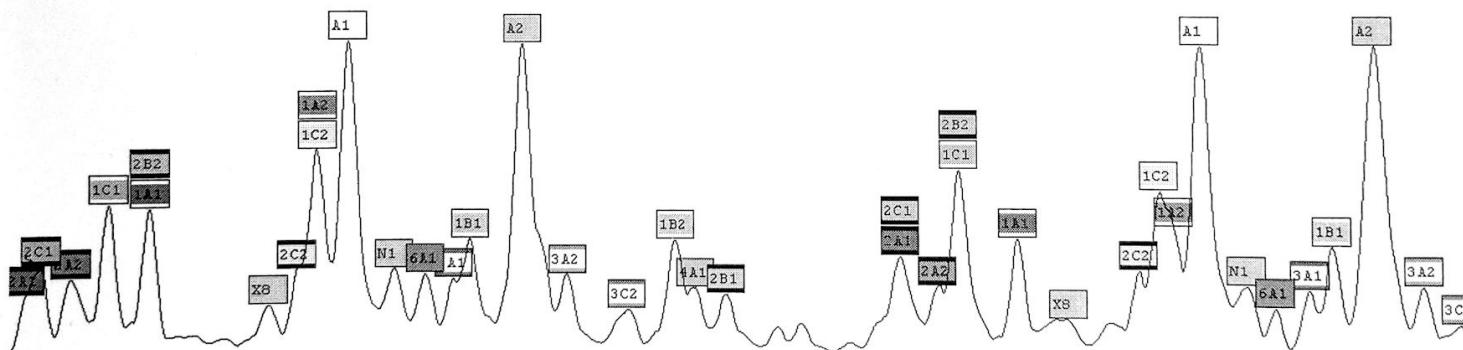


New computational tools for rotational analysis of infrared spectra of linear molecules: Application to the ν_4 and ν_3 band systems of deuterobromoacetylene



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Abstract

A novel spectrum analysis program for the rotational analysis of vibration-rotation spectrum has been developed by the author for peak assignment and calculation of the molecular parameters. The program structure and usage are explained.

Two band systems, ν_4 and ν_3 , of deuterobromoacetylene (DCCBr) have been rotationally analyzed from the high resolution (0.004 cm^{-1}) infrared spectrum in the wavenumber range 450 to 650 cm^{-1} . The assignment problems arising from high number of hot bands and resulting peak overlapping are discussed as well as various solutions to them implemented in the analysis software.

22 perpendicular bands from the ν_4 band system and 6 in the ν_3 band system belonging to isotopic species DCC^{79}Br and DCC^{81}Br have been rotationally analysed. For 10 of the 22 perpendicular bands the Q -branches could also be analysed. The analyzed bands in the ν_4 system include all bands originating from the ground state, ν_5 states and ν_4 states.

The total number of peak assignments in the ν_4 band system was 3140, an average of 98 assignments per band. The upper and lower vibrational states have been determined for all analyzed bands. Rotational parameters B and D have been obtained with combination difference fit for the ground state and with reduced wavenumber fitting for all other states.

Four of the ν_4 system bands experience rotational l -resonance in the upper state and have been analyzed with nonlinear least squares fits taking into account the relevant resonance parameters.

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1. Introduction

The progress in science is usually divided into two distinct categories: building theories that are more advanced and performing experiments that are more accurate. In the field of spectroscopy the advancement of theories is characterized by more accurate predictions of molecular energy levels and the advancement of experiments means spectra with higher resolution, lower noise and lower detection threshold.

This division neglects an important step in the practical scientific work, the process of *analyzing* the data. In spectroscopy this means the understanding of the spectrum in terms of the theory. A scientist wants obtain a theoretical explanation for every peak in the spectrum and calculate values of various parameters of the theoretical model as determined by the spectrum.

The main aim of this work has been to discuss this data analysis step in the case of high resolution infrared spectra of linear molecules. The experimental data for the work have been measured by commercially available high resolution FTIR spectrometer and the theoretical model used for the energy level calculations has been available and widely used for many years. However, a good spectrum and accurate theory do not mean simple spectrum analysis. On the contrary, DCCBr, having two isotopic species and many low lying vibrational states, provides a complex spectrum with many overlapping hot bands. Good tools are required for the analysis work to be bearable and the results to be reliable.

A sophisticated software application has been developed to aid the process of spectrum fitting. The program suits for the rotational analysis of any linear molecule. Currently it has been used in addition to DCC⁷⁹Br and DCC⁸¹Br for HCC⁷⁹Br, HCC⁸¹Br, HCCH and CO. The analysis methods implemented in the software become especially useful in case of very dense, complicated and overlapping band systems such as the v₄ system of DCCBr analyzed here.

No rotational analysis of any bands of the DCCBr molecule has been published to date. Vaittinen^[13] has done currently unpublished rotational analysis of the v₅ band system. A low resolution infrared study of the molecule with normal mode analysis was done in 1961^[12].

Rotational analysis of bands of other haloacetylenes and the acetylene itself have been published by various researchers in recent years. Some of the fundamental band systems of HCCBr, including the v₃ and v₄ systems studied here, has been analysed by Vaittinen et. al^[18]. Borro et. al have performed research on bands of HCCF^[2,5], DCCF^[2] and HCCl^[5,6]. A large work of over 120 band systems of

HCCF in the wavenumber range 1700 to 7500 cm⁻¹ complete with vibration analysis has been done by Holland et. al^[3].

The far infrared studies of the low lying vibrational states have been complemented by near infrared analysis of some overtone and combination bands of haloacetylenes. Due to the weakness of the overtone transitions and lack of sensibility of fourier transform interferometers, laser spectrometers have to be used for the experiments in that energy range, making the experiments somewhat more difficult^[6]. The overtone studies include band systems of HCCF^[1,6] and HCCl^[1,7] and HCCBr^[17].

Unfortunately, most sources confine their research reports to the their theoretical energy level model and the results of their analysis and do not discuss the details of the implementation of their analysis.

In the present work, as many as possible bands in both studied band systems have been assigned and rotationally analysed using the developed software.

2. Theory

Vibrational Normal modes of DCCBr

In the harmonic oscillator approximation^[16], all third, fourth and higher order terms in the vibrational potential energy Hamiltonian operator are ignored so that only quadratic terms remain:

$$1) \quad V_{vib} = \sum_r \phi_r x_r^2 + \sum_{r < r'} \phi_{rr'} x_r x_{r'}$$

Where the coordinates x_r are some internal coordinates of the molecule and ϕ the potential energy term coefficients. With a suitable linear transformation, so called G matrix transformation^[21], a new set of coordinates can be found where the cross terms disappear:

$$2) \quad V_{vib} = \sum_r \alpha_r q_r^2$$

where the coordinates q_r are called the *normal coordinates* of the molecule and α the new normal mode potential coefficients. Table 1 shows approximately the resulting normal mode coordinates of DCCBr. One needs to remember that while the different normal modes are fairly localized to different bonds of the molecule, they actually involve all of the atoms.

Table 1: Approximate normal modes of DCCBr

Stretching modes	Bending modes (doubly degenerate)
V_1	V_4
V_2	V_5
V_3	

Hence in the normal mode approximation, the molecule becomes a collection of independent harmonic vibrators and the vibrational energy becomes a sum of harmonic oscillator energies^[15]:

$$3) \quad E_{harm} = \sum_r \omega_r (v_r + \frac{1}{2})$$

Where index r spans through all normal modes of the molecule.

Higher order vibrational models

For a more realistic analysis of the vibrations, additional cubic and quartic terms must be added to the potential energy function (1). The corresponding Shrödinger equation becomes then impossible to solve exactly and the *variation theory* and *perturbation theory*^[16] must be used to obtain an approximate solution.

A Hamiltonian matrix with harmonic oscillator wavefunctions as the basis functions is set up. Taking into account with perturbation theory the off-diagonal matrix elements caused by the anharmonic potential energy terms leads to diagonal matrix elements of the form^[15]:

$$4) \quad \langle v | H_{vib} / hc | v \rangle = \sum_r \omega_r (v_r + \frac{1}{2}) + \sum_{r \leq r'} x_{rr'} (v_r + \frac{1}{2})(v_{r'} + \frac{1}{2})$$

For a linear molecule, such as DCCBr, experiencing vibrational angular momentum in the doubly degenerate bending modes, additional g terms arise in the perturbation analysis^[3]. It is convenient to study the energy levels relative to ground state energy i.e., subtract ground state energy from the formula (4). It is also convenient to replace the harmonic wavenumbers ω_r with the first (anharmonic) transition wavenumbers \tilde{v}_r . This leads to diagonal elements of form^[3]:

$$5) \quad \begin{aligned} \langle v | H_{vib} / hc | v \rangle &= \sum_r \tilde{v}_r v_r + \sum_r x_{rr} (v_r^2 - v_r) + \sum_{r < r'} x_{rr'} v_r v_{r'} \\ &+ \sum_t g_{tt} (l_t^2 - v_t) + \sum_{l < l'} g_{ll'} l_l l_{l'} \end{aligned}$$

Off diagonal matrix elements

Equation (5) alone can provide decent approximate values for those vibrational energy levels that are located far away from each other. How

$$6) \quad \langle v_1, v_2, v_3, v_4^{l_4}, v_5^{l_5} | H_{vib} | v_1, v_2, v_3 - 1, v_4^{l_4}, (v_5 + 2)^{l_5} \rangle = k_{355} [v_3(v_5 + l_5 + 2)(v_5 - l_5 + 2)/8]^{1/2}$$

For example, in the simplest case:

$$7) \quad \langle 0,0,1,0^0,0^0 | H_{vib} | 0,0,0,0^0,2^0 \rangle = k_{355}/\sqrt{2}$$

In addition to elements that differ by one in v_3 and two in v_5 , there would be similar element for instance, between basis functions that differ one in v_2 and two in v_1 . However, in such case the energies of the mixing states would be far away from each other and the effect of the mixing is contained in the perturbation analysis.

Vibrational l -resonance matrix element

This elements connects states that differ from each other by the values of the vibrational angular momentum quantum numbers l . It has the form[4]:

$$8) \quad \langle v_1, v_2, v_3, v_4^{l_4}, v_5^{l_5} | H_{vib} | v_1, v_2, v_3, v_4^{l_4-2}, v_5^{l_5+2} \rangle = \frac{1}{4} r_{45} \left\{ [(v_4 + 1)^2 - (l_4 - 1)^2][(v_5 + 1)^2 - (l_5 + 1)^2] \right\}^{1/2}$$

$$\text{For example, in the simples case: } \langle 0,0,0,1^{+1},1^{-1} | H_{vib} | 0,0,0,1^{-1},1^{+1} \rangle = r_{45}$$

The mixing caused by vibrational 1-resonance is accounted in this work by using the linear combinations $\frac{1}{\sqrt{2}} [\langle 0,0,0,1^{+1},1^{-1} | + \langle 0,0,0,1^{-1},1^{+1} |]$ (with Σ^+ symmetry) and $\frac{1}{\sqrt{2}} [\langle 0,0,0,1^{+1},1^{-1} | - \langle 0,0,0,1^{-1},1^{+1} |]$ (with Σ^- symmetry) as basis functions instead of the unmixed ones. This results in some of the originally off-resonance elements of equation (8) becoming diagonal elements.

Effective parameters

Note that the parameters of diagonal element formula (5) are strictly speaking defined to include *all* off-diagonal resonances. Hence, when strong resonances are handled in this work with matrix diagonalisation and only weak resonances left to the parameters of (5) they are not used quite in the original sense. This should be kept in mind when comparing the results with those of other studies.

Table 2: Vibrational resonance blocks relevant to this work

V	Symmetry	Basis functions in the block	Off-diagonal elements in the block	
0	Σ	$ 000\ 0^00^0, \Sigma\rangle$		
1	Π	$ 000\ 0^01^1, \Pi\rangle$		
2	Σ	$ 001\ 0^00^0, \Sigma\rangle, 000\ 0^02^0, \Sigma\rangle$	$\frac{1}{\sqrt{2}}k_{355}$	Fermi resonance
	Π	$ 000\ 1^10^0, \Pi\rangle$		
	Δ	$ 000\ 0^02^2, \Delta\rangle$		
3	Σ^+	$ 000\ 1^11^1, \Sigma^+\rangle$		
	Σ^-	$ 000\ 1^11^1, \Sigma^-\rangle$		
	Π	$ 001\ 0^01^1, \Pi\rangle, 000\ 0^03^1, \Pi\rangle$	$\sqrt{3}k_{355}$	Fermi resonance
	Δ	$ 000\ 1^11^1, \Delta\rangle$		
	Φ	$ 000\ 0^03^3, \Phi\rangle$		
4	Σ	$ 002\ 0^00^0, \Sigma\rangle, 001\ 0^02^0, \Sigma\rangle, 000\ 2^00^0, \Sigma\rangle, 000\ 0^04^0, \Sigma\rangle$	k_{355}	Fermi resonance
	Π	$ 000\ 1^12^0, \Pi\rangle, 000\ 1^12^2, \Pi\rangle$		
	Δ	$ 001\ 0^02^2, \Delta\rangle$		
	Φ	$ 000\ 1^12^2, \Phi\rangle$		

The resonance blocks

A systematic method has been developed to gather together for variational calculation all possible states with similar energies that might be in resonance with each. In this *resonance block* method, the basis function are arranged primarily according to their energy level and secondarily by their symmetry. This breaks up the original huge Hamiltonian matrix to many small matrixes so that each matrix contains levels with similar energy and same symmetry. This speeds up the diagonalisation process dramatically.

In this study, only v_5 , v_4 and v_3 are included in the analysis since we do not have any data concerning the higher energy modes v_1 and v_2 . The blocks are formed in practice by noting that the energy ratios of v_5 , v_4 and v_3 are roughly 1:2:2. Hence, if we invent a *block quantum number* V , which is defined as:

$$9) \quad V = 2v_3 + 2v_4 + v_5$$

so that combinations of v_5 , v_4 and v_3 that produce same V have approximately same energy and are hence included in same block. That block is further broken into sub-blocks according to the symmetry species of the states.

Note, that when one goes high up in energy, the energy levels in a block will spread to a large width and states of other bands will spread to the energy area of the block. However, this does not usually cause problems as most states are not connected by resonance matrix elements so that their overlap does not matter.

Blocks of this study

Since very low lying vibrational energy states have been studied here, the application of the resonance blocks becomes particularly simple: most blocks are just 1×1 in size. The values of Fermi resonance elements have been calculated from equation (6). The resonance blocks that include the vibrational states studied in this work are listed in Table 2.

In the higher energy range both the number of the interacting states inside resonance blocks and the sizes of the off-diagonal matrix elements compared to the diagonal elements increase increasing rapidly the mixing of different states^[3].

Rotational energy level structure

Quantum mechanical treatment of a rigid rotor leads to^[16]:

$$10) \quad E_J^{rot} = B[J(J+1) - k^2]$$

Where B is called the rotational constant, J is the total angular momentum quantum number and k is the vibrational angular momentum quantum number rising from the two double degenerate bending modes. Perturbation treatment adds a higher order centrifugal distortion term to the rotational energy. The energy of the levels, including the vibrational energy, becomes^[15]:

$$11) \quad E_{aJ}^{tot} = E_a^{vib} + E_{aJ}^{rot} = E_a^{vib} + B_a[J(J+1) - k^2] - D_a[J(J+1) - k^2]^2$$

Where D is called the centrifugal distortion constant. Even higher order terms such as $H_a[J(J+1) - k^2]^3$ will arise to the energy expression with higher order perturbation treatment, but their coefficients are very small and usually are not needed in the rotational analysis.

Parity sub-levels

Those vibration-rotation levels that possess non-zero vibrational angular momentum ($k \neq 0$) are further broken down to two sub levels, called the e and f parity levels^[15]. In classical terms, this can

be understood as the bending vibration taking place in the plane of rotation or perpendicular to that plane. In the zero rotation limit the e / f separation vanishes and one expects the band origins of e and f bands to converge together.

Rotational l-resonance

This type of resonance couples vibration-rotation states whose vibration angular momentum differs by two quantas from each other. The coupling off-diagonal matrix element is^[3]:

$$12) \quad \langle v_t^{l_t+1}, v_s^{l_s}, J, k+1 | H | v_t^{l_t-1}, v_s^{l_s}, J, k-1 \rangle = \frac{1}{4} [q_{t0} + q_{ts} J(J+1)] [(v_t + 1)^2 - l_t^2]^{\frac{1}{2}} [J(J+1) - k(k+1)]^{\frac{1}{2}} [J(J+1) - k(k-1)]^{\frac{1}{2}}$$

where q_{t0} and q_{ts} are the l -resonance constants and t and s are indexes of the doubly degenerate normal modes in resonance. In DCCBr $t = 4$ and $s = 5$. In this study the relevant resonance element of this type is between the states $000\ 1^11^1,\Sigma^+$ and $000\ 1^11^1,\Delta$ for which the element becomes:

$$13) \quad \langle 1^1, 1^1, J, \Delta | H | 1^{-1}, 1^1, J, \Sigma^+ \rangle = \frac{1}{2} [q_{t0} + q_{ts} J(J+1)] [J(J+1) - 2]^{\frac{1}{2}} [J(J+1)]^{\frac{1}{2}}$$

Note that only vibration-rotation states with same J can be coupled to each other. Hence, simple only 2×2 matrixes result for each J and must be diagonalised to obtain the perturbed energy levels.

Band Origin and Band Center

Consider the total rotational-vibrational energy of a molecule in vibrational state a is according to equation (11):

$$E_{aJ}^{tot} = E_a^{vib} + B_a [J(J+1) - k^2] - D_a [J^2(J+1) - k^2]^2$$

The term E_a^{vib} is the pure vibrational energy of the state and obtained by setting $J = 0$ and $k = 0$ then the energy level formula. G_v is sometimes used instead of E_a^{vib} and has the same meaning. However, for the states that possess vibrational angular momentum $k \neq 0$ another energy definition, the *center energy*, G_c can be used as well. G_c is calculated by setting only $J = 0$ in the equation (11):

$$14) \quad G_c = E_a^{vib} - B_a k^2 - D_a k^4$$

Note that for the vibrational levels with $k = 0$, pure vibrational energy and center energy are the same. Due to two different possibilities for the vibrational energy in $k \neq 0$ states, there are also two different definitions for the vibrational transition energy. *Band center*, v_c , is the difference between two center energies whereas *band origin*, v_0 , is the difference between two pure vibrational energies.

Selection rules and transition energies

The wavenumber of a transition to another vibrational level from J'' to J' can be calculated from equation (11) simply by subtracting the energies of the two levels from each other:

$$15) \quad \tilde{\nu} = \Delta E_{vib} + B' [J'(J'+1) - k'^2] - D' [J'(J'+1) - k'^2]^2 - \\ B'' [J''(J''+1) - k''^2] + D'' [J''(J''+1) - k''^2]^2$$

Where J' and J'' are the rotational quantum numbers of the upper and lower vibrational states.

Vibrational selection rules

DCCBr, being a linear molecule with no center of inversion, belongs to the $C_{\infty v}$ symmetry point group. It has a C_∞ axis and an infinite number of vertical σ_v planes (see Figure 1).

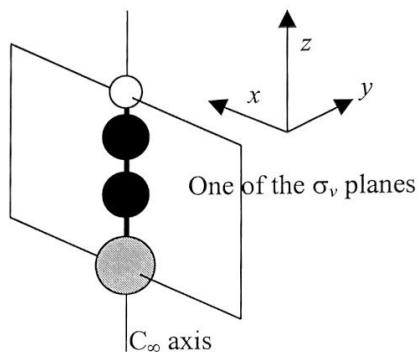


Figure 1: Symmetry operations of DCCBr

For a vibrational transition of a molecule to be allowed, the product of the lower and upper vibrational state symmetries must contain a species of translation^[15]. Inspecting the character table of DCCBr (Table 3) one can see that such transitions are Σ^+ transitions (creating so called *parallel* bands) and the Π transitions creating *perpendicular* bands.

From the band systems studied in this work, the v_3 system is a parallel band system, transitions being induced by electric field that make the C – Br bond oscillate parallel to the molecular axis.

Table 3: Character table for the DCCBr point group $C_{\infty v}$ ^[15]

$C_{\infty v}$	I	$2C_\infty^\phi$	$\infty \sigma_v$	
Σ^+	1	1	1	T_z
Σ^-	1	1	-1	R_z
Π	2	$2\cos\phi$	0	$(T_x, T_y), (R_x, R_y)$
Δ	2	$2\cos 2\phi$	0	
Φ	2	$2\cos 3\phi$	0	
...	

The v_4 system, on the other hand, is a perpendicular band system, the transitions being induced by an electric field oscillating perpendicular to the molecular axis and making the D – C – C bend angle to oscillate.

Rotational selection rules

For the possible rotational transitions, the selection rule is $\Delta J = \pm 1$ for those transitions where the parity is not changed. These kind of transitions create bands with P - and R -branches in both band systems. In the v_3 band system these are the only type of transitions because as a parallel band the parity of the upper and lower state must be same. In the v_4 system other type of transition is possible, where $\Delta J = 0$ and the parity changes from e to f or f to e . These kind of transitions create strong and dense Q -branches in v_4 system.

Allowed transition energies

Using the selection rules for J one obtains three possibilities for a vibration-rotation transition:

For P -branch transitions ($J'' = J' + 1$):

$$16) \quad \tilde{\nu}_P = \Delta E_{vib} + B' [J'(J'+1) - k'^2] - D' [J'(J'+1) - k'^2]^2 - \\ B'' [(J'+1)(J'+2) - k''^2] + D'' [(J'+1)(J'+2) - k''^2]^2$$

For R -branch transitions ($J'' = J' - 1$):

$$17) \quad \tilde{\nu}_R = \Delta E_{vib} + B' [J'(J'+1) - k'^2] - D' [J'(J'+1) - k'^2]^2 - \\ B'' [J'(J'-1) - k''^2] + D'' [J'(J'-1) - k''^2]^2$$

For Q -branch transitions ($J'' = J'$):

$$18) \quad \tilde{\nu}_Q = \Delta E_{vib} + B' [J'(J'+1) - k'^2] - D' [J'(J'+1) - k'^2]^2 - \\ B'' [J'(J'+1) - k''^2] + D'' [J'(J'+1) - k''^2]^2$$

Peak m value

For purposes of fitting peaks from P - and R -branches it is useful to define m , closely related to J :

$$19) \quad \text{In } P\text{-branch} \quad m = -J' - 1 \quad \Rightarrow \quad J' = -m - 1 \quad J'' = J' + 1 = -m$$

$$20) \quad \text{In } R\text{-branch} \quad m = J' \quad \Rightarrow \quad J' = m \quad J'' = J' - 1 = m - 1$$

The transition energies of equations (16) and (17) can be expressed in terms of m for both branches:

$$21) \quad \tilde{\nu} = \Delta E_{vib} + B' [m(m+1) - k'^2] - D' [m(m+1) - k'^2]^2 - \\ B'' [m(m-1) - k''^2] + D'' [m(m-1) - k''^2]^2$$

This is the real reason for using m instead for J' or J'' : all P - and R -branch peaks can be expressed with a single equation (21) instead of two separate equations (16) and (17). Hence the various polynomial fitting algorithms become more convenient when m is used as the x -variable.

Statistical tools

Polynomial fits

Consider an n th degree polynome $y = b_0 + b_1x + \dots + b_nx^n$. To obtain the coefficients b_0 to b_n that fit best (i.e., produce the smallest total square deviation of the data points from the fitted polynome) we set up a matrix [19]:

$$22) \quad X = \begin{pmatrix} \sum \mu_i & \sum \mu_i x_i & \dots & \sum \mu_i x_i^n \\ \sum \mu_i x_i & \sum \mu_i x_i^2 & \dots & \sum \mu_i x_i^{n+1} \\ \dots & \dots & \dots & \dots \\ \sum \mu_i x_i^n & \sum \mu_i x_i^{n+1} & \dots & \sum \mu_i x_i^{2n} \end{pmatrix} \quad B = \begin{pmatrix} b_0 \\ b_1 \\ \dots \\ b_n \end{pmatrix} \quad Y = \begin{pmatrix} \sum \mu_i y_i \\ \sum \mu_i x_i y_i \\ \dots \\ \sum \mu_i x_i^n y_i \end{pmatrix}$$

Then the coefficients are obtained from the matrix equation:

$$23) \quad B = X^{-1}Y$$

Composite error

In this work, various molecular parameters are determined from polynomial fits performed for the peak wavenumber data. In addition to the values of the parameters, it is essential to obtain the standard errors for them. The standard errors of the polynome coefficients are readily obtained from the polynomial fits, and the values of the parameters are calculated from these with various formulas. When calculating the errors of the parameters, the formula for the error of the sum of values is needed [19]:

$$24) \quad E_{tot} = \sqrt{E_1^2 + E_2^2}$$

Where E_1 and E_2 are the standard errors of the two values to be added together and E_{tot} is the error of the resulting sum.

When doing least square sum fits to the experimental data, the weights of the individual peaks in the fits should be given as the inverse square of their estimated standard errors of their positions:

$$25) \quad W_{peak} = 1/E_{peak}^2$$

There are also some fits (like the ground state combination difference) where one data point is obtained per two observed peaks. In such situation, one must decide what weights to give to the

resulting data points as a function of the weights given to the individual peaks. Using the equation (25) for the relation of weight and error of individual peak and equation (24) for the compounded error, one gets:

$$26) \quad W_{tot} = \left(\frac{1}{W_1} + \frac{1}{W_2} \right)^{-1}$$

where W_1 and W_2 are the weights of data to be added or subtracted from each other and W_{tot} is the weight given to the data point.

3. Experimental Data

The spectra analyzed in this work were recorded in Wuppertal University, Germany with a Bruker high resolution FTIR spectrometer. The energy range observed was 450 to 650 cm^{-1} . The spectrum waveform data and calibrated peak lists from the ν_4 band region ν_3 band region were provided to the author of this work for analysis.

General appearance of the spectrum

Figure 2 shows the 455 – 514 cm^{-1} region containing the ν_4 band system. Figure 3 shows the 570 – 650 cm^{-1} region containing the ν_3 band system of DCCBr. Note that the ν_3 spectrum is partly overlapped by the ν_4 band system of the molecule HCCBr which was present as impurity in the DCCBr sample. Especially note the Q -branches in the center of the HCCBr ν_4 system. The strong peaks on the right hand side of the ν_3 system are due to CO_2 , another impurity.

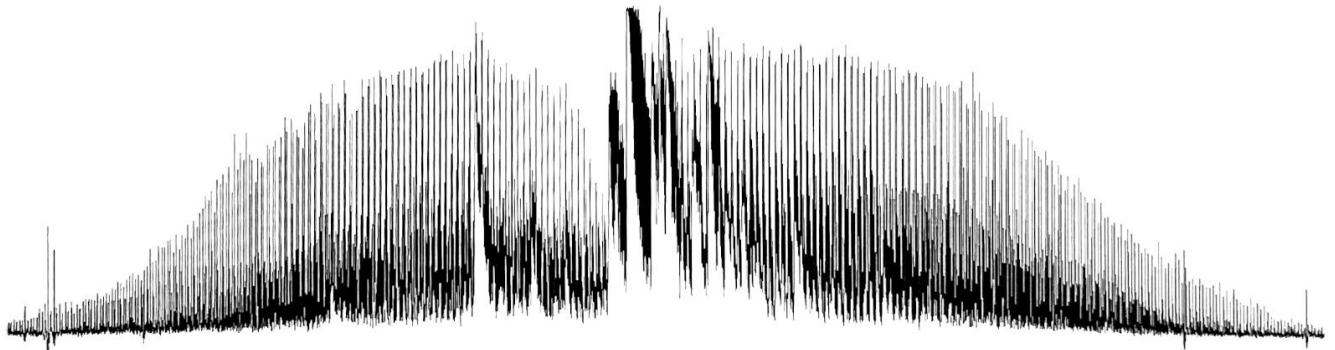


Figure 2: DCCBr ν_4 band system at 455 to 514 cm^{-1}

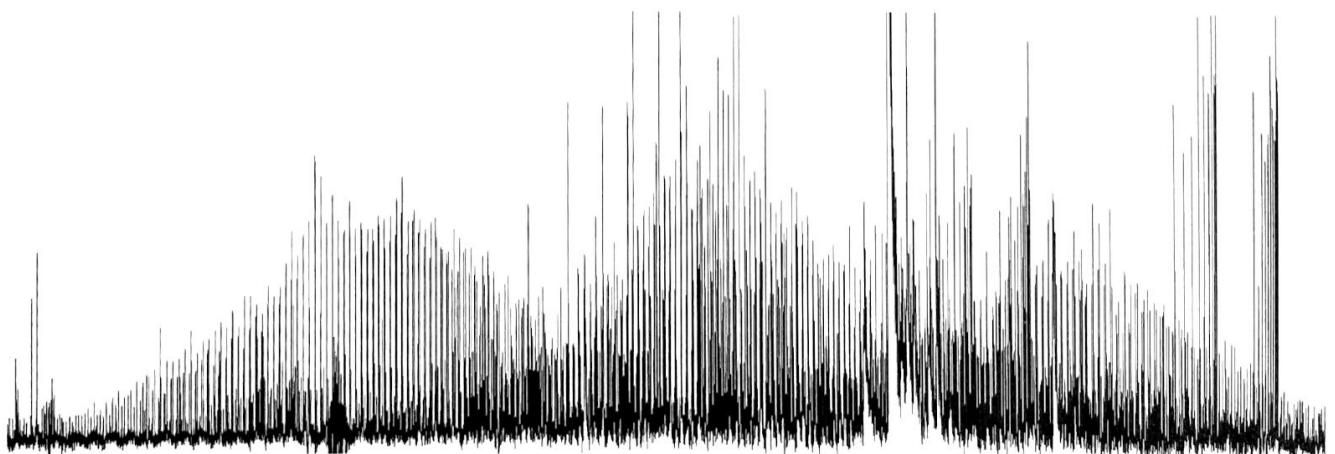


Figure 3: DCCBr ν_3 band system at 570 to 650 cm^{-1}

Figure 4 shows a region of the ν_4 spectrum, two wavenumbers wide, magnified 25 times from Figure 2. Two strong ground state bands, one for each isotopic species of the molecule, can be clearly seen to rise above the rest of the peaks. The separation of the peaks in the ground state bands can be seen to be about 0.25 cm^{-1} leading to a rough estimate of 0.125 cm^{-1} for the rotational constant B of the molecule.

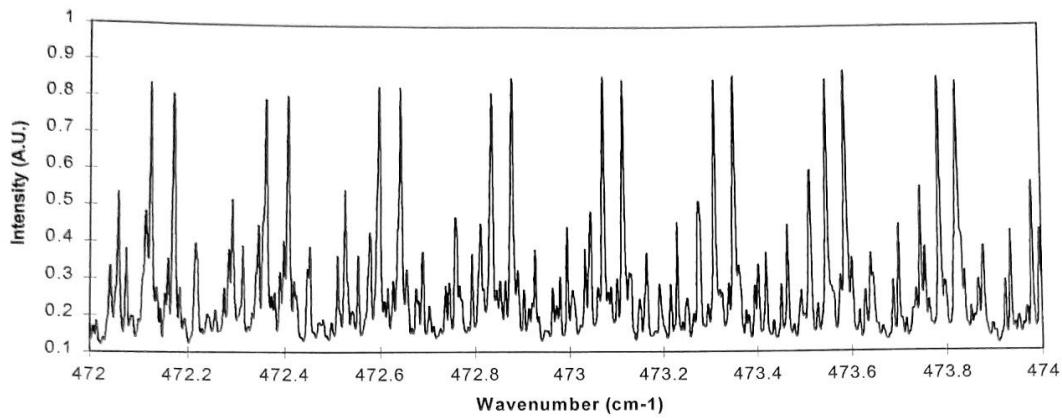


Figure 4: 472 to 474 cm^{-1} region of ν_4

Hot bands

Many weaker bands can be seen as well in the Figure 4. These weak bands are hot bands whose lower state is some vibrationally excited state. They are weaker because in accordance with the Boltzman energy distribution their lower state population is much smaller compared to the ground vibrational state population^[20]. Many molecules, such as acetylene, have only extremely weak hot bands because they lack any low lying vibrational states. On the other hand, the lowest excited states of DCCBr are at roughly 280 cm^{-1} for the ν_5 state (bromine bending), 480 cm^{-1} for the ν_4 state (deuterium bending) and $2\nu_5$ at 560 cm^{-1} . At least these three states can be expected to result in detectable hot bands in the spectrum.

Typical $2B$ wide region

The width of the spectral region in Figure 5 is similar in size with $2B$ where B is typical rotational constant (0.12 cm^{-1}). While the B -constants of the vibrationally excited states differ from those of the ground state, the difference is rather small and hence every $2B$ region (about 0.25 cm^{-1}) of the spectrum is expected to contain a single peak of each band.

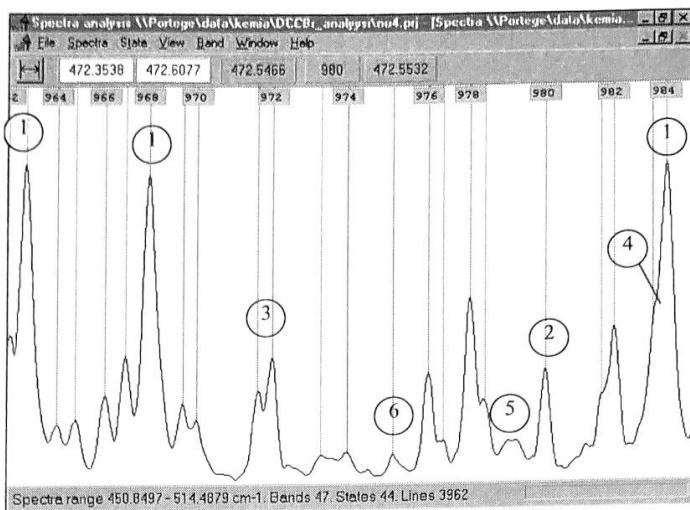


Figure 5: 472.35 to 472.61 cm^{-1} region of ν_4 system (program screen shot)

The region should be expected to enclose one peak from most bands. The yellow vertical lines show the positions of peaks that peak finding program has found. Note that the peak analysis software was able to detect peaks even in the edge of other peaks, but there is naturally a limit to how small or bad peaks should be detected.

Few points can be noted directly about the peaks in Figure 5:

- ① Peaks belonging to the ground state bands of DCC^{79}Br and DCC^{81}Br . These bands dominate the spectrum since the Boltzmann distribution of energy levels shows that large part of molecules are at the ground vibrational state in room temperature.
- ② An example of a good quality hot band peak which is strong and distinct resulting in accurate peak position. Less than half of all detected peaks are as good in quality as this one.
- ③ Two peaks near each other but peak centers still well separated. Their positions should be expected to deviate from theoretical value only a small amount.
- ④ The peak finding algorithm is by using self deconvolution able to spot peaks that appear only as bumps in the edge of other, larger peaks. There is naturally a limit to this ability: very small peaks next to very large ones are not detected. And even for peaks detected in this manner there is expected to be exceptionally large error in the calculated peak position.
- ⑤ When two small peaks merge together their positions are often lost as the resulting form is too flat to yield any proper peak position. (Even if the peaks would be strong enough on their own)
- ⑥ Example of a peak just large enough to be registered. Its position should not be expected to be as accurate as for a strong peak.

While the number of detected peaks could be easily increased by lowering the detection threshold of the peak finding program, eventually noise becomes a problem. If detection limit is too low, random noise peaks will simply fill the whole spectral range.

Peak crossings

Due to because different rotational constants of different states, peaks in different bands do not occur exactly at same intervals. Hence the peak pattern seen in Figure 5 repeats in a slightly different form when the view is shifted by $2B$ to left or right. When the spectra is scrolled in $2B$ steps it looks as if the peaks of different bands move relative to each other. Some peaks approach each other, merge together due to the limited resolution, and separate again in different order.

Figure 6 shows one such crossing that occurs in the region of $492.72 \dots 494.49 \text{ cm}^{-1}$. Each image is showing a region of spectrum of equal width, each separated $2B$ from the previous one. One can see a peak of a weaker band (marked with arrow) approaching from left, merging with the strong peak for duration of 5 m -values and leaving from the other side. It is important to note that in the middle of the merging, the combination peak can be seem to be look a very well defined and good quality peak single peak although it results from two separate transitions.

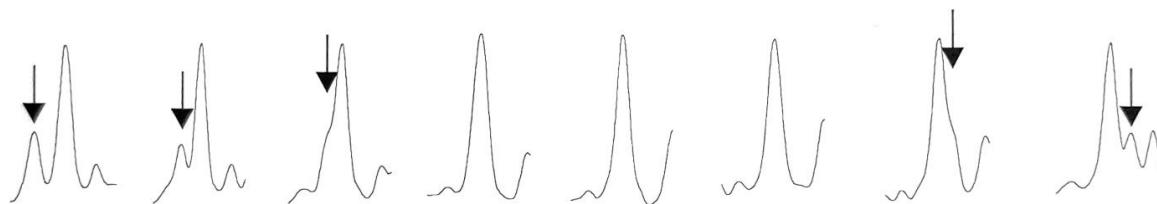


Figure 6: Weaker band crossing a ground state band near 493.5 cm^{-1}

It is clear from Figure 6, that much information is lost in these crossings. The position of the weaker band peaks during the merging is almost completely ambiguous, but even the stronger band peak center can be expected to show deviation from expected theoretical value due to the crossing. Since the spectrum is very dense of peaks with various intensities, these crossings are common: for some weaker bands it is not uncommon that over half of the peaks are masked by stronger peaks in this way. There are even some weak bands that are visible during just a few, say five, consequent m -values and are below or above this region permanently covered by other peaks. There is little hope in analyzing such bands with present resolution.

The peak crossings and resulting peak merging is the main source of problems in the analysis process causing potentially unassignable bands, incorrect peak and branch assignments and errors in calculated parameters. Any program to analyze the spectrum must somehow be resistant to these

deviations from exact. Since the amount of peak merging depends very highly on the resolution of the spectra, even slight improvement in resolution aids greatly the analysis of the weaker hot bands. Finally, one can make a rough estimation of the amount of bands that should be analyzable from the ν_4 band system. The number of visible hot bands can be estimated to be about 20 from the number of detected peaks in a $2B$ wide region (Figure 5). The real number of analyzable bands should be expected to be lowered from this figure due to many of the bands that have peaks in Figure 5 being too weak for analysis. On the other hand, some peaks in Figure 5 might actually be merged peaks from two different bands that can both be analyzed.

The Q -branches

As the selection rules show (see page 14), there will be Q -branches present in the perpendicular ν_4 band system. Figure 7 shows the main Q -branch area in the center of ν_4 band system. Compare with Figure 2 that shows the whole ν_4 .

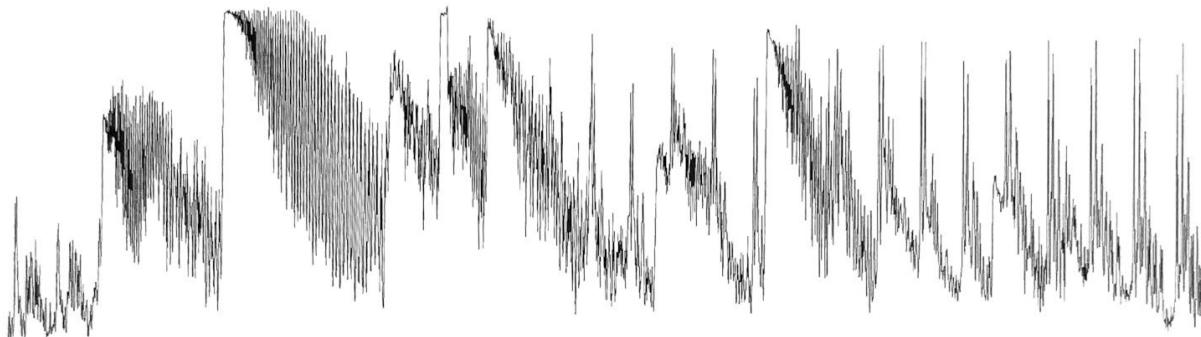


Figure 7: Main Q -branch area of ν_4 in the range 479.27 to 486.35 cm^{-1}

Figure 8 shows the second Q -branch from left in Figure 7. This is also the strongest Q -branch, having the ground states of DCC⁷⁹Br and DCC⁸¹Br as lower states. One can see here that the peaks of the different isotopic species are merged to rather high m -values until they are resolved to separate peaks.

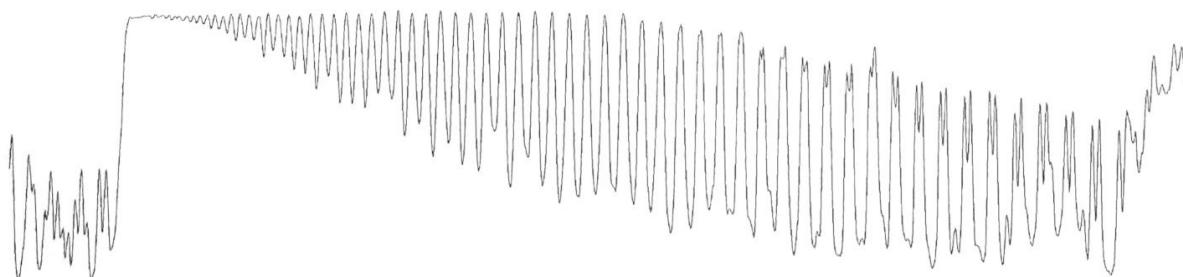


Figure 8: Ground state Q -branches from Figure 7 (480.426 to 481.571 cm^{-1})

4. Fitting the spectrum

There are two distinct tasks in spectrum fitting. The first is to *assign* as many as possible peaks in the spectrum. This means to determine the exact spectral transition that causes the peak to exist in the spectrum: the lower vibrational state, the upper vibrational state and the rotational J quantum numbers of the upper and lower state. The second task is to calculate rotational and vibrational parameters of the lower and upper states by fitting various functions to the peak wavenumber data. This fitting is mostly linear least squares in case of a n^{th} degree polynomial fitting function. Iterative nonlinear least squares fitting must be used in the case of resonance bands where the energy levels are not any more described by equation (11). Whereas the latter fitting task is very straightforward and easily performed by computer programs, the former assignment task is in some cases very tedious.

Peak assignment

Looking at the DCCBr spectrum of Figure 4 and Figure 5, few notes can be made.

First, The strongest peaks can be immediately assigned to ground vibrational lower state of the two isotopic species respectively. The assignment of hot band peaks to various vibrational lower states cannot be made directly although the strongest hot band peaks can be expected to originate from the various v_5 or v_4 lower states.

Second, since the peak pattern repeats in a roughly similar manner at every $2B$ intervals (about 0.25 cm^{-1} in DCCBr) it is often easy to *follow a band* i.e., after locating one peak, find other peaks in the band with consequent m -quantum numbers. This is trivial for the ground state bands and becomes more and more difficult when the band becomes weaker due to many of the peaks of the band being overlapped by stronger peaks as shown in Figure 6.

Fourth order fit a P - or R -branch

While finding a series of consequent peaks of a band can be done to some degree by eye and intuition, suitable prediction algorithms can be very handy.

Consider the term values for transitions expressed in m as shown in equation (21). The equation can be expressed in different powers of m :

$$27) \quad \tilde{v} = m^4 [D'' - D'] - 2m^3 [D'' + D'] + m^2 [B' - B'' - D'(1 - 2k'^2) + D''(1 - 2k''^2)] + \\ m[B' + B'' + 2D'k'^2 - 2D''k''^2] + [B''k''^2 - B'k'^2 - D'k'^4 + D''k''^4 + \Delta E_{\text{vib}}]$$

At first sight the presented fourth order fit might seem not useful in the initial prediction of new peak position in the band since we do not know the m -values of the peaks: only the relative m -values of a series of band peaks.

We can replace the m in equation (27) with $m_a + \Delta m$ where m_a means the assigned m -value and Δm is the unknown error in m -assignments:

$$28) \quad \tilde{v} = (m_a + \Delta m)^4 [D'' - D'] - 2(m_a + \Delta m)^3 [D'' + D'] + \\ (m_a + \Delta m)^2 [B' - B'' - D'(1 - 2k'^2) + D''(1 - 2k''^2)] + \\ (m_a + \Delta m)[B' + B'' + 2D'k'^2 - 2D''k''^2] + [B''k''^2 - B'k'^2 - D'k'^4 + D''k''^4 + \Delta E_{vib}]$$

which can be arranged as a fourth order polynome in powers of m_a :

$$\begin{aligned}
& \tilde{v} = m_a^4 (D'' - D') + \\
& m_a^3 (4\Delta m [D'' - D'] - 2[D'' + D']) + \\
& m_a^2 (6\Delta m^2 [D'' - D'] - 6\Delta m [D'' + D'] + B' - B'' - D'(1 - 2k'^2) + D''(1 - 2k''^2)) + \\
& m_a \left(4\Delta m^3 [D'' - D'] - 6\Delta m^2 [D'' + D'] + \right. \\
& \left. 2\Delta m [B' - B'' - D'(1 - 2k'^2) + D''(1 - 2k''^2)] + [B' + B'' + 2D'k'^2 - 2D''k''^2] \right) + \\
& \left(B''k''^2 - B'k'^2 - D'k'^4 + D''k''^4 + \Delta E_{vib} + \Delta m^4 [D'' - D'] - (2\Delta m^3)[D'' + D'] + \right. \\
& \left. \Delta m^2 [B' - B'' - D'(1 - 2k'^2) + D''(1 - 2k''^2)] + \Delta m [B' + B'' + 2D'k'^2 - 2D''k''^2] \right)
\end{aligned}$$

Hence it is clear that a fourth order polynomial fit in m_a , the assigned m -values, should fit the peak wavenumbers of a P- or R-branch even if m_a is in error. Since equation (29) has six unknowns (D' , D'' , B' , B'' , Δm and ΔE_{vib}) but only five coefficient values are returned from the fit, the values of the constants can not be solved. However, the aim at this point is not to calculate parameter values but to use the fit prediction of new lines in the branch. Solving the optimal coefficients of equation (29) using the assigned peaks allows one to predict new peak wavenumbers by using unassigned m_a values in the equation with solved coefficient. Naturally, the prediction will become more accurate when new peaks are assigned.

Fourth order fit can also to some degree help to get over peak crossings such as the one in Figure 6. But with very slow crossings (where the weaker peak is merged to a larger for very many m_a -values) following the band becomes uncertain and the danger of assigning peaks from two separate bands to a single “band” becomes real. This is because the predicted peak positions will differ from the actual ones the more the further one goes from the assigned area.

Combining the P- and R-branches

Even if a band can be assigned over occasional peak crossings, the Q -branch area in the center of v_4 band system (Figure 7) is virtually impossible to bridge through. The range of the area filled with

strong Q -branches is over 7 wavenumbers wide which means that most bands will be invisible there for approximately 30 peaks (30 times $2B$ distance of 0.25 cm^{-1} is about 7 cm^{-1}). Also note that the P - and R -branch peaks are rather weak in the center area, increasing the masking effect of the Q -branches. There is very little chance that a fourth order polynomial fit can give accurate enough prediction on the other side of the Q -area based on few peak assignments on the other side.

Combination difference prediction

The solution used here for finding out which P - and R -branches belong to the same band uses the ground state combination difference (GSCD) expression. In this method the wavenumbers of band peaks from P - and R -branches having the same upper state rotational quantum number J' are subtracted from each other. Starting from the expressions for peak wavenumbers in P - and R -branches of equations (16) and (17) it can be shown (for details, see Appendix 1) that the expression of the difference takes form:

$$30) \quad \tilde{\nu}_r - \tilde{\nu}_p = (4B'' - 6D'')\left(J' + \frac{1}{2}\right) - 8D''\left(J' + \frac{1}{2}\right)^3$$

where B'' is the rotational constant of lower vibrational state of the transition and D'' is the centrifugal distortion constant. Note that the corresponding constants of upper state have cancelled out because we have subtracted from each other two terms that have same upper state. J' is the rotational quantum number of the upper state and can be calculated from the m value with the equations (19) and (20).

In the expression (30) there are four types of unknowns: wavenumbers of P -branch lines $\tilde{\nu}_p$, wavenumbers of R -branch lines $\tilde{\nu}_R$, the rotational constants B'' and D'' and the rotational quantum number J' . In the familiar ground state combination difference method (as described on page 28) the wavenumbers $\tilde{\nu}_p$ and $\tilde{\nu}_R$ and the quantum numbers J' are known and a fit is made to solve the unknown B'' and D'' . Here the aim is different: to predict the wavenumbers of band peaks in the other branch, say $\tilde{\nu}_R$, when we know peak wavenumbers in the other, $\tilde{\nu}_p$, and the B'', D'' and J' .

Guessing the unknowns

But we do *not* know B'' , D'' and J' . We might know the B'' and D'' constants for some possible lower states but we do not know which of those states is the one for the analyzed band. Also, we know the relative m values (from which J' is obtained) of the peaks in the assigned branch but there is likely to be an unknown error Δm in each assignment. Hence, we guess. We guess the lower state *and* the Δm . After making the guesses, line positions from the other branch can be predicted and checked whether they match well the actual line positions. If the match is good, we have with one

blow found the line positions in the opposing branch, the lower state and the correct shift of m . If the match is not good, another combination of Δm and lower state can be tried.

What is “good” and “not good” match between the predicted lines in the other branch and actual line positions is of course a matter of judgement. In practice, a *fitness* value, for example the mean square deviation of predicted peaks from nearest actual lines, can be calculated by the software for very many combinations and the best performing combinations are viewed to the user for selection. If an outstanding combination is found, the peaks in both branches can be automatically combined to a single band with *P*- and *R*-branches. Then peak assignment can be then continued further with the additional aid of knowing the band lower state constants and correct peak m -values.

Fitness calculation

The aim of Fitness function is to calculate a numerical measure describing how well the predicted lines calculated with equation (30) match the lines assigned in the other branch. The reason for producing a numerical value describing the accuracy of the prediction is that only then we can use an automatic computer algorithm to select the few tolerable combinations of lower state and Δm from the many thousands of bad ones.

The first and simplest idea is to calculate the fitness value as the mean of the square differences of predicted line positions to the nearest assigned ones. Two immediate problems arise: the two series of peaks assigned from *P*- and *R*-branches might not be from exactly opposite locations. The *P*-branch peaks could be, for example, with actual m -values 20...35 and the *R*-branch peaks they are compared to with actual m -values 27...37. Also, there might be gaps in the peak assignments of the

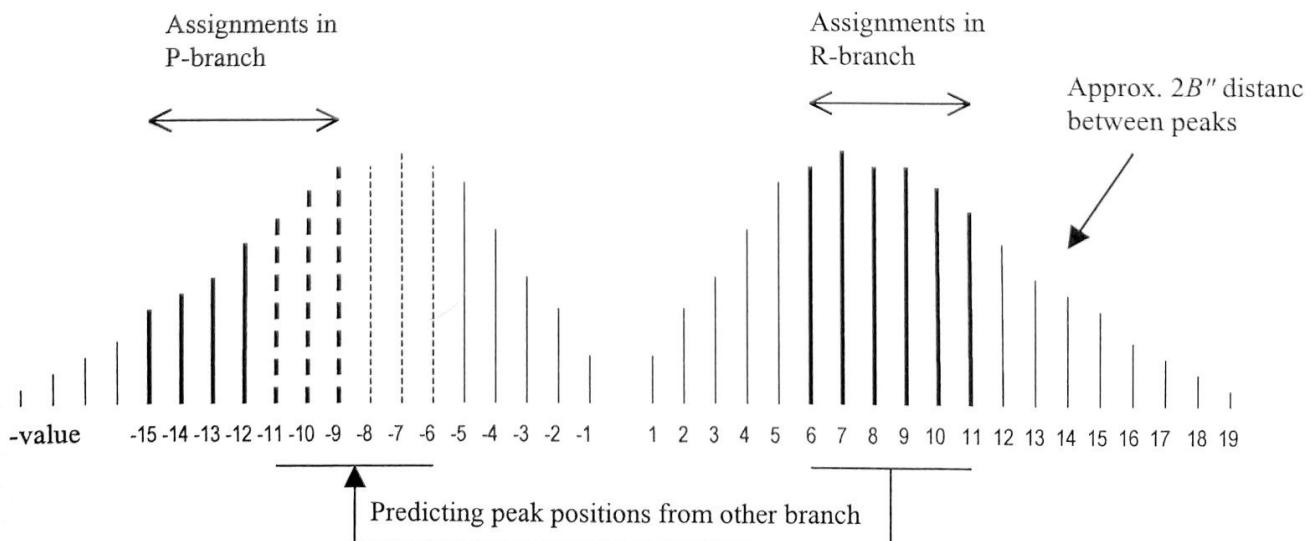


Figure 9: Peak prediction and branch comparison

other branch, leading to very large deviations.

Both of these problems can be solved by discarding those peak comparisons where the deviation of the predicted wavenumber from the nearest assigned one was more than the value of the lower state rotational constant B'' . Because the approximate distance between lines of a band is $2B''$ there should always be assigned line nearer than B'' if that m -value is assigned in the branch. The idea is illustrated in Figure 9 where only the thick dotted lines are used in the fitness calculation.

Selecting a suitable fitness function

The aim of the fitness function is of course to provide as small value for the correct combination of opposing branch, lower state and Δm as possible and as large value all the incorrect combinations i.e., to make the correct combination stand out well from the group of thousands of incorrect ones. It turned out during the analysis that calculating the fitness function as an ordinary mean square difference does achieve this optimally. Because of the very large number of combinations evaluated, there are bound to be some incorrect combinations producing quite good fitness *by chance*. On the other hand, there might be peak overlaps or similar problems in the assignments of correct combination that make the fitness value of the correct combination somewhat poor.

After extensive experimentation with different possibilities of fitness function F calculations, following formula was chosen:

$$31) \quad F = \exp\left(\frac{1}{W} \sum_{n=1}^a w_n [\ln(d_n^2) + I_n]\right) \quad \begin{cases} d = \max(|v_{pred} - v_{ass}|, 0.0001 \text{ cm}^{-1}) \\ I = \max\left(\frac{I_P}{I_R}, \frac{I_R}{I_P}\right) - 1 \end{cases}$$

where v_{pred} is the predicted wavenumber and v_{ass} is the nearest assigned wavenumber in the other branch. The summation runs through all assigned peaks (a = number of assignments) for which $(v_{pred} - v_{ass}) < B''$ as explained above. w is the weight given for predictions and W is the sum of the weights. I is the *Intensity factor* which is calculated from I_P and I_R , the intensities of the P - and R -branch peaks respectively

this was that one can not demand even a correct prediction to be more accurate than the standard error other than by chance.

The reason for the better performance of formula (41) over arithmetic mean raises from its better ability to value very small differences between predicted and observed wavenumbers and on the other hand its habit not pay too much attention to occasional large deviations that might be caused by peak overlaps. Due to these two reasons it tends to select better the correct combination of the lower state and m shift (see page 61 for discussion of the performance of the method).

Getting started

The method of combining branches assumes, that a selection of lower state constants are known and that the selection includes the lower state of the band that is analyzed. In the beginning of the analysis process this is not usually the case – no rotational constants might be known. In such situation one first needs to find the ground state B and D constants by combination difference calculation of some well resolved ground state band in any band system (v_1 , v_2 or v_1 band systems are preferable since they lack the disturbing Q -branches).

After finding the ground state constants, one can proceed to analyze all the ground state bands of all band systems and from the analysis obtain the parameters for singly excited states. These parameters can be further used to find and analyze hot bands originating from singly excited states and gain parameters for doubly excited states and so on.

This starting process was greatly aided in this study by the previous work by Olavi Vaittinen^[13] who had analyzed the v_5 band system obtaining rotational parameters for the ground state, v_5 state and $2v_5$ state. Those were used as a starting point in this study.

Parameter fitting

When lines assigned from P - and R -branches have been combined to a full band as explained above, the next stage of the band analysis can begin. Now more powerful fitting methods become available for rotational parameter determination and peak prediction in order to make additional peak assignments.

Direct polynomial fit

The most straightforward fit to the peak wavenumber data is the fourth order polynomial fit described by equation (27) above shown again here:

$$\tilde{v} = m^4 [D'' - D'] - 2m^3 [D'' + D'] + m^2 [B' - B'' - D'(1 - 2k'^2) + D''(1 - 2k''^2)] + \\ m[B' + B'' + 2D'k'^2 - 2D''k''^2] + [B''k''^2 - B'k'^2 - D'k'^4 + D''k''^4 + \Delta E_{vib}]$$

By looking at the equation we can see that when points with $x = m$ and $y = \tilde{v}$ are plotted, a fourth order polynome should fit the data points giving a curve $y = c_4x^4 + c_3x^3 + c_2x^2 + c_1x^1 + c_0$. We can further see that the constants D' and D'' can be calculated from the fit coefficients c_4 and c_3 , B' and B'' further from c_2 and c_1 and finally ΔE_{vib} from c_0 using the formulas:

$$32) \quad \begin{aligned} D'' &= \frac{1}{2}c_4 - \frac{1}{4}c_3 & D' &= -\frac{1}{2}c_4 - \frac{1}{4}c_3 \\ B'' &= \frac{1}{2}[c_1 - c_2 - D' + D''] & B' &= \frac{1}{2}[c_2 + c_1 + D'(1 - 4k'^2) - D''(1 - 4k''^2)] \\ \Delta E_{vib} &= c_0 - B''k''^2 + B'k'^2 + D'k'^4 - D''k''^4 \end{aligned}$$

Note that value of the vibrational angular momentum quantum number k must be known for both upper and lower vibrational level. This is usually not a problem: lower state is known from the branch combination procedure as explained above and upper state can in most cases be determined from the lower state and type of transition.

Ground state combination difference fit (GSCD)

Consider the equation (30), the wavenumber difference of P - and R -branch peaks that have the same upper level. Dividing the equation by $J' + \frac{1}{2}$ gives:

$$33) \quad \frac{\tilde{v}_r - \tilde{v}_p}{J' + \frac{1}{2}} = 4B'' - 6D'' - 8D''(J' + \frac{1}{2})^2$$

We can see that taking peak pairs from P - and R -branches and plotting points $x = (J' + \frac{1}{2})^2$, $y = (\tilde{v}_r - \tilde{v}_p)/(J' + \frac{1}{2})$ will yield a first degree fit $y = C_0 + C_1x$ with $C_0 = 4B'' - 6D''$ and $C_1 = -8D''$. The rotational parameters are hence given by:

$$34) \quad D'' = -\frac{1}{8}C_1 \quad B'' = \frac{1}{4}(C_0 + 6D'')$$

Reduced wavenumber fit for upper state parameters (FitUp)

Consider the equation (15) giving the peak wavenumbers in terms of J' , shown again here:

$$35) \quad \tilde{v} = \Delta E_{vib} + B'[J'(J'+1) - k'^2] - D'[J'(J'+1) - k'^2]^2 - \\ B''[J''(J''+1) - k''^2] + D''[J''(J''+1) - k''^2]^2$$

When we subtract from both sides of equation (35) the so called *reducing* expression:

$$36) \quad Z = B''[(J'(J'+1) - k'^2) - (J''(J''+1) - k''^2)] - \\ D''[(J'(J'+1) - k'^2)^2 - (J''(J''+1) - k''^2)^2]$$

we obtain, after simplification:

$$37) \quad \tilde{v} - Z = \Delta E^{vib} + (B' - B'') [J'(J'+1) - k'^2] - (D' - D'') [J'(J'+1) - k'^2]^2$$

Note that the reducing expression Z uses only lower state constants which are supposed to be known at this stage of the band analysis. Also the J'' and J' values can be calculated from the m -values that are used in peak assignments using equations (19) and (20). It turns out that for both P - and R -branches apply:

$$38) \quad \begin{aligned} J'(J'+1) &= m(m+1) \\ J''(J''+1) &= m(m-1) \end{aligned}$$

Hence Z can be calculated for each assigned band peak. Looking at the reduced energy expression (37) we can note that plotting points with $x = J'(J'+1) - k'^2$ and $y = \tilde{v} - Z$ gives a second order curve $y = C_0 + C_1x + C_2x^2$ with

$$39) \quad \Delta E^{vib} = C_0, \quad B' = B'' + C_1, \quad D' = D'' - C_2.$$

Comparing the different fitting methods

One might wonder, why three different types of fit have been introduced. After all, do not the two latter ones (GSCD and FitUp) only give the same information that direct polynomial fit has already given? In principle this is true and the analysis program could well do its job with only direct fourth order polynomial fit. However, both GSCD and FitUp method have some merits that justifies their existence in the analysis program.

The first point concerns about the standard errors for the parameters obtained from the different types of fits. Smaller standard error means more accurate parameter values so it is always desirable to use the fit that provides the minimum standard errors for the desired parameters. The standard errors for polynomial fits tend to correlate with two main factors: the number of data points and the order of the fit (linear, second order polynome and so on). More datapoints means more accuracy and higher order polynome means less accuracy. The latter factor raises probably from the fact that there is more flexibility in the fitting function with higher degree and changes in some coefficient can be to some degree compensated by the change in the others.

For a given band, the number of data points for the direct polynomial fit and reduced wavenumber fit is equal to the number of peak assignments. On the other hand, GSCD calculation requires P - and R -branch peak wavenumbers to be subtracted from each other and hence creates only one datapoint per *two* peak assignments in best case. Actually things get often even worse, since the two peaks to be subtracted from each other must have same upper level J . It often happens that for a P -

branch peak assignment with given upper J there is *no* corresponding assignment in R -branch due to peak overlapping or similar reason. It was not uncommon in the present work that a band having more than 90 assignments had only some 25 datapoints generated for GSCD due to many assigned peaks not having assigned counterparts in the other branch.

It turns out that the number of datapoints is the most important factor in accuracy and hence GSCD provides the worst accuracy of the three fits, giving some 3 to 5 times larger standard errors for the ground state parameters than the direct polynomial fit. FitUp is on the other hand most accurate of the three, having maximum number of data points and lower polynome degree than the direct polynomial fit. Still, the usefulness of FitUp is limited by the fact that it provides accurately not the upper state parameters themselves but their differences to the fixed ground state parameters: ΔB and ΔD . Since the ground state parameters do have to be received from somewhere, we have to resort to the less accurate methods of direct polynomial fit or GSCD to obtain them. This inaccuracy will be transferred to the upper state parameters in the calculation $B' = B'' + \Delta B$ and hence FitUp can be only as accurate as are the known lower state parameters. Table 4 summarizes the properties of different fitting methods utilized in the analysis program.

Table 4: Comparison of different fitting methods

	Direct polynomial fit	Reduced wave-number fit (FitUp)	Combination difference (GSCD)
# of datapoints	# of assigned peaks	# of assigned peaks	< ½ of assigned peaks
Fit polynome degree	4	2	1
Parameters obtained	$B'', D'', B', D', \Delta E_{\text{vib}}$	$\Delta B, \Delta D, \Delta E_{\text{vib}}$	B'', D''
Relative error ¹	7–10	1	30 – 50
Special advantages	+ Gives all parameters with one fit.		+ Upper state perturbations do not matter
Special disadvantages		– Errors in ground state parameters limit the B' and D' accuracy.	– Only correctly paired peaks can be used as a data point.

¹ The relative accuracy means that for given band assignments, the error in parameters that direct polynome fit gives tend to be 5 to 10 times larger than the error FitUp gives for the parameter value differences. Similarly, GSCD produces the largest fit errors, 30 to 50 times those of FitUp. These numbers are an estimate based on this work and seem to have quite similar values for all analyzed bands.

The relative advantages and disadvantages of the fits lead to following conclusions:

- 1) Direct polynomial fit should be used to obtain the ground state parameters from a good ground state band.
- 2) FitUp should be used for all other parameter fits. The error of the ground state parameters will be the limiting factor in the parameters of most states. Only in very weak hot bands the error in FitUp will be larger than the error in the fixed ground state parameters.
- 3) GSCD fit should be used only when ground state parameters need to be fitted and there are perturbations in the upper level.

All of the three different types of fit methods are implemented in the software with the details of their implementation found from the chapter ***WinAnalyse technical documentation*** and instructions for their usage in the chapter ***8. WinAnalyse Users Manual***.

Fitting Q-branches

The fitting methods for *Q*-branches differ only slightly from those for *P*- and *R*-branches. In practice there are few differences.

First, for *Q*-branches one cannot do a prediction analysis similar to the combination calculation that combines *P*- and *R*-branches to a band and also gives the correct lower state and *m*-values of the peaks. Hence the lower vibrational state and *m*-values must be obtained in some other way. The way to find the lower state of a *Q*-branch is to observe the location of the *Q*-branch: each *Q*-branch has its origin at the same energy as the corresponding band with *P*- and *R*-branches. Hence it is useful to assign and combine first all possible *P*- and *R*-branches and then deduce the lower state of the *Q*-branches by looking at a transition diagram similar to those in Figure 13, Figure 14 and Figure 17 in the chapter ***6. Results***. Note that for hot bands the lower state of the *Q*-branch can have a different parity than the corresponding *P,R*-branches.

Second, the problems of overlapping peaks are different in *Q*-branches. *Q*-branches dominate the spectrum in the center area over *P*- and *R*-branches that are generally weak there. On the other hand, the different *Q*-branches do cause overlap problems among themselves. There are usually at least two *Q*-branches overlapping, namely those of the different isotopic species. Such situation can be well seen in the Figure 8, where the peaks of the two isotopic species are first merged together for many *m*-values and only in the right hand part of the figure resolved to separate peaks. In such situation one must simply assign the merged peaks to the bands of both isotopic species.

The overlapping can be worse, though. When four or more Q -branches are located on top of each other, the result can be more or less impossible to analyze with the present resolution.

Since it is rather easy to follow a Q -branch (i.e., find peaks with consequent m -values) there is usually little need for peak prediction. However, the fourth order fit of equation (29) works as well for Q -branches as for P - and R -branches if needed even when the correct m -values are not known.

FitUp for Q -branches

The only difference in the reduced wavenumber fit (FitUp) for Q -branches compared to P - and R -branches is that we have to use slightly different formula for the reducing factor Z . Instead of the Z formula of PR-branches in equation (36) we use:

$$40) \quad Z = B''[(J'(J'+1)-k'^2)-(J'(J'+1)-k''^2)] - \\ D''[(J'(J'+1)-k'^2)^2 - (J'(J'+1)-k''^2)^2]$$

Note that the only difference is that the $J''(J''+1)$ have been replaced by $J'(J'+1)$ since for Q -branches $J'' = J'$. When this reducing expression is subtracted from the wavenumbers of Q -branch peaks, we get, after simplification:

$$41) \quad \tilde{v} - Z = \Delta E^{vib} + (B' - B'')[(J'(J'+1)-k'^2)] - (D' - D'')[J'(J'+1)-k'^2]^2$$

Which is exactly same formula as the one for PR-branches in equation (37). Hence, a second order fit is formed and same type of upper state information obtained as with P - and R -branches.

The accuracy of the FitUp calculation is of course in theory same for P,R -branches and Q -branches. However, often less peaks are observed for Q -branches decreasing the accuracy. For example the standard error for band origin tends to be 5–10 times larger for a Q -branch than the corresponding combination of P - and R -branches.

Finding the correct m -values

One can see from the image of a Q -branch in Figure 8 that in the beginning of the branch the peak merge together so tightly that one cannot deduce the rotational m -quantum numbers of peaks just by counting the number of peaks from the beginning of the branch. Therefore one must guess and there is likely to be a systematic error in the m -values. But for the FitUp method described above to produce correct upper state parameters, the correct m -values must be known.

As well as the ground state determination problem, the m -value problem is solved by the position of the corresponding P,R -branches. In theory the band origins of the Q -branch and PR -branch should be same (in practice small deviation should be expected due to inaccuracies in the fits). Hence one can try different shifts of m -values for the Q -branch and find the shift that produces a band origin

nearest to the one produced by the P - and R -branches. In most cases this is a reliable method for m -value assignment. What adds to the reliability is that the two Q -branches of the different isotopic species are analyzed separately. If the same m -values are found for both as expected the likeliness of correct assignment is increased.

The analysis program features an automated routine for the Q -branch m -adjustment as described on page 64 in the chapter **7. WinAnalyse technical** documentation. The usage of the function is described on page 81 in the chapter **8. WinAnalyse Users Manual**.

Predicting new peak positions

One can note by observing the fitting equation for direct polynomial fit (27) and the equation for FitUp (37) that both can be used to predict new peak positions as well as parameter determination. New yet unassigned values can be given for m (or J') in these equations after the fit has been performed and hence obtain predicted wavenumbers. In practice it makes little difference which one of them is used for prediction: both perform equally well for non-perturbed bands and equally badly in the case of perturbations in the upper vibrational state.

Analysis of l -Resonance bands

Consider two vibrational states X and Y that are connected with rotational l -resonance as described by the off-diagonal matrix element of equation (13) so that the energy levels are not any more described by the $J(J+1)$ polynomial expansion.

If such resonance exists on the lower vibrational state of the band the ground state combination difference formula (30) fails and the band cannot be found. If, on the other hand, upper state is the perturbed one, the GSCD formula works since it depends only on the unperturbed lower state parameters B'' and D'' . Hence the P - and R -branches of the band can be combined in the normal manner using the method described on page 23. What fails in that case is the polynome fit for upper state parameters (equation 37). It produces large deviations of the predicted wavenumbers from the assigned ones especially when a large numbers of peaks of the are assigned.

Although the peaks of the latter type of resonant band can be assigned, the upper state rotational constants resulting from polynomial fit or FitUp are worthless due to the resonance. In such case both bands must be fitted together diagonalising the 2×2 diagonal resonance matrixes described above. This is not a polynomial fit and hence an iterative nonlinear fitting must be used for the rotational parameters B'_X and D'_X (band X), B'_Y and D'_Y (band Y) and the resonance parameters q and q_J of equation (13).

5. The analysis project

The spectrum analysis of the present work was carried out between 18.12.1995 and 22.4.1997. The analysis was started with three separate Fortran77 command line programs provided by Olavi Vaittinen. Working with the original programs was very slow, and required much manual work by the user including typing long lists of peak wavenumbers to input files. More and more improvements were added to the programs and in the summer 1996 the first version of the present windows-based systems was programmed.

The developments of the current version of the software has proceeded hand in hand with the spectrum analysis. More powerful features have been added to assign ever more difficult hot bands with a high level of automatisation.

One of the major problems that prompted the development of the software was noticed in spring 1996. Many bands had been analyzed with the old (though improved) Fortran programs when the author noticed that some of the analyzed “bands” were in fact sharing the same P-branch! It appeared that with such dense spectrum and numerous lower states it was possible to obtain a good fit even with incorrect pairing of the *P*- and *R*-branches. This was not easily detectable with the old programs.

System of peak assignment

When peaks overlap it is always a matter of judgement, whether the resulting combination peak should be assigned to none, one or both of the peaks and what weights should be used in the possible assignments.

The final assignment is always based on intuition, but as strict and well defined rules of assignment as possible were used in the final assignments of this work. Strict rules were used in order to obtain equal treatment of different band, aiding the comparison of bands. Well defined rules provide easily repeatable results as other researchers can use same assignment system. The final rules of assignment used were following:

- 1) Well formed spectrum peaks that were caused by single transitions of a single band and large enough (larger than about one quarter of the maximum peak of the band) were assigned with weight of unity.

Assignment with reduced weight of 0.05 to 0.5 depending on situation was performed for:

- 2) Relatively weak peaks, about less than one quarter in size relative to the strongest peaks in the band. Especially in the edges of the band and near the center.
- 3) Peaks that were overlapped by other peaks in the case that the other peak was larger than about one third but not larger than three times the peak in question.
- 4) Most common reduced weight used was 0.2 and 75% of all reduced weights were between 0.1 and 0.3 inclusive.

No assignment was made when one or more of the following applied:

- 5) Peak was too weak to be detected by the peak finding software (although visible in the spectrum waveform)
- 6) Peak was overlapped by another peak that was over about three times stronger than the peak in question. Note that no assignment was done in this case even if the wavenumber of the combination peak was accidentally very near the predicted wavenumber.
- 7) Peak was overlapped by another peak of similar size in such way that the nearest observed wavenumber was further than 0.002 cm^{-1} from the predicted wavenumber

Note especially, that in the described system of assignment, a single detected peak that was created by spectral transitions of many bands could be assigned to some or all of the bands in question. (See Figure 23 on page 55 for a good example of complex multiple assignments).

Resonance bands

Because the band with l -resonance in their upper state do not fit the normal $J(J+1)$ polynomial expansion, they create a typical ‘wobbling’ fit where the residual systematically oscillates from side to side. On the other hand, if only a few peaks are fitted from a resonant band, a good fit can be accidentally found (when the fit parameters try to adjust to the resonance) but then the parameters of the fit, B' and D' , will have typically very weird values and are completely unreliable. For example, the band 1C1 has a very weak resonance pair 1D1 for which only 36 peaks could be fitted. Hence the residuals of the fit were small but the D' parameter obtained before resonance analysis ($-0.055 \times 10^{-7} \text{ cm}^{-1}$) is clearly in error. (See the Table 5 in the next chapter for details)

The resonance bands were analyzed with a Fortran program provided by Olavi Vaittinen and modified by the author to the Fortran90 specification. The program uses iterative fit to obtain best values for the rotational parameters and l -resonance parameters q and q_J .

6. Results

Peak assignments

22 perpendicular bands from the ν_4 band system and 6 in the ν_3 band system were rotationally analysed (11 and 3 bands, respectively, for both isotopic species). For 10 of the 22 perpendicular bands the Q -branches could also be analysed.

All bands in the ν_4 band system contained a total of 3140 peak assignments, an average of 98 assignments per band. This can be compared to the total number of detected peaks in the band system, 3962, keeping in mind that multiple assignments can be made for the same peak with the software. Figure 10 shows the peak assignments in a typical region of the spectrum.

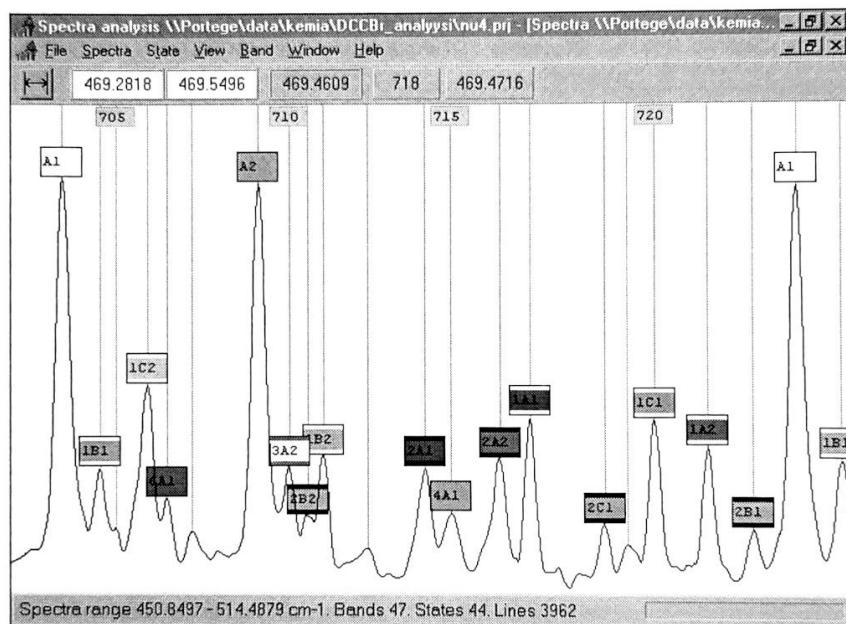


Figure 10: Final peak assignments in a typical region of the ν_4 system

Note that while most of the visible bands have been analyzed, there are clearly some unassigned peaks remaining. These typically belong to bands that are so badly overlapped by others that the P/R-branch combination procedure has not yielded any result for them with the present data.

Figure 11 displays assignments of a typical hot band, 2B1, originating from a ν_4 lower state. Total of 141 peaks were assigned in the band. m -values of the peaks are displayed in the assignment labels. Note the Q -branch system located in the $m = 0$ position as expected.

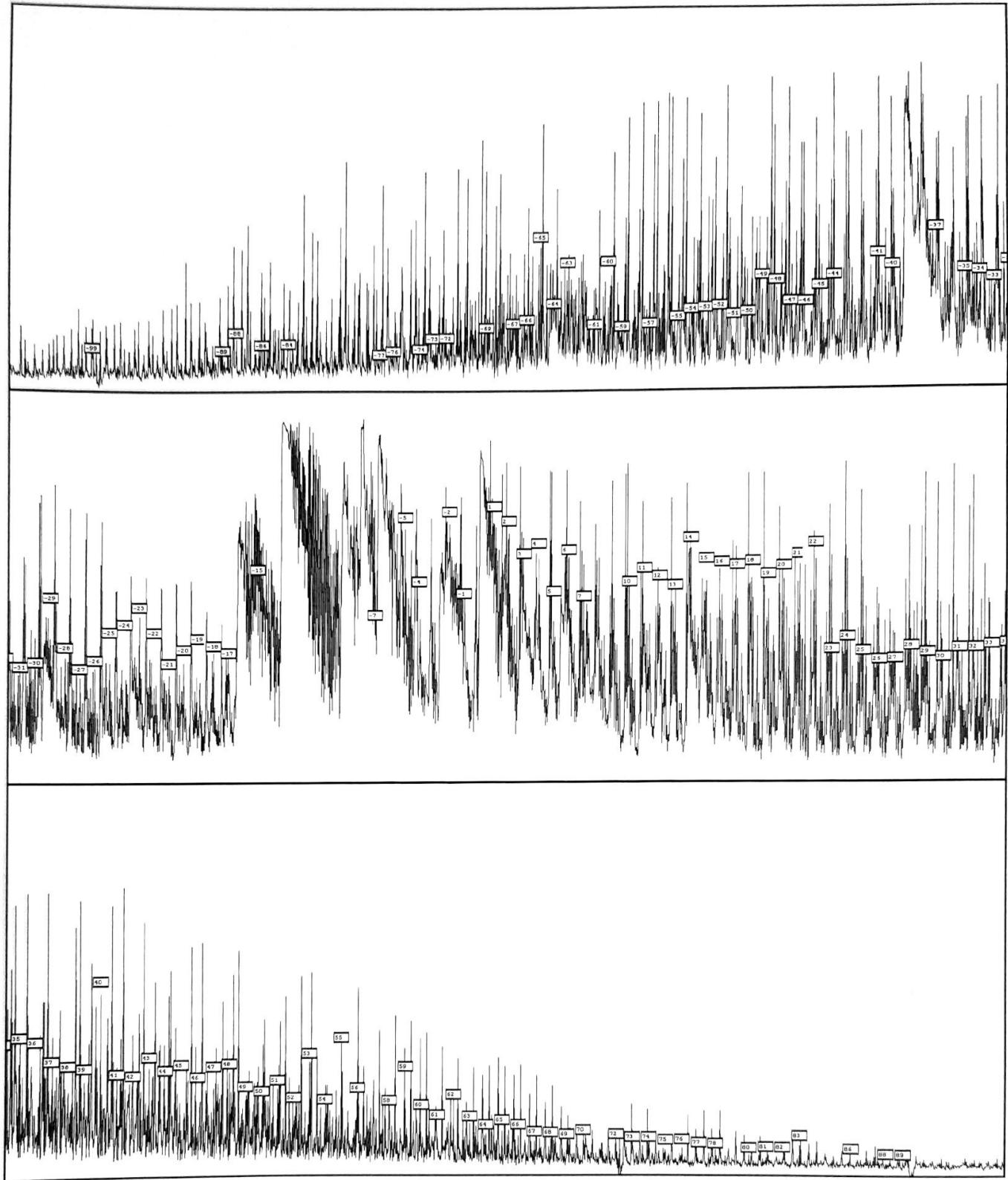


Figure 11: The 2B1 band with transitions $000\ 2^20^0,\Delta,e \leftarrow 000\ 1^10^0,\Pi,e$.

Rotational analysis results

Table 5 and Table 6 contain the parameters found for the analyzed bands of DCC⁷⁹Br and DCC⁸¹Br. *Name* is the code of the band as used in the fitting software. It is displayed here so that the band can

easily be referred to in the text. *Type* can be either Q (for *Q*-branches, where $\Delta J = 0$) or PR (for P,R-branches, where $\Delta J = \pm 1$). The type code includes as a subscript the number of the band system where the band is found, which in this work is 3 for the v_3 band system or 4 for the v_4 band system.

The *Ass* column shows the total number of assigned peaks in the band and the *Min m* and *Max m* columns show the minimum and maximum *m* value of the assigned peaks respectively.

The calculated standard errors in the last digits are displayed after the parameter values in parenthesis. For example, 0.1234(7) means 0.1234 ± 0.0007 . The maximum error in last digit is 15 i.e., an error of 0.123(16) would be shown as 0.12(2). The root mean square deviation of peaks from their predicted values varied from 0.00015 cm^{-1} to 0.00058 cm^{-1} for analyzed *P*- and *R*-branches and from 0.00029 cm^{-1} to 0.00107 cm^{-1} for analyzed *Q*-branches. This represents a good accuracy compared to the nominal spectral resolution of 0.004 cm^{-1} used in the experiment. In FitUp calculation the ground state parameters with smallest standard errors have been used as the fixed ground state parameters

Table 5: Analyzed vibration-rotation bands of DCC⁷⁹Br

Name	Type	Upper State	Lower State	B'/cm ⁻¹	D' × 10 ⁷ /cm ⁻¹	ΔG _v /cm ⁻¹	Ass m	Min m	Max m	Notes
A1	PR ₄	000 1 ⁰ 0 ⁰ ,Σ, e	000 0 ⁰ 0 ⁰ ,Σ, e	0.1220209(7)	0.2031(8)	480.65936(2)	207	-112	117	
Q1	Q ₄	000 1 ⁰ 0 ⁰ ,Σ, f	000 0 ⁰ 0 ⁰ ,Σ, e	0.1220929(7)	0.2031(8)	480.65926(14)	59	19	85	
C1	PR ₃	001 0 ⁰ 0 ⁰ ,Σ, e	000 0 ⁰ 0 ⁰ ,Σ, e	0.1217441(7)	0.1727(8)	603.43506(4)	149	-83	79	
1C1	PR ₄	000 1 ¹ 1 ¹ ,Δ, e	000 0 ⁰ 1 ¹ ,Π, e	0.1223791(2)	(0.2071)	481.70252(14)	138	-87	78	a
1D1	PR ₄	000 1 ¹ 1 ¹ ,Σ ⁺ , e	000 0 ⁰ 1 ¹ ,Π, e	0.1223725(2)	(0.2071)	482.48018(10)	36	-28	29	a
1Q1	Q ₄	000 1 ¹ 1 ¹ ,Σ ⁻ , f	000 0 ⁰ 1 ¹ ,Π, e	0.1223800(8)	0.193(3)	479.70139(14)	32	8	41	
1R1	Q ₄	000 1 ¹ 1 ¹ ,Δ, f	000 0 ⁰ 1 ¹ ,Π, e	0.1223791(8)	0.215(16)	482.1928(2)	31	16	51	
1E1	PR ₃	001 0 ⁰ 1 ¹ ,Π, e	000 0 ⁰ 1 ¹ ,Π, e	0.1220262(7)	0.1862(9)	612.84070(11)	112	-69	80	
1A1	PR ₄	000 1 ¹ 1 ¹ ,Σ, f	000 0 ⁰ 1 ¹ ,Π, f	0.1223822(5)	0.2111(5)	479.70077(11)	134	-93	92	
1B1	PR ₄	000 1 ¹ 1 ¹ ,Δ, f	000 0 ⁰ 1 ¹ ,Π, f	0.1223780(5)	0.2048(5)	482.19192(8)	143	-88	84	
1S1	Q ₄	000 1 ¹ 1 ¹ ,Σ ⁺ , e	000 0 ⁰ 1 ¹ ,Π, f	0.1224781(10)	0.189(2)	482.4816(8)	53	15	68	b
1F1	RP ₃	001 0 ⁰ 1 ¹ ,Π, f	000 0 ⁰ 1 ¹ ,Π, f	0.1221837(5)	0.1803(5)	612.84084(10)	112	-76	83	
2A1	PR ₄	000 2 ⁰ 0 ⁰ ,Σ, e	000 1 ⁰ 0 ⁰ ,Π, e	0.1221908(7)	0.2104(8)	474.34509(8)	125	-91	75	
2B1	PR ₄	000 2 ² 0 ⁰ ,Δ, e	000 1 ⁰ 0 ⁰ ,Π, e	0.1221859(7)	0.1992(8)	484.14426(9)	141	-99	89	
2C1	PR ₄	000 2 ² 0 ⁰ ,Δ, f	000 1 ⁰ 0 ⁰ ,Π, f	0.1221856(7)	0.2040(8)	484.14415(9)	120	-85	86	
2Q1	Q ₄	000 2 ⁰ 0 ⁰ ,Δ, e	000 1 ⁰ 0 ⁰ ,Π, f	0.1221939(9)	0.221(2)	474.3437(4)	31	21	51	
3A1	PR ₄	000 1 ¹ 2 ⁰ ,Π, e	000 0 ⁰ 2 ⁰ ,Σ, e	0.1224471(9)	0.2550(12)	481.66853(14)	95	-87	81	
3B1	PR ₄	000 1 ¹ 2 ² ,Φ, e	000 0 ⁰ 2 ² ,Δ, e	0.1226987(10)	0.206(2)	483.73539(10)	73	-56	73	
4A1	PR ₄	001 1 ⁰ 0 ⁰ ,Π, e	001 0 ⁰ 0 ⁰ ,Σ, e	0.1218314(3)	0.1586(4)	483.3474(4)	63	-79	76	d
6A1	PR ₄	000 1 ¹ 3 ¹ ,Δ, e	000 0 ⁰ 3 ¹ ,Π, e	0.122624(2)	0.247(5)	482.8569(4)	42	-56	66	c

Notes

- a These bands form a rotational l -resonance pair that has been fitted with nonlinear least squares method. The resonance parameters found were $q_4 = 0.974(2) \cdot 10^{-4} \text{ cm}^{-1}$ and $q_{4J} = 0.78(13) \cdot 10^{-10} \text{ cm}^{-1}$. The D constants had to be fixed in the fit to obtain converge and they were fixed to the respective ground state value. This fixing also renders the other obtained parameters somewhat unreliable. Note also that the obtained q_{4J} constant is here about ten times smaller than with the DCC⁸¹Br isotope but has a smaller error.
- b This Q -branch experiences rotational l -resonance in the upper state leading to large residuals in the fit. It has been anyhow analyzed with the standard linear formulas (assuming no resonance) so the rotational parameters might be slightly in error.
- c There is a slight uncertainty with the assignment of this band. The symmetry of the upper state could be also Σ^+
- d There is a slight uncertainty with the assignment of this band.

Table 6: Analyzed vibration-rotation bands of DCC⁸¹Br

Name	type	Upper State	Lower State	B'/cm ⁻¹	D' × 10 ⁷ /cm ⁻¹	ΔG _v /cm ⁻¹	Ass m	Min m	Max m	Notes
A2	PR_4	000 1 ¹ 0 ⁰ , Σ , e	000 0 ⁰ 0 ⁰ , Σ , e	0.1213484(7)	0.2005(8)	480.65928(3)	202	-105	107	
Q2	Q_4	000 1 ¹ 0 ⁰ , Σ , f	000 0 ⁰ 0 ⁰ , Σ , e	0.1214202(7)	0.2018(9)	480.65942(11)	65	19	86	
C2	PR_3	001 0 ⁰ 0 ⁰ , Σ , e	000 0 ⁰ 0 ⁰ , Σ , e	0.1210834(7)	0.1689(9)	602.07575(5)	156	-88	87	
1C2	PR_4	000 1 ¹ 1 ¹ , Δ , e	000 0 ⁰ 1 ¹ , Π , e	0.1217033(4)	0.208(4)	481.70586(13)	144	-79	89	a
1D2	PR_4	000 1 ¹ 1 ¹ , Σ^+ , e	000 0 ⁰ 1 ¹ , Π , e	0.1216965(5)	0.188(7)	482.47338(11)	36	-33	32	a
1Q2	Q_4	000 1 ¹ 1 ¹ , Σ^- , f	000 0 ⁰ 1 ¹ , Π , e	0.1217111(9)	0.229(4)	479.70112(2)	33	10	42	
1R2	Q_4	000 1 ¹ 1 ¹ , Δ , f	000 0 ⁰ 1 ¹ , Π , e	0.1217033(9)	0.195(3)	482.1918(3)	25	16	43	
1E2	PR_3	001 0 ⁰ 1 ¹ , Π , e	000 0 ⁰ 1 ¹ , Π , e	0.1213618(6)	0.1827(7)	611.58288(10)	114	-71	80	
1A2	PR_4	000 1 ¹ 1 ¹ , Σ^- , f	000 0 ⁰ 1 ¹ , Π , f	0.1217075(5)	0.2083(5)	479.70113(11)	116	-89	88	
1B2	PR_4	000 1 ¹ 1 ¹ , Δ , f	000 0 ⁰ 1 ¹ , Π , f	0.1217036(5)	0.2023(5)	482.19252(8)	151	-90	94	
1S2	Q_4	000 1 ¹ 1 ¹ , Σ^+ , e	000 0 ⁰ 1 ¹ , Π , f	0.1218066(9)	0.1983(13)	482.4713(10)	63	15	79	b
1F2	RP_3	001 0 ⁰ 1 ¹ , Π , f	000 0 ⁰ 1 ¹ , Π , f	0.1215198(5)	0.1771(6)	611.58288(9)	109	-75	71	
2A1	PR_4	000 2 ⁰ 0 ⁰ , Σ , e	000 1 ¹ 0 ⁰ , Π , e	0.1215170(7)	0.2077(9)	474.34189(6)	131	-84	102	
2B1	PR_4	000 2 ² 0 ⁰ , Δ , e	000 1 ¹ 0 ⁰ , Π , e	0.1215121(7)	0.1966(9)	484.14436(1)	136	-95	90	
2C1	PR_4	000 2 ² 0 ⁰ , Δ , f	000 1 ¹ 0 ⁰ , Π , f	0.1215125(7)	0.2028(9)	484.14415(9)	93	-73	79	
2Q1	Q_4	000 2 ⁰ 0 ⁰ , Δ , e	000 1 ¹ 0 ⁰ , Π , f	0.1215257(9)	0.2316(14)	474.3411(7)	33	23	73	
3A2	PR_4	000 1 ² 0 ⁰ , Π , e	000 0 ² 0 ⁰ , Σ , e	0.1217615(9)	0.2510(14)	481.64815(11)	89	-62	95	
3C2	PR_4	000 1 ¹ 2 ² , Φ , f	000 0 ⁰ 2 ² , Δ , f	0.1220225(14)	0.202(2)	482.6385(2)	57	-56	51	

Notes

- a These bands form a rotational l -resonance pair that has been fitted with nonlinear least squares method. The resonance parameters found: $q_4 = 0.947(6) \cdot 10^{-4} \text{ cm}^{-1}$, $q_{4J} = 0.6(3) \cdot 10^{-9} \text{ cm}^{-1}$. Note that the size of the q_{4J} constant is not much larger than the error limit i.e., it is not

well defined. Compare with the DCC⁷⁹Br isotope where the value is ten times smaller but better defined (that might be a more realistic value).

- b This *Q*-branch experiences rotational *l*-resonance in the upper state leading to large residuals in the fit. It has been anyhow analyzed with the standard linear formulas (due to lack of suitable software for *Q*-branch resonance analysis) so the rotational parameters might be slightly unreliable.

Transition diagrams

Figure 12 to Figure 18 display graphically all theoretically possible transitions (as described in the chapter selection rules on page 13) from a selection of low lying vibrational states along with the bands observed in this work. Names of the observed bands of DCC⁷⁹Br are located upper in each box on top of band lines. Name of corresponding DCC⁸¹Br band is lower in the boxes. Dashed line in a state box indicates that the state is perturbed by a resonance and is not suitable for normal $J(J+1)$ expansion analysis. The boxes of *e* / *f* substates of vibrational state possessing vibrational angular momentum are drawn together to emphasize that there is really only one vibrational state in question and that the *e* / *f* separation rises from rotation.

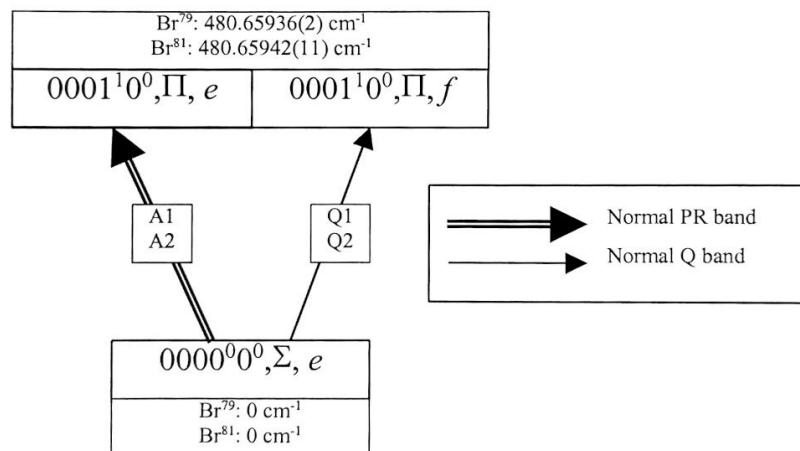


Figure 12: v_4 band system bands originating from the ground state

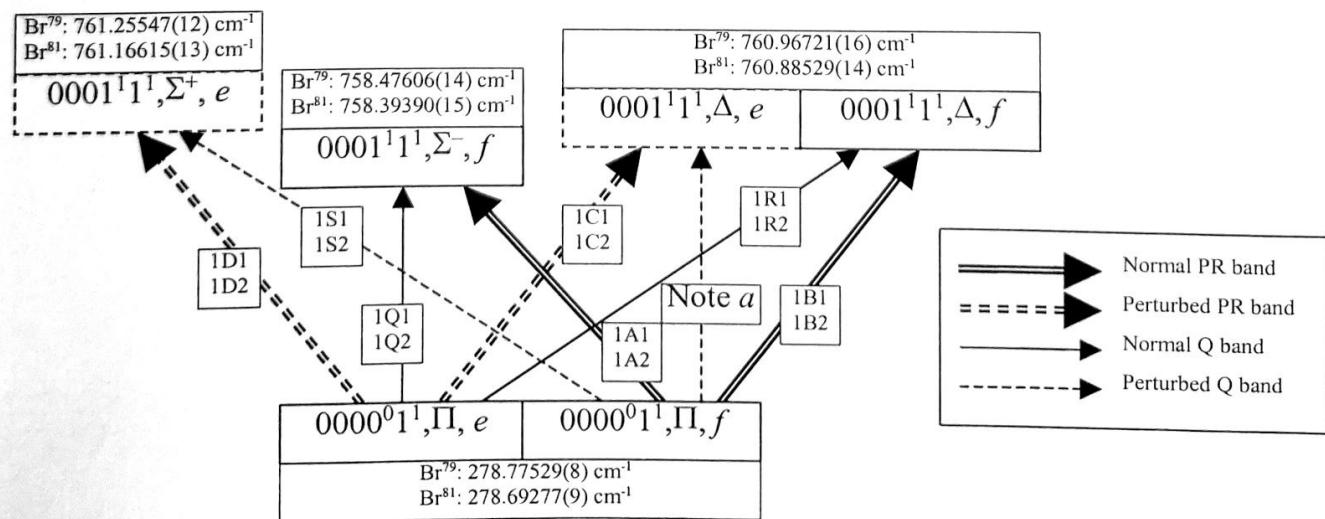


Figure 13: v_4 band system bands originating from v_5 states

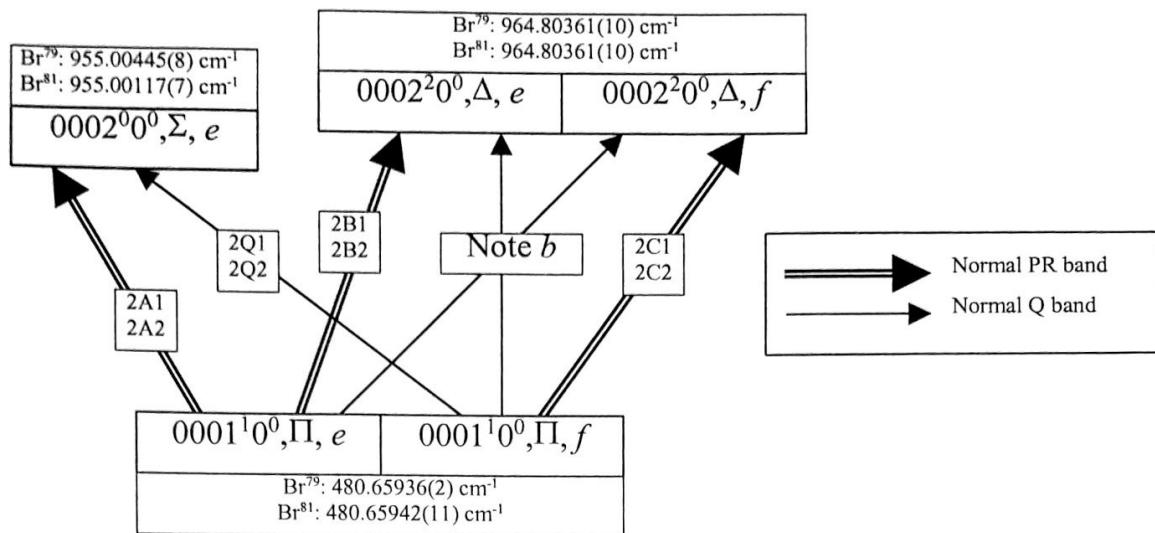


Figure 14: ν_4 band system bands originating from ν_4 states

Notes

- a This Q -branch is too dense for analysis due to resonance in the upper state which causes the peaks to turn back and merge into one square-looking blob.

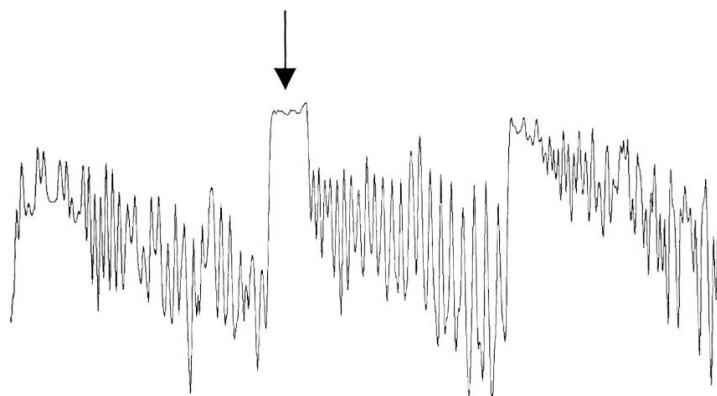


Figure 15: Resonant Q -branch pair turning back into itself (range 481.52 to 482.36 cm^{-1})

- b These two Q -branches and the two additional similar Q -branches from other isotope form a system of four overlapping Q -branches shown in Figure 16. This system proved unanalysable despite prolonged attempts. Higher resolution might help to assign the system.

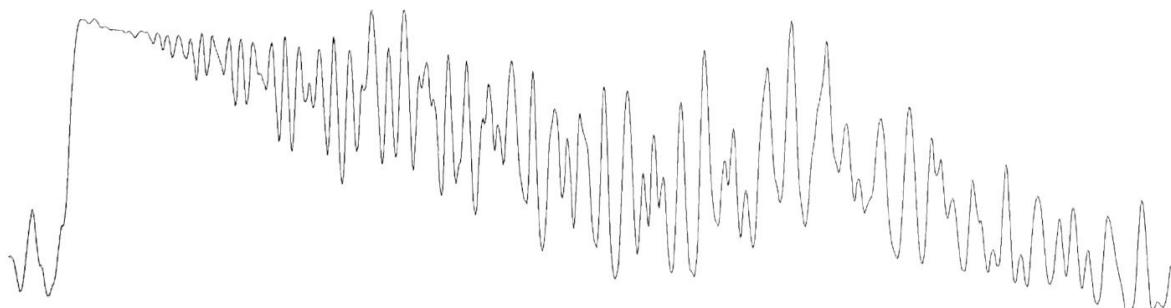


Figure 16: Four overlapping Q -branches produce an unanalysable mess in the region from 483.75 to 484.41 cm^{-1}

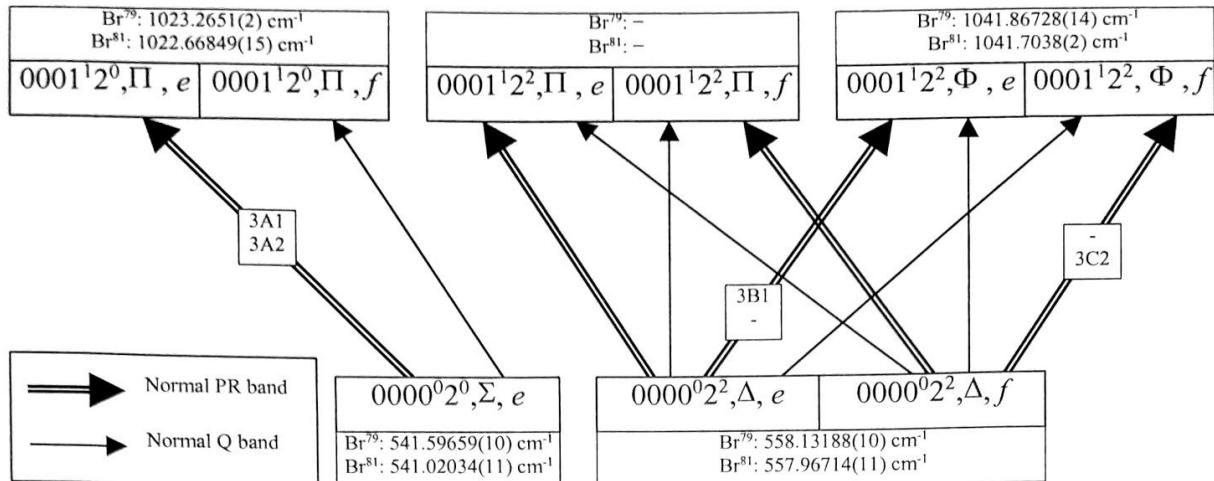


Figure 17: v_4 band system bands originating from $2v_5$ states

Bands that miss a label were either so weak that they were not found (in case of P - and R -branches) or found but too low quality for rotational analysis (in case of Q -branches)

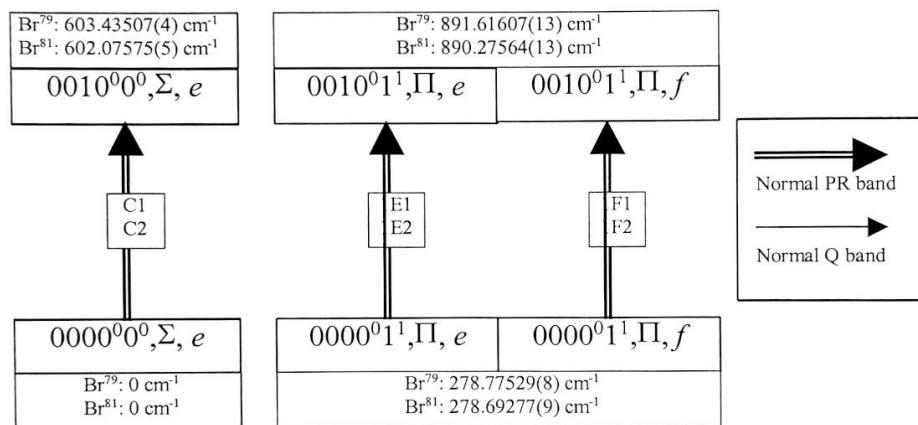


Figure 18: v_3 band system bands

Note that bands having resonance in the *lower* state (e.g. $0001^{11}\Sigma^+, e$ and $0001^{11}\Delta, e$) could not be found or analyzed with the present software.

State parameters

The rotational parameters B and D for the ground states of both isotopic species were obtained with standard ground state combination difference (*GSCD*, see page 28 of theory for details of the method) calculation of the bands A1 and A2. The vibrational energy of the ground states is defined to be exactly zero.

The algorithm used by the software for band upper state parameter determination (*FitUp*, see page 28 of the theory for details of the method) does not give the absolute B , D or E_{vib} values. Instead it

gives ΔB , ΔD and ΔE_{vib} , the differences to the fixed lower state parameters. The actual upper state parameters have to be calculated then with formulas such as $B' = B'' + \Delta B$.

This final addition must be taken into account when observing the standard errors obtained for the parameters. While the *FitUp*-algorithm usually provides relatively accurate values for ΔB , ΔD and ΔE_{vib} , the standard errors in the lower state parameters are usually significantly larger and hence limiting factor in the upper state parameter accuracy. The errors of the upper state parameters are calculated using the formula (24) on page 15.

After the upper state parameters have been obtained, they have further been used as lower state parameters in the analysis of bands originating from that state. Some lower state parameters have been obtained from other sources (references displayed in Table 6 and Table 7).

Multiple bands might provide parameters for the same upper state. For example, the *e* and *f* sub bands of same vibrational band have in theory the same band origin. In practice the values differ by small random amount. If the quality of the bands providing the same upper state parameters is of comparable quality (measured by the standard deviation of the fit), the final state parameters have been calculated as an average of the band results. If, on the other hand, the fit error of one of the bands is significantly lower than others, the fit of that band only are used for the upper state parameter determination. This is typically the case with *P,R*-branches and respective *Q*-branches: the error of the *P,R*-branch origin is usually smaller than that of the *Q*-branch origin and hence the band origin is taken directly from the *P,R*-branch origin.

Table 7 and Table 8 summarize the best possible parameters found for the vibrational states of $DCC^{79}Br$ and $DCC^{81}Br$ respectively.

Table 7: DCC⁷⁹Br vibrational state parameters

State	G _v /cm ⁻¹	Parity e /f	B /cm ⁻¹	D×10 ⁷ /cm ⁻¹	Source	Notes
000 0 ⁰ 0 ⁰ ,Σ 0		e	0.1219223(7)	0.2021(8)	Band A1 GSCD	
000 0 ⁰ 1 ¹ ,Π 278.77529(8)		e	0.1221849(7)	0.2071(8)	[Ref Olavis table 1]	
		f	0.1223051(5)	0.2073(5)	[Ref Olavis table 1]	
000 1 ¹ 0 ⁰ ,Π 480.65936(2)		e	0.1220209(7)	0.2031(8)	Band A1 FITUP	
		f	0.1220929(7)	0.2031(8)	Band Q1 FITUP	
000 0 ⁰ 2 ⁰ ,Σ 541.59659(10)		e	0.1223491(9)	0.2484(12)	[Ref Olavis table 1]	
000 0 ⁰ 2 ² ,Δ 558.13188(10)		e	0.1225665(1)	0.209(2)	[Ref Olavis table 1]	a
		f	0.1225661(7)	0.2122(10)	[Ref Olavis table 1]	a
001 0 ⁰ 0 ⁰ ,Σ 603.43507(4)		e	0.1217441(7)	0.1727(8)	Band C1 FITUP	
000 1 ¹ 1 ¹ ,Σ ⁺ 761.25547(12)		e	0.1223725(2)	(0.2071)	Band 1C1,1D1 <i>l</i> -resonance FitUp	b
000 1 ¹ 1 ¹ ,Σ ⁻ 758.47606(14)		f	0.1223822(5)	0.2111(5)	Band 1A1 FITUP	
000 1 ¹ 1 ¹ ,Δ 760.96721(16)		e	0.1223791(2)	(0.2071)	Band 1C1,1D1 <i>l</i> -resonance FitUp	b
		f	0.1223780(5)	0.2048(5)	Band 1B1 FITUP	
001 0 ⁰ 1 ¹ ,Π 891.61607(13)		e	0.1220262(7)	0.1862(9)	Band 1E1 FITUP.	
		f	0.1221837(5)	0.1803(5)	Band 1F1 FITUP	
000 2 ⁰ 0 ⁰ ,Σ 955.00445(8)		e	0.1221908(7)	0.2104(8)	Band 2A1 FITUP	
000 2 ⁰ 0 ⁰ ,Δ 964.80361(10)		e	0.1221859(7)	0.1992(8)	Band 2B1 FITUP	
		f	0.1221856(7)	0.2040(8)	Band 2C1 FITUP	
000 1 ¹ 2 ⁰ ,Π 1023.2651(2)		e	0.1224471(9)	0.2550(12)	Band 3A1 FITUP	
		f	—	—		
000 1 ¹ 2 ² ,Φ 1041.86728(14)		e	0.1226987(1)	0.206(2)	Band 3B1 FITUP	
		f	—	—		

Notes

- a Note that the difference of *e* and *f* sub state parameters is smaller than the error limit i.e., They are same in the scope of this work.
- b These two states are in rotational *l*-resonance. The parameters have been found with nonlinear fit that includes the resonance. The *D*-constants had to be fixed to ground state value for the fit to converge. This might cause the other parameters found to be somewhat inaccurate. The resonance parameters found were $q_4 = 0.974(2) \cdot 10^{-4} \text{ cm}^{-1}$ and $q_{4J} = 0.78(13) \cdot 10^{-10} \text{ cm}^{-1}$.

Table 8: DCCBr⁸¹ vibrational state parameters

State	G _v /cm ⁻¹	Parity e /f	B /cm ⁻¹	D×10 ⁷ /cm ⁻¹	Source	Notes
000 0 ⁰ 0 ⁰ ,Σ 0		e	0.1212503(7)	0.1995(8)	Band A2 GSVD	
000 0 ⁰ 1 ¹ ,Π 278.69277(9)		e	0.1215111(6)	0.2037(6)	[Ref Olavis table 2]	
		f	0.1216318(5)	0.2047(5)	[Ref Olavis table 2]	
000 1 ¹ 0 ⁰ ,Π 480.65942(11)		e	0.1213484(7)	0.2005(8)	Band A1 FITUP	
		f	0.1214202(7)	0.2018(9)	Band Q1 FITUP	
000 0 ⁰ 2 ⁰ ,Σ 541.02034(11)		e	0.1216655(9)	0.2448(14)	[Ref Olavis table 2]	
000 0 ⁰ 2 ² ,Δ 557.96714(11)		e	0.1218895(13)	0.201(2)	[Ref Olavis table 2]	a
		f	0.1218914(14)	0.201(2)	[Ref Olavis table 2]	a
001 0 ⁰ 0 ⁰ ,Σ 602.07575(5)		e	0.1210834(7)	0.1689(9)	Band C2 FITUP	
000 1 ¹ 1 ¹ ,Σ ⁺ 761.16615(13)		e	0.1216965(5)	0.188(7)	Band 1C2,1D2 <i>l</i> -resonance FitUp	b
000 1 ¹ 1 ¹ ,Σ ⁻ 758.39390(15)		f	0.1217075(5)	0.2083(5)	Band 1A2 FITUP	
000 1 ¹ 1 ¹ ,Δ 760.88529(14)		e	0.1217033(4)	0.208(4)	Band 1C2,1D2 <i>l</i> -resonance FitUp	b
		f	0.1217036(5)	0.2023(5)	Band 1B2 FITUP	
001 0 ⁰ 1 ¹ ,Π 890.27564(13)		e	0.1213618(6)	0.1827(7)	Band 1E2 FITUP.	
		f	0.1215198(5)	0.1771(6)	Band 1F2 FITUP	
000 2 ⁰ 0 ⁰ ,Σ 955.00117(7)		e	0.1215170(7)	0.2077(9)	Band 2A2 FITUP	
000 2 ⁰ 0 ⁰ ,Δ 964.80361(10)		e	0.1215121(7)	0.1966(9)	Band 2B2 FITUP	
		f	0.1215125(7)	0.2028(9)	Band 2C2 FITUP	
000 1 ¹ 2 ⁰ ,Π 1022.66849(15)		e	0.1217615(9)	0.2510(14)	Band 3A2 FITUP	
		f	—	—		
000 1 ¹ 2 ² ,Φ 1041.704(2)		e	—	—		
		f	0.1220221(14)	0.202(2)	Band 3C2 FITUP	

Notes

- a* Note that the difference of *e* and *f* substate parameters is smaller than the error limit i.e., They are same in the scope of this work.
- b* These two states are in rotational *l*-resonance. The parameters are unperturbed ones found with nonlinear fit. The resonance parameters found: $q_4 = 0.947(6) \cdot 10^{-4} \text{ cm}^{-1}$, $q_{4J} = 0.6(3) \cdot 10^{-9} \text{ cm}^{-1}$. Note that the size of the q_{4J} constant is not much larger than the error limit i.e., it is not well defined.

Table 9: Isotopic vibrational comparison

State	^{79}Br G _v /cm ⁻¹	^{81}Br G _v /cm ⁻¹	ΔG_v /cm ⁻¹	Formula, from Equation (6) on page 8	Notes
000 0 ⁰ 0 ⁰ , Σ	0	0	0	0	a
000 0 ⁰ 1 ¹ , Π	278.77529(8)	278.69277(9)	0.08252(12)	\tilde{v}_5	b
000 1 ¹ 0 ⁰ , Π	480.65936(2)	480.65942(11)	0	\tilde{v}_4	c
000 0 ⁰ 2 ⁰ , Σ	541.59659(10)	541.02034(11)	0.57625(15)	$2\tilde{v}_5 + 2x_{55}^* - 2g_{55}^*$ + Fermi	b, d
000 0 ⁰ 2 ² , Δ	558.13188(10)	557.96714(11)	0.16474(15)	$2\tilde{v}_5 + 2x_{55}^* + 2g_{55}^*$	b, d
001 0 ⁰ 0 ⁰ , Σ	603.43507(4)	602.07575(5)	1.35932(8)	\tilde{v}_3 + Fermi	b, e
000 1 ¹ 1 ¹ , Σ^+	761.25547(12)	761.16615(13)	0.08932(17)	$(\tilde{v}_4 + \tilde{v}_5 + x_{45} - g_{45}) + r_{45}$	b, f
000 1 ¹ 1 ¹ , Σ^-	758.47606(14)	758.39390(15)	0.0822(2)	$(\tilde{v}_4 + \tilde{v}_5 + x_{45} - g_{45}) - r_{45}$	b, f
000 1 ¹ 1 ¹ , Δ	760.96721(16)	760.88529(14)	0.0819(2)	$\tilde{v}_4 + \tilde{v}_5^* + x_{45}^* + g_{45}^*$	b, f
001 0 ⁰ 1 ¹ , Π	891.61607(13)	890.27564(13)	1.34043(19)	$\tilde{v}_3 + \tilde{v}_5$	b, g
000 2 ⁰ 0 ⁰ , Σ	955.00445(8)	955.00117(7)	0.00328(13)	$2\tilde{v}_4 + 2x_{44}^* - 2g_{44}^*$	h
000 2 ² 0 ⁰ , Δ	964.80361(10)	964.80361(10)	0	$2\tilde{v}_4 + 2x_{44}^* + 2g_{44}^*$	c, i
000 1 ¹ 2 ⁰ , Π	1023.2651(2)	1022.66849(15)	0.5966(3)	$\tilde{v}_4 + 2\tilde{v}_5 + 2x_{55}^* + 2x_{45} - 2g_{55}^*$	b, f
000 1 ¹ 2 ² , Π	–	–	–	$\tilde{v}_4 + 2\tilde{v}_5 + 2x_{55}^* + 2x_{45} + 2g_{55}^* - 2g_{45}$	
000 1 ¹ 2 ² , Φ	1041.86728(14)	1041.704(2)	0.1632	$\tilde{v}_4 + 2\tilde{v}_5 + 2x_{55}^* + 2x_{45} + 2g_{55}^* + 2g_{45}$	b, f

Notes

- a Note that the vibrational energies are measures relative to the ground vibrational state.
- b Mode involves Br bending or stretching and the Br⁷⁹ species has higher vibrational energy as expected from its lighter mass.
- c State does not involve Br bending or stretching and consequently the difference between the vibrational energies is found to be zero (i.e., smaller than the standard error).
- d Compare this with the difference in 000 0⁰1¹, Π states. As the amplitude of the Br-vibration increases, the difference between the energies of the two isotopic species increases. This is expected since in higher energy vibrations the Br-atoms move faster and the difference of their kinetic energy becomes larger due to mass difference.
- e Note that the isotopic effect is larger in the stretching vibration than in bending.
- f Note that the state has similar size isotopic difference with the state that is otherwise equal but does not have quanta on D bending (v_4)
- g This mode includes one quanta of stretching and bending. Compare with the states 000 0⁰1¹, Π and 001 0⁰0⁰, Σ and note that the isotopic energy difference is nearly determined by the latter.
- h Compare with the state 000 1¹0⁰, Π . Note that when the energy of the vibration increases, some modes start to develop a noticeable (although small) isotopic difference. This is expected because actually all atoms of the molecule are involved in all of the vibrational modes at least slightly.
- i Compare the pair 000 2⁰0⁰, Σ / 000 2²0⁰, Δ with the pair 000 0⁰2⁰, Σ / 000 0⁰2², Δ and note that in both airs the isotopic energy difference is larger with the Σ states.

Vibrational analysis

Using the found energies and respective formulas for those energies in Table 9, parameters for the effective Hamiltonian can be estimated. Figure 19 and Figure 20 display the values for the parameters as calculated in Appendix 2. Some parameter values have been taken from a HCCBr study in ref [13]. The parameters taken from HCCBr study are those that involve only the bromine bending and stretching and can hence be assumed to have similar values in DCCBr.

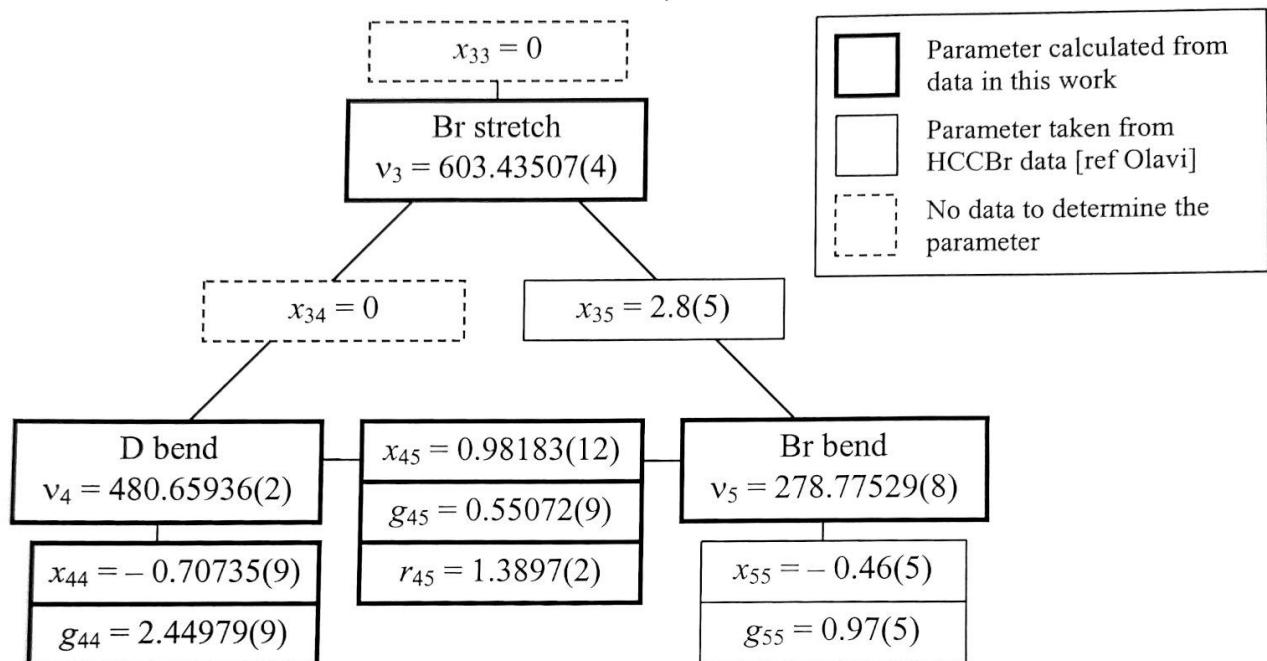


Figure 19: DCC-⁷⁹Br estimated vibrational anharmonicity parameters (in cm⁻¹)

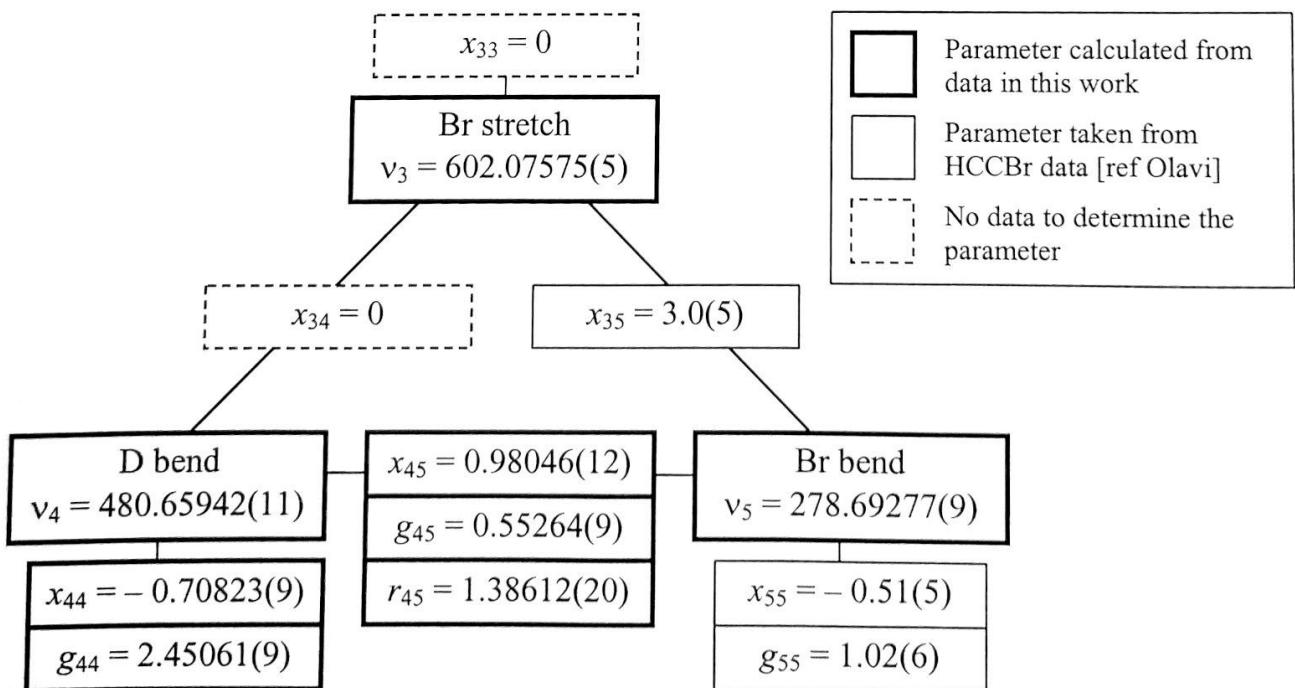


Figure 20: DCC-⁸¹Br estimated vibrational anharmonicity parameters (in cm⁻¹)

Conclusions

Suggestions for extended research

It would be difficult to analyze any more bands from the spectrum of this work, especially the ν_4 system. On the other hand, improving the spectral resolution would dramatically aid the analysis of further bands (and existing bands with higher accuracy). A higher resolution spectrum (0.002 cm^{-1} compared to 0.004 cm^{-1}) of ν_3 has already been recorded by the author in Helsinki and higher resolution can be seen to aid the peak resolving significantly. Detail of the comparison of the new spectrum to the spectrum used in this work is viewed in Figure 20. It is immediately clear that much more weak lines are resolved. This aids greatly finding and fitting of weak hot bands.

ν_4 band system spectrum of same quality is planned to be recorded soon. In that band system, the aid of higher resolution will be even more clear because of its greater number of bands and greater density of peaks. It is likely that many $2\nu_5$ and ν_3 lower state hot bands can be fitted with the high resolution data. Fitting these new spectra is planned in near future and it is likely to be efficient because the peaks already assigned in old low quality spectrum can be automatically transferred to the new spectrum and then more resolved lines can be easily added.

New spectra of resolution 0.002 cm^{-1} measured by the author

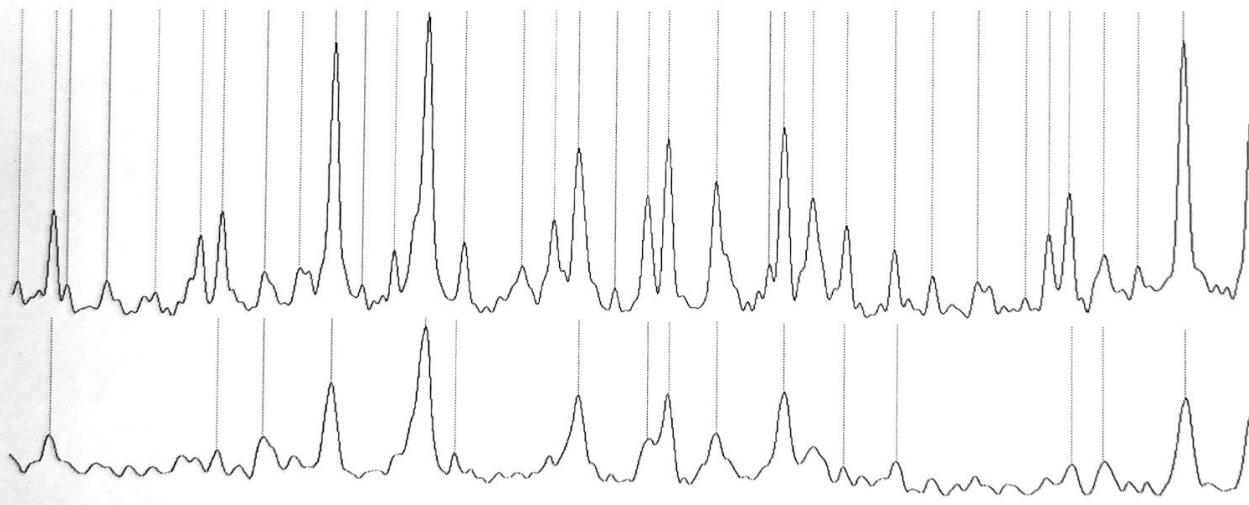


Figure 21: Comparison of the new and old spectrum (sample from ν_3 band system)

Higher degree fitting

There were indications in some strong bands, especially the ground state bands of v_3 band system, that the $J(J+1)$ expansion with B terms and D terms would need an additional H term, resulting in equation:

$$42) \quad E_{aJ}^{rot} = B_a [J(J+1) - k^2] - D_a [J(J+1) - k^2]^2 + H_a [J(J+1) - k^2]^3$$

There were three indications that a H -term would be needed:

- 1) When only about 100 peaks were fitted in m -range ± 60 the fit was still excellent.
- 2) Adding to the fit peaks with high m -values (all the way to ± 110), the residuals started to show larger and larger systematic deviation from the values predicted with the two-term expansion.
- 3) A sixth order polynome produced again an excellent fit even with high m peaks included (note that the highest power of J or m that result from equation (45) is six).

While it is impossible at this writing to use H -terms in the *FitUp* routine, such modification to the software would be straightforward and is planned to be done by the author in near future.

7. WinAnalyse technical documentation

Introduction

This technical documentation is intended mainly for scientific programmers interested in developing the software further but it is highly recommended reading for anyone using the software for spectrum analysis. This chapter explains the inner structure and operation of the program and also provides some additional insights to the general analysis problems. The documentation explains, how the spectrum fitting ideas introduced in the previous chapter (*Fitting The Spectra*) are realized into a working and highly automated package.

WinAnalyse is programmed with Borland Delphi 2.0, a 32-bit Windows95 based program development system. The system was chosen because of the ease in which a convenient and powerful graphical user interface can be developed with it. Pure mathematical calculations are of course also an important part of the program, but because all calculations, for example the ground state combination difference fit, can be carried out in fractions of a second on a Pentium-based system, speed considerations were not as important in choosing the development system as systems graphical abilities and development ease. Delphi excels in these areas with its readily available collection of graphical objects such as windows, tables, dialog-boxes, and menus available directly for the programmer to use.

WinAnalyse consists of over 4600 lines of source code, broken down into 12 separate units of 100 to 1000 lines each, each being responsible of certain strictly defined areas of program functionality. The executable is 450 kilobytes in size. Some 500 hours of time has been used for program development alone, not counting the time used for spectrum analysis with the program. *WinAnalyse* features include visual spectrum and assignment display with multiple functions, multiple data tables, automatic real time parameter fitting and peak prediction and powerful multiband storage capabilities. As a 32-bit program, all available system memory is fully utilized. Spectrum files of 100.000 points and more are processed with ease.

With such a large project, special attention has been paid for high quality program code, modularity, code reusability and good naming of variables and procedures. The object support of Delphi has made it possible to divide the code in many compact objects, making program modifications, improvements and debugging a painless task. It should not be difficult for other programmers to develop the system further with the aid of this documentation. Also all the objects of the software can be used separately independent of each other in other programs. For example the

SpectraWindow object that handles spectrum viewing on the display could be used to view the spectrum in a application that controls a spectrometer.

Structure of the this documentation

This technical documentation is structured by the Delphi-objects that make up the program. The higher level objects are discussed first and the chapter proceeds to lower level objects. With each object the most important *methods* of the object (procedures belonging to an object are called methods). Small units with minor importance are not discussed.

AnalyseWindow object

Found in unit	ANALWIN.PAS
Lines of code	1150
Parent object	TForm (Delphi standard object for a Window)

Analysewindow is the main object of the *WinAnalyse* program. It is responsible for displaying the main window of the application, setting up the application main menu and responding to the menu commands. Although the object is a long one, most of its methods are short ones that are activated by a certain menu command and that send proper messages to lower level objects to carry out the desired operations. They are in most cases self-explanatory and not explained in detail here. Analysewindow also brings together all the other Windows (such as the spectra window) that other object are responsible for.

Important methods

FormCreate	Called when the Analysewindow is created when the program is started. Initializes some global variables and creates a Win95 registry key to store program information.
LoadSpectraFile	Creates a new spectra object, asks the filename to load and calls the ReadSpectra method of the spectra object to load the spectra waveform.
LoadLineFile	Asks line file name and calls the LoadLines method of spectra object to load the lines.
RefreshStatusInfo	Displays in the bottom of the window information about the total spectra range and number of lines.
Options1Click	Responds to the File/Options menu command. Fills the current options settings to the OptionDialog object and reads the new values after dialog processing.
SaveProject	Creates a file for project saving and writes the general project parameters to the file. Calls the SaveBands and SaveStates methods of MyFit object to save the fitted bands and found state parameters.
LoadProjectGeneral	Reads the general project parameters from the project file.
TileFour, TileThree, TileTwo, TileOne and TileOneVertical	Arrange the sub-windows if the AnalyseWindow neatly on the screen.
UpdateBandType	Enables and disables certain menu commands in the band menu based on the type of band that is selected.

SpectraFileConversion1Click Responds to the **Spectra / Spectra File Conversion** menu command. Asks the name of the spectra file to convert to other format and calls the specific spectra loading routines in the **spectra** object depending on the type of the spectra to convert. Finally calls the **WriteSpectra** method of the **spectra** object to save the converted spectra.

SpecWin object

Found in unit SPECWIN.PAS

Lines of code 660

Parent object TForm (Delphi standard object for a Window)

The *SpecWin* object was the starting point of the whole *WinAnalyse* program and is still in a way the heart of the program. Originally the program was meant to be only a visual aid at looking at the spectrum waveform instead of relying on cumbersome multipage printouts of the spectrum. The sophisticated analysis and calculation functions were added later.

Spectra Window displays the spectrum information provided by the **Spectra** object and band assignment information provided by the **Fit** object. For a good of the Spectra Window, see the Figure 28 on page 71 in the program users manual.

The main drawing routine is **DrawGraphics**. *DrawGraphics* displays the spectrum Waveform with the method **DrawSpectra**. On top of the spectrum, line position markers are drawn with **DrawPeakMarkers**. Peak assignment labels are added with **DrawAssignmentLabels** method, prediction labels with **DrawPredictedLabels** and prediction lines with the method **DrawPredictedLines**.

The spectrum can be displayed with any zoom level. Routines responsible of viewing window setting are **ZoomIn** and **ZoomOut** for zooming coupled with **Scroll** and **ScrollLarge** for view scrolling. Viewing and zooming can also are controlled by mouse through the methods **FormMouseDown**, **FormMouseMove**, **FormMouseUp**.

Assignments can be made in the spectra window and are performed by **AutomaticAssign1Click** method.

Procedure DrawGraphics

DrawGraphics is called automatically by Windows every time the spectrum window needs to be redrawn due to becoming visible or being resized, for instance. The **startx** and **endx** input parameters define the area of the window to be redrawn. *DrawGraphics* can be used to redraw only small horizontal part of the window; this is used when the window has been scrolled and the new area that became visible has to be drawn.

`DrawGraphics` calculates the first and last wavenumber of the area to be drawn (variables `drawstart` and `drawend`) and also the first and last peak number that are located in the area (variables `FirstLine` and `LastLine`). These are passed to various drawing routines that `DrawGraphics` calls: **DrawSpectra** to draw the spectra waveform, **DrawPeakMarkers** to draw the peak marker lines, **DrawAssignmentLabels** to draw the assignment label boxes, **DrawPredictedLines** to draw the prediction marker lines and **DrawPredictedLabels** to draw the prediction marker boxes.

Procedure **DrawSpectra**

DrawSpectra method draws the spectra waveform by calling **DrawSpectraLow** (when the zoom level is small i.e., large wavenumber range is visible) or **DrawSpectraHigh** (when the zoom level is large i.e., small wavenumber range is visible).

Procedure **DrawSpectraHigh**

DrawSpectraHigh goes through the horizontal screen area to be redrawn one pixel at a time. For each pixel it finds the vertical position of the spectrum waveform with the **WaveToWindowY** method and draws a continuos line displaying the spectrum by calling the **LineTo** method of **Canvas** object (the drawing surface of the spectra windows).

DrawSpectraHigh routine performs well, when the zoom level is high so that there is not much details visible (Figure 22, left). On lower zooming levels, peaks can be missed and the procedure **DrawSpectra** (that uses supersampling) should be used. Note that the **DrawSpectra** method selects automatically the correct routine to use depending on the zoom level.

Figure 5 on page 19 is a good example of highly zoomed spectrum where *DrawSpectraHigh* has been used.

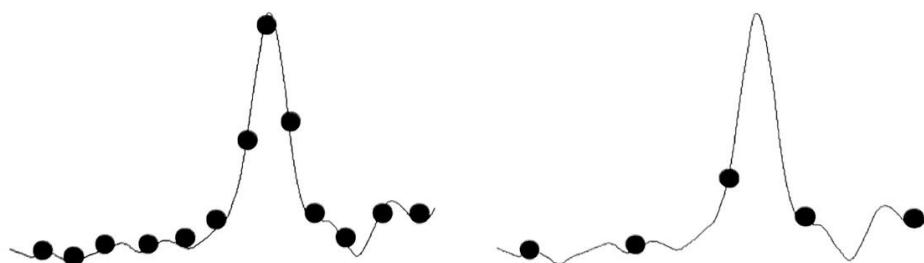


Figure 22: *DrawSpectraHigh* procedure performs well on high zoom levels when samples are taken dense on the spectrum data (left). When zoom level is too low (right), *DrawSpectraHigh* misses peaks because sampling grid is too sparse.

Procedure DrawSpectraLow

To solve the peak missing problem present in the DrawSpectraHigh routine at low zoom levels (see Figure 22), another routine, *DrawSpectraLow*, was programmed. This procedure takes multiple samples per each vertical pixel row (*supersampling*) and finds the lowest and highest intensity value in the pixels range. A vertical line is then drawn at the pixel column between the lowest and highest intensity values.

Figure 2 on page 17 is a good example of lowly zoomed spectrum drawn with DrawSpectraLow.

Procedure DrawPeakMarkers

This procedure draws yellow vertical lines at the wavenumber positions of detected spectrum peaks. It iterates through the lines in the area to be drawn and fetches the line wavenumbers from the **Line** array of **Spectra** object. Screen position of the line is calculated with **WaveToWindowX** method and line drawn with the **MoveTo** and **LineTo** methods of the canvas object (which represents the drawing surface of the window).

Finally, small labels are drawn on top of every nth peak marker line to show the number of the line. Methods **Rectangle** and **TextOut** of the canvas object are used for this.

Procedure DrawAssignmentLabels

DrawAssignmentLabels draws small two-colored boxed on top of the peaks that have been assigned to some bands. The procedure draws labels either to top of all assigned peaks (when the **DrawAllBandLabels** flag is set) or only on top of the selected band.

All *m*-values are iterated through all bands and drawing is performed only for those assigned lines that fall within the drawn region defined by the parameters **FirstLine** and **LastLine**. Band assignment information is fetched from the **band** table of the **Fit** object.

Depending on the value of the **LabelType** flag, either the *m*-value of the assignment or the band name of the assignment is written to the assignment label. Procedure **DrawBandLabel** is called to perform the actual drawing job.

Note that same line can be assigned to more than one band i.e., there can be multiple assignments on one peak. For example of this, see the second peak from left on the Figure 28 on page 71. To avoid overlapping of assignment labels, the second assignment label must be drawn higher than the first, third one still higher and so on. This has been accomplished by keeping a variable **Assignments** for each line and incrementing it after each drawn assignment. Assignment label position is then shifted according to the value of the variable.

Procedure DrawPredictedLabels

At one point the Spectra Window displayed only blue prediction lines for the selected band. It became soon clear, however, that labels similar to the assignment labels as described above would be useful also in the predicted line positions of *all* bands. This would allow the user to see what transition(s) is responsible for certain spectrum feature even if the feature is so badly formed that it hasn't been assigned to some of the peaks causing it. The prediction labels becomes especially useful in a multiple peak overlap situation. The aid that prediction labels give to spectrum understanding is clear from Figure 23 below that shows one of the more complex areas of the ν_4 band system spectrum.

DrawPredictedLabels iterates through all m -values of all bands and draws small labels to the predicted positions for the *nonassigned* m -values. Band prediction information is fetched from the **band** table of the **Fit** object, more precisely from the bands **pred** (prediction) table. The prediction labels are drawn with the procedure **DrawBandLabel** and look like assignment labels but have yellow border instead of black.

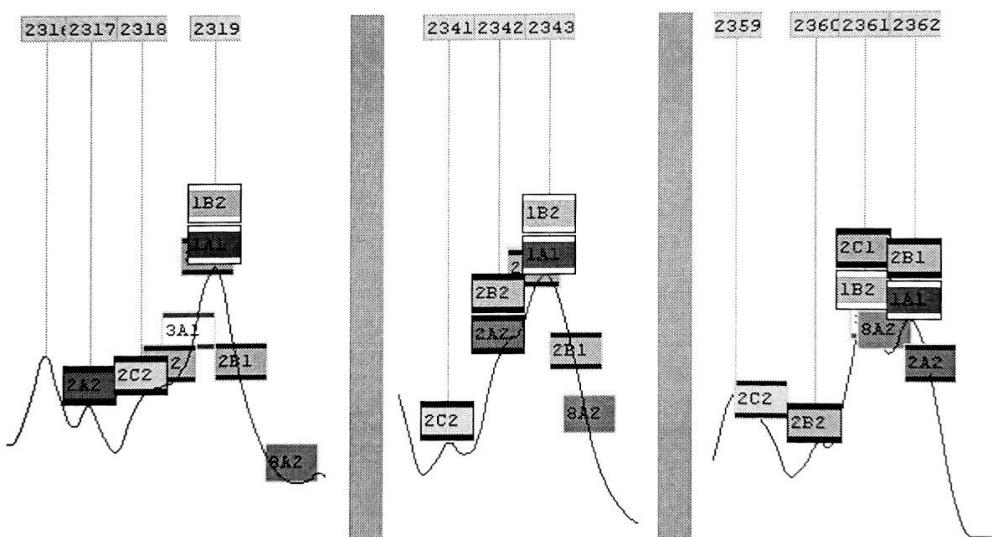


Figure 23: Three images of the assigned spectrum in 2B steps near 485.98 cm^{-1} . Note that some assignment labels with black borders have been replaced by prediction labels with yellow bordered.

Procedure DrawPredictedLines

Draws blue vertical lines at the predicted line positions for the selected band. Lines are drawn to all predicted positions, whether assigned or unassigned. Works much like the **DrawPredictionLabels** (see above) but uses for drawing the **DrawVertLine** method instead of **DrawBandLabel**.

Procedure Scroll

It is useful for the spectrum visual analysis to move within the spectrum in small rapid steps, creating an illusion of continuous scrolling. The scrolling routine is activated by the hot keys CTRL+B and CTRL+N.

Procedure *Scroll* performs the scrolling using the **CopyRect** method: the whole contents of the Spectra Window is copied few pixels to left or right, depending on the direction of scrolling. Then the **DrawGraphics** method is used to fill the new area that has became visible of the spectrum.

Procedures FormMouseDown, FormMouseMove, FormMouseUp and ZoomIn

These three methods allow the user to select a portion of the viewed area of the spectrum in order to zoom to it (with the **ZoomIn** method). When the left mouse button is pressed down, the **FormMouseDown** method sets the **DoingSelection** flag. When the mouse pointer is moved, the **FormMouseMove** method is called by Windows. If the DoingSelection flag is set, this method inverts the new portion of the selection and updates the variables that define the selection. **FormMouseUp** causes the DoingSelection flag to be cleared.

ZoomIn method calculates the new spectral range to be viewed depending on the selection and triggers a window redraw using the windows **Invalidate** method.

Procedure LineAssignment

Pressing the right mouse button causes the **FormMouseDown** method to call *LineAssignment* method that allows the user to add or remove assignments of the peak nearest the pointer. The method finds first the line nearest to the mouse pointer with **NearestLine** method of the **Spectra** object and marks it with a black vertical line. Then it sets up a pop-up menu with options to assign the nearest line or remove assignments. Finally it pops up the menu with **popup** method of the **LineMenu** object. Separate methods **AutomaticAssign1Click**, **RemoveAllAssignments1Click** or **RemoveAssignment1Click** will be called by windows depending on the menu option user chooses.

Procedure AutomaticAssign1Click

This method is called when user selects the menu command “Automatic Assignment” from the pop-up menu (see above). The method adds the line nearest the cursor as determined previously by the **LineAssignment** method as an assignment to the selected band by calling the **AddAssignment** method of the **SelBand** object. The *m*-value to use in the assignment is obtained by calling the **PredictedM** method of the same band (PredictedM finds the predicted peak nearest to the wavenumber of the selected peak).

Other important methods

WaveToWindowX	Function that converts a given wavenumber to screen x-coordinate using information about the spectral range currently viewed and screen size.
IntensityToWindowY	Function that converts a given spectra absorption intensity (0...1) to screen y-coordinate using information about the screen size.
WaveToWindowY	Function that finds the spectra absorption intensity at given wavenumber by calling Spectra objects Value method and further converts the result to screen y-coordinate using the IntensityToWindowY .
ScrollLarge	Scrolls a full screen by setting new values for the ViewStart and ViewEnd variables and redrawing the screen.

Spectra object

Found in unit SPECTRA.PAS

Lines of code 370

Parent object None

The *Spectra* object serves as a container for the spectral data (waveform and peaks). It provides few but important services processing the spectral data such as loading and saving the spectrum or peaks, finding the spectrum value at given wavenumber

function Value

This function returns the value of the spectrum absorption intensity at requested wavenumber. Because the spectrum intensity data is provided only in discrete points, the Value function uses 3rd order polynome (*bicubic*) interpolation to calculate the intensity value between data points. The idea of the interpolation is shown in Figure 24: two points of spectral data are taken from both sides of the required wavenumber, a third order function going through the points is constructed and value of the function at the requested wavenumber is returned to the calling procedure.

$$43) \quad y(x) = a_3(x - x_0)^3 + a_2(x - x_0)^2 + a_1(x - x_0) + y_0$$

where the points of spectral data used are (x_0, y_0) to (x_3, y_3) and coefficient a_1 to a_3 are calculated with formulas:

$$44) \quad \begin{aligned} a_3 &= \frac{1}{d} [3(y_1 - y_0) - \frac{3}{2}(y_2 - y_0) + \frac{1}{3}(y_3 - y_0)] \\ a_2 &= \frac{1}{d^2} [-\frac{5}{2}(y_1 - y_0) + 2(y_2 - y_0) - \frac{1}{2}(y_3 - y_0)] \\ a_1 &= \frac{1}{d^3} [\frac{1}{2}(y_1 - y_0) - \frac{1}{2}(y_2 - y_0) + \frac{1}{6}(y_3 - y_0)] \end{aligned}$$

Where d is the wavenumber distance between the points.

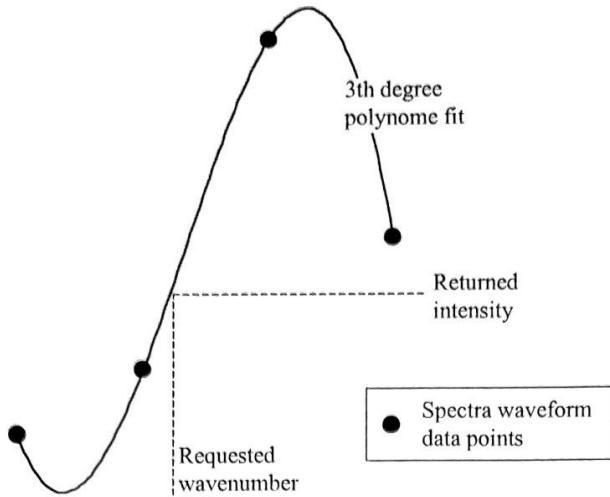


Figure 24: Spectrum smoothing with polynome interpolation

function NearestLine

Finds the number of the line in the line table nearest to a requested wavenumber. This low-level routine is used by many higher level methods, for example the combine branches method (see page 59 for description) to find how near the predicted lines are actual lines of the spectrum.

Because the lines are ordered in the line table by increasing wavenumber there is no need to iterate through all (usually many thousands) of lines. Instead, *NearestLine* method uses a powerful division search can be performed where the estimated time to find the nearest line is proportional to the logarithm of number of lines.

Other important methods

ReadSpectra	Loads the spectra waveform from a given standard format file.
WriteSpectra	Writes the spectra waveform to a given file in standard format.
ReadDIVSpectra	Reads a spectra in DIV binary format for conversion purposes.
ReadDATSpectra	Reads a spectra in DAT ASCII format for conversion purposes.
Normalise	Scales the spectral intensity data to range 0...1 for conversion purposes.
Invert	Inverts the spectral intensity data for conversion purposes.
LoadLines	Loads given ASCII format peak list file and sets the data to the peak table in memory.
Crop	Allows a wavenumber portion of the spectra waveform to be separated from the rest. A large spectra can be broken into different band system ranges for example.

Fit object

Found in unit	FIT.PAS
Lines of code	550
Parent object	None

Fit object acts as a container for all the **band** objects that are used to store and manipulate spectral assignments and **state** records that store the vibrational state parameter information. The *Fit* object itself provides methods that affect multiple bands or manipulate states, the main service being the combination P- and R-branches to a PR-band (the theory of which is explained in chapter *Combining the P- and R-branches* on page 23).

procedure CombineHalfbands and CombineHalfbandsGlobal

There are two main methods for combining P- and R-bands to a PR-band, *CombineHalfbands* and *CombineHalfbandsGlobal*. Both use the GSCD formula of equation (30) as explained on page 24 to predict line positions in the other branch based on peak assignments of the selected band. Both iterate through all possible lower state candidates that have their **use** flag set and all Δm values within the range defined by the global parameter **MaxModelError**. Both call functions from the **band** object to calculate a fitness value estimating the accuracy of the prediction.

There is one important difference. *CombineHalfbands* iterates through all the assigned bands that have been assigned in the opposing branch and compares the predicted line positions to the line positions assigned to those bands band by band. If, for example, the selected band is a P-branch then the routine looks up all the assigned R-branches and looks how well they fit with the selected branch. On the other hand, *CombineHalfbandsGlobal* tests the predicted line positions *directly against the peaks in the spectra* regardless of their assignments.

CombineHalfbands calls the **Fitness** method of the selected band to calculate the fitness value for the combination of lower state, Δm and opposing branch. *CombineHalfbandsGlobal* calls the **FitnessGlobal** method of the selected band and the fitness value is calculated for the combination of lower state and Δm . Both procedures fill the **BestComb** table with the information of the best combinations found while working and afterwards call the **Fill** method of the **CombTable** object to display the result of the combination analysis.

Both methods have their merits and are therefore available for the user to choose depending on the situation. The advantage of *CombineHalfbands* is that the combinations it produces tend to be more reliable – they have after all been put together from two assigned sequences of peaks that the user

has considered satisfactory. On the other hand, sequence is always only a sequence and the global version of the procedure can sometimes find more combinations when no more are found with `CombineHalfbands`.

MergeToPR

`CombineHalfbands` and `CombineHalfbandsGlobal` do not perform the actual branch combination – they simply show the user the different alternatives. When the user has selected the desired combination, `MergeToPR` does the actual branch joining.

Other important methods

<code>LoadStates</code>	Loads from an ASCII disk file the state parameters in state table.
<code>SaveStates</code>	Saves to an ASCII disk file the state parameters in state table.
<code>LoadBands</code>	Loads bands from the project file by calling the <code>Load</code> method for each band.
<code>SaveBands</code>	Saves bands to the project file by calling the <code>Save</code> method for each band.
<code>CopyLowerState</code>	Copies fitted lower state parameters from the selected band to the state table.
<code>CopyUpperState</code>	Copies fitted upper state parameters from the selected band to the state table.
<code>SeparateBand</code>	Breaks a <i>PR</i> -band back into <i>P</i> - and <i>R</i> -branches.
<code>SortBands</code>	Sorts the bands according to name, lower state or band origin.

Band object

Found in unit BAND.PAS

Lines of code 870

Parent object None

Here comes the interesting stuff: *Band* objects hold all the assignments made in the spectrum and they also are subject of all the calculations and fits described in the chapter *Fitting the Spectra* starting at page 22. If the `SpectraWindow` object is the heart of the program, *Band* object is definitely the brains.

A *band* object contains a `PeakTable` array for assigned peaks and for predicted peaks. These arrays have a `Peak` record for each possible value of m . *Band* also has two `State` records to store the calculate upper state and lower state parameters.

The calculating methods of *band* object fall into two categories. First there are the routines that are used in branch prediction and combination as described in the chapter *Combining the P- and R-branches* on page 23. This category includes the methods `CombPredLines`, `Fitness` and `FitnessGlobal`. In the second category are the fitting functions described in the chapter *Parameter fitting* starting at page 27 that are designed to obtain rotational parameters of the vibrational states

and predict new peak positions. Here are the procedures **Calculate**, **PredictPolynome**, **Fitup**, **GSCD** and **SolveQOptimalM**.

procedure CombPredLines

CombPredLines starts the branch combination process. This procedure is called by **Fitness** and **FitnessGlobal** to calculate the predicted positions of lines in the other branch, using the formula (30) on page 24 for the wavenumber difference between the *P*- and *R*-branch lines. It can either predict *P*-lines based on *R*-assignments or *R*-lines based on *P*-assignments.

Function Fitness

Fitness calculates a number representing, how well the lines from the other branch predicted with GSCD formula (30) match the actual lines in the spectra. The details of the theory behing **Fitness** is described on page 25.

It might happen that only few – or even none – of the predicted lines coincide with those assigned in the other branch. In such situation **Fitness** – or **CombineBranches** that uses it – doesn't produce good results and one should attempt to use the **CombineHalfbandsGlobal** that utilizes *FitnessGlobal* (see below) which is not restricted by peak assignments in the other branch.

Performance of the fitness selection

Figure 25 shows the results of a typical combination analysis using **CombineBranches** and **Fitness**. A total of 9000 combinations (15 opposing bands \times 20 Δm values \times 30 lower states) has been calculated to and 10 best fitting combinations are tabulated in the figure. Column **Band2** is the name of the opposing branch used in the combination. Column **Lower** is the number of the lower state (as found in the state table) used in the GSCD formula for predicted lines. Column **Terms** shows how many peak prediction–observation pairs were used to calculate the fitness value. Columns **Delta m1** and **Delta m2** show the required *m*-value shifts in both branches for the combination. We can see the best combination having significantly better fitness than even the second best. The fully automatic calculation took 3 seconds.

N	Band2	Delta m1	Delta m2	Lower	Fitness	Terms
1	1C1	3	0	3	0.11	62
2	1C1	3	0	33	3.89	62
3	X2	-10	-9	28	5.81	10
4	X2	-8	-7	4	9.14	12
5	X10	6	9	31	9.24	5
6	X2	-8	-7	30	13.31	12
7	1A2	-4	-12	34	15.55	46
8	1A2	-4	-12	30	15.62	46
9	1C1	3	0	29	16.46	63
10	1A2	-4	-12	4	16.79	46

Best (and correct) combination stands out clearly

Figure 25: Best fitting combinations found by the method *Fitness* (program screen shot)

In the end of this study the performance of the final version of the combination algorithm was tested by breaking all the 28 analyzed PR-bands to their respective P- and R-branches and letting the software to try to combine them back. For 25 of the 28 bands the program gave the best fitness to the single correct combination out of the 9000 candidates. Even for the rest three bands the correct combination was among the best four combinations ones listed by the program.

Note that it is possible in the program to limit the number of lower states used in the combination analysis if, for example, all the bands from certain lower states have already been found.

function FitnessGlobal

FitnessGlobal attempts to connect P- and R-branches to a PR-band as **Fitness** (see above), but it compares the predicted peaks directly to the peaks of the spectrum in the band system. Figure 26 shows a typical result of combination analysis done using the method **CombineHalfbandsGlobal** that uses the *FitnessGlobal*. The fitness value itself is calculated with formula (31) as with **Fitness**. Note that Figure 26 does not have values in **Band2** or **Delta m2** columns since no assignments of other branches are observed.

N	Band2	Delta m1	Delta m2	Lower	Fitness	Terms
1		0		3	0.18	
2		0		33	4.08	
3		0		29	19.76	
4		0		31	30.82	
5		0		39	121.19	
6		6		43	183.26	
7		0		43	204.02	
8		0		16	241.97	
9		-5		15	252.13	
10		4		43	264.98	

Best (and correct) combination stands out clearly

Figure 26: Best fitting combinations found by the *GlobalFitness*

FitnessGlobal is slightly less sophisticated in its idea, but it can sometimes help in situations where the regular **Fitness** becomes useless due to incomplete assignment, for example.

Calculate

Calculate is a high level routine for all calculations. It decides which fits to perform depending on the status of calculation flags. The ground state combination difference fit is performed with the **GSCD** method if **CalcGSCD** flag is set. Then, depending on the value of the **PredictionMode** flag, either direct polynomial prediction is performed with the **PredictPolynome** method or reduced wavenumber fit is performed by calling the **Fitup** method. In the former case, the degree of the polynomial fit is in most cases set to four (as explained in the chapter *Fourth order fit a* on page 22) but lowered if there are only few assignments.

Procedure PredictPolynome

Fits a fourth order polynome in m to the assigned peaks of the spectrum according to the equation (27), or – if the absolute m values are not known – according to the equation (29). *PredictPolynome* sets up arrays that hold the X-values, Y-values and the weights to be used in the fit and calls the procedure **PolynomeFit** (see page 66) to perform the actual fitting.

After the fit, *PredictPolynome* calculates the predicted wavenumbers for each m -value peak from the obtained polynome $y = c_4x^4 + c_3x^3 + c_2x^2 + c_1x + c_0$ and fills them to the **Pred** table of the band. Then the values of the rotational parameters B'', D'', B', D' and ΔE_{vib} as shown in the equation (32). The errors for the parameters are calculated using the formula (24) on page 15.

Procedure Fitup

Fitup performs the reduced wavenumber fit as described by equation (37) on page 29. It constructs arrays that hold the X-values ($J'(J'+1) - k'^2$), Y-values ($\tilde{\nu} - Z$) and the weights to be used in the fit for each assigned peak and calls the procedure **PolynomeFit** (see page 66) to perform the actual second order polynomial fit. The *FitUp* method works for both PR- and Q-branches since the reduction factors Z are calculated by the method **ReducingFactor** using either the formula (36) (for PR-bands) or (40) (for Q-branches).

After the polynome coefficients in the $y = c_2x^2 + c_1x + c_0$ have been determined, *Fitup* calculates the predicted wavenumbers for all m -values and the values of the upper state rotational parameters and ΔE_{vib} as in the equation (39). The errors for the parameters are calculated using the formula (24) on page 15.

Procedure GSCD

GSCD method performs a ground state combination difference calculation on the band to obtain lower state rotational parameters, as described by the (33) on page 28. It constructs arrays that hold the X-values ($(J' + \frac{1}{2})^2$), Y-values ($(\tilde{\nu}_r - \tilde{\nu}_p)/(J' + \frac{1}{2})$) and the weights. There will be one data point per each pair of assignments from *P*- and *R*-branches having the same upper state rotational quantum number J' . Weight calculation for the GSCD datapoints is done using the formula (26) as described on page 16.

A first degree fit is done to the data with the **PolynomeFit** method and lower state parameters calculated from the fit coefficients with the formula (34).

Procedure SolveQOptimalM

This procedure attempts to find correct shift of m -values for a *Q*-branch whose m -assignments are uncertain. The idea of the method – aligning the origin of the *Q*-branch with a corresponding PR-band – is described in the chapter **Finding the correct m-values** on page 32. The method asks user through a input dialog box the name of the PR-band to be used to adjust the center of the band. It then iterates through a large number of m shifts and for each shift calls the **Fitup** method to calculate the corresponding band origin. The m shift that produces the minimum difference between the band origins is recorded and after the iteration user may choose to make the shift.

function PredictedM

This function estimates for a given wavenumber the nearest m number in the band. It is used in the automatic assignment of peaks: for the peak wavenumber *PredictedM* can give a suitable m -value to use in the assignment.

The predicted m -value is found simply by iterating through the **Pred** table of the band and finding the predicted peak that is nearest the requested wavenumber. The Pred table has been filled with predicted wavenumbers by the fits in **PredictPolynome** of **Fitup** (see above).

If the number of assignments in the band is so small (0,1 or 2) that no fit has been yet performed, different heuristics is used. With 1 or 2 datapoints the m -value is taken to be the next unassigned value. With 0 datapoints the m -value is taken *ad hoc* to be -30, 10 or 30 depending on the band type (remember that the m -values need not to be correct in the beginning of a band analysis)

Other important methods

Load	Loads the band data (assignments and parameters) from the given project file.
Save	Loads band data (assignments and parameters) to a given project file.
Refresh	Refreshed the data in all windows that contain information about the band: the Spectra Window, Band table and Band assignment table.
EditProperties	Displays the Band Properties dialog box and allows the user to edit band parameters.
ReducingFactor	Calculates the reducing factor Z (as defined in equation (36) on page 28 and equation (40) on page 32) for the band for a given m -value. Used by the FitUp method.
DrawBandLabel	Draws the two colored square band label for the band as featured for example in Figure 10.
NearestAss	Finds the band assignment that is nearest to the given wavenumber.
Assignments	Returns the number of assignments in the band.
FindNext	Searches for the next assigned m -value in the band starting at given position.

TableForm object

Found in unit	TableFormUnit.PAS
Lines of code	650
Parent object	TForm (Delphi standard object for a Window)

In addition to the Spectra Window, there are various tables displaying relevant data, namely, states, assigned bands, peak assignments, GSCD details, branch combinations and combination details. See for example the Figure 27 on page 68. These tables have been constructed in the program with the *TableForm* object. TableForm is a window containing a Delphi **StringGrid** component that forms the actual table.

procedure SavetoFile1Click

Data in any table can be saved to ASCII text disk file. This makes it easy to transfer the results obtained to a word processor for publishing purposes without the need to copy them from screen. This method used standard Pascal file handling routines to write the file.

procedure DrawResidual

This procedure is used by BandDetail table, GSCD detail table Combination detail table to draw small bars displaying graphically the residuals i.e., wavenumber differences between the predicted and observed wavenumbers. *DrawResidual* calculates the color code do that the color the residual box will be drawn by depends on the size and the direction of the residual. It uses the **Rectangle** method of the **canvas** object to draw the box.

procedure Fill

Each of the different types of tables has a *Fill* procedure of its own, setting up the relevant data to the table. Fill procedures use the **Cells** property of the **StringGrid** component to write the data to the table. Different filling routines obtain their data from different sources. For example, the Fill routine of **BandDetail** table (showing the assignments of the selected band) fetches the assignment data from the **SelBand** object.

procedure Edit (applies to BandDetail table and StateTable)

Two of the tables have *Edit* procedures that allow the user to modify data in the tables. These procedures verify the values user has inputted and transfer if further to the relevant data structures.

procedure Select

The *Select* procedure allows the program to respond, when the user selects certain row of a table. For example, when the user selects a row in the peak assignment table, the Select methods sends a message to the **SpectraWindow** object causing it to display the area of the spectra where the selected assignment is located.

SqrMatrix object (*Square matrix object for linear algebra*)

Found in unit	LINALG.PAS
Lines of code	160
Parent object	None

All the fits used by the present version of the program are polynomial fits and linear in their nature. Such fits can be performed by matrix inversion as described in the chapter ***Polynomial fits*** on page 15. The *LinAlg* unit and its *SqrMatrix* (Square Matrix) object provide the necessary machinery for performing a polynomial fit of any degree and all the procedures that use fitting in the analysis program use them. It should be noted that this unit is completely independent and can be easily transferred to any other program project that requires linear algebra calculation.

Procedure PolynomeFit

PolynomeFit takes as input parameters an array of X-values, Y-values and Weights. It uses a **SqrMatrix** object, representing a square matrix, and calculates the elements of the matrix according to the formulas (22). The matrix is then inverted by calling its **Invert** method and polynome coefficients calculated from equation (23).

The RMS (Root Mean Square) error is calculated after the fit and, using the RMS value, the errors of obtained polynome coefficients. Results are returned to the calling procedure in the **Coeff** and **CoeffErr** arrays.

Other important methods

Invert	Performs matrix inversion for a SqrMatrix object to solve a system of linear equations.
Transpose	Performs matrix transposition for a SqrMatrix object.

8. WinAnalyse Users Manual

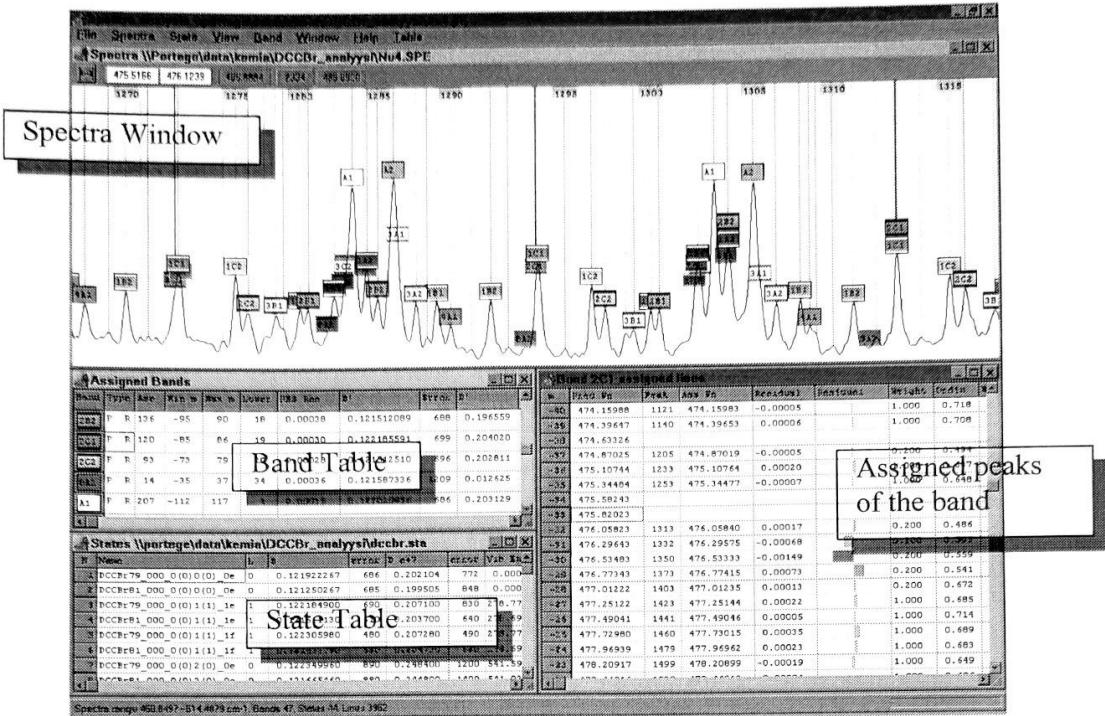


Figure 27: Some of the windows of the spectrum analysis application

Introduction

An extensive and user friendly computer application has been developed along the analysis work to automate the analysis process to as great extent as possible. Program is suitable for the rotational analysis of all linear molecules. This section explains the usage of the program from the users point of view. No mathematical or theoretical understanding is needed to read this section, but references are provided to other part of this document that explain the inner workings of the program (the chapter **7. WinAnalyse technical** documentation at page 50), the underlying theory (the **chapter Error! Reference source not found.**) and underlying mathematical methods of the analysis (the chapter **4. Fitting the spectrum**).

The program is freeware and the executable, Delphi 2.0 source code and demonstration data files (including the data files for the analysis of this work) can be requested from the author through internet by sending mail to robert@iki.fi.

It is recommended that any user of the program reads through this documentation (user manual and the program technical documentation) once before starting to use analyze his or her spectrum.

Starting an analysis

System requirements

- PC system with 486/33 processor (Pentium recommended)
- 16 MB RAM
- Microsoft Windows95 or WindowsNT 4.0 operating system.
- SuperVGA display with 800 × 600 resolution (1024 × 768 recommended) and 256 colours (16 bit colour recommended).

Installation

Simply copy the executable file **analyse.exe** to a suitable folder. It is also recommended that a separate folder is kept for the data files, one folder per molecule.

Spectrum waveform input file

Two data files describing the spectrum are needed to begin the analysis. First is the *spectrum waveform file*, which simply lists the intensity of the absorption at constant wavenumber intervals. The spectrum filename must have end with **.SPE**. The file is an ASCII text file and looks following:

```
Spectra Data File
StartWavenumber 450.84971993
EndWavenumber 514.48785307
Points 35904
Intensity List:
0.1135
0.1065
0.1099
...
```

The **points** means the number of intensity datapoints which is equal to the number of lines in the spectrum file after the **Intensity list** line. **StartWavenumber** and **EndWavenumber** are the wavenumbers of the first and last point in the intensity list, respectively.

The intensity data is assumed by the program to be scaled between 0 and 1. However, a file with different intensity range can be read by the program, scaled to the 0...1 range with the menu command **spectra / normalize** and saved in correct form with the menu command **Spectra / Save spectra file**.

The distribution package contains a sample spectrum waveform file **CO_Fundamental.SPE** that contains the infrared FTRI spectrum of carbonmonoxide fundamental transition.

The program is able to convert few other spectrum formats to the one it uses. The conversion is started with **Spectra / Spectra File Conversion** menu command and the two supported formats are:

DIV Format This is a binary format produced by the Bruker calibration software. The spectrum data for this project was originally in DIV format.

DAT format. This is a ASCII text format and looks like this:

```
480.12334    45.6  
480.12365    40.2  
480.12389    15.6  
...
```

Where the first column contains the wavenumbers and the second column the respective intensities. note that the wavenumbers do not have to be equally spaced in this format. The program converts the data to regular evenly spaced format by interpolation and resampling.

Spectrum peak listing input file

A separate file must be provided by the user listing the peaks in the spectrum and looks following:

```
Lines 2385  
1      575.103977    0.9183  0.0411  4.3    0.2    0.9561  
2      575.188647    0.9579  0.0212  3.4    0.08   0.9728  
3      575.805783    0.9343  0.0377  5.61   0.24   0.8348  
...
```

First row of the file contains the word “Lines” and the number of peaks in the file.

The first column is the line number and must proceed in increments of one. Second column is the peak wavenumber in cm^{-1} and third is the peak intensity. The last four columns contain peak information that is not presently used by the program (Ordinate, Width, E.W., Asymmetry) and can be set to zeros.

Note that in the program the spectrum waveform is only as a visual aid. All calculations is performed using the spectrum peak listing. Hence it is more important for the peak listing wavenumbers to be properly calibrated than the spectrum waveform.

Note that separate software must be used to analyze the spectrum contour for peak positions. WinAnalyse does not currently have a peak detection algorithm.

Setting up a new analysis project

- Start the WinAnalyse program
- Open the spectrum file with menu command **Spectra / Load Spectra File**
- If necessary, normalise the spectra intensities to the display range with menu command **Spectra/Normalize**. If the spectra is upside down, invert it with **Spectra/Invert**. After changes, save the spectra with **Spectra / Save Spectra File** command.
- Load the line file with menu command **Spectra / Load Line File**.
- Zoom some part of the spectra with **Ctrl + Z** to see that the line markers are correctly positioned on the peaks. Zoom some peak on high magnification. If the markers are not exactly aligned with peaks, shift the waveform slightly with **Spectra / Horizontal Shift** menu

command. Remember that the calculations are done with the peak list data and are not affected by any modifications to the waveform. After changes, save the spectra with **Spectra / Save Spectra File** command.

- Tile the windows by pressing **F6**.
- Initiate a state table with the menu command **State / New**.
- Save the state file with menu command **State / Save State File**. Give a name to the file. A typical state file name contains the name of the molecule whose states it contains.
- Initiate the first band to analyse with the menu command **Band / New**. Accept the settings of the dialog box.
- Give the menu command **File / Save Project** to save your project and give a name to the project. A typical project file name contains the name of the band system that is analysed in it.

The analysis project has now been initiated. Try exiting the program, starting it again and loading the project with **File / Load Project** menu command. Note that every time you save your project, all relevant data (states, band assignments and project settings) are saved.

The Spectra Window

Although spectra analysis with the software is in many respects automatic, a good visual view of the spectra is an invaluable aid in the fitting process. This view is provided by the spectra window, in many respects a central part of the software. To play around with the spectra window with all the elements included, you can load a demonstration project Nu4.PRJ that is provided with the program distribution files. The implementation of the spectra window in the analysis program is described in the software technical documentation on page 52.

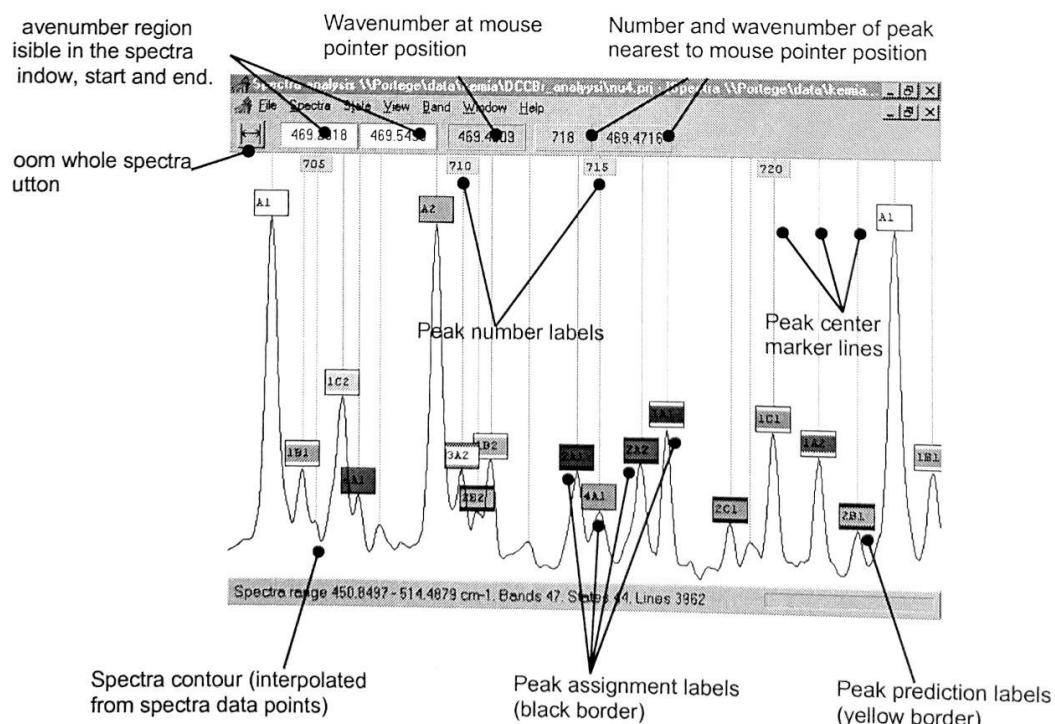


Figure 28: The spectra window

Spectra window elements

Look at the Spectra Window shown in Figure 28.

Spectra contour shows the measured absorption at different wavenumbers using the data from the spectra data file of the current project. Because the spectra is recorded only in discrete points, the data is interpolated to form a smooth curve. See page 53 for implementation of the spectra drawing in the program.

Peak marker lines show the center positions of the absorption peaks as listed in the peak data file. Only these line positions are used in the automatic fitting calculations. The spectra contour is provided for visual aid only and is not used in the analysis calculations in any way. Peak marker lines can be hidden or shown with menu command *View* → *Line Markers* or pressing F2. Peak marker lines are drawn by the *DrawPeakMarkers* procedure (description on page 54)

Peak marker numbers. Every nth peak marker line has a small label showing the number of the line in the line data file. The density of the labels (value of n in the “every nth peak”) can be changed in the *options*-window, displayed with the menu command *File* → *Options* or hotkey Ctrl + O.

Peak assignment labels. The fitting of the spectra consists of assigning the peaks of the spectra (as shown by the peak marker lines) to different bands and rotational quantum numbers of the molecule. Peak assignment labels, small boxes with black frame and two color code, show the assignments that have been made. Labels with same colors belong to same band. The colors and other band properties can be changed in the *band options window* (see chapter **Working with bands** on page 80). When peaks of two different bands overlap, the merged peak can be assigned to both bands as is seen with some peaks in Figure 28.

The text in the labels can show either the three letter band name (as in the Figure 28), the rotational *m*-quantum number assigned to the peak or nothing. The labeling mode can be changed in the *options*-window, displayed with the menu command *File* → *Options* or hotkey CTRL+O. Peak assignment labels can be shown or hidden with the menu command *View* → *All Bands* or by pressing F3. Alternatively, only the labels of the selected band can be shown with command *View* → *Selected Band* or by pressing Shift + F3.

There are also some special display modes concerning the peak marker labels accessible from the *options*-window. The *only m=0 peaks visible* option hides all other labels that those having *m* = 0. Since *m* = 0 peaks are located in the start of the *Q*-branch of the band, this mode is useful for quick identification of *Q*-branches in the assigned spectra. The *Hide Halfbands* option can be used to tidy up the screen somewhat when only complete PR-bands and *Q*-branches. The term halfbands refers

to some series of peaks in *P*- or *R*-branch that have not yet been combined. These halfbands are not really fully assigned, so hiding them allows one to view only the fully assigned peaks.

The peak assignment labels are drawn by *DrawAssignmentLabels* procedure in the *TspectraWindow* object. For implementation information, see page 54.

Peak prediction labels look much like the peak assignment labels (see previous section) but instead of marking assigned peak positions, they point to predicted peak positions of various bands. The visual difference is that prediction labels have red frames instead of the black frames of assignment labels and they can be located in any position on the spectra contour instead of being restricted to the peak marker positions like true assignments. Prediction labels are drawn only for full PR-branches and *Q*-branches, not for *P*- or *R*-branches. They can be hidden or displayed with the menu command *View* → *Prediction* markers or pressing key F4.

Peak positions are predicted and marked only inside the assigned range of *m*-values and certain range outside that range. The extent of the prediction range outside assigned *m*-values is five by default but can be changed to any integer value in the *options*-dialog box, displayed with the menu command *File* → *Options* or hotkey Ctrl + O. For example, if the prediction range is three and peaks have been assigned for *m*-values 6,7,8,10 and 11, the positions of peaks with *m*-values 3,4,5,9,12,13 and 14 will be displayed – three extra *m*-values on both sides in addition to the gaps in the assigned range.

The formulas used in the prediction depend on the type of the branch and are described in the chapter **Peak assignment** starting at page 22. The prediction labels are drawn in the program by the *DrawPredictedLabels* procedure (see page 55 for implementation details) and the prediction of peak positions if done by the *Calculate*, *PredictPolynome* and *Fitup* procedures of the Band-object (see page 63)

Predicted peak markers work much like peak prediction labels: they show the calculated peak positions (see previous section). There are some differences, however. First, predicted peak markers are blue lines instead of labels. Second, they are only drawn for the selected band, not all bands. Note that in Figure 28 there are two predicted peak markers visible and both are drawn for peaks of the A1 band, the selected band. Third, they are also drawn for *P*- and *R*-halfbands (and are useful in their assignment!) Fourth, they are drawn also on top of already assigned peaks, not only on yet unassigned ones. Like the prediction labels, predicted peak markers can be toggled on or off with the menu command *View* → *Prediction* markers or pressing key F4.

Selecting the zoom level

There are two main ways to control, which portion of the spectra is shown in the spectra window: selecting the zoom level (*how large* wavenumber range is visible at one time) and selecting the visible area (*what* range is visible). For maximum flexibility, both of these variables can be changed continuously and over a large range.

Table 10: Selecting the zoom level

<i>In order to...</i>	<i>Do the following...</i>
Reset the view to the whole spectra in memory	Press the  button in the top left part of the spectra window
Zoom a region to fit the whole spectra window	Select the desired region by dragging with mouse from the start to the end of the region. Then press Ctrl + Z (Zoom).
Increase the zoom level by 25%	Press Ctrl + Z (Zoom) without selecting region.
Decrease the zoom level by 25%	Press Ctrl + X (UnZoom)

Vertical zoom level and vertical scrolling

If the spectra does not fill vertically the whole spectra window or if there is need to look more closely to some spectra feature, the vertical magnification level can be changed. Select the menu command **File / Options** and change the field **Vertical Zoom %** to desired value.

The spectra can be also shifted vertically with the key combinations Ctrl + Q and Ctrl + A.

Selecting the region to show

When a region of the spectra is zoomed in the spectra window, the view can be scrolled to left or right to show new regions.

<i>In order to...</i>	<i>Do the following...</i>
Scroll the spectra window left (to smaller wavenumbers) by small steps.	Press and hold down Ctrl + B
Scroll the spectra window right (to larger wavenumbers) by small steps.	Press and hold down Ctrl + N

Scroll the spectra window left by 75% of the visible range.	Press Ctrl + V
Scroll the spectra window right by 75% of the visible range.	Press Ctrl + M
Change the size of the scrolling step when the spectra is scrolled with Ctrl + B or Ctrl + N	Select menu command <i>File</i> → <i>Options</i> . Change parameter “Scroll Step” to desired value.

Note the location of the scrolling keys: four consequent keys V,B,N and M in the lower right corner of the keyboard. Hence they need not to be remembered by the keys but rather by their position.

Moving from one area of the spectra to another can take much time by ordinary scrolling if the zoom level is high. Instead, lower first the zoom level by pressing Ctrl+X a few times, then scroll to desired region and finally zoom again to desired zoom level by pressing Ctrl+Z a few times.

Note that whereas there should be only one project file for a band system, all projects of the same molecule can share the same state file. In fact, it should include even all isotopic species. For example, for deuterobromoacetylene, a state file could include rotational parameters for vibrational states of DCC⁷⁹Br, DCC⁸¹Br, HCC⁷⁹Br and HCC⁸¹Br. The state file is an ASCII text file and can be easily modified with any text editor if necessary.

The vibrational state information is used for two purposes. Firstly, to store the results of the analysis, secondly, to store the lower state parameters in the automatic analysis of the bands.

For the first purpose, it makes sense to keep in the table some rows even for yet unsolved vibrational states for completeness and to remind us of them. For example, the vibrational state window in Figure 29 the states number 21 and 22 (DCC⁷⁹Br0001¹¹, Σ ,e) have zeros in their data fields, waiting to be filled later with the analysis results.

Vibrational state information										
N	Name	L	B	error	D e+7	error	Vib Energy	error	Used?	Comment
15	DCCBr79_000_0(0)3(1)_le	1	0.122522200	2000	0.247700	5200	0.000000	0	Yes	Olaavin table1. Tarkastettu.
16	DCCBr81_000_0(0)3(1)_le	1	0.121838000	2100	0.233900	4200	0.000000	0	Yes	Olaavin table2. Tarkistettu.
17	DCCBr79_000_1(1)0(0)_le	1	0.122020504	7	0.202825	7	480.659360	14	Yes	Band2 sovitus.
18	DCCBr81_000_1(1)0(0)_le	1	0.121348108	11	0.199806	12	480.659277	17	Yes	Band1 sovitus.
19	DCCBr79_000_1(1)0(0)_lf	1	0.122092520	0	0.202800	0	480.659277	20	Yes	Oma vanha sovitus QFIT:11ä
20	DCCBr81_000_1(1)0(0)_lf	1	0.121419930	0	0.201100	0	480.659277	20	Yes	Oma vanha sovitus QFIT:11ä
21	DCCBr79_000_1(1)1(1)_0e	0	0.000000000	0	0.000000	0	0.000000	0	Yes	Häiriötä bandissa 1C1
22	DCCBr81_000_1(1)1(1)_0e	0	0.000000000	0	0.000000	0	0.000000	0	Yes	Häiriötä bandissa 1C2

Figure 29: Vibrational state information window

Columns of the state table

State number is assigned automatically to each new state. Bands refer to their lower stated by the state number, so the same state should always have the same state number. Hence, new states should be always added to the end of the table and states in between of the table should not be removed (otherwise the numbering scheme changes). Due to this limitation it is advised that the user creates an “empty” state for each possible state that might be encountered during the fitting process *before* starting the fitting process in a convenient order. [A possible improvement to the program would be to add an unchangeable state code to each state and use that as a reference so that numbers could change.]

State name is an arbitrary user defined name for the state, up to 40 characters long. It should show at least the molecule in question (in case of multiple isotopic species) and number of vibrational quantas on each vibrational mode. Often some types of symmetry labeling has to be included as well to distinguish states from each other. For example, deuterobromoacetylene has a state DCC⁷⁹Br0001¹¹, Σ ,e where DCC⁷⁹Br shows . Due to lack of superscripts and Greek symbols, this state would be given the name such as DCCBr79_000_1(1)1(1)_0e in the program. Users should be

consistent in state naming. This is obtained best by inputting all the states to the state table in one go before starting the fitting process.

State l-number. This is the total vibrational angular momentum of the state. Linear molecules can possess vibrational angular momentum if their bending modes are excited. The l-number must be stored in the state information because it is used in the energy level calculations.

Rotational constant B in units of cm^{-1} . For definition of this constant, see the theory on page 11.

Centrifugal constant D in units of $10^7 \times \text{cm}^{-1}$. For definition of this constant, see page 11.

Vibrational Energy parameter stores the relative zero-rotation energy of the state relative to the vibrational ground state of the molecule. For states whose parameters have been obtained by fitting bands originating from the ground state, this energy is equal to the band origin of those bands. For states whose parameters have been obtained by fitting hot bands, the energy equals the vibrational energy of the lower state plus the band origin of the band.

Errors in B, D and Energy are displayed as error in the last decimal places of the value. For example:

Table 11: Representation of parameter errors in the tables

	State / Band Table display	Meaning
Example 1	B 0.121836755 Error 345	B value = 0.121836755 B error = 0.000000345
Example 2	D e+7 0.207130 error 640	D value = 0.207130 $\times 10^{-7}$ D error = 0.000640 $\times 10^{-7}$

Inputting state parameters manually

If any B and D parameters are known for any vibrational states, they can – and should – be written to the state table before starting the actual analysis. These parameters will be used by the program as possible lower state parameters in the band combination analysis (as explained on pages 23 and 59) and it is recommended to have them at least for the ground state to begin with.

New states can be added to the state table with menu command **State / New**. The parameter values of the state table can be edited simply by selecting the desired field and typing a value. Note that the error values are inputted exactly as described in Table 11.

Assigning a PR-branch directly

If the spectra is of good quality and not very dense, one might be able to see the *m*-values of the peaks directly from the spectra. In such situation a new band can be made with **Band / New**

command and the band type set directly to **PR**. After few assignments have been added, the *m*-values can be shifted manually to their correct positions with the menu command **Band / Shift m values**.

Assigning peaks to a band from a P- or R-branch

- Press **F6** to tile the windows.
- Make a new band with the menu command **Band / New**.
- In the *Band Properties* dialog box, write a three-letter name for the band to the **Band Code** edit box and choose colours for the band. Select the band type: P or R.
- Find a suitable series of lines in some band.
- In the spectra window, click with right mouse button a peak belonging to the band and select the command **Automatically Assign to band...**
- The assignment window should now show the assigned peak.
- Find the next peak of the band (having a one larger *m*-value) and assign it in the similar way. Do this also for the third peak.
- When three (or more) peaks have been assigned, you should see the blue prediction lines appearing and the **Pred Wn** column of the assignment window filling up with predicted wavenumbers. If you do not see the blue lines, select menu command **View / Prediction markers**.
- Now you can start to assign more peaks based on the predictions. First select a row from the assignment window that has not yet been assigned. If the blue predicted line is closer to the correct peak than any other peak, *double click* the row in the assignment table. Assignment will be automatically added.
- Continue assigning the peaks of the band and note that the predictions get more accurate as more assignments are added. You do not need to assign a peak for every *m*-value i.e., you can leave gaps without assignments if, for example, the peak has been overlapped by another one. You should be able to cross minor peak overlaps using the predictions.
- If some peak of the band is of bad quality, you can still assign it but with a lower weight. Assign it in the normal manner, type a new weight value (between 0 and 1) to the **weight** field of the assignment in the assignment table and press **Enter**.
- Assign only so many peaks from the branch that you can without being uncertain about the assignments. Some 15 peaks should be enough for proceeding to the branch combination but if you can assign easily more, do so.

You can later modify the settings of the band (colors, calculation modes etc.) by selecting its row from the band table and choosing the menu command **Band / Properties**.

Assigning all possible P-and R-branches

Before you proceed to combination of bands, you should assign as many as possible P- and R-branches as explained above. This is because the branch combination algorithm expects all the branches to be assigned for analysis.

Combining P- and R-branches to PR-band

- Assign all possible P-branches.
- Check that you have all relevant lower state constants inputted to your state table and that all of them have value **Yes** in the **Use** column.
- Select a R-branch band.
- Select a menu command **Band / HalfBand /Combine Branches**.
- After some processing, the **Branch Combination Results** table is displayed. Inspect the combinations. Note that you can look at combination details in the corresponding window after selecting the combination. Read the chapter **Fitness** on page 25 in the technical documentation if you do not know what the combinations mean.

If no good combination is found, the reason can be one or more of the following:

- 1) You do not have the correct lower state parameters in the state table.
- 2) You have not assigned the corresponding portion of the other branch of the band. To check this case, run the **Combine Branches Global** algorithm with **Shift + F8** and see if you get any better results.
- 3) You have not been careful in your P- and R-branch assignments and some of your “bands” are actually a collection of peaks from multiple bands. (It happens! Be careful!)

If the combination was successful i.e., there was a combination that had good fitness, decent lower state, enough terms and looked good in the combination details, go on: combine the halfbands to a PR-band by double-clicking the combination row in the combinations table.

There are two additional measures that should be checked to be sure that the combination has been correct:

- 1) If a *Q*-branch is expected to be located in the center of the PR-band, go and see if there is one.
- 2) Look in the right hand side of band table and locate two *delta* columns next to the calculated lower state constants *B''* and *D''*. These show the difference of the lower state constants found by fitting this band and the fixed constants in the state table. The difference is shown in same way as the error (see Table 11 for details) and it should be rather small. One should get little worried if the delta is larger than the error of the corresponding parameter. If it's more than

three times the error there is likely to be errors in the assignments. But go on and assign more peaks of the band and look if the deltas get smaller. Note that if there is perturbation in the upper state, the lower state constants must be calculated with GSCD (see a mark to the GSCD box in band properties dialog box).

After the band has been combined to a PR-band, proceed to assign all possible peaks of the band that you can. After the combination there should be so many peak assigned on so broad area that the predictions should be of good quality and trustworthy. Use lower weight in peak assignments where necessary.

Working with Bands

- When assignment of bands lines changes (new assignments added or old ones removed) program calculates automatically and quickly all the defined fits and updates the positions of the predicted lines.
- The band assignment data is stored in the project file. This file is a text file and can be easily edited by manually with a text editor if, for example, you want to remove a large portion of the assignments of a band.
- If you notice that two *R*-branches which you have started to assign in different locations are actually part of the same *R*-branch, you can combine them to one with The **Band / HalfBand / Merge** command. Before that you must, though, shift the m-values of the other one to be in compliance with the other (**Band / Shift m values**).

Band Properties

Band properties can be later changed (and band information looked at) by double-clicking the band row in the band table or selecting the band row and selecting the menu command **Band / Properties**.

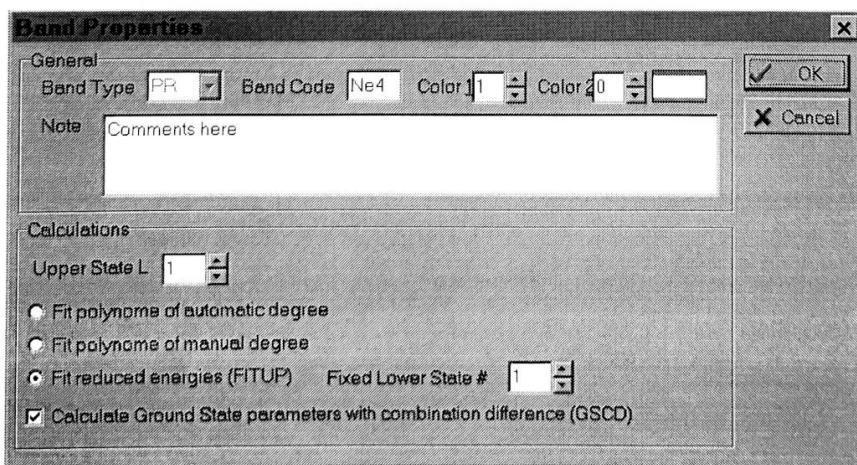


Figure 30: The band properties dialog box

Upper State L quantum number of the upper state should be set to the corresponding field. This number defines the amount of vibrational angular momentum on the upper state and although the effect it has on calculations is small, it is needed to obtain correct parameters. For definition, see equation (11) page 11 (where symbol k instead of L for the total vibrational angular momentum).

Type of fit to perform. Automatic polynomial fit will use polynome of degree 1...4 depending on the number of assignments (mostly degree = 4). With the manual degree setting even higher degrees can be used. Hint: try degree 6 to include the effect of H term in the $J(J+1)$ expansion. Fitup option calculates the upper state values with high accuracy (see page 63 for more information on Fitup).

GSCD calculation can be performed for a PR-band if ground state parameters are not known or if there is perturbation on the upper state and lower state parameters want to be calculated.

Fitting a Q-branch

- Make a new band and give Q for its type.
- Start assigning the peaks of the Q -branch in the same way as the peaks of P- or R-branches

Transferring band parameters to the state table

When a band (PR or Q) has been fitted to completion, the upper state parameters that FitUp has provided for it should be transferred to the state table so that they can be used as lower state parameters for new yet unanalyzed bands. To do so:

- Select from the band table the band whose upper state parameters are to be copied.
- Select from the state table the state where the parameters should be copied to
- Give menu command **State / Get Upper State From Band**. Write a name for the state.

Note that the calculated lower state parameters can be copied as well to a state using the **State / Get Lower State From Band** command.

Options

Choosing the menu command File / Options or pressing Ctrl+O brings up the options window:

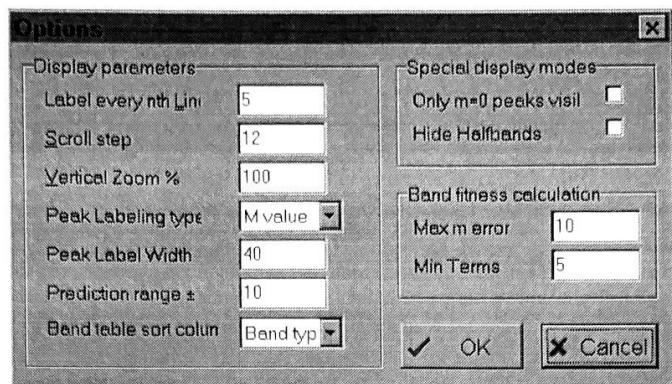


Figure 31: The Options dialog box

Max M Error defines how large number of Δm values are tested in the branch combination process. Higher number means more accidentally good combinations and slower processing but might find the correct combination if the initial m -assignments are very far from the correct ones.

Min Terms defines how many terms there must be at minimum to compare in the branch combination process.

Rest of the options are explained on the *Spectra Window* chapter on page 71.

Exporting results

When the analysis process is completed, the parameters obtained – bands, states and peak assignments – can be saved to ASCII disk files. This is in order to read them to word processors so they can be used in articles easily. For this feature, activate the desired table and select the menu command **Table / Save to File**.

Program Hotkey summary

- Ctrl+L** Load a project file
Ctrl+S Save the project file and all related files.
Ctrl+O Display the options dialog box

Navigation keys are at the bottom of the keyboard:

- Ctrl+B** Scroll spectra to left (smaller wavenumbers) a small step.
Ctrl+N Scroll spectra to right (larger wavenumbers) a small step.
Ctrl+V Scroll spectra to left (smaller wavenumbers) 75% screen.
Ctrl+M Scroll spectra to right (larger wavenumbers) 75% screen.
Ctrl+Z Zoom in 25% or selected region if selection is made
Ctrl+X Zoom out 25%
Ctrl+Q Scroll vertically up.
Ctrl+A Scroll vertically down.
F4 Toggle peak prediction markers visible / invisible.
F2 Toggle peak and assignment markers visible / invisible.
F3 Toggle all band assignment markers / selected band assignment markers.
F6 Tile Band window
Shift+F6 Tile combination windows
F7 Tile one window
Shift+F7 Tile one window vertically
F8 Combine Branches
Shift+F8 Combine Branches Global
F9 Refresh the calculations (usually not needed since calculations are automatic after changes)

9. References

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10. Appendixes

Appendix 1: the separation of P- and R-branch peaks

Consider two transitions that both have same upper state rotational quantum number J' , but other has $J'' = J' + 1$ (P-branch), other $J'' = J' - 1$ (R-branch). The *differences* of P- and R-branch line wavenumbers is:

$$(45) \quad \begin{aligned} \tilde{v}_r - \tilde{v}_p &= \Delta E_{vib} + B' [J'(J'+1) - k'^2] - D' [J'(J'+1) - k'^2]^2 - \\ &\quad B'' [J'(J'-1) - k''^2] + D'' [J'(J'-1) - k''^2]^2 - \\ &\quad \Delta E_{vib} - B' [J'(J'+1) - k'^2] + D' [J'(J'+1) - k'^2]^2 + \\ &\quad B'' [(J'+1)(J'+2) - k''^2] - D'' [(J'+1)(J'+2) - k''^2]^2 \end{aligned}$$

The upper-state terms cancel and rest simplifies to:

$$(46) \quad \begin{aligned} \tilde{v}_r - \tilde{v}_p &= \Delta E_{vib} + B'' [(J'+1)(J'+2) - J'(J'-1)] - \\ &\quad D'' [(J'+1)(J'+2) - k''^2]^2 - (J'(J'-1) - k''^2)^2 \end{aligned}$$

Note especially that the k -constant in the B'' term has canceled out. A large approximation is not done when k :s are removed from the D'' term as well since 1) D'' term is very small compared to B'' term. 2) typical J -values are from 10 to 100, typical k -values 0 to 2. Hence the terms that are approximately J^2 are 100 to 10000 times greater than k^2 . 3) Some of the k -including terms (like k^4) would cancel out when opening the brackets – this is not seen now since the k :s are removed before opening in order to keep expressions simple.

Removing k :s gives:

$$\tilde{v}_r - \tilde{v}_p = B'' [(J'+1)(J'+2) - J'(J'-1)] - D'' [((J'+1)(J'+2))^2 - (J'(J'-1))^2]$$

The first term simplifies:

$$\begin{aligned} B'' [(J'+1)(J'+2) - J'(J'-1)] &= B'' [(J'^2 + 3J' + 2) - (J'^2 - J')] = \\ B'' [J'^2 + 3J' + 2 - J'^2 + J'] &= B'' [4J' + 2] = 4B'' [J' + \frac{1}{2}] \end{aligned}$$

The second term simplifies:

$$\begin{aligned} & -D'' \left[((J'+1)(J'+2))^2 - (J'(J'-1))^2 \right] \\ &= -D'' \left[(J'^2 + 3J' + 2)^2 - (J'^2 - J')^2 \right] \\ &= -D'' \left[(J'^4 + 6J'^3 + 13J'^2 + 12J' + 4) - (J'^4 - 2J'^3 + J'^2) \right] \\ &= -D'' [8J'^3 + 12J'^2 + 12J' + 4] \\ &= -D'' [6J' + 3] - D'' [8J'^3 + 12J'^2 + 6J' + 1] \\ &= -6D'' \left[J' + \frac{1}{2} \right] - 8D'' \left[J' + \frac{1}{2} \right]^3 \end{aligned}$$

And the total difference simplifies to:

$$47) \quad \tilde{v}_r - \tilde{v}_p = (4B'' - 6D'') \left(J' + \frac{1}{2} \right) - 8D'' \left(J' + \frac{1}{2} \right)^3$$

Which is the result used in the text.

Appendix 2: Calculating vibration parameters

Numerical values are for DCC⁷⁹Br, but parameters are calculated in the same way for the species DCC⁸¹Br.

D bend anharmonicity x_{44} / g_{44}

$$000\ 2^00^0,\Sigma - 000\ 2^20^0,\Delta \Rightarrow g_{44} = 2.44979(9) \text{ cm}^{-1}$$

$$000\ 2^00^0,\Sigma + 000\ 2^20^0,\Delta \Rightarrow x_{44} = -0.70735(9) \text{ cm}^{-1}$$

Br bend – D bend anharmonicity $x_{45} / g_{45} / r_{45}$

$$000\ 1^11^1,\Sigma^+ - 000\ 1^11^1,\Sigma^- \Rightarrow r_{45} = 1.3897(2) \text{ cm}^{-1}$$

$$000\ 1^11^1,\Sigma^+ + 000\ 1^11^1,\Sigma^- - 2 \times 000\ 1^11^1,\Delta \Rightarrow g_{45} = 0.55072(9) \text{ cm}^{-1}$$

$$000\ 1^11^1,\Sigma^+ + 000\ 1^11^1,\Sigma^- + 2 \times 000\ 1^11^1,\Delta \Rightarrow x_{45} = 0.98183(12) \text{ cm}^{-1}$$

Rotation vibrational dependence – Alpha parameters

$$B_v = B_0 - \sum_r \alpha_r v_r \Rightarrow \alpha_r = B_0 - B_1$$

For the doubly degenerate modes $\alpha_r = B_0 - \frac{1}{2}(B_{1e} + B_{1f})$

DCC⁷⁹Br $\alpha_3 = 0.0001782(10) \text{ cm}^{-1}$, $\alpha_4 = -0.0001346(8) \text{ cm}^{-1}$, $\alpha_5 = -0.0003227(8) \text{ cm}^{-1}$

DCC⁸¹Br $\alpha_3 = 0.0001669(10) \text{ cm}^{-1}$, $\alpha_4 = -0.0001340(7) \text{ cm}^{-1}$, $\alpha_5 = -0.0003211(8) \text{ cm}^{-1}$