Report on DUO calculations

Methods and results

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1 | Introduction

This report provides an overview of the methods and the results about the simulations I have done with the DUO software during my internship (February – July 2025) in the RbCs team of the Cornish Labs. DUO is a computer program for computing rotational and rovibrational spectra of diatomic molecules[1]. In the present work, I aimed to reproduce simulations about direct imaging of diatomic molecules[2]. DUO can solve the Schrödinger equation for multiple coupled electronic states (open-shell diatomic, excited states with spin-orbit coupling...). Transition dipole moment can also be added to compute absorption/emission spectra. DUO also has the capacity of fitting experimental data to models, however this will not be studied here. In order to analyse the data, I used some fortran code besides python codes. Fortran is way faster than python for some purpose, but I everything could be done in python (for a longer running time).

After reviewing briefly the method of resolutions in DUO, a tutorial describing the input file for a basis input file will be given and then a brief overview of the informations given in the output files. Then, the results of the simulations will be presented.

Some of the output files (which contains the input file) and fortran codes are available at: https://github.com/ThomasLjn/DUO_report_Durham

2 | Theoretical background

2.1 Methods of resolutions

The methods used in DUO are well described in[1], I will simply do a summary of the main ideas of the section 2 of this paper.

The non relativistic Hamiltonian of a diatomic molecule can be writte as:

$$\hat{H}_{tot} = \hat{H}_e + \hat{H}_\mu + \hat{H}_{vib} + \hat{H}_{rot} + \tag{1}$$

Where $\hat{H}_e$ is the electronic Hamiltonian, with $\{\xi_i\}_i$ the set of electronic coordinates, r is the internuclear distance and V the Coulomb electrostatic interactions between all particles:

$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N_e} \nabla_i^2 + V(r, \xi_i) \tag{2}$$

$\hat{H}_\mu$ is the mass-polarization term, where m_N is the total nuclear mass.

$$\hat{H}_\mu = -\frac{\hbar}{2m_N} \sum_{i=1}^{N_e} \sum_{j=1}^{N_e} \nabla_i \cdot \nabla_j \tag{3}$$

$\hat{H}_{vib}$ is the vibrational kinetic energy operator, with μ the reduced mass of the molecule.

$$\hat{H}_{vib} = -\frac{\hbar^2}{2\mu} \frac{dr}{dr^2} \tag{4}$$

$\hat{H}_{rot}$ is the rotational Hamiltonian and can be expression in terms of the body-fixed rotational angular momentum operator $\hat{\mathbf{R}} = \hat{\mathbf{J}} - \hat{\mathbf{L}} - \hat{\mathbf{S}}$ where $\hat{\mathbf{L}}$ is the total angular momentum, $\hat{\mathbf{J}}$ the electron orbital angular momentum and $\hat{\mathbf{S}}$ the spin angular momentum. With $\hat{K}$ an angular momentum, we can define the ladder operators: $\hat{K}_\pm = \hat{K}_x \pm \hat{K}_y$. We can then express the rotational Hamiltonian:

$$\hat{H}_{rot} = \frac{\hbar^2}{2\mu r^2} \hat{\mathbf{R}}^2$$

$$= \frac{\hbar^2}{2\mu r^2} \big[\big(\hat{J}^2 - \hat{J}_z^2 \big) + \big(\hat{L}^2 - \hat{L}_z^2 \big) + \big(\hat{S}^2 - \hat{S}_z^2 \big) \tag{5}$$

$$+ \big(\hat{J}_+ \hat{S}_- + \hat{J}_- \hat{S}_+ \big) - \big(\hat{J}_+ \hat{L}_- + \hat{J}_- \hat{L}_+ \big) + \big(\hat{S}_+ \hat{L}_- + \hat{S}_- \hat{L}_+ \big) \big]$$

The input of DUO is the electronic potential. It is assumed that the electronic problem has already been solved. The subsequent objective is to resolve the vibrational problem, which is known as the uncoupled problem. The construction of a basis of vibrational functions is a prerequisite for the expansion of rovibrational wavefunctions. In this basis of functions, the complete rovibronic Hamiltonian is solved (coupled problem). In the case of the addition of certain couplings, these are included in the full Hamiltonian. In conclusion, the wavefunction of each rovibrational state is expressed as an expansion

in the basis set of function labelled by $|n\rangle$ = $|$state, $J,\Omega,\Lambda,S,\Sigma,v\rangle$, with τ the parity ($\pm$), λ a counting index:

$$\Phi_\lambda^{J,\tau} = \sum_n C_{\lambda,n}^{J,\tau} |n\rangle \qquad (6)$$

In the general case, the only goof quantum numbers (*i.e.* labels associated with the eigenvalues of symmetry operators) are the total angular momentum value J and the parity τ. Other numbers are estimated by DUO by looking at the highest coefficient in this expansion.

3 | Installation and compilation of DUO

In this part, I am assuming that the reader has access to a linux terminal. If you are using windows, you can use Windows Subsystem for Linux (WSL).

This part is in majority based on DUO documentation: https://duo.readthedocs.io/en/latest/index.html.

3.1 Download DUO from github

An old but still working version is the `MOLPRO` branch: https://github.com/Trovemaster/Duo/tree/MOLPRO. In order to download this specific branch, the following command line can be used:

```
git clone -b MOLPRO https://github.com/Trovemaster/Duo.git .
```

If you want to have the last version of DUO (might not work ?), you can just type:

```
git clone https://github.com/Trovemaster/Duo.git .
```

3.2 Download fortran compiler

Multiple free fortran compilers are available from internet. I am personally using `gfortran`. You may also need to install `gcc`, but it should be installed by default. Here is how to install them using `apt` package manager (for instance the default one in Ubuntu distribution):

```
sudo apt-get install gfortran
sudo apt-get install gcc
```

3.3 Changing the Makefile

Makefile (`makefile`) is a file containing all the information about the files compilation. In order to start it and then compile the code, go to the main folder (where DUO files are) and type `make` in the terminal. If a `makefile` is found, it should start the compilation. If it is not working, it can be that the default `makefile` is not well written for you compiler. If you install gfortran, then the default file is not the right one to use. In the folder `MAKEFILES` is the file `makefile_gfortran`: this is the one that needs to be used. Then you can use the following commands to properly compile duo, assuming you are in the main directory of DUO:

```
cp MAKEFILES/makefile_gfortran makefile
make
```

The default name for the DUO executable in the MOLPRO branch is `j-duo_0506.x`. You can change it directly in the `makefile` file, or using the `mv j-duo_0506.x new_name.x` command.

3.4 Run your first simulation

The following command can be used to start a simulation. Note that the < and > characters are mandatory since they tell to the fortran program where to read and where to write.

```
./duo.x < input_file > output_file
```

4 ┃ DUO I/O

4.1 Input file

Everything said here is based on personal experience with the software and on the documentation (available in the DUO folder as `manual.pdf` but a more recent version is available in the website: https://duo.readthedocs.io/en/latest/index.html).

> ℹ️ In DUO files, the comments lines are surrounded by parenthesis, for instance:
>
> **(this is a comment)**

4.1.1 System defintion

The first lines of the input file will be the the definition of the system:

```
1  ( === Global Setup === )
2  atoms Rb-87 Cs-133
3  nstates 3
4  jrot 0 - 5
5  (Symmetry is Cs(M) for heternuclear and C2v(M) for homonuclear)
6  symmetry Cs(M)
```

- `atoms`: specifies the two atoms and isotopes
- `nstates`: number of potential energy curves (PEC)
- `jrot`: specifies the set of total angular momentum quantum numbers to be computed. Can be integers, half-integers or range. *e.g*: `jrot 2.5, 0.5, 10.5 - 12.5, 20.5`. The first `J` in the `jrot` list will be used to define the reference zero-point-energy (ZPE) value for the run.
- `symmetry`: Optional keywork specifying the molecular permutation-inversion symmetry group

4.1.2 Definition of the grid

```
1  ( === Grid definition === )
2  grid
3  npoints  800
4  range  2.5, 15.0
5  (units angstrom)
6  type 0
7  end
```

- `grid` and `end`: keywords that specifies the beggining and the end of the grid definition section.
- `npoints`: number of grid points
- `units`: optionnal here, default unit is `angstrom`. can be `bohr`
- `range`: minimal and maximum internuclear distance for the calculation.
- `type`: can be 0, 1, 2, 3 or 4. `0` is default and correspond to a uniform distribution. For detail about the other type of grid definitions, see the documentation.

4.1.3 Vibrational basis set

```
1   VibrationalBasis
2   vmax 300 300 200 400
3   end
```

where the `vmax` argument specifies the number of vibrational levels for each PEC included in the basis. If only one integer n is provided, then it will compute for each PEC the lowest-energy n vibrational levels.

4.1.4 Eigensolver

```
1   EigenSolver
2   nroots 100
3   ZPE 24.794637558396
4   end
```

- **nroots**: number of energy levels of the coupled problem to be computed (for any of the specified values of jrot).
- **enermax**: to select the energy levels of the coupled problem to be computed
- **ZPE**: allows to explicitly input the zero-point energy (ZPE) of the molecule (in cm^{-1}). This affects the value printed, as Duo always prints energy of rovibronic levels by subtracting the ZPE. Example:

> ℹ️ If both **nroots** and **enermax** are specified then only levels satisfying both criteria are selected. Note that the present **enermax** threshold is distinct from the VibrationalBasis input.

4.1.5 Potential energy curves

The PEC can be implemented using built-in functions or by giving values on a grid. In both cases, the other keywords than `type` are the same. For a complete list of the built-in functions, please see the documentation and/or manual. I figured that some of the built-in functions are not specified in the documents. You can find them in the `functions.f90` file, defining all the functions.

- **poten**: number/ID of the PEC
- **lambda**: Λ quantum number
- **mult**: $2S + 1$ value, spin multiplicity
- **symmetry**: + or −, symmetry of the state. Only if Λ = 0
- **units**: units for length and energy
- **type**: built-in function (e.g `EMO`, see documentation) or `grid`

Below one example with `type EMO` and one with `type grid`.

```
1   poten 1
2     name "A1Sigma+"
3     lambda 0
4     mult 1
5     symmetry +
6     type EMO
```

```
7    units angstrom cm-1
8  values
9    Te 9994.328
10   Re  5.12209398917506
11   Ae 15383.992
12   RREF  5.1
13   PL  3
14   PR 3
15   NL 17
16   NR 17
17   a0 0.449325692555731
18   a1 0.0322192612584081
19   a2 0.00894469540557293
20   ...
21   a16 3.34614495243100
22   a17 0.108832960764537
23  end
```

```
1  poten 1
2  name "X1Sigma+"
3  symmetry +
4  lambda 0
5  mult  1
6  units cm-1
7  units angstroms
8  type grid
9  Interpolationtype Cubicsplines
10 values
11 2.800000 13071.271547
12 2.825814 12221.936011
13 2.851628 11434.746517
14 ...
15 13.900000 3831.655762
16 end
```

4.1.6 Couplings

Two examples will be given, one dipole and one spin-orbit coupling. More coupling are detailed in the documentation. Note that some optionnal keywords are not mentionned here but can be found in the documentation, such as `Interpolationtype`.

- `spin-orbit 1 2` or `dipole 1 2`: coupling between PEC 1 and PEC 2.
- `name`: name of the coupling – only for prints.
- `lambda, spin, sigma`: Λ, S and Σ quantum number for both PEC. Other keywords exists, as `mult`... See documentation for more, depending on the systems.
- `units`: distance and energy units.
- `factor`: scaling factor (energy)
- `type`: build-in function or `grid`

Examples:

```
1  ( 1. Spin-Orbit: A 1Sigma+ ~ b 3Pi_0 coupling --- V_A-b0 = -sqrt(2)*xi_Ab0 - Kruzins
   Table II [cite: 8] )
2  spin-orbit 1 2               ( Couples state 1 and state 2 )
3    name "<A|HSO|b0>"
4    lambda 0 1
5    spin   0 1
6    sigma  0 -1
7    units angstrom cm-1
```

```
8      factor 1
9      type HH
10     values
11       De 91.536963
12       Aatom 184.6795
13       re 5.529408
14       a 1.820259
15       b 0.455345
16       c 0.487451
17     end
```

```
1   dipole 2 1
2     name "1X <- 1A"
3     units angstrom
4     units debye
5     lambda 0 0
6     spin 0.0 0.0
7     type grid
8     values
9       2.1 6.052659749799999
10      2.2 8.8239254136
11      2.3 9.770471623999999
12      2.4 9.6825272124
13      2.5 9.663718291999999
14      2.6 9.7076904978
15      2.7 9.789280544399999
16      2.8 9.8952713526
17      ...
18    end
```

4.1.7 Computing spectra

```
1   intensity
2     absorption
3     Thresh-Einstein 1e-10
4     temperature 1.0
5     linelist name_of_file
6     J, 0, 1
7     freq-window -0.1, 22000.0
8     energy low -0.1, 30.0, upper 8000.0 12000.0
9   end
```

- **intensity**: keyword used for the transition section
- **absorption** or **emission**: speficies if it needs to compute absorption or emission
- **Thresh-Einstein**: threshold on the Einstein coefficients. Other thresholds exists, but I think this one is the most relevant (see documentation).
- **temperature**: for computing partition function, dummy variable in my case.
- **J**: specifies the J levels that have to be taken into account in the computation of the transition. Uncorrelated to the **jrot** keyword at the beggining but takes the same kind of arguments.
- **freq-window**: frequency windows (in cm^{-1}) for the transitions.
- **energy low ... high**: energy range of the lower state and the higher state. You can be restrictive in order to have fewer transitions to compute. They do not include the ZPE.
- **linelist**: filename prefix of the output file (**.trans** and **.states** file)

4.1.8 Writting the wavefunctions to the disk

In order to write the wavefunctions to the disk, the following code can be used. It will generate two files, one with the vibrational basis functions (values on a grid) and one with the expansion coefficients. `filename` is the prefix for the output checkpoint files.

```
1  checkpoint
2  eigenfunc save
3  filename chk/file_name
4  end
```

4.2 Output file

4.2.1 .out file

This file contains almost every piece of information relevant to the simulation. Subsequent to the header, in which the author's information and the physical constants utilised by DUO are documented, the input file is printed. This can be advantageous because it ensures the availability of a secure copy of each input file utilised. Subsequently, a series of data pertaining to the atoms is enumerated, such as the atomic mass, the nuclear spin, and the reduced mass of the molecule. Subsequently, the grid and the PEC are printed. This process may be useful for performing a sanity check and plotting the PEC. addresses the coupling and dipoles in a similar manner. Subsequently, details pertaining to the contracted vibrational basis are displayed. While these may not be of particular pertinence in this context, they can be consulted to ascertain the overall functionality of the system.

The solutions to the coupled problem for each J will subsequently be printed, with the process commencing with the line entitled `Eigenvalues for J = 0.0`. The organisation of these elements will be by (J, p) blocks, where p denotes the parity. The variable i denotes the number of the state in this particular block. The term 'state' is employed to denote the ID of the `poten` object that possesses the highest coefficient in the expansion.

```
1  Eigenvalues for J =      0.0
2
3       J    i        Energy/cm  State   v  lambda spin   sigma    omega  parity
4       0.0  1      8724.961402    2      0    1     1.0    -1.0     0.0    +    ||b3pi0
5       0.0  2      8774.806113    2      1    1     1.0    -1.0     0.0    +    ||b3pi0
```

If the keyword `intensity` is used, then the transition informations will also be printed with this format:

```
Linestrength S(f<-i) [Debye**2], Transition moments [Debye],Einstein coefficient A(if) [1/s],and Intensities [cm/mol]

   J Gamma <-  J  Gamma Typ      Ei    <-      Ef      nu_if        S(f<-i)          A(if)           I(f<-i)      State v lambda sigma  omega <-State v lambda sigma  omega
  1.0  A"   <- 0.0  A'    R    8749.7904 <-   24.7946  8724.9957   4.25724090E-01  2.95600291E+04  4.00321843E-16 ( 3  0 -1   1.0     0.0 )<-( 1  0  0   0.0    0.0 )
  1.0  A"   <- 0.0  A'    R    8760.6475 <-   24.7946  8735.8529   4.40336960E-06  3.06889506E-01  4.14578037E-21 ( 3  0 -1   0.0    -1.0 )<-( 1  0  0   0.0    0.0 )
  1.0  A"   <- 0.0  A'    R    8799.6350 <-   24.7946  8774.8404   2.80408206E-01  1.98056618E+04  2.65183064E-16 ( 3  1 -1   1.0     0.0 )<-( 1  0  0   0.0    0.0 )
```

4.2.2 .states and .trans files

The `.states` and `.states` files are generated if the keyword `intensity` is used.

The `.states` file is a list of the states involed in the transitions, each state is described by the following line:

```
n E         g J +/- e/f State  v |Λ| |Σ| |Ω|

1 24.794638 1 0 +   e X1Sigma+ 0  0   0    0

2 74.239245 1 0 +   e X1Sigma+ 1  0   0    0
```

- n: State counting number.
- E: State energy in cm^{-1}.
- g: State degeneracy.
- J: Total angular momentum.
- +/-: Total parity.
- e/f: Rotationless parity.
- State: Electronic state label.
- v: State vibrational quantum number.
- Λ: Absolute value of Λ (projection of the electronic angular momentum).
- Σ: Absolute value of Σ (projection of the electronic spin).
- Ω: Absolute value of Ω = Λ + Σ (projection of the total angular momentum).

Example:

The `.trans` file is described the transitions:

```
        nf              ni  A_fi           v_fi
        1031             1  2.6862E+07     10478.783294
        1032             1  4.0242E+08     10490.670223
        1033             1  3.1481E+01     10511.503749
        1034             1  7.3507E+04     10513.099485
        1035             1  4.5985E+08     10539.090003
```

- nf : Upper state counting number.
- ni: Lower state counting number.
- A_{fi}: Einstein-A coefficient in s^{-1}.
- v_{fi}: Transition wavenumber in cm^{-1}.

4.2.3 .chk files

The checkpoints files are created if the keyword `checkpoint` is used. Two files are created: one describing the vibrational basis function with values on the grid, and one giving the expansion coefficients.

The `_vib.chk` file contains the vibrational part of the basis set in the grid representation, where the each basis function is given in a block. The first line specifies the sate (number, energy, electronic state and vibrational quantum number) followed by the grid values. Example:

```
 499      13130.039181     2  97    A1Sigma+
  -0.195571629589E-19
  -0.417810529718E-19
  -0.105896656706E-18
```

```
  -0.718567118181E-18
...
```

the `_vectors.chk` file contains the expansion coefficients of the eigenfunction in terms of the Duo vibrational basis set functions. The first eight lines describe the system. The line 9 is a header describing each column:

- `#`: counting number in the current (J, parity) block
- `J, p`: rotational quantum number, parity
- `Coeff`: coefficient $C_i^{J,p}$ of the expansion
- `St, vib,Lambda, Spin, Sigma, Omega`: quantum number of the current state of the vibrational basis
- `ivib`: unique basis set number, correspond at the first column in the `_vib.chk` file. It is a counting number including all electronic states.

Example:

```
Molecule = Rb-87           Cs-133
 masses   =     86.909180531000    132.905451961000
 Nroots   =       300
 Nbasis   =       900
 Nestates =         3
 Npoints  =       800
 range    =     2.5000000    15.0000000
X1Sigma+, A1Sigma+, b3pi0,    <- States
     |  # |   J | p |           Coeff.  | St vib Lambda Spin    Sigma    Omega
ivib|
       1    0.0  0   0.100000000000E+01  1   0   0     0.0      0.0      0.0    1
       1    0.0  0   0.000000000000E+00  1   1   0     0.0      0.0      0.0    2
       1    0.0  0   0.000000000000E+00  1   2   0     0.0      0.0      0.0    3
       1    0.0  0   0.000000000000E+00  1   3   0     0.0      0.0      0.0    4
       1    0.0  0   0.000000000000E+00  1   4   0     0.0      0.0      0.0    5
```

5 | Potential energy curve and coupling functions

The potential energy curves, the spin-orbit coupling function and the transition dipole moments are all represented in Figure 1. The electronic ground state potential energy curve is from ref.[3]. The uncoupled excited states potential energy curves and spin-orbit coupling functions are from Ref.[4]. The electronic transition dipole moment between the $X^1\Sigma^+$ and $A^1\Sigma^+$ electronic states is from Ref.[5]. The spin-orbit coupling is introduced directly into DUO.
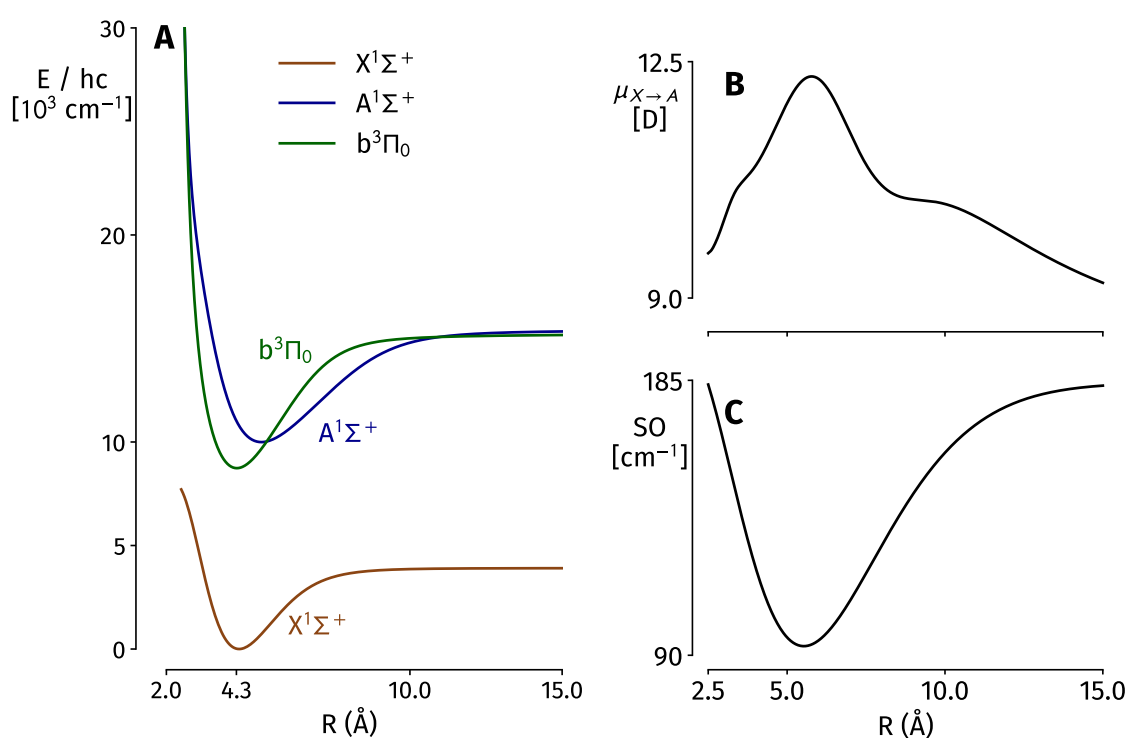

Figure 1 - **A**: Potential energy curves of the relevant electronic states of RbCs molecule[3,4]. **B** Transition dipole moment between $X^1\Sigma^+$ and $A^1\Sigma^+$ states[3]. **C**: Spin-orbit coupling between $A^1\Sigma^+$ and $b^3\Pi^0$ states[4].

6 | Characterisation

6.1 Impact of the number of grid points

While performing simulations, a multitude of degrees of freedom can exert an influence on the precision of the calculation. It is imperative to verify that our computation has indeed reached convergence.

The initial evaluation focuses on the quantity of grid points. The initial 40 vibrational energy levels with $J = 0$ of the $X^1\Sigma^+$ electronic state of the RbCs molecule were computed for varying numbers of grid points, whilst maintaining the same internuclear range. As demonstrated in Figure 2, the energy displays exponential convergence with the number of grid points. It may be posited that, in accordance with this plot, utilising 300 grid points would be adequate. However, it is suggested that a more prudent approach would be to employ a point count of approximately 500 to 800, thereby ensuring convergence for higher vibrational levels. The choice between affordable precision and computation time is a constant compromise. In this instance the computational was sufficiently quick to permit utilisation of 800-1000 grid points without encountering any difficulties. It was ensured that a sufficient quantity of basis functions was employed in this instance to guarantee that this was not the limiting factor.
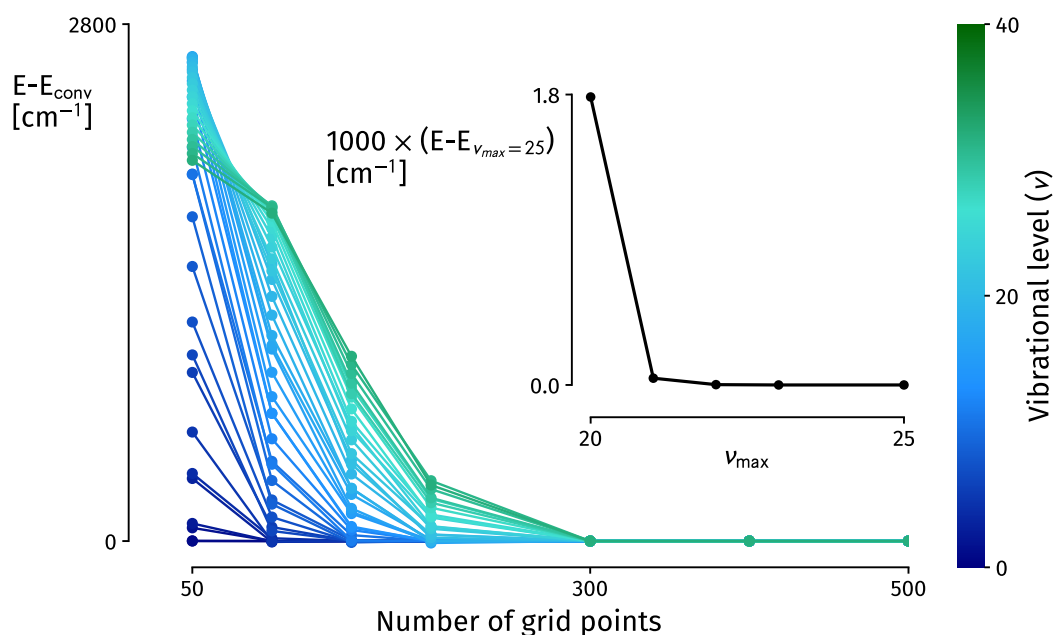

Figure 2 - Vibrational energy levels ($J = 0$) of the $X^1\Sigma^+$ electronic state of the ^{87}Rb^{133}Cs molecule, compared to the converged value for different numbers of grid points. The converged value is taken as the energy at 900 grid points. For this comparaison, v_{max}=100. The inset shows the same study against the number of vibrational basis function. The data are for $v = 20, J = 10$ of the electronic ground state and for 900 grid points.

6.2   Impact of the size of the basis

The inset of Figure 2 shows how the energy of a rotationally excited state converge with the number of basis functions. It is recommended by the authors of the code to use a basis of size $1.25 \times v_{max} + 2$ to compute rotationally excited states up to v_{max}[1]. It is always better to have a bit more functions to ensure the convergence, if the computation is not too slow.

6.3   Reproducing LEVEL16 results

With LEVEL16 code, the implementation of any form of coupling between states is impossible. The $b^3\Pi_0$ and the $A^1\Sigma^+$ states were pre-mixed in Python, using a 2 x 2 Hamiltonian. The off-diagonal terms of this Hamiltonian correspond to the spin-orbit coupling terms. Subsequently, the newly obtained eigenstates were employed as the input states for the simulations. With DUO, it is possible to input the uncoupled states and specify the coupling, which must result in greater accuracy and physical realism. Nevertheless, as a demonstration of the underlying principle, it is encouraging to observe that DUO and LEVEL16 produce consistent results when the same input is utilised.

With the LEVEL16 code, it is impossible to put any coupling between states. I pre-mixed the $b^3\Pi_0$ and the $A^1\Sigma^+$ states in python (using a 2×2 Hamiltonian, the off-diagonal terms are the spin-orbit coupling terms) and use the new eigenstates as input states. In DUO, one can input the uncoupled states and specify the coupling, which will be more accurate and physically correct. However, as a proof of principle, it is nice to see that DUO and LEVEL16 are giving the same results for the same input. As demonstrated by Figure 3, the difference in the energies between the two codes is neglectable.
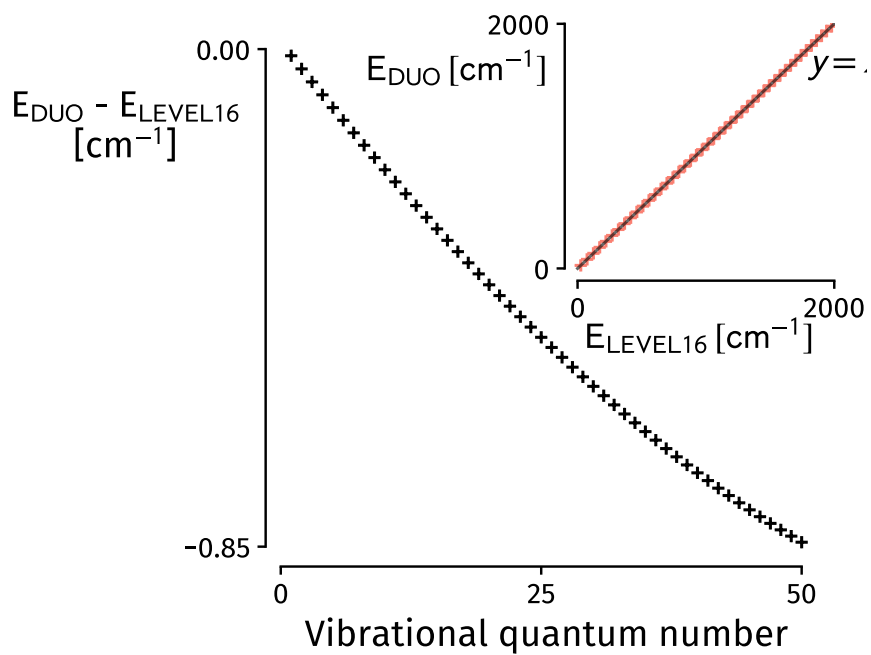
Figure 3 - Comparison between energies computed with LEVEL16 or DUO for the J=0 states of the $X^1\Sigma^+$ potentiel of RbCs molecule. The difference is shown in the same plot while the inset shows. In the DUO simulation, v_{max} = 100 and n_{grid} = 800.

7 | Mixing coefficients

In the RbCs molecule, the $A^1\Sigma$ and $b^3\Pi_0$ states are coupled by spin-orbit interactions. The potential energy curves and the spin-orbit functions utilised in this study were derived from Ref.[4]. The computed rovibrational states are found to exhibit a mixture, rather than a pure attribution to any single state. In the DUO system, the utilisation of the 'checkpoint' keyword allows for the storage of expansion coefficients in a file. The proportion α of $A^1\Sigma$ or $b^3\Pi_0$ of one particular state λ can then be computed from the Equation 6, where the electronic state is denoted Λ. The following equation is to be solved: $\alpha_\lambda^\Lambda = \sum_n (C^J, \tau)^2 \delta_{\text{state}, \Lambda}$.

It is evident that, in the case of the simulation being populated with only these two electronic states, the calculation of a single α_λ is sufficient, since $\alpha_\lambda^{A^1\Sigma^+} = 1 - \alpha_\lambda^{b^3\Pi_0}$.

Table I from the supplementary data of Ref[4] gives some experimental energies and computed mixing coefficients (see Listing 1). The main goal of this part is to see wheter it is possible to reproduce these data using DUO calculations. For these calculations, I only included the spin-orbit coupling, the $A^1\Sigma^+$ and the $b^3\Pi_0$ states. Other couplings could be added to have more precision if needed.

```
========================================================
N    i    J    Eexpt      Ecalc      Del      A%    b0%    b1%    b2%
========================================================
1    0    139   10928.612   10928.614   -0.002   73    26.9   0.1    0
2    0    141   10935.797   10935.802   -0.005   73.5  26.4   0.1    0
3    0    142   10939.419   10939.429   -0.01    73.7  26.2   0.1    0
4    0    143   10943.074   10943.078   -0.004   73.9  26     0.1    0
5    0    148   10961.676   10961.679   -0.003   73.7  26     0.3    0
6    0    149   10965.471   10965.477   -0.006   73.3  26.3   0.4    0
7    0    150   10969.302   10969.306   -0.003   72.7  26.8   0.5    0
8    0    151   10973.163   10973.169   -0.006   71.8  27.5   0.7    0
9    0    125   10607.937   10607.936    0.001   50    50     0      0
```

Listing 1 - Extract of TableI.txt, N is the line number, i refers to the isotope and J is the rotational quantum number. Del is the difference between their simulation and experimental energies[4].

The isotope of interest is $^{87}\text{Rb}^{133}\text{Cs}$. Subsequently, it is imperative to implement a preliminary filtration process on the designated file, with the condition of `i=1`. In consideration of the symmetry of the the $A^1\Sigma$ state, a comparison is to be made exclusively with those states that exhibit $(-1)^J$ parity. Conversely, states with the opposite parity will not be mixed and will be 100% $b^3\Pi_0$ states.

Following the computation of rovibrational states with DUO, for J ranging from 0 to 10 and from 70 to 80, a comparison can be made by searching for the state with the correct parity and J value that has the closest energy to E_{exp} from Table I. Subsequently, all the pertinent information can be written in file (cf. Listing 4). In order to facilitate the analysis, it is first possible to retrieve all the state information from the `.out` file, and then write them in a separate file (cf. Listing 2). The same process can be repeated for the mixing coefficient (cf Listing 3). The process of opening large files can be time-consuming; therefore, it is advisable to undertake the preliminary step of formatting the file in order to reduce the time taken.

The resultant extract of the formatted file, which was produced by the analysis code, can be found in Listing 2, Listing 3 and Listing 4. Figure 4 provides a comprehensive overview of the differences between the Table I[4] and the calculations from DUO. The magnitude of the energy difference is consistently less than 1 ~ cm^{-1}, and in the majority of cases, it is less than 0.1 ~ cm^{-1}. The points that exhibit the optimal match in terms of mixing coefficients are those that demonstrate the closest proximity in energy to the experimental values. The figure is indicative of a trend, with the points exhibiting the highest differences in mixing coefficients being those with the highest vibrational quantum number *v* and the highest energy difference with the litterature.

```
1   J       i(#)         E state  v lambda spin  sigma  omega parity
2   0.0      1     8724.9614   2   0   1   1.0   -1.0   0.0 +
3   0.0      2     8774.8061   2   1   1   1.0   -1.0   0.0 +
4   0.0      3     8824.5188   2   2   1   1.0   -1.0   0.0 +
5   0.0      4     8874.0994   2   3   1   1.0   -1.0   0.0 +
```

Listing 2 - Example of formatted `.out` file

```
1   # Root  J Par SumCoeffSq(St=1) SumCoeffSq(St=2)
2       1  0.0 0   0.00489879      0.99510121
3       2  0.0 0   0.00518921      0.99481079
4       3  0.0 0   0.00551109      0.99448891
5       4  0.0 0   0.00586926      0.99413074
6       5  0.0 0   0.00000000      0.00000000
7       6  0.0 0   0.00626953      0.99373047
```

Listing 3 - Example of formatted `.chk` file

```
1     I p  J   v      Eexpt         Eduo    diff A_duo b0_duo A_paper b0_paper
2    ---- - --- ------------ ------------ ------- ------ ------ ------- --------
3    114 -  71  12   10477.0490   10476.8858  -0.16  60.18  39.82  65.60   34.30
4    114 +  72  11   10478.9660   10478.8331  -0.13  62.71  37.29  67.00   32.90
5    114 -  73  11   10480.9040   10480.7928  -0.11  64.85  35.15  68.30   31.60
6    114 +  74  11   10482.8620   10482.7666  -0.10  66.66  33.34  69.30   30.60
7    114 -  75  11   10484.8390   10484.7562  -0.08  68.15  31.85  70.30   29.60
8    114 +  76  11   10486.8340   10486.7630  -0.07  69.38  30.62  71.10   28.80
9    114 -  77  11   10488.8510   10488.7885  -0.06  70.39  29.61  71.70   28.20
10   105 -  71   7   10374.3460   10374.3173  -0.03  70.94  29.06  71.30   28.70
11   105 +  72   7   10376.2450   10376.2158  -0.03  71.37  28.63  71.70   28.30
12   105 -  73   7   10378.1660   10378.1377  -0.03  71.76  28.24  72.00   28.00
13   105 +  74   7   10380.1080   10380.0832  -0.02  72.10  27.90  72.30   27.60
```

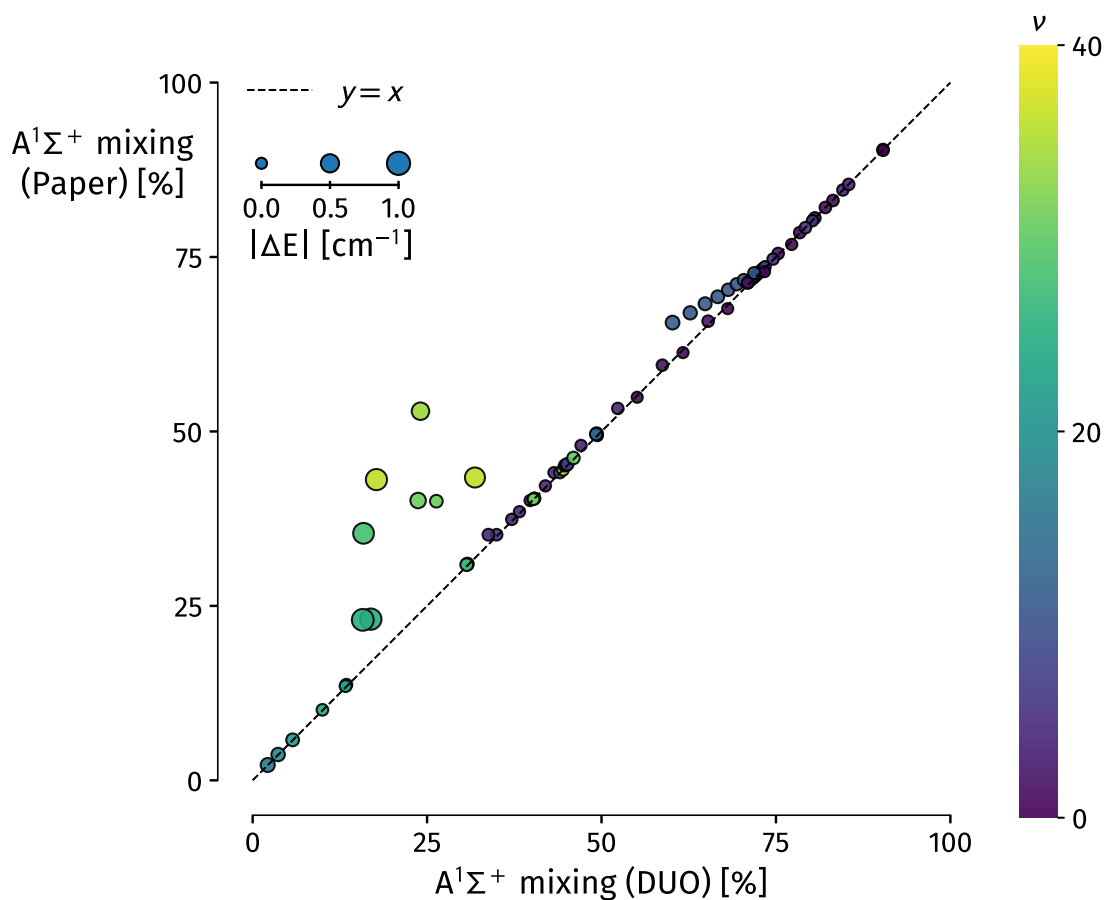Listing 4 - Example of computed difference output file

Figure 4 - Comparison between the $A^1\Sigma^+$ mixing coefficient given in Table I[4] and the ones computed with DUO. The size of the circle are related to the absolute difference in cm^{-1} between the experimental energy of Table I and the computed energy in DUO. The color is related to the vibrational quantum number of each computed state.

8 | Transitions

8.1 Absorption and emissions

This section will concentrate on computing transitions from the state $\left|X^1\Sigma^+, v'' = 0, J = 1\right\rangle$ to some excited states $\left|A^1\Sigma^+ - b^3\Pi_0, v', J' = 0\right\rangle$. The same method can be used to compute other transitions. The simulations were conducted with the three states and the spin-orbit coupling. For each potential energy curve, the number of vibrational basis functions was 300. The grid was delineated from a minimum radius of 2.5 angstroms to a maximum radius of 15 angstroms and a total of 800 grid points. From the initial state, one of the most probable transition absorption is to the state $\left|A^1\Sigma^+ - b^3\Pi_0, v' = 20, J' = 0\right\rangle$, with a transition energy of 10692.5409 cm^{-1} (Top part of Figure 5). This excited state will mainly decay to the ground state ($J = 1$), see the bottom part of the Figure 5.

8.2 Lifetimes

Figure 6 shows the lifetime of some excited eigenstates of the $A^1\Sigma^+ - b^3\Pi_0$ complex. This quantity is computed with 800 grid points and 400 basis functions for each potential energy curve. The lifetime is the sum of the decay Einstein coefficients, where f is a $X^1\Sigma^+$ rovibrational state:

$$\gamma_i = \sum_f A_{i,f} \tag{7}$$

The figure shows some difference with the direct imaging paper figure[2] (Figure 9). I tried to increase the number of grid points and the number functions in the vibrational basis but nothing changed. A first hypothesis was about the accuracy of the dipole moments/PEC but in fact it should not be caused by that since:
- They are the same that claimed by the paper
- The differential linewidth plot is very similar and is calculated from the wavefunctions and the transition dipole moment

The main differences are the states with "low" value of γ (around 2 MHz): they have an higher lifetime than in the direct imaging paper and also at high energy, the trend is not the same as in the paper.
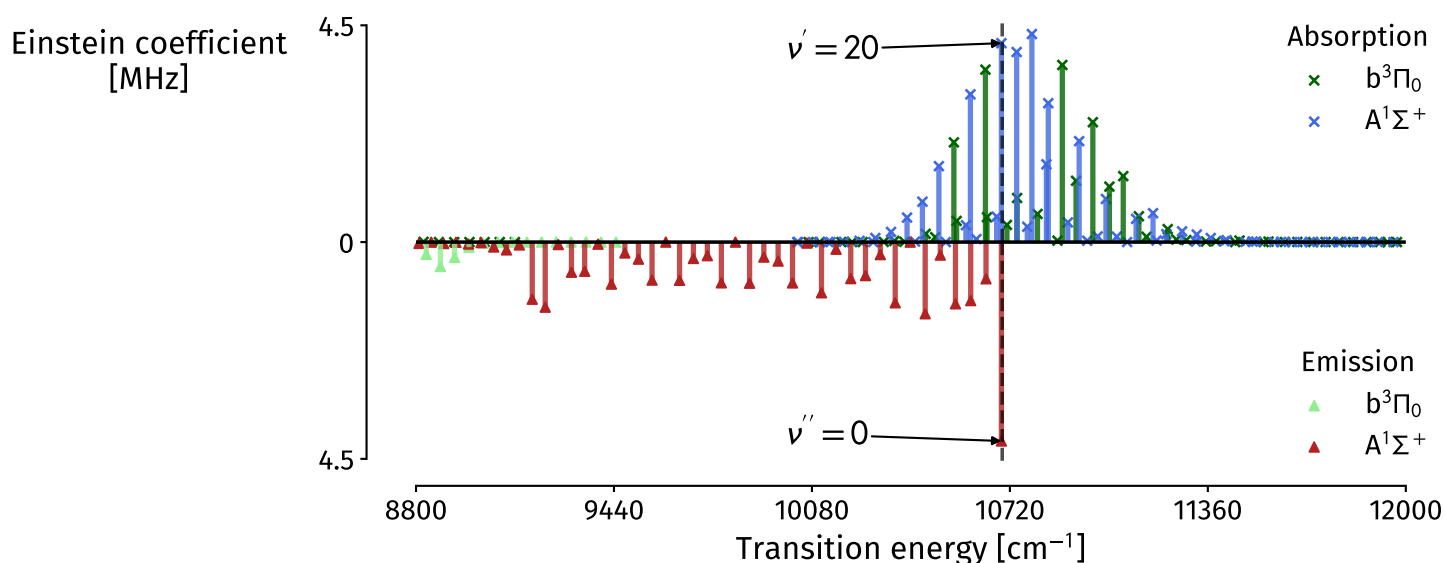
Figure 5 - Einstein coefficients in MHz over the transition energy in cm^{-1}. The top of the plot is related to the emission spectra from the ground state to the excited complex. The bottom of the plot is related to the emission from the excited $v' = 20, J = 0$ state to the electronic ground state. The states labels ($A^1\Sigma^+$ and $b^3\Pi_0$) are the output from DUO and related to the highest coefficient in the expansion (Equation 6).
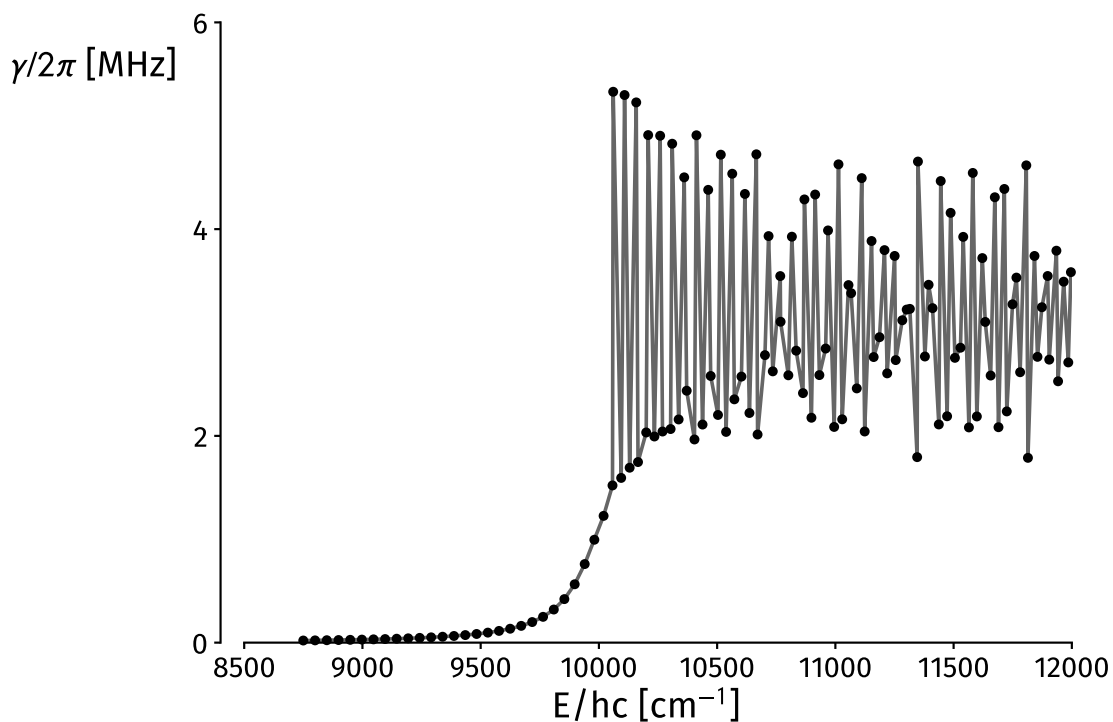

Figure 6 - Lifetime γ of eigenstates of the $J' = 0$ $A^1\Sigma^+$ – $b^3\Pi_0$ complex of RbCs molecule. The reference in energy is the minimum of potential of the $X^1\Sigma$ + potential energy curve.

9 | Differential transition width Γ

The objective of this section is to compute the differential transition width Γ, defined in the direct imaging paper[2] with DUO software. With the particular choice of target excited states, Γ can be computed with , where $\hbar\omega_{\text{t-im}} = E_t - E_{\text{im}}$ where E_{im} is the eigenenergy of the imaging state. $\mu_{n'}$ is a vibrational matrix element that we will need to compute.

$$\Gamma = \frac{4}{3}\frac{1}{4\pi\varepsilon_0\hbar c^3}\left(\frac{\left|c_0\right|^2}{3} - \frac{\left|c_1\right|^2}{6}\right)w_{\text{t-im}}^3\left|\mu_{n'}\right|^2 \tag{8}$$

Because our target vibrational states are coupled between $A^1\Sigma^+$ and $b^3\Pi_0$ states, then the wavefunction is given by Equation 9[2] where the index n' labels eigenstates by order of their eigenenergies. DUO calculations can give access to the $f_{A,n'}(R)$ and $f_{b,n'}(R)$, using Equation 6.

$$\left|\Psi_{t,n'}\right\rangle = \frac{1}{\sqrt{4\pi}}\left(f_{A,n'}(R)\left|A^1\Sigma^+\right\rangle + f_{b,n'}(R)\left|b^3\Pi_0\right\rangle\right) \times \left|i_{\text{Rb}}m'_{\text{Rb}}\right\rangle\left|i_{\text{Cs}}\,m'_{\text{Cs}}\right\rangle \tag{9}$$

With this notations, the vibrational matrix element $\mu_{n'}$ can be defined[2]:

$$\mu_{n'} = \int_0^\infty f_{A,n'}(R)d_{A\leftarrow X}(R)\varphi_{\text{perp}(R)}R^2\,dR \tag{10}$$

Where φ_{perp} is a state definde in the direct imaging paper as the initial state for the perpendicular dispersive imaging. It is defined as the energetically lowest $J = 1$ hyperfine state. In first approximation, that φ_{perp} wavefunction will be the same as the $v = 0, J = 1$ state of the electronic ground state. As hyperfine interactions are very weak compared to the other interactions here, the effect on the wavefunction can be neglected.

9.1 Computing the wavefunctions

Using the `checkpoint` keyword, the basis functions and the expansion coefficients can be written in a file. Because each coefficient is associated with a basis function of a specific electronic state, it is possible to compute only the wavefunction associated to the $A^1\Sigma^+$ state for instance.

In DUO, the wavefunctions are normalized on a grid, with r_i the points on the grid and Δr the grid step:

$$\sum_i \left|\psi(r_i)\right|^2 = \Delta r \tag{11}$$

In the direct imaging paper, it looks like (not directly mentionned) that the wavefunctions are normalized such that

$$\int_0^\infty |\psi(R)|^2 R^2\,dR = 1 \tag{12}$$

A first analysis can be to compute and write the wavefunctions (separated between the two coupled electronic states) in a separated file. Then, the wavefunctions can be plotted. Figure 7 shows the contributions of each excited electronic state to the global wavefunction. The quantity plot is the $f_{A,n'}$ and $f_{b,n'}$ defined in Equation 9. The right pannel shows the wavefunction of the electronic ground state ($v = 0, J = 1$). Here, the wavefunctions are devided by $\sqrt{\Delta r}$ to account for normalization factor from the vibrational basis functions. One can also plot the basis wavefunctions and verify the normalization condition in DUO.
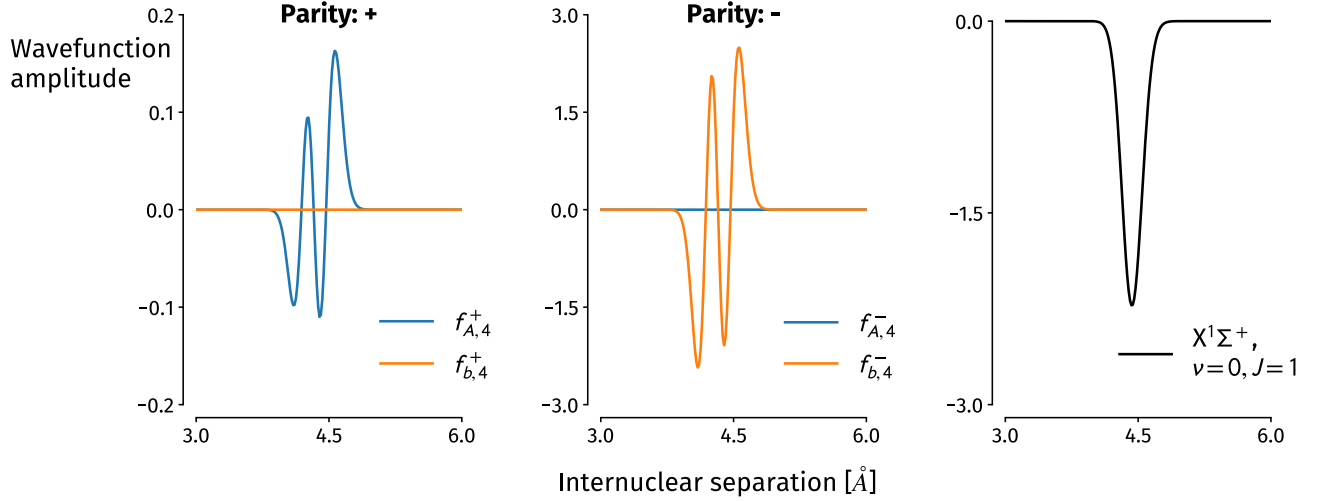
Figure 7 - Wavefunction amplitude for $v = 4, J = 0$ states of the excited complex, for both parities. The right pannel shows the wavefunction of the vibronic ground state for $J = 1$, which will be used for $\left| \varphi_{\text{perp}} \right\rangle$.

9.2 Integral computation

In order to compute $\mu_{n'}$, an integral has to be computed. In this analysis, the trapezoid rule (Equation 13) has been used. With 900 grid points, it should be accurate enough but other more precise methods (as the Simpson method) can also be used.

The trapezoid method equation involved multiplying by the grid step Δr. One can either devide the wavefunctions computed by DUO with $\sqrt{\Delta r}$ or devide the computed integral by Δr at the end. This is equivalent.

$$\int_{r_{\min}}^{r_{\max}} f(R) \, dR \simeq \sum_{i=1}^{N} \frac{f(r_{i+1}) - f(r_i)}{2 \times \Delta r_i} \tag{13}$$

However, between the direct imaging papier[2] and DUO computation, the wavefunctions are not normalized the same way. To account for this difference, we integrand (Equation 10) has to be devided by R^2. So the correct matrix element to compute is:

$$\mu_{n'}^{\text{DUO}} = \frac{1}{\Delta r} \int_{0}^{\infty} f_{A,n'}(R) d_{A \leftarrow X}(R) \varphi_{\text{perp}(R)} \, dR \tag{14}$$

The integrals has been computed for 100 eigenstates of the excited complex with $J = 0$ and then written in a file. At each step a new file is written, this allows faster analysis

and checkup of the code. Γ can be computed with these integrals, the result is shown in Figure 8. The highest value is 202 kHz, which is very close to the 201 kHz of the litterature[2].
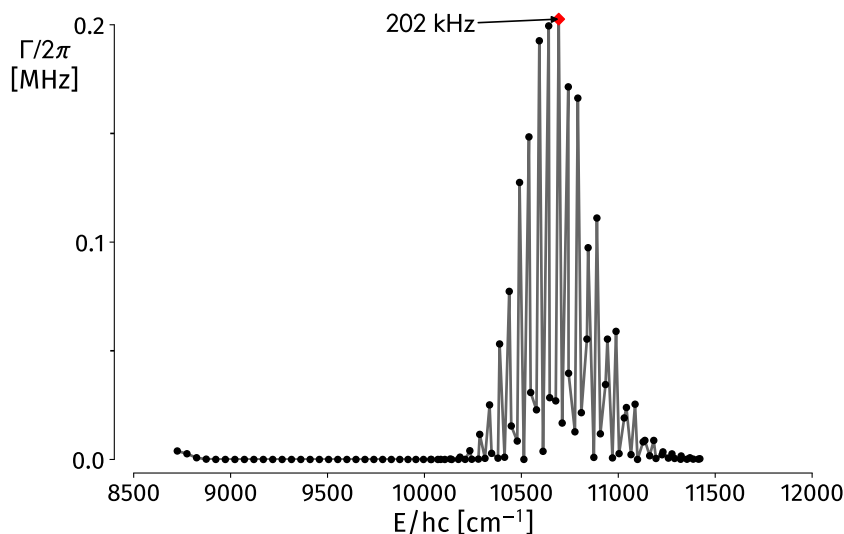

Figure 8 - Differential transition linewidth of eigenstates of the $J' = 0$ $A^1\Sigma^+ - b^3\Pi_0$ complex of $^{87}Rb^{133}Cs$ molecule.

The figure 8 from the direct imaging paper[2] can then be "reproduced", as shown in fig Figure 9. A similar graphical chart as in the paper has been used for better comparison between both figures. The value of the relevant $\frac{\gamma}{\Gamma}$ points are 12 and 19 in the article. The results of DUO simulations gives 9 and 20, which is still close. The issue the probably in the lifetime computation, since it is the plot with the most differences.
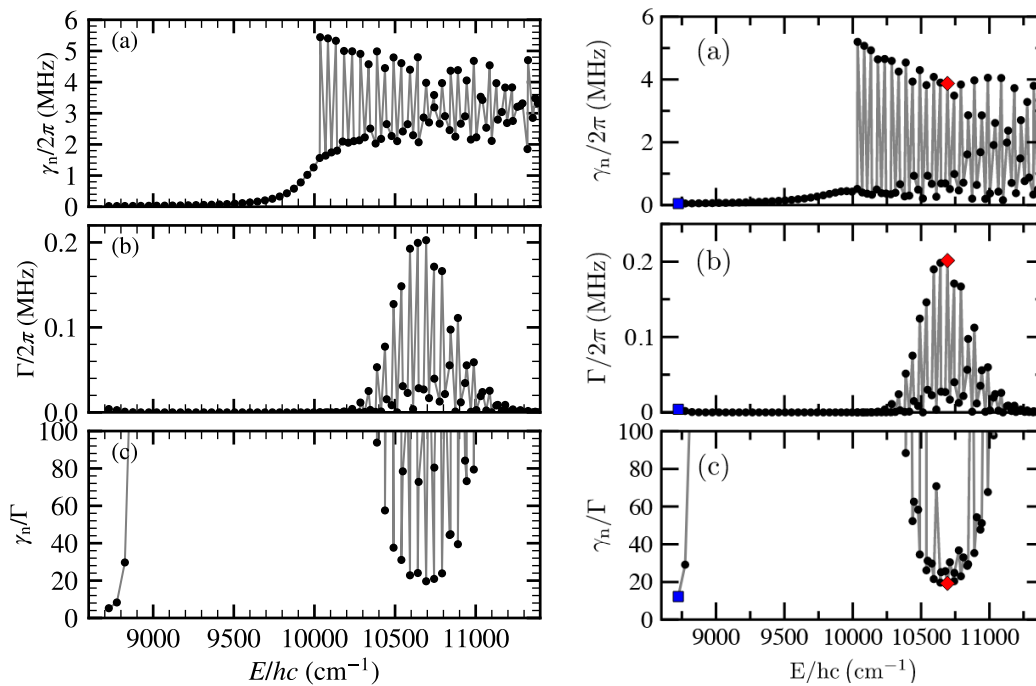
Figure 9 - Lifetime (top panel), transition linewidth (middle panel) and ratio of both (bottom panel) of eigenstates of the $J' = 0$ $A^1\Sigma^+ - b^3\Pi_0$ complex of RbCs molecule. Left pannel: DUO simulations. Right pannel: direct imaging paper[2]

10 | Results on NaRb

Using the exact same methods and protocoles and using the PEC, dipole moment and spin-orbit coupling mentionned in the direct imaging paper[2], the following figures are showing the lifetime, differential transition width and the ratios as before but for the NaRb molecule. We can see that as for RbCs molecule, the differential transition width is in very good agreement with the paper. However, the lifetime is of the good order of magnitude but not accurate enough to have the right ratios.
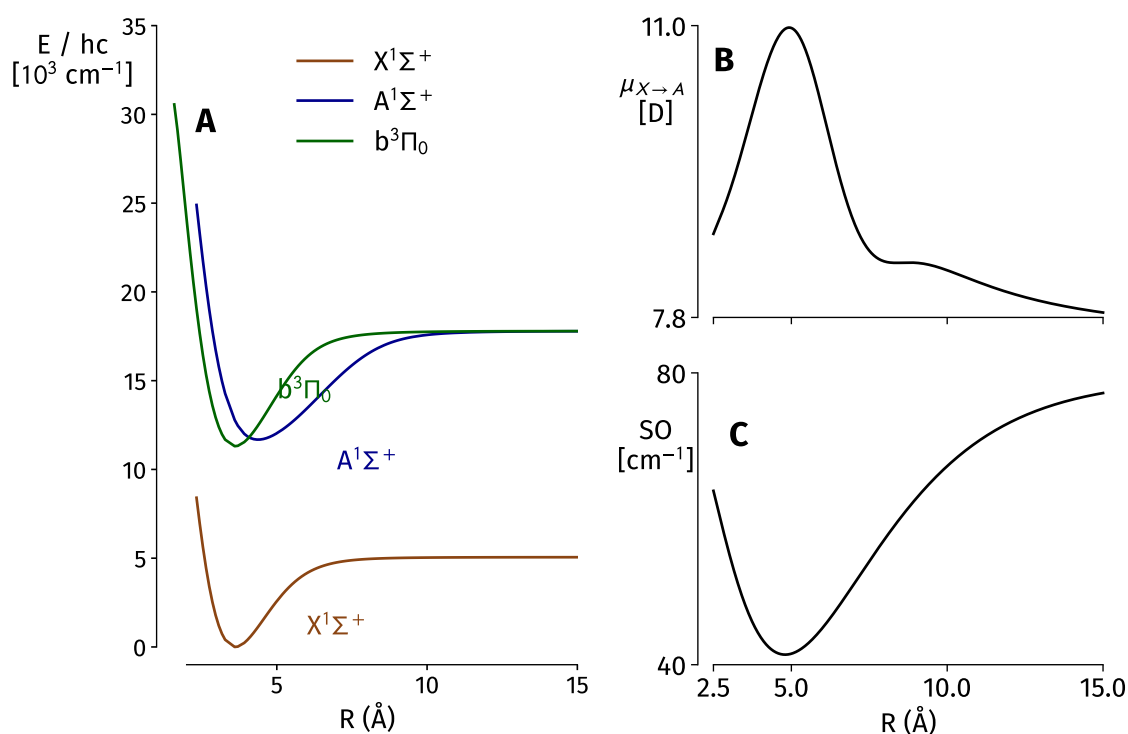

Figure 10 - **A**: Potential energy curves of the relevant electronic states of NaRb molecule. **B** Transition dipole moment between $X^1\Sigma^+$ and $A^1\Sigma^+$ states. **C**: Spin-orbit coupling between $A^1\Sigma^+$ and $b^3\Pi^0$ states.
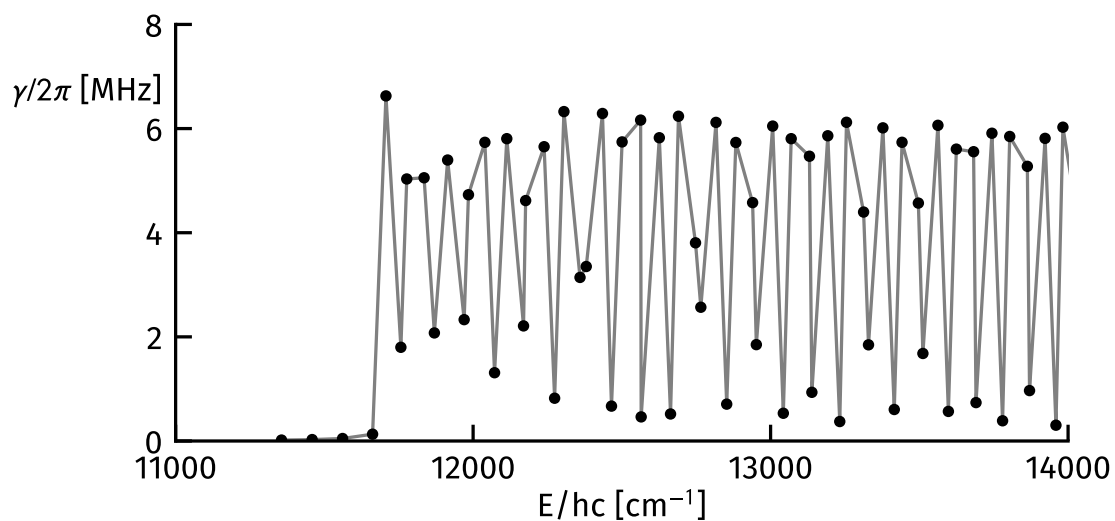
Figure 11 - Lifetime γ of eigenstates of the $J' = 0$ $A^1\Sigma^+ - b^3\Pi_0$ complex of NaRb molecule. The reference in energy is the minimum of potential of the $X^1\Sigma$ + potential energy curve.
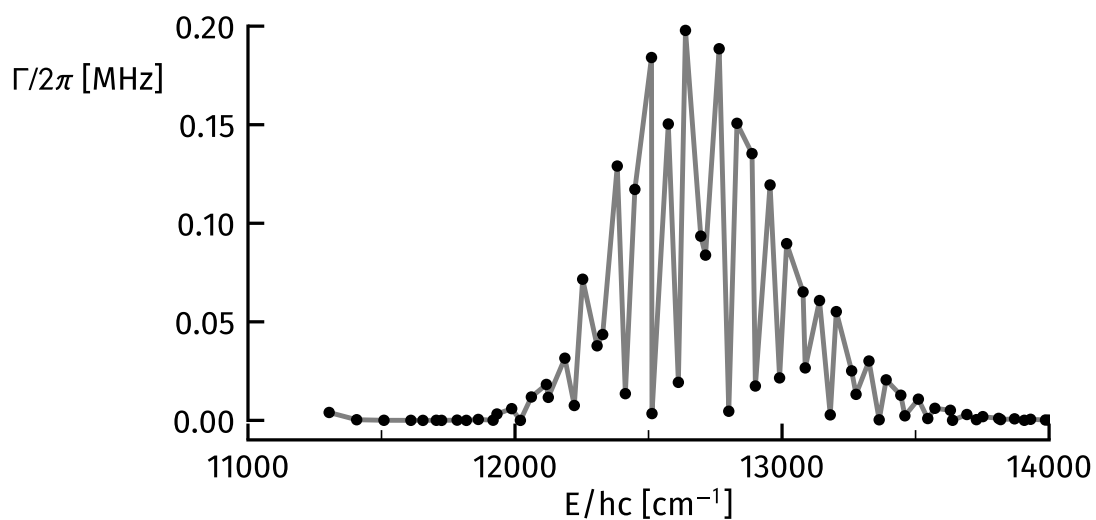

Figure 12 - Differential transition linewidth of eigenstates of the $J' = 0$ $A^1\Sigma^+ - b^3\Pi^0$ complex of NaRb molecule
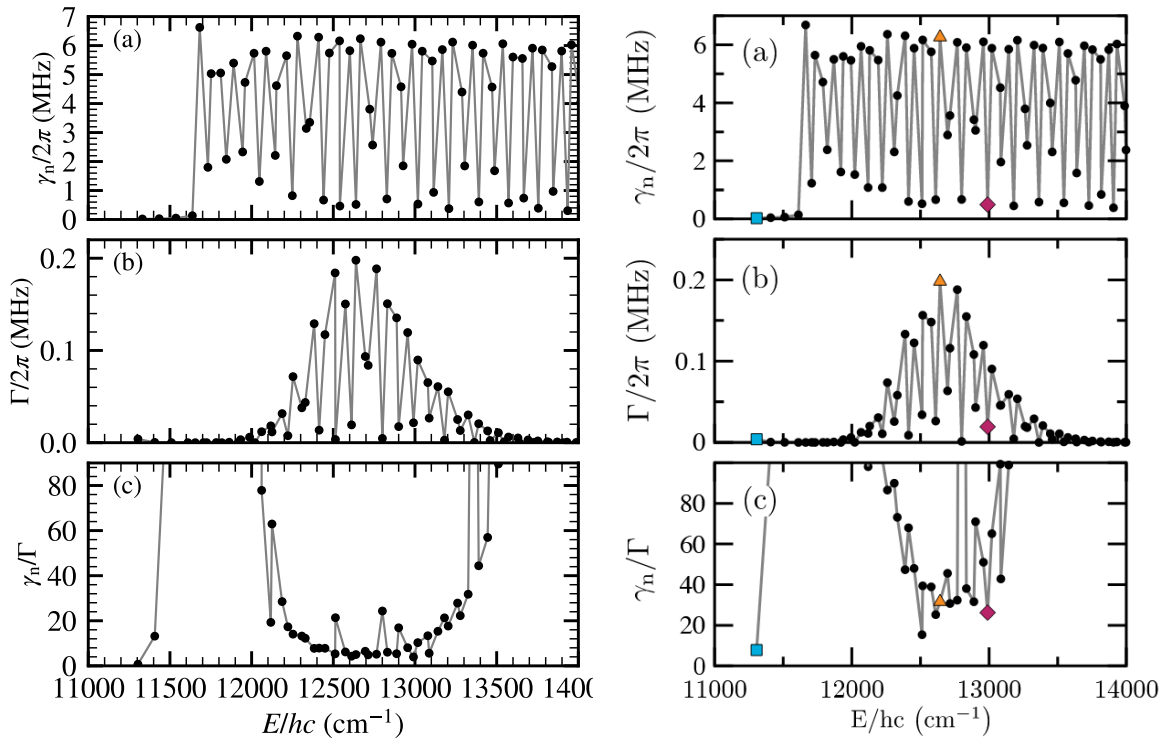
Figure 13 - Lifetime (top panel), transition linewidth (middle panel) and ratio of both (bottom panel) of eigenstates of the $J' = 0$ $A^1\Sigma^+$ – $b^3\Pi_0$ complex of NaRb molecule. Left pannel: DUO simulations. Right pannel: direct imaging paper[2]

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