INFIA—Program for Rotational Analysis of Linear Molecule Spectra

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ABSTRACT: A software package for spectral rotation analysis is described. The INFIA a program features multiple simultaneous views of the analysis data, including a spectrum view with assignment markers; a Loomis–Wood-type view; and lists of assignments, bands, and vibrational states. Automatic combination difference prediction and parameter calculation are included for linear molecules, but the program can also be used to assign spectra for symmetric top molecules. The interactive nature of the program combined with the high level of automation makes possible rapid and reliable analyses even for difficult spectra with many overlapping bands and high peak densities.   © 1999 John Wiley & Sons, Inc.   J Comput Chem 20: 610–622, 1999

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Introduction

The development of high-resolution laser and FTIR spectrometers has made possible measurements of rotationally resolved spectra of linear molecules such as haloacetylenes.[1,2] Such spectra contain information about rotational, vibrational, and rovibrational molecular parameters. However, extracting this information through peak assignment and least-squares fitting of parameters can be quite tedious, time consuming, and prone to er-

rors. Problems arise especially with molecules that have a large mass and several low-energy vibrational modes, and hence high density of peaks.

Despite the work involved, many laboratories still use rather manual methods for the assignment and fitting of such spectra. These methods rely on printed spectra, printed peak lists, and command line programs that read text input files and produce text output files.

On the other hand, there has been, for several decades, progress toward more visual, interactive, and computer-aided approaches to the analysis. Two-dimensional spectrum peak diagrams by Loomis and Wood[3] were developed further by Scott and Rao[4] and Nakagava and Overend[5] to aid pattern identifications and assignments of complex

spectra. Whereas these early versions used a printed Loomis−Wood diagram, the more recent Loomis−Wood applications by Winnewisser et al.[6] and Launila[7] use computer graphics and are more interactive in their approach.

Although the Loomis−Wood assignment programs leave the actual assignment to the analyst there are attempts for automatization of the whole assignment process with computer codes. A program by Moruzzi[8] uses Ritz−combinations and polynomial extrapolation to determine transition assignments automatically. Although very effective in proper conditions, its usability is somewhat reduced by the need for loose selection rules, requirement of a set of initial assignments, and problems that missing peaks may cause.

A new spectrum analysis program called INFIA is presented in this article. INFIA combines into one program interactive spectrum and Loomis−Wood windows, interactive data tables, automatic parameter fitting, peak prediction, and assignment utilities. The calculation capabilities include nonlinear least-squares optimization for linear molecules with rotational and anharmonic resonances. The calculations of the parameters in the current version are restricted to linear molecules, but the assignment and spectrum display capabilities can also be used for other types of molecules. An example analysis of some fundamental and overtone band systems of $DCC^{79}Br$ and $DCC^{81}Br$ is given in a separate work.[9]

Theory

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[10]:

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

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 state v. With some vibrational states, it is necessary to add a higher order term, $H_v[J(J+1) - k_v^2]^3$, to eq. (1) to obtain an accurate fit of rotational energies for high J values. The vibrational term values, G_v, and rota-

tional constants, B_v, that are obtained from the rotational analysis can be used further in the vibrational analysis.

ROTATIONAL RESONANCES

Occasionally, nearby vibration−rotation states interact strongly with each other through some vibrationally off-diagonal Hamiltonian operator terms.[11] 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 onto 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[3]:

$$\langle v_t^{l_t+1}, J, k+1|H/hc_0|v_t^{l_t-1}, J, k-1\rangle$$
$$= \tfrac{1}{4}q_t\left[(v_t+1)^2 - l_t^2\right]^{1/2}$$
$$\times\left[J(J+1) - k(k+1)\right]^{1/2}$$
$$\times\left[J(J+1) - k(k-1)\right]^{1/2} \quad (2)$$

where $|v_t^{l_t}, J, k\rangle$ refers to the vibration−rotation state with v quanta on vibrational bending mode t leading to 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 $q_t = q_{t0} + q_{tJ}J(J+1) + \cdots$.

TRANSITIONS

Formulas for allowed vibration−rotation transition wave numbers can be deduced from eq. (1) with the appropriate selection rules. For example, for P branch transitions ($\Delta J = -1$) one obtains[12]:

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

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 wave number formulas of P and R branches can be combined by defining an auxiliary quantum number, m, by:

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

This leads to a single formula:

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

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

Peak Assignment

The high-resolution spectrum of some band systems of deuterobromoacetylene[9] is used in the examples of this article. Figure 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 prediction of new peak positions for assignment.

STARTING ASSIGNMENT OF A BAND

The first step of the analysis of a vibration−rotation band system with INFIA software 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.[1]

Figure 2 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 abundance creating the series of doublets seen in the spectrum. The visual identification of bands is aided in the INFIA by the flexible zooming and scrolling capabilities of the spectrum.

Some peaks from the visually identified new band are assigned rotational m quantum numbers by clicking on the peaks. The correct m values do not need to be known at this stage: the possible systematic error in the m assignments can be corrected later with combination difference predic-
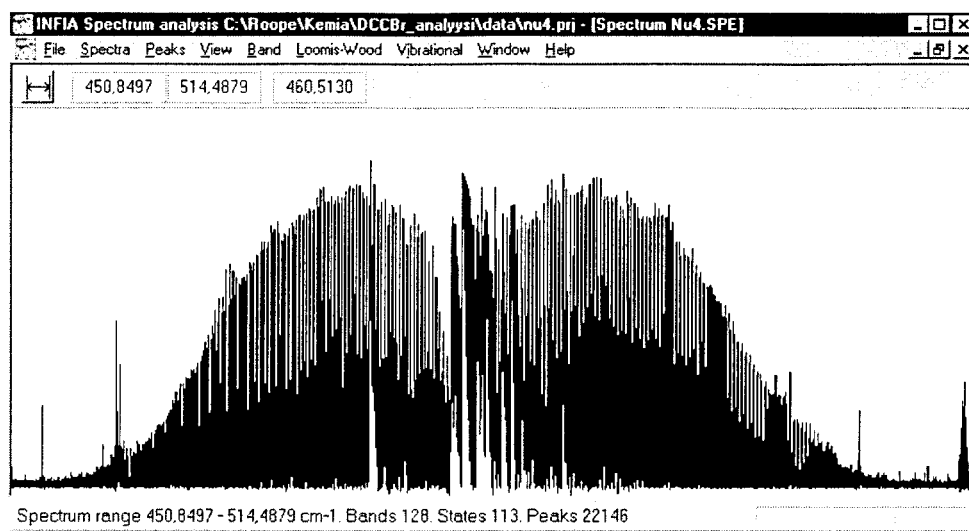
FIGURE 1. The ν_4 band system of DCCBr in the wave number region 450.85−514.50 cm^{-1} as shown by the INFIA program.
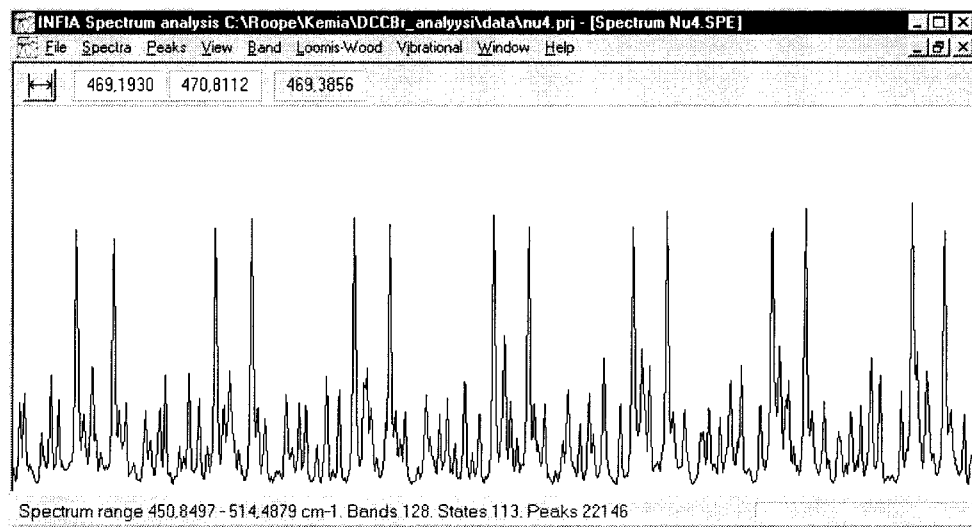
FIGURE 2. Part of the ν_4 band system of DCCBr in the wave number region 469.193–470.811 cm^{-1} as shown by the INFIA program. The strong peak duplets correspond to transitions from ground vibrational states of DCC^{79}Br and DCC^{81}Br isotopomers. Weaker peaks belong to various hot bands.

tion. Figure 3 shows some trial assignments of peaks of a hot band.

POLYNOMIAL PREDICTION

Expansion of the transition wave number formula of eq. (5) leads to a fourth order polynomial in m. Even if there is a systematic error in all m assignments (e.g., 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 wave numbers and can be used for prediction purposes.

This kind of polynomial prediction has been built into the INFIA software. When some peaks have been assigned, predicted wave numbers can be calculated automatically and displayed to aid further assignment. Predictions can be recalculated easily after adding or removing assignments. Peak wave numbers are calculated within the assigned range and in both directions, away from the assigned range, by a user-defined amount.

Figure 4 shows a typical working setup of the 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 wave numbers with the polynomial fit. The assignment table shows, for each m value, the peak status (predicted or assigned), observed and calculated wave numbers, and their difference in a numeric and a graphical format. The spectrum window shows a vertical prediction line below the spectrum curve for the m value of -40, corresponding to a spectrum peak that has not yet been assigned. To aid
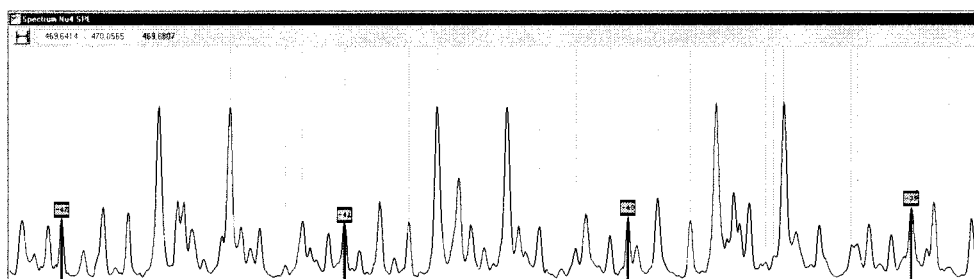
FIGURE 3. Trial m quantum number assignments of some peaks of a hot band seen in the INFIA spectrum window.
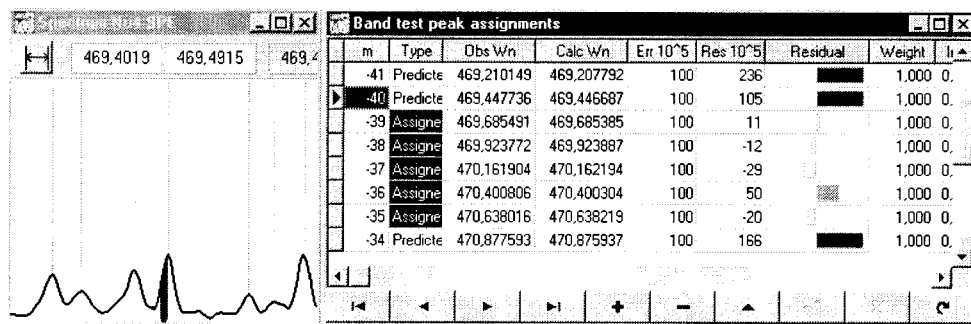
FIGURE 4. New *P* branch band with five preliminary assignments. The spectrum window and the assignment table can be viewed and used together.

the simultaneous use of the two views, the spectrum view automatically shows the assignment selected from the assignment table.

Peak assignment with the aid of 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 wave number in the assignment table can be converted to an assignment to the nearest spectrum peak.

COMBINATION DIFFERENCE PREDICTION

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

First, it may be difficult to locate the peaks that belong to the other branch of the band by using just the polynomial prediction. There can be a large wave number 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 those in Figure 1. Second, one must determine the lower vibrational state of the band. This problem arises in band systems with many hot bands and several isotopic species. Third, one has to determine the correct rotational *m* values of the peaks.

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[1, 12]:

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

where $\tilde{\nu}_R$ is the wave number of a peak from the *R* branch, $\tilde{\nu}_P$ is the wave number 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. (6) can be used to predict line positions in the *R* branch. Note that in order to use the combination difference method for assignment of some band, some lower state parameters B'' and D'' must be known beforehand from analysis of some other bands or previous works.

The predicted *R* branch line positions can be compared with 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 wave numbers suggests that they are correct.

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. With a single command, INFIA calculates predicted *R* branch wave numbers for all 400 combinations, evaluates the predictions against the spectrum and constructs a report of the best combinations.

Fitness Function

For each tested combination of *m* shift and lower state, INFIA calculates a number with a "fitness" function, describing how well the predicted lines match the observed ones. This makes possi-

ble the automatic selection of the best candidate combinations.

The most straightforward example of such a fitness function would be the average square difference deviation of predicted and observed lines. However, for reasons related to the pattern of deviations that different combinations produce, a function using logarithm performs better in selecting the correct combination as opposed to incorrect ones. The fitness function, F, in INFIA is calculated by:

$$F = \frac{1}{N} \sum_{n=1}^{N} \ln\left(\frac{d_n}{d_{\min}}\right)^2 \qquad (7)$$

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

$$d_n = \max\left(|\tilde{\nu}_{n,obs} - \tilde{\nu}_{n,pred}|, d_{\min}\right) \qquad (8)$$

where $\tilde{\nu}_{n,pred}$ is the wave number predicted from the R branch using assignment n from the P branch and the combination difference formula of eq. (6). $\tilde{\nu}_{n,obs}$ is the wave number of the closest actual spectrum peak in the R branch.

$d_{\min}$ is the average precision of measured wave numbers. 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.

In addition to the fitness value, F, an intensity fitness function F_{int} is calculated for each combination by:

$$F_{int} = \frac{1}{N} \sum_{n=1}^{N} \left[\max\left(\frac{I_{n,P}}{I_{n,R}}, \frac{I_{n,R}}{I_{n,P}}\right) - 1\right]^2 \qquad (9)$$

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 wave number in the R branch. The basis for F_{int} calculation is that the peaks from band P and R branches with the same lower state J are expected to have similar intensities. F_{int} has a value of zero if these intensities are exactly equal for all assignments and gets increasingly higher for worse cases. 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 wave number measurements. One should also be aware that effects, such as Coriolis resonance[13] or the Herman−Wallace effect,[14,15] can disturb the intensities in a way that is not taken into account by eq. (9).

Results of Combination Difference Prediction

The branch combination analysis produces a report table like the one in Figure 5. The table in Figure 5 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. Forty different m shifts and 32 lower state candidates were attempted, giving a total of 1280 combinations. The ten combinations with the best F values are listed. The best combination has an m shift of -5, $DCC^{79}Br$ as the isotopic species, and $|000\ 0^01^1\ \Pi\ e\rangle$ (singly excited CCBr bending) as the lower state.

To aid the user in choosing the correct combination among the best ones, predicted peak positions can be inspected manually. When one combination has been chosen to be the correct one, the two

N	Delta m	Molecule	Lower State	Fitness	IntFitnes
1	-5	DCC79Br	000_0(0)1(1)_1e	1.9	4.39
2	-5	DCC81Br	000_0(0)2(2)_2f	15.8	4.63
3	-5	DCC81Br	000_0(0)2(2)_2e	23.4	4.61
4	1	DCC81Br	000_0(0)2(2)_2f	38.3	5.43
5	-2	DCC81Br	000_0(0)2(2)_2e	38.4	9.47
6	13	DCC81Br	000_0(0)1(1)_1e	38.5	12.10
7	2	DCC81Br	000_1(1)1(1)_2f	38.9	9.18
8	-6	DCC79Br	000_0(0)1(1)_1e	39.6	6.46
9	2	DCC81Br	000_1(1)1(1)_2e	39.9	10.61
10	-2	DCC81Br	000_0(0)2(2)_2f	40.1	8.71

FIGURE 5. Results from a branch combination analysis of a hot band in the $2\nu_4$ band system of DCCBr. The ten best fitting lower state and m shift combinations are listed along with their respective fitness values and intensity fitness values.

branches can be combined automatically into a single band with the correct lower state and the correct m assignments.

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 for accurate prediction of new peaks. Working with the spectrum window together with the assignment table, such as in Figure 4, 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 poor quality and which are left totally unassigned due to severe overlap.

ASSIGNMENT OF Q BRANCHES

In addition to the P and R branches present in all band systems, INFIA can also be used to analyze Q branches in perpendicular band systems. Figure 6 shows the strongest Q-branch pair of the ν_4 band system of DCCBr. Peak m assignments (in Q branches $m = J' = J''$) are shown for both isotopic species. The wave number 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. (6) cannot be used to assign the lower state or m values for Q branches. Instead, the lower state can be deduced directly from the position of the Q branch after 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 the closest agreement between the band origins are assumed to be correct.

Parameter Optimization

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 wave numbers. For bands without rovibrational resonances the most straightforward way is to fit a polynomial in m to the transition wave numbers. 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 wave numbers are recalculated automatically. The results are shown in a script window like the one in Figure 7. Vibrational term values and rotational parameters are shown for both the lower and upper state.

REDUCED WAVE NUMBER 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
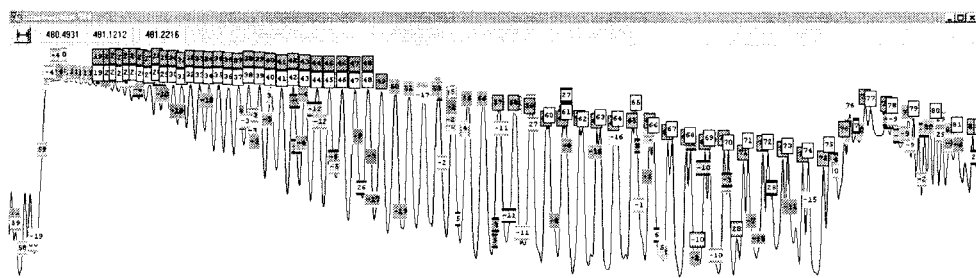
FIGURE 6. Strong Q branches of the fundamental DCCBr bands in the ν_4 band system. Note that the respective peaks of the two isotopic species are completely merged at low m values.

```
Prepared optimization data for 1 bands: DA2a
(No off-diagonal resonance elements)
Fit results for band DA2a of DCC79Br
RMS Error of the fit = 0.00011
State 000_1(1)0(0)_1e (L=1) of DCC79Br parameters:
Energy    10^0  = 480.659357(14) (fixed)
B         10^0  = 0.12202007(19)   delta to fixed = -26(24) (worse than existing)
D         10^8  = 2.0224(16)   delta to fixed = -33(19) (worse than existing)
H         10^14 = 0.00(0) (fixed)
State 000_3(1)0(0)_1e (L=1) of DCC79Br parameters:
Energy    10^0  = 1433.216006(23)  delta to fixed = -4(34) (BETTER than existing)
B         10^0  = 0.12224462(19)   delta to fixed = -26(24) (worse than existing)
D         10^8  = 2.0657(16)   delta to fixed = -33(19) (worse than existing)
H         10^14 = 0.00(0) (fixed)
Predicting peak positions...
Calculation completed.
```

FIGURE 7. Script view of the results of a fourth order polynomial calculation of a band. All parameter values are in cm^{-1}.

accuracy, it is reasonable to fix them to the previously known values in the linear least-squares calculation. This allows for determination of upper state parameters with higher accuracy due to the reduced degree of the resulting polynomial. In practice, the calculated lower state rotational energies, $B''[m(m-1) - k''^2] - D''[m(m-1) - k''^2]^2$, are added to each observed transition wave number, $\tilde{\nu}_{PR}$, of eq. (5), yielding *reduced wave numbers*:

$$\tilde{\nu}_{red} = \Delta G + B'[m(m+1) - k'^2]$$
$$- D'[m(m+1) - k'^2]^2 \qquad (10)$$

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

In INFIA, the use of a reduced wave number fit is similar to the free polynomial fit, producing calculated wave numbers and a result script similar to the one shown in Figure 7.

Reduced wave number fit can be used to determine upper state parameters for Q branches as well as for P and R branches when the lower state energy of eq. (10) is calculated in the appropriate way. INFIA takes care of this automatically when the type of the band (PR or Q) has been defined.

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 wave numbers accurately. However, with sufficiently weak resonances, all observed peaks can be fitted with a polynomial 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, rotational and anharmonic resonances can be explicitly taken into account in the parameter fitting. Information about the relevant rotational resonances of the molecules analyzed are stored in the resonance table shown in Figure 8. The user defines the states in resonance and the type of resonances in the table. When calculation of a band is requested, INFIA automatically searches 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.

Nonlinear least-squares optimization is consequently executed to find parameter values, including relevant resonance parameters. For the calculation 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[16] using finite difference gradients. If parameter values are poorly known before refinement, the simplex method[17] can be chosen instead. After calculation has converged, predicted wave numbers are recalculated for all the bands involved and the results are

FIGURE 8. Resonance database of INFIA is used to store information about rotational resonances present in the analysed molecules. All parameter values are in cm^{-1}.

displayed in a script similar to the reduced wave number fit script in Figure 7.

From the user's 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 branches and combination of *P* and *R* branches—are performed in the same way as for the nonresonance bands. However, note that the combination difference formula of eq. (6) can only be used for bands whose *lower* state is free of rovibrational resonances.

Dealing with Complex Spectra

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 Figure 9. This database stores the vibrational term values and rotational parameters of the vibrational states analyzed. If

the present band belongs to a resonance group, the optimized resonance parameters are also transferred to the resonance database shown in Figure 8.

The state and resonance databases are used for three purposes. First, they automate 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 regarding 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 different fits, such as the one in Figure 7, show for each parameter its deviation from its existing value in the state database and relative accuracy.

FIGURE 9. State table stores the parameter values that have been found in the analysis for various vibrational states.

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 important 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 Figure 10. Assignment labels are color coded according to the band and they can display either the band name (as in Fig. 10) 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.
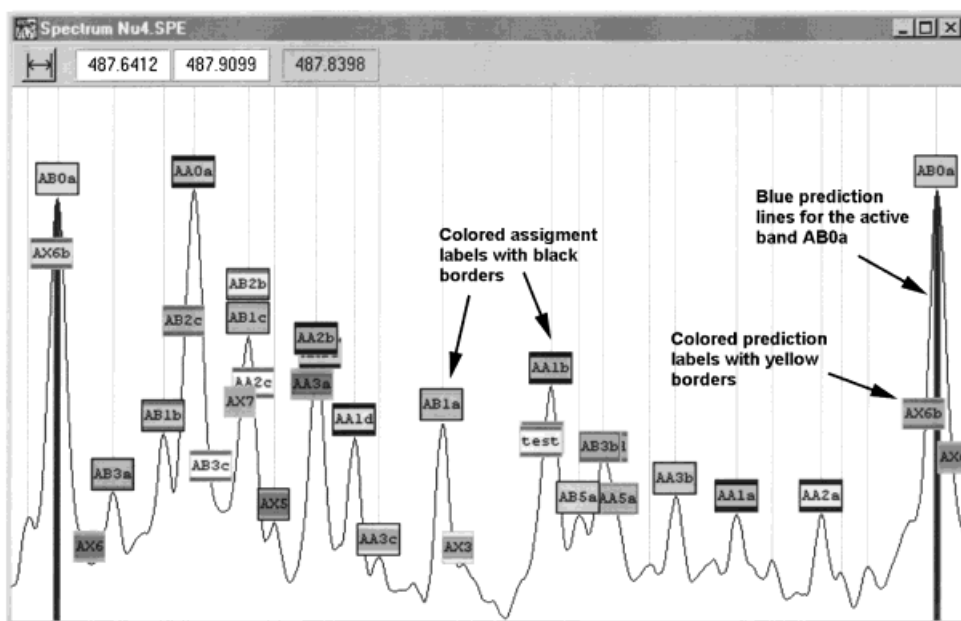
LOOMIS–WOOD VIEW

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.[4–6] A Loomis–Wood image shows the spectrum peaks as dots on a two-dimensional display as seen in Figure 11. The x axis is defined by the rotational m quantum number of the selected band and the y axis by the wave number deviation of

the peak from the calculated wavenumber of the selected band. Therefore, the selected band is straightened to the x axis and other bands are seen as strings of dots with different slopes and curvatures. In INFIA, the dots have a color according to the band they have been assigned to, and brightness according to the peak intensity. 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 at any zoom level. It can be used to assign peaks to the selected band by clicking them. This is usually the most rapid way to start the assignment of a new band. The Loomis–Wood view can be used in combination with the regular spectrum view and assignment table as shown in Figure 12. All three views are connected so that selecting a peak in one of them causes the same peak to be shown in all three.

Program Implementation

INFIA is a WINDOWS 95 program with about 5000 lines of code in 20 units. It has been written with Borland Delphi 3.[18] INFIA can utilize all available system memory, thus enabling the analysis of spectra of any size and number of peaks. Hard-

FIGURE 10. Details of a band system showing peaks from multiple overlapping fundamental and hot bands of DCCBr along with assignment labels, prediction labels, and prediction lines.
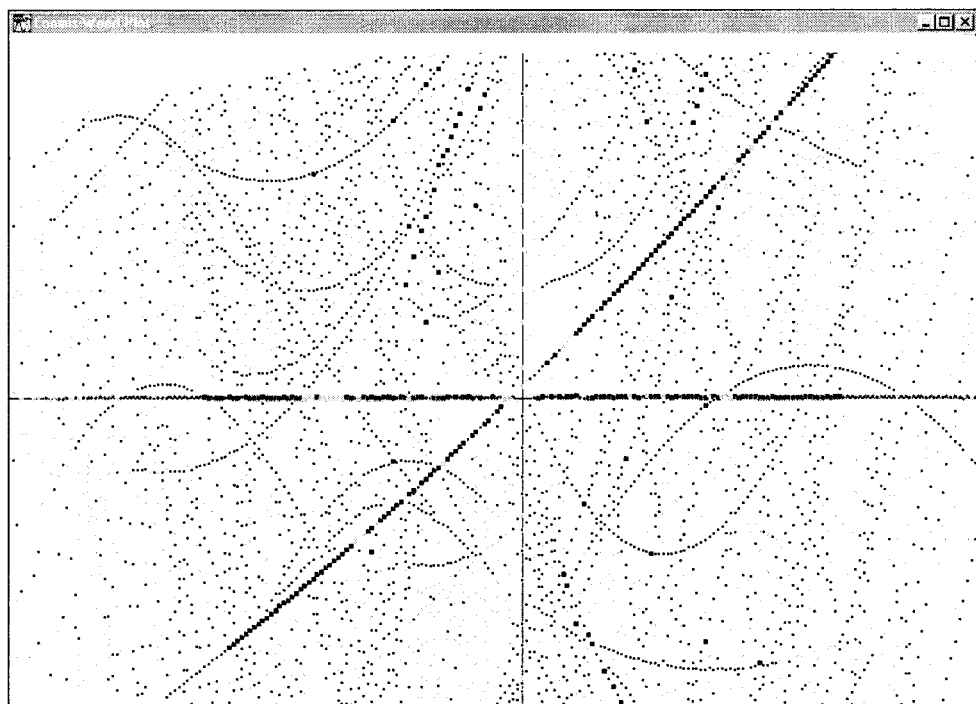
FIGURE 11. Loomis–Wood image of the $2\nu_4$ band system of DCCBr. Spectrum peaks are displayed as dots. The x axis is defined by the rotational m quantum number of the selected band and the y axis by the wave number deviation of the peak from the selected band calculated wave number.
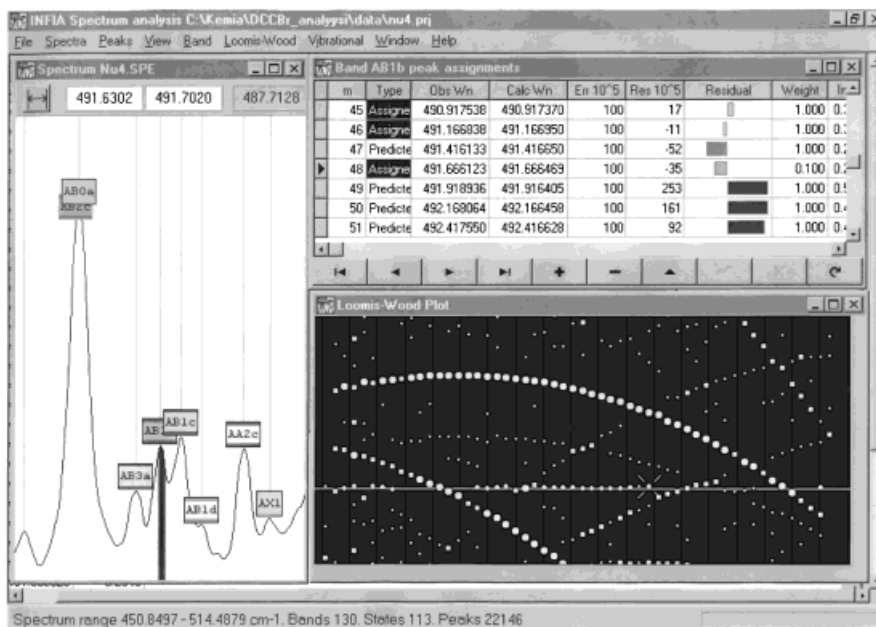
FIGURE 12. Working simultaneously with the spectrum window, assignment list, and Loomis–Wood view.

ware recommendations include a Pentium processor, 32 MB of RAM, and fast graphics with at least a 1024 × 768 resolution and 65,536 colors.

INFIA uses objects to represent relevant entities such as vibrational states, bands, spectral parameters, assignments, and peaks. The high level of object orientation allows efficient transfer of data from a program module to another and results in robust, clean, and easily understood program code.

Discussion

The INFIA software has been used to analyze the ν_4, ν_3, $\nu_4 + \nu_5$, and $2\nu_4$ band systems of DCCBr. Results of this project have been published in a separate study.[10] The integrated approach of the program has proven to free the analyst from many routine tasks that can take considerable time. It also reduces the possibility of human error which is a characteristic of more manual approaches.

The inclusion of both spectrum and Loomis−Wood windows provides the best total view to the spectrum. Whereas a Loomis−Wood image is good in giving the overall view of a band system, it cannot properly present the subtle details of the spectrum in complex overlapping peak systems. These details can be quickly observed in the spectrum window of INFIA due to the automatic connection of the two views. This combination of windows enables more bands and peaks to be assigned with higher reliability, thus increasing the amount of information obtainable from any spectrum. We are not aware of any other analysis program providing such a feature.

Furthermore, the integration of the spectrum viewing and assignment tools with complete parameter calculation methods eliminates many manual steps, saving time and increasing reliability. When using separate programs for assignment and parameter fitting, one faces the problem of interface between the programs. The communication between them is usually implemented with ASCII data files, resulting in slower, more rigid, and less complete data exchange than between different modules of a single program. For example, the assignment program might not be able the to take feedback from the fitting program in the form of predicted peak wave numbers, forcing the analyst to rely on polynomial prediction. In INFIA, program modules pass data to each other in flexible object packages and the peaks predicted after resonance calculation are immediately visible and available for assignment. For the Loomis−Wood view this means that even bands with rotational resonances can be straightened without resorting to very high-order polynomials.

Using combination differences for peak assignment is commonly used in the field but INFIA automates the method to a previously unseen level while maintaining a high level of reliability. In manual combination difference analysis it can take several minutes to inspect one assignment combination, whereas INFIA can inspect some 500 combinations in 1 second and reliably find those most likely to be correct. The power of the fitness function used by INFIA is reflected in the fact that, for over 95% of the 88 DCCBr bands analyzed, the correct combination also had the best fitness value. We consider this quite impressive given that several hundreds of combinations were evaluated for each band and the spectrum was full of severe peak overlaps.

When working with spectra with a high density of peaks, the danger of misassignment is always present. For example, seemingly good polynomial fits can be created from a set of peaks that do not actually belong to the same band. Several features of INFIA increase the reliability of assignment in such difficult conditions. Clear assignment labeling of peaks in the spectrum and Loomis−Wood views, efficient combination difference prediction, automatic comparison of calculated parameters with previous ones, and clear display of the observed minus calculated deviation patterns help to confirm correct assignments.

Options for the future development of INFIA include methods for analysis of spectra of other types of molecules. Although the present version of the program can already be used to view and assign such spectra, it does not include parameter fitting routines for these molecules. However, due to the modularity of the program, such addition is expected to be rather straightforward.

INFIA is available freely from the author via the Internet.

Acknowledgments

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