pybranch.py : A python script to obtain transition probabilities from Fourier transform spectra

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1 Description of program pybranch.py

This program is used to calculate experimental branching fractions and transition probabilities from measurements of atomic spectra. The program is usually used with spectral line lists from intensity-calibrated spectra from Fourier transform spectrometers, but could in principle be used with any calibrated spectra that meet the input requirements. The program takes a set of linelists and computes a weighted average branching fraction (F_{ki}) for each line from an upper level k to lower level i, using the calibrated integrated intensities and signal-to-noise (S/N) ratios. It combines these branching fractions with the level lifetime to obtain the transition probability.

The program prints out the calibrated intensities and S/N ratios for all the lines observed from a particular upper level in each spectrum. The user then chooses one line to use as a reference to put all of the intensities on the same scale. If the reference line is not observed in a particular spectrum, the intensity scale of that spectrum can be set by using a normalization factor calculated from a strong transfer line that is observed in both that spectrum and other spectra that can be calibrated from the reference line (see Section 3.2.4 of Sikström et al. [2002]). The program can use calculated transition probabilities to calculate a residual from lines that have not been observed .

The program is written in python 3 and uses tkinter for the interface. Additional python packages that are used are:

- glob: Used for unix-style pathname pattern expression for compatibility with Windows.
- tkinter.scrolledtext: This is used for the scrolled text section that is used to display the results

The following sections describe the different input files that are required for the program. The final section describes the way in which the calculations are done and how the uncertainties of the results are estimated.

2 The branchrc.py and branchgrep.py files

The resource file for pybranch - BRANCHRC.PY - contains default values for many of the filenames and parameters used in the script. The values of these parameters should be set before the program is first run to match what is required for anaylzing the spectra. The parameters are as follows:

upper_level: Initial value for the upper level. This can be changed in the interface.

file_name: The filename used for the results. The extension '.log' will be written to this. All of the information written to the scrolling text section is written to this file. The name can be changed in the interface.

reference_level: The intensity of all the lines in each file will be multiplied by a scaling factor so that the intensity of the line to this level is 1000 in each file. The value can be changed in the interface.

transfer_file: The name of a file where the line to the reference_level does not appear, so that the lines need to be multiplied by a different scaling factor determined by the transfer_level. The value can be changed in the interface.

transfer_level: The lower level of a line in the transfer file that is seen in at least one other file that contains the line to the reference_level. All the lines in the transfer file are multiplied by a scaling factor so that the intensity of the line to the transfer_level is the same as the weighted average of the intensities of the lines to the transfer level in the other files. The value can be changed in the interface.

identified_lines_file: A file that contains previous identifications of lines in the spectrum. Its format is described in section 3. Its value can be changed in the interface.

lifetime_file: A file containing the energy levels and lifetimes in the spectrum. The value is fixed.

delfile: Initial value of a file containing a line that needs to be deleted because its intensity is wrong for some reason (blend, mis-identification etc.). The value can be changed in the interface.

delval: Initial value of a lower level of the line that is wrong in the delfile. The value can be changed in the interface.

lifetime_unc: The uncertainty of the lifetimes in the lifetime file. Its value is fixed.

all_spectrum_files: A regular expression used to match the files containing lines and their intensities.

calc_file: A file containing calculated transition probabilities that is used to compare with the measurements and to estimate a residual.

discrim: A wavelength discriminator to match the observations with the calculations.

unc_cal: A calibration uncertainty estimated from the repeatability of the observations of the calibration file.

The file BRANCHGREP.PY contains two functions that are required for the use of the Unix command *grep* on Windows machines.

3 Input files

All files use a key to identify the energy levels being used. This key must be common to all the files used, although other energy level descriptions may be used elsewhere in the file. This enables the program to match the same energy level from different sources, even when the value of the level may be different (e.g. values from older calculations, compared with modern measurements)

Identified lines file: A file of previously-identified lines, separated by column. The format is:

Column 1: Wavenumber of transition.

Column 2: Lower energy level value in cm^{-1}.

Column 3: Upper energy level value in cm^{-1}.

Column 4: Lower configuration key - this must match the format in the energy levels and lifetimes file. Can't contain spaces.

Column 6: Upper configuration key - this must match the format in the energy levels and lifetimes file. Can't contain spaces.

Column 7: Optional notes (e.g. intensities).

An example is:

```
 8503.122    36101.52   84604.64      d5____a2G3 -     1F4p__u2F2*       21
48491.0570       0.00   48491.06      d5____a6S2 -     5D4p__z6P2*     2500
48474.553    20517.79   68992.35      d5____a4G3 -     3G4p__y4H4*       28
48473.07     20519.27   68992.35      d5____a4G4 -     3G4p__y4H4*        4
48451.940    25033.67   73485.61      d5____b4D3 -     3D4p__w4D3*       69
```

Lifetimes file: File of energy levels and lifetimes. The format is:

Column 1: Energy level - any format but can't contain spaces.

Column 2: J value.

Column 3: Energy level value in cm^{-1}.

Column 4: Parity - 0 or 1.

Column 5: Lifetime in ns. If none, should be '-'.

Column 6: Energy level key. This must match the format in the identified lines file.

An example is:

```
5D4p__z6F4* 4.5     47464.55            0 4.2 5D4p__z6F4
5D4p__z6F5* 5.5     47751.62            0 4.0 5D4p__z6F5
d5____d2D2  2.5     47354.44            1 - d5____d2D2
d5____d2D1  1.5     47372.53            1 - d5____d2D1
```

Calculations file: File of calculations to be used for comparison. The format is:

Column 1: Wavenumber. Does not need to be an exact match to the wavenumbers in the spectra or identified lines file but should match within the discriminator specified in the branchrc.py file.

Column 2: The calculated transition probability in units of 10^6 s^{-1}. This is used for comparison with the measured transition probabilities and also for calculating the residuals.

Last column: The energy level key. This must match the format in the identified lines file and the lifetimes file.

An example is:

```
45246.3400    0.3883     2209.435    -2.94411  1.5   21824.11* 1|4P3)      1.5   67070.45* a3F4p_y4F1*
45246.6100    4.1274     2209.422    -1.91757   .5   21823.84* 1|4P3)      1.5   67070.45* a3F4p_y4F1*
45247.9300    4.0368     2209.357    -1.92724  2.5   21822.52* 1|4P3)      1.5   67070.45* a3F4p_y4F1*
45358.6800    0.0220     2203.962    -4.01645  2.5   19797.88* 2|5D4)4D    2.5   65156.56* a3F4p_z4G2*
45359.9400    0.2962     2203.901    -2.66596  3.5   20024.01* 2|5D4)4D    4.5   65383.95* a3F4p_z4G4*
45459.0000    0.1568     2199.098    -3.04100  2.5   19797.88* 2|5D4)4D    3.5   65256.88* a3F4p_z4G3*
```

Branching ratio files: Set of files of measured relative line intensities in units of photons per second. The filenames should match the pattern specified in 'all_spectrum_files' variable in the branchrc.py file. The first line has three numbers:

- The resolution of the spectrum in cm^{-1}.
- The lower wavenumber limit of the calibration in cm^{-1}
- The upper wavenumber limit of the calibration in cm^{-1}.

These three numbers are used to calculate the uncertainties of the branching fractions and transition probabilities.

The following lines contain the parameters of the spectral lines in each of the files, with the following format:

Column 1: S/N ratio of the line

Column 2: Calibrated, integrated intensity of the line

Column 3: Full width at half maxiumum (FWHM) of the line. Used to calculate the uncertainty of the intensity

Column 5: Wavenumber of the transition in cm^{-1}.

Column 7: Lower level key of the transition. Must match the key in the lifetimes file.

Column 9: Upper level key of the transition. Must match the key in the lifetimes file.

An example is:

```
0.09 32000. 46000.
4      19090   130.04 3043.665   32855.131   II   d5____b4F4 - a3F4p_z4G5*
5      19630   117.26 3035.418   32944.389   II   3F4s__a4F2 - a3P4p_y4D1*
10     41560   142.82 3004.795   33280.144   II   3F4s__a4F3 - a3P4p_y4D2*
6      13610   110.76 3000.811   33324.329   II   d5____a2F3 - 3H4p__z2G4*
8      26890   121.93 2995.621   33382.062   II   3H4s__a4H4 - 3H4p__z4H3*
7      24410   162.60 2993.318   33407.744   II   3H4s__a4H5 - 3H4p__z4H4*
106   310900   150.52 2990.063   33444.107   II   3H4s__a4H3 - 3H4p__z4H3*
```

4 Interface

The main interface is shown in Figure 1. The left side of the interface has the buttons and entry fields for the files and levels of interest. The right side contains a scrolled text section with the results of the actions. The buttons and entry fields are as follows:

Quit button: Closes all files and quits the program.

Results button: First prints out the values of the residuals - i.e. transition probabilities in units of 10^6 s^{-1} of lines that were not observed in any spectra, but were included in the calculations. These are used to calculate a residual that is used in the calculation of the branching fraction. The program then prints out the Summary section, with the line wavenumber, lower energy level, weighting factor, measured branching fractions and uncertainty, transition probabilities and uncertainties, and the value in the theoretical calculations.

Save As : The filename used for the output. All of the information in the scrolled text section is written to this file.

ID'd lines file: The file containing a list of previously identified lines. The lines in this file are printed in the first block in the scrolled text field.

Upper Level: The upper level of interest. The format must be that used in the lifetimes file

Reference Level: The lower level used for putting all of the intensities in the separate files on the same scale. The intensity of this line is set to 1000 in all the files and the other lines adjusted accordingly. The results are printed in the second block in the scrolled text field in Fig. 1.

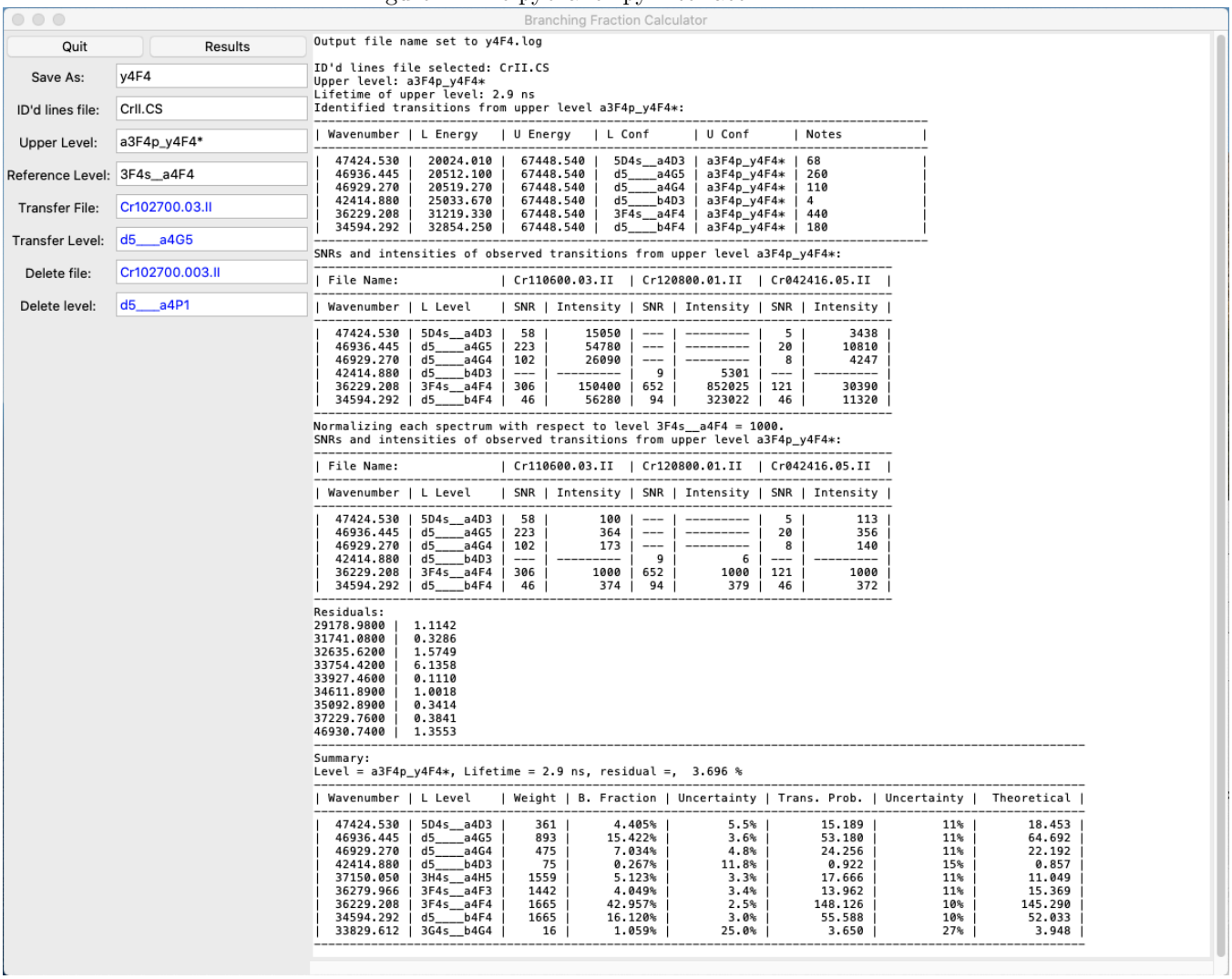
Transfer File: This is the name of a file that does not contain the line to the reference level. The intensities in this file must be set using a transfer level that gives a line in both the transfer file and in at least one other file that contains the reference level. A weighted average intensity and uncertainty is calculated from all the other files that contain both the transfer level and the reference level and the intensity of the transfer line is set to that value. The uncertainties of the intensities of all the lines in the transfer file are then added in quadrature to the uncertainty of the weighted average intensity.

Transfer Level: Used with the "Transfer File" entry.

Delete File: Used to delete lines in specific files that appear to be erroneous

Delete Level: The level to delete in the "Delete File"

Figure 1: The pybranch.py interface




```
Output file name set to y4F4.log

ID'd lines file selected: CrII.CS
Upper level: a3F4p_y4F4*
Lifetime of upper level: 2.9 ns
Identified transitions from upper level a3F4p_y4F4*:
-------------------------------------------------------------------------------------------
| Wavenumber | L Energy   | U Energy   | L Conf      | U Conf      | Notes           |
-------------------------------------------------------------------------------------------
|  47424.530 |  20024.010 |  67448.540 |  5D4s__a4D3 | a3F4p_y4F4* | 68              |
|  46936.445 |  20512.100 |  67448.540 |  d5____a4G5 | a3F4p_y4F4* | 260             |
|  46929.270 |  20519.270 |  67448.540 |  d5____a4G4 | a3F4p_y4F4* | 110             |
|  42414.880 |  25033.670 |  67448.540 |  d5____b4D3 | a3F4p_y4F4* | 4               |
|  36229.208 |  31219.330 |  67448.540 |  3F4s__a4F4 | a3F4p_y4F4* | 440             |
|  34594.292 |  32854.250 |  67448.540 |  d5____b4F4 | a3F4p_y4F4* | 180             |
-------------------------------------------------------------------------------------------
SNRs and intensities of observed transitions from upper level a3F4p_y4F4*:
-------------------------------------------------------------------------------------------
| File Name:               | Cr110600.03.II  | Cr120800.01.II  | Cr042416.05.II  |
-------------------------------------------------------------------------------------------
| Wavenumber | L Level     | SNR | Intensity | SNR | Intensity | SNR | Intensity |
-------------------------------------------------------------------------------------------
|  47424.530 | 5D4s__a4D3  |  58 |     15050 | --- | --------- |   5 |      3438 |
|  46936.445 | d5____a4G5  | 223 |     54780 | --- | --------- |  20 |     10810 |
|  46929.270 | d5____a4G4  | 102 |     26090 | --- | --------- |   8 |      4247 |
|  42414.880 | d5____b4D3  | --- | --------- |   9 |      5301 | --- | --------- |
|  36229.208 | 3F4s__a4F4  | 306 |    150400 | 652 |    852025 | 121 |     30390 |
|  34594.292 | d5____b4F4  |  46 |     56280 |  94 |    323022 |  46 |     11320 |
-------------------------------------------------------------------------------------------
Normalizing each spectrum with respect to level 3F4s__a4F4 = 1000.
SNRs and intensities of observed transitions from upper level a3F4p_y4F4*:
-------------------------------------------------------------------------------------------
| File Name:               | Cr110600.03.II  | Cr120800.01.II  | Cr042416.05.II  |
-------------------------------------------------------------------------------------------
| Wavenumber | L Level     | SNR | Intensity | SNR | Intensity | SNR | Intensity |
-------------------------------------------------------------------------------------------
|  47424.530 | 5D4s__a4D3  |  58 |       100 | --- | --------- |   5 |       113 |
|  46936.445 | d5____a4G5  | 223 |       364 | --- | --------- |  20 |       356 |
|  46929.270 | d5____a4G4  | 102 |       173 | --- | --------- |   8 |       140 |
|  42414.880 | d5____b4D3  | --- | --------- |   9 |         6 | --- | --------- |
|  36229.208 | 3F4s__a4F4  | 306 |      1000 | 652 |      1000 | 121 |      1000 |
|  34594.292 | d5____b4F4  |  46 |       374 |  94 |       379 |  46 |       372 |
-------------------------------------------------------------------------------------------
Residuals:
29178.9800 |  1.1142
31741.0800 |  0.3286
32635.6200 |  1.5749
33754.4200 |  6.1358
33927.4600 |  0.1110
34611.8900 |  1.0018
35092.8900 |  0.3414
37229.7600 |  0.3841
46930.7400 |  1.3553
-------------------------------------------------------------------------------------------------------------
Summary:
Level = a3F4p_y4F4*, Lifetime = 2.9 ns, residual =,  3.696 %
-------------------------------------------------------------------------------------------------------------
| Wavenumber | L Level     | Weight | B. Fraction | Uncertainty | Trans. Prob. | Uncertainty |  Theoretical |
-------------------------------------------------------------------------------------------------------------
|  47424.530 | 5D4s__a4D3  |    361 |      4.405% |        5.5% |       15.189 |         11% |       18.453 |
|  46936.445 | d5____a4G5  |    893 |     15.422% |        3.6% |       53.180 |         11% |       64.692 |
|  46929.270 | d5____a4G4  |    475 |      7.034% |        4.8% |       24.256 |         11% |       22.192 |
|  42414.880 | d5____b4D3  |     75 |      0.267% |       11.8% |        0.922 |         15% |        0.857 |
|  37150.050 | 3H4s__a4H5  |   1559 |      5.123% |        3.3% |       17.666 |         11% |       11.049 |
|  36279.966 | 3F4s__a4F3  |   1442 |      4.049% |        3.4% |       13.962 |         11% |       15.369 |
|  36229.208 | 3F4s__a4F4  |   1665 |     42.957% |        2.5% |      148.126 |         10% |      145.290 |
|  34594.292 | d5____b4F4  |   1665 |     16.120% |        3.0% |       55.588 |         10% |       52.033 |
|  33829.612 | 3G4s__b4G4  |     16 |      1.059% |       25.0% |        3.650 |         27% |        3.948 |
-------------------------------------------------------------------------------------------------------------
```

5 Calculations and Uncertainties

The calculation of the branching fractions, transition probabilities, and their uncertainties follows the analysis of Sikström et al. [2002]. The transition probability between an upper level, k and lower level, i, is obtained by combining a measurement of the lifetime of the upper level τ_k with the branching fraction, F_{ki} :

$$F_{ki} = I_{ki} / \sum_j I_{kj} \tag{1}$$

where I_{ki} is the intensity of the line in photons/s and the sum is over all of the decay channels from the upper level k. The transition probability A_{ki} is then calculated from τ_k using:

$$A_{ki} = F_{ki} / \tau_k \tag{2}$$

The following components of uncertainty are included in the PYBRANCH.PY script:

1. The statistical uncertainty U_{stat} of the line intensity is estimated from equation 10 of Sikström et al. [2002] as

$$U_{stat} = \frac{1.5}{(S/N)\sqrt{n}} \tag{3}$$

   where n is the number of points per FWHM. n is calculated from the resolution in the first line of the branching ratio files and the FWHM in the third column.

2. The uncertainty with which the response of the spectrometer and imaging system can be measured is estimated from repeated observations of the calibration lamp on the same day. As noted in Section 3.2.1 of Sikström et al. [2002], applying this uncertainty directly to each line would be an overestimate, as lines close together in wavenumber will have a much smaller uncertainty in the calibration than lines well-separated in wavenumber. The script thus multiplies the uncertainty by a factor $\Delta\sigma / W_\sigma$, where $\Delta\sigma$ is the separation of the line from the strongest line from the upper level of interest, and W_σ is the total width of the observed calibration spectrum, given in the first line of each branching ratio file.

3. The uncertainty of strong lines in each spectrum is limitied to a minimum of 6 % to ensure that strong lines receive similar weighting in the average. The 6 % minimum uncertainty was taken from the estimated calibration uncertainty and applied after combining the calibration and statistical uncertainties in quadrature.

4. The inverse square of the uncertainty of the line in each spectrum is applied as a weighting factor to calculate F_{ki} for each spectral line. The uncertainty of F_{ki} is then then derived from the first two terms in equation 7 of Sikström et al. [2002].

5. In cases where the reference line is not seen in one or more spectra, a transfer line is used to calculate a normalizing factor f to put the spectrum on the same intensity scale as the other spectra. The uncertainty of this normalizing factor $u(f)$ is derived from the weighted average of the quadrature sum of the uncertainty of the reference line $u(I_{ref,j})$ in each normalized spectrum, j, and the uncertainty of the transfer line $u(I_{trans,j})$ in each normalized spectrum:

$$u(f) = \Sigma_j \sqrt{u(I_{trans,j})^2 + u(I_{ref,j})^2} \tag{4}$$

   The uncertainty of the normalizing factor is added in quadrature to the uncertainty of each line in spectrum not containing the reference line.

6. The residuals are applied as a correction to the lifetime before calculating F_{ki} and transition probability. The relative uncertainty of the residuals, is estimated as 50 %, as in Section 3.3 of Sikström et al. [2002]. As noted in Sikström et al. [2002], its influence on the uncertainties of the measured lines is small provided that the residuals themselves are small.

References

C. M. Sikström, H. Nilsson, U. Litzén, A. Blom, and H. Lundberg. Uncertainty of oscillator strengths derived from lifetimes and branching fractions. *J. Quant. Spectrosc. Radiat. Transfer*, 74:355–368, 2002. doi: 10.1016/S0022-4073(01)00258-8.