Infia — a program for rotational analysis of linear molecule spectra

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Abstract

A software package for spectrum analysis is described. With Infia software, high resolution vibration-rotation spectra of linear molecules can be analysed interactively and visually. Routine tasks are minimised by the automatic features of the program such as assignment of peak with combination difference prediction. Detection of spectral structures is aided by multiple simultaneous views to the data, including a Loomis-Wood type view. The program is designed especially for difficult spectra with many overlapping bands, high density of peaks and possibility for incorrect assignments.

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1 Keyphrases

1. High resolution infrared spectroscopy

2. Automatic spectrum analysis

3. Vibration-rotation spectrum

4. Loomis-Wood

5. Linear molecules

2 Introduction

The development of high resolution laser and FTIR spectrometers has allowed measurement of rotationally resolved spectra of linear molecules such as acetylene [?] and its halogenated derivatives [?, ?]. Rotational energy level structures these molecules can be usually described by simple well known formulas [?]. Assigning the spectra and obtaining the respective spectral parameters can, however, be quite tedious, time consuming and prone to misassignments. Problems arise especially with molecules that have a high mass and several low-energy vibrational modes. They produce spectra with a high density of peaks and severe peak overlap problems and require good tools for the analysis work to be bearable and the results to be reliable.

To free the spectroscopist to as great extent as possible from the routine tasks in spectrum analysis and to increase the overall reliability and effectiveness of the process, semiautomatic interactive spectrum analysis software Infia has been

developed. Visual and user friendly interface has been a major design goal so that the usage of the program can be learned quickly and that it can be used even in student work. All analysis data is stored in databases reducing the need to type thousands of numbers into several text input files. The software has been used to analyze some fundamental and overtone band systems of $DCC^{79}Br$ and $DCC^{81}Br$. The results of this study have been published separately [?].

3 Theory

3.1 Energy levels

The total vibration-rotation term value of a linear molecule at a vibrational state v and with a total angular momentum quantum number J is given by

$$G = G_v + B_v \left[J \left(J + 1 \right) - k_v^2 \right] - D_v \left[J \left(J + 1 \right) - k_v^2 \right]^2 \tag{1}$$

where G_v is the vibrational term value, B_v and D_v are the rotational and centrifugal distortion constants and k_v is the vibrational angular momentum quantum number of the state v. With some vibrational states, it is necessary to add a higher order term $H_v \left[J \left(J + 1 \right) - k_v^2 \right]^3$ to Eq. (1) to obtain an accurate fit of rotational energies for high J values. The vibrational term values G_v and rotational constants B_v that are obtained from the rotational analysis can be further used in the vibrational analysis.

3.2 Rotational resonances

Occasionally nearby vibration-rotation states interact strongly with each other through some vibrationally off-diagonal Hamiltonian operator terms [?]. If the Hamiltonian term involves the rotational motion of the molecule, the resulting interactions are called rotational resonances. These include the rotational l-resonance and the Coriolis resonance. In these cases the polynomial expression of Eq. (1) does not adequately produce the observed energy levels. Instead, the calculation requires a separate Hamiltonian matrix to be set up for each value of J. The unperturbed energies are placed to the diagonal of these matrices and resonance elements to off-diagonal positions. Resonance energies are obtained with matrix diagonalization. For example, for the rotational l-resonance, the off-diagonal elements are given by [?]

$$
\begin{aligned}
&\left\langle v_t^{l_t+1}, J, k+1 \right| H/hc_0 \left| v_t^{l_t-1}, J, k-1 \right\rangle \\
&= \tfrac{1}{4} q_t \left[(v_t+1)^2 - l_t^2 \right]^{\frac{1}{2}} \left[J(J+1) - k(k+1) \right]^{\frac{1}{2}} \left[J(J+1) - k(k-1) \right]^{\frac{1}{2}}
\end{aligned}
\tag{2}
$$

where $\left| v_t^{l_t}, J, k \right\rangle$ refers to the vibration-rotation state with v quanta on vibrational bending mode t raising l_t quanta of vibrational angular momentum and with total vibrational angular momentum quantum number k. Parameter q_t is the l-resonance parameter consisting of a constant and a J dependent part and is given by $q_t = q_{t0} + q_{tJ} \ J(J+1) + \cdots$.

3.3 Transitions

Formulas for allowed vibration-rotation transition wavenumbers can be deduced from Eq. (1) with the appropriate selection rules. For example, for P branch

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transitions ($\Delta J = -1$) one obtains [?]

$$\tilde{\nu}_P = \Delta G + B' \left[J' \left(J' + 1 \right) - k'^2 \right] - D' \left[J' \left(J' + 1 \right) - k'^2 \right]^2 - \qquad (3)$$

$$B'' \left[\left(J' + 1 \right) \left(J' + 2 \right) - k''^2 \right] + D'' \left[\left(J' + 1 \right) \left(J' + 2 \right) - k''^2 \right]^2$$

where B' and D' are the rotational constants of the upper state, B'' and D'' are the rotational constants of the lower state and $\Delta G = G'_v - G''_v$ is the vibrational *band origin*. The transition wavenumber formulas of P and R branches can be combined by defining an auxiliary quantum number m by

$$m = -J' - 1 \quad \text{(in the } P \text{ branch) and} \qquad (4)$$

$$m = J' \quad \text{(in the } R \text{ branch).}$$

This leads to a single formula

$$\tilde{\nu}_{PR} = \Delta G + B' \left[m \left(m + 1 \right) - k'^2 \right] - D' \left[m \left(m + 1 \right) - k'^2 \right]^2 - \qquad (5)$$

$$B'' \left[m \left(m - 1 \right) - k''^2 \right] + D'' \left[m \left(m - 1 \right) - k''^2 \right]^2 ,$$

allowing the peaks of both branches to be fitted with a single polynomial.

Approximations $D' = D'' = 0$, $B' = B'' = B$ and $k' = k'' = k$ yield

$$\tilde{\nu}_{PR} = \Delta G + 2B \cdot m \qquad (6)$$

which explains the familiar pattern of peaks separated by approximately $2B$ in the vibration rotation bands. A *band system* consists of a number of partly overlapping bands located in the same spectral region and includes *fundamental* or *overtone* bands that originate from the ground vibrational state and *hot bands* originating from various vibrationally excited states.

Figure 1:

4 Peak assignment

The high resolution spectrum of deuterobromoacetylene (DCCBr) will be used in the examples of this article. Fig. 1 displays the ν_4 (the DCC bending) band system of DCCBr.

Spectrum analysis consists of *assigning* spectrum peaks by determining the upper and lower vibration-rotation state of each peak and *fitting* molecular energy level functions to the assigned transitions so that optimized molecular parameters are obtained. In practice, these two phases overlap as the determination of molecular parameters by fitting the set of assigned peaks allows the prediction of new peak positions for assignment.

4.1 Starting the assignment of a band

The first step of the analysis of a vibration-rotation band is the visual identification of some peaks that are part of the band. The basis for the identification is that the band peaks occur at approximately $2B$ intervals as can be seen in Eq. (6). No knowledge of the lower vibrational state, isotopic species or correct J values of the peaks are needed at this point. However, it is common to start the analysis of a band system from the strongest band because it can be implicitly assigned to the ground lower state and the most abundant isotopic species.

Fig. ?? shows a small range of the ν_4 band system. DCCBr has two isotopic

species, $DCC^{79}Br$ and $DCC^{81}Br$ in almost equal abundances and one can easily spot the two sets of peaks belonging to the fundamental bands of each isotopic species.

The visual identification of bands is aided in the Infia software by the flexible zooming capabilities. Any window size and any zoom level can be selected quickly and the wavenumber region can be scrolled.

Some peaks from the visually identified new band are assigned rotational m quantum numbers according to Eq. (4). Although the correct m values can in some simple cases be directly seen from the peak intensity distribution, the possible systematic error in the original m assignments can be corrected later. In Infia, the initial assignments are made by clicking the peak in the spectrum window and giving the assumed m value. Fig. ?? shows some trial assignments of peaks of a hot band.

4.2 Polynomial prediction

Expansion of the transition wavenumber formula of Eq. (5) leads to a fourth order polynomial in m. Such polynomial fit can be used for prediction purposes in the initial phases of band assignment. Even if there is a systematic error in all m assignments (for example, peak with $m = 6$ is assigned as $m = 10$ and $m = 7$ as $m = 11$, etc.) a fourth order polynomial in m still fits the wavenumbers — the effect of the error is only incorporated into the resulting polynomial coefficients.

This kind of polynomial prediction has been built into the Infia software. When some peaks have been assigned, predicted wavenumbers are automati-

cally calculated and displayed to aid further assignment. Predictions can be easily recalculated after adding or removing assignments. Peak wavenumbers are calculated within the assigned range and to both directions away from the assigned range by an user defined amount.

Fig. ?? shows a typical working setup of Infia program with the spectrum window and the assignment table placed side by side. Five peaks have been assigned from a hot band and the program has automatically predicted peak wavenumbers with the polynomial fit. The assignment table shows for each m value the peak status (predicted or assigned), observed and calculated wavenumbers and their difference in a numeric and a graphical format. The spectrum window shows a vertical prediction line below the spectrum curve for m value of -40 corresponding to a spectrum peak that has not yet been assigned. To aid the simultaneous use of the two views, the spectrum view automatically shows the assignment that is selected from the assignment table.

Peak assignment with the aid of the automatic prediction can be continued in two ways. Assignments can be made as in the initial assignment phase by clicking peaks from the spectrum view. Alternatively a predicted wavenumber in the assignment table can be converted to an assignment to the nearest spectrum peak.

4.3   Combination difference prediction

When a large portion of a P or R branch has been preliminary assigned, one faces several potential problems.

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First, it can be difficult to locate the peaks that belong to the other branch of the band just by using the polynomial prediction. There can be a long wavenumber range in the center of the band where peaks are weak and totally overlapped by peaks from other bands. The situation is made worse in perpendicular band systems due to several Q branches like the ones in Fig. ??.

Second, one has to determine the lower vibrational state of the band. This problem arises in band systems with many hot bands and several isotopic species. When the lower state is determined, the upper vibrational state can usually be deduced using the vibrational selection rules, but sometimes even this requires additional reasoning and comparison of different bands.

Third, one has to determine the correct rotational m values of the peaks. In the preliminary assigned values, there might be a constant error in the m values that needs to be corrected.

There are several potential solutions to these problems, one of which is implemented in the Infia software and described here. We call the present approach *combination difference prediction* according to the familiar combination difference formula [?, ?]

$$\tilde{\nu}_R - \tilde{\nu}_P = \left(2B'' - 6D''\right)\left(J' + \tfrac{1}{2}\right) - 8D''\left(J' + \tfrac{1}{2}\right)^3 \tag{7}$$

where $\tilde{\nu}_R$ is the wavenumber of a peak from R branch, $\tilde{\nu}_P$ is the wavenumber of the P branch peak with the same upper state J and B'' and D'' are the rotational parameters of the lower state. When some peaks from a P branch have been assigned with trial J (or m) values and a trial vibrational lower state, Eq. (??) can be used to predict line positions in the R branch (similarly,

observed R branch peaks can be used to predict P branch peaks but this will not be discussed further). The predicted R branch line positions can be compared to actual peak positions in the spectrum to test whether the trial lower state and m assignments were correct. A good match of predicted and actual peak wavenumbers suggests that they are correct.

One advantage of this method is that possible upper state resonances do not disturb it. One shortcome is that the rotational parameters of some vibrational states must be already known beforehand and that the lower state of the analyzed band must be among the known states. This problem will be discussed later.

The comparison of predicted and actual peak positions is done fully automatically in the Infia software. The program tries different shifts in all m assignments and different lower state parameters. For example, with an m shift range of ± 10 and with 20 lower state candidates there are 400 possible combinations of m assignment and lower state. Infia calculates predicted R branch wavenumbers for all 400 combinations, evaluates the predictions against the spectrum and constructs a report of the best combinations. The whole process takes a few seconds on a Pentium class computer.

4.3.1 Fitness functions

The automatic selection of the best combinations out of the hundreds that are tested requires the definition of a *fitness* function that returns a single value for a given combination. The fitness function should reflect the quality of the

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match between the predicted and observed peaks and hence the probability that the combination is the correct one. With such a function the combinations can be sorted according to their probability of being the correct one and the best ones can be automatically selected for manual inspection.

It is not straightforward to define a fitness function that would systematically produce small fitness values for correct combinations and large for incorrect ones. With a dense spectrum and a large number of trial combinations it becomes inevitable that some incorrect lower state and m combinations will produce a rather good agreement of predicted and observed lines just by chance. On the other hand, even if the combination is correct, many of the R branch peaks that correspond to the predicted peaks might be badly shifted or missing due to peak overlap. The latter is observed especially in weak hot bands. For these reasons simple fitness function definitions such as the average square difference deviation of predicted and observed lines are not the most efficient in picking out the correct combination.

To develop a well performing fitness function, one must examine more closely the pattern of observed minus predicted wavenumber deviations of some correct combinations and of some incorrect but accidently good combinations. Let the wavenumber precision of good spectrum peaks be $d_{\min}$, typically about 0.0001 cm^{-1} in high resolution work in the far infrared region. In the correct combinations there typically are many deviations in the order of $d_{\min}$ and some deviations in the order of $20 \times d_{\min}$ due to peak overlap. On the other hand, accidentally good incorrect combinations have usually very few deviations near

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$d_{\min}$ and instead perform well because there are by accident exceptionally few badly fitting of the order $20 \times d_{\min}$. These combinations tend to have almost all of their deviations in the "average" $5 \times d_{\min}$ range.

These characteristics can be exploited by many different functions, the one used in Infia software being the logarithm function. Logarithm rewards a combination that has many particularly small deviations and is forgiving towards a few bad ones. The fitness function F in Infia is calculated by

$$F = \frac{1}{N} \sum_{n=1}^{N} \ln \left(\frac{d_n}{d_{\min}} \right)^2 \tag{8}$$

where N is the number of peaks in the assigned branch and d_n is given by

$$d_n = \max \left(\left| \tilde{\nu}_{n,obs} - \tilde{\nu}_{n,pred} \right|, d_{\min} \right) \tag{9}$$

where $\tilde{\nu}_{n,pred}$ is the wavenumber predicted from the R branch using assignment n from the P branch and combination difference formula of Eq. (??). $\tilde{\nu}_{n,obs}$ is the wavenumber of the closest actual spectrum peak in the R branch. The effective deviation d_n is used in the program instead of the actual deviation $\tilde{\nu}_{obs} - \tilde{\nu}_{pred}$ because a match better than $d_{\min}$ must be due to chance and should not rewarded. The presented fitness function has the property that for a perfect combination ($d_n = d_{\min}$ for all peaks) it has the value of zero and worse combinations produce increasingly higher values of F.

The fitness analysis of Infia program implementation has been further improved in four ways. First, an user defined percentage of the worst matching predictions are removed before the calculation of the average. Since all combinations tend to produce some bad matches, this removal helps to limit the

comparison of peak pairs to the more appropriate ones. Second, the predicted wavenumbers in the R branch are calculated with Eq. (??) using the *calculated* (instead of observed) wavenumbers in the P branch. They usually represent better the true line positions and in addition enable the filling of unassigned gaps in the P branch. Third, the user can choose the set of lower states and range of m shifts that are attempted in the combination analysis. For example, from the set of lower states one can leave out those that are impossible due to band intensity considerations. Fourth, in addition to the fitness function F, an *intensity fitness* function F_{int} has been defined by

$$F_{int} = \frac{1}{N} \sum_{n=1}^{N} \left[\max \left(\frac{I_{n,P}}{I_{n,R}}, \frac{I_{n,R}}{I_{n,P}} \right) - 1 \right]^2 \tag{10}$$

where $I_{n,P}$ is the intensity of assigned peak n in the P branch and $I_{n,R}$ intensity of the peak nearest the predicted wavenumber in the R branch. The basis for F_{int} calculation is that the peaks from bands P and R branches with the same lower state J are expected to have similar intensities when no strong perturbations are present. F_{int} has a value of zero if these intensities are exactly equal for all assignments and its value gets increasingly higher for combinations that produce worse matches for the intensities.

The intensity fitness function is not as a clear measure of the quality of the combination as the regular fitness function F due to the low accuracy of the peak intensity measurements relative to the wavenumber measurements. One should also be aware that there are effects, such as Coriolis resonance [?] or the Herman-Wallace effect [?, ?], that the simple intensity comparison of Eq. (??) does not take into account and that can cause the P and R branch

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peaks to have significantly different intensities. Nevertheless, in most cases, F_{int} provides a valuable additional confirmation of the correctness or incorrectness of a combination.

The branch combination analysis produces a report table such as the one in Fig. ??. The table in Fig. ?? has been formed by the combination analysis of an unknown R branch with 85 preliminary assignments in the $2\nu_4$ band system of DCCBr. 40 different m shifts and 32 lower state candidates were tried, giving a total of 1280 combinations. The ten combinations with best F values are listed in the table. The best combination has an m shift of -5, $DCC^{79}Br$ as the isotopic species and $\left|000\ 0^0 1^1\ \Pi\ e\right\rangle$ (singly excited CCBr bending) as the lower state. The performance of the fitness calculation is reflected in the fact that for over 95% of the 88 DCCBr bands that have been analyzed with Infia, the correct combination also had the best fitness value although several hundrets of combinations were evaluated in each case and there was severe peak overlap in the spectrum.

To aid the user in choosing the correct combination among the best ones, their peak deviation pattern can be manually inspected. When a combination is selected in the results table in Fig. ??, the predictions produced by the combination are shown in the spectrum view as predicted peaks and can be compared to the acrual peak positions in the spectrum.

When one combination − if any − has been decided to be the correct one, the two branches can be automatically combined to a single band with the correct lower state and the correct m assignments. If the results produced by the new

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band appear to be contradictory at some later stage, the band can be again separated to P and R branches and new combinations can be attempted.

4.4   Final assignment

After successful combination of the P and R branches, assignment of the rest of the peaks in the band is straightforward. The large number of assigned peaks at this stage allows an accurate prediction of new peaks. Working with the spectrum window together with the assignment table as in Fig. ?? allows rapid and reliable assignment of the remaining peaks. In the final assignment it is also determined, which peaks are assigned with reduced weight due to bad quality and which are left totally unassigned due to severe overlaps.

4.5   Assignment of Q Branches

In addition to the P and R branches present in all bands systems, Infia can also be used to analyze Q branches in perpendicular band systems. Fig. ?? shows the strongest Q branch pair of ν_4 band system of DCCBr. Peak m assignments (in Q branches $m = J' = J''$) are shown for both isotopic species. The wavenumber expressions used in Q branch analyses are similar to the corresponding expressions of P and R branches shown in Eqs. 3 and 5. The main results in terms of the assignment is that a polynomial fit can be used for predictive purposes as for the P and R branches.

The combination difference prediction of Eq. (??) cannot be used to assign the lower state or m values for Q branches. Instead, the lower state can

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be deduced directly from the position of the Q branch after the analysis of the respective P and R branches. The final m assignments are based on the comparison of the calculated vibrational band origin for the Q branch and the respective P and R branches. The m assignments that produce closest agreement between the band origins are assumed to be correct.

5 Parameter optimization

5.1 Direct polynomial fit

When a band has been assigned, rotational and vibrational parameters can be calculated by least squares optimization of energy level parameters to the assigned wavenumbers. For bands without rovibrational resonances the most straightforward way is to fit a polynomial in m to the transition wavenumbers. Expanding Eq. (5) yields a fourth order polynomial in m. A linear least squares calculation yields five coefficients from which the rotational parameters B'', B', D'' and D' and the vibrational band origin ΔG are calculated. Additional terms in H' and H'' can be used in the rotational energy level expression, yielding a sixth order polynomial in m.

In Infia software, fourth (or sixth) order polynomial fits to the assignments of the current band can be performed at any point with a single command. In addition to the parameter calculation, the predicted wavenumbers are automatically recalculated. The results are shown in a script window like the one in Fig. ??. Vibrational term values and rotational parameters are shown for both the

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lower and upper state.

5.2   Reduced wavenumber fit

The lower state parameters of a band are often known before its analysis. If the lower state parameters are previously known with high enough accuracy, it is reasonable to fix them to the previously known values in the linear least squares calculation. This allows the determining of the upper state parameters with higher accuracy due to reduced degree of the resulting polynomial. In practice, the calculated lower state rotational energies $B'' \left[m \left(m - 1 \right) - k''^2 \right] - D'' \left[m \left(m - 1 \right) - k''^2 \right]^2$ are added to each observed transition wavenumber $\tilde{\nu}_{PR}$ of Eq. (5) yielding *reduced wavenumbers*

$$\tilde{\nu}_{red} = \tilde{\nu}_{PR} + B'' \left[m \left(m - 1 \right) - k''^2 \right] - D'' \left[m \left(m - 1 \right) - k''^2 \right]^2 \qquad (11)$$
$$= \Delta G + B' \left[m \left(m + 1 \right) - k'^2 \right] - D' \left[m \left(m + 1 \right) - k'^2 \right]^2 .$$

The reduced wavenumbers can be fitted with the linear least squares method to a second order polynomial of the expression $m \left(m + 1 \right) - k'^2$ to obtain upper state parameters B' and D'.

In Infia software the usage of reduced wavenumber calculation is similar to the free polynomial fit. An example of a result script produced by it is shown in Fig. ??.

Reduced wavenumber fit can be used to determine upper state parameters for Q branches as well as for the P and R branches when the lower state energy of Eq. (??) is calculated in the appropriate way. Infia software takes care of

this automatically when the type of the band (PR or Q) has been defined.

5.3 Resonance fit

When two or more vibrational states are in rotational resonance, such as the rotational l-resonance described by the matrix element Eq. (2), polynomial expressions do not fit the rotational wavenumbers accurately. However, even in the polynomial calculation the effects of the resonance to the transition wavenumbers can sometimes be absorbed to the polynomial coefficients to large extent. Hence a resonance is often noticed only after assigning peaks in a wide m region and even then the deviations produced can be small. With sufficiently weak resonances, all observed peaks can be fitted with a polynomial fit with no observable deviations. In such cases one must keep in mind that the resulting parameters are effective parameters rather than the true B and D rotational parameters.

In the Infia software, information about the relevant rotational resonances of the analyzed molecules are stored in the resonance table shown in Fig. ??. The user defines the states in resonance and the type of the resonances in the table. When calculation of a band is requested, Infia searches automatically the resonance table for resonances that involve the current band. If such resonances are found, an assignment data set is formed using all bands in the present band system that are in resonance with each other.

Non-linear least squares optimization is consequently executed to find parameter values, including the relevant resonance parameters. For the calcula-

tion of energy levels, a Hamiltonian matrix is set up and diagonalized for each J value. Optimization is performed by iterative refinement of the parameters. The default optimization method is the Gauss-Newton prediction [?] using finite difference gradients. If parameter values are poorly known before refinement, the Simplex method [?] can be chosen instead. After the calculation has converged, predicted wavenumbers are recalculated for all the bands involved and the results are displayed in a script such as Fig. ??.

From the users point of view, the resonance calculation differs from the polynomial calculation only by lasting somewhat longer. In addition the first stages of band analysis — initial assignment of a portion of peaks from other branch and combination of P and R branches — are performed in the same way as they are done for the non-resonance bands. Note however, that the combination difference formula of Eq. (??) can only be used for bands whose *lower* state is free of rovibrational resonances.

6 Dealing with complex spectra

6.1 State Database

After the user decides that the assignment of a band or a group of resonance bands is complete, the final parameters are transferred to the *state parameter database*, shown in Fig. ??. This database stores the vibrational term values and rotational parameters of the analyzed vibrational states. If the present band belongs to a resonance group, the optimized resonance parameters are

also transferred to the resonance database shown in Fig. ??.

The state and resonance databases are used for three purposes. First, they automatize the collection and storage of the calculation results, display them in an organized fashion and provide methods for exporting the results to ASCII-files used in publications. Second, the databases serve as an easily accessible source of state parameters for the combination difference prediction method. Third, they provide initial parameter values for the iterative refinement methods used in resonance calculation.

In the situations where different bands provide information of the same vibrational state, the state database can be used to compare the resulting parameter values in order to select the most accurate ones. The comparison is performed automatically by Infia. The result scripts of Figs. ??, ?? and ?? show for each parameter its deviation from its existing value in the state database and relative accuracy (better, same or worse).

6.2 Building up the vibrational energy level structure

Due to the combination difference prediction method used by Infia, the lower state parameters of the analyzed bands must be known beforehand. This suggests a cumulative approach in the parameter determination described in following.

First, the ground state parameters of the analyzed molecule must be obtained from a previous (possibly microwave) study. If such a study is not available, one has to attempt to assign some ground state bands directly. These bands

are easily detected due to their high intensity and their m assignments can be based on the position of the zero-gap [?] or the Q branch. The ground state parameters are then obtained by polynomial calculation.

Next, one can assign and analyze ground state bands from all the measured band systems using the combination difference prediction. If their polynomial fit gives more accurate values for the ground state parameters, these parameters replace the old values in the state database. Reduced wavenumber calculations of the ground state bands give various excited state rotational parameters that are placed to the state database.

Now all the hot bands originating from the newly found vibrational states can be assigned from all the band systems, giving still more vibrational state parameters as a result. More upper state parameters will be determined by reduced wavenumber fits and even more hot bands become accessible. This process is repeated until all the bands in the measured band systems have been analyzed.

If additional band systems are measured at a later stage, they can be rapidly analyzed using the previously known parameters with combination difference prediction. State parameters can also be manually entered to the state database if they are available from some other study.

6.3   Spectrum view with many bands

When many bands have been analyzed from a complex band system, it becomes increasingly difficult to find additional new bands. Therefore it becomes impor-

tant to present a clear view of the spectrum and assignments that have been made. The spectrum window of the Infia program handles this task as shown in Fig. ??. Assignment labels are color coded according to the band and they can display either the band name as in Fig.?? or the assigned m value. The spectrum positions with predicted peaks are shown by prediction labels and, for the selected band, with blue prediction lines.

6.4   The Loomis-Wood view

In some complicated band systems, even a detailed view of the spectrum is not enough for the efficient detection and assignment of weak bands. For such cases the Infia software includes an alternative Loomis-Wood type view of the spectrum [?]. A Loomis-Wood image shows the spectrum peaks as dots on a two-dimensional display as seen in Fig. ??. The x axis is defined by the rotational m quantum number of the selected band and the y axis by the wavenumber deviation of the peak from the selected band calculated wavenumber. Therefore the selected band is straightened to the x axis and other bands are seen as strings of dots with different slopes and curvatures. It is significantly easier to locate new bands from this view than from a conventional spectrum view.

The Loomis-Wood view can be displayed in any size and zoom level. It can be used to assign peaks to the selected band by clicking them. This is usually the most rapid way to assign a new band. The Loomis-Wood view can be used in combination with the regular spectrum view and assignment table as shown in Fig. ??. All three views are connected so that selecting a peak in one of

them causes the same peak to be shown in all three.

6.5 Reliability of assignment

When working with a complicated spectrum, care must be taken to ensure that the peaks are correctly assigned. When the density of peaks is high, seemingly good polynomial fits can be created from peaks that do not actually belong to the same band. The danger of misassignment is especially large for weak hot bands that have large portion of their peaks totally overlapped by the lines of stronger bands.

Infia software offers many possibilities for ensuring correct peak and band assignment. With these guidelines, a high reliability for assignment can be obtained even for weak bands of low quality.

First, in the combination difference method for the lower state and m assignment, the correct combination should stand out having clearly better fitness value than all other combinations. The manual inspection of the combination should show no systematic deviations in the predicted versus observed wavenumbers. Second, deviations of calculated minus observed wavenumbers for a completely assigned band should be generally small relative to the average peak wavenumber precision. The deviation should not display any systematic pattern. These requirements must be met both by the free polynomial calculation and by the reduced wavenumber calculation.

Third, when two or more bands have a common lower state, their analysis must yield similar values for the lower state rotational parameters. Infia

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automatically compares the new fit results to the existing values in the state database and reports deviations.

Fourth, for perpendicular bands there must be a corresponding Q branch found close to the band center ($m = 0$). Fifth, observation of the l-doubling [?] in bands where it is expected adds to the reliability of the assignment. This effect is best observed in the Loomis-Wood view. Sixth, when the analyzed molecule possesses more than one isotopic species, all bands occur in groups with one member for each species. This produces a familiar pattern in the Loomis-Wood view that adds to the reliability of their assignment.

Seventh, if a vibrational calculation is performed after the rotational analysis, only small deviations of calculated and observed wavenumbers should occur.

7   Program implementation

Infia is an object oriented program with about 5000 lines of code in 20 units. The modular design of the program enables rapid debugging and easy addition of new features. Physically Infia is a 32-bit Windows95 program that has been developed using Borland Delphi 3.0 [?]. Delphi was chosen due to its capability of a rapid user interface design and its object oriented programming approach. As a 32-bit program, all available system memory can be utilized. Hence there are no limits for size of the spectra or number of peaks or assignments. Hardware recommendations include a Pentium processor, 32 MB of RAM and fast graphics with at least a 1024×768 resolution and 65536 colors. Operating system can

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be either Windows95 or NT4.

7.1   Data structures

Infia uses object database for the storage of the analysis data. The object oriented data storage increases the robustness of the program and makes addition of new features easy. The database consists of five object tables containing the molecules, vibrational states, bands, assignments and peaks of the analysis project. The data fields and relations between the objects (implemented as pointers) are presented in Fig. ??. Some additional important objects and their descriptions are presented in Table ??.

8   Discussion

The Infia software has been used successfully to analyze the $\nu_4, \nu_3, \nu_4 + \nu_5$ and $2\nu_4$ band systems of DCCBr. Results of this project have been published in a separate paper [?]. The program has proven to free the spectrum analyst from many routine tasks that take considerable time and are prone to human errors in more manual approaches. Furthermore, with the advanced views to the data, more bands and peaks can be often assigned, enabling higher amount of information being obtainable from any spectrum.

Future possible developments of the program involve analysis of non-linear molecule spectra. With the spectrum views and general optimization modules present, this addition should be rather straightforward. Another considered extension is the vibrational calculation, that is usually performed after the ro-

Object	Description
AnalyseWindow	Main object of the WinAnalyse program. Responsible for displaying the main window of the application, setting up the application main menu and responding to the menu commands by calling lower level methods of other objects.
SpecWin	SpecWin object creates the spectrum window that displays the spectrum curve, peak markers and assignment labels as shown in Fig. ??.
Spectrum	The Spectra object serves as a container for the spectum data. It provides services for processing and accessing this data such as calculating the interpolated spectrum intensity at given wavenumber and performing baseline correction.
FitData	Central storage and manipulation of data for linear or nonlinear parameter optimization. Includes resonance calculation methods.
Newton	Nonlinear least squares optimization object with the Gauss-Newton method. Works on data in Fitdata object.
Simplex	Nonlinear least squares optimization object with Simplex method. Works on data in Fitdata object.
Matrix	Matrix object capable of inversion, eigenvalue analysis etc. through IMSL mathematics libraries.
LoomisForm	Object displaying the Loomis-Wood plot of the spectrum and performing assignments through it.

Table 1:

tational analysis of the measured spectra.

9   Acknowledgments

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