INSTITUTO DE ESTUDOS AVANÇADOS - DIVISÃO DE FOTÔNICA

ASAS Software (Beta 1.0)
Analysis and Simulation of Atomic Spectra

by

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SUMMARY

1. Introduction 3

2. Installing and uninstalling 5

3. Database 12

3.1. Remarks on level databases 12

3.2. Remarks on lines databases 13

4. How to use the program 15

4.1. Editing databases 15

4.2. Rotine: Transitions From a Level 16

4.2.1. Input 17

4.2.2. Output 18

4.3. Rotine: Possible Transitions 23

4.3.1. Input 23

4.3.2. Output 24

4.4. Rotine: Spectra Simulation 26

4.4.1. Input 26

4.4.2. Output 27

4.5. Rotine: Electronic Temperature 30

4.5.1. Input 31

4.5.2. Output 34

5. References 37

1. INTRODUCTION

The goal of ASAS (Analysis and Simulation of Atomic Spectra) software is to facilitate the planning and data analysis of atomic spectroscopy experiments particularly that in the field of atomic photoionization by multiphoton or multi-step process. Furthermore, the ASAS allows users to build their own database according to their research field. The ASAS software was developed in Visual Basic using Visual Studio editor Microsoft® the 2010®. The program permits interactivity between the output data obtained through their routines and all graphs are constructed from the GNUPLOT graphing program [1]. The ASAS software is compatible with Windows XP/Vista/7/8. It is only necessary to install the Microsoft.NET Framework v4.0, or superior, available in http://www.microsoft.com/download/ .

The current beta version of the ASAS consists of four subroutines each one requiring parameters compiled by the user and organized in databases:

a) *Transitions From a Level*: this routine identify possible transitions from a particular energy level considering the energy levels parity and total angular momentum *J* selection rules for dipole momentum transitions (absorption or emission of electromagnetic radiation). The routine can also calculate second photon absorption transitions.

b) *Possible Transitions*: this routine identify possible transitions from any initial energy level to any other energy level within a defined region of the spectrum, applying energy levels parity and total angular momentum *J* selection rules for dipole momentum transitions.

c) *Spectra Simulation*: this routine simulates spectra (atoms or molecules) in the spectral range and linewidth defined by the user employing Lorentz lineshapes. The spectra can be emission or absorption depending on the input data.

d) *Electronic Temperature*: this routine calculates the electronic temperature of atoms in an experimental environment through the Boltzmann Plot and employs the least square method.

The ASAS software provides examples of database for neutral dysprosium, erbium, neodymium, neonium and titanium (Dy I, Er I, Nd I, Ne I and Ti I), compiled from recent literature data [2, ,3, 4, 5]. The user can create a database for the element of interest (atom or

atomic ion), according to the program proper formatting (see section 3). Spectroscopic data for a large number of atoms and ions can be found in NIST database [2].

Theoretical and experimental details of atomic spectroscopy will be not discussed here but excellent texts can be found for example in [6], [7] and [8]. Next sections present details of ASAS software: installation and uninstallation, the database formatting (pre-requisite for the proper functioning of the routine functions) and how to use of the routines.

2. INSTALLING AND UNINSTALLING

Installing ASAS software requires the following steps:

1) Run the file *Install ASAS Beta 1.0.exe* and the screen showed in Figure 1 is displayed. Click *Next* to continue.

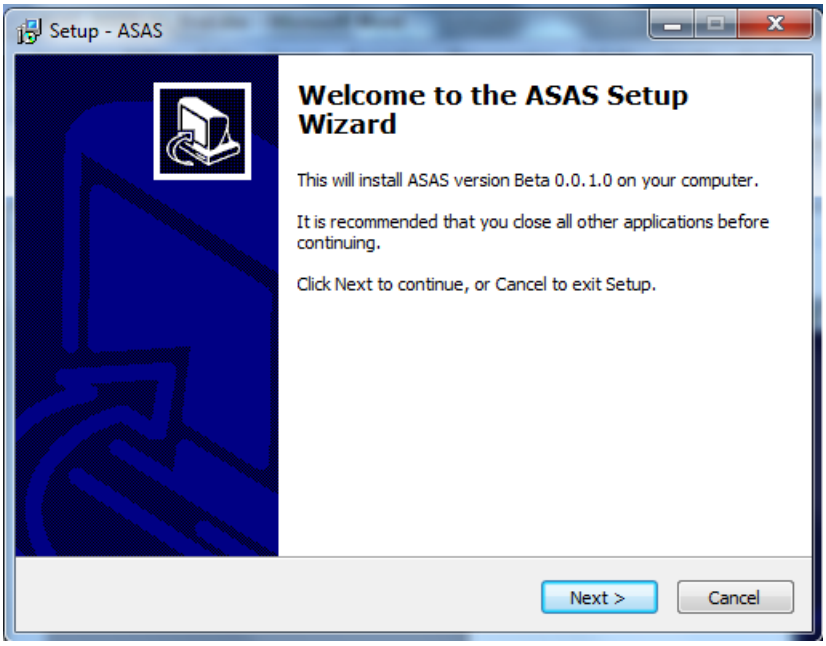


Figure 1. Initial installing screen.

2) A *License Agreement* screen appears (Figure 2). If you agree, select *I accept the agreement* and click *Next*.

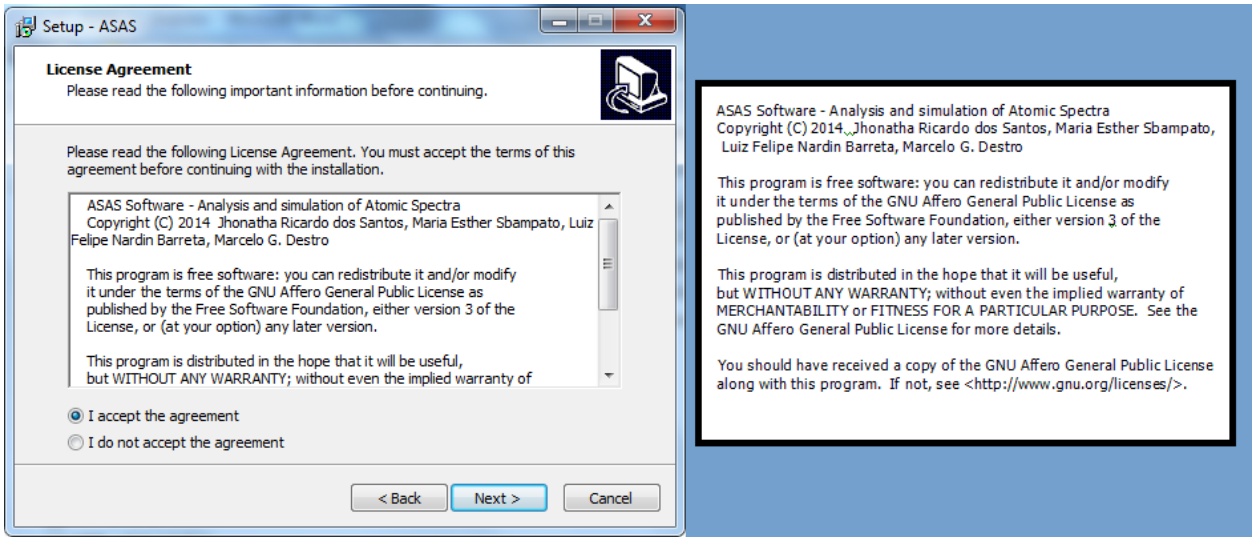


Figure 2. License Agreement screen (left) and the License Agreement (right).

3) A screen with a warning about the directory choice for the ASAS software installation appears. To avoid bad program operation make sure you have administrator privileges on it. Click *Next*.

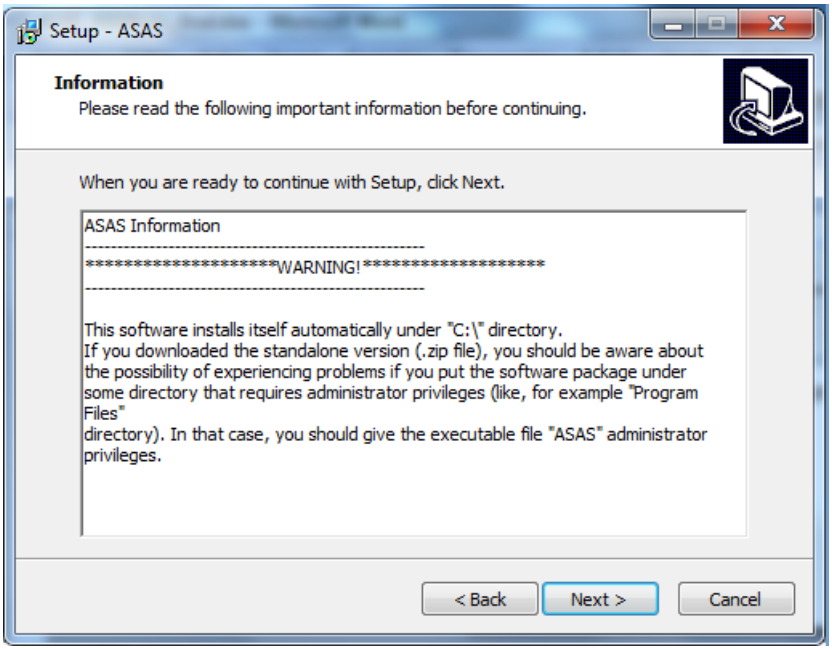


Figure 3. Warning screen about directory for ASAS software installation.

4) Select the path where the file will be installed. Example *C:/ASAS* (default, Figure 4). Click *Next*.

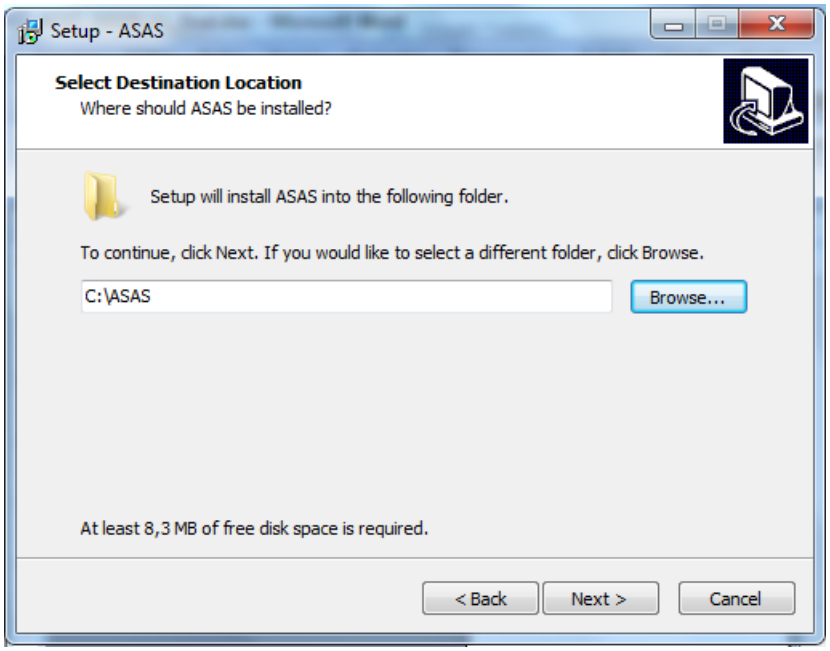


Figure 4. Choosing the program directory.

5) Choose the shortcut name in *Start Menu* folder (default: ASAS, Figure 5). Click *Next*.

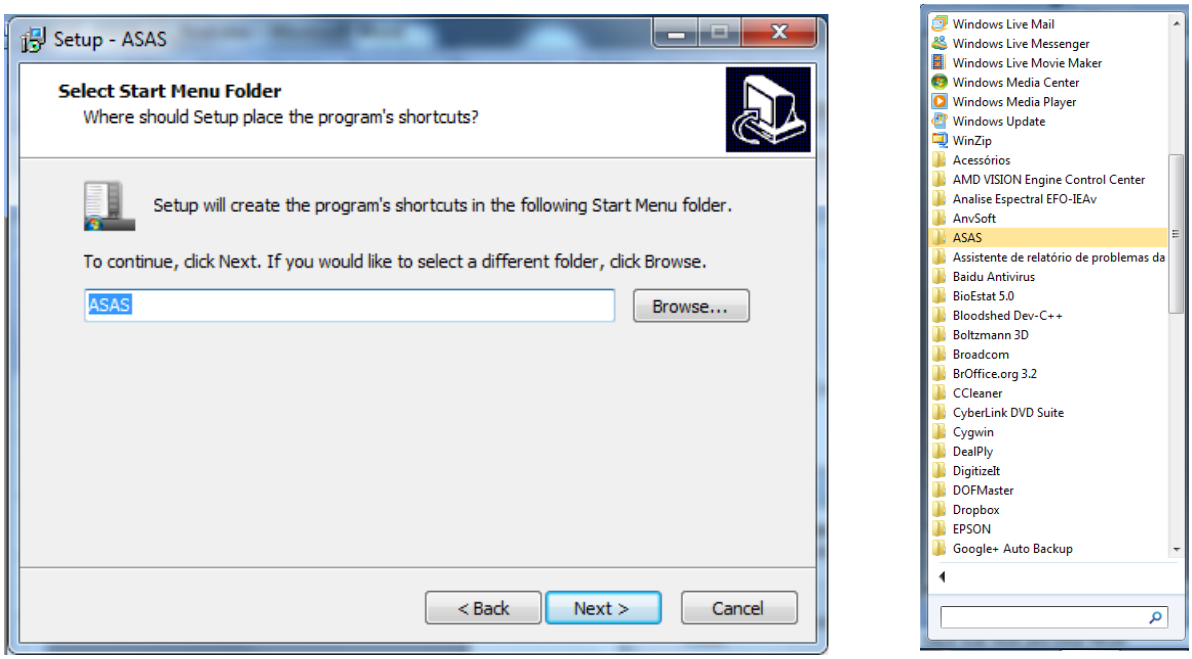


Figure 5. *Left*: Choosing Start Menu folder for the shortcut. *Right*: ASAS shortcut obtained.

6) Select the button *Create a desktop icon* (Figure 6) to create a desktop shortcut. Click *Next*.

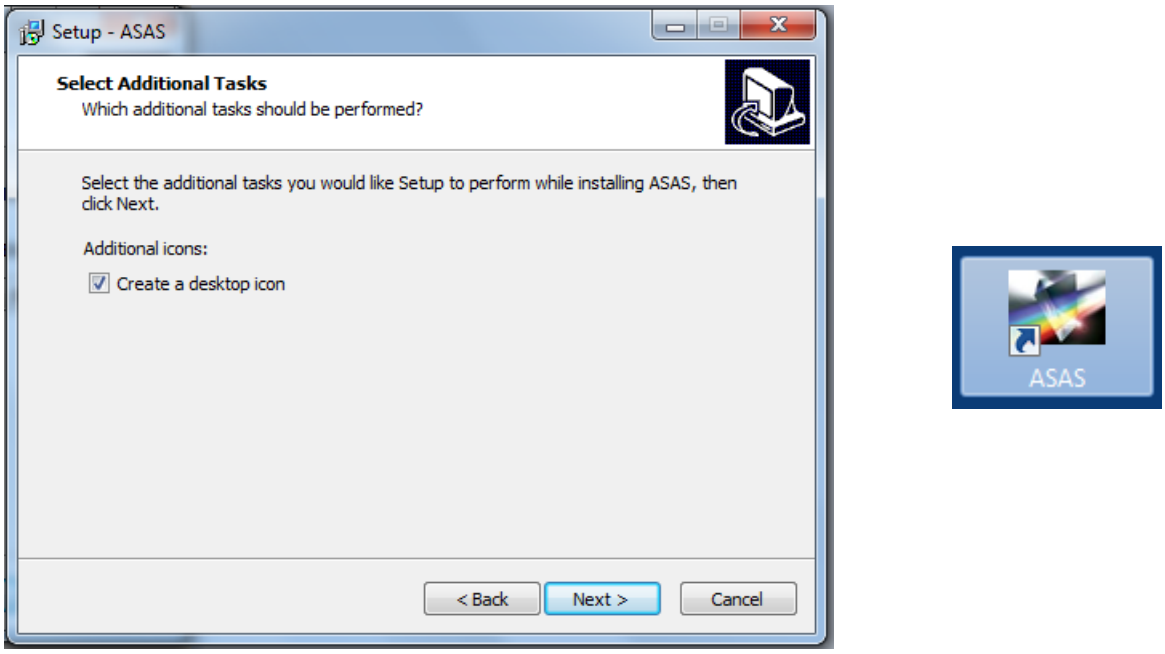


Figure 6. *Left*: Creating a desktop icon. *Right*: ASAS desktop icon.

7) Click *Install* (Figure 7). A screen with the GNUPLOT program use permission appears. (Figure 8). Click *Next*.

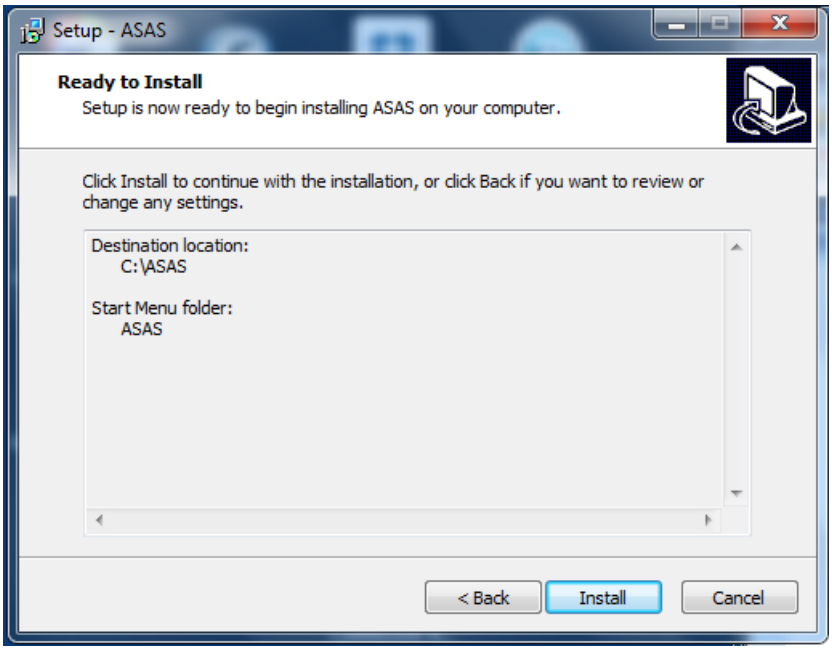


Figure 7. Program installation screen. In this example, the software was installed directly in the C:\ folder.

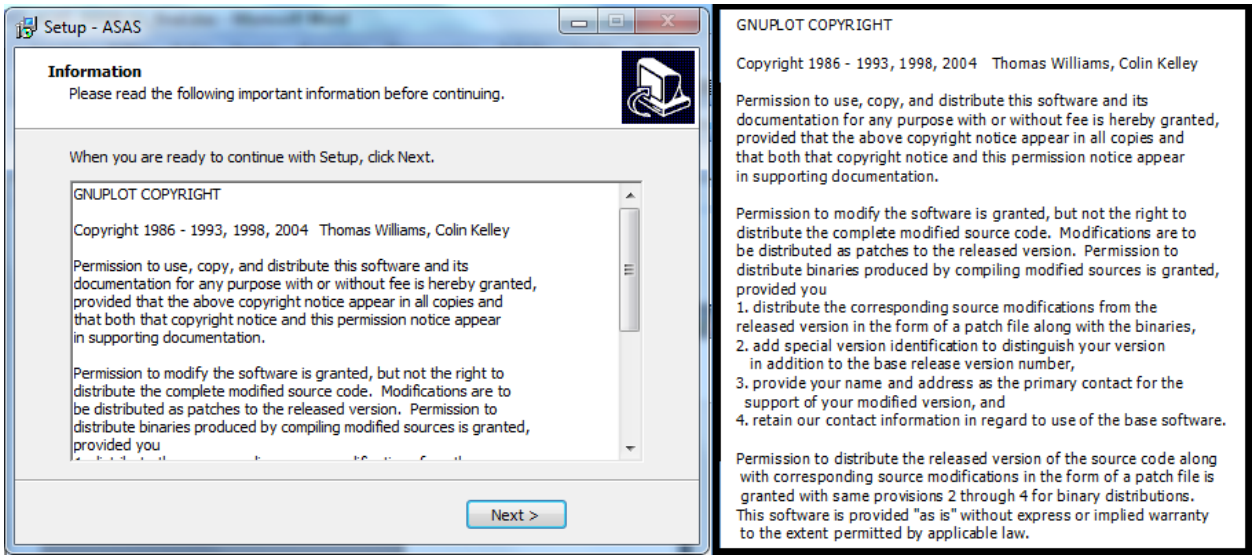


Figure 8. The GNUPLOT program use permission screen.

8) To complete the installation and launch ASAS select the option *Launch ASAS* and Click *Finish* (Figure 9). Figure 10 shows the main screen of the ASAS software. Now the user can choose the desired routine or edit databases.

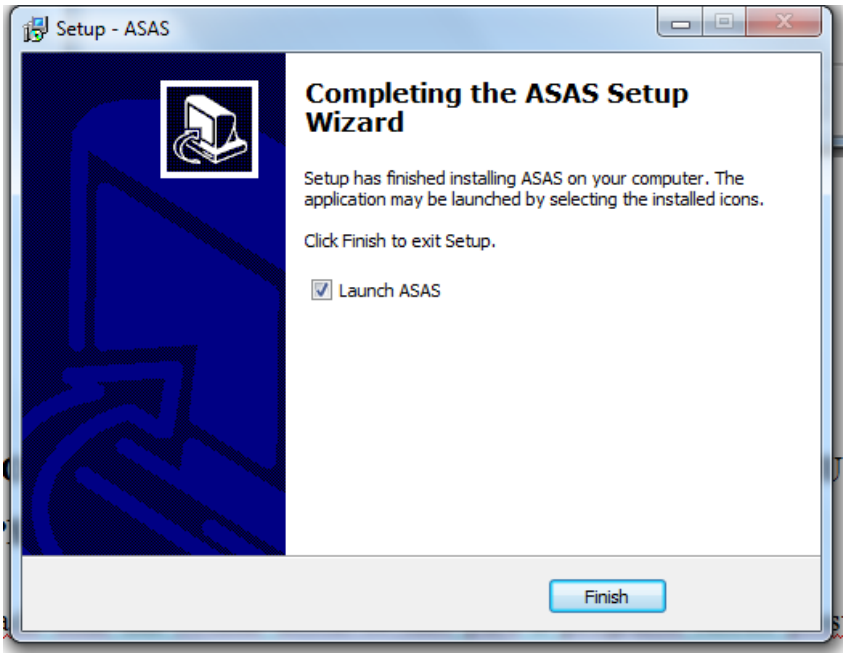


Figure 9. Completing the ASAS setup.

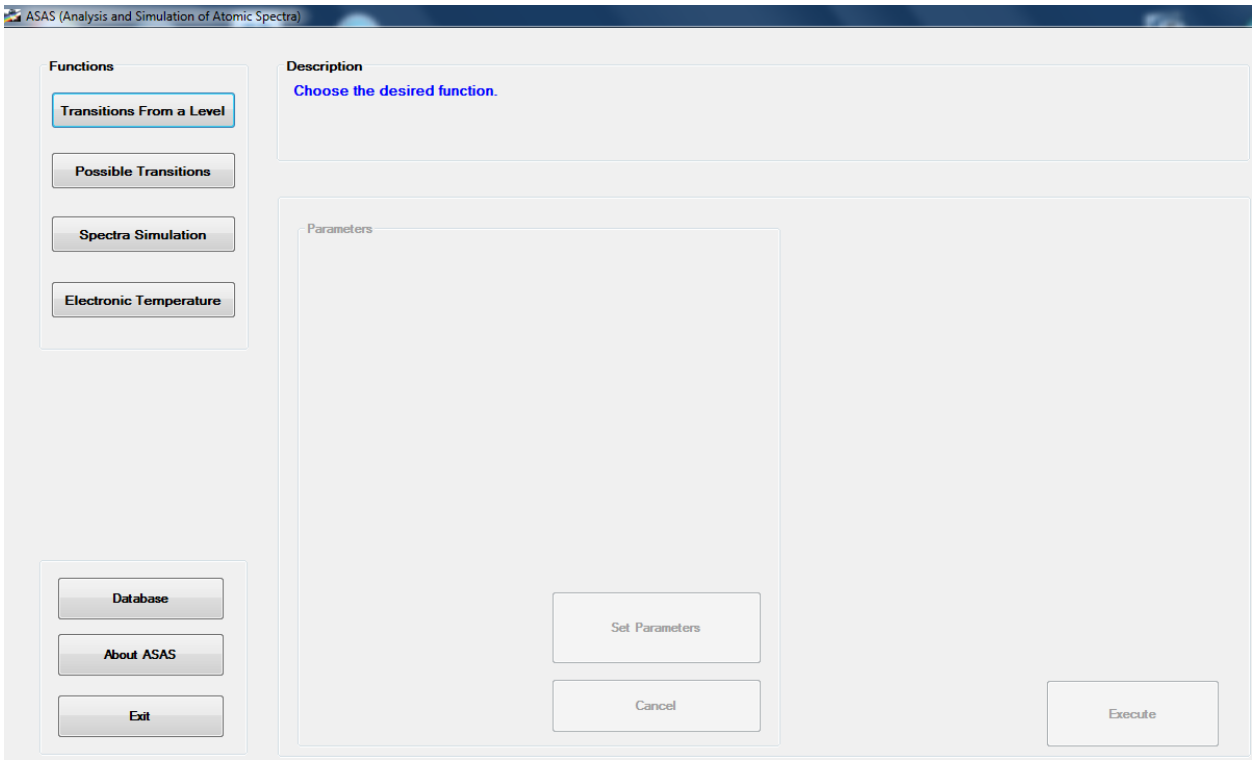


Figure 10. Main screen of the ASAS software.

9) To uninstall ASAS run the program *unins000.exe* that is in the same directory of the main program (Figure 11).

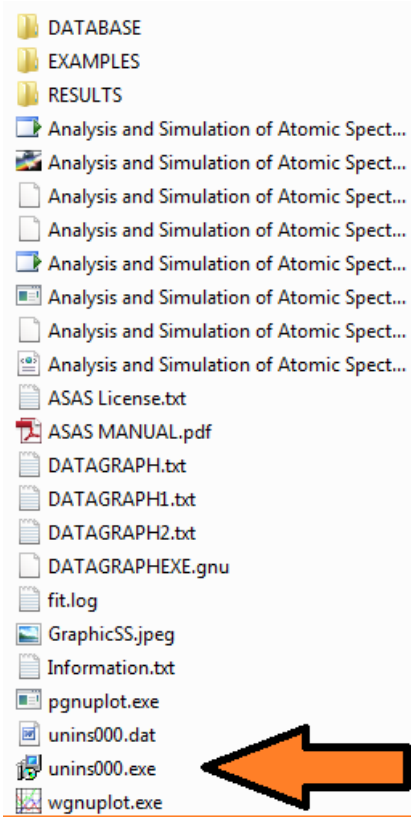


Figure 11. ASAS directory highlighting the uninstalling program.

As soon as the ASAS software is installed three directories inside ASAS folder are created: *DATABASE*, *EXAMPLES* and *RESULTS* (Figure 12). **To work properly the databases of the atoms must be stored inside the correct folder created by the installer** as explained below. Inside the *DATABASE* folder there are two different directories: *LINES* and *LEVELS*. Details about *DATABASE* are discussed in section 3. The *RESULTS* folder include 4 directories: *TRANSITIONS FROM* a *LEVEL*, *POSSIBLE TRANSITIONS*, *SPECTRA SIMULATION* and *ELECTRONIC TEMPERATURE* and form the default path to save the calculated results (details in sections 0, 4.3, 4.4 and 4.5). Inside *EXAMPLES* folder there are examples of files to be used in *SPECTRA SIMULATION* (option: *External Files*, section 4.4.1,) and *ELECTRONIC TEMPERATURE* (section 4.5.1) routines.

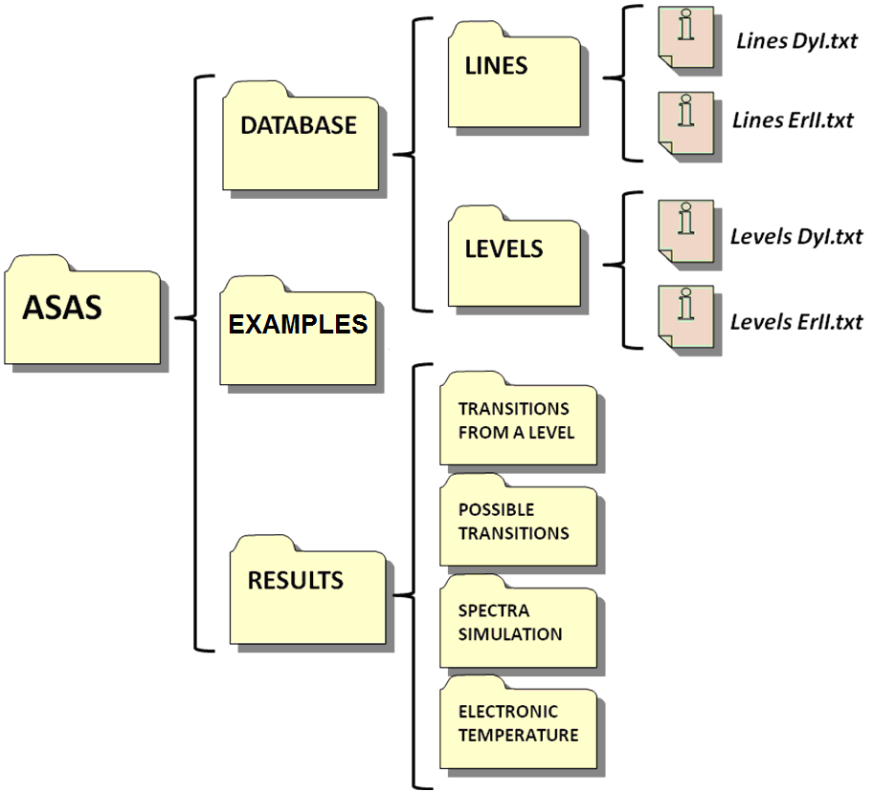


Figure 12. ASAS file/folder structure.

3. DATABASE

The database is divided into *txt* files according to the element. The files may be modified as required but it is necessary to keep the file structure as explained below. **Databases improperly formatted lead to wrong results or routines malfunctioning**.

The data are organized in two directories; one of them contains parameters related to the energy levels of the element (*LEVELS*) and the other parameters related to electromagnetic radiation emission (or absorption) transitions between the energy levels (*LINES*). The *txt* file name of the energy levels consists of the word "*Levels*", space (" "), the atomic symbol followed by the roman numeral determining the ionization stage ("I", "II" and so on). The *txt* file name of the lines consists of the word "*Lines*", space (" "), the atomic symbol followed by the roman numeral determining the ionization stage ("I", "II" and so on). Example: *Levels DyI.txt* (energy levels for neutral dysprosium); *Lines DyII.txt* (absorption/emission lines for dysprosium once ionized, Dy^+). **ASAS software is not sensitive to uppercase or lowercase letters.**

Databases for Er I, Dy I, Nd I, Ti I and Ne I are provided during the ASAS installation and can be used as examples for construction of other elemental databases. **Note that double 0 ("00") found in databases means that the date was not obtained in the consulted literature and serves to differentiate from real zero values** (this is not relevant to the correct operation of the program)**. Decimal points can be represented either by points (".") or by commas (",").**

3.1. REMARKS ON LEVEL DATABASES

Levels*<space> <atomic symbol><roman numeral indicating ionization state >*.txt

Insensible to uppercase or lowercase letters. Example: *Levels ERI.txt* or *LEVELS eri.txt*

The energy levels *txt* files **must** contain five columns separated by space (any number of spaces) containing the following data (Figure 13) (**unknowing values may be indicated by "00" to differentiate from real zero values**):

a) column 1: quantum number of total angular momentum of the energy level, *J*;
b) column 2: energy of the level *E*, in cm^{-1} units;
c) column 3: parity of the wave function ψ that describes the energy level - number **01** for odd function, **02** for even functions and **00** if the parity is not known;
d) column 4: energy level lifetimes, *t*, in nanoseconds (ns) units;

e) column 5: uncertainties of the energy levels lifetimes, δt, in nanoseconds (ns) units.

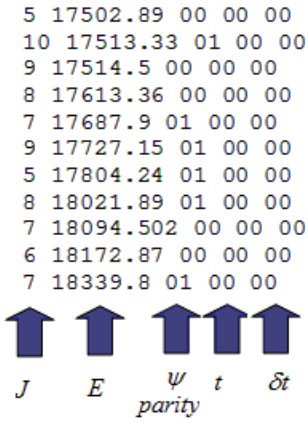


Figure 13. Levels database formatting (*File*: Levels DyI.txt). See text for definitions.

3.2. REMARKS ON LINES DATABASES

Lines*<space> <atomic symbol><ionization roman>*.txt

Insensible to uppercase or lowercase letters. Example: *Lines ERI.txt* or *lines eri.txt*

The lines *txt* files **must** contain ten columns separated by space (any number of spaces) containing the following data (Figure 14) (**unknowing values may be indicated by "00" to differentiate from real zero values**):

a) column 1: number of the line (*n*, sequencial);
b) column 2: wavelength in vacuum, λ_0, of the line center, in nm;
c) column 3: wavelength in air, λ_{air}, of the line center, in nm;
d) column 4: relative intensities, *RI*, of the line, in arbitrary units;
e) column 5: atomic transition probability (spontaneous emission Einstein coefficient), *A*, in s^{-1} units;
f) column 6: uncertainties of the atomic transition probability, δA, in s^{-1} units;
g) column 7: energy of the lower level, E_l , in cm^{-1} units ;
h) column 8: quantum number of total electronic angular momentum of the lower level, J_l;
i) column 9: energy of the upper level, E_u, in cm^{-1} units ;
j) column 10: quantum number of total electronic angular momentum of the upper level, J_u.

```
20 343.41709 343.3190 5 2320000 116000 0 8 29119.110 9
21 344.45296 344.3540 5 285000 28500 4134.230 7 33165.770 8
22 348.43133 348.3320 5 1210000 145200 4134.230 7 32834.290 6
23 351.20190 351.1015 1000 9400000 470000 4134.230 7 32607.880
24 357.24582 357.1438 1000 4800000 240000 4134.230 7 32126.160
25 357.43378 357.3320 5 1030000 92700 4134.230 7 32111.440 6
26 357.81030 357.7080 5 2770000 166200 4134.230 7 32082.000 6
27 359.04799 358.9460 5 326000 26080 0 8 27851.430 8
28 360.43582 360.3330 5 1290000 77400 4134.230 7 31878.420 7
29 360.45284 360.3500 5 560000 61600 7050.610 6 34793.490 6
30 362.79086 362.6870 5 600000 36000 4134.230 7 31698.320 7
```

Figure 14. Lines database formatting (*File*: Lines DyI.txt). See text for definitions.

4. HOW TO USE THE PROGRAM

<u>Input parameters</u>: decimal points can be represented either by points (“.”) or by commas (“,”).

4.1. EDITING DATABASES

a) Click *Database* button (*Main Screen*, Figure 10).

b) Click *Open File* button and choose the file to be edited (Figure 15).

c) The user can modify data (*Edit Line* button) or include data (*Include Data Line* button). Once a line of the table is selected, the parameters are shown in the *Edit Line* spaces and they can be modified. If *Include Data Line* is clicked, a new line at the end of the table is opened and the parameters can be edited. After entering the values in one line, click *Save Changes* button. To delete data, click *Delete* button.

d) Any changes will be saved over the original file just after the button *Save All Changes* **is selected.**

e) To delete all changes, click *Cancel All Changes* button.

f) To exit the database editing click *Exit* button. If the *Save all Changes* button is not clicked before the *Exit* one, the changes will not be saved.

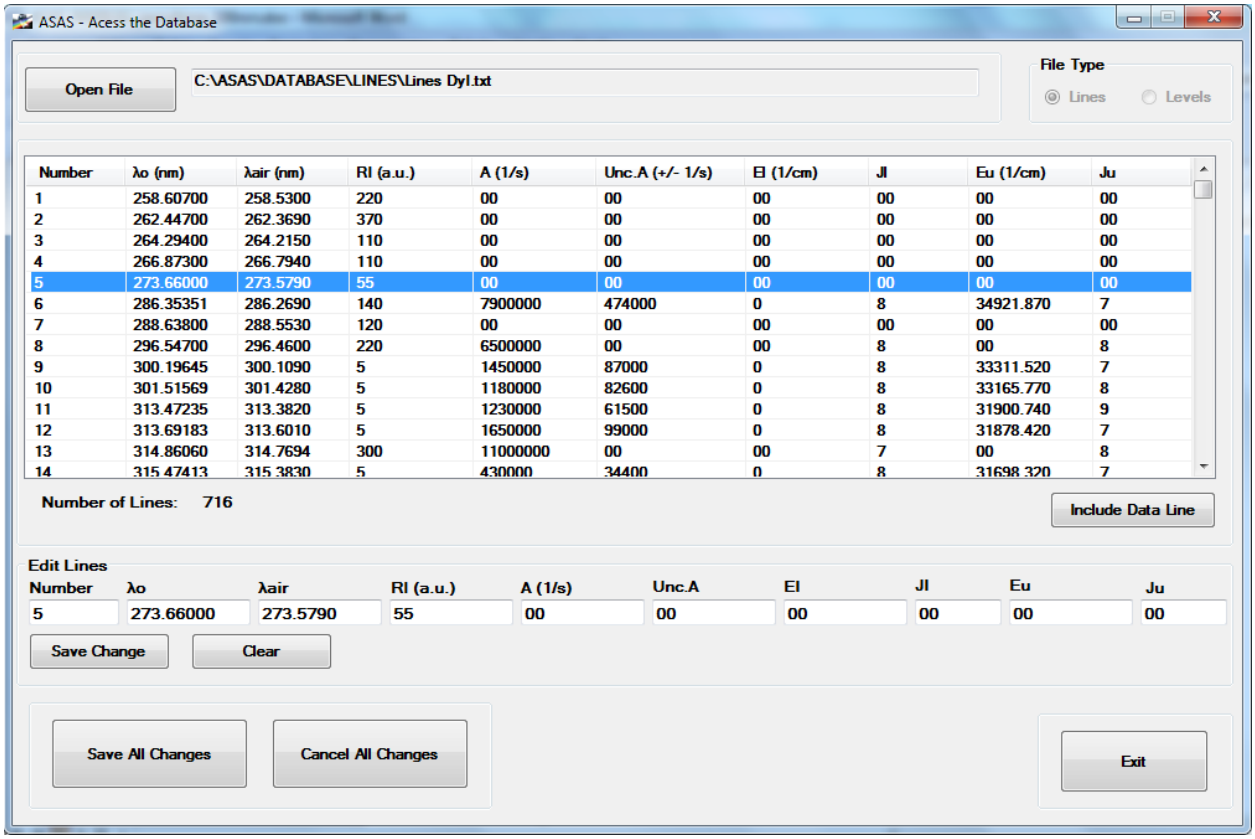


Figure 15. Editing database screen.

4.2. ROTINE: TRANSITIONS FROM A LEVEL

This routine works with *Levels* databases but *Lines* databases are also required because the transitions obtained thought energy levels are compared with that of the *Lines* database.

Figure 16 shows the screen obtained once the *Transitions From a Level* button is clicked on *Main Screen* (Figure 10). The ASAS *Transitions From a Level* routine determines the optical transitions that obey **just the more restrictive selections rules for electronic transitions of atoms involving absorption/emission of electromagnetic radiation**:

a) for the total angular momentum, *J*:

$$\Delta J = 0, \pm 1, \text{ but if } J = 0, \Delta J \neq 0$$

b) the wavefunction that describes the atom in the energy levels involved in the electronic transition must present opposite parity:

$$even \Leftrightarrow odd$$

Sometimes the level parity is not known and the database presents the value “00”; in this case, the software bypass the parity selection rule and transitions from even and oven levels are presented. The user must pay attention on this. When studding spectroscopy of small atoms, other selection rules must be considered (particularly those involving total spin, *S*, and total orbital momentum, *L*, are important for small atoms) [7,9].

Besides one photon transition, the routine permits verify possible second photon transitions (absorption) from the upper energy level of the first photon transition.

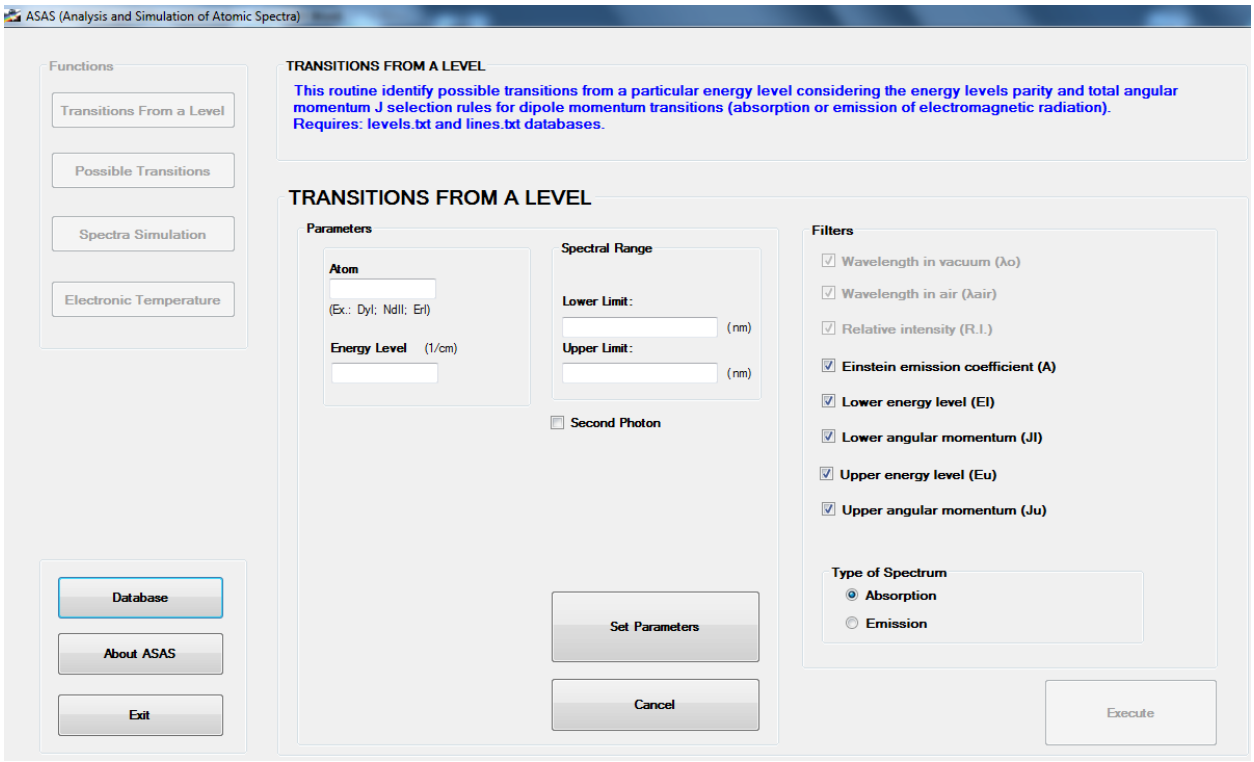


Figure 16. ASAS *Transitions From a Level* Screen.

4.2.1. INPUT

1. To use the *Transitions From a Level* routine (Figure 16), first inform the following parameters:

a) *Atom*: only the atom symbol and the roman that define the ionization state, obeying the nomenclature used in the database.

b) *Energy Level*, in cm^{-1}: energy of the initial level of the desired transition (the user must provide an energy level that is in the *Level* database, with all the significant; if the data is not correctly informed, the routine is canceled and an advice is given).

c) *Spectral Range*: *Lower Limit* and *Upper Limit*, in nm units. Spectral range where the lines should be found. **The routine considers that these limits are in vacuum** (for details, see Appendix 1**).**

d) The user can select the *Second Photon* option if desirable. In that case the routine will verify possible second photon transitions from the upper level of each first photon transition found in the chosen region (**only absorption**). The range of the second photon transition can be the same as the first photon (default) or another one (enter new values). **The routine considers that these spectral range limits are given in vacuum.**

e) The *Filter* options permit to chosen the informations that will be saved in the output file.

f) Select *Absorption* or *Emission* in the *Type of Spectrum* option. The routine will find absorption or emission lines from the initial energy level (**only for one photon transition**).

2. Click *Set Parameter* button. If the input parameters are ok the *Execute* button is released. If some data is not properly entered, the *Execute* button is not liberated and the user is advised to correct the parameter.

3. Click *Execute* button.

At any time the program can be stopped using the *Cancel* button. In this case, the *Main Screen* (Figure 10) is displayed.

4.2.2. OUTPUT

Case 1: The *Second Photon* button is *of*; the screen showed in Figure 17 is obtained (the parameters used are shown in the figure legend). If the line is not present in the *Lines.txt* file of the atom, it is identified as a *0* line number. The following options are possible:

a) *Save* button: to save the obtained data on a file:

- Default path: /ASAS/RESULTS/TRANSITIONS FROM A LEVEL/
- Default filename: Transitions of [*Atomx*] From Level 0 ([*Lower Limit*] nm – [*Upper Limit*] nm) [*Type of Spectrum*].txt

The user can modify the path and the filename.

b) *Print* button: to print the table of results on a printer.

c) *Exit* button: to return *Transitions From a Level* Screen (Figure 16).

It is important to note that the program can find many lines that obey the two considerate selections rules but there are not listed in *Lines.txt* database. This may be due to the following reasons: a) some lines could be very weak (low Einstein Spontaneous Emission Coefficients) and were not observed in the literature experiments; b) the transitions involve levels with low electronic relative population in ordinary laboratory temperature experiments; c) another relevant selection rule for the specific atom was not considerate. If some of the calculated transitions are NOT prohibited by any selection, they can be observed in experiments

involving high electronic temperatures (discharges, plasmas) or multiphoton absorption of laser radiation.

The routine allows visualizing two kinds of graphics: the *Arrows Diagram* (Figure 18) or the *Spectrum Simulation* (Figure 19). For both the option *Known Possible Transitions* shows **only** lines that are present in *Lines.txt* database; the option *All Possible Transitions* shows all the lines obtained considering the two selection rules (section 0).

The graphics can be constructing using both wavelength in air (click *Vacuum* option) or wavelength in vacuum (click *Air* option). The wavelength in air is calculated employing the Ciddor Equation [10,11] (see Appendix 1**)**, **valid for wavelengths from below 350 nm to above 1700 nm**. If the routine is used outside this range, use only the *Vacuum* option.

To obtain a simulated spectrum using *Spectrum Simulation* **option, the user must inform the lines full width at half maximum**, *FWHM*, in nm units.

Once *All Possible Transitions* **is selected in the *Spectrum Simulation*, lines not present is** *Lines.txt* **database are attributed with an intensity 20% of the more intense one found in database between the spectral range limits. If there are no lines in this spectral range, the value "100" is used.**

After one of the graphics is obtained, the following options are possible (Default path: /ASAS/RESULTS/TRANSITIONS FROM A LEVEL/):

a) *Save Plot*:

- Default filename:

Arrows Diagram: Arrows Diagram - Transitions of [*Atomx*] From Level [*Energy Level*] ([*Lower Limit*] nm – [*Upper Limit*] nm) [*Type of Spectrum*].jpeg

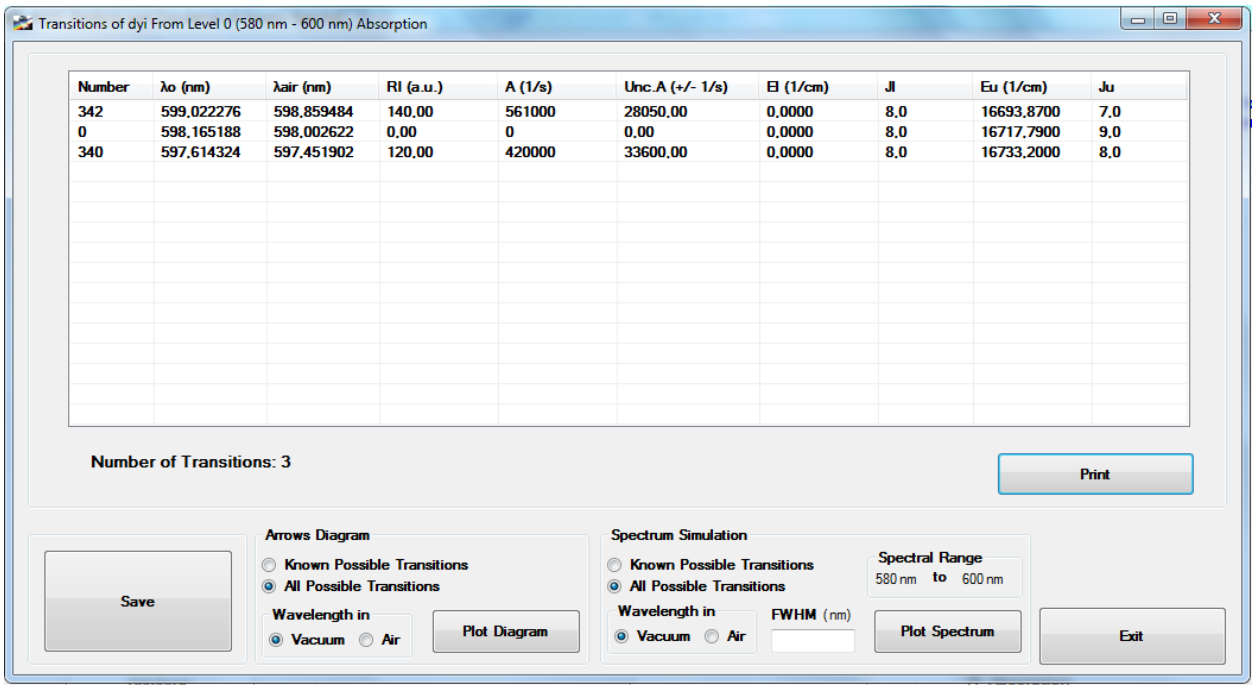
Spectrum Simulation: Simulated Spectra - Possible transitions of (A*tomx*) From Level [*Energy Level*] ([*Lower Limit*] nm – [*Upper Limit*] nm) [*Type of Spectrum*].jpeg

b) *Save Data Plot* (only available for the *Spectrum Simulation* option)

- Default filename:

Simulated Spectrum - Possible transitions of [*Atomx*] from level [*Energy Level*] cm^{-1} ([*Lower limit* nm – *Upper limit*] nm).txt

c) *Exit*: back to previous screen (Figure 17).



Number	λo (nm)	λair (nm)	RI (a.u.)	A (1/s)	Unc.A (+/- 1/s)	El (1/cm)	Jl	Eu (1/cm)	Ju
342	599,022276	598,859484	140,00	561000	28050,00	0,0000	8,0	16693,8700	7,0
0	598,165188	598,002622	0,00	0	0,00	0,0000	8,0	16717,7900	9,0
340	597,614324	597,451902	120,00	420000	33600,00	0,0000	8,0	16733,2000	8,0

Figure 17. Possible transitions obtained thought *Transitions From a Level* Routine (*Atom*: DyI; *Energy Level*: 0 cm^{-1}; *Lower Limit*: 580 nm; *Upper Limit*: 600 nm; *Second Photon* button: of; *Type of Spectrum*: Absorption; *Filters*: all clicked.).

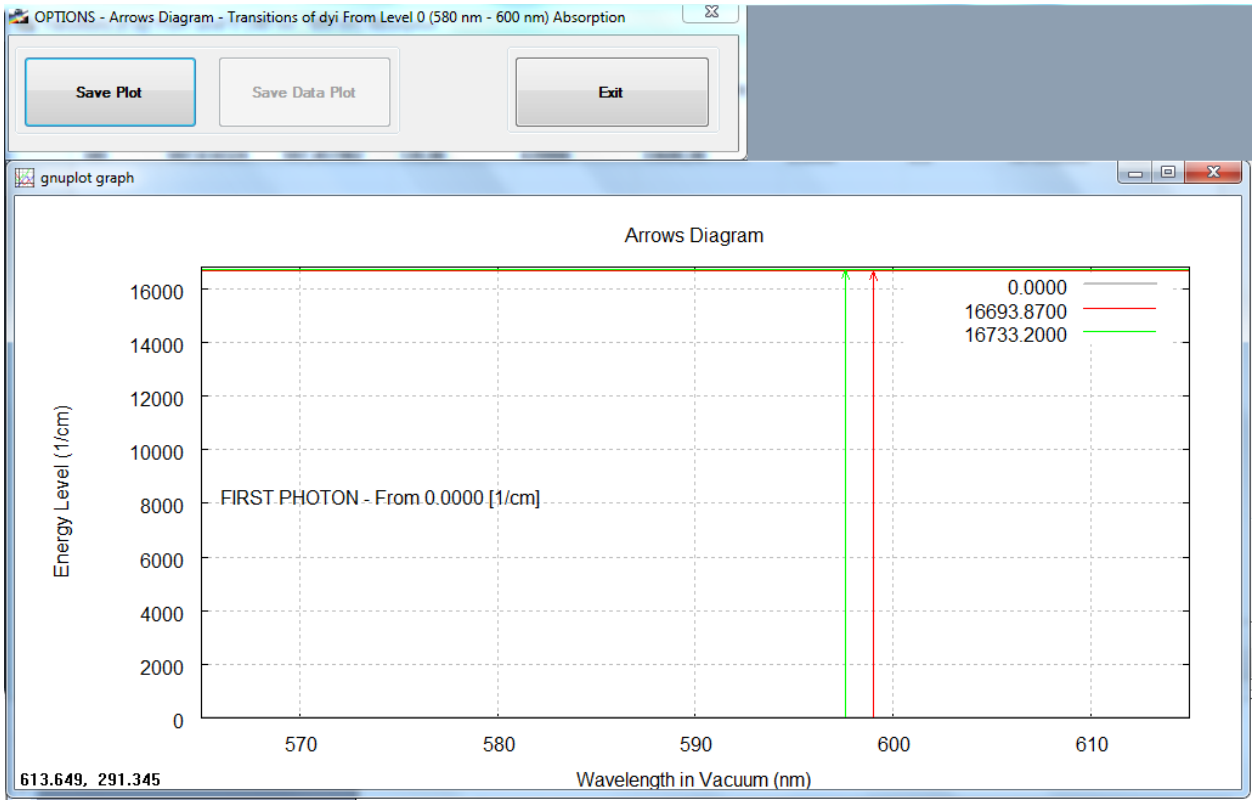


Figure 18. Arrows Diagram obtained with *Known Possible Transitions* option clicked in Figure 17 screen. Note that the photon transition at 598.1652 nm (Figure 17) is not shown (this transition is not in *LinesDyI.txt* datafile employed)

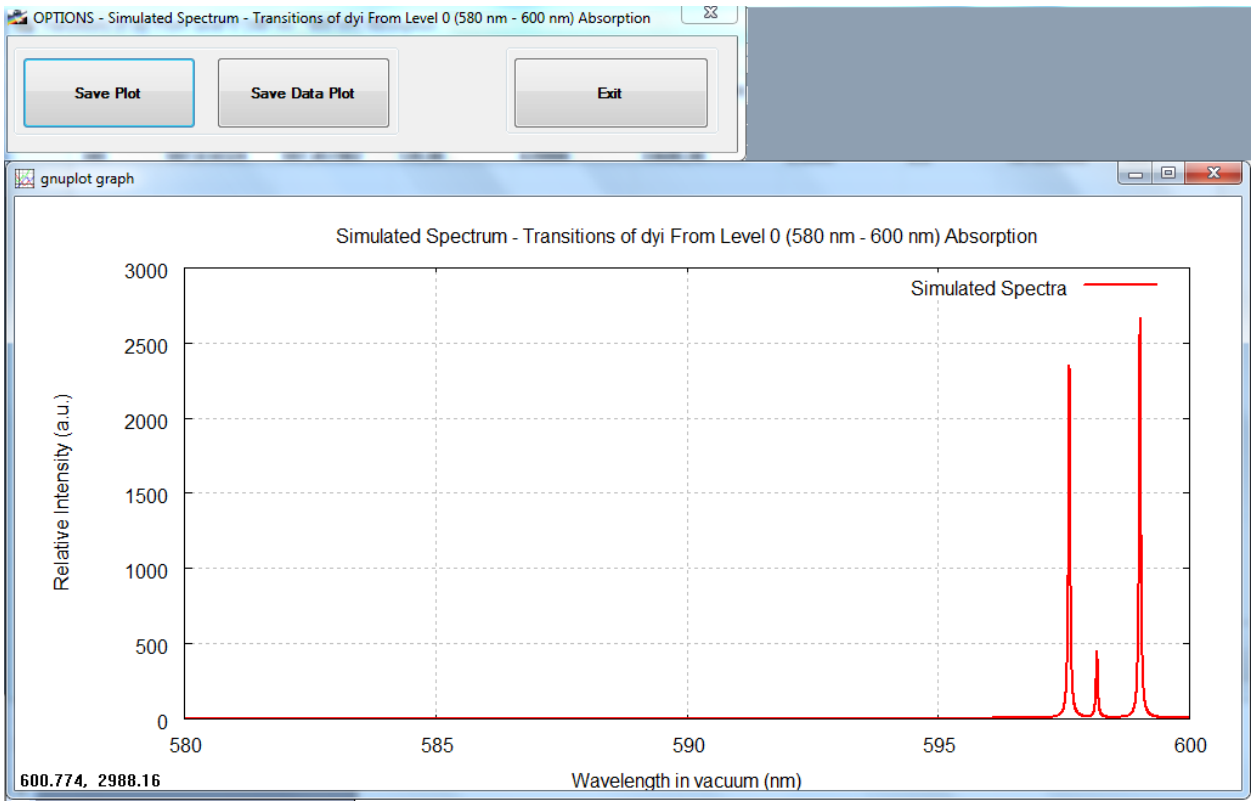


Figure 19. Simulated spectrum obtained with *All Possible Transitions* option clicked in Figure 17 screen (*FWHM*: 0.02 nm). The intensity of the line at 598.1652 nm (not present in DyI.txt database) was considerate as 20% of the more intense line in the simulation spectral range.

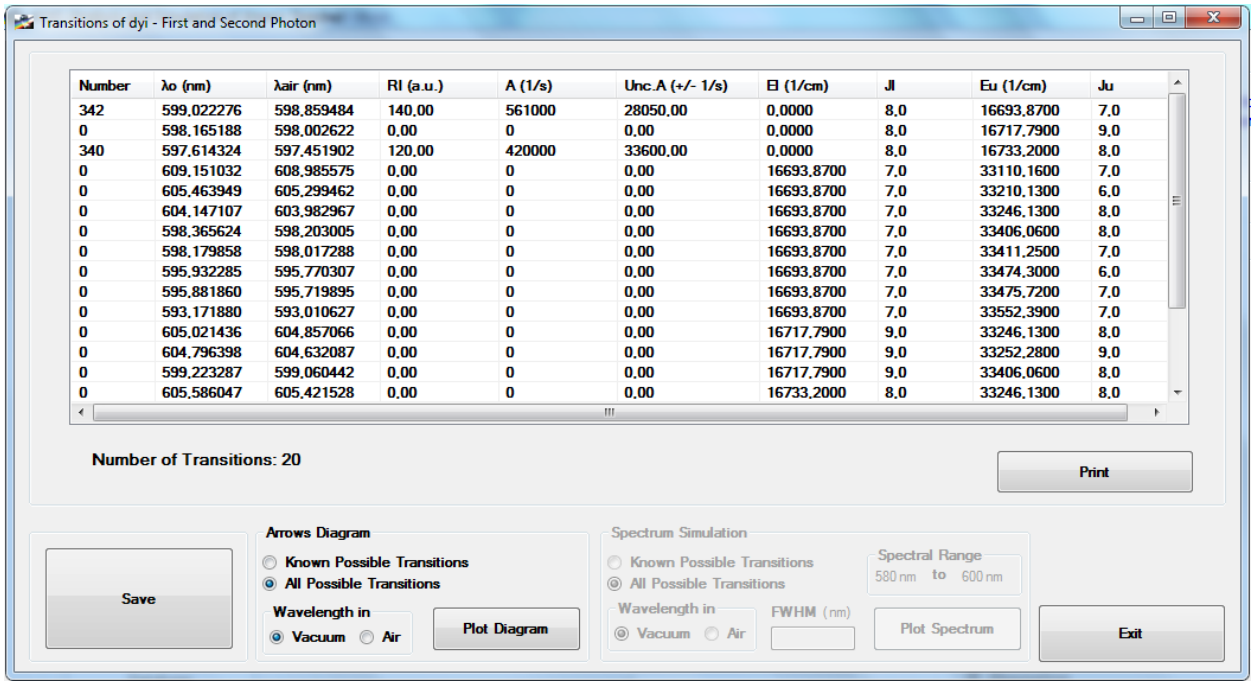
Case 2: The *Second Photon* button is on (*Type of Spectrum*: *Absorption*); the screen showed in Figure 20 is obtained (see employed parameters in the figure legend).

Only *Arrows Diagram* is possible, choosing between *All Possible Transitions* or *Known Possible Transitions*, as explained in Case 1. The *Save* (Default filename: Transitions of [*Atomx*]- First and Second Photon.txt), *Print* and *Exit* buttons are similar to the Case 1. When *Plot Diagram* is clicked two screens are obtained. In the inferior screen it is visualized the first and second photons absorption possible paths each of them with a different color (Figure 21*)* and on the superior screen the following options are possible:

a) *Save Plot*:

- Default filename: Arrows Diagram - Transitions of [*Atomx*]- First and Second Photon.txt

b) *Exit*: back to previous screen (Figure 20).



Number	λo (nm)	λair (nm)	RI (a.u.)	A (1/s)	Unc.A (+/- 1/s)	El (1/cm)	Jl	Eu (1/cm)	Ju
342	599,022276	598,859484	140,00	561000	28050,00	0,0000	8,0	16693,8700	7,0
0	598,165188	598,002622	0,00	0	0,00	0,0000	8,0	16717,7900	9,0
340	597,614324	597,451902	120,00	420000	33600,00	0,0000	8,0	16733,2000	8,0
0	609,151032	608,985575	0,00	0	0,00	16693,8700	7,0	33110,1600	7,0
0	605,463949	605,299462	0,00	0	0,00	16693,8700	7,0	33210,1300	6,0
0	604,147107	603,982967	0,00	0	0,00	16693,8700	7,0	33246,1300	8,0
0	598,365624	598,203005	0,00	0	0,00	16693,8700	7,0	33406,0600	8,0
0	598,179858	598,017288	0,00	0	0,00	16693,8700	7,0	33411,2500	7,0
0	595,932285	595,770307	0,00	0	0,00	16693,8700	7,0	33474,3000	6,0
0	595,881860	595,719895	0,00	0	0,00	16693,8700	7,0	33475,7200	7,0
0	593,171880	593,010627	0,00	0	0,00	16693,8700	7,0	33552,3900	7,0
0	605,021436	604,857066	0,00	0	0,00	16717,7900	9,0	33246,1300	8,0
0	604,796398	604,632087	0,00	0	0,00	16717,7900	9,0	33252,2800	9,0
0	599,223287	599,060442	0,00	0	0,00	16717,7900	9,0	33406,0600	8,0
0	605,586047	605,421528	0,00	0	0,00	16733,2000	8,0	33246,1300	8,0

Figure 20. Possible transitions obtained thought *Transitions From a Level* Routine (*Atom*: DyI; *Energy Level*: 0 cm^{-1}; *Lower Limit*: 580 nm; *Upper Limit*: 600 nm; *Second Photon* button: on; *Lower Limit*: 590 nm; *Upper Limit*: 610 nm *Filters*: all clicked).

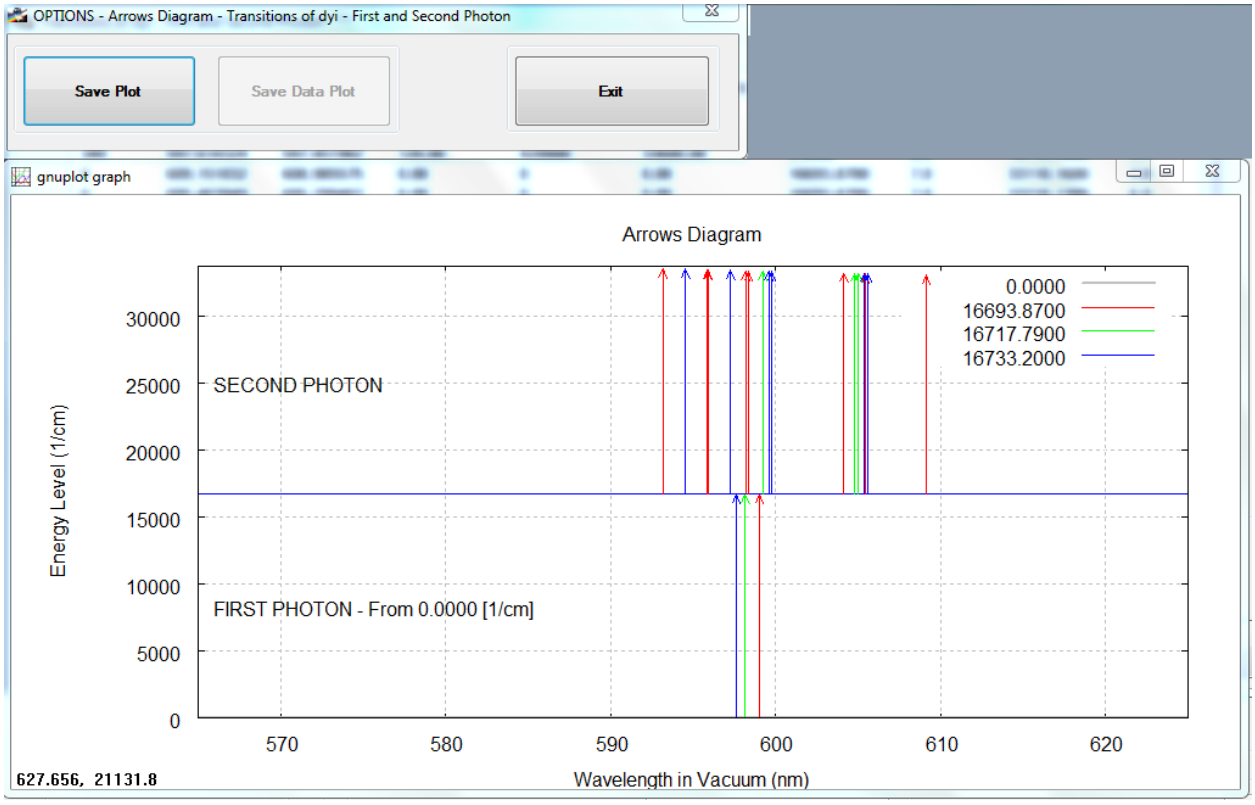


Figure 21. Arrows Diagram obtained with *All Possible Transitions* option clicked in Figure 20 screen.

To restart the routine with other parameters, it is necessary to click *Cancel* on *Transition From a Level* screen (Figure 16), and choose the *Transition From a Level* in the *Main Screen* (Figure 10). The previously used parameters are automatically placed as default.

4.3. ROTINE: POSSIBLE TRANSITIONS

The *Possible Transitions* routine identify possible transitions from any initial energy level to any other energy level within a defined region of the spectrum, applying energy levels parity and total angular momentum *J* selection rules for dipole momentum transitions. The *Levels* databases are used (see section 3.1).

4.3.1. INPUT

1. To use the routine *Possible Transitions* (Figure 22), first inform the following parameters:

    a) *Atom*: only the atom symbol and the roman that define the ionization state, obeying the nomenclature used in the database.
    b) *Spectral Range*: *Lower Limit* and *Upper Limit*, in nm units. Spectral range where the lines should be found. **The routine considers that these limits are in vacuum** (for details, see Appendix 1). **The maximum range must be 10 nm**.
    c) The *Filter* options permit to chosen the informations that will be saved in the output file.

2. Click *Set Parameter* button. If the input parameters are ok the *Execute* button is released. If some data is not properly entered, the *Execute* button will not be liberated and the user will be advised to correct the parameter.

3. Click *Execute* button.

At any time the program can be stopped using the *Cancel* button. In this case, the *Main Screen* (Figure 10) is displayed.

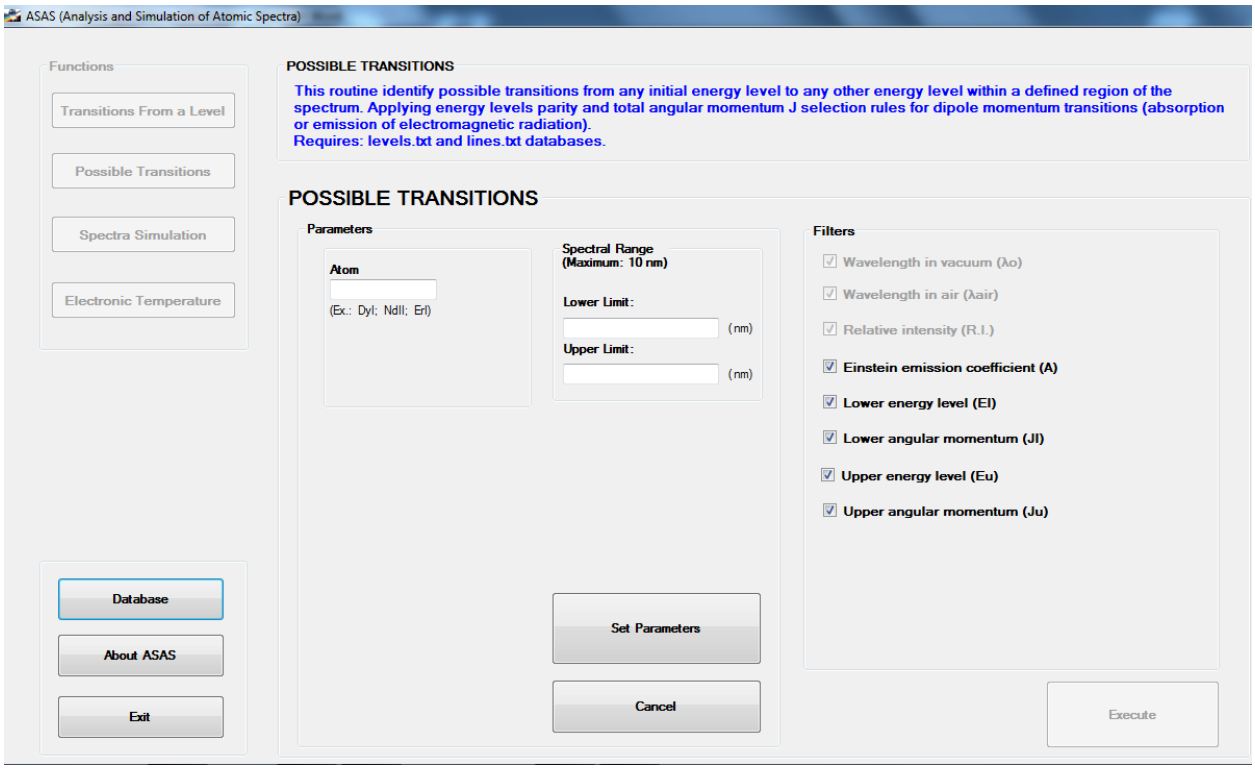


Figure 22. ASAS *Possible Transition* screen.

4.3.2. OUTPUT

After *Execute* button is clicked the screen showed in Figure 23 is obtained (the parameters used are shown in the figure legend). If the line is not present in the *Lines.txt* file of the atom, it is identified as a *0* line number. The following options are possible:

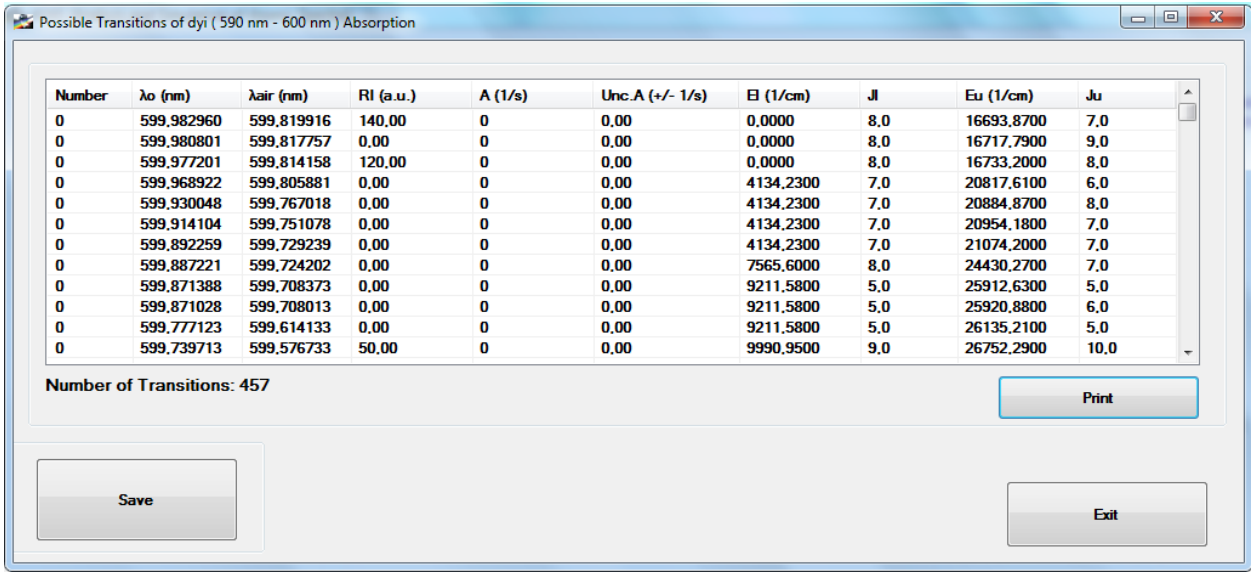
a) *Save* button: to save the obtained data on a file:

- Default path: /ASAS/RESULTS/POSSIBLE TRANSITIONS/
- Default filename: Possible Transitions of [*Atomx*] ([*Lower Limit*] nm – [*Upper Limit*] nm).txt

The user can modify the path and the filename.

b) *Print* button: to print the table of results on a printer.

c) *Exit* button: to return *Possible Transitions* Screen (Figure 22).



Number	λo (nm)	λair (nm)	RI (a.u.)	A (1/s)	Unc.A (+/- 1/s)	El (1/cm)	Jl	Eu (1/cm)	Ju
0	599,982960	599,819916	140,00	0	0,00	0,0000	8,0	16693,8700	7,0
0	599,980801	599,817757	0,00	0	0,00	0,0000	8,0	16717,7900	9,0
0	599,977201	599,814158	120,00	0	0,00	0,0000	8,0	16733,2000	8,0
0	599,968922	599,805881	0,00	0	0,00	4134,2300	7,0	20817,6100	6,0
0	599,930048	599,767018	0,00	0	0,00	4134,2300	7,0	20884,8700	8,0
0	599,914104	599,751078	0,00	0	0,00	4134,2300	7,0	20954,1800	7,0
0	599,892259	599,729239	0,00	0	0,00	4134,2300	7,0	21074,2000	7,0
0	599,887221	599,724202	0,00	0	0,00	7565,6000	8,0	24430,2700	7,0
0	599,871388	599,708373	0,00	0	0,00	9211,5800	5,0	25912,6300	5,0
0	599,871028	599,708013	0,00	0	0,00	9211,5800	5,0	25920,8800	6,0
0	599,777123	599,614133	0,00	0	0,00	9211,5800	5,0	26135,2100	5,0
0	599,739713	599,576733	50,00	0	0,00	9990,9500	9,0	26752,2900	10,0

Figure 23. Possible transitions obtained through *Possible Transitions* routine (*Atom*: DyI; ; *Lower Limit*: 590 nm; *Upper Limit*: 600 nm; *Filters*: all clicked).

To restart the routine with other parameters, it is necessary to click *Cancel* on *Possible Transitions* screen (Figure 23), and choose the *Possible Transitions* in the *Main Screen* (Figure 10). The previously used parameters are automatically placed as default.

4.4. ROTINE: SPECTRA SIMULATION

The *Spectra Simulation* routine can work with both the *Lines.txt* database as a user *file.txt* containing line centers (first column) and intensity (second column) to calculate simulated spectra of atoms through the Lorentz curves. The program can be employed to simulate atomic or molecular spectra if using the *file.txt* option. Figure 24 shows the ASAS *Spectra Simulation* screen.

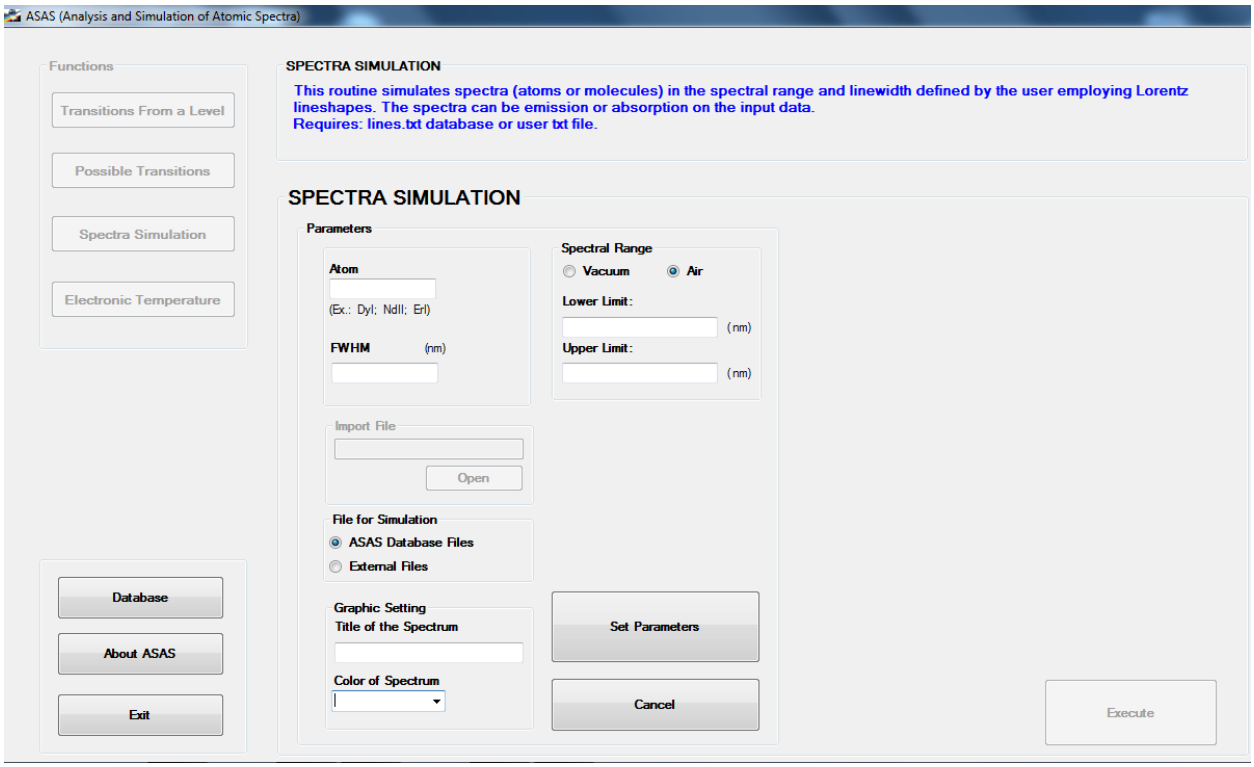


Figure 24. ASAS *Spectra Simulation* screen.

4.4.1. INPUT

1. To use the routine *Spectra Simulation* (Figure 24) first inform the following parameters:

a) Filename with the parameters for simulation (line centers and their intensities):

a.1 <u>If *Lines* database is used (default):</u>

Atom: only the atom symbol and the roman that define the ionization state, obeying the nomenclature used in the database. Only lines with R.I. above 0 in the database are simulated.

a.2 <u>If an external file.txt is used:</u>

- Select External Files in the Files for Simulation option.
- Click *Import File* and localize the data file. This file must contain two columns separated by spaces. The first one must contain the line centers and the other their

intensity. In *EXAMPLES* folder there is an example of an external file (Sp_I2_Molecule_597p9_nm_to_598p1nm.txt, some lines of iodine molecule between 597.9 nm and 598.1 nm, which can be simulated with a FWHM of 0.0002 nm, for example).

b) *Spectral Range*: *Lower Limit* and *Upper Limit*, in nm units. These limits can be providing in vacuum or in air (Default: *Spectral Range* in *Air*.)

c) The full width at half maximum (*FWHM*) in nm. This parameter can be available by the experimental results or theoretically considering the experimental resolution and predominant broadening mechanisms (see Appendix 2). This parameter defines the spectrum resolution.

d) The *Graphics Settings* options permit to chosen the color (default: red) and the title of the spectrum (default: Simulated Spectrum of [*Atomx*] if *Lines.txt* database is used and Simulated Spectrum of [*path\file.txt*] if a user *file.txt* is employed).

2. Click *Set Parameter* button. If the input parameters are ok the *Execute* button is released. If some data is not properly entered, the *Execute* button will not be liberated and the user will be advised to correct the parameter.

Attention: The maximum points per spectrum must be 200000 (see Appendix 2**). If this number of points is exceeded, the user is prompted to decrease the spectral region or to increase the FWHM.**

3. Click *Execute* button. Examples of simulated spectra are shown in Figure 25 and Figure 26.

At any time the program can be stopped using the *Cancel* button. In this case, the *Main Screen* (Figure 10) is displayed.

4.4.2. OUTPUT

After *Execute* button is clicked two screens (Figure 25) are obtained (the parameters used in the simulation are shown in the figure legend). The following options are possible in the superior screen:

a) *Save Plot* button: to save the obtained data on a file:

- Default path: /ASAS/RESULTS/SPECTRA SIMULATION/

•Default filename: Simulated Spectrum of [*Atomx*] in [*Vacuum* or *Air*] ([*Lower Limit*] nm – [*Upper Limit*] nm).jpeg

The user can modify the path and the filename.

b) *Save Data Plot* button: to save the data of the simulated spectrum:

- Default path: /ASAS/RESULTS/SPECTRA SIMULATION/
- Default filename: Simulated Spectrum of [*Atomx*] in [*Vacuum* or *Air*] ([*Lower Limit*] nm – [*Upper Limit*] nm).txt

c) *Exit* button: to return *Spectra Simulation* screen (Figure 24).

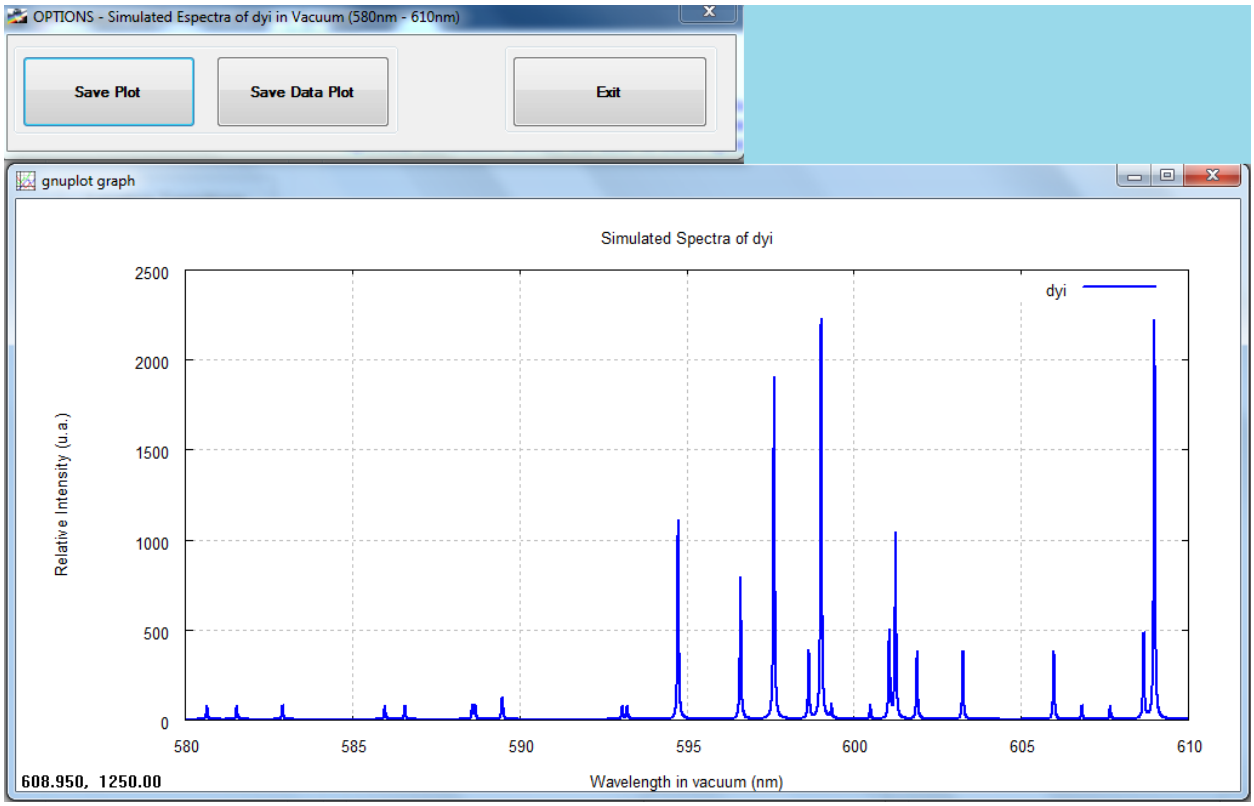


Figure 25. Simulated spectrum obtained with *Spectra Simulation* routine (*File for Simulation*: *ASAS Database Files Atom*: DyI; *Spectral Range*: vacuum *Lower limit*: 580 nm *Upper limit*: 600 nm; *Graphics Settings: Title* default *Color* blue; *FWHM*: 0.02 nm).

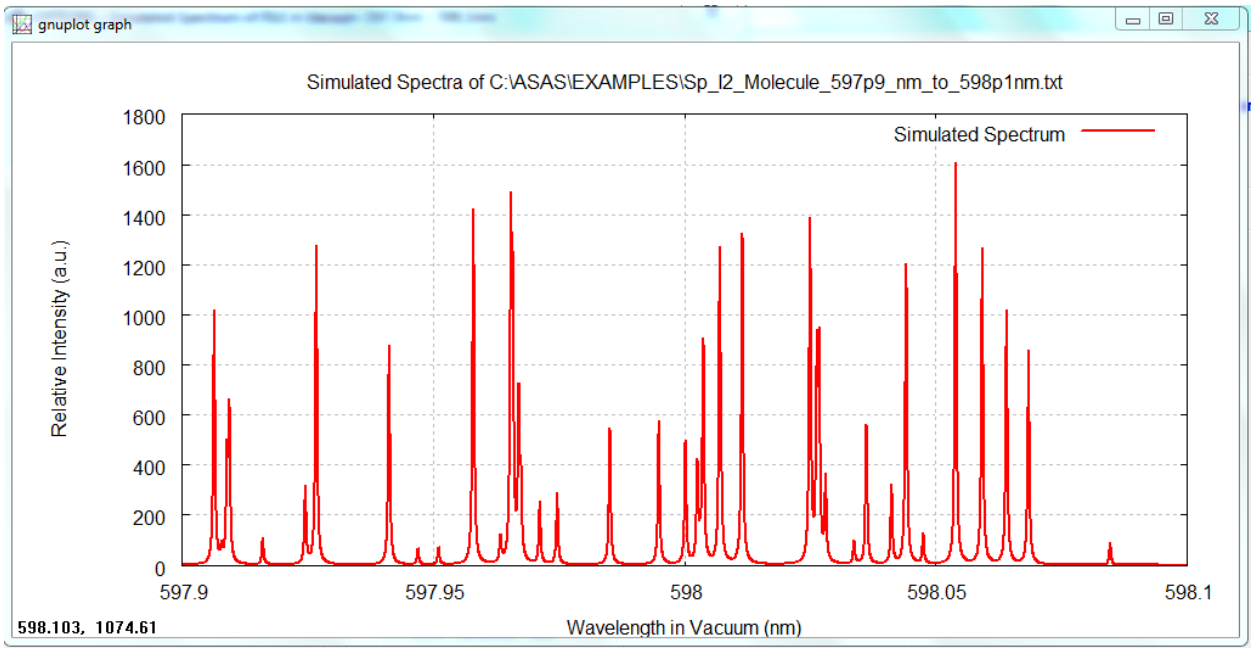


Figure 26. Simulated spectrum obtained with *Spectra Simulation* routine (*File for Simulation*: *External File* Sp_I2_Molecule_579p54_nm_to_579p71nm.txt; *Spectral Range:* air *Lower limit*: 574.54 nm; *Upper limit*: 579.71nm; *Graphics Settings: Title* default *Color* red; *FWHM*: 0.0002 nm).

To restart the routine with other parameters, it is necessary to click *Cancel* on *Spectra Simulation* screen (Figure 24), and choose the *Spectra Simulation* in the *Main Screen* (Figure 10). The previously used parameters are automatically placed as default.

4.5. ROTINE: ELECTRONIC TEMPERATURE

The *Electronic Temperature* routine requires the atom/atomic ion *Lines.txt* database and the experimental intensities of some of the lines with Einstein Emission Coefficient known. Equations are discussed in Appendix 3 and details can be found in references [12] and [13].

The lines intensities can be entered directly by keyboard during the program execution or being provided in a *file.txt* format, with three columns (Figure 27) separated by spaces: the first should contains the line number, the second, the experimental intensity and the third, the deviation in experimental intensity measurements. **The line number requires that the user visualize previously the atom *Lines* database to enter the correct line number**. Figure 28 shows the ASAS *Electronic Temperature* screen.

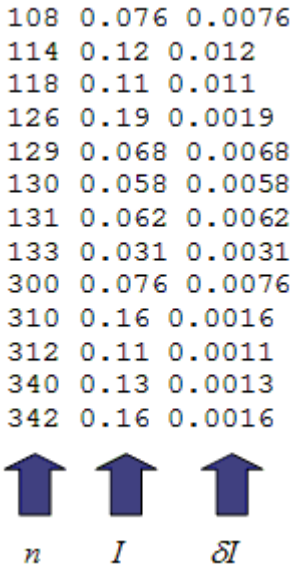


Figure 27. *File.txt* format with the data required for electronic temperature calculation (in the example, line emissions intensities for DyI in a hollow cathode discharge, 1 mbar of argon, 10 mA current [14]. The lines can be provided in random order.

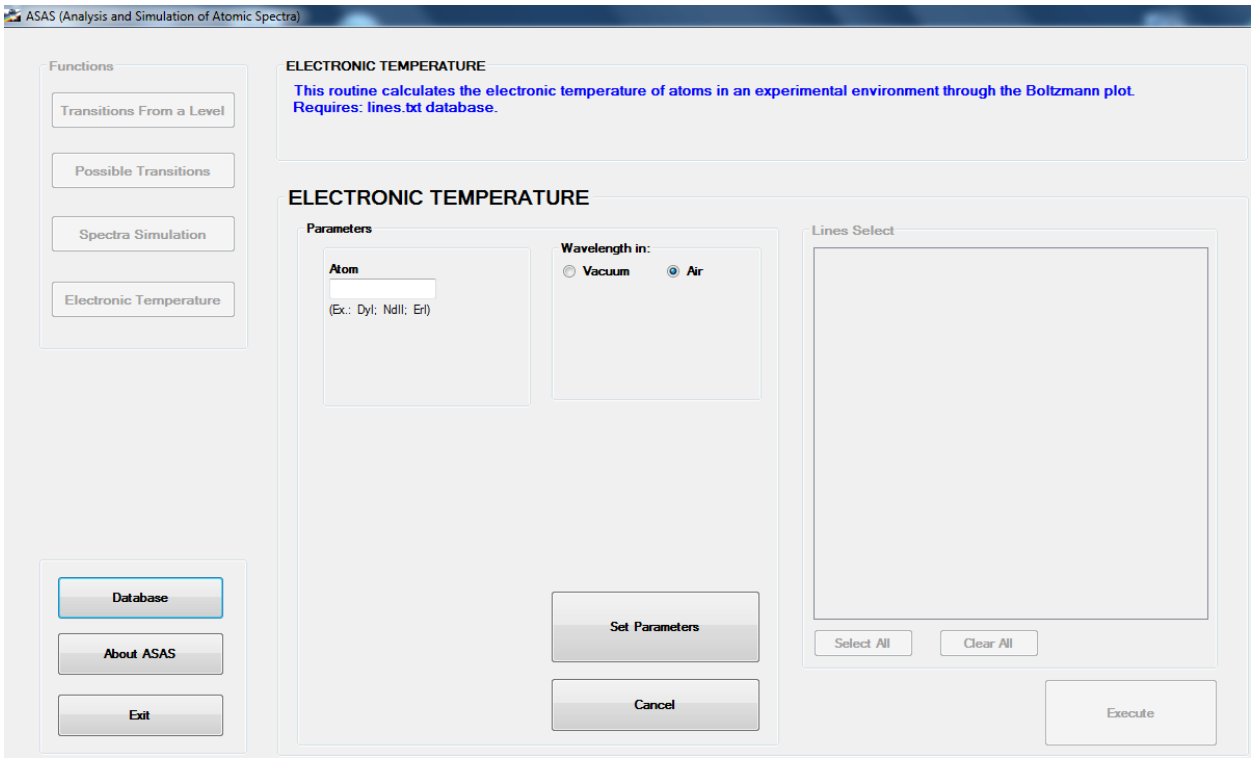


Figure 28. ASAS *Electronic Temperature* screen.

4.5.1. INPUT

1. To use the *Electronic Temperature* routine (Figure 28) first inform:

    a) *Atom*: only the atom symbol and the roman that define the ionization state, obeying the nomenclature used in the database.

    b) Select *Wavelength*: *Vacuum* or *in Air* .It depends on the experimental spectrum registered by the user. Default: *Wavelength* in *Air*.

2. Click *Set Parameter* button. If some data is not properly entered, the *Execute* button will not be liberated and the user will be advised to correct the parameter. If the input parameters are ok the *Execute* button is released and all the lines (wavelength in vacuum or in air) with known Einstein Spontaneous Emission Coefficients (A_E) inside the database of the atom are displayed in the *Lines Select* table (Figure 29). Two actions are possible:

    a) <u>If the experimental intensities is entered by keyboard</u>:

- select the lines whose intensities were measured experimentally;
- Click *Execute*. A table with the selected lines is shown;
- Click one line at a time and provide the intensity and its uncertainty data on the proper space. Click *Save* after each line data inclusion (Figure 30);

- After all the data are entered, the user can save the file using *Save Data of Table* option (default path: ASAS/RESULTS/ELECTRONIC TEMPERATURE; default filename: Data of Table - Electronic Temperature in the Atom [*Atomx*].txt). The file is saved in the format that can be read by the routine, item b) below.

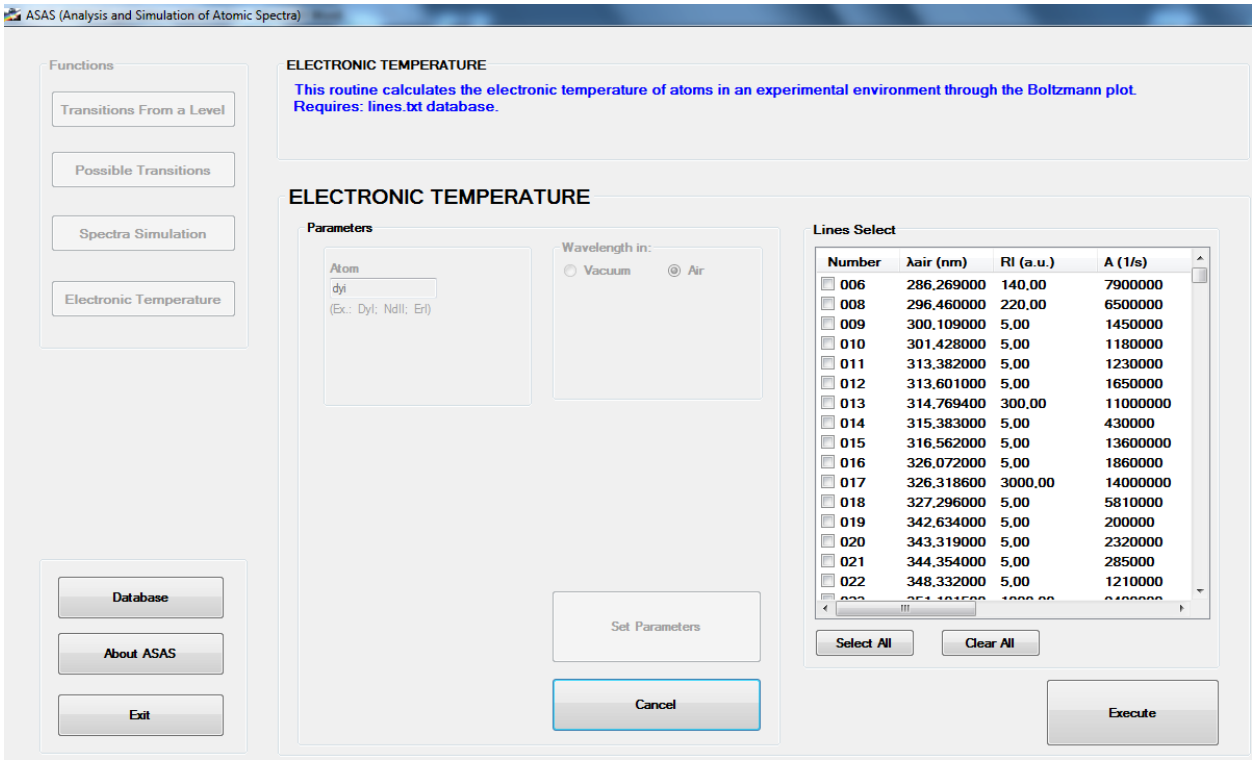


Figure 29. *Electronic Temperature* screen after *Set Parameter* button is clicked.

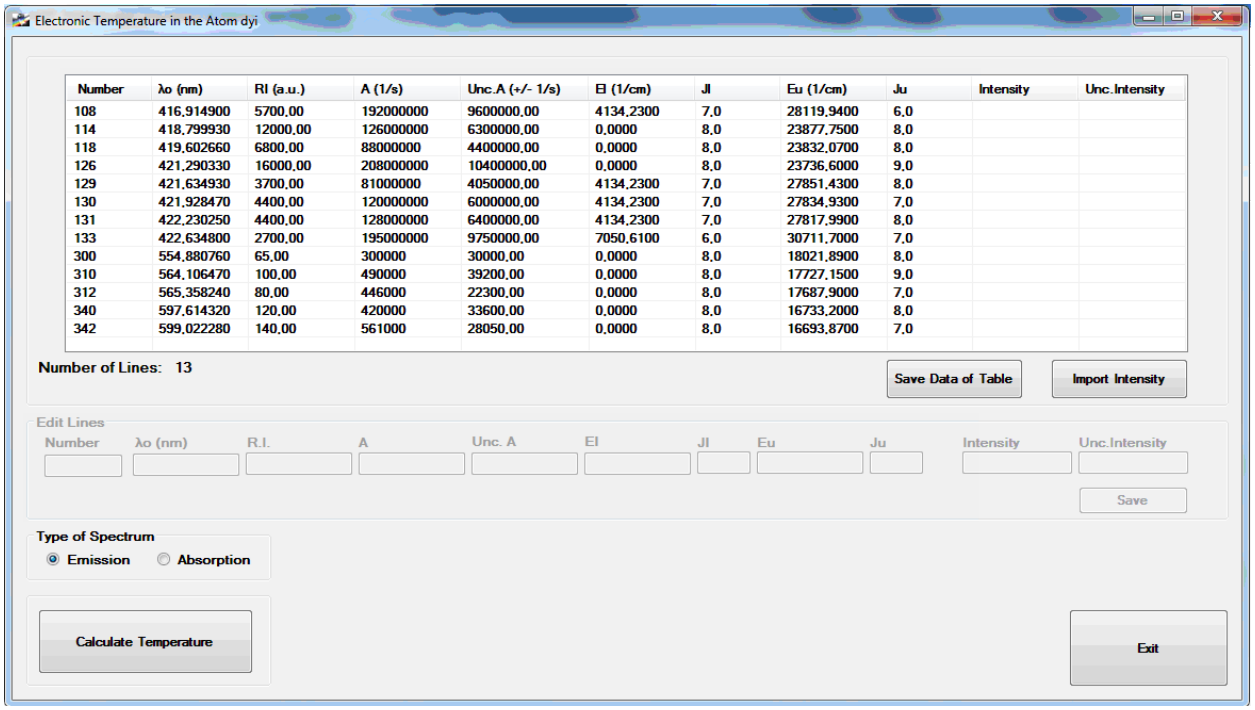


Figure 30. *Electronic Temperature* screen opened when some lines are selected. (*Atom*: DyI).

b) <u>If a file.txt data is going to be used</u>:

- Select *Select All* option. The screen showed in Figure 31 is opened.

- Click *Import Intensity* and localize the user *file.txt* with the intensity data. After this, the lines included in the file will contain their intensities included in the table (Figure 32).

  c) If necessary, the user can edit some of the data using the *Edit* and *Save* buttons (Figure 32). The modified file can be saved in a *.txt* file using *Save Data of Table* button.

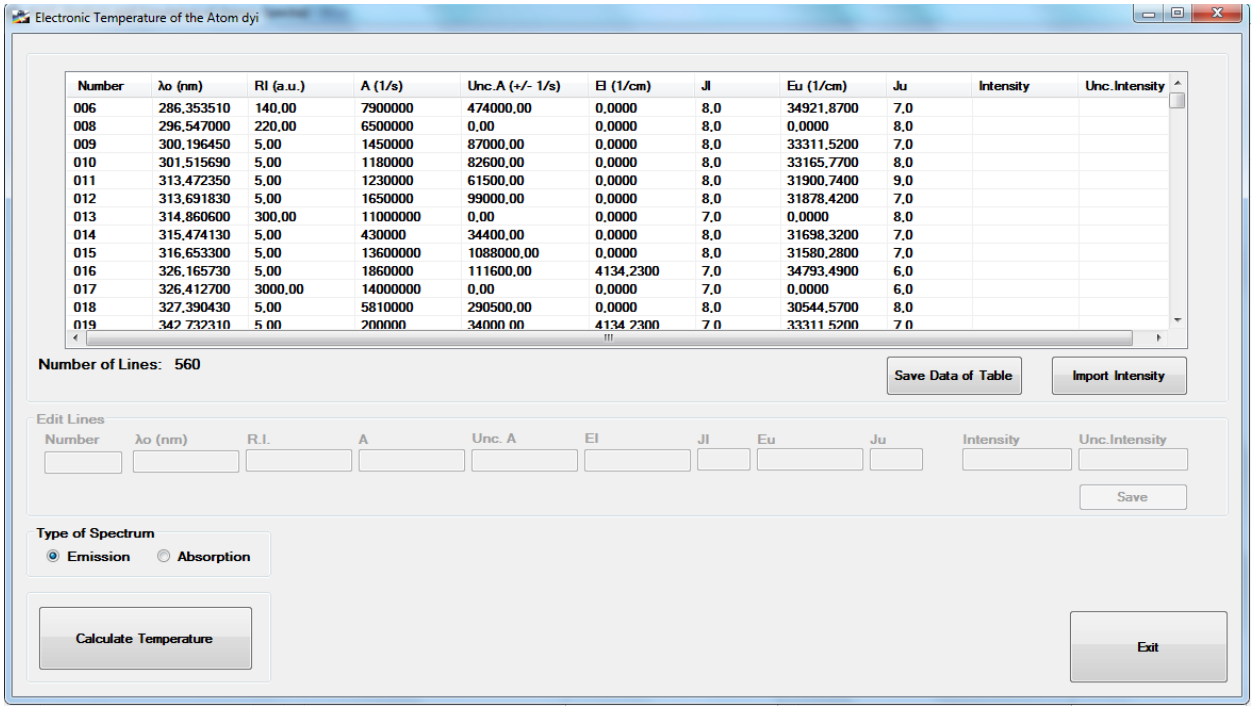


Figure 31. *Electronic Temperature* screen opened when *Select All+ Execute* are clicked.

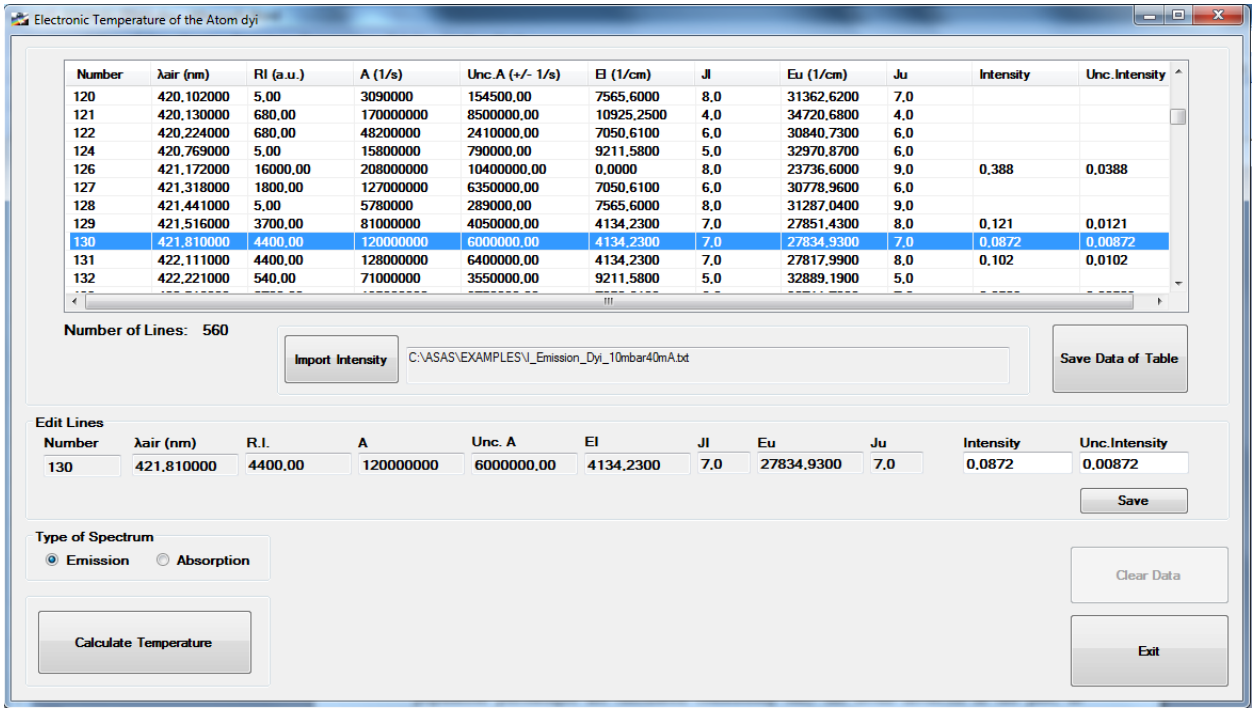


Figure 32. *Electronic Temperature* screen after the file.txt with intensity data is opened.

3. Choose *Type of Spectrum* (*Emission* or *Absorption*)

4. Click *Calculate Temperature*.

4.5.2. OUTPUT

After *Calculate Temperature* is clicked the screen showed in Figure 33 is obtained. The electronic temperature with its error and the correlation factor are shown in red (see Appendix 3). A table containing the following data are also presented: number of the line, wavelength (in nm, vacuum or air depending the user entry), lower energy level of the transition for absorption spectrum or upper energy level of the transition for emission spectrum (cm^{-1}) and the population (%) of the lower or upper energy levels for absorption or emission spectra, respectively. These population percentages are calculated considering only the levels involved in the plot, as explained in Appendix 3.

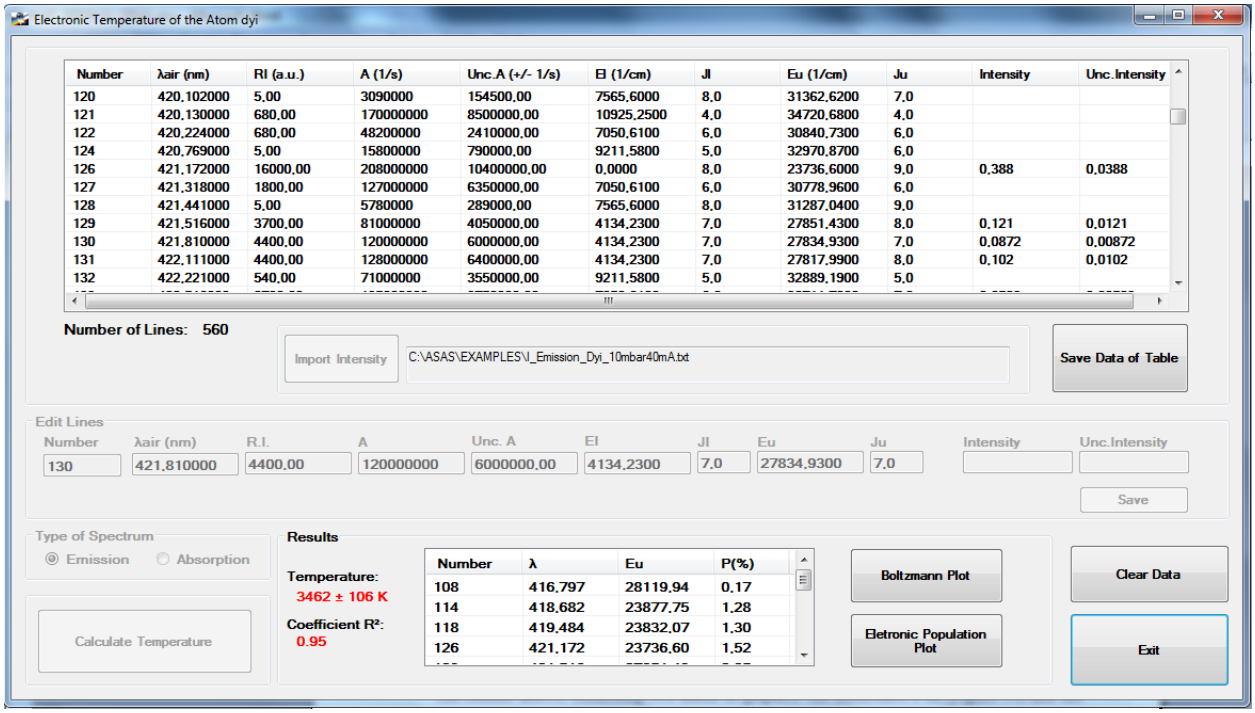


Figure 33. *Electronic Temperature* screen after *Calculate Temperature* button is clicked.

The routine allows visualizing two kinds of graphics: the *Boltzmann Plot* (Figure 34) and the *Electronic Distribution Plot* (Figure 35).

Once one of the graphics is obtained, the following options are possible (Default path: /ASAS/RESULTS/ELECTRONIC TEMPERATURE/):

d) *Save Plot*:

- Default filename:

Boltzmann Plot: Plot Boltzmann -Electronic Temperature in the Atom [*Atomx*] – [*Emission* or *Absorption*] Spectrum.jpeg

Electronic Population: Electronic Population Plot - Electronic Temperature in the Atom [*Atomx*] – [*Emission* or *Absorption*] Spectrum.jpeg

e) *Save Data Plot*

- Default filename:

Boltzmann Plot: Plot Boltzmann -Electronic Temperature in the Atom [*Atomx*] – [*Emission* or *Absorption*] Spectrum.txt

Electronic Population: Electronic Population Plot - Electronic Temperature in the Atom [*Atomx*] – [*Emission* or *Absorption*] Spectrum.txt

f) *Exit*: back to previous screen (Figure 33).

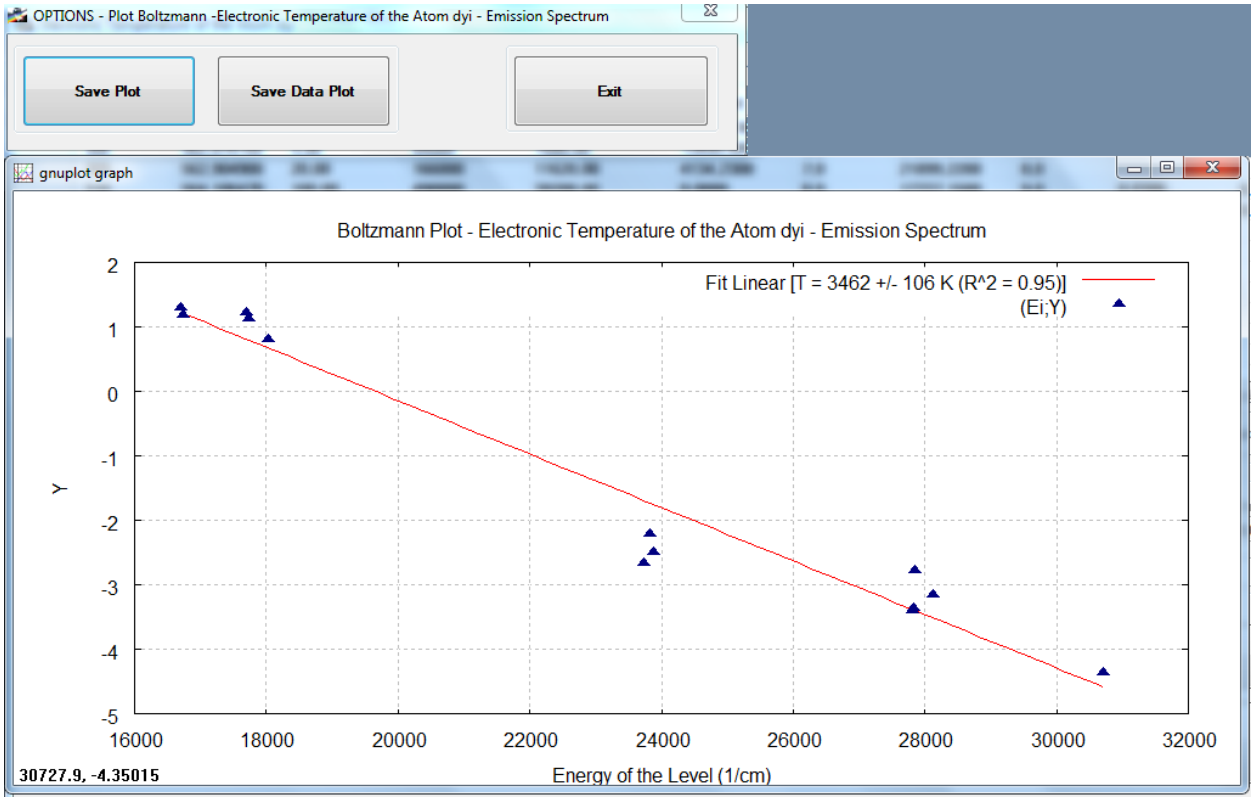


Figure 34. Results obtained after *Boltzmann Plot* is selected in Figure 33 screen.

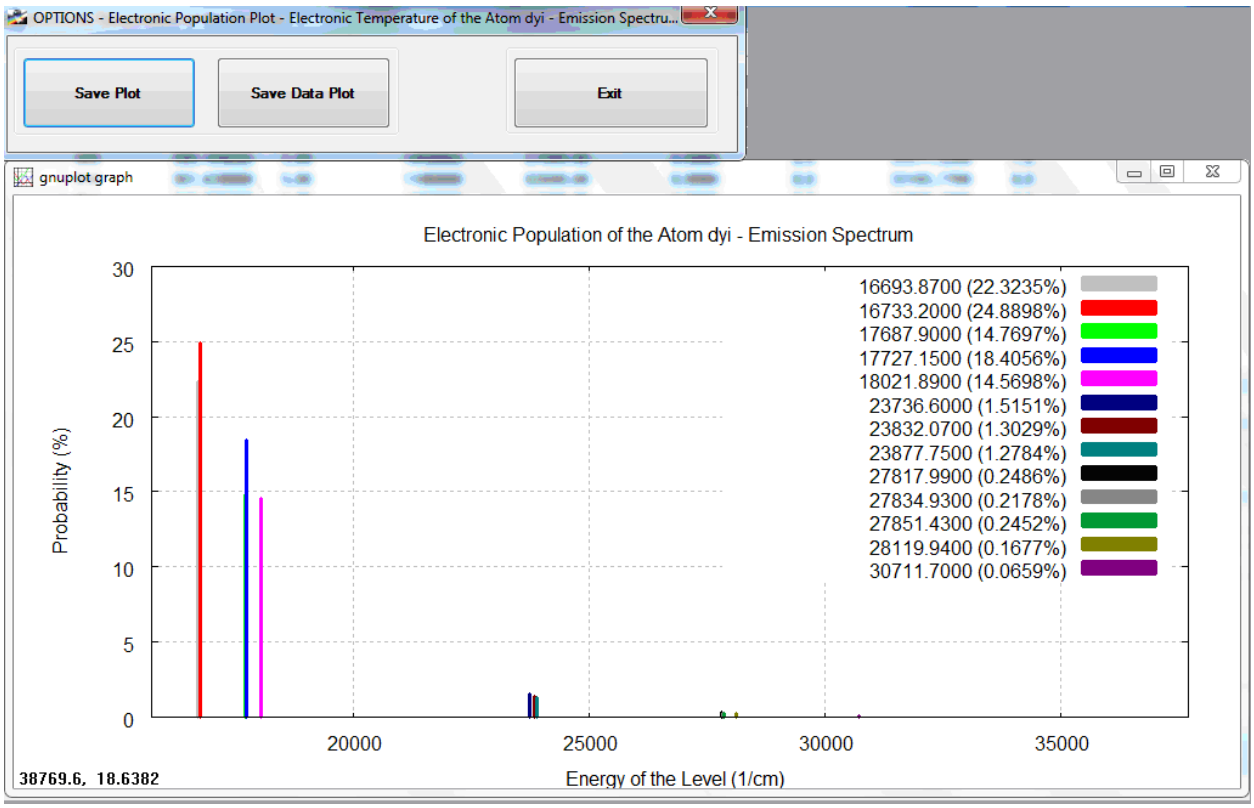


Figure 35. Results obtained after *Electronic Population Plot* is selected in Figure 33 screen.

To use another measured intensities for the same atom, click *Clear Data* on *Electronic Temperature* screen, Figure 33, and enter the new data.

To restart the routine with other atom parameters, it is necessary to click *Exit* on Figure 33 screen, *Cancel* on *Electronic Temperature* screen (Figure 28), and choose the *Electronic Temperature* in the *Main Screen* (Figure 10). The previously used parameters are automatically placed as default.

5. REFERENCES

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Appendix 1. Wavelength in Vacuum and in Air

The wavelength in vacuum is related with the energy of the transition thought the equation:

$$\lambda_o = \frac{hc}{E_u - E_l}. \qquad \text{A1.1}$$

Experimentally, the wavelength is obtained in air and its value depends on the air composition (humidity, CO_2 concentration), temperature and pressure; being:

$$\lambda_{air} = \frac{\lambda_o}{n} \lambda_{ar} = \lambda_{vácuo}/n, \qquad \text{A1.2}$$

where n is the refraction index in air. The refraction index can be calculated using the Ciddor Equation [10,11], valid between 300 nm and 1700 nm and considering a standard air with the following composition: 20°C, 50% humidity, 450 ppb CO_2 concentration and 1 atm pressure:

$$n = 1.00035396 - 4.19823.10^{-7}\lambda + 8.38492.10^{-10}\lambda^2 - 7.77411.10^{-13}\lambda^3 + 2.76285.10^{-16}\lambda^4.$$

$$n = 1{,}00035396 - 4{,}19823 \times 10^{-7}\lambda + 8{,}38492 \times 10^{-10}\lambda^2 - 7{,}77411 \times 10^{-13}\lambda^3 + 2{,}76285 \times 10^{-16}\lambda^4 \qquad \text{A1.3}$$

Appendix 2. Shape Functions and Broadening Mechanisms

Spectral lines are not completely narrow. The atom (or molecule) do not emit (or absorb) strictly monochromatic radiation but show an intensity profile (line shape) around each line center with a finite full width at half maximum (FWHM). The principal broadening mechanisms are: natural (lorentzian line shape), pressure (lorentzian line shape), Doppler (Gaussian line shape) and instrumental [6].

The *Spectra Simulation* routine (beta 1.0 version) simulates spectra in the spectral range defined by the user considering lorentzian line shape:

$$I(\lambda) = \frac{FWHM}{2} \frac{1}{\left(\frac{FWHM}{2}\right)^2 + (\lambda - \lambda_0)^2}. \qquad \text{A2.1}$$

To assure the graphic resolution, the interval between two points of the spectrum is defined as $\Delta\lambda$=FWHM/10. The number of points, *N*, in a Spectral Range is obtained through:

$$N = \frac{10.Spectral\ \ Range}{FWHM}. \qquad \text{A2.2}$$

The number of points per spectrum is limited to 200000. If the spectrum to be simulated exceeds this number of points, the user is alerted to decrease the spectral range or use a larger value of FWHM.

Appendix 3. Boltzmann Statistics and the Electronic Temperature

The ratio of atoms (or molecules) in an upper excited state to a lower energy state can be calculates from the Maxwell-Boltzmann equation, also called Boltzmann distribution:

$$\frac{N_i}{N_T} = \frac{g_i \; e^{\frac{E_i}{kT}}}{\sum_i g_i \; e^{\frac{E_i}{kT}}}, \qquad \text{A3.1}$$

where N_i is the number of atoms in the state of energy E_i,, N_T the total number of atoms, T, the absolute temperature (K), g_i, the level degeneracy (number of states having equal energy, g_i = $2.J_i+1$, where J_i is the total angular quantum number of the level i and k, the Boltzmann constant ($1.380662.10^{-16}$ erg/K).

One of the methods most frequently used for determination of excitation temperature (T_{ext}) is the Boltzmann plot [12]. Excitation sources like Hollow Cathode Lamp (HCL) emit radiation in enough intensity to be measured by laboratory detectors. Following the Boltzmann distribution, A3.1, and neglecting self-absorption, the lines intensity of the atoms are related to T_{ext} by [12]:

$$I_{ul} = \left(\frac{hc}{\lambda}\right) N_T \frac{g_u}{\sum_i g_i \; e^{-\frac{E_i}{kT_{exc}}}} A_{ul} e^{-\frac{E_u}{kT_{exc}}}, \qquad \text{A3.2}$$

where I_{ul} refers to the line intensity for the transition between the upper level u to the lower level l of the emitting species, T_{exc} is the excitation temperature (K), g_u, the upper level degeneracy E_u, the energy of the upper level, A_{ul} stands for the probability of the transition per unit of time (Einstein probability for spontaneous transition), h, the Planck constant ($6.626176.10^{-27}$ erg.s) and c, the light velocity in vacuum ($2.99792458.10^{10}$ cm/s). The sum $\sum_i g_i \; e^{-\frac{E_i}{kT_{exc}}}$ is the total partition function that is constant for each atom at a specific T_{ext}. In the Boltzmann plot method, A3.2 can be expressed as the following:

$$\ln\left[\frac{I_{ul}\lambda}{g_u A_{ul}}\right] = C - \frac{E_u}{kT_{exc}}, \qquad \text{A3.3}$$

where C contains the contributions of all the constant parameter of A3.2 equation. The angular coefficient, b, of the $\ln\left[\frac{I_{ul}\lambda}{g_u A_{ul}}\right] \times E_u$ plot is related with the excitation temperature:

$$T_{exc} = \frac{1}{kb} \qquad \text{A3.4}$$

if E_u is given in ergs.

The error of the temperature resulting from the Boltzmann plot method is calculated by [13]:

$$\frac{\Delta T_{exc}}{T_{exc}} = \frac{k_B T_{exc}}{\sqrt{\sum_{i=1}^{n} E_{u;i}^2 - \frac{1}{n}\left(\sum_{i=1}^{n} E_{u;i}\right)^2}} . \left(\frac{\Delta I_{ul}}{I_{ul}} + \frac{\Delta A_{ul}}{A_{ul}} \right), \qquad \text{A3.5}$$

where n is the number of the lines employed in the plot, $\frac{\Delta I_{ul}}{I_{ul}}$ is the error of the emission of the lines and $\frac{\Delta A_{ul}}{A_{ul}}$ is the error of the Einstein coefficient. ASAS software considers a medium error for both, $\frac{\Delta I_{ul}}{I_{ul}}$ and $\frac{\Delta A_{ul}}{A_{ul}}$.

When an absorption spectrum is being analyzed to obtain a Boltzmann plot, the intensity of each line, the absorbance, **A**, is measured experimentally as:

$$\mathbf{A}(\lambda) = -\log\left(\frac{I(\lambda)}{I_0(\lambda)} \right), \qquad \text{A3.6}$$

where $I_0(\lambda)$ is the radiation intensity and $I(\lambda)$, the radiation intensity after passing through the sample (transmitted radiation). In this case, the Boltzmann Plot is obtained using:

$$\ln\left[\frac{\mathbf{A}}{g_l B_{lu}} \right] = C - \frac{E_l}{kT_{exc}} \qquad \text{A3.7}$$

and the temperature error is calculated by A3.4 replacing E_u by E_l and I_{ul} by **A**.

The electronic population percentages in *Electronic Temperature* routine are calculated using A3.1 and considering only the energy levels employed to obtain the Boltzmann Plot.