



4<sup>th</sup> winter School of Computational Chemistry  
Sharif University of Technology

# SPECTROSCOPY

Fluorescence & phosphorescence

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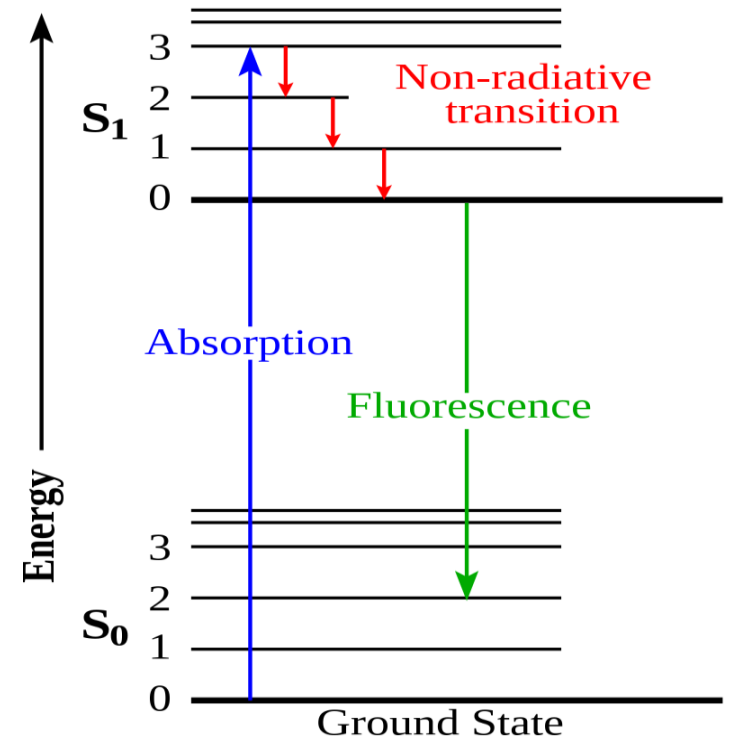
February 15, 2024



## □ Fluorescence

A form of **luminescence**,

where a molecule **absorbs** light of a specific energy (usually ultraviolet) and then **emits** light of lower energy (usually visible). This emitted light has a longer wavelength than the absorbed light, causing the phenomenon to be visible under specific conditions.



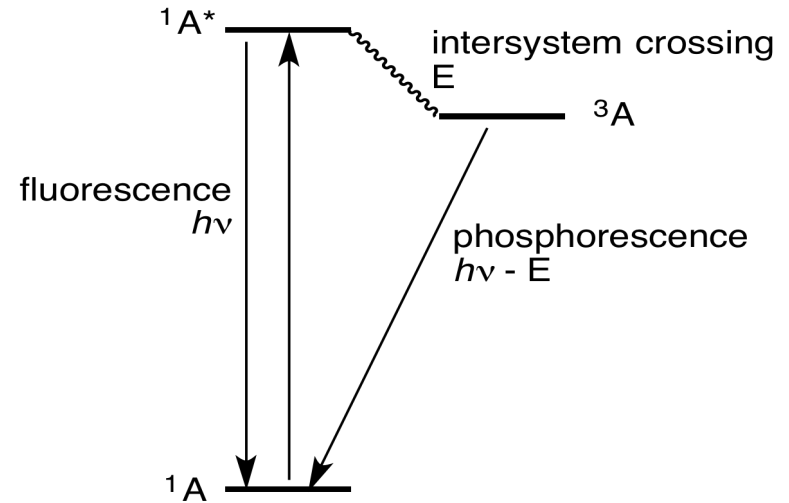
## ☐ Radiative transitions

involve the absorption of a photon, if the transition occurs to a higher energy level, or the emission of a photon, for a transition to a lower level.

## ☐ nonradiative transitions

Nonradiative transitions arise through several different mechanisms:

1. **Vibrational relaxation:** Relaxation of the excited state to its lowest vibrational level. This process involves the dissipation of energy from the molecule to its surroundings, and thus it cannot occur for isolated molecules.
2. **Internal conversion (IC):** It occurs when a vibrational state of an electronically excited state can couple to a vibrational state of a lower electronic state.
3. **intersystem crossing (ISC):** This is a transition to a state with a different spin multiplicity. In molecules with large spin-orbit coupling, intersystem crossing is much more important than in molecules that exhibit only small spin-orbit coupling. ISC can be followed by phosphorescence.



**1.Excitation:** A molecule in its ground state ( $S_0$ ) absorbs a photon with enough energy to jump to an excited state ( $S_1$  or higher). This energy excites an electron from a lower energy orbital to a higher energy one.

**2.Internal Conversion (Non-radiative relaxation):** In most cases, the molecule doesn't stay in the excited state for long. It loses some energy through vibrations and rotations (internal conversion) to reach a lower vibrational level within the same excited state ( $S_1'$ ).

**3.Fluorescence Emission:** From the lower vibrational level of the excited state ( $S_1'$ ), the molecule returns to the ground state ( $S_0$ ) by emitting a photon. This emitted photon has less energy (longer wavelength) than the absorbed one because some energy was lost during internal conversion.

**4.Stokes Shift:** The difference in energy between the absorbed and emitted photon is called the Stokes shift. It's usually small for molecules in solution and larger for gases due to less interaction with surrounding molecules.

## □ What types of molecules and materials exhibit fluorescence?

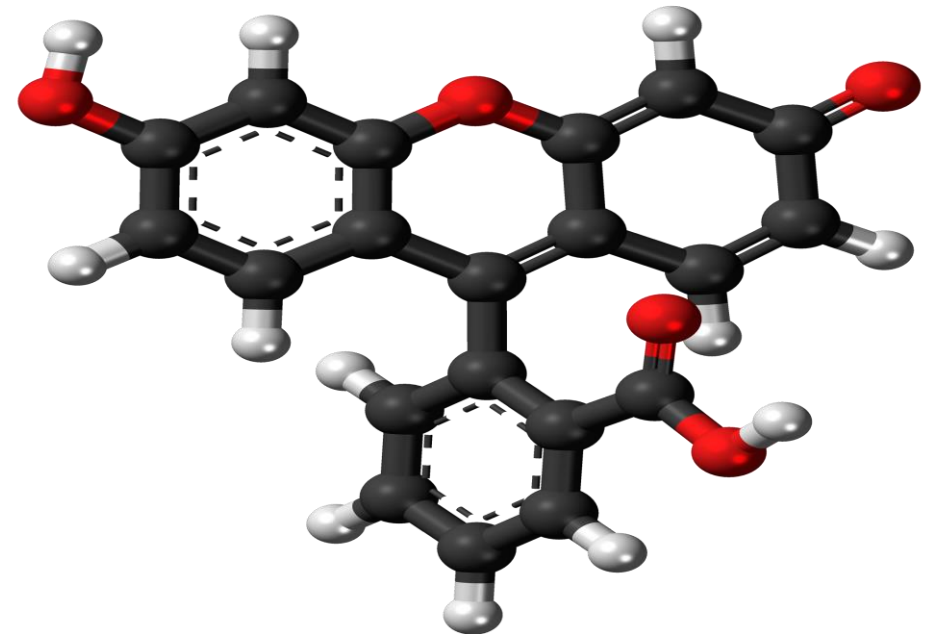
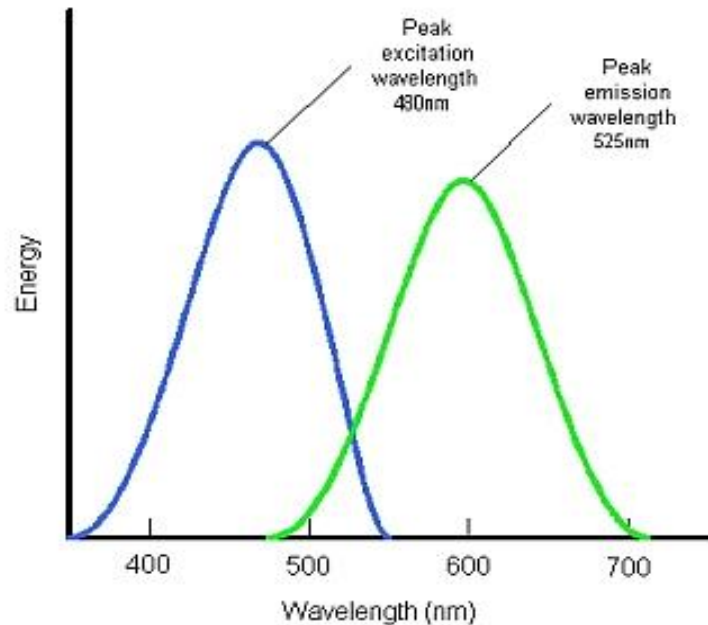
There are many molecules that are luminescent in nature such as;

- a few of the amino acids
- chlorophylls
- natural pigments

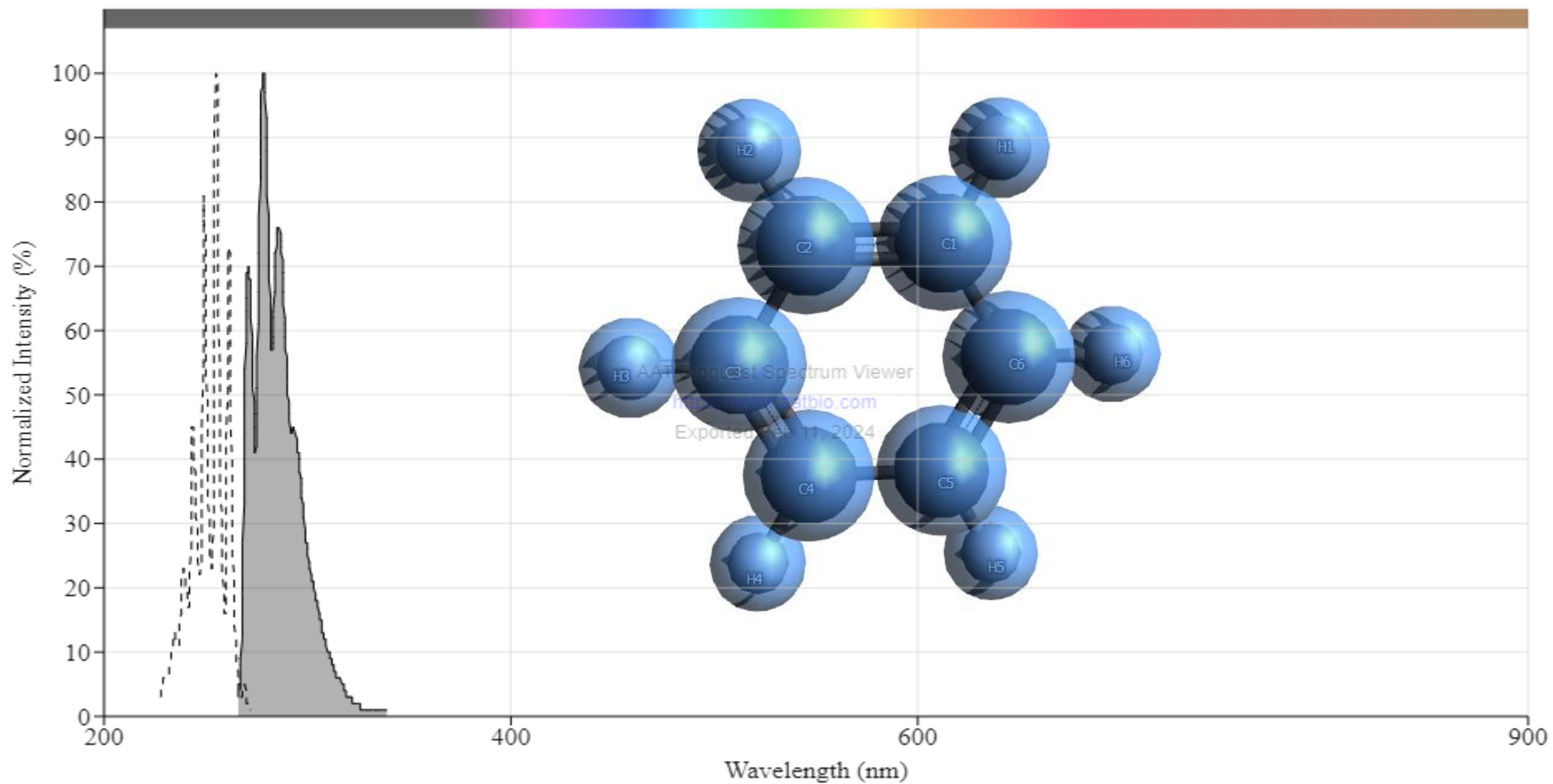
Typically, organic fluorescent molecules have **aromatic rings** and **pi-conjugated electrons** in them. Depending on their size and structure, organic dyes can emit from the UV out into the near-IR.

## Example: Fluorescein

Imagine a fluorescein molecule, commonly used in **highlighters** and **biological markers**. When exposed to ultraviolet light (**around 490 nm**), an electron in the molecule gets excited to a higher energy level. While in the excited state, the molecule loses some energy through vibrations (**non-radiative relaxation**) and settles to a lower vibrational level. Finally, it returns to the ground state by emitting a photon with longer wavelength (**around 530 nm**), appearing green to our eyes.



## ☐ Benzene as an Example in orca





# Computational steps

## G.S.

---

Step 1. Optimize the ground state.  $\longrightarrow$  GS.XYZ file

Step 2. Make sure that the optimized geometry is at minimum (not Maximum)!!  $\longrightarrow$  GS.hess file

## E.S.

---

Step 3. Perform a TD calculation to get an insight to electronic absorption spectrum.  $\longrightarrow$  Absorption spectrum

Step 4. Optimize the first excited state.  $\longrightarrow$  ES.XYZ file

Step 5. Make sure that the optimized geometry of step 3 is at minimum (not Maximum)!!  $\longrightarrow$  ES.hessian file

---

## Fluorescence

Step 6. Now calculate the Fluorescence spectrum by ESD module.  $\longrightarrow$  .spectrum file

## Step 1: Optimize the ground state

✓ check “optimization convergence”

# optimization of Benzene

! B3IYP def2-SVP OPT

\* xyz 0 1

```
H   -1.07840   2.14729  -0.63710
C   -0.60344   1.20171  -0.35657
C   -1.35780   0.03418  -0.30082
H   -2.42630   0.06083  -0.53738
C   -0.75430  -1.16745   0.05573
H   -1.34791  -2.08618   0.09970
C    0.60350  -1.20168   0.35649
H    1.07838  -2.14725   0.63705
C    1.35781  -0.03415   0.30077
H    2.42623  -0.06105   0.53755
C    0.75435   1.16750  -0.05578
H    1.34788   2.08625  -0.09964
```

\*

Item	value	Tolerance	Converged
Energy change	-0.0000087388	0.0000050000	NO
RMS gradient	0.0000100626	0.0001000000	YES
MAX gradient	0.0000314702	0.0003000000	YES
RMS step	0.0000240702	0.0020000000	YES
MAX step	0.0000606448	0.0040000000	YES
.....			
Max (Bonds)	0.0000	Max (Angles)	0.00
Max (Dihed)	0.00	Max (Improp)	0.00

Everything but the energy has converged. However, the energy appears to be close enough to convergence to make sure that the final evaluation at the new geometry represents the equilibrium energy. Convergence will therefore be signaled now

```
*****HURRAY*****
***           THE OPTIMIZATION HAS CONVERGED           ***
*****
```

## Step 2. Make sure that the optimized geometry is at minimum (not Maximum)!!

```
# Frequency calculation of Benzene
```

```
! B3IYP def2-SVP freq
```

```
%pal nprocs 3
```

```
end
```

```
* xyzfile 0 1 benzene-opt.xyz
```

For nonlinear  $C_6H_6$  molecule the vibrational degrees of freedom is :

$$3N-6 = (3 \times 12) - 6 = 30$$

```
-----  
VIBRATIONAL FREQUENCIES  
-----  
Scaling factor for frequencies = 1.000000000 (already applied!)  
  
0:      0.00 cm**-1  
1:      0.00 cm**-1  
2:      0.00 cm**-1  
3:      0.00 cm**-1  
4:      0.00 cm**-1  
5:      0.00 cm**-1  
6:      418.59 cm**-1  
7:      418.70 cm**-1  
8:      620.39 cm**-1  
9:      620.42 cm**-1  
10:     694.27 cm**-1  
11:     733.75 cm**-1  
12:     869.86 cm**-1  
13:     870.25 cm**-1  
14:     1003.34 cm**-1  
15:     1003.76 cm**-1  
16:     1014.03 cm**-1  
17:     1018.35 cm**-1  
18:     1039.21 cm**-1  
19:     1057.08 cm**-1  
20:     1057.18 cm**-1  
21:     1161.55 cm**-1  
22:     1183.39 cm**-1  
23:     1183.44 cm**-1  
24:     1363.00 cm**-1  
25:     1365.41 cm**-1  
26:     1508.35 cm**-1  
27:     1508.43 cm**-1  
28:     1650.19 cm**-1  
29:     1650.23 cm**-1  
30:     3162.46 cm**-1  
31:     3172.03 cm**-1  
32:     3172.11 cm**-1  
33:     3186.27 cm**-1  
34:     3186.37 cm**-1  
35:     3195.65 cm**-1
```

No imaginary frequency

Step 3. Perform a TD calculation to get an insight to electronic absorption spectrum.

```
#absorption of Benzene(TD job)
```

```
! B3LYP def2-SVP
```

```
% pal nprocs 3 end
```

```
% TDDFT
```

```
nroots 10
```

```
end
```

```
* xyzfile 0 1 benzene-opt.xyz
```

```
-----
```

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

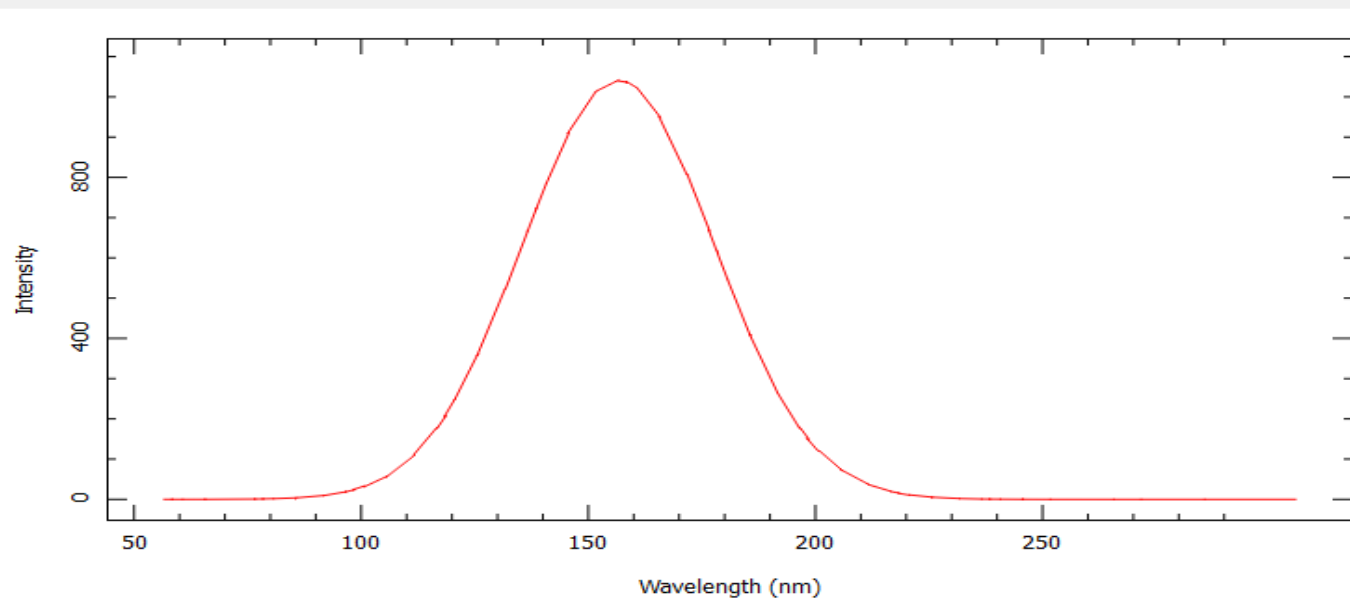
```
-----
```

State	Energy (cm <sup>-1</sup> )	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (au)
1	44304.7	225.7	0.000000038	0.00000	-0.00050	-0.00017	0.00005
2	52156.9	191.7	0.000000151	0.00000	-0.00018	0.00090	-0.00033
3	60370.1	165.6	0.000000000	0.00000	-0.00000	0.00000	0.00000
4	60373.3	165.6	0.000000000	0.00000	-0.00000	-0.00000	-0.00000
5	62225.1	160.7	0.000000901	0.00000	-0.00201	-0.00076	-0.00038
6	63093.0	158.5	0.000174377	0.00091	-0.00233	0.02952	-0.00572
7	63094.0	158.5	0.000103446	0.00054	0.02230	0.00219	0.00614
8	63178.4	158.3	0.008611568	0.04487	-0.05191	0.03895	0.20165
9	63848.1	156.6	0.959868326	4.94925	1.57612	-1.44536	0.61321
10	63849.6	156.6	0.960202945	4.95086	-1.50031	-1.64306	-0.01667

```
-----
```

Display visual cues

## Spectra Visualization



Absorption Load data... Advanced &lt;&lt; Close

Appearance Export Image CD Settings Absorption Settings

Spectra Type Transition Electric dipole X min 156.618052  Label peaks

X Units nm X max 225.709688

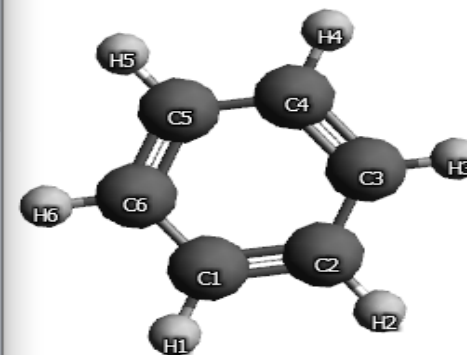
Line Shape Gaussian Points per Peak 10

Peak Width 50.00

Energy Shift 0.00



225.71	0.000000
191.73	0.000000
165.64	0.000000
165.64	0.000000
160.71	0.000001
158.50	0.000174
158.49	0.000103
158.28	0.008612
156.62	0.959868
156.62	0.960203



Export Data

Export Spectra Data

### Step 3. ESD as an alternative module to calculate absorption

```
# absorption spectrum of Benzene- vertical gradient approximation (VG)-FC LEVEL
```

```
!B3LYP DEF2-SVP TIGHTSCF ESD(ABS)
```

```
%pal nprocs 3 end
```

```
%TDDFT NROOTS 10
```

```
    IROOT 1
```

```
END
```

```
%ESD GSHESSIAN "benzene-freq.hess"
```

```
    HESSFLAG VG #DEFAULT
```

```
    END
```

```
* xyzfile 0 1 benzene-opt.xyz end
```

```
-----
```

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

```
-----
```

State	Energy (cm-1)	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (au)
1	44304.9	225.7	0.000000037	0.00000	0.00049	0.00017	-0.00005
2	52157.3	191.7	0.000000152	0.00000	0.00018	-0.00091	0.00033
3	60370.1	165.6	0.000000000	0.00000	-0.00001	0.00000	0.00000
4	60373.2	165.6	0.000000000	0.00000	0.00000	0.00000	0.00000
5	62224.8	160.7	0.000000894	0.00000	-0.00199	-0.00080	-0.00037
6	63092.7	158.5	0.000174727	0.00091	-0.00233	0.02956	-0.00572
7	63093.7	158.5	0.000103635	0.00054	0.02232	0.00223	0.00614
8	63178.0	158.3	0.008611716	0.04487	0.05181	-0.03899	-0.20167
9	63848.5	156.6	0.959880310	4.94928	-1.56921	1.45290	-0.61313
10	63850.0	156.6	0.960216116	4.95089	1.50755	1.63640	0.01949

```
-----
```

AS you can see if you run the absorption calculation under FC level of theory of transition dipole moment in the case of Benzene molecule, the data points related to HT term are zero in .spectrum file.

Energy	TotalSpectrum	IntensityFC	IntensityHT
10828.022679	9.816798e-07	9.816798e-07	0.000000e+00
10848.966630	9.836254e-07	9.836254e-07	0.000000e+00
10869.910581	9.855712e-07	9.855712e-07	0.000000e+00
10890.854532	9.875173e-07	9.875173e-07	0.000000e+00
10911.798483	9.894637e-07	9.894637e-07	0.000000e+00
10932.742434	9.914104e-07	9.914104e-07	0.000000e+00
10953.686386	9.933573e-07	9.933573e-07	0.000000e+00
10974.630337	9.953045e-07	9.953045e-07	0.000000e+00
10995.574288	9.972519e-07	9.972519e-07	0.000000e+00
11016.518239	9.991997e-07	9.991997e-07	0.000000e+00
11037.462190	1.001148e-06	1.001148e-06	0.000000e+00
11058.406141	1.003096e-06	1.003096e-06	0.000000e+00
11079.350092	1.005045e-06	1.005045e-06	0.000000e+00
11100.294043	1.006993e-06	1.006993e-06	0.000000e+00
11121.237994	1.008943e-06	1.008943e-06	0.000000e+00
11142.181945	1.010892e-06	1.010892e-06	0.000000e+00
11163.125896	1.012842e-06	1.012842e-06	0.000000e+00
11184.069847	1.014792e-06	1.014792e-06	0.000000e+00
11205.013798	1.016742e-06	1.016742e-06	0.000000e+00
11225.957749	1.018692e-06	1.018692e-06	0.000000e+00
11246.901700	1.020643e-06	1.020643e-06	0.000000e+00
11267.845651	1.022594e-06	1.022594e-06	0.000000e+00
11288.789602	1.024546e-06	1.024546e-06	0.000000e+00
11309.733553	1.026497e-06	1.026497e-06	0.000000e+00
11330.677504	1.028449e-06	1.028449e-06	0.000000e+00
11351.621455	1.030402e-06	1.030402e-06	0.000000e+00
11372.565406	1.032354e-06	1.032354e-06	0.000000e+00
11393.509357	1.034307e-06	1.034307e-06	0.000000e+00
11414.453308	1.036260e-06	1.036260e-06	0.000000e+00
11435.397259	1.038212e-06	1.038212e-06	0.000000e+00

### Step 3. ESD as an better alternative module to calculate absorption with considering Herzberg Teller term

# absorption spectrum of Benzene- vertical gradient-considering Herzberg-Teller term (HT)

```
!B3LYP DEF2-SVP TIGHTSCF ESD(ABS)
```

```
%pal nprocs 12 end
```

```
%TDDFT NROOTS 5
```

```
    IROOT 1
```

```
    END
```

```
%ESD GSHESSIAN "benzene-freq.hess"
```

```
    DOHT TRUE
```

```
    HESSFLAG VG #DEFAULT
```

```
    LINES VOIGT
```

```
    LINEW 75
```

```
    INLINEW 200
```

```
END
```

```
* xyzfile 0 1 benzene-opt.xyz end
```

Energy	TotalSpectrum	IntensityFC	IntensityHT
10838.494655	5.025105e-02	1.321586e-06	5.024973e-02
10869.910581	5.040031e-02	1.325522e-06	5.039898e-02
10901.326508	5.054960e-02	1.329460e-06	5.054827e-02
10932.742434	5.069893e-02	1.333399e-06	5.069759e-02
10964.158361	5.084828e-02	1.337338e-06	5.084695e-02
10995.574288	5.099767e-02	1.341278e-06	5.099633e-02
11026.990214	5.114709e-02	1.345220e-06	5.114574e-02
11058.406141	5.129654e-02	1.349162e-06	5.129519e-02
11089.822067	5.144602e-02	1.353105e-06	5.144466e-02
11121.237994	5.159553e-02	1.357049e-06	5.159417e-02
11152.653920	5.174507e-02	1.360994e-06	5.174371e-02
11184.069847	5.189465e-02	1.364940e-06	5.189328e-02
11215.485773	5.204426e-02	1.368887e-06	5.204289e-02
11246.901700	5.219389e-02	1.372835e-06	5.219252e-02
11278.317626	5.234357e-02	1.376784e-06	5.234219e-02
11309.733553	5.249327e-02	1.380734e-06	5.249189e-02
11341.149479	5.264301e-02	1.384685e-06	5.264162e-02
11372.565406	5.279278e-02	1.388637e-06	5.279139e-02
11403.981333	5.294258e-02	1.392589e-06	5.294119e-02
11435.397259	5.309242e-02	1.396543e-06	5.309102e-02
11466.813186	5.324228e-02	1.400498e-06	5.324088e-02
11498.229112	5.339219e-02	1.404454e-06	5.339078e-02
11529.645039	5.354212e-02	1.408410e-06	5.354071e-02



#### Step 4. Optimize the first excited state

(YOU CAN JUMP FROM THIS STEP IF YOU WANT TO RUN , VG APPROXIMATION IN FLUORESCENCE JOB)!!!

```
# Excited state geometry optimization of Benzene
```

```
! B3LYP def2-SVP OPT
```

```
%pal nprocs 3  
end
```

```
%TDDFT NROOTS 1
```

```
    IROOT 1       #specify the excited state you want to optimize
```

```
    END
```

```
* xyzfile 0 1 benzene-opt.xyz end
```

Step 5. Make sure that the optimized geometry of step 4 is at minimum (not Maximum)!!

```
# Excited state frequency calculation of Benzene
```

```
! B3IYP def2-SVP freq
```

```
%pal nprocs 12 end
```

```
%TDDFT NROOTS 1
```

```
IROOT 1
```

```
END
```

```
* xyzfile 0 1 benzene-S1-opt.xyz #optimized geometry of E.S.
```

```
-----  
VIBRATIONAL FREQUENCIES  
-----
```

```
Scaling factor for frequencies = 1.000000000 (already applied!)
```

```
0:      0.00 cm**1  
1:      0.00 cm**1  
2:      0.00 cm**1  
3:      0.00 cm**1  
4:      0.00 cm**1  
5:      0.00 cm**1  
6:     313.15 cm**1  
7:     313.77 cm**1  
8:     399.07 cm**1  
9:     522.63 cm**1  
10:    536.13 cm**1  
11:    625.30 cm**1  
12:    641.66 cm**1  
13:    649.04 cm**1  
14:    784.76 cm**1  
15:    785.45 cm**1  
16:    829.99 cm**1  
17:    961.04 cm**1  
18:    982.83 cm**1  
19:    983.93 cm**1  
20:    994.93 cm**1  
21:   1173.57 cm**1  
22:   1173.64 cm**1  
23:   1180.29 cm**1  
24:   1362.31 cm**1  
25:   1439.52 cm**1  
26:   1439.99 cm**1  
27:   1491.86 cm**1  
28:   1567.62 cm**1  
29:   1571.13 cm**1  
30:   3142.83 cm**1  
31:   3158.35 cm**1  
32:   3160.77 cm**1  
33:   3177.67 cm**1  
34:   3178.71 cm**1  
35:   3193.51 cm**1
```

No imaginary frequency

## Step 6. Now calculate the Fluorescence spectrum by ESD module

You can choose any of the described methods to obtain the PES by choosing the HESSFLAG

```
# fluorecence spectrum of Benzene-Vertical Gradient approximation (VG)
```

```
!B3LYP DEF2-SVP TIGHTSCF ESD(FLUOR)
```

```
%pal nprocs 2 end
```

```
%TDDFT NROOTS 5
```

```
    IROOT 1
```

```
    END
```

```
%ESD GSHESSIAN "benzene-freq.hess"
```

```
    HESSFLAG VG #DEFAULT
```

```
    LINES VOIGT
```

```
    LINEW 75
```

```
    INLINEW 200
```

```
    END
```

```
* xyzfile 0 1 benzene-opt.xyz end
```

```
The calculated fluorescence rate constant is    4.233354e+01 s-1  
with 100.00% from FC and 0.00% from HT
```

```
The fluorescence spectrum was saved in    benzene-fluorescence-VG-FC.spectrum
```

## Fluorescence rate

- When you select **ESD(FLUOR)** on the main input, the rate will be printed on the output at the end, with the **contributions from FC and HT** discriminated.
- **If you use CPCM,**  
it will be multiplied by the square of the **refractive index.**
- **In case you calculate a rate without CPCM** (and still want to consider the solvent), don't forget to multiply the final rate for this factor!

## The ideal model: Adiabatic Hessian

```
!B3LYP DEF2-SVP TIGHTSCF ESD(FUOR)
%TDDFT NROOTS 5
      IROOT 1
END
%ESD  GSHESSIAN      "BEN.hess"
      ESHESSIAN      "BEN_S1.hess"
      DOHT            TRUE
      LINES           VOIGT
      LINEW           75
      INLINEW        200
END
* XYZFILE 0 1 BEN.xyz
```

## FLUORESCENCE rate considering solvent

**n= 1.3749** refractive index of hexan

```
(0.00002 0.00000),  
(-0.00058 0.00000)  
Calculating correlation function: ...done  
Last element of the correlation function: 0.000000,-0.000000  
Computing the Fourier Transform: ...done  
  
The calculated fluorescence rate constant is 1.688355e+06 s-1*  
with 0.00% from FC and 100.00% from HT  
  
*The rate is multiplied by the square of the refractive index  
  
The fluorescence spectrum was saved in BASENAME.spectrum
```

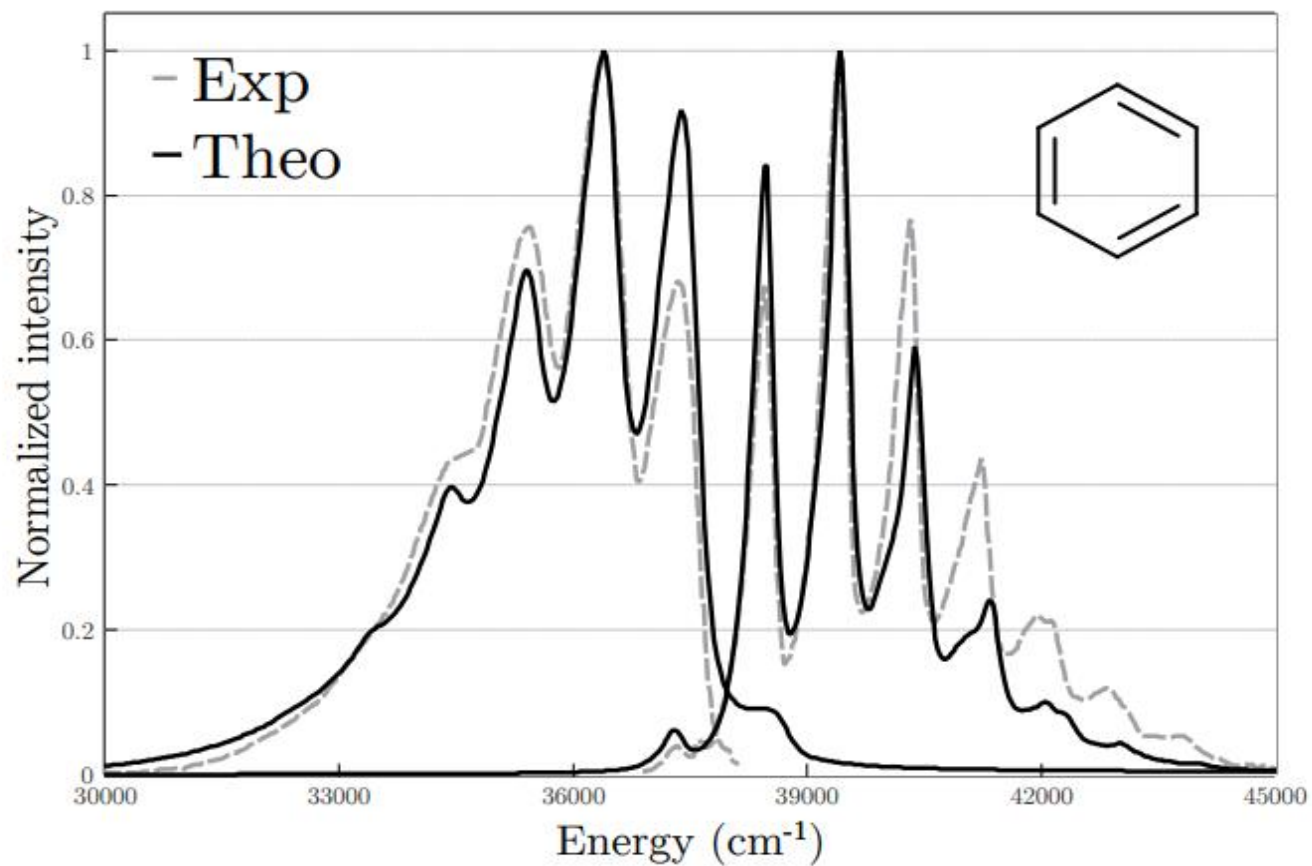
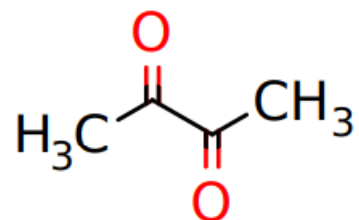


Figure 8.43: Predicted absorption (right) and emission (left) spectrum for benzene in hexane at 298.15 K.

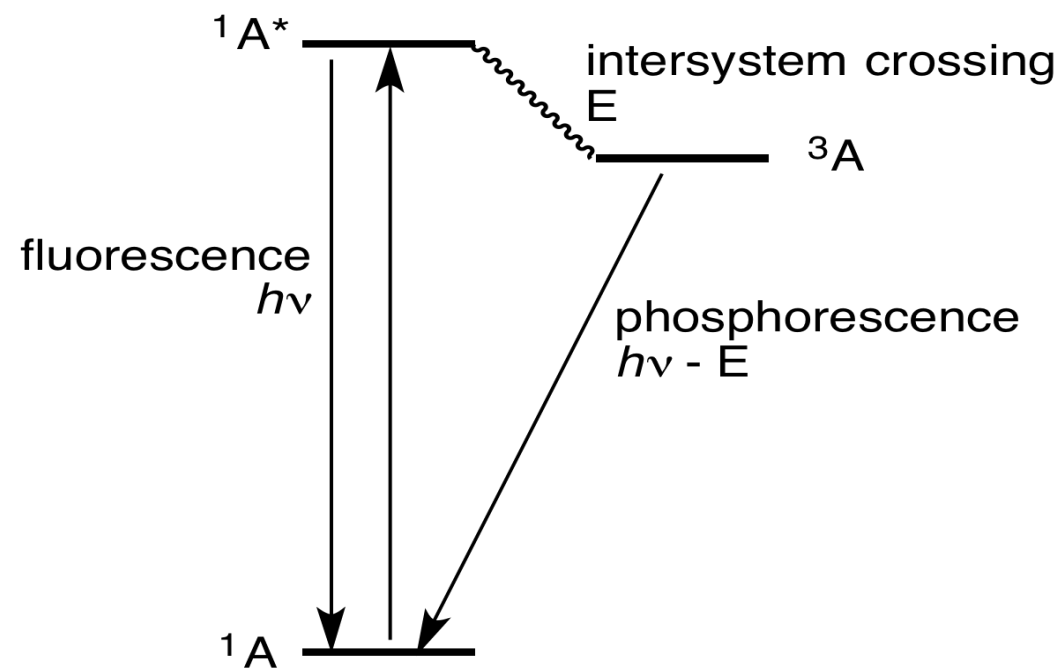
# Phosphorescence



## □ nonradiative transitions

Nonradiative transitions arise through several different mechanisms:

1. **Vibrational relaxation:** Relaxation of the excited state to its lowest vibrational level. This process involves the dissipation of energy from the molecule to its surroundings, and thus it cannot occur for isolated molecules.
2. **Internal conversion (IC):** It occurs when a vibrational state of an electronically excited state can couple to a vibrational state of a lower electronic state.
3. **intersystem crossing (ISC):** This is a transition to a state with a different spin multiplicity. In molecules with large spin-orbit coupling, intersystem crossing is much more important than in molecules that exhibit only small spin-orbit coupling. ISC can be followed by phosphorescence.





```
!B3LYP DEF2-TZVP(-F) CPCM(ETHANOL) OPT FREQ
```

```
%pal nprocs 12  
end
```

```
%TDDFT NROOTS 5  
IROOTMULT TRIPLET
```

```
END
```

```
* XYZ 0 1
```

```
C -0.82240 -0.05739 0.00515  
C 0.42295 0.77803 0.02146  
H -0.85252 -0.69527 0.89195  
H -0.85090 -0.66429 -0.90325  
H -1.69889 0.59680 0.01431  
C 1.74379 0.02561 -0.01818  
C 2.98907 0.86121 -0.00686  
H 3.01366 1.50199 -0.89176  
H 3.86561 0.20724 -0.02398  
H 3.02300 1.46514 0.90332  
O 0.42398 2.00161 0.06749  
O 1.74282 -1.19814 -0.05965
```

```
*
```

```

      .------.
-----|Geometry convergence|-----
Item           value           Tolerance     Converged
-----|-----|-----|-----
Energy change  -0.0000051987    0.0000050000    NO
RMS gradient   0.0000696215        0.0001000000    YES
MAX gradient   0.0002157857            0.0003000000    YES
RMS step       0.0010425126        0.0020000000    YES
MAX step       0.0032771019        0.0040000000    YES
.....
Max(Bonds)     0.0001      Max(Angles)  0.03
Max(Dihed)     0.19       Max(Improp) 0.00
-----|-----|-----|-----

```

Everything but the energy has converged. However, the energy appears to be close enough to convergence to make sure that the final evaluation at the new geometry represents the equilibrium energy. Convergence will therefore be signaled now

```

*****HURRAY*****
***      THE OPTIMIZATION HAS CONVERGED      ***

```

-----  
 TD-DFT/TDA EXCITED STATES (SINGLETs)  
 -----

the weight of the individual excitations are printed if larger than 1.0e-02

```
STATE 1: E= 0.093415 au    2.542 eV    20502.3 cm**-1 <S**2> = 0.000000
        22a -> 23a :    0.992038 (c= -0.99601086)

STATE 2: E= 0.146693 au    3.992 eV    32195.4 cm**-1 <S**2> = 0.000000
        21a -> 23a :    0.971978 (c= -0.98588942)
        22a -> 24a :    0.023777 (c= -0.15419839)

STATE 3: E= 0.232210 au    6.319 eV    50964.3 cm**-1 <S**2> = 0.000000
        18a -> 23a :    0.988264 (c= 0.99411444)

STATE 4: E= 0.237018 au    6.450 eV    52019.5 cm**-1 <S**2> = 0.000000
        21a -> 23a :    0.024567 (c= 0.15673813)
        22a -> 24a :    0.964175 (c= -0.98192419)

STATE 5: E= 0.243610 au    6.629 eV    53466.3 cm**-1 <S**2> = 0.000000
        14a -> 23a :    0.022405 (c= -0.14968427)
        19a -> 23a :    0.942147 (c= 0.97064252)
        20a -> 24a :    0.014711 (c= 0.12128949)
```

-----  
 TD-DFT/TDA EXCITED STATES (TRIPLETs)  
 -----

the weight of the individual excitations are printed if larger than 1.0e-02

```
STATE 1: E= 0.073747 au    2.007 eV    16185.6 cm**-1 <S**2> = 2.000000
        21a -> 24a :    0.012117 (c= 0.11007604)
        22a -> 23a :    0.983341 (c= 0.99163538)

STATE 2: E= 0.126403 au    3.440 eV    27742.2 cm**-1 <S**2> = 2.000000
        21a -> 23a :    0.942745 (c= -0.97095055)
        22a -> 24a :    0.050525 (c= -0.22477761)

STATE 3: E= 0.164139 au    4.466 eV    36024.4 cm**-1 <S**2> = 2.000000
        14a -> 24a :    0.013102 (c= -0.11446532)
        15a -> 23a :    0.039416 (c= 0.19853403)
        19a -> 24a :    0.028231 (c= -0.16802161)
        20a -> 23a :    0.913246 (c= 0.95563893)

STATE 4: E= 0.184854 au    5.030 eV    40570.8 cm**-1 <S**2> = 2.000000
        14a -> 23a :    0.076816 (c= 0.27715652)
        19a -> 23a :    0.857824 (c= 0.92618762)
        20a -> 24a :    0.055831 (c= -0.23628635)

STATE 5: E= 0.223362 au    6.078 eV    49022.3 cm**-1 <S**2> = 2.000000
        12a -> 23a :    0.027067 (c= -0.16451986)
        16a -> 23a :    0.028576 (c= -0.16904473)
        18a -> 23a :    0.919664 (c= 0.95899126)
        21a -> 24a :    0.016341 (c= -0.12783354)
```

-----  
 ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS  
 -----

State	Energy (cm <sup>-1</sup> )	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (au)
1	20502.3	487.8	0.000177856	0.00286	0.00152	-0.00047	-0.05342
2	32195.4	310.6	0.000000018	0.00000	-0.00014	0.00041	0.00003
3	50964.3	196.2	0.000272333	0.00176	0.00356	0.00198	-0.04174
4	52019.5	192.2	0.000000314	0.00000	0.00081	0.00115	0.00004
5	53466.3	187.0	0.000000956	0.00001	-0.00008	-0.00048	0.00238
6	16185.6	617.8	spin forbidden (mult=3)				
7	27742.2	360.5	spin forbidden (mult=3)				
8	36024.4	277.6	spin forbidden (mult=3)				
9	40570.8	246.5	spin forbidden (mult=3)				
10	49022.3	204.0	spin forbidden (mult=3)				

-----

Summary of contributions to the inner energy U:

Electronic energy	...	-306.35941421 Eh	
Zero point energy	...	0.09042794 Eh	56.74 kcal/mol
Thermal vibrational correction	...	0.00287689 Eh	1.81 kcal/mol
Thermal rotational correction	...	0.00141627 Eh	0.89 kcal/mol
Thermal translational correction	...	0.00141627 Eh	0.89 kcal/mol
-----			
Total thermal energy		-306.26327684 Eh	

#optimozation and frequency calculation of ground triplet state

!B3LYP DEF2-TZVP(-F) CPCM(ETHANOL) OPT FREQ

%pal nprocs 12

end

\* XYZfile 0 3 biacetyl-opt-freq-td.xyz

```
-----|-----  
-----|Geometry convergence|-----  
Item          value          Tolerance    Converged  
-----|-----  
Energy change -0.0000017027      0.0000050000    YES  
RMS gradient  0.0000641872      0.0001000000    YES  
MAX gradient  0.0002283065      0.0003000000    YES  
RMS step      0.0007200790      0.0020000000    YES  
MAX step      0.0026066969      0.0040000000    YES  
.....  
Max (Bonds)   0.0001      Max (Angles)  0.03  
Max (Dihed)  0.15      Max (Improp)  0.00  
-----|-----
```

```
*****HURRAY*****  
***      THE OPTIMIZATION HAS CONVERGED      ***  
*****
```

```
Summary of contributions to the inner energy U:  
Electronic energy      ...  -306.35867333 Eh  
Zero point energy      ...    0.09017746 Eh    56.59 kcal/mol  
Thermal vibrational correction ...    0.00290623 Eh    1.82 kcal/mol  
Thermal rotational correction ...    0.00141627 Eh    0.89 kcal/mol  
Thermal translational correction ...    0.00141627 Eh    0.89 kcal/mol  
-----|-----  
Total thermal energy      -306.26275710 Eh
```

```

NAME = biacetyl-phosphorescence.inp
| 1> # phosphorescence spectrum of biacetyl
| 2>
| 3> !B3LYP DEF2-TZVP(-F) TIGHTSCF CPCM(ETHANOL) ESD(PHOSP) RI-SOMF(1X)
| 4> %TDDFT NROOTS 20
| 5> DOSOC TRUE
| 6> TDA FALSE
| 7> IROOT 1
| 8> END
| 9> %ESD GSHESSIAN "BIA.hess"
| 10> TSHESSIAN "BIA_T1.hess"
| 11> DOHT TRUE
| 12> DELE 17130
| 13> END
| 14> * XYZFILE 0 1 BIA.xyz
| 15> $NEW_JOB
| 16> !B3LYP DEF2-TZVP(-F) TIGHTSCF CPCM(ETHANOL) ESD(PHOSP) RI-SOMF(1X)
| 17> %TDDFT NROOTS 20
| 18> DOSOC TRUE
| 19> TDA FALSE
| 20> IROOT 2
| 21> END
| 22> %ESD GSHESSIAN "BIA.hess"
| 23> TSHESSIAN "BIA_T1.hess"
| 24> DOHT TRUE
| 25> DELE 17130
| 26> END
| 27> * XYZFILE 0 1 BIA.xyz
| 28> $NEW_JOB
| 29> !B3LYP DEF2-TZVP(-F) TIGHTSCF CPCM(ETHANOL) ESD(PHOSP) RI-SOMF(1X)
| 30> %TDDFT NROOTS 20
| 31> DOSOC TRUE
| 32> TDA FALSE
| 33> IROOT 3
| 34> END
| 35> %ESD GSHESSIAN "BIA.hess"
| 36> TSHESSIAN "BIA_T1.hess"
| 37> DOHT TRUE
| 38> DELE 17130
| 39> END
| 40> * XYZFILE 0 1 BIA.xyz
| 41>
| 42> *****END OF INPUT*****
=====

```



biacetyl-phosphorescence



biacetyl-phosphorescence\_job2



biacetyl-phosphorescence\_job3

## JOB 1

The calculated phosphorescence rate constant is  $5.058676e+00 \text{ s}^{-1}$ \*  
with 87.20% from FC and 12.80% from HT

\*The rate is multiplied by the square of the refractive index

The phosphorescence spectrum was saved in biacetyl-phosphorescence.spectrum

Total run time: 5 hours 8 minutes 40 seconds

\*\*\*\*ORCA ESD FINISHED WITHOUT ERROR\*\*\*\*

Timings for individual modules:

Sum of individual times	...	19107.607 sec (= 318.460 min)	
GTO integral calculation	...	0.517 sec (= 0.009 min)	0.0 %
SCF iterations	...	61.282 sec (= 1.021 min)	0.3 %
CIS module	...	524.852 sec (= 8.748 min)	2.7 %
ESD module	...	18520.956 sec (= 308.683 min)	96.9 %

## JOB 2

The calculated phosphorescence rate constant is  $1.981669e+00 \text{ s}^{-1}$   
with 14.02% from FC and 85.98% from HT

\*The rate is multiplied by the square of the refractive index

The phosphorescence spectrum was saved in `biacetyl-phosphorescence_job2.spectrum`

Total run time: 4 hours 31 minutes 51 seconds

\*\*\*\*ORCA ESD FINISHED WITHOUT ERROR\*\*\*\*

Timings for individual modules:

Sum of individual times	...	16939.504 sec (= 282.325 min)	
GTO integral calculation	...	0.458 sec (= 0.008 min)	0.0 %
SCF iterations	...	31.566 sec (= 0.526 min)	0.2 %
CIS module	...	595.598 sec (= 9.927 min)	3.5 %
ESD module	...	16311.882 sec (= 271.865 min)	96.3 %



## JOB 3

The calculated phosphorescence rate constant is  $9.646268e+02 \text{ s}^{-1}$ \*  
with 94.55% from FC and 5.45% from HT

\*The rate is multiplied by the square of the refractive index

The phosphorescence spectrum was saved in biacetyl-phosphorescence\_job3.spectrum

Total run time: 3 hours 53 minutes 54 seconds

\*\*\*ORCA ESD FINISHED WITHOUT ERROR\*\*\*

Timings for individual modules:

Sum of individual times	...	14508.568 sec (= 241.809 min)	
GTO integral calculation	...	0.568 sec (= 0.009 min)	0.0 %
SCF iterations	...	24.271 sec (= 0.405 min)	0.2 %
CIS module	...	448.758 sec (= 7.479 min)	3.1 %
ESD module	...	14034.970 sec (= 233.916 min)	96.7 %

\*\*\*ORCA TERMINATED NORMALLY\*\*\*

TOTAL RUN TIME: 0 days 14 hours 2 minutes 39 seconds 518 msec

## Calculation of rates

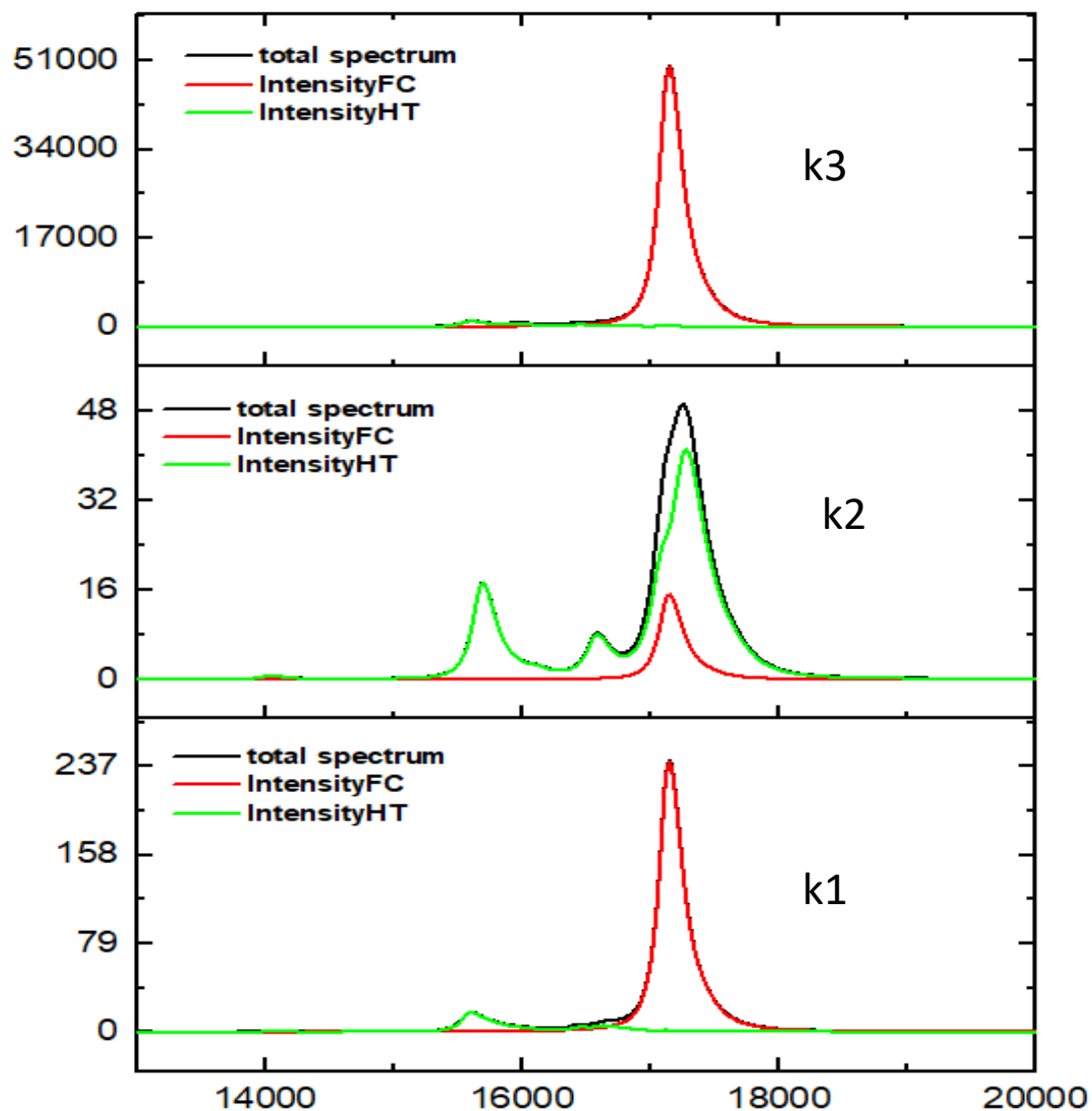
The calculation of the Phosphorescence rate is a little more involved, for there are three triplets that contribute so that the observed rate must be taken as an average of the three:

$$k_{av}^{phosp} = \frac{k_1 + k_2 + k_3}{3}$$

To be even more strict and account for the Boltzmann population distribution at a given temperature T:

$$k_{av}^{phosp} = \frac{k_1 + k_2 e^{-(\Delta E_{1,2}/k_B T)} + k_3 e^{-(\Delta E_{1,3}/k_B T)}}{1 + e^{-(\Delta E_{1,2}/k_B T)} + e^{-(\Delta E_{1,3}/k_B T)}}$$

where  $\Delta E_{1,2}$  is the energy difference between the first and second states, and so on.



$E$  singlet = -306.26233263 Eh

$E$  triplet = -306.35867333 Eh

Adiabatic difference energy = 0.9634070 hartree

After completion of each calculation, the rates for the three triplets were

$K_1 = 7.47 \text{ s}^{-1}$ ,

$K_2 = 0.80 \text{ s}^{-1}$  and

$K_3 = 542 \text{ s}^{-1}$ .

In the figure, the final calculated rate is about  $183 \text{ s}^{-1}$ , while the best experimental value is  $102 \text{ s}^{-1}$  (at 77K), with about 40% deriving from the HT effect

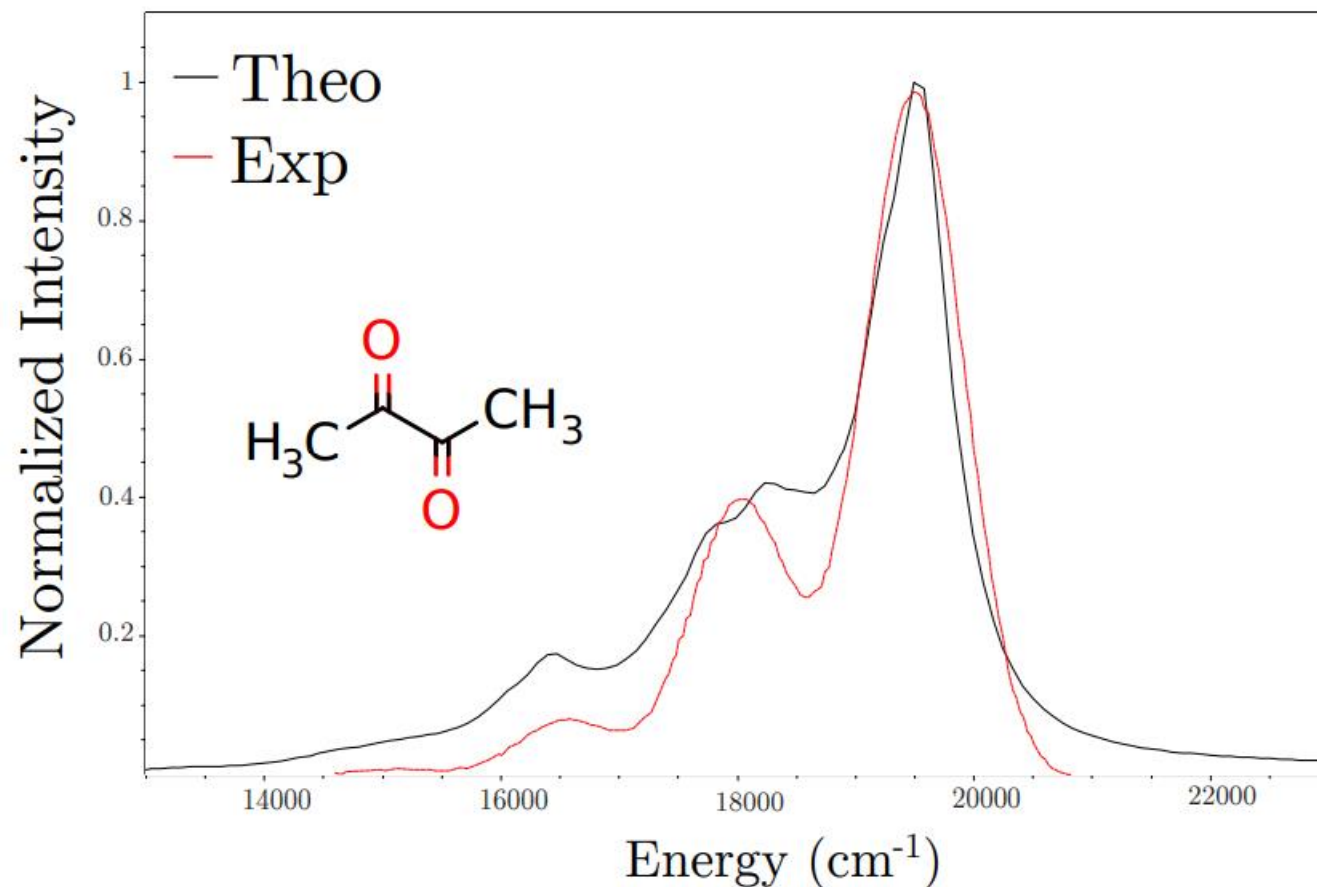


Figure 8.46: The experimental (dashed red) and theoretical (solid black, displaced by about  $2800 \text{ cm}^{-1}$ ) phosphorescence spectra for biacetyl, in ethanol at 298 K.