MOMAP

Tutorial 01 with g09

Fluorescence Spectrum Calculation

MOMAP

Molecular Material Property Prediction Package

Version 2019

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MOMAP Tutorial 01 with g09

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MOMAP Tutorial

- Fluorescence Spectrum Calculation

Azulene is an organic compound and an isomer of naphthalene. Whereas naphthalene is colorless, azulene is dark blue. Two terpenoids, vetivazulene (4,8-dimethyl-2-isopropylazulene) and guaiazulene (1,4-dimethyl-7-isopropylazulene), that feature the azulene skeleton are found in nature as constituents of pigments in mushrooms, guaiac wood oil, and some marine invertebrates.

MOMAP is able to simulate fluorescence spectrum and calculate the corresponding radiative decay rate constant based on the TVCORF_SPEC and TVSPEC_SPEC subprograms. The TVCORF_SPEC subprogram is used to calculate thermal vibration correlation function (TVCF), while the TVSPEC_SPEC subprogram is used to simulate fluorescence spectrum.

To begin the TVCORF_SPEC and TVSPEC_SPEC calculations, we need the evc results. The evc calculation can use outputs from other QC programs, such as Gaussian, TURBOMOLE, ChemShell, Dalton, MOLPRO, DFTB and MOPAC *etc*. It can also read data from the output files, including vibrational frequencies and force constant matrix, and calculate normal mode displacement, Huang-Rhys factor, reorganization energy and Duschinsky rotation matrix between initial and final electronic states under both internal coordinate and Cartesian coordinate.

Thus, the basic steps involved in the calculations are as follows:

1. Gaussian calculations
2. Vibration analysis *etc*.
3. Fluorescence spectrum calculation

Contents

Gaussian Calculations

Optimization calculation on ground state (S_0)

Once the initial geometry is obtained, we have to find the optimized S_0 geometry. The route section is set as **`#p opt b3lyp/6-31g*`**, which indicates an optimization calculation at `B3LYP/6-31G*` level.

The initial geometry gaussian S_0 input file (`azulene-s0.com`) is as follows:

```
%chk=azulene-s0.chk
%mem=4GB
%nprocl=1
%nprocs=8
#p opt freq B3LYP/6-31G*

azulene-s0 optimization

0 1
 C                 2.01378743   -1.48849852    0.00000000
 C                 2.28995141   -0.11795315    0.00000000
 C                 1.39185815    0.95357383    0.00000000
 C                 0.78413689   -2.15418449    0.00000000
 C                 0.00000000    0.93285810    0.00000000
 C                -0.50398383   -1.61065958    0.00000000
 C                -0.89316505   -0.27406276    0.00000000
 H                 2.88919252   -2.13621797    0.00000000
 H                 3.34387207    0.15083266    0.00000000
 H                 1.84191311    1.94635990    0.00000000
 H                 0.83658347   -3.24058384    0.00000000
 H                -1.32037398   -2.33298523    0.00000000
 C                -0.84567310    2.05536637    0.00000000
 H                -0.51364908    3.08694089    0.00000000
 C                -2.17758707    1.61062710    0.00000000
 H                -3.04994479    2.25593917    0.00000000
 C                -2.21339978    0.20656494    0.00000000
 H                -3.10314368   -0.41207657    0.00000000
```

We use g09 to do the geometry optimization.

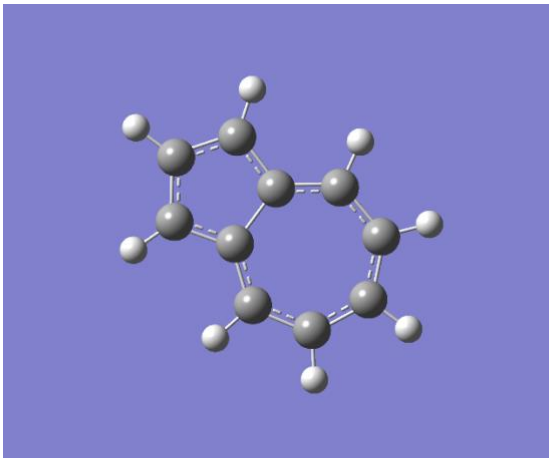


Fig. 1 Optimized S_0 geometry

Optimization calculation on lowest singlet excited state (S_1)

With the optimized S_0 geometry at hand, we can start optimizing S_1 geometry using the optimized S_0 geometry as the initial structure. The route section is set as `#p td opt b3lyp/6-31g*`, which indicates an optimization calculation at `B3LYP/6-31G*` level using the TDDFT method.

The initial gaussian S_1 input file (`azulene-s1.com`) is as follows:

```
%chk=azulene-s1.chk
%mem=4GB
%nprocl=1
%nprocs=8
#p opt freq td B3LYP/6-31G*

azulene-s1 optimization

0 1
 C                2.01378700   -1.48849900    0.00000000
 C                2.28995100   -0.11795300    0.00000000
 C                1.39185800    0.95357400    0.00000000
 C                0.78413700   -2.15418400    0.00000000
 C                0.00000000    0.93285800    0.00000000
 C               -0.50398400   -1.61066000    0.00000000
 C               -0.89316500   -0.27406300    0.00000000
 H                2.88919300   -2.13621800    0.00000000
 H                3.34387200    0.15083300    0.00000000
 H                1.84191300    1.94636000    0.00000000
 H                0.83658300   -3.24058400    0.00000000
 H               -1.32037400   -2.33298500    0.00000000
 C               -0.84567300    2.05536600    0.00000000
 H               -0.51364900    3.08694100    0.00000000
 C               -2.17758700    1.61062700    0.00000000
 H               -3.04994500    2.25593900    0.00000000
 C               -2.21340000    0.20656500    0.00000000
 H               -3.10314400   -0.41207700    0.00000000
```

Again, use g09 to do the S_1 optimization. Note that the initial geometry should be the optimized the S_0 geometry.

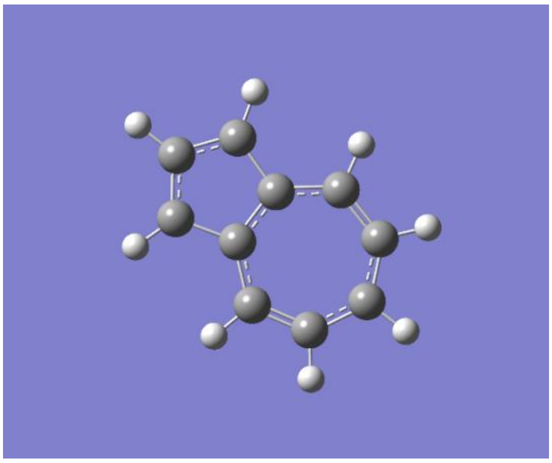


Fig. 2 Optimized S_1 geometry

TIPS: To obtain the optimized ground state geometry, use **Gaussview** to open `azulen-s0.log` file, and save as `azulene-s1.com`. Then, modify the first few lines of `azulene-s1.com` to suit for S1 optimization.

Calculate non-adiabatic coupling matrix element (NACME)

Unlike rad_FL calculation, The NACME should be obtained before performing a nonrad calculation.

After finding the optimized S_1 geometry, we can calculate NACME at this geometry.
The route section is set as the following line:

```
#p td b3lyp/6-31g(d) prop=(fitcharge,field) iop(6/22=-4, 6/29=1, 6/30=0, 6/17=2)
```

The initial gaussian nacme input file (`azulene-nacme.com`) is as follows:

```
%chk=azulene-nacme.chk
%mem=4GB
%nprocl=1
%nprocs=8
#p td B3LYP/6-31G* prop=(fitcharge,field) iop(6/22=-4,6/29=1,6/30=0,6/17=2) nosymm

azulene excited state nacme calculation

0 1
 C                2.00781300   -1.54567700    0.00000000
 C                2.29335100   -0.16097300    0.00000000
 C                1.43666200    0.92263700    0.00000000
 C                0.74217000   -2.17592100    0.00000000
 C                0.00000000    0.87899800    0.00000000
 C               -0.52457900   -1.62505800    0.00000000
 C               -0.85006100   -0.22497100    0.00000000
 H                2.86853900   -2.20838800    0.00000000
 H                3.35493800    0.08558900    0.00000000
 H                1.88767400    1.91181300    0.00000000
 H                0.77544500   -3.26524800    0.00000000
 H               -1.36541000   -2.31420500    0.00000000
 C               -0.84651000    2.06953900    0.00000000
 H               -0.46545900    3.08512900    0.00000000
 C               -2.19214700    1.68790200    0.00000000
 H               -3.04949000    2.34818800    0.00000000
 C               -2.21739500    0.28941600    0.00000000
 H               -3.10206800   -0.33823600    0.00000000
```

Again, use g09 to do the NACME calculation.

Now, all the Gaussian related calculations are done.

In the following calculations, we need the gaussian *.fchk files, we use the Gaussian built-in command **`formchk`** to generate the *.fchk file based on output *.chk. The *.fchk file contains readable force constant matrix information that is needed in dushin calculation.

```
$ formchk azulene-s0.chk
$ formchk azulene-s1.chk
$ formchk azulene-nacme.chk
```

TIPS: To obtain the optimized excited state geometry for NACME calculation, use **Gaussview** to open `azulen-s1.log` file, and save as `azulene-nacme.com`. Then, modify the first few lines of `azulene-nacme.com` to suit for NACME calculation.

Vibration Analysis

The evc calculation requires the basic information on initial and final electronic states. Thus, to begin an evc calculation, you need to designate the related file names in MOMAP input file (i.e., momap.inp).

For the Gaussian output files, you have to provide the corresponding .fchk files as well, as done in the last section.

The momap.inp for evc calculation is straightforward and is shown as follows:

```
[evc]$ cat momap.inp
do_evc     = 1                       # toggle dushin rotation effect, 1 or 0

&evc
  ffreq(1)  = "azulene-s0.log"       # log file of ground state
  ffreq(2)  = "azulene-s1.log"       # log file of excited state
/
```

TIPS: In each directory, there exists a README file, just follow the instructions in README to carry out the operations. For example, the README in evc is shown as follows:

```
                      How to run MOMAP

1) Copy the following gaussian files from upper directory:

  ../gaussian/azulene-s0.fchk
  ../gaussian/azulene-s0.log
  ../gaussian/azulene-s1.fchk
  ../gaussian/azulene-s1.log

  to this directory.

2) Change momap.inp accordingly.

3) Run MOMAP to do the calculation by the following command:
   ./run
```

Copy the following gaussian output files from upper directory:

```
../gaussian/azulene-s0.fchk
../gaussian/azulene-s0.log
../gaussian/azulene-s1.fchk
../gaussian/azulene-s1.log
```

to this evc work directory.

A run file is also created, and is shown as follows:

```
#!/bin/sh

momap -input momap.inp -np 4
```

Users may modify the `run` file, for example, by changing the `-n` option from 4 to 8, and perform the calculation by running the script file:

```
$ ./run
```

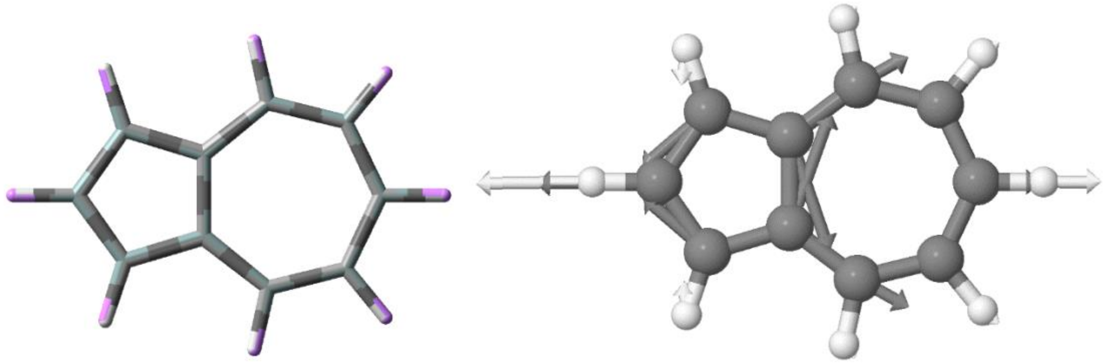
The result files are as follows:

```
[evc]$ ls
azulene-nacme.log   azulene-s1.log  evc.dint.dat  evc.out       nodefile
azulene-s0.fchk     evc.cart.abs    evc.dx.v.xyz  evc.vib1.xyz  README
azulene-s0.log      evc.cart.dat    evc.dx.x.com  evc.vib2.xyz  ref
azulene-s1.fchk     evc.dint.abs    evc.dx.x.xyz  momap.inp     run
```

- **evc.cart.dat**: includes frequency, Huang－Rhys factor, and Duschinsky matrix (Cartesian coordinate system).
- **evc.dint.dat**: includes frequency, Huang－Rhys factor, and Duschinsky matrix (D solved by using internal coordinate system).
- **evc.cart.abs**: Duschinsky matrix file, used to plot 2D Duschinsky figure.
- **evc.cart.nac**: Projection of NACME to normal modes.
- **evc.cart.inp**: Projection of derivatives of transition dipoles to normal modes.
- **evc.dx.x.com**: Molecular overlapping figure of two electron states (viewed by using Gaussview)
- **evc.dx.x.xyz**: Molecular overlapping figure of two electron states (viewed by using Jmol)
- **evc.dx.v.xyz**: Molecular displacement vectors of two electron states (viewed by using Jmol)
- **evc.vib1.xyz**: Molecular vibrational vectors at ground state (viewed by using Jmol)
- **evc.vib2.xyz**: Molecular vibrational vectors at excited state (viewd by using Jmol)
- **evc.out**: evc log file

Except for `ffreq(1)` and `ffreq(2)` parameters, the `evc` program also allows user to project reorganization energy onto the internal coordinate, to take account of isotope effect, and to configure many other advanced settings *etc*., please refer to the **MOMAP User Guide** for details.

Please check the reorganization energy results between `evc.cart.dat` and `evc.dint.dat`. If the energy difference is small (< 1000 cm^{-1}), then use the results in `evc.cart.dat` to do the next calculations. However, if the energy difference is large, then use `evc.dint.dat` to do the next calculations.



evc.dx.x.com **evc.dx.v.xyz**

Electron vibration coupling

Adiabatic Excitation Energy

Before we can calculate the Fluorescence Spectrum, we need to known the adiabatic excitation energy E_{ad}. The adiabatic excitation energy is the energy difference between the relaxed excited state energy and the ground state energy.

From the S_0 Gaussian log file, locate the last line with "`SCF Done`" in the output `azulene-s0.log` file in order to find the single point energy at the optimized S_0 geometry.

For example, you may use the following commands:

```
$ cat azulene-s0.log | grep "SCF Done"
```

In this example, the last line with "`SCF Done`" is like the following:

```
SCF Done:  E(RB3LYP) =  - 385.838172128    A.U.
```

Thus, we have the energy E_{gs} at optimized ground state geometry:

E_{gs} = - 385.838172128 a.u.

From the S_1 Gaussian log file, locate the last line with "`Total Energy, E(TD-HF/TD-KS)`" in the output `azulene-s1.log` file in order to find the single point energy at the optimized S_1 geometry.

For example, you may use the following commands:

```
$ cat azulene-s1.log | grep "Total Energy, E(TD-HF/TD-KS)"
```

In this example, the last line with "`Total Energy, E(TD-HF/TD-KS)`" is like the following:

```
Total Energy, E(TD-HF/TD-KS) =  -385.763080213
```

Then, we have the single point energy E_{es} at the optimized S_1 geometry:

E_{es} = - 385.763080213 a.u.

From the above obtained ground state S_0 and excited state S_1 energies, we can obtain the adiabatic excitation energy E_{ad}:

$E_{ad} = E_{es} - E_{gs}$ = [(-385.763080213) - (-385.838172128)] a.u

= 0.075092 a.u

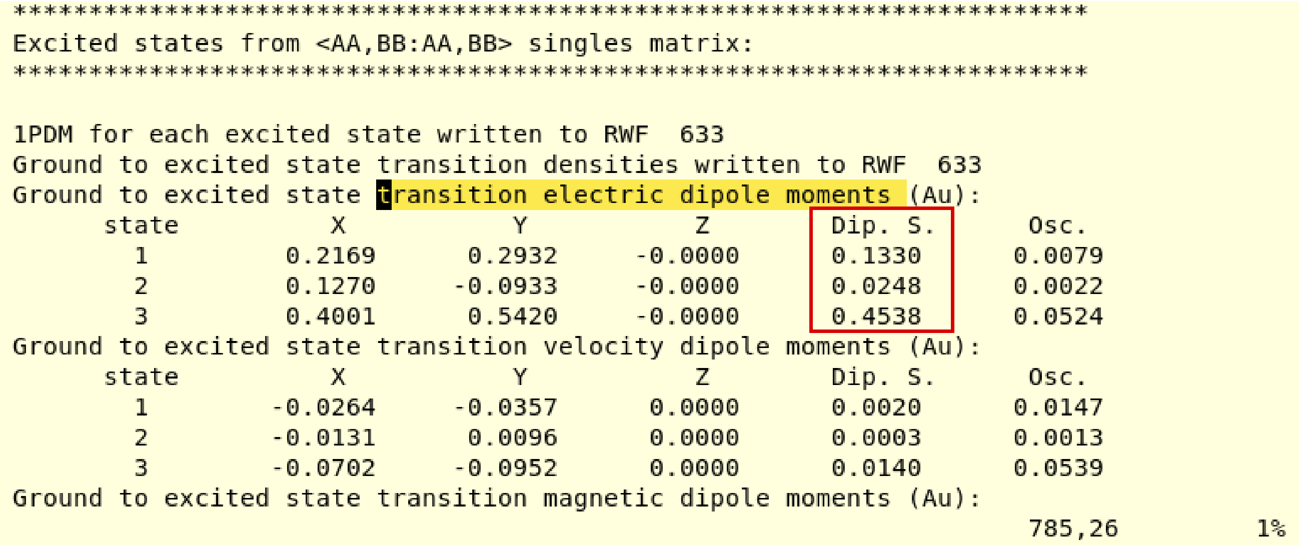
TIPS: To find the energies, users may use **Gaussview** to open the Gaussian log file, from the menu item **Results → Summary** to obtain the value, which is valid for both the ground state and excited state.

Electronic Transition Dipole

To calculate the spectrum by using the sum-over-states approach, we need the electronic transition dipole data.

The Gaussian log file for the optimized S1 excited state has already included the Dipole Square of Electronic Transition Dipole Absorption (EDMA) and the Dipole Square of Electronic Transition Dipole Emission (EDME) information.

Open `azulene-s1.log` file with `vim`, for example, search the string "`transition electric dipole moments`", the first match is shown as follows:



```
**********************************************************************
Excited states from <AA,BB:AA,BB> singles matrix:
**********************************************************************

1PDM for each excited state written to RWF  633
Ground to excited state transition densities written to RWF  633
Ground to excited state transition electric dipole moments (Au):
      state          X           Y           Z        Dip. S.      Osc.
        1         0.2169      0.2932     -0.0000      0.1330      0.0079
        2         0.1270     -0.0933     -0.0000      0.0248      0.0022
        3         0.4001      0.5420     -0.0000      0.4538      0.0524
Ground to excited state transition velocity dipole moments (Au):
      state          X           Y           Z        Dip. S.      Osc.
        1        -0.0264     -0.0357      0.0000      0.0020      0.0147
        2        -0.0131      0.0096      0.0000      0.0003      0.0013
        3        -0.0702     -0.0952      0.0000      0.0140      0.0539
Ground to excited state transition magnetic dipole moments (Au):
                                                                785,26          1%
```

Focus on the "`Dip. S.`" column, this is the Dipole Square of the calculated Electronic Transition Dipole Absorption (EDMA), take note the data of the first excited state, i.e., `0.1330`, this is the value of the expected EDMA. Thus, we have:

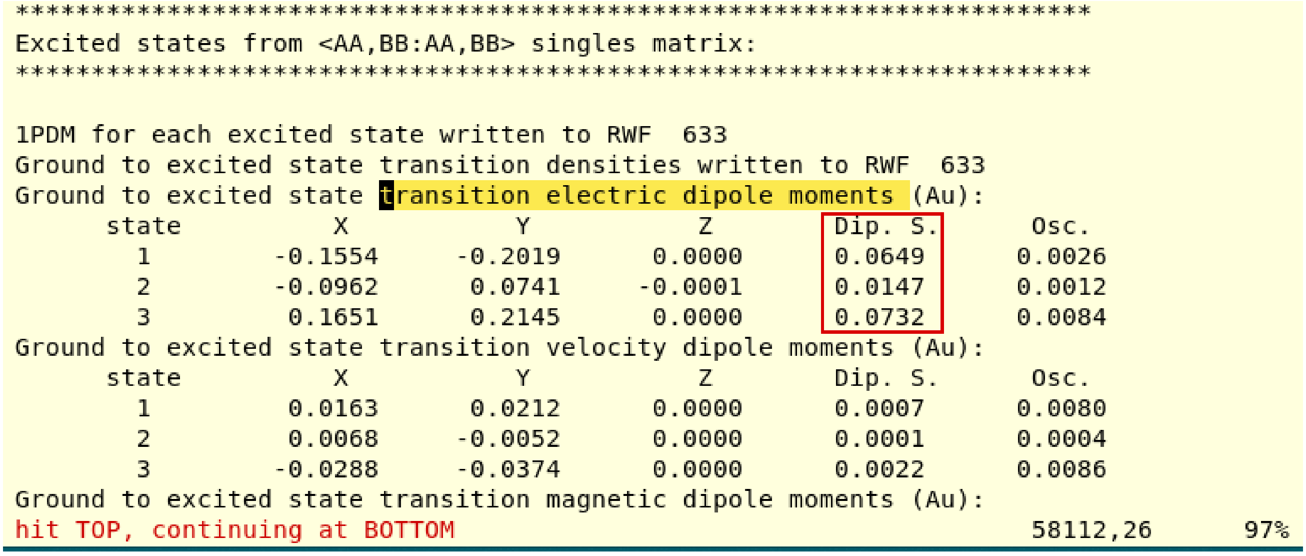
$$\mu_{\text{trans}} = \sqrt{\mu_{\text{trans}}^{2}} = \sqrt{0.1330}\ \text{a.u.} = 0.36469\ \text{a.u.}$$

$$= 0.36469\ \text{a.u.} \times 2.5417\ \text{Debye/a.u.}$$

$$= 0.92694\ \text{Debye}$$

This is the value of parameter `EDMA` needed in our momap.inp file.

If the Linux command `vim` is used, press `SHIFT + N`, the search jumps to the last occurrence of "`transition electric dipole moments`", shown as follows:



```
**********************************************************************
Excited states from <AA,BB:AA,BB> singles matrix:
**********************************************************************

1PDM for each excited state written to RWF  633
Ground to excited state transition densities written to RWF  633
Ground to excited state transition electric dipole moments (Au):
      state          X           Y           Z        Dip. S.      Osc.
        1         -0.1554     -0.2019      0.0000      0.0649      0.0026
        2         -0.0962      0.0741     -0.0001      0.0147      0.0012
        3          0.1651      0.2145      0.0000      0.0732      0.0084
Ground to excited state transition velocity dipole moments (Au):
      state          X           Y           Z        Dip. S.      Osc.
        1          0.0163      0.0212      0.0000      0.0007      0.0080
        2          0.0068     -0.0052      0.0000      0.0001      0.0004
        3         -0.0288     -0.0374      0.0000      0.0022      0.0086
Ground to excited state transition magnetic dipole moments (Au):
hit TOP, continuing at BOTTOM                                     58112,26       97%
```

Again, focus on the "`Dip.  S.`" column, this is the Dipole Square of the calculated Electronic Transition Dipole Emission (EDME), take note the data of the first excited state, i.e., `0.0649`, this is the value of the expected EDME. Thus, we have:

$$\mu_{\text{trans}} = \sqrt{\mu_{trans}^{2}} = \sqrt{0.0649}\ \text{a.u.} = 0.254755\ \text{a.u.}$$

$$= 0.254755\ \text{a.u.} \times 2.5417\ \text{Debye/a.u.}$$

$$= 0.64751\ \text{Debye}$$

Again, this is the value of parameter `EDME` needed in our momap.inp file.

TIPS: If the optimization and frequency calculations are separate, then the data of EDME and EDMA should be taken from the log file of excited state geometry optimization.

Fluorescence Spectrum Calculation

Nonradiative rate k_{ic}

Create a directory `kic` and go to that directory, in this directory, we further create two directories `evc` and `kic`.

To start the calculation, you need a `*.dat` file, a MOMAP control file, and optionally a parallel control file. The `*.dat` file is obtained from the previous mentioned `evc` calculation. A MOMAP control file is used to control how `TVCORF_SPEC` and `TVSPEC_SPEC` subprograms behavior. An optional parallel control file is used to control how many computing processes will be used.

To begin with, the first step is to do an `evc` calculation. Note we also need the non-adiabatic coupling matrix element (NACME) calculation log file, that is, `azulene-nacme.log`, to do the nonradiative rate calculation.

Go to the directory `evc`, copy the following gaussian files from upper directory:

```
../../gaussian/azulene-s0.fchk
../../gaussian/azulene-s0.log
../../gaussian/azulene-s1.fchk
../../gaussian/azulene-s1.log
../../gaussian/azulene-nacme.log
```

to this work directory.

Create a `momap.inp` file with its contents as follows:

```
[kic/evc] cat momap.inp
do_evc      = 1

&evc
  ffreq(1)   = "azulene-s0.log"      # log file of ground state
  ffreq(2)   = "azulene-s1.log"      # log file of excited state
  fnacme     = "azulene-nacme.log"   # log file of NACME
/
```

Also create a `run` file and change it with execution attribute (e.g., `chmod a+rx run`), the `run` file is very simple, and is shown as follows:

```
#!/bin/sh

momap -input momap.inp -np 4
```

Users may modify the `run` file, for example, by changing the `-n` option from 4 to 8, and perform the calculation by running the script file:

```
$ ./run
```

When the calculation finishes, the result files are as follows:

```
[kic/evc]$ ls
azulene-nacme.log  azulene-s1.log  evc.dint.abs  evc.dx.x.xyz   momap.inp  run
azulene-s0.fchk    evc.cart.abs    evc.dint.dat  evc.out        nodefile
azulene-s0.log     evc.cart.dat    evc.dx.v.xyz  evc.vib1.xyz   README
azulene-s1.fchk    evc.cart.nac    evc.dx.x.com  evc.vib2.xyz   ref
```

Please check the reorganization energy results between `evc.cart.dat` and `evc.dint.dat`. If the energy difference is small (< 1000 cm^{-1}), then use the results in `evc.cart.dat` to do the next calculations. However, if the energy difference is large, then use `evc.dint.dat` to do the next calculations.

For example, we can use the Linux command `cat` and `grep` to do the job:

```
$ cat  evc.cart.dat evc.dint.dat  | grep "Total reorganization energy"

Total reorganization energy     (cm-1):        3390.305348      3453.436666
Total reorganization energy     (cm-1):        3412.711425      3449.528917
```

As can be seen, the energy difference is indeed rather small.

Once the `evc` calculation is done, we then go to the `kic` directory.

Copy the following `evc` files from upper directory:

```
../evc/evc.cart.dat
../evc/evc.cart.nac
```

to this `kic` work directory.

Create a `momap.inp` with its contents as follows:

```
[kic/kic]$ cat momap.inp
do_ic_tvcf_ft   = 1                      # toggle internal conversion correlation function, 1 or 0
do_ic_tvcf_spec = 1                      # toggle internal conversion spectrum, 1 or 0

&ic_tvcf
  DUSHIN        = .t.                    # toggle Duschinsky rotation effect, .t. or .f.
  Temp          = 300 K                  # temperature
  tmax          = 1000 fs                # integral interval of correlation function
  dt            = 1   fs                 # integration timestep of correlation function
  Ead           = 0.075092 au            # adiabatic excitation energy difference between two states
  DSFile        = "evc.cart.dat"         # input dushin file
  CoulFile      = "evc.cart.nac"         # input nacme info file
  Emax          = 0.3 au                 # upper bound of spectrum frequency
  logFile       = "ic.tvcf.log"          # output file for logging
  FtFile        = "ic.tvcf.ft.dat"       # output file for correlation function info
  FoFile        = "ic.tvcf.fo.dat"       # output file for spectrum function info
/
```

Also create a `run` file and change it with execution attribute (e.g., `chmod a+rx run`), the `run` file is shown as follows:

```
#!/bin/sh

momap -input momap.inp -np 4  &> log &
```

Users may modify the `run` file, for example, by changing the `-n` option from 4 to 8, and perform the calculation by running the script file:

```
$ ./run
```

When the calculation finishes, the result files are shown as follows:

```
[kic/kic]$ ls
evc.cart.dat  ic.tvcf.fo.dat  ic.tvcf.log      momap.inp   README     run
evc.cart.nac  ic.tvcf.ft.dat  ic.tvcf.ft.gnu   log         nodefile   ref
```

The Internal conversion (IC) rate constant can be found at the end of `ic.tvcf.log` file. The relationship between IC rate constant and energy gap can be obtained from `ic.tvcf.fo.dat` file.

Filename	Meaning
ic.tvcf.fo.dat	Output file for spectrum function
ic.tvcf.ft.dat	Output file for correlation function
ic.tvcf.log	Output file for logging

Then use the following commands to generate the correlation function plot to check for convergence:

```
$ gnuplot *.gnu
$ ps2png *.eps
```

Or if your gnuplot has terminal `pngcairo`, then you can generate the png files in one step:

```
$ gnuplot *.gnu-png
$ display *.png
```

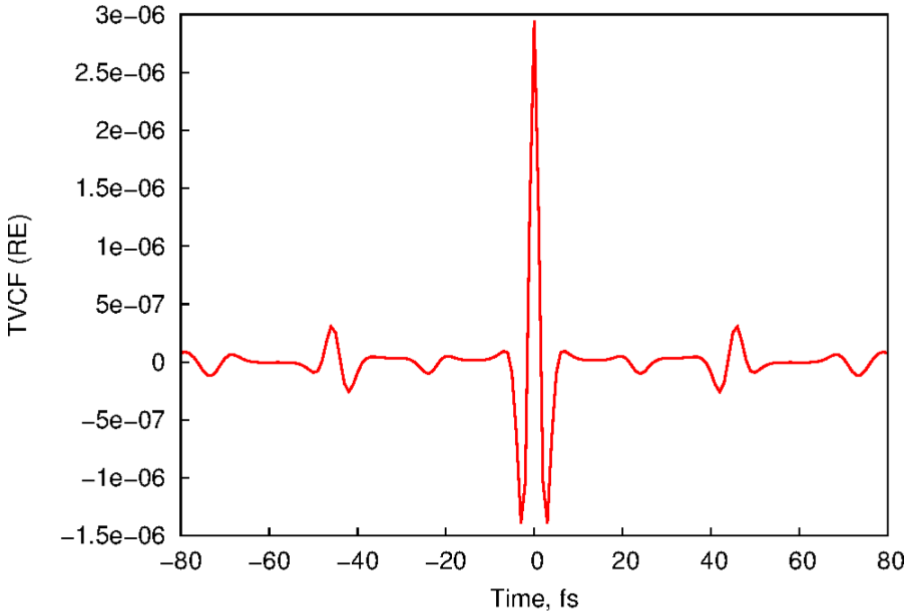
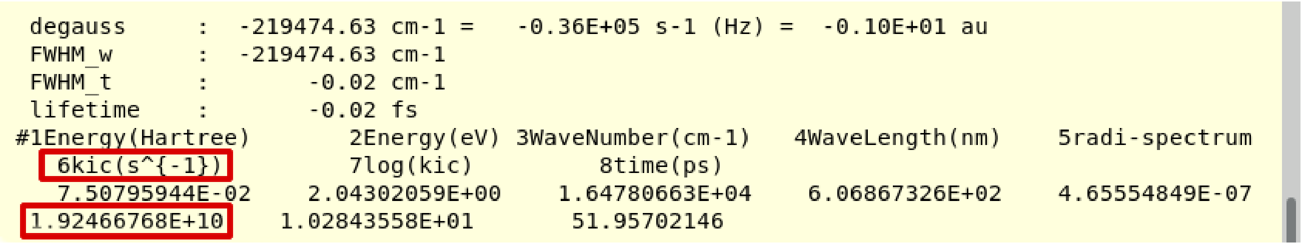


Fig. 3 Distribution of time *vs* real part of a converged correlation function

Once the correlation function is known to be converged, we can obtain the nonradiative rate at the end of the `ic.tvcf.log` file. From the file, we can obtain the internal conversion radiative rate k_{ic} for azulene molecule is **1.92466768×10^{10}** s^{-1}, as shown below.



```
 degauss     :  -219474.63 cm-1 =   -0.36E+05 s-1 (Hz) =  -0.10E+01 au
 FWHM_w      :  -219474.63 cm-1
 FWHM_t      :       -0.02 cm-1
 lifetime    :       -0.02 fs
#1Energy(Hartree)       2Energy(eV) 3WaveNumber(cm-1)   4WaveLength(nm)     5radi-spectrum
   6kic(s^{-1})         7log(kic)         8time(ps)
   7.50795944E-02     2.04302059E+00     1.64780663E+04     6.06867326E+02     4.65554849E-07
 1.92466768E+10     1.02843558E+01       51.95702146
```

Radiative rate k_r

Next, we create a directory `kr` and go to that directory.

Copy the following `evc` files from upper directory:

`../evc/evc.cart.dat`

to this `kr` work directory.

Create a `momap.inp` with its contents as follows:

```
[kr]$ cat momap.inp
do_spec_tvcf_ft     = 1                     # toggle correlation function calculation, 1 or 0
do_spec_tvcf_spec   = 1                     # toggle fluorescence spectrum calcluation, 1 or 0

&spec_tvcf
  DUSHIN        = .t.                       # toggle Duschinsky rotation effect, .t. or .f.
  Temp          = 300 K                     # temperature
  tmax          = 1000 fs                   # integration time
  dt            = 1   fs                    # integration timestep
  Ead           = 0.075092 au               # adiabatic excitation energy
  EDMA          = 0.92694 debye             # electronic dipole moment of absorption (GS)
  EDME          = 0.64751 debye             # electronic dipole moment of emission (ES)
  FreqScale     = 1.0                       # frequency scaling factor
  DSFile        = "evc.cart.dat"            # input dushin file
  Emax          = 0.3 au                    # upper bound of spectrum frequency
  dE            = 0.00001 au                # output energy interval
  logFile       = "spec.tvcf.log"           # output file for logging
  FtFile        = "spec.tvcf.ft.dat"        # output file for correlation function info
  FoFile        = "spec.tvcf.fo.dat"        # output file for spectrum function info
  FoSFile       = "spec.tvcf.spec.dat"      # output file for spectrum info
/
```

Also create a `run` file and change it with execution attribute (e.g., `chmod a+rx run`), the `run` file is shown as follows:

```
#!/bin/sh

momap -input momap.inp -np 4  &> log &
```

Users may modify the `run` file, for example, by changing the `-n` option from 4 to 8, and perform the calculation by running the script file:

```
$ ./run
```

When the calculation finishes, the result files are shown as follows:

```
[kic/kic]$ ls
evc.cart.dat    README              spec.tvcf.ft.dat    spec.tvcf.spec.gnu
log             ref                 spec.tvcf.ft.gnu
momap.inp       run                 spec.tvcf.log
nodefile        spec.tvcf.fo.dat    spec.tvcf.spec.dat
```

The radiative decay rate constant can be found at the end of `spec.tvcf.log` file, while the fluorescence spectrum information can be obtained from `spec.tvcf.spec.dat`.

Plot the data from file `spec.tvcf.spec.dat` by using columns 3, 5, and 6, in Linux, we can use **Gnuplot** to do the plotting, the plot script is shown as follows:

```
[sumstat]$ cat spec.tvcf.spec.gnu
reset
set nogrid
set lmargin 10
set pointsize 1.0
set encoding iso_8859_1
set term postscript eps enhanced color 20
set xlabel "Wave number, cm^{-1}" offset 0,0
set ylabel "Intensity, a.u." offset 0,0

set xtics nomirror
set ytics nomirror

set xrange [5000:30000]
set yrange [0:1.15]

set output "spec.tvcf.spec.eps"

plot  \
  "spec.tvcf.spec.dat"  u 3:5 t "Absorption" w l lw 3 lt 1, \
  ""  u 3:6 t "Emission" w l lw 3 lt 2
```

Then use the following commands to generate the correlation and spectrum plots:

```
$ gnuplot *.gnu
$ ps2png *.eps
Or  if your gnuplot has terminal  pngcairo,
$ gnuplot *.gnu-png
$ display *.png
```

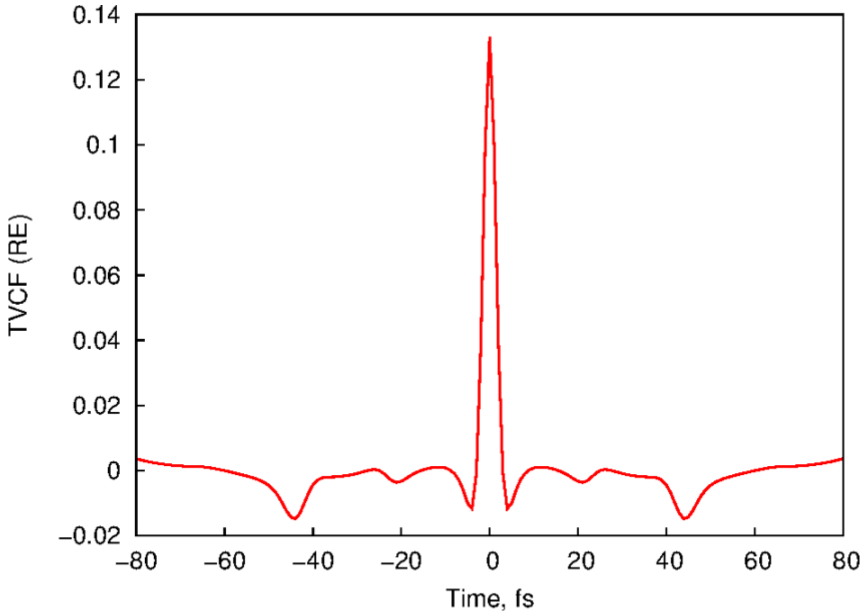


Fig. 4 Distribution of time *vs* real part of a converged correlation function

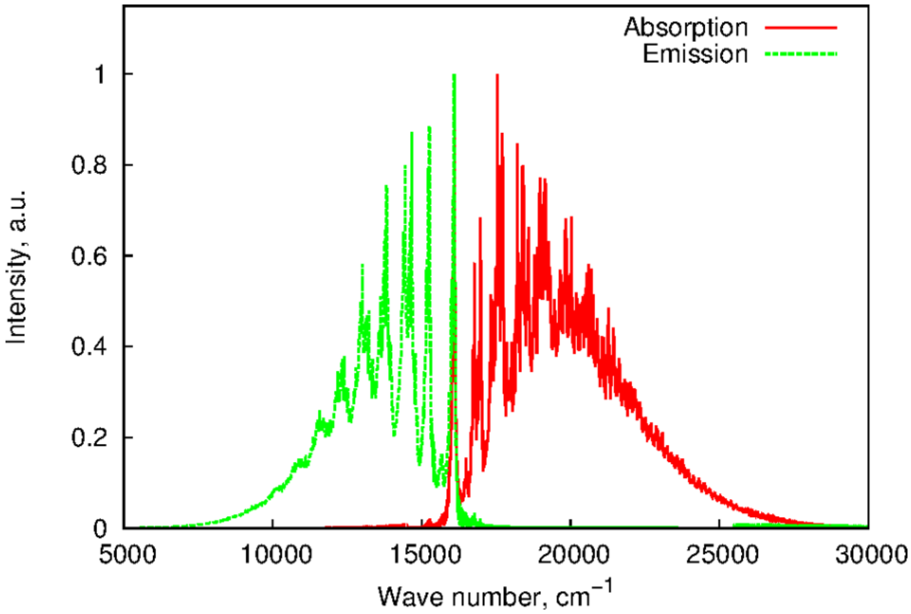


Fig. 5 Absorption and emission spectrum

The script ps2png is used to convert a .eps file to .png file, with its contents as follows:

```
$ cat  ~/bin/ps2png
#!/usr/bin/perl -w
#
# ps2png [resolution] file...
#
# Convert a postscript file to PNG, using the gs (GhostScript) command.   The
# resolution defaults to 200, which is a readable compromise for most screens.
# The files should be postscript files.  You can omit a .ps suffix and  we'll
# assume it.

# Author: John Chambers <jc@trillian.mit.edu>

$ENV{LD_LIBRARY_PATH} = '/usr/X11R6/lib/:/usr/eecs/lib:/usr/lib:/usr/lib/aout';

if ( @ARGV == 0 )
{
   print "Usage: ps2png [resolution] file...\n";
   exit $?;
}

if (($res = $ARGV[0]) =~ /^\d+$/) {shift @ARGV} else {$res = 200}

file: for $file (@ARGV) {
    if ($file =~ /(.*)\.(\w*ps)$/i) {
        $fili = $file;
        $filo = "$1.png";
    } else {
        if      (-f ($fili = "$file.ps" )) {$filo = "$file.png";
        } elsif (-f ($fili = "$file.eps")) {$filo = "$file.png";
        } elsif (-f ($fili = "$file.PS" )) {$filo = "$file.PNG";
        } else {
            print STDERR "Can't find postscript file for $file.\n";
            next file;
        }
    }
    system "gs -q -DNOPAUSE -sDEVICE=ppmraw -r$res -sOutputFile='|pnmcrop|pnmtopng > $filo' -- $fili";
    if ($?) {
        print STDERR "Conversion of \"$fili\" failed with exit status $?.\n";
        exit $?;
    }
}
```

TIPS: The ps2png script needs the pnmcrop and pnmtopng commands, which can be resolved by installing the netpbm packages:

```
$ yum install netpbm netpbm-progs          #    provide pnmcrop & pnmtopng etc.
```

Sum-over-states Approach

Similar to the above calculations, first we copy the following files from upper directory:

```
../gaussian/azulene-s0.fchk
../gaussian/azulene-s0.log
../gaussian/azulene-s1.fchk
../gaussian/azulene-s1.log
../evc/evc.cart.dat
```

to a work directory, say, `sumstat`.

Create a `momap.inp` with its contents as follows:

```
[sumstat]$ cat momap.inp
do_spec_sums    = 1                # if use sum-over-states approach, 1 or 0

&spec_sums
  DSFile        = "evc.cart.dat"   # input evc file
  Ead           = 0.075092 au      # adiabatic excitation energy
  dipole_abs    = 0.92694 debye    # Electronic Transition Dipole Absorption
  dipole_emi    = 0.64751 debye    # Electronic Transition Dipole Emission
  maxvib        = 10               # maximum vibration quantum number
  if_cal_ic     = .t.              # if do internal conversion analysis, .t. or .f.
  promode       = 24               # promotion mode (internal conversion)
  FC_eps_abs    = 0.1              # eps of Franck-Condon factor (absorption)
  FC_eps_emi    = 0.1              # eps of Franck-Condon factor (emission)
  FC_eps_ic     = 0.1              # eps of Franck-Condon factor (internal conversion)
  FreqScale     = 1.0              # frequency scaling factor
  FreqEPS       = 0.01             # eps of frequency
  Seps          = 0.00001          # eps of Huang-Rhys coupling constant
  eps           = 0.00             #
  debug         = .false.          #
  FWHM          = 500   cm-1       # broadening factor, full width at half maximum
  blocksize     = 1000             #
  testpoints    = 1000             #
  TEST          = .f.              #
  flog          = "spec.sums.log"  # output log file
  reduce_eps    = 0.001            #
/
```

Also create a `run` file and change it with execution attribute (e.g., `chmod a+rx run`), the `run` file is shown as follows:

```
#!/bin/sh

momap -input momap.inp -np 4  &> log &
```

Then, perform the calculation by running the script file:

```
$ ./run
```

Finally, the result files are shown as follows:

```
[sumstat]$ ls
azulene-s0.fchk  momap.inp          spec.sums.abs.dirac.dat  spec.sums.emi.short.dat
azulene-s0.log   nodefile           spec.sums.abs.long.dat   spec.sums.ic.dat
azulene-s1.fchk  README             spec.sums.abs.short.dat  spec.sums.ic.dirac.dat
azulene-s1.log   ref                spec.sums.emi.dat        spec.sums.log
evc.cart.dat     run                spec.sums.emi.dirac.dat  spec.sums.spec.dat
log              spec.sums.abs.dat  spec.sums.emi.long.dat
```

Filename	Meaning
`spec.sums.abs.dirac.dat`	Absorption spectrum and vibrational transition quantum numbers
`spec.sums.emi.dirac.dat`	Emission spectrum and vibrational transition quantum numbers
`spec.sums.ic.dirac.dat`	Internal conversion and vibrational transition quantum numbers with the set `promode` as promotion mode
`spec.sums.log`	Logging file for sums-over-states aproach
`spec.sums.spec.dat`	Absorption and emission spectrum

Plot the data from file `spec.sums.spec.dat` by using columns 4, 7, and 13, in Linux, we can use Gnuplot to do the plotting, the plot script is shown as follows:

```
[sumstat]$ cat spec.sums.spec.gnu
reset
set nogrid
set lmargin 10
set pointsize 1.0
set encoding iso_8859_1
set term postscript eps enhanced color 20
set xlabel "Wave number, cm^{-1}" offset 0,0
set ylabel "Intensity, a.u." offset 0,0

set xtics nomirror
set ytics nomirror
set yrange [0:1.15]
set output "spec.sums.spec.eps"

plot  \
  "spec.sums.spec.dat"  u 4:7 t "Absorption" w l lw 3 lt 1, \
  ""  u 4:13 t "Emission" w l lw 3 lt 2
```

Then use the following commands to generate the graph:

```
$ gnuplot *.gnu
$ ps2png *.eps
Or  if your gnuplot has terminal  pngcairo,
$ gnuplot *.gnu-png
$ display *.png
```

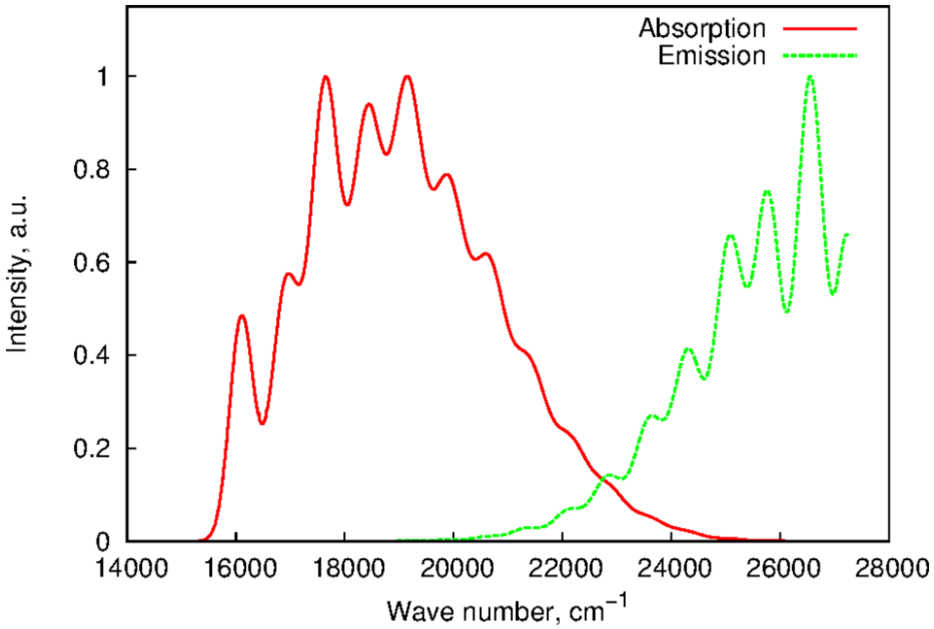


Fig. 6 Absorption and emission spectrum by using sum-over-states approach

Verify Convergence of Correlation Function

Correlation function must be converged before obtaining any calculation results. To verify, plot a graph using the first 2 columns in spec.tvcf.ft.dat, which are time and real part of the correlation function (TVCF_RE). TVCF_RE should be very close to zero and stop oscillating before it reaches the integration time limit. Figure 7 shows the distribution of a converged correlation function.

The Gnuplot plot script for the figure is shown as follows:

```
[sumstat]$ cat spec.tvcf.ft.gnu
reset
set nogrid
set lmargin 10
set pointsize 1.0
set encoding iso_8859_1
set term postscript eps enhanced color 20
set xlabel "Time, fs" offset 0,0
set ylabel "TVCF (RE)" offset 0,0
set xtics nomirror
set ytics nomirror

set xrange [-80:80]
set output "spec.tvcf.ft.eps"
plot "spec.tvcf.ft.dat"  u 1:2 t "" w l lw 3 lt 1
```

Then use the following commands to generate the graph:

```
$ gnuplot *.gnu
$ ps2png *.eps
Or  if your gnuplot has terminal  pngcairo,
$ gnuplot *.gnu-png
$ display *.png
```

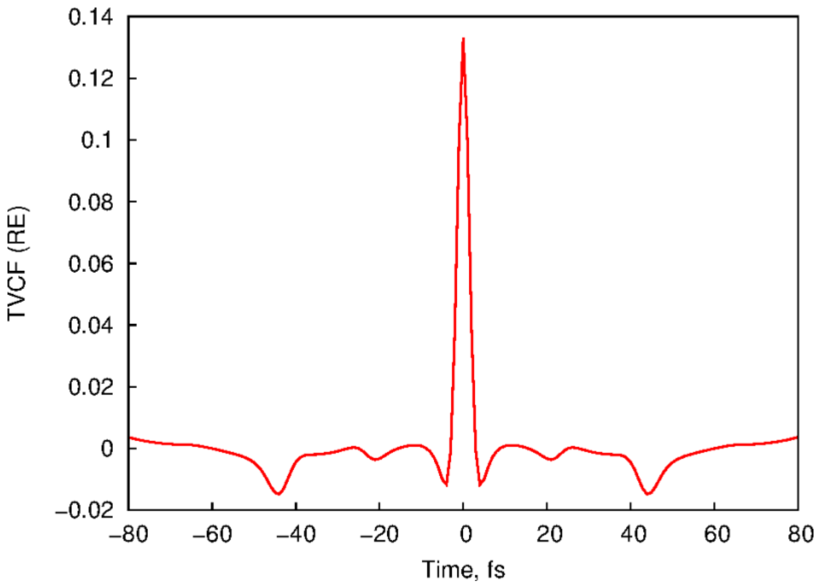


Fig. 7 Distribution of time vs real part of a converged correlation function