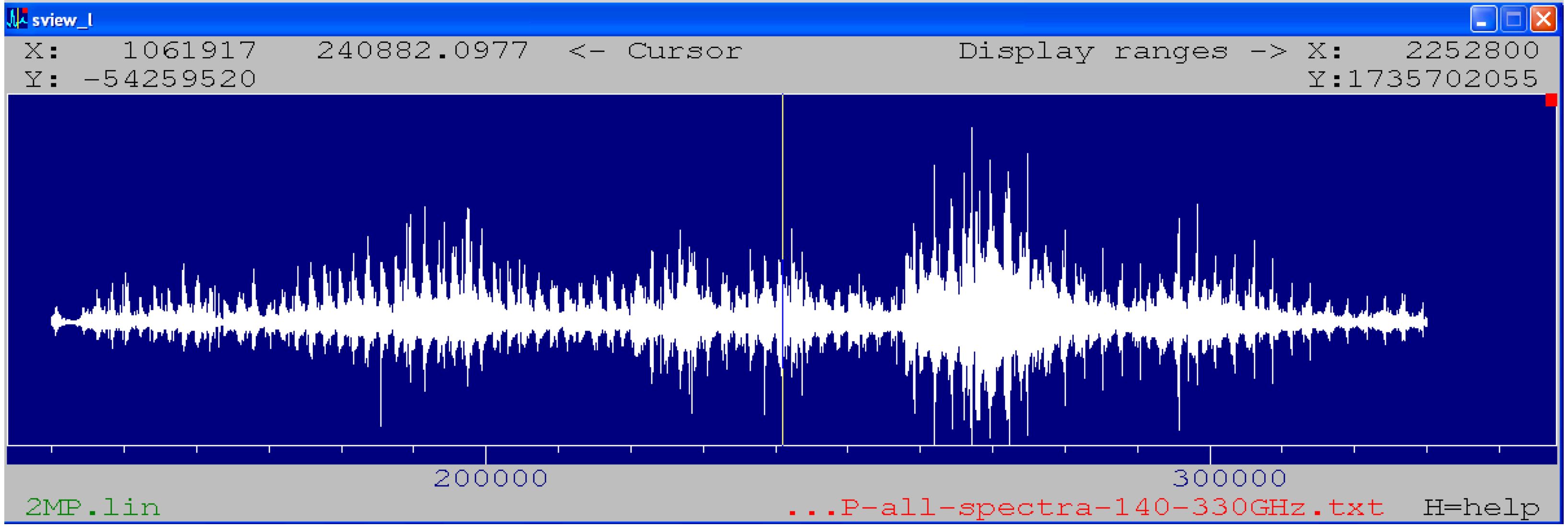
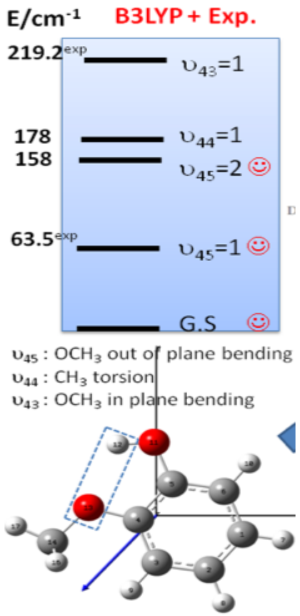
Tutorial: analysis of a rotational mm-wave spectra

Arnaud Cuisset, Laboratoire de Physico-Chimie de l'atmosphère,
Dunkerque, France

Ground state analysis of 2-Methoxyphenol (guaïacol)



```
X:    1061917   240882.0977  <- Cursor          Display ranges -> X:    2252800
Y: -54259520                                                      Y:1735702055
2MP.lin                          ...P-all-spectra-140-330GHz.txt    H=help
```



The frequency multiplier chain (70 – 900 GHz)

Source

Commercial frequency multiplier chain (VDI)

Electronic source associated with **multipliers**

Cell

Simple or double pass 1.20m absorption cell

P= 8µbar (flow)

Detection

Good S/N ratio : 2F frequency modulation (25.5kHz)

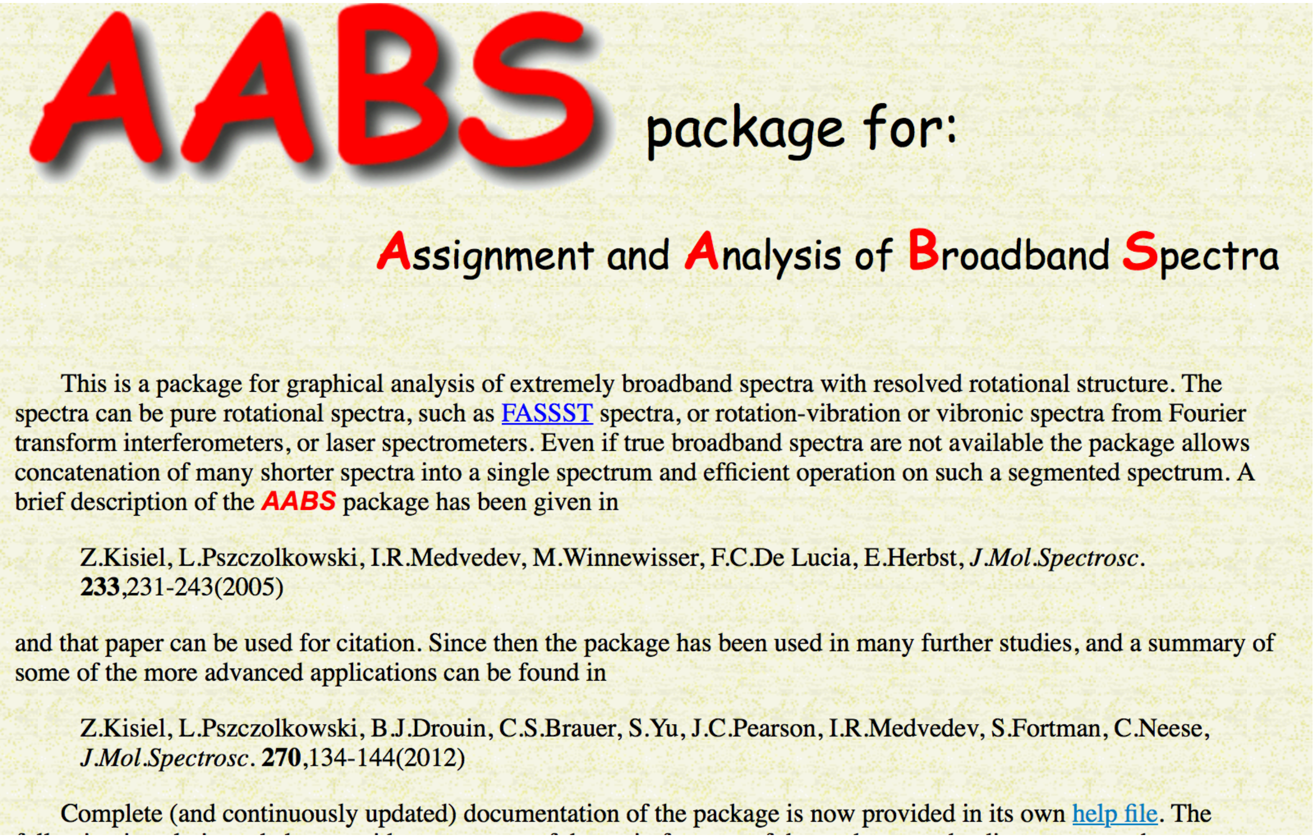
High spectral resolution (10kHz), Doppler limit.

High sensitivity : InSb He cooled bolometer (4K)

3 main factors may explain the large density of lines and complicate the spectroscopic analysis:

- Small rotational constants (C<1GHz) – rotational transitions observed up to high J levels ($J''_{max}=175$)
- Several conformers significantly populated at room temperature
- Rotational transitions in low-frequency vibrational states

The AABS package from Z. Kisiel (http://info.ifpan.edu.pl/~kisiel/aabs/aabs.htm)



AABS package for:

Assignment and **A**nalysis of **B**roadband **S**pectra

This is a package for graphical analysis of extremely broadband spectra with resolved rotational structure. The spectra can be pure rotational spectra, such as FASSST spectra, or rotation-vibration or vibronic spectra from Fourier transform interferometers, or laser spectrometers. Even if true broadband spectra are not available the package allows concatenation of many shorter spectra into a single spectrum and efficient operation on such a segmented spectrum. A brief description of the ***AABS*** package has been given in

Z.Kisiel, L.Pszczolkowski, I.R.Medvedev, M.Winnewisser, F.C.De Lucia, E.Herbst, *J.Mol.Spectrosc*. **233**,231-243(2005)

and that paper can be used for citation. Since then the package has been used in many further studies, and a summary of some of the more advanced applications can be found in

Z.Kisiel, L.Pszczolkowski, B.J.Drouin, C.S.Brauer, S.Yu, J.C.Pearson, I.R.Medvedev, S.Fortman, C.Neese, *J.Mol.Spectrosc*. **270**,134-144(2012)

Complete (and continuously updated) documentation of the package is now provided in its own help file. The

ELSEVIER

Journal of Molecular Spectroscopy 233 (2005) 231–243

www.elsevier.com/locate/jms

Rotational spectrum of *trans–trans* diethyl ether in the ground and three excited vibrational states

Zbigniew Kisiel [a,*], Lech Pszczółkowski [a], Ivan R. Medvedev [b], Manfred Winnewisser [b], Frank C. De Lucia [b], Eric Herbst [b]

[a] *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland*

[b] *Department of Physics, The Ohio State University, Columbus, OH 43210-1106, USA*

ELSEVIER

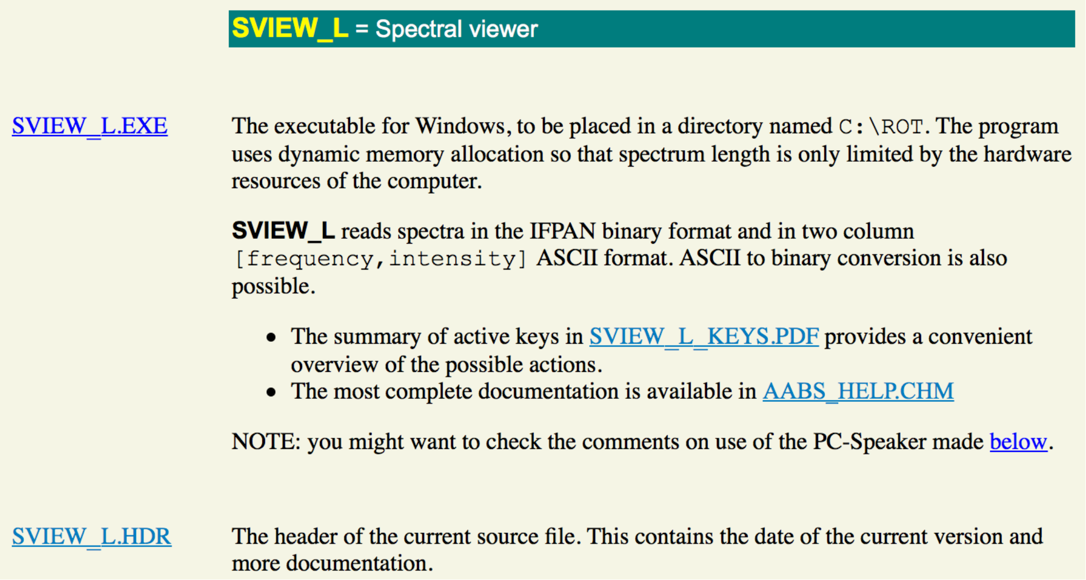
Journal of Molecular Spectroscopy 233 (2005) 231–243

www.elsevier.com/locate/jms

Rotational spectrum of *trans–trans* diethyl ether in the ground and three excited vibrational states

Zbigniew Kisiel [a,*], Lech Pszczółkowski [a], Ivan R. Medvedev [b], Manfred Winnewisser [b], Frank C. De Lucia [b], Eric Herbst [b]

The SVIEW_L and ASCP_L programs



SVIEW_L = Spectral viewer

SVIEW_L.EXE

The executable for Windows, to be placed in a directory named `C:\ROT`. The program uses dynamic memory allocation so that spectrum length is only limited by the hardware resources of the computer.

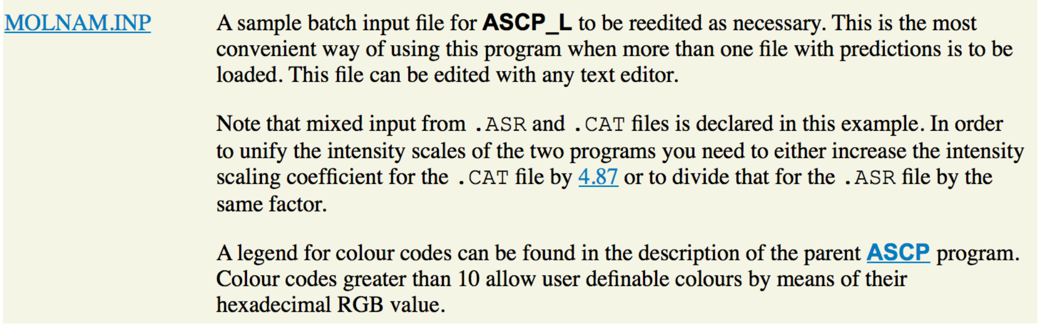
SVIEW_L reads spectra in the IFPAN binary format and in two column `[frequency,intensity]` ASCII format. ASCII to binary conversion is also possible.

- The summary of active keys in SVIEW_L_KEYS.PDF provides a convenient overview of the possible actions.
- The most complete documentation is available in AABS_HELP.CHM

NOTE: you might want to check the comments on use of the PC-Speaker made below.

SVIEW_L.HDR

The header of the current source file. This contains the date of the current version and more documentation.

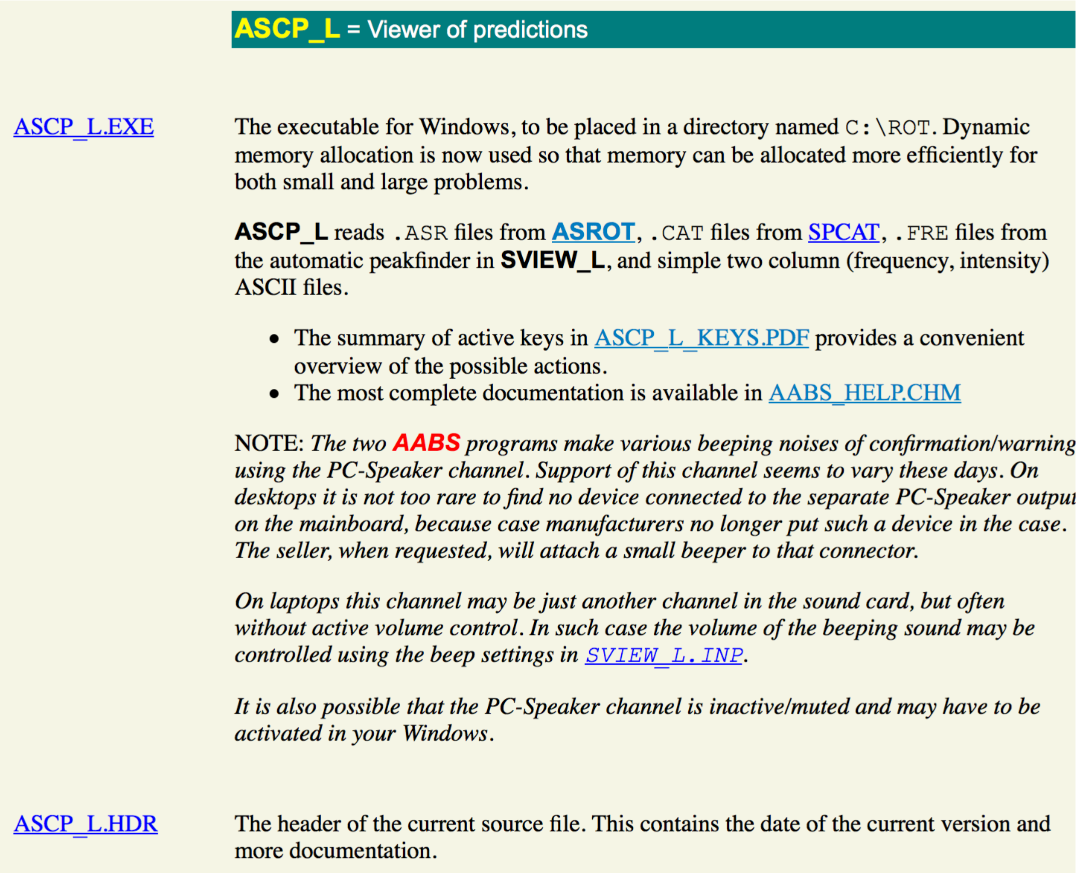


MOLNAM.INP

A sample batch input file for **ASCP_L** to be reedited as necessary. This is the most convenient way of using this program when more than one file with predictions is to be loaded. This file can be edited with any text editor.

Note that mixed input from `.ASR` and `.CAT` files is declared in this example. In order to unify the intensity scales of the two programs you need to either increase the intensity scaling coefficient for the `.CAT` file by 4.87 or to divide that for the `.ASR` file by the same factor.

A legend for colour codes can be found in the description of the parent **ASCP** program. Colour codes greater than 10 allow user definable colours by means of their hexadecimal RGB value.



ASCP_L = Viewer of predictions

ASCP_L.EXE

The executable for Windows, to be placed in a directory named `C:\ROT`. Dynamic memory allocation is now used so that memory can be allocated more efficiently for both small and large problems.

ASCP_L reads `.ASR` files from **ASROT**, `.CAT` files from SPCAT, `.FRE` files from the automatic peakfinder in **SVIEW_L**, and simple two column (frequency, intensity) ASCII files.

- The summary of active keys in ASCP_L_KEYS.PDF provides a convenient overview of the possible actions.
- The most complete documentation is available in AABS_HELP.CHM

NOTE: *The two* ***AABS*** *programs make various beeping noises of confirmation/warning using the PC-Speaker channel. Support of this channel seems to vary these days. On desktops it is not too rare to find no device connected to the separate PC-Speaker output on the mainboard, because case manufacturers no longer put such a device in the case. The seller, when requested, will attach a small beeper to that connector.*

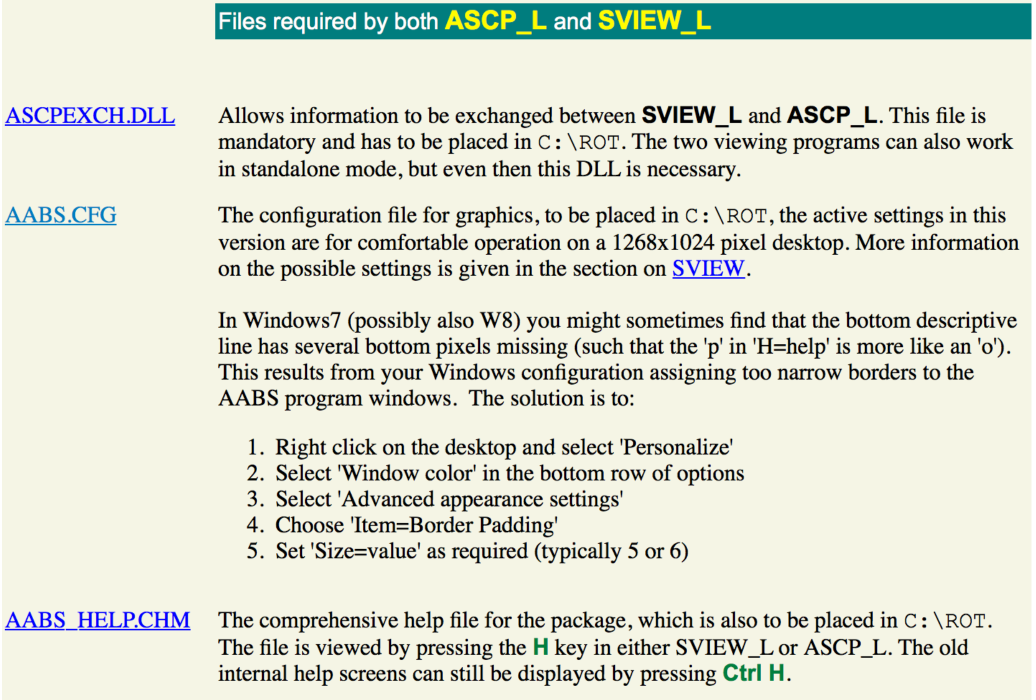
On laptops this channel may be just another channel in the sound card, but often without active volume control. In such case the volume of the beeping sound may be controlled using the beep settings in `SVIEW_L.INP`.

It is also possible that the PC-Speaker channel is inactive/muted and may have to be activated in your Windows.

ASCP_L.HDR

The header of the current source file. This contains the date of the current version and more documentation.

The SVIEW_L and ASCP_L programs



Files required by both **ASCP_L** and **SVIEW_L**

ASCPEXCH.DLL

Allows information to be exchanged between **SVIEW_L** and **ASCP_L**. This file is mandatory and has to be placed in `C:\ROT`. The two viewing programs can also work in standalone mode, but even then this DLL is necessary.

AABS.CFG

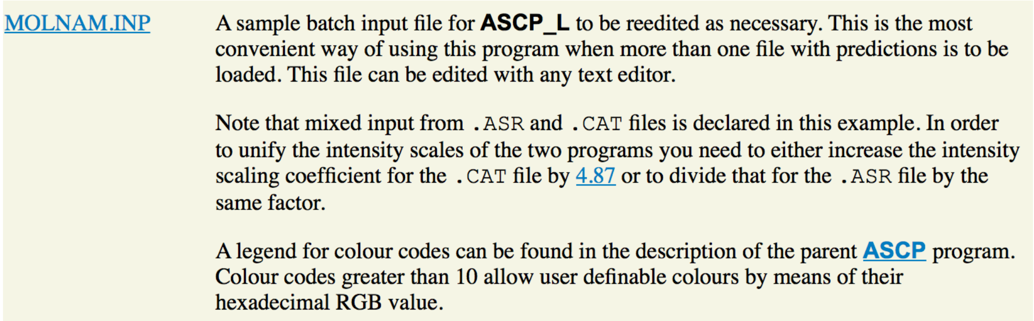
The configuration file for graphics, to be placed in `C:\ROT`, the active settings in this version are for comfortable operation on a 1268x1024 pixel desktop. More information on the possible settings is given in the section on SVIEW.

In Windows7 (possibly also W8) you might sometimes find that the bottom descriptive line has several bottom pixels missing (such that the 'p' in 'H=help' is more like an 'o'). This results from your Windows configuration assigning too narrow borders to the AABS program windows. The solution is to:

1. Right click on the desktop and select 'Personalize'
2. Select 'Window color' in the bottom row of options
3. Select 'Advanced appearance settings'
4. Choose 'Item=Border Padding'
5. Set 'Size=value' as required (typically 5 or 6)

AABS_HELP.CHM

The comprehensive help file for the package, which is also to be placed in `C:\ROT`. The file is viewed by pressing the **H** key in either SVIEW_L or ASCP_L. The old internal help screens can still be displayed by pressing **Ctrl H**.

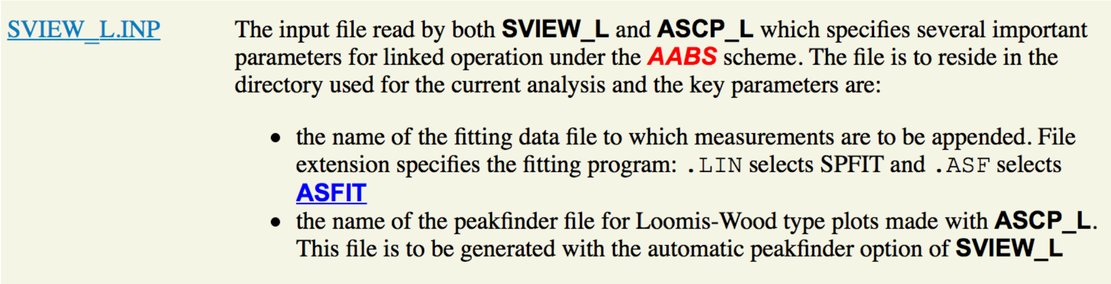


MOLNAM.INP

A sample batch input file for **ASCP_L** to be reedited as necessary. This is the most convenient way of using this program when more than one file with predictions is to be loaded. This file can be edited with any text editor.

Note that mixed input from `.ASR` and `.CAT` files is declared in this example. In order to unify the intensity scales of the two programs you need to either increase the intensity scaling coefficient for the `.CAT` file by 4.87 or to divide that for the `.ASR` file by the same factor.

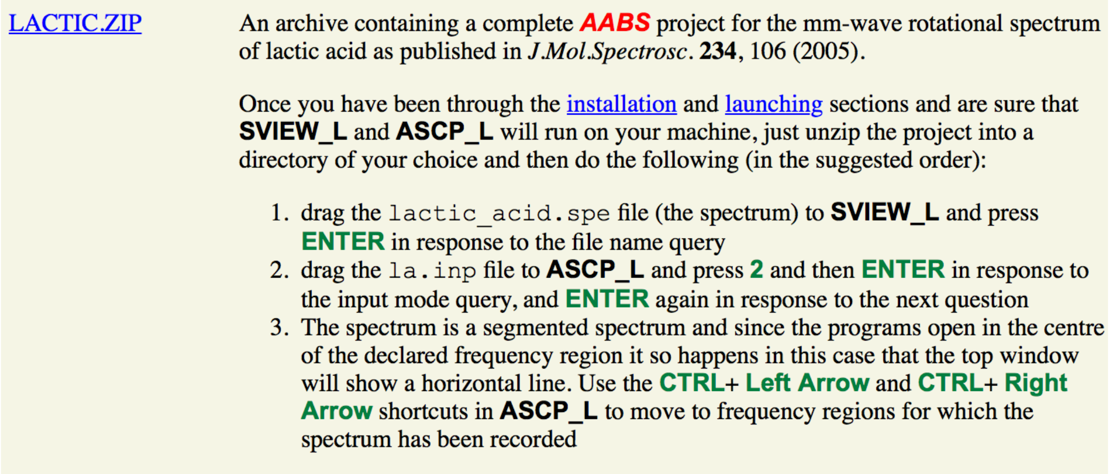
A legend for colour codes can be found in the description of the parent **ASCP** program. Colour codes greater than 10 allow user definable colours by means of their hexadecimal RGB value.



SVIEW_L.INP

The input file read by both **SVIEW_L** and **ASCP_L** which specifies several important parameters for linked operation under the ***AABS*** scheme. The file is to reside in the directory used for the current analysis and the key parameters are:

- the name of the fitting data file to which measurements are to be appended. File extension specifies the fitting program: `.LIN` selects SPFIT and `.ASF` selects **ASFIT**
- the name of the peakfinder file for Loomis-Wood type plots made with **ASCP_L**. This file is to be generated with the automatic peakfinder option of **SVIEW_L**



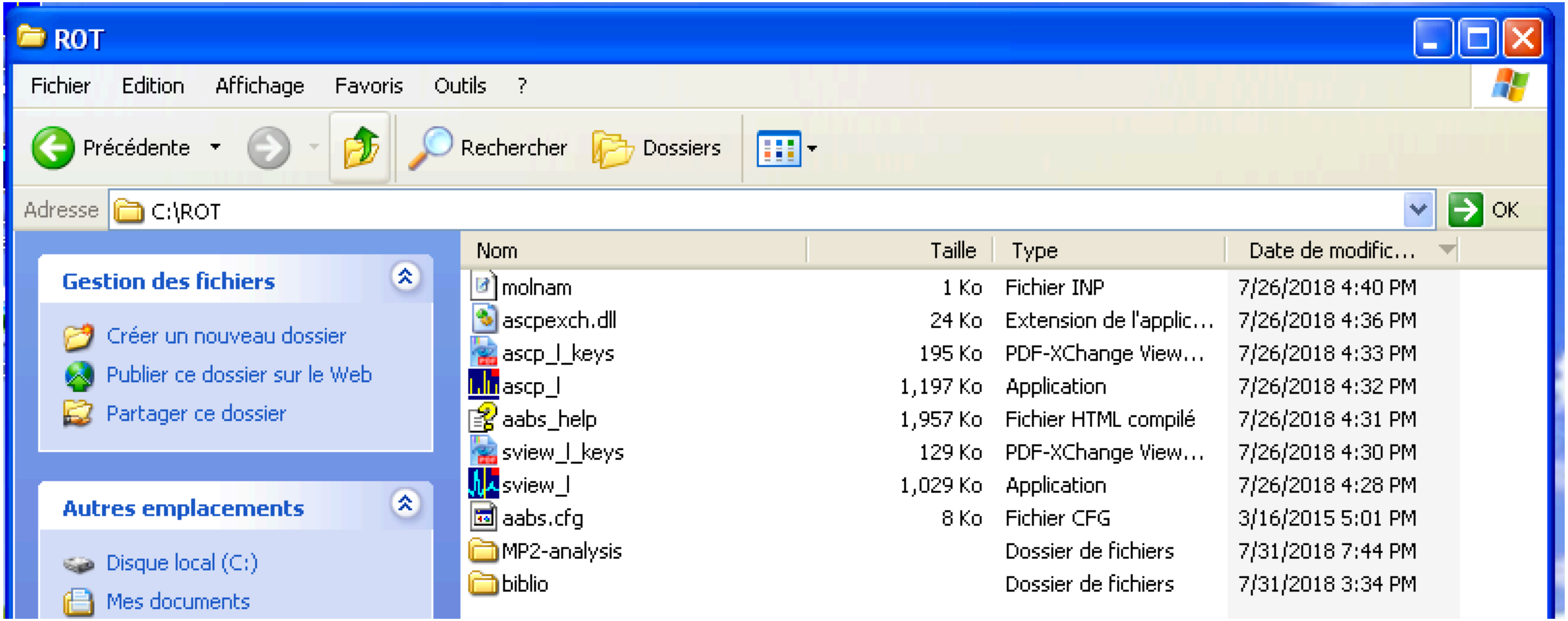
LACTIC.ZIP

An archive containing a complete ***AABS*** project for the mm-wave rotational spectrum of lactic acid as published in *J.Mol.Spectrosc*. **234**, 106 (2005).

Once you have been through the installation and launching sections and are sure that **SVIEW_L** and **ASCP_L** will run on your machine, just unzip the project into a directory of your choice and then do the following (in the suggested order):

1. drag the `lactic_acid.spe` file (the spectrum) to **SVIEW_L** and press **ENTER** in response to the file name query
2. drag the `la.inp` file to **ASCP_L** and press **2** and then **ENTER** in response to the input mode query, and **ENTER** again in response to the next question
3. The spectrum is a segmented spectrum and since the programs open in the centre of the declared frequency region it so happens in this case that the top window will show a horizontal line. Use the **CTRL+ Left Arrow** and **CTRL+ Right Arrow** shortcuts in **ASCP_L** to move to frequency regions for which the spectrum has been recorded

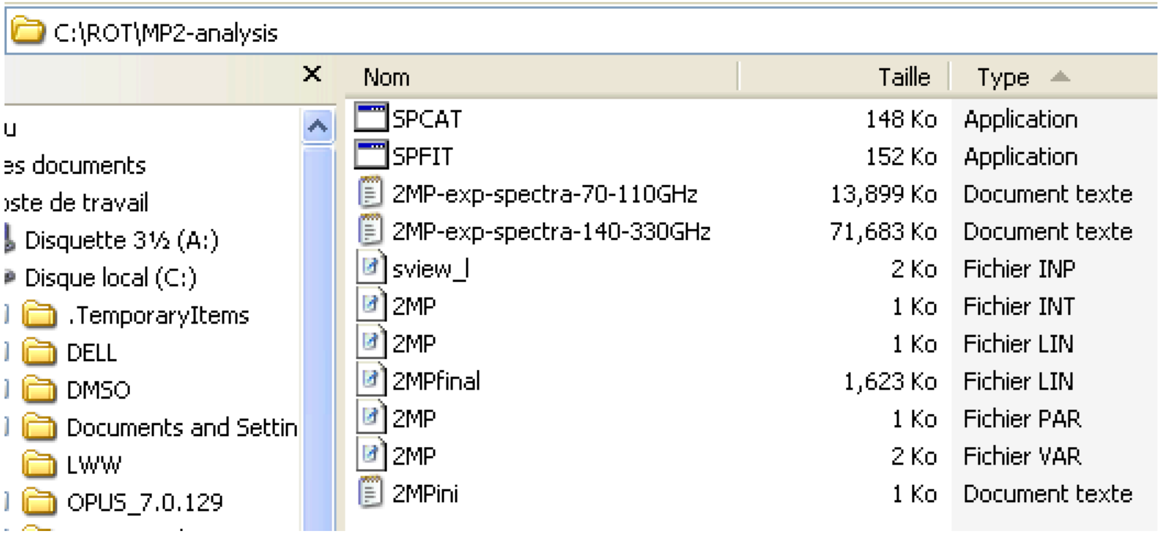
The SVIEW_L and ASCP_L programs: in the C:\ROT directory



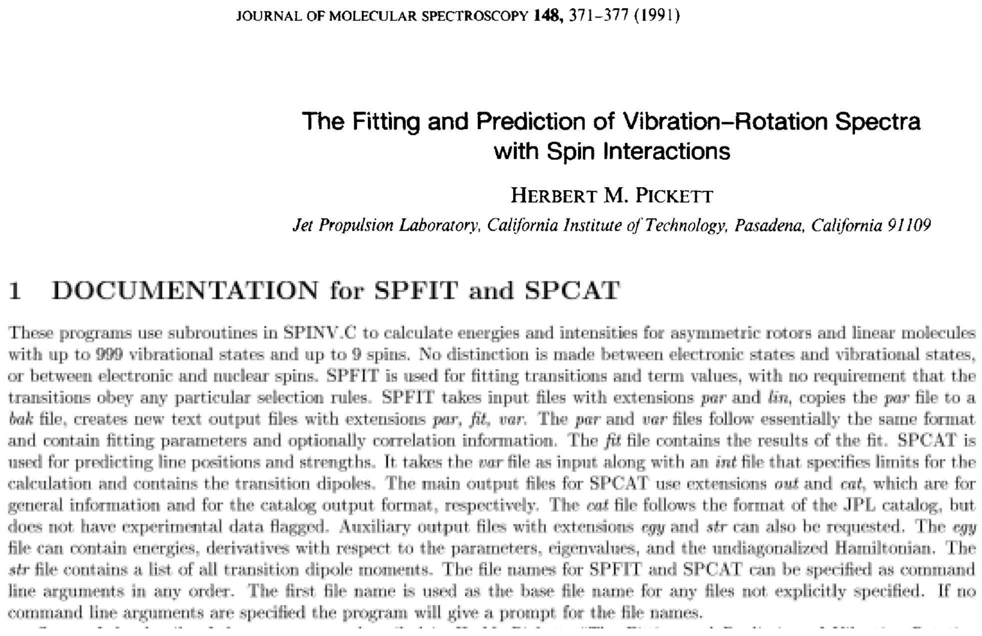
Adresse C:\ROT

Nom	Taille	Type	Date de modific...
molnam	1 Ko	Fichier INP	7/26/2018 4:40 PM
ascpexch.dll	24 Ko	Extension de l'applic...	7/26/2018 4:36 PM
ascp_l_keys	195 Ko	PDF-XChange View...	7/26/2018 4:33 PM
ascp_l	1,197 Ko	Application	7/26/2018 4:32 PM
aabs_help	1,957 Ko	Fichier HTML compilé	7/26/2018 4:31 PM
sview_l_keys	129 Ko	PDF-XChange View...	7/26/2018 4:30 PM
sview_l	1,029 Ko	Application	7/26/2018 4:28 PM
aabs.cfg	8 Ko	Fichier CFG	3/16/2015 5:01 PM
MP2-analysis		Dossier de fichiers	7/31/2018 7:44 PM
biblio		Dossier de fichiers	7/31/2018 3:34 PM

The SPCAT and SPFIT programs from H. M. Pickett (https://spec.jpl.nasa.gov)



Nom	Taille	Type
SPCAT	148 Ko	Application
SPFIT	152 Ko	Application
2MP-exp-spectra-70-110GHz	13,899 Ko	Document texte
2MP-exp-spectra-140-330GHz	71,683 Ko	Document texte
sview_l	2 Ko	Fichier INP
2MP	1 Ko	Fichier INT
2MP	1 Ko	Fichier LIN
2MPfinal	1,623 Ko	Fichier LIN
2MP	1 Ko	Fichier PAR
2MP	2 Ko	Fichier VAR
2MPini	1 Ko	Document texte



JOURNAL OF MOLECULAR SPECTROSCOPY **148,** 371–377 (1991)

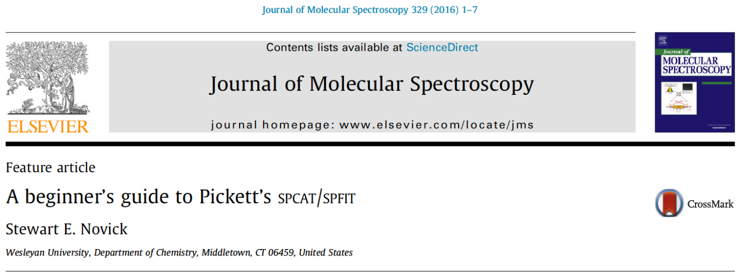
The Fitting and Prediction of Vibration–Rotation Spectra with Spin Interactions

HERBERT M. PICKETT

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

1 DOCUMENTATION for SPFIT and SPCAT

These programs use subroutines in SPINV.C to calculate energies and intensities for asymmetric rotors and linear molecules with up to 999 vibrational states and up to 9 spins. No distinction is made between electronic states and vibrational states, or between electronic and nuclear spins. SPFIT is used for fitting transitions and term values, with no requirement that the transitions obey any particular selection rules. SPFIT takes input files with extensions *par* and *lin*, copies the *par* file to a *bak* file, creates new text output files with extensions *par*, *fit*, *var*. The *par* and *var* files follow essentially the same format and contain fitting parameters and optionally correlation information. The *fit* file contains the results of the fit. SPCAT is used for predicting line positions and strengths. It takes the *var* file as input along with an *int* file that specifies limits for the calculation and contains the transition dipoles. The main output files for SPCAT use extensions *out* and *cat*, which are for general information and for the catalog output format, respectively. The *cat* file follows the format of the JPL catalog, but does not have experimental data flagged. Auxiliary output files with extensions *egy* and *str* can also be requested. The *egy* file can contain energies, derivatives with respect to the parameters, eigenvalues, and the undiagonalized Hamiltonian. The *str* file contains a list of all transition dipole moments. The file names for SPFIT and SPCAT can be specified as command line arguments in any order. The first file name is used as the base file name for any files not explicitly specified. If no command line arguments are specified the program will give a prompt for the file names.



Journal of Molecular Spectroscopy 329 (2016) 1–7

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

ELSEVIER

Feature article

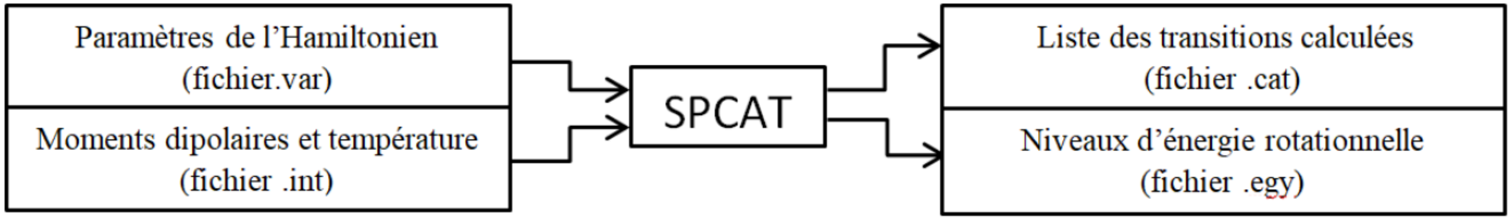
A beginner's guide to Pickett's SPCAT/SPFIT

Stewart E. Novick

Wesleyan University, Department of Chemistry, Middletown, CT 06459, United States

The SPCAT and SPFIT programs from H. M. Pickett (https://spec.jpl.nasa.gov)

Calculation of a theoretical spectrum from Hamiltionien parameters



Paramètres de l'Hamiltonien (fichier.var)

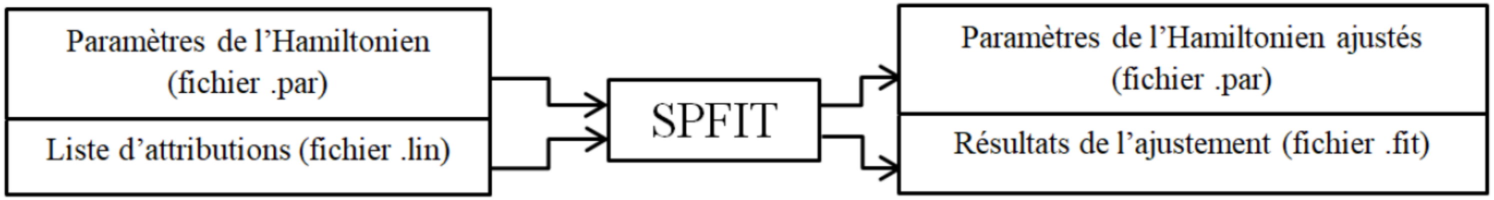
Moments dipolaires et température (fichier .int)

SPCAT

Liste des transitions calculées (fichier .cat)

Niveaux d'énergie rotationnelle (fichier .egy)

Fit of Hamiltionien parameters from experimental frequency transitions



Paramètres de l'Hamiltonien (fichier .par)

Liste d'attributions (fichier .lin)

SPFIT

Paramètres de l'Hamiltonien ajustés (fichier .par)

Résultats de l'ajustement (fichier .fit)

Preparation of the .int file for SPCAT

A set of initial parameters are required:

- **Ab initio parameters**
- **Previous studies in the litterature**

Intramolecular structure and dynamics of mequinol and guaiacol in the gas phase: Rotationally resolved electronic spectra of their S_1 states

José Arturo Ruiz-Santoyo, Marcela Rodríguez-Matus, José Luis Cabellos, John T. Yi, David W. Pratt, Michael Schmitt, Gabriel Merino, and Leonardo Álvarez-Valtierra

Citation: The Journal of Chemical Physics **143**, 094301 (2015);

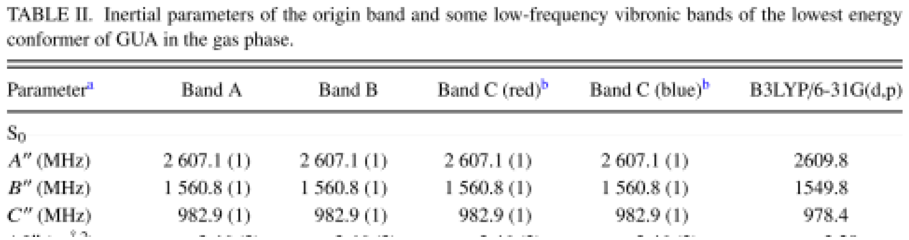
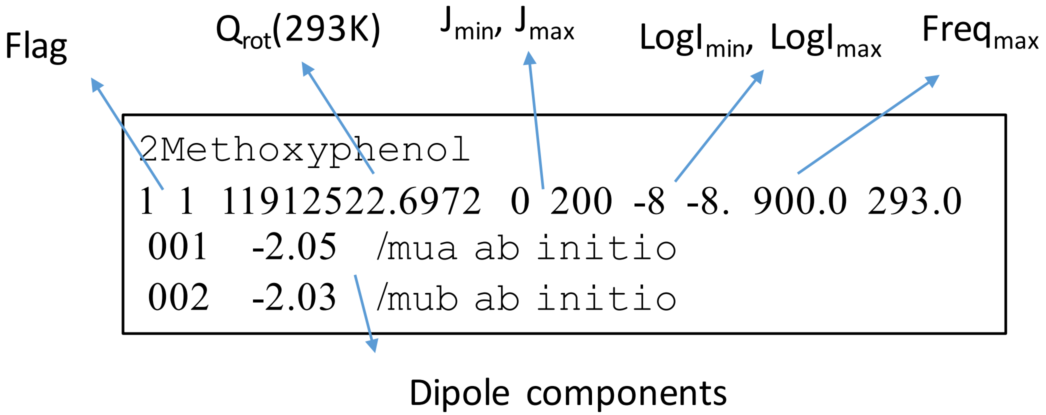


TABLE II. Inertial parameters of the origin band and some low-frequency vibronic bands of the lowest energy conformer of GUA in the gas phase.

Parameter[a]	Band A	Band B	Band C (red)[b]	Band C (blue)[b]	B3LYP/6-31G(d,p)
S_0					
A'' (MHz)	2 607.1 (1)	2 607.1 (1)	2 607.1 (1)	2 607.1 (1)	2609.8
B'' (MHz)	1 560.8 (1)	1 560.8 (1)	1 560.8 (1)	1 560.8 (1)	1549.8
C'' (MHz)	982.9 (1)	982.9 (1)	982.9 (1)	982.9 (1)	978.4

The « 2MP.int » file



Flag

Q_{rot}(293K)

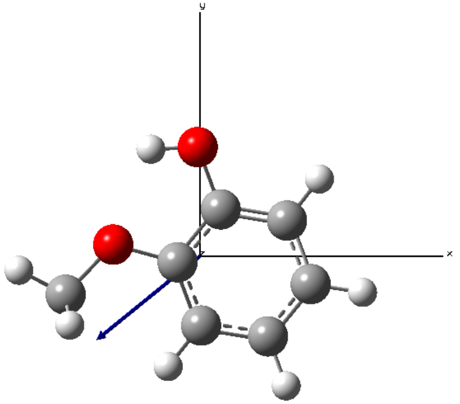
J_{min}, J_{max}

$LogI_{min}$, $LogI_{max}$

$Freq_{max}$

```
2Methoxyphenol
1  1  11912522.6972  0  200  -8  -8.  900.0  293.0
 001    -2.05   /mua ab initio
 002    -2.03   /mub ab initio
```

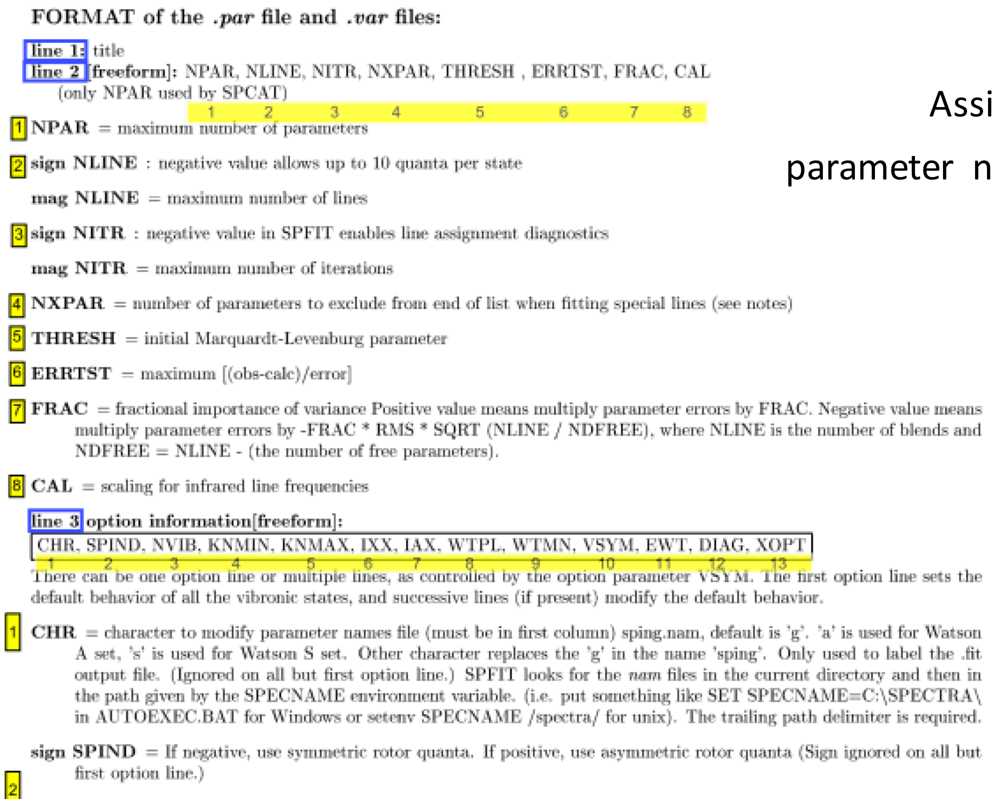
Dipole components



Structure and dipole orientation calculated at the B3LYP/6-31G(d,p) level of theory

$$Q_{rot} = \sum_{J,K_a,K_c} (2J+1) e^{-\frac{E(rot)_i}{kT}} \simeq \sqrt{\frac{\pi}{A_{PAM} B_{PAM} C_{PAM}} \left(\frac{k_B T}{h}\right)^3}.$$

Preparation of the .var file for SPCAT



FORMAT of the *.par* file and *.var* files:

line 1: title
line 2 [freeform]: NPAR, NLINE, NITR, NXPAR, THRESH , ERRTST, FRAC, CAL
(only NPAR used by SPCAT)

1 2 3 4 5 6 7 8

1 **NPAR** = maximum number of parameters

2 **sign NLINE** : negative value allows up to 10 quanta per state

mag NLINE = maximum number of lines

3 **sign NITR** : negative value in SPFIT enables line assignment diagnostics

mag NITR = maximum number of iterations

4 **NXPAR** = number of parameters to exclude from end of list when fitting special lines (see notes)

5 **THRESH** = initial Marquardt-Levenburg parameter

6 **ERRTST** = maximum [(obs-calc)/error]

7 **FRAC** = fractional importance of variance Positive value means multiply parameter errors by FRAC. Negative value means multiply parameter errors by -FRAC * RMS * SQRT (NLINE / NDFREE), where NLINE is the number of blends and NDFREE = NLINE - (the number of free parameters).

8 **CAL** = scaling for infrared line frequencies

line 3 option information[freeform]:

CHR, SPIND, NVIB, KNMIN, KNMAX, IXX, IAX, WTPL, WTMN, VSYM, EWT, DIAG, XOPT

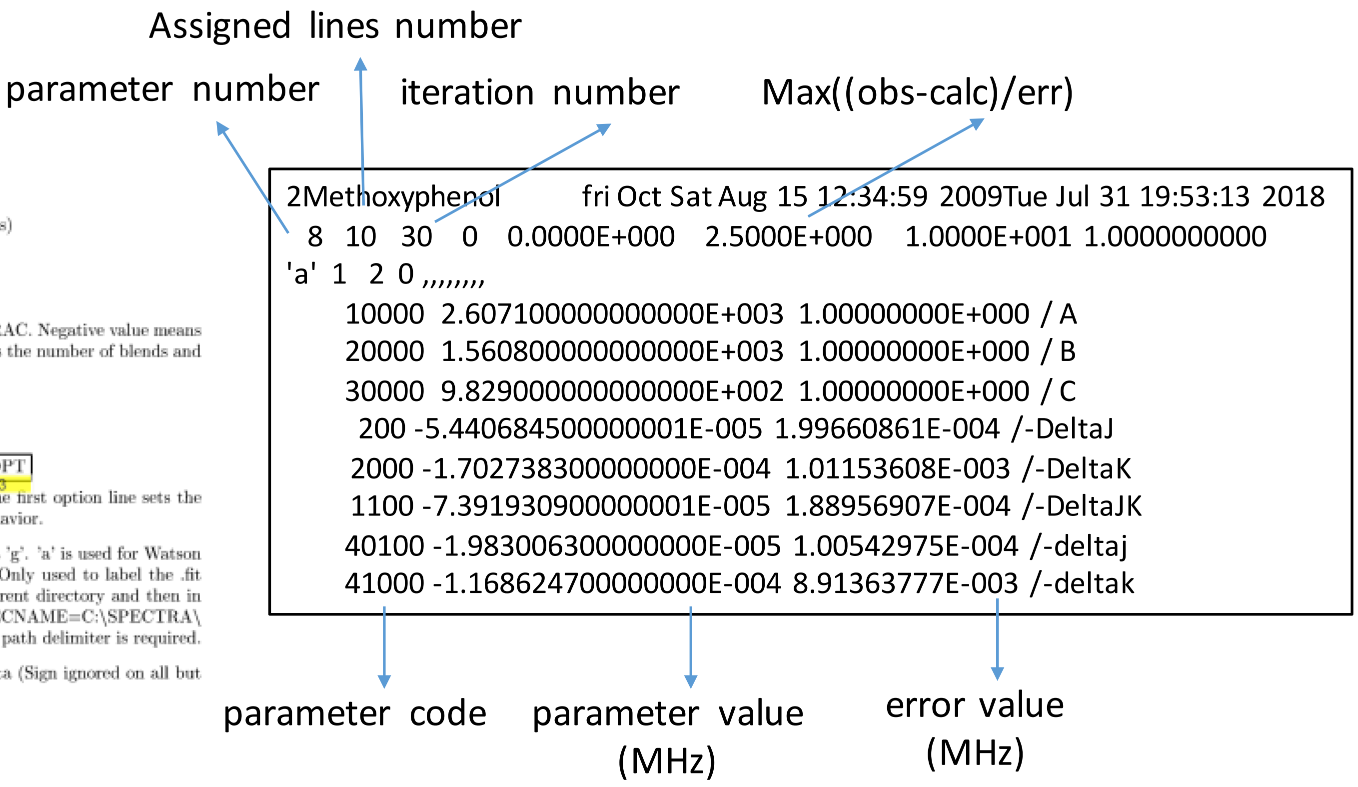
1 2 3 4 5 6 7 8 9 10 11 12 13

There can be one option line or multiple lines, as controlled by the option parameter VSYM. The first option line sets the default behavior of all the vibronic states, and successive lines (if present) modify the default behavior.

1 **CHR** = character to modify parameter names file (must be in first column) sping.nam, default is 'g'. 'a' is used for Watson A set, 's' is used for Watson S set. Other character replaces the 'g' in the name 'sping'. Only used to label the .fit output file. (Ignored on all but first option line.) SPFIT looks for the *nam* files in the current directory and then in the path given by the SPECNAME environment variable. (i.e. put something like SET SPECNAME=C:\SPECTRA\ in AUTOEXEC.BAT for Windows or setenv SPECNAME /spectra/ for unix). The trailing path delimiter is required.

sign SPIND = If negative, use symmetric rotor quanta. If positive, use asymmetric rotor quanta (Sign ignored on all but first option line.)

2



Assigned lines number

parameter number

iteration number

Max((obs-calc)/err)

```
2Methoxyphenol          fri Oct Sat Aug 15 12:34:59  2009Tue Jul 31 19:53:13  2018
 8   10    30    0    0.0000E+000    2.5000E+000    1.0000E+001 1.0000000000
'a'  1   2  0 ,,,,,,,,
      10000  2.607100000000000E+003  1.00000000E+000 / A
      20000  1.560800000000000E+003  1.00000000E+000 / B
      30000  9.829000000000000E+002  1.00000000E+000 / C
        200 -5.440684500000001E-005  1.99660861E-004  /-DeltaJ
       2000 -1.702738300000000E-004  1.01153608E-003  /-DeltaK
       1100 -7.391930900000001E-005  1.88956907E-004  /-DeltaJK
      40100 -1.983006300000000E-005  1.00542975E-004  /-deltaj
      41000 -1.168624700000000E-004  8.91363777E-003  /-deltak
```

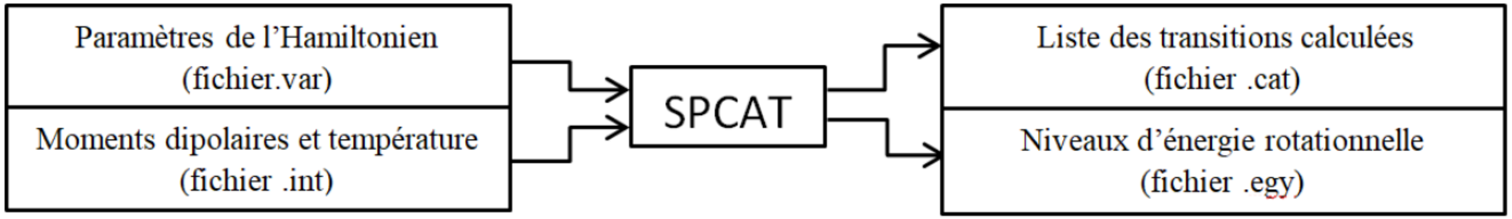
parameter code

parameter value
(MHz)

error value
(MHz)

Run the SPCAT.exe with 2MP.int and 2MP.var

Calculation of a theoretical spectrum from Hamiltionien parameters



Paramètres de l'Hamiltonien
(fichier.var)

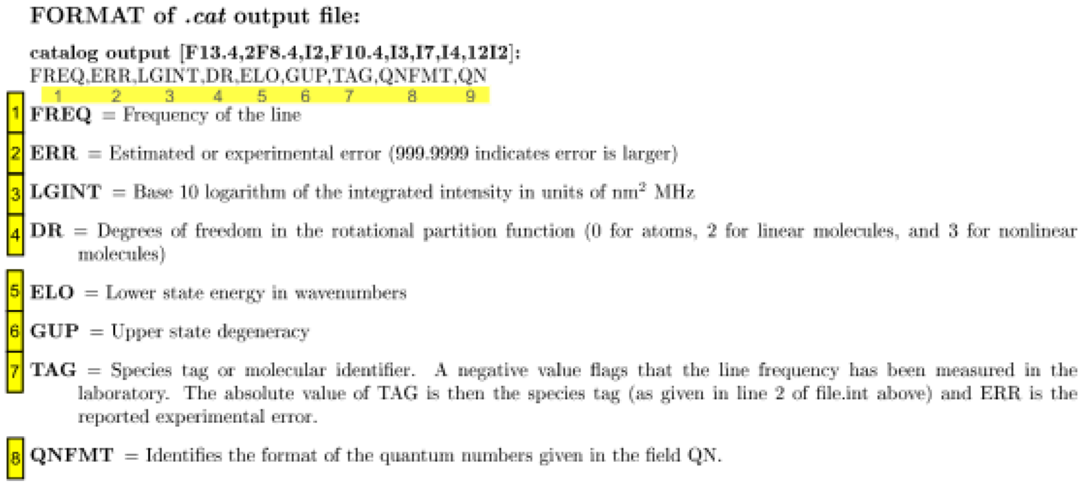
Moments dipolaires et température
(fichier .int)

SPCAT

Liste des transitions calculées
(fichier .cat)

Niveaux d'énergie rotationnelle
(fichier .egy)

The .cat file:



FORMAT of *.cat* output file:

catalog output [F13.4,2F8.4,I2,F10.4,I3,I7,I4,12I2]:
FREQ,ERR,LGINT,DR,ELO,GUP,TAG,QNFMT,QN
1 2 3 4 5 6 7 8 9

1 **FREQ** = Frequency of the line

2 **ERR** = Estimated or experimental error (999.9999 indicates error is larger)

3 **LGINT** = Base 10 logarithm of the integrated intensity in units of nm^2 MHz

4 **DR** = Degrees of freedom in the rotational partition function (0 for atoms, 2 for linear molecules, and 3 for nonlinear molecules)

5 **ELO** = Lower state energy in wavenumbers

6 **GUP** = Upper state degeneracy

7 **TAG** = Species tag or molecular identifier. A negative value flags that the line frequency has been measured in the laboratory. The absolute value of TAG is then the species tag (as given in line 2 of file.int above) and ERR is the reported experimental error.

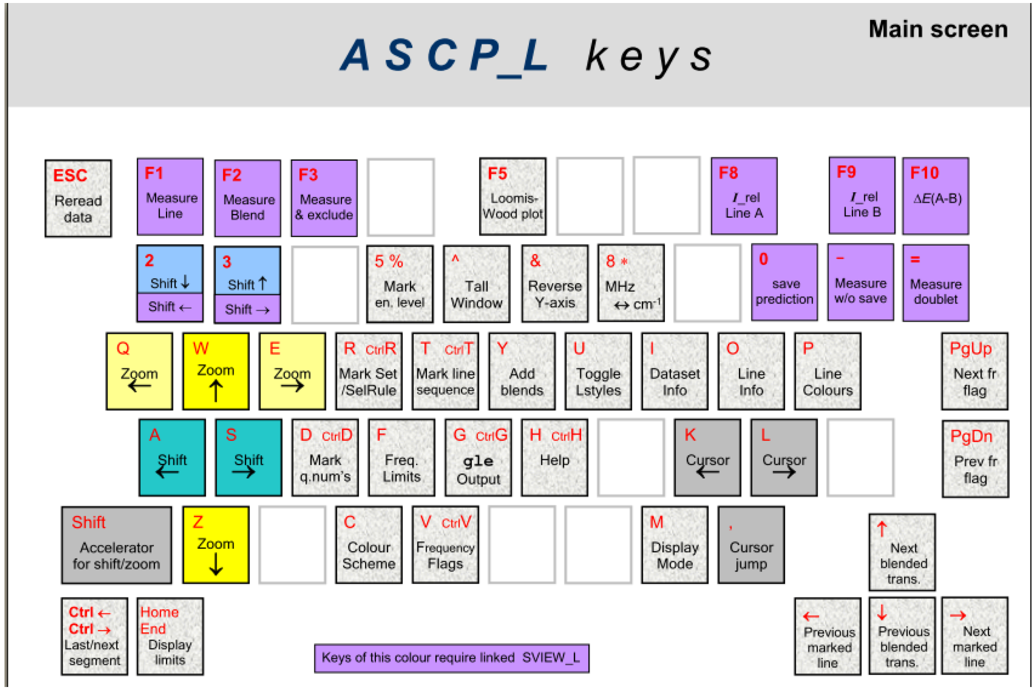
8 **QNFMT** = Identifies the format of the quantum numbers given in the field QN.

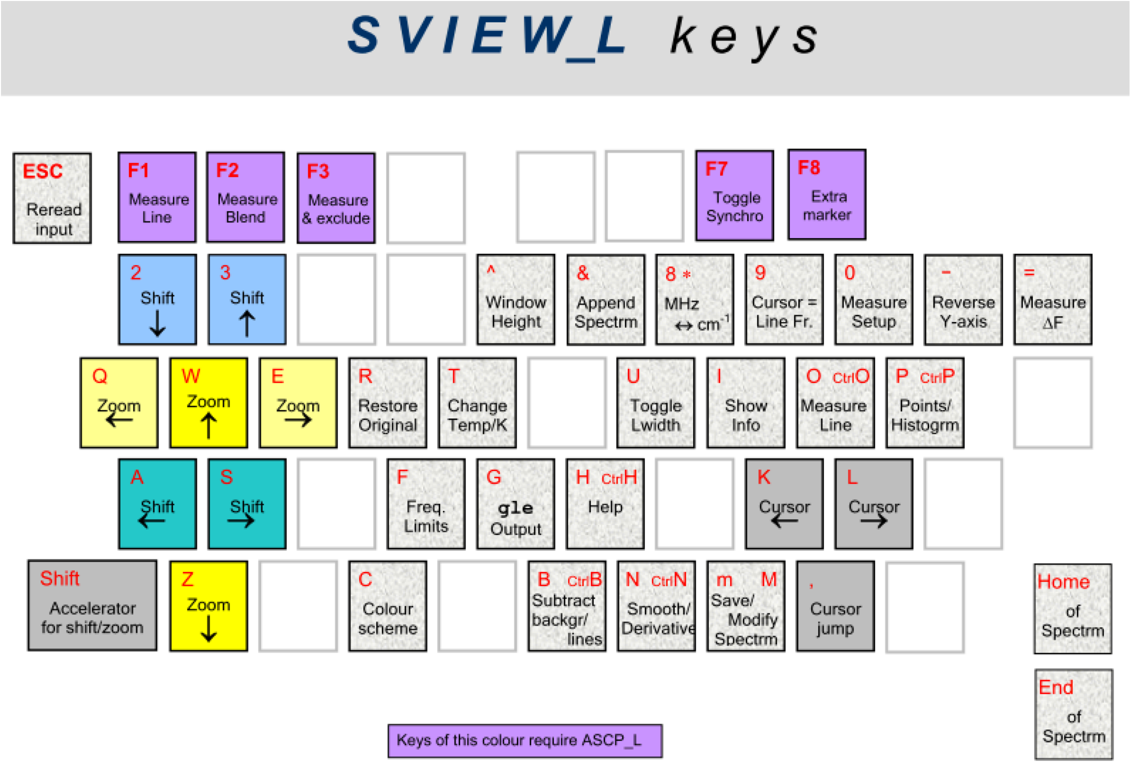
```
16266.6925  0.3410 -7.9660 3  36.2539 53   1140426 11 15 0   26 10 16 0
16362.1615  0.9045 -7.9839 3  33.7719 51   1140425 11 14 0   25 10 15 0
17285.6577  0.8001 -7.9597 3  33.1954 51   1140425 10 15 0   25  9 16 0
17448.5289  0.6098 -7.8875 3  42.0718 57   1140428 12 16 0   28 11 17 0
17603.5800  0.6297 -7.9052 3  38.8003 55   1140427 11 16 0   27 10 17 0
17660.3738  1.3937 -7.9654 3  31.3739 49   1140424 11 13 0   24 10 14 0
18126.2580  0.4183 -7.8500 3  44.8285 59   1140429 12 17 0   29 11 18 0
18206.8077  1.2487 -7.8836 3  39.3875 55   1140427 12 15 0   27 11 16 0
```

Ready to use ASCP_L.exe and SVIEW_L.exe

ASCP_L reads the .cat file from SPCAT

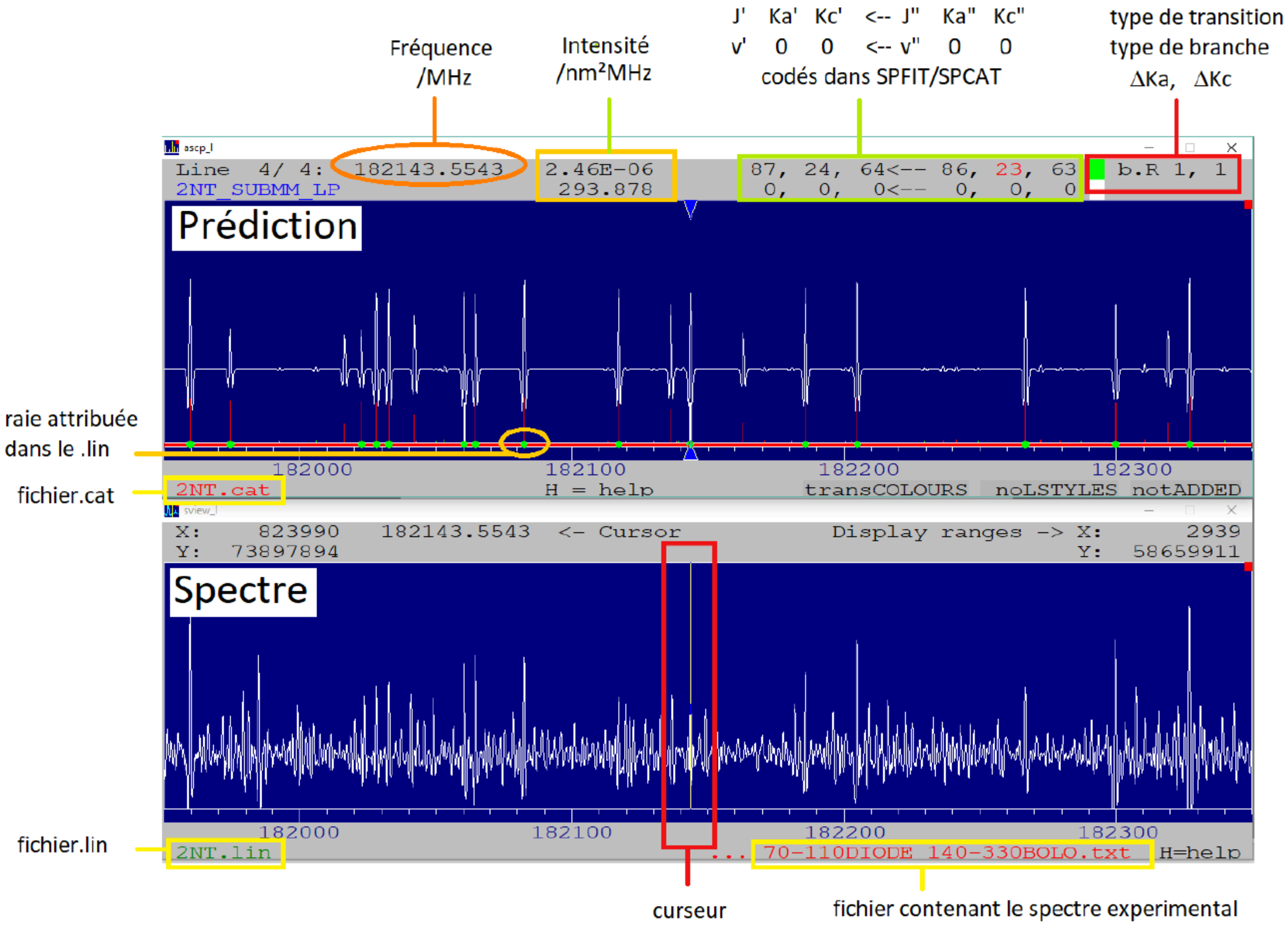
SVIEW_L reads the experimental data and is synchronized with ASCP_L





ASCP_L prepares the .lin file for SPFIT

Ready to use ASCP_L.exe and SVIEW_L.exe



Fréquence /MHz

Intensité /nm²MHz

J' Ka' Kc' <-- J" Ka" Kc"
v' 0 0 <-- v" 0 0
codés dans SPFIT/SPCAT

type de transition
type de branche
ΔKa, ΔKc

```
ascp_l
Line   4/ 4:  182143.5543   2.46E-06     87, 24, 64<-- 86, 23, 63   b.R 1, 1
2NT_SUBMM_LP                 293.878       0,  0,  0<--  0,  0,  0
```

```
2NT.cat                  H = help          transCOLOURS  noLSTYLES notADDED
```

```
sview_l
X:     823990    182143.5543   <- Cursor        Display ranges -> X:      2939
Y:   73897894                                                    Y:  58659911
```

```
2NT.lin                                 ... 70-110DIODE 140-330BOLO.txt  H=help
```

raie attribuée dans le .lin

fichier.cat

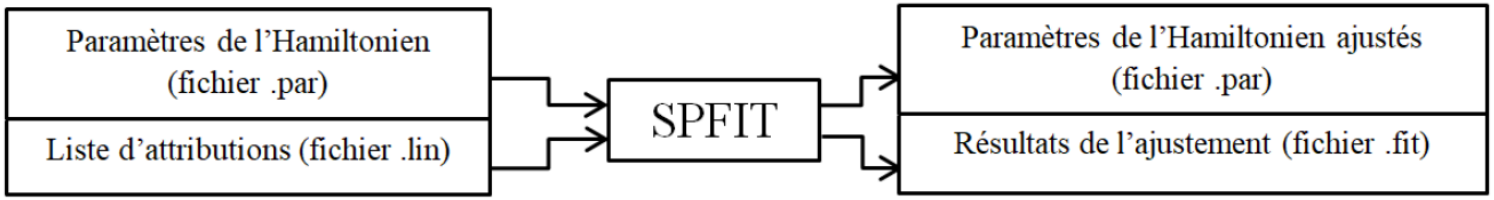
fichier.lin

curseur

fichier contenant le spectre experimental

Run the SPFIT.exe with 2MP.lin and 2MP.par

Fit of Hamiltionien parameters from experimental frequency transitions


Paramètres de l’Hamiltonien (fichier .par)

Liste d’attributions (fichier .lin)

SPFIT

Paramètres de l’Hamiltonien ajustés (fichier .par)

Résultats de l’ajustement (fichier .fit)

The .lin file:

The .lin file generated by ASCP_L:

```
32  4 28 31  4 27  0  0  0  0  0  0   71641.161538   0.100000  1.00000
33  3 30 32  3 29  0  0  0  0  0  0   71656.706616   0.100000  1.00000
34  2 32 33  2 31  0  0  0  0  0  0   71679.139339   0.100000  1.00000
35  1 34 34  1 33  0  0  0  0  0  0   71705.197857   0.100000  1.00000
36  0 36 35  0 35  0  0  0  0  0  0   71732.698745   0.100000  1.00000
```

The .lin file accepted by SPFIT:

```
32  4 28  0 31  4 27  0  0  0  0  0   71641.161538   0.100000  1.00000
33  3 30  0 32  3 29  0  0  0  0  0   71656.706616   0.100000  1.00000
34  2 32  0 33  2 31  0  0  0  0  0   71679.139339   0.100000  1.00000
35  1 34  0 34  1 33  0  0  0  0  0   71705.197857   0.100000  1.00000
36  0 36  0 35  0 35  0  0  0  0  0   71732.698745   0.100000  1.00000
```

FORMAT of the *.lin* file:

line 1–NLINE [12I3,freeform]: QN,FREQ,ERR,WT

QN = 12-integer field of quantum numbers. Interpreted in a multiple I3 format as the quantum numbers for the line (upper quanta first, followed immediately by lower quanta). Unused fields can be used for annotation. The entire field is printed in file.fit

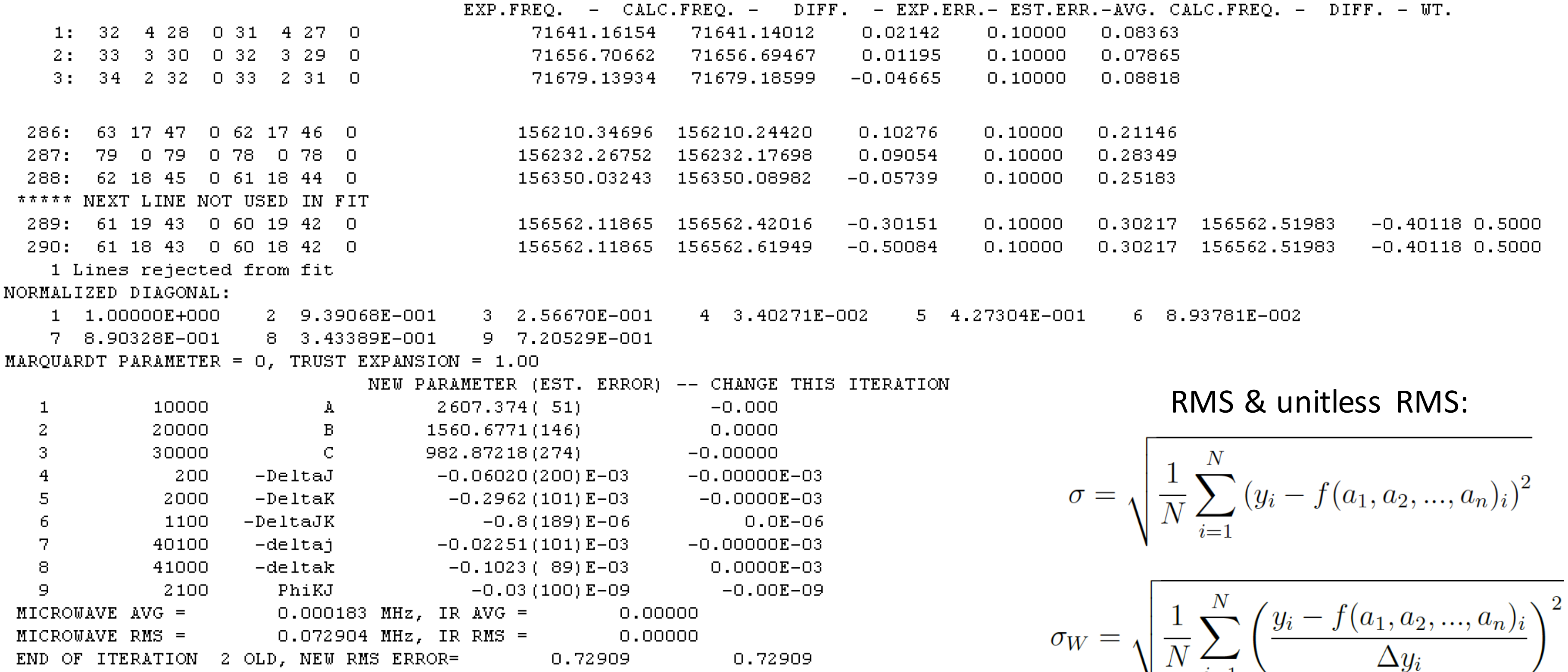
FREQ = frequency in MHz or wavenumbers

ERR = experimental error. Minus sign means that the frequency and error are in units of wavenumbers. FREQ and ERR will be converted internally to units of MHz.

WT = relative weight of line within a blend (normalized to unity by program)

Run the SPFIT.exe with 2MP.lin and 2MP.par

The .fit file:



```
                                         EXP.FREQ.  -  CALC.FREQ. -   DIFF.  - EXP.ERR.- EST.ERR.-AVG. CALC.FREQ. -  DIFF. - WT.
    1:  32  4 28  0 31  4 27  0                71641.16154   71641.14012    0.02142    0.10000   0.08363
    2:  33  3 30  0 32  3 29  0                71656.70662   71656.69467    0.01195    0.10000   0.07865
    3:  34  2 32  0 33  2 31  0                71679.13934   71679.18599   -0.04665    0.10000   0.08818

  286:  63 17 47  0 62 17 46  0               156210.34696  156210.24420    0.10276    0.10000   0.21146
  287:  79  0 79  0 78  0 78  0               156232.26752  156232.17698    0.09054    0.10000   0.28349
  288:  62 18 45  0 61 18 44  0               156350.03243  156350.08982   -0.05739    0.10000   0.25183
 ***** NEXT LINE NOT USED IN FIT
  289:  61 19 43  0 60 19 42  0               156562.11865  156562.42016   -0.30151    0.10000   0.30217  156562.51983   -0.40118 0.5000
  290:  61 18 43  0 60 18 42  0               156562.11865  156562.61949   -0.50084    0.10000   0.30217  156562.51983   -0.40118 0.5000
    1 Lines rejected from fit
NORMALIZED DIAGONAL:
    1  1.00000E+000    2  9.39068E-001    3  2.56670E-001    4  3.40271E-002    5  4.27304E-001    6  8.93781E-002
    7  8.90328E-001    8  3.43389E-001    9  7.20529E-001
MARQUARDT PARAMETER = 0, TRUST EXPANSION = 1.00
                                NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION
   1         10000           A        2607.374( 51)           -0.000
   2         20000           B       1560.6771(146)           0.0000
   3         30000           C       982.87218(274)         -0.00000
   4           200     -DeltaJ        -0.06020(200)E-03     -0.00000E-03
   5          2000     -DeltaK         -0.2962(101)E-03      -0.0000E-03
   6          1100    -DeltaJK            -0.8(189)E-06          0.0E-06
   7         40100     -deltaj        -0.02251(101)E-03     -0.00000E-03
   8         41000     -deltak         -0.1023( 89)E-03       0.0000E-03
   9          2100       PhiKJ           -0.03(100)E-09        -0.00E-09
 MICROWAVE AVG =        0.000183 MHz, IR AVG =        0.00000
 MICROWAVE RMS =        0.072904 MHz, IR RMS =        0.00000
 END OF ITERATION  2 OLD, NEW RMS ERROR=        0.72909         0.72909
```

RMS & unitless RMS:

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(y_i - f(a_1, a_2, \ldots, a_n)_i\right)^2}$$

$$\sigma_W = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{y_i - f(a_1, a_2, \ldots, a_n)_i}{\Delta y_i}\right)^2}$$