed, obviously according to the selection rules. The separation of transitions in such sequences, with J changing stepwise by 1, can be written in the first approximation as

$$\Delta\tilde{\nu}(J+1, J) = \tilde{\nu}(J+1) - \tilde{\nu}(J) \\ = 2B'm + (B' - B'')J(J+1) + \dots, \quad (1)$$

where m equals $-J, 0, J+1$ for the $P, Q,$ and R branches (with $\Delta J = -1, 0, +1$), respectively, and B' and B'' are the upper and lower state rotational constants, respectively. The idea of the LW diagram is to arrange the segments of the spectrum in such a way that the reference points, which are wavenumbers in the spectrum differing by $2B'$ and corresponding approximately to the distance between successive transitions in the branch with J differing by 1, are aligned vertically in the center of the LW diagram. Each horizontal ‘line’ of the LW diagram is a representation of the spectrum in the neighborhood of such reference point where the spectral lines are shown as peak symbols. In the semi-graphical LW diagram of one of the previous programs [3] these symbols were digits from 0 to 9 with the value denoting absorbance at the peak maximum. Such representation of the spectrum in a text mode for was chosen to keep the refresh time of the LW diagram after each assignment action at a reasonable rate. The use of a graphical representation with high-resolution graphics, needed in cases of congested spectra, has become available only with the increased processor/graphics speed of personal computers. In the present setup we are using triangle symbols with their height corresponding to absorbance at peak maximum to represent the peaks of the spectrum.

The described arrangement of lines in the LW diagram means that if there were no difference between the upper and lower state B' and B'' rotational constants and their centrifugal distortion, the series of peak symbols of the particular branch would appear as a straight vertical line of peak symbols in the center of the LW diagram. The difference between B' and B'' rotational constants and their centrifugal distortion in the real spectrum is translated into a slant and curved pattern of peak symbols in the LW diagram.

In our program design, we have slightly modified the definition of the reference points in the center of the LW diagram so that they correspond to transition wavenumbers predicted from the table of energies

$$\tilde{\nu}_{\text{calc}}(J'', J', K^*, \Delta K^*) = [E_{\text{upper}}(J', K^* + \Delta K^*) - E_{\text{lower}}(J'', K^*)]/hc, \quad (2)$$

where K^* stands for the set of quantum numbers which are constrained in the particular branch for which the LW diagram is constructed. In the current case of symmetric top molecules, for which this first version of the program has

been developed, K^* represents a set of two values: the rotational quantum number K and the quantum number l of the vibrational angular momentum. The program can also handle the special case of series, which have for example instead of a fixed value of K the difference $J - K$ fixed to 0, 1, ..., which is useful in perturbed bands to trace levels with a similar amount of perturbation. An analogous algorithm will be used in the case of asymmetric molecules where K would translate to K_a for a prolate asymmetric rotor or to K_c for an oblate rotor, with the other the K_c/K_a being constrained to the $J - K_a/J - K_c$ difference, respectively. With this approach one can define in principle branches for any kind of molecule with only an appropriate correspondence of the set of K^* quantum numbers assigned to transitions and the entries $E(J, K^*)$ in the file of energies.

The displacement $\delta\tilde{\nu}$ of the peak from the center of the LW diagram is given by

$$\delta\tilde{\nu}(J'', J') = \tilde{\nu}_{\text{obs}}(J'', J') - \tilde{\nu}_{\text{calc}}(J'', J') + \tilde{\nu}_{\text{corr}}(J'), \quad (3)$$

where we have with no loss of generality omitted the K^* quantum numbers. If the correction function $\tilde{\nu}_{\text{corr}}(J')$ is set to zero, $\delta\tilde{\nu}$ is simply the difference between the observed and calculated transition frequencies. Because for a particular branch in the LW diagram also the difference $\Delta J = J' - J''$ is a constrained value, the correction function $\tilde{\nu}_{\text{corr}}(J')$ is a function of the upper state J quantum number only. Minimizing the differences $\delta\tilde{\nu}$ by least-squares fitting of the empirical coefficients $a_0, a_1, a_2, \dots, b_1, b_2, \dots$ of

$$\begin{aligned} \tilde{\nu}_{\text{corr}}(J) = & a_0 + a_1 J(J+1) + a_2 [J(J+1)]^2 + \dots \\ & + b_1 [J(J+1)]^{1/2} + b_2 [J(J+1)]^{3/2} + \dots \end{aligned} \quad (4)$$

results in aligning the series of peak symbols of the studied branch along the central vertical line of the LW diagram.

As has been already mentioned, the use of a single LW diagram can help to identify visually transitions in the spectrum that belong to one spectral branch, but the correct assignment of quantum numbers can be verified only by checking the consistency with other branches in the spectrum through fitting of the whole rovibrational band. The idea of linking together several LW diagrams, in which the displayed branches share the same J -series of the upper state used in Ref. [3], makes possible to subject the related branches to a stringent check by CD in an interactive manner. This can be explained with the help of Fig. 1, where the three branches related by CD are the P , Q , and R branches with $\Delta J = -1, 0, +1$, respectively. In this scheme, the common upper rovibrational level, the three transitions, which share this upper level, and the three distinct lower rovibrational levels are drawn in bold lines. The CD checking is based on the assumption, that the spacings between the rovibrational levels (the three rotational levels of the lower vibrational state, in the present example) are known with high accuracy from a previous study. Therefore even if the upper state energy is known only approximately, these three transitions with a common upper level must have more or less the same difference $\delta\tilde{\nu}$ between the prediction

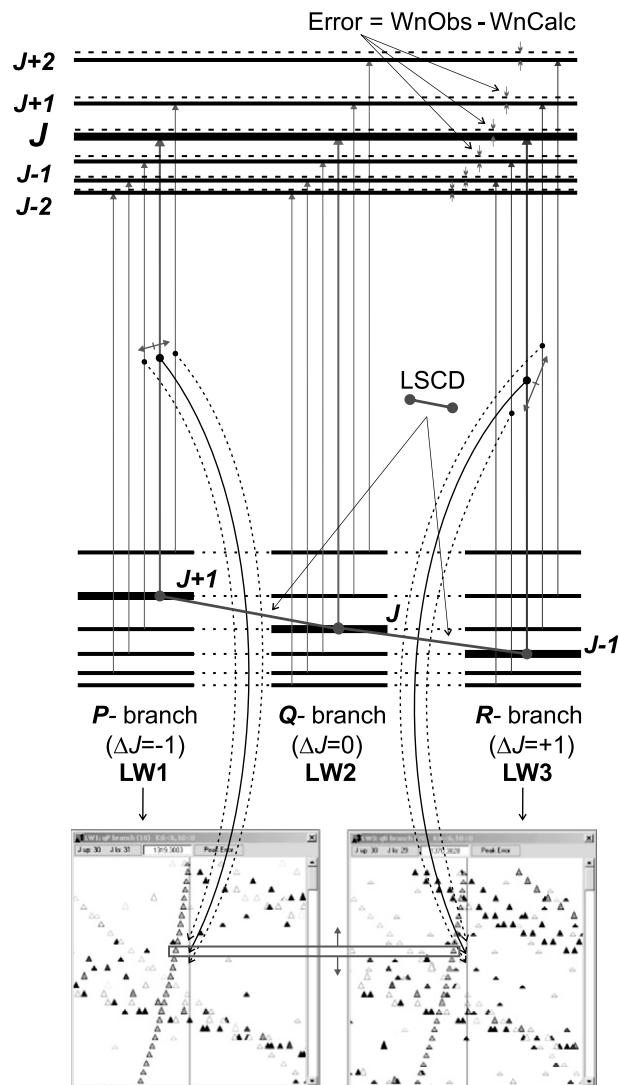


Fig. 1. Relation between the transition wavenumbers calculated from the table of energies (upper part of the figure) and the Loomis–Wood diagrams (lower part in which two diagrams corresponding to the P and R branches are shown). Peak symbols of transitions, which are related by LSCD, are shown in the rectangle. Navigation of the cursor in the LW diagram of the active branch is synchronized with all other related LW diagrams and also with the table of energies, so that the transitions currently selected for CD checks share a common upper level. The currently selected levels and transitions are drawn in bold. Adding a correction function to upper state energies from the table (full lines) moves them to the values corresponding to experimental observations (dashed lines). Minimizing differences between observed and calculated wavenumbers results in aligning the series of line markers of all related branches along the vertical lines in the center of the LW diagrams.

and the corresponding line found in the spectrum. A coincidence of three transitions satisfying the CD relation can be of course accidental, but it can hardly occur for many consecutive triads of transitions that share a common upper level. A series of such triads satisfying the CD relations provides a reliable check of assignments of quantum numbers to transition wavenumbers. In addition to this, such series must be displayed as continuous patterns of

the same shape in all related LW diagrams, as shown in the lower part of Fig. 1.

It is not difficult in this program setup to have these displacements displayed in all opened LW diagrams and synchronized as the cursor is navigated around one of the LW diagrams, from one peak marker to another. In this way the CD checking of correct assignment of quantum numbers, without the necessity of exact fitting of the upper state levels, is made fast and interactive. Such relation between the three linked branches (LW diagrams) also means that minimizing the residuals $\delta\tilde{\nu}$ in one of the branches by fitting the correction function $\tilde{\nu}_{\text{corr}}(J')$ minimizes the residuals in all other related branches as well, when they are correctly assigned.

The current program is not limited to have only three branches linked together with CD. The only limitation is that only three of any number of branches, which share the same series of upper levels, can be displayed simultaneously in the Loomis–Wood diagrams. Their selection is accomplished by the flexible design of the Branches window described in detail in the next section. This feature represents an advantage for example in assigning asymmetric rotor spectra, where more relaxed selection rules for dipole allowed transitions provide more branches reaching the common upper level. In symmetric rotors, this feature allows for example simultaneous CD checking of allowed and perturbation allowed transitions.

3. Main components and features of the LWW program

The main components (windows) of the LWW (Loomis–Wood for Windows) program are shown in the scheme in Fig. 2. We give here only a brief description of their functions and relations and we refer the reader for details to the home page of the program at <http://www.lww.amu.edu.pl>, where a complete documentation of the program with graphical illustrations are available. The web page also contains illustrative examples of typical assignment tasks as well as special features of the current program related to treatment of local resonances and simultaneous assignments of hot and overtone bands.

The basic logical unit, to which the LWW program refers, is a *project*. It is a collection of files used and generated by the program, for convenient access usually stored in one computer directory. When a new project is started, a *project file*, which contains all necessary information for opening (loading) the project repeatedly, is created in the project directory. Starting a new project requires the basic information about the rovibrational spectrum and the corresponding rovibrational energies. It is assumed that the spectrum is available at least in the form of a peak list file. If the plot of the spectrum is not available, the program can generate a simulated one from the peak list. If the file of energies is not available, the LWW program can still be used as a simple tool for viewing and plotting selected sections of the spectrum.

The LWW program desktop has four basic windows that are permanently open and cannot be closed by the user. These are shown in the scheme of Fig. 2 with shaded window title bars.

- **Spectrum** window – contains the plot of the IR spectrum and is synchronized with the Assignments and Loomis–Wood windows as described further. It is equipped with zooming tools and can be used for exporting bitmaps for plotting selected sections of the spectrum.
 - **Vibrational States** window – contains the list of vibrational levels that were automatically detected in procedure of reading the energy file.
 - **Branches** window – is the control center of the program. It contains a table of all branches in the project and controls the display/assignment actions in the Assignments and Loomis–Wood windows. This window is used for defining the branches, which the user wants to have included in the project and from here the LW diagrams of selected branches are opened.
 - **Assignments** window – contains in its table all necessary information about the transitions in the branch, selected as the active branch in the Branches window, sorted by the J quantum number. Each line of the table, corresponding to one J value, contains the wavenumber predicted from the table of energies (WnCalc), the nearest matching wavenumber found in the peak list of the spectrum (WnObs), their difference (Error) and the uncertainty (Unc) attributed to the assigned peak. In this window assignments can be done either for individual transitions or for whole sequences of transitions. In the same way, deleting of assignments and changing of uncertainties is obviously possible.
- Besides this minimum configuration, two other types of windows are usually open in the process of making assignments
- **Loomis–Wood (LW)** window(s) – contain the Loomis–Wood diagrams of the branches that can be related by lower state combination differences. Peaks of the spectrum are shown here as triangular peak markers. Up to three LW windows can be opened at a time. The LW window, in which the cursor is being navigated, corresponds to the *active branch*, whose content is displayed at the same time in the Assignments window. We denote the other two LW windows (and corresponding branches) as *related windows (branches)*. The active/related status is easily toggled from one window to another. The LW window of the active branch also serves for making assignments and assignments made here are fully synchronized with the Assignments window. This means that every assignment action in either of the LW/Assignments windows leads to a corresponding update in its counterpart. The synchronization also means that as the cursor is moved from one line of the Assignments table to another, its counterpart in the LW window is placed on the corresponding peak marker. All actions in

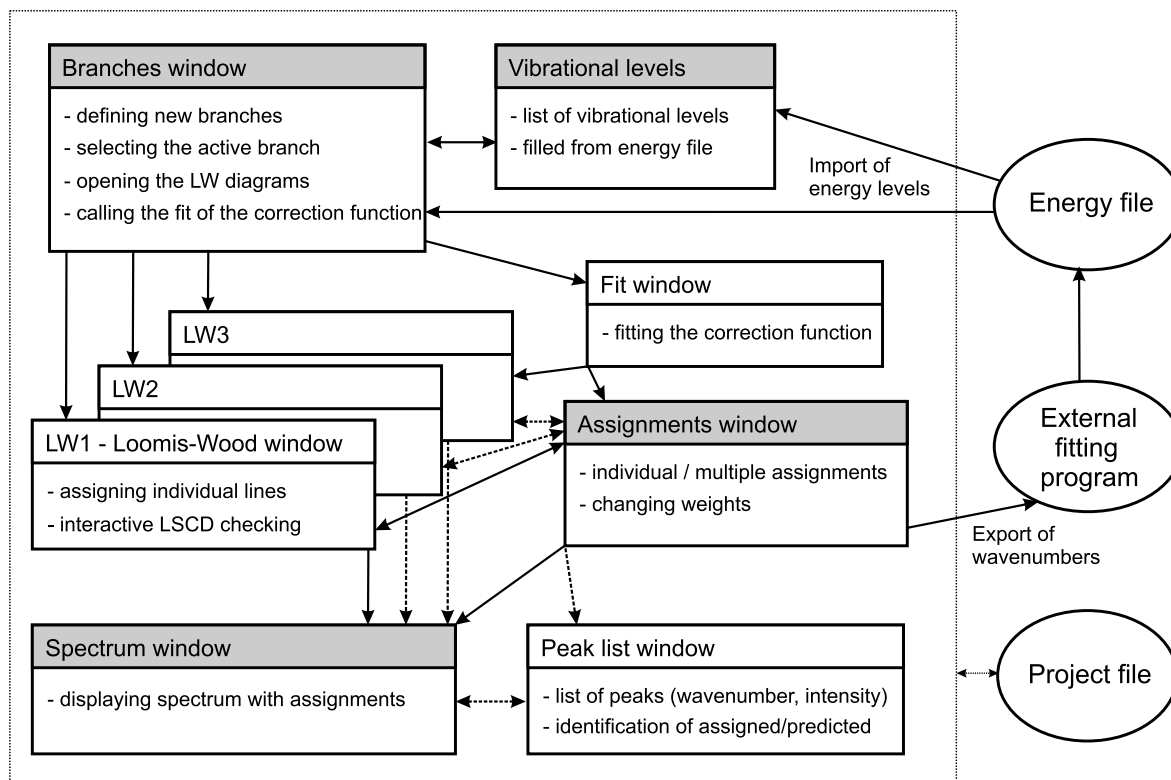


Fig. 2. Scheme of the main components (windows) of the LWW program. Windows that are opened only permanently have shaded window title bars. Lines with two-sided arrows denote the full bi-directional synchronization between the assignments and LW windows. The dashed lines correspond to the 1-to-3 relations between the assignments window and the LW windows in the sense that the table in the assignments window corresponds to the currently selected active branch in one of the LW windows. Lines with one-sided arrows denote actions called from a 'higher-level' window with no such interactive feedback from the 'lower-level' window.

these two types of windows are further synchronized with the Spectrum window as described in the next paragraph.

- **Peak List** window – contains the list of wavenumbers and peak intensities corresponding to the spectrum displayed in the **Spectrum** window. Each peak also carries the information to which transition it is assigned and/or tentatively related by prediction. There is a multi-directional synchronization in the chain Spectrum-Assignments-LW windows. When the cursor is navigated around the peaks of the spectrum in the LW/Assignments windows, the corresponding peak in the Spectrum window is placed to its center and the corresponding line in the Peak list window gets highlighted.

The last window necessary in assignment procedures is the **Fit** window, used for fitting the coefficients of the correction function $\tilde{\nu}_{\text{corr}}(J')$. Its function is described in detail in the next section with discussion of assignment strategies.

The most frequent actions of assignment procedures are programmed so that they can be accessed easily by pressing hot keys or they have associated function buttons in the main windows of the LWW program. They can be of course accessed through the items of the main LWW program menu, where many more functions are available. Out of these it is worth mentioning the procedures that

facilitate the link to fitting the assigned spectrum with an external program.

We have found it useful to separate the calculations of rovibrational energies from the assignment program already in the previous generation of the Loomis–Wood program [3]. However, the import of rovibrational energies into the assignment program and export of assigned data into external fitting was one of its weak points. Therefore we have paid much attention to making this step easy and flexible, so that the present LWW program can be linked to virtually any fitting program. For this purpose, two user-programmed import/export interfaces have been integrated into the program package. They are both based on an interactive definition of the I/O format template, which is saved for repeated use in the project file.

For convenience, the LWW program package provides also built-in tools for converting the usual format of Fourier-transform spectra (Bruker Giessen-format) to the internal representation of the spectrum. It provides also a utility for merging two or more spectra into one project. This feature becomes useful in combined analyses of fundamental/hot band/overtone spectra when it is necessary to have spectra from two distant regions displayed in the spectrum window. Together with a flexible management of branches that can be opened in LW windows simultaneously, this allows to link with CD branches, which need

not have the lower levels in the same vibrational level. This feature, which has not been considered in the previous implementation of CD checking [3], can for example combine levels of the vibrational ground and fundamental states in the lower state combination differences and assign with appropriate CD checking the hot and overtone bands simultaneously.

4. Typical assignments strategies with LWW

Every spectrum analysis has to be started from a first more or less approximate prediction of energy levels. Because we assume that the program serves mainly to assigning infrared rovibrational spectra, we assume that the rotational energies of the lower vibrational state pertaining to the band, not necessarily the vibrational ground state, are known with accuracy suitable for lower state combination difference checking. This also means that in some favorable cases we can make simple predictions of the upper state level by simply adding the vibrational energy to all ground state levels. This is usually sufficient in weakly perturbed states to identify visually series of transitions in the LW diagrams, for which CD checking can be started. The first assignments in the branch have to be done one by one in the LW windows where it is possible to assign lines which need not be close to the center of the diagram (i.e. close to the prediction), but which have partners in the related LW windows with approximately the same errors. These initial trial assignments are followed by fitting the correction function, which aligns the series close to the center of the LW diagram. For the content of the Assignments window this means that the peaks found closest to the predictions correspond to correct assignments in the branch and can be then assigned in whole series by ‘just a mouse click’. Such series can be highlighted by dragging the mouse cursor across the selection of lines in the table of the Assignments window and then the assignment action can be performed on all of them by a cursor click. In the same way, assignment of whole series of transitions can be deleted or their weighting for the fit can be changed by modifying their uncertainty. If now the assignment of quantum numbers to the series is correct, the series in all related LW diagrams should appear aligned in the same way, i.e. with the same shape and errors. In non-resonant cases, fitting of the simple polynomial correction function should always put the series to their center. Weak local resonances can be identified as series broken in the same way and having approximately equal errors in all LW windows. Therefore even in such resonant cases, transitions with rather large errors, but consistent in all LW windows, can be safely assigned before any quantitative fitting of the resonance in the upper state is done. For easier assessment of local resonances the program has an interactive tool for displaying plots of reduced energies.

The easy export and import of data to external fits allows performing iterative fitting during the assignment procedures. The selected portions of assigned data can be

exported to files in a format, which is directly used as input for fitting in a corresponding external program. The refined energies are then easily returned into the LWW. When the corrected energies are read into the assignment project, the user can use them for recalculating only individual branches selected in the Branches window or all branches in one run. One can work in this way with multiple energy files. For this purpose each branch carries the information about the file of energies from which it was predicted. It should be noted that the recalculation of wavenumber predictions in the branches does not change the once assigned transitions, unless these are re-assigned by the user.

The representation of rovibrational energies by a table, rather than by a direct calculation within the assignment program, is obviously an advantage in cases when the lower vibrational state is already perturbed, which is a very frequent case in studies of hot bands. It also allows linking together LW diagrams of allowed and perturbation-allowed branches, which has not been possible in of the previous version of the LW-CD program [3].

In cases of straightforward assignments of not too much perturbed bands the program significantly accelerates the assignment procedures, which is useful in handling spectra with thousands of lines.

For spectra with no visual clue for initial steps of assignments, there are several useful utilities that facilitate the assignment attempts. In congested spectra, for example, it is possible to simplify the LW diagrams by filtering out lines with high and low intensities, which simplifies the LW diagrams and makes the continuous patterns emerge. When it is difficult to predict the upper state energies with sufficient accuracy that would show at least some patterns in the LW diagrams, there is a possibility of simple step-wise changing of any coefficient of the correction function and redrawing the LW diagrams after each change, allowing for trial-and-error seek for emerging LW patterns.

With the easy and interactive way of assignment actions related to displaying the corresponding sections of the spectrum, one can also effectively perform trial-and-error attempts of assignments based on recognition of some typical line patterns directly in the plot of the spectrum. In such approach, the interactive CD checking immediately rules out incorrect assignments.

5. Perspectives of future developments

The original development of the LWW program has been done for the case of symmetric rotors. However, the general internal representation of rovibrational energies in the LWW program by a table allows for an input of energies from any external source. This is already supported in the current version by the user-programmable format template that can be used both for importing energies and exporting assigned wavenumbers. This will enable in future development linking for example to the general asymmetric rotor fitting program SPFIT [9]. The change of meaning of the quantum numbers that are fixed in the

definition of branches will be easily handled, because this requires code changes only in a limited and well defined set of procedures, leaving the rest of the program unchanged. It will also allow for inclusion of additional quantum numbers pertaining to e.g. large-amplitude or hyperfine splittings.

The LWW program has been designed primarily for assigning rovibrational or rovibronic bands, but it offers a possibility of a straightforward extension to assigning simultaneously rotational spectra within any vibrational level appearing in the file of energies. This development is planned together with the above-mentioned extensions to the case of asymmetric rotors and molecules with large-amplitude or hyperfine splittings.

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