Spectroscopy exercise: Raman scattering, UV-Visible and absorption spectra

Sahar Ashtari
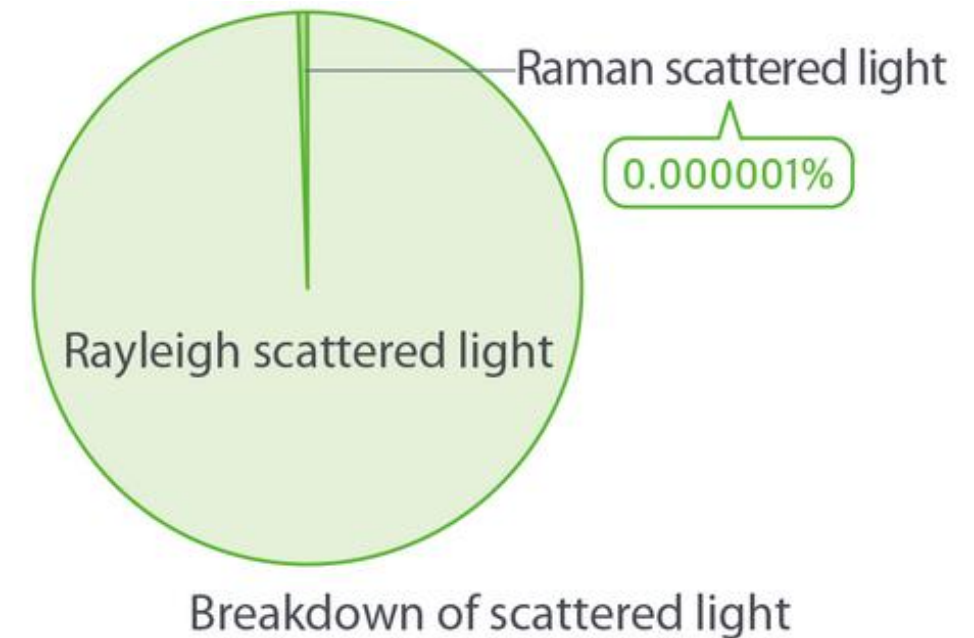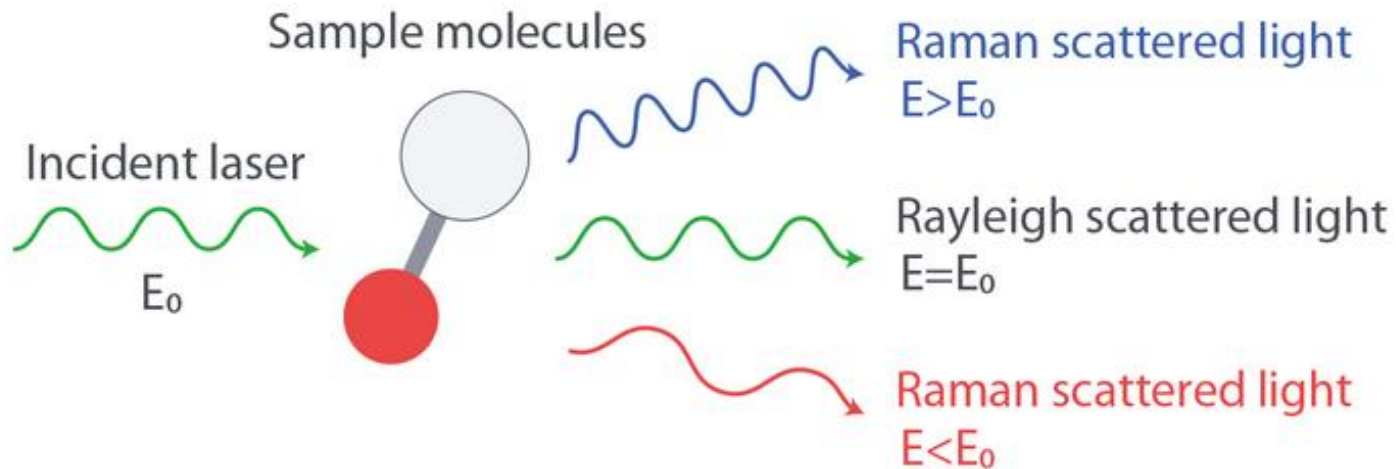
Raman scattering

The normal Raman signals represent the inelastic scattering of the incident light after its absorption by the molecule induces a vibrational and rotational excitation.

Raman and Krishnan, 1928

Landsberg and Mandelstam, 1928

Sample molecules

Incident laser

E_0

Raman scattered light
$E > E_0$

Rayleigh scattered light
$E = E_0$

Raman scattered light
$E < E_0$

Raman scattered light

0.000001%

Rayleigh scattered light
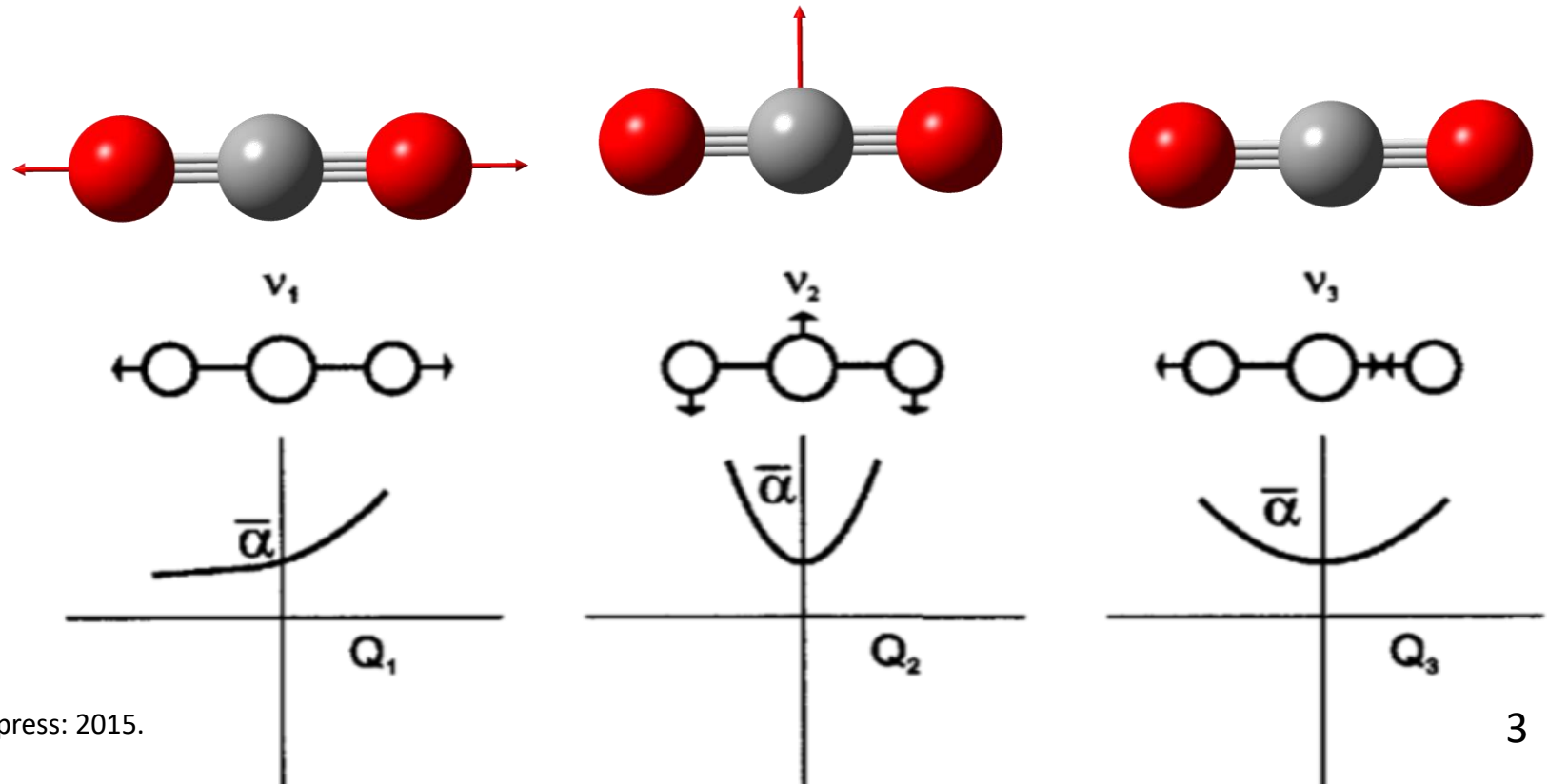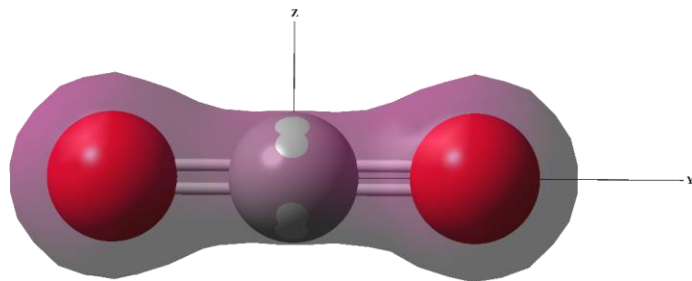
Breakdown of scattered light

Raman selection rules

During this phenomena, the change in the polarizability of the system for each normal mode gives rise to the intensity of the Raman bands

$$(\partial\alpha/\partial Q_K)_{Q_k=0} \neq 0$$

-CO_2 example:

Bernath, P. F., *Spectra of atoms and molecules*. Oxford university press: 2015.

Raman scattering calculations in Orca

In order to predict the Raman spectrum of a compound one has to know the derivatives of the polarizability with respect to the normal modes.

In Orca, a numerical frequency run combined with a polarizability calculation will calculate the Raman spectrum too.

Key words:

NumFreq: command, runs a numerical frequency calculation.
%elprop Polar 1 end: block, runs a polarizability calculation.

Raman practice:

Calculate the static Raman spectrum for H_2CO molecule using the following coordinates, at RHF/STO-3G level of theory.

c	0.000000	0.000000	-0.533905
o	0.000000	0.000000	0.682807
h	0.000000	0.926563	-1.129511
h	0.000000	-0.926563	-1.129511

Open a text editor of your choice (like NotePad or NotePad++) and start making the ORCA input file. After you are finished save the file with the .inp extension.

```
1  ! RHF STO-3G TightSCF SmallPrint
2  ! Opt NumFreq
3  %elprop Polar 1
4  end
5  * xyz 0 1
6  c 0.000000 0.000000 -0.533905
7  o 0.000000 0.000000 0.682807
8  h 0.000000 0.926563 -1.129511
9  h 0.000000 -0.926563 -1.129511
10 *
11
```

Check the output file for normal termination and analyse/visualize the results of the calculation.

Before the calculation of Raman activities, the numerical frequency calculation is performed.

```
<<< Energy and Gradient at the input geometry >>>

<<< Energy and Gradient at displaced geometries >>>
      <<<Displacing    1/coordinate 1  (+)>>>
      <<<Displacing    1/coordinate 1  (-)>>>
      <<<Displacing    1/coordinate 2  (+)>>>
      <<<Displacing    1/coordinate 2  (-)>>>
      <<<Displacing    1/coordinate 3  (+)>>>
      <<<Displacing    1/coordinate 3  (-)>>>
      <<<Displacing    2/coordinate 1  (+)>>>
      <<<Displacing    2/coordinate 1  (-)>>>
      <<<Displacing    2/coordinate 2  (+)>>>
      <<<Displacing    2/coordinate 2  (-)>>>
      <<<Displacing    2/coordinate 3  (+)>>>
      <<<Displacing    2/coordinate 3  (-)>>>
      <<<Displacing    3/coordinate 1  (+)>>>
      <<<Displacing    3/coordinate 1  (-)>>>
      <<<Displacing    3/coordinate 2  (+)>>>
      <<<Displacing    3/coordinate 2  (-)>>>
      <<<Displacing    3/coordinate 3  (+)>>>
      <<<Displacing    3/coordinate 3  (-)>>>
      <<<Displacing    4/coordinate 1  (+)>>>
      <<<Displacing    4/coordinate 1  (-)>>>
      <<<Displacing    4/coordinate 2  (+)>>>
      <<<Displacing    4/coordinate 2  (-)>>>
      <<<Displacing    4/coordinate 3  (+)>>>
      <<<Displacing    4/coordinate 3  (-)>>>
```

Check the output file for normal termination and analyse/visualize the results of the calculation.

Under the title "RAMAN SPECTRUM" we can find the activities (in $Å^4$/AMU) and the Raman depolarization ratios:
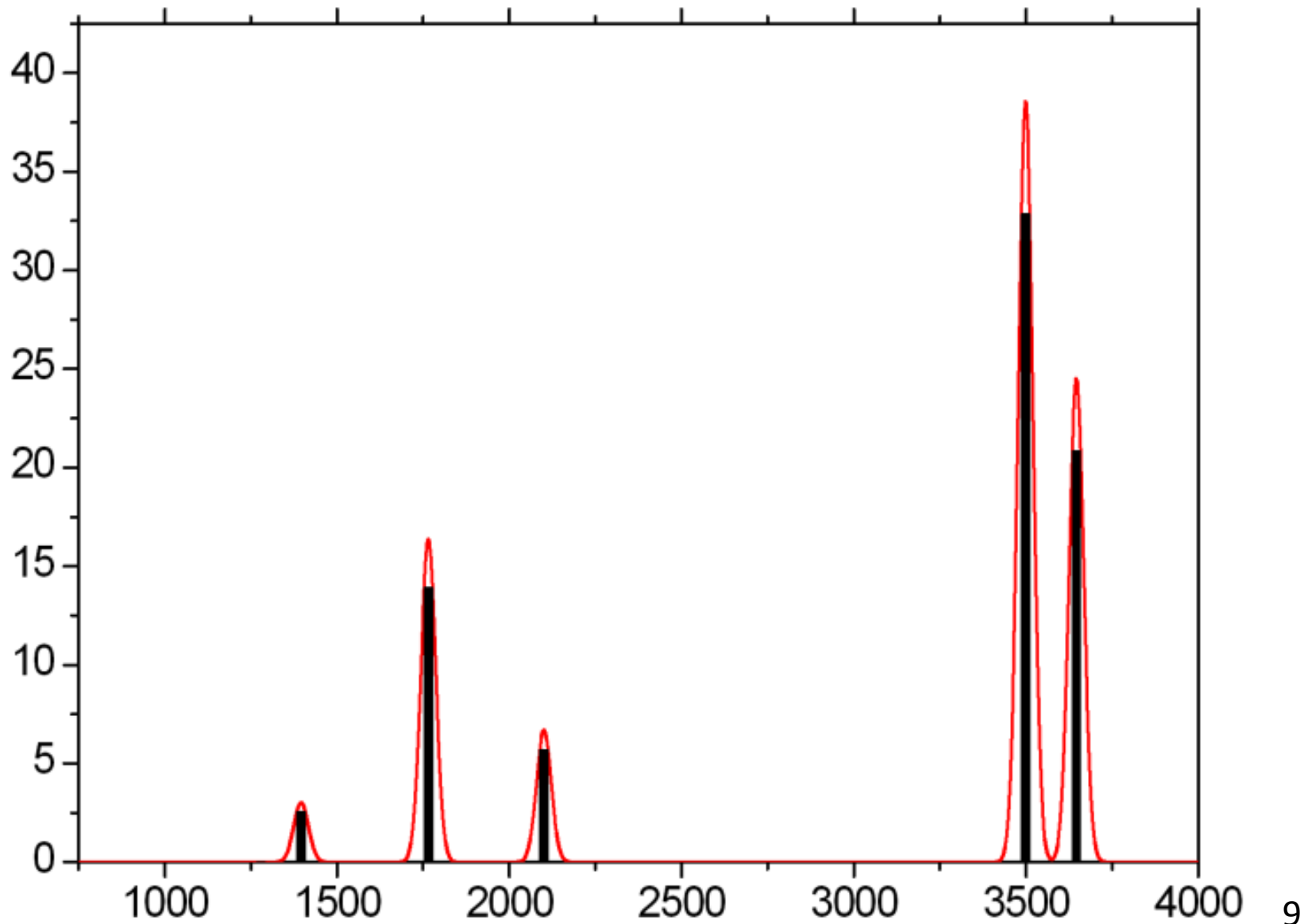
```
-------------
RAMAN SPECTRUM
-------------

 Mode       freq (cm**-1)    Activity    Depolarization
-----------------------------------------------------------------
    6:          1277.66       0.000000        0.000000
    7:          1397.45       0.000000        0.000000
    8:          1767.01      16.386770        0.707350
    9:          2099.21       6.702060        0.075705
   10:          3499.49      38.647287        0.186526
   11:          3645.45       0.000000        0.000000

The first frequency considered to be a vibration is 6
The total number of vibrations considered is 6
```

Visualize the Raman spectrum using "orca_mapspc myoutput.out raman -w50" in the command line in the folder of the output.

For more details on the basic options, call orca **mapspc** without any input.

We can also use Avogadro to visualize the Raman spectrum.

We can also use Avogadro to visualize the Raman spectrum.

UV-Visible spectroscopy

Most molecules and ions absorb energy in the ultraviolet or visible range. The absorbed photon excites an electron to higher energy molecular orbitals, an excited state.
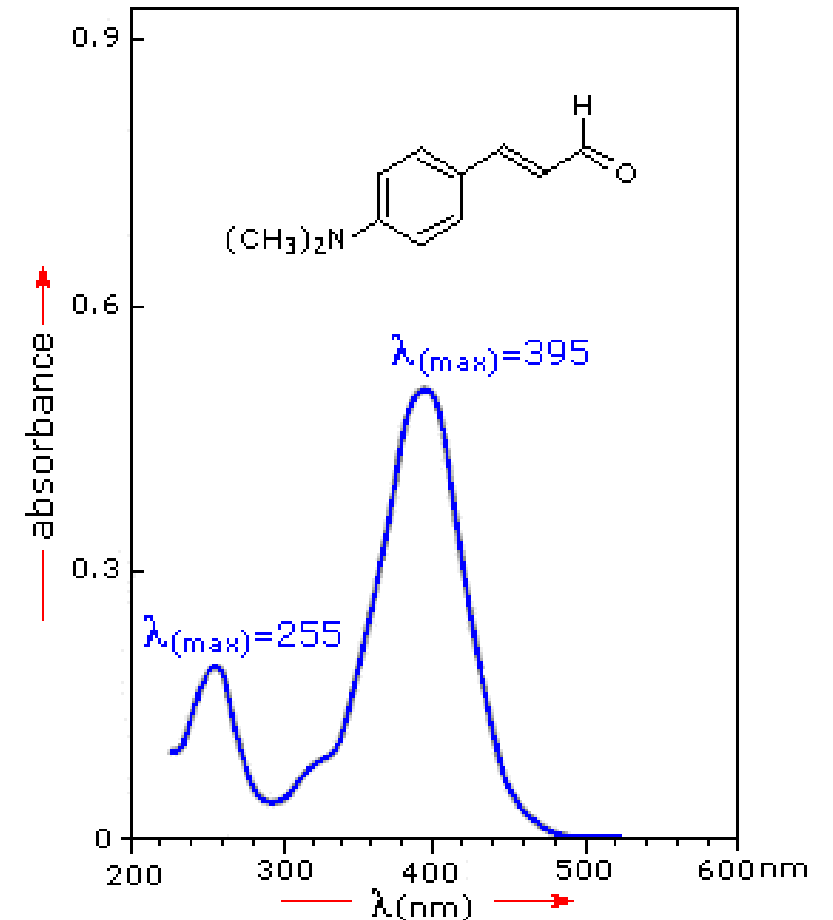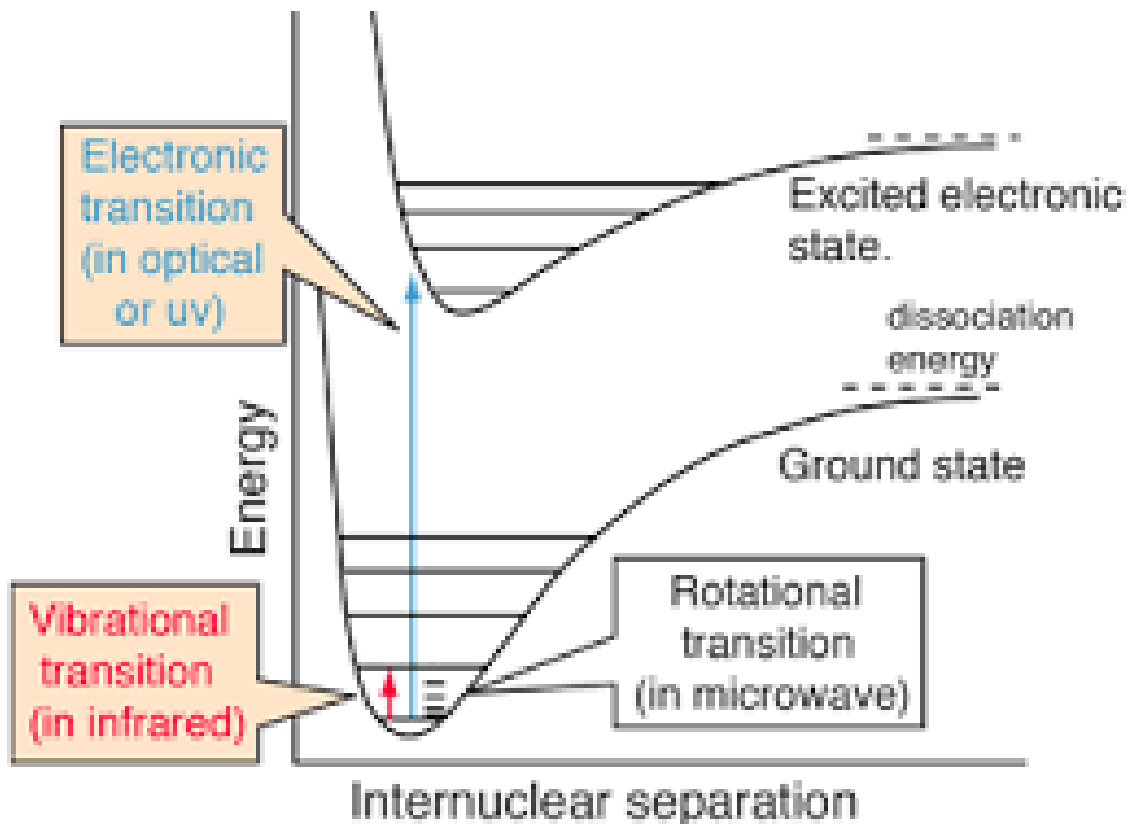
Excited-state calculations with ORCA

With ORCA, we can use TD-DFT, single-excitation CI (CIS) and RPA to calculate excitation energies, absorption intensities and CD intensities. Here we focus on **TD-DFT** method.

 Key words:

      The simplest input only requires the number of roots in the **%TDDFT NROOTS 10 END** block.

      We can determine the triplet excitation energies in addition to the singlets for closed shell reference systems using the **%TDDFT TRIPLETS TRUE END** block.

      For methods with implemented analytical gradient calculation, a given state can be selected for geometry optimization with the help of the **Iroot** keyword.

In TD-DFT, the oscillator strength fI, which determines the probability of a singlet excitation happening through the absorption of light, is given by

$$f_I = \frac{2}{3}\Delta_I \left| \sum_{ia} \sqrt{\frac{2\Delta_{ia}}{\Delta_I}} F_{ia,I}^S \overbrace{\langle\varphi_i|\vec{r}|\varphi_a\rangle}^{\overrightarrow{d_{ia}}} \right|^2$$

$$\underbrace{\phantom{\sum_{ia} \sqrt{\frac{2\Delta_{ia}}{\Delta_I}} F_{ia,I}^S \langle\varphi_i|\vec{r}|\varphi_a\rangle}}_{\overrightarrow{d_I}}$$

Here $\overrightarrow{d_{ia}}$ is the transition dipole moment of the single orbital transition i → a. Their linear combination determines the transition dipole moment $\overrightarrow{d_I}$ of the excitation, from which the oscillator strength is then calculated.

UV-Visible spectroscopy practice:

predict the absorption spectrum for COH_2, using the following coordinates, at B3LYP/DEF2-SVP level of theory.

```
! B3LYP DEF2-SVP
%TDDFT NROOTS 10
END
* int 0 1
C 0 0 0 0.00 0.0 0.00
O 1 0 0 1.20 0.0 0.00
H 1 2 0 1.08 120 0.00
H 1 2 3 1.08 120 180.00
*
```

After the termination of the calculations, we can find the excitation energies, the single orbital transitions involved and their contribution under "TD-DFT/TDA EXCITED STATES (SINGLETS)" in the output.

```
----------------------------------------
TD-DFT/TDA EXCITED STATES (SINGLETS)
----------------------------------------

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

STATE   1:  E=    0.147972 au       4.027 eV     32476.0 cm**-1 <S**2> =    0.000000
      7a ->    8a  :       0.998161 (c= -0.99907991)

STATE   2:  E=    0.304471 au       8.285 eV     66823.6 cm**-1 <S**2> =    0.000000
      7a ->    9a  :       0.995298 (c=  0.99764613)

STATE   3:  E=    0.336509 au       9.157 eV     73855.1 cm**-1 <S**2> =    0.000000
      5a ->    8a  :       0.992904 (c= -0.99644587)

STATE   4:  E=    0.357673 au       9.733 eV     78500.2 cm**-1 <S**2> =    0.000000
      6a ->    8a  :       0.245470 (c= -0.49544897)
      7a ->   10a  :       0.729621 (c=  0.85417881)

STATE   5:  E=    0.390095 au      10.615 eV     85615.9 cm**-1 <S**2> =    0.000000
      4a ->    8a  :       0.996612 (c=  0.99830471)

STATE   6:  E=    0.408972 au      11.129 eV     89758.9 cm**-1 <S**2> =    0.000000
      7a ->   11a  :       0.996262 (c=  0.99812904)

STATE   7:  E=    0.427641 au      11.637 eV     93856.3 cm**-1 <S**2> =    0.000000
      4a ->   10a  :       0.016113 (c= -0.12693649)
      5a ->    9a  :       0.027984 (c= -0.16728341)
      5a ->   11a  :       0.023415 (c= -0.15302044)
      5a ->   17a  :       0.010868 (c=  0.10424909)
      6a ->    8a  :       0.620793 (c=  0.78790421)
      7a ->   10a  :       0.241904 (c=  0.49183710)
      7a ->   14a  :       0.029849 (c= -0.17276957)
```

We can also find the oscillator strengths and transition electric dipole moments under "ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS"

```
-------------------------------------------------------------------------------------------
             ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS
-------------------------------------------------------------------------------------------
State     Energy     Wavelength   fosc             T2          TX          TY          TZ
          (cm-1)       (nm)                      (au**2)       (au)        (au)        (au)
-------------------------------------------------------------------------------------------
   1      32476.0      307.9     0.000000000     0.00000     0.00000    -0.00000     0.00000
   2      66823.6      149.6     0.137503568     0.67742    -0.00000     0.82306    -0.00000
   3      73855.1      135.4     0.002198722     0.00980     0.00000     0.00000    -0.09900
   4      78500.2      127.4     0.007957520     0.03337    -0.18268     0.00000     0.00000
   5      85615.9      116.8     0.000000000     0.00000     0.00000    -0.00000    -0.00000
   6      89758.9      111.4     0.017916546     0.06571    -0.00000     0.25635     0.00000
   7      93856.3      106.5     0.535168085     1.87716    -1.37010     0.00000    -0.00000
   8      94588.3      105.7     0.004140266     0.01441    -0.00000    -0.00000     0.12004
   9     106443.0       93.9     0.084604300     0.26167    -0.51154     0.00000     0.00000
  10     106543.4       93.9     0.000000000     0.00000    -0.00000     0.00000     0.00000
```

The visualization of the absorption spectrum can be done in Avogadro using spectra in extensions menu and then changing to absorption:
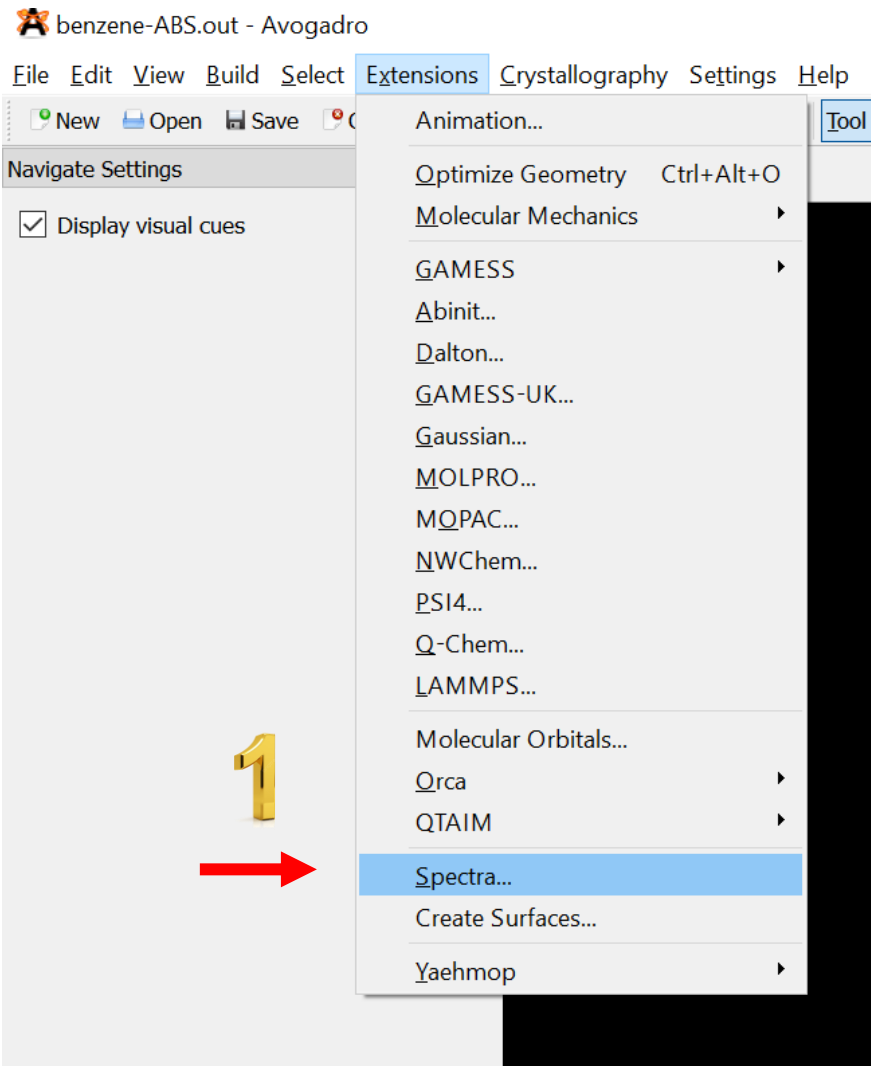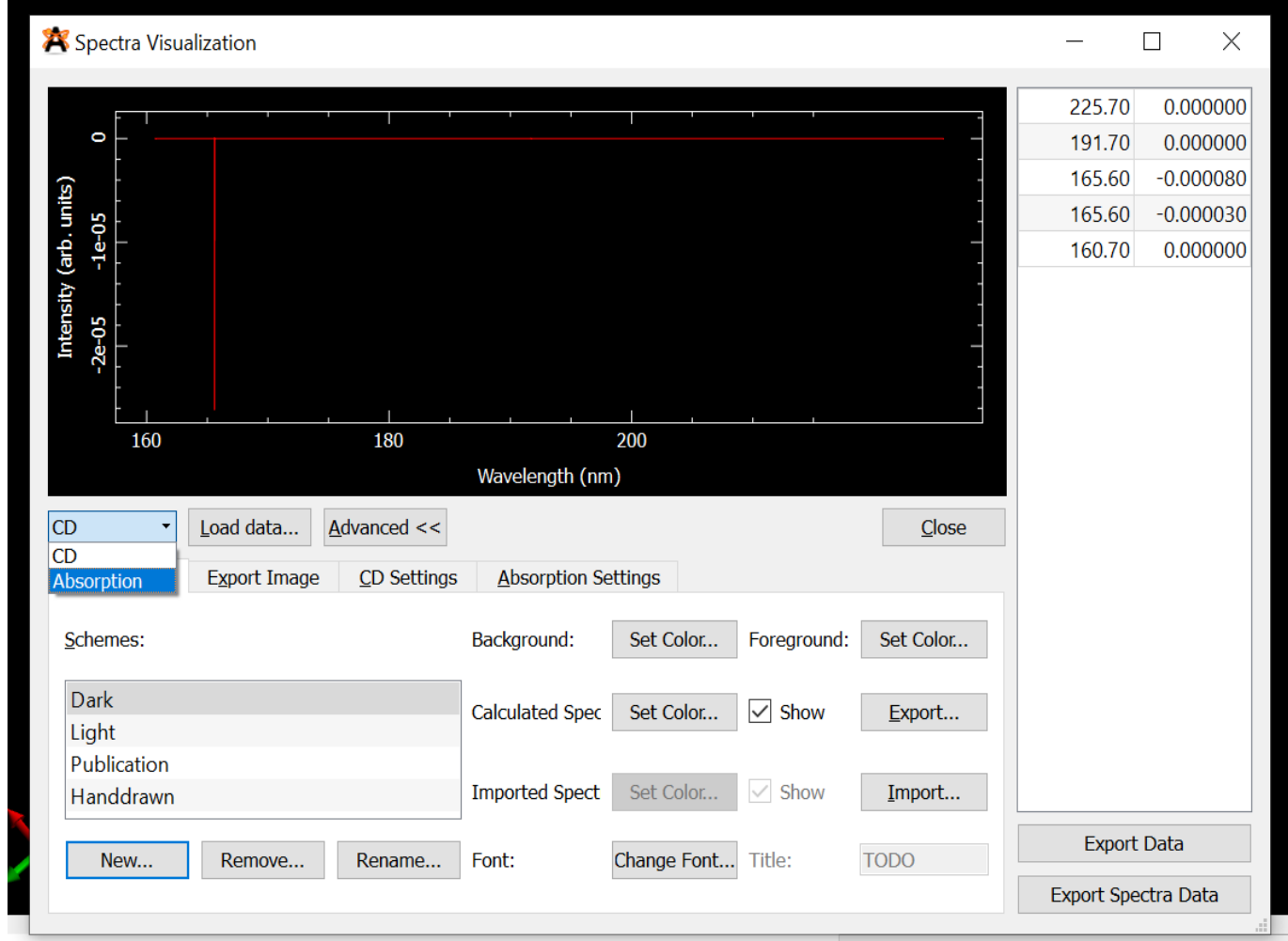
We can change the units, peak width and other spectral characteristic through Advanced>>Absorption Settings.

19

Further analysis can be done on the nature of the orbitals involved in each excitation using Charge difference density (CDD) figures using "**orca_plot gbwfilename –i**".


```
        1 - Enter type of plot
        2 - Enter no of orbital to plot
        3 - Enter operator of orbital (0=alpha,1=beta)
        4 - Enter number of grid intervals
        5 - Select output file format
        6 - Plot CIS/TD-DFT difference densities
        7 - Plot CIS/TD-DFT transition densities
        8 - Set AO(=1) vs MO(=0) to plot
        9 - List all available densities

       10 - Generate the plot
       11 - exit this program
Enter a number: 5
File-Format is presently: 5
     1 -   2D    Origin format
     2 -   2D    HPGL format
     3 -   2D    Gnuplot binary format
     4 -   2D    Gnuplot ascii format
     5 -   3D    gOpenMol binary
     6 -   3D    gOpenMol ASCII
     7 -   3D    Gaussian cube
     8 -   3D    simple format
Enter Format: 7
Current-settings:

PlotType        ... MO-PLOT
MO/Operator     ... 0 0
Output file     ... C:\Users\Admin\Desktop\TCCW2024\myexcercise\TDDFT\uv-s.cisdp10.plt
Format          ... Grid3d/Cube
Resolution      ... 40 40 40
Boundaries      ...      -8.020452      9.267671 (x direction)
                        -8.767475      8.767475 (y direction)
                        -7.000000      7.000000 (z direction)
```

20

Further analysis can be done on the nature of the orbitals involved in each excitation using Charge difference density (CDD) figures using "**orca_plot gbwfilename –i**".

```
PlotType         ... MO-PLOT
MO/Operator      ... 0 0
Output file      ... (null)
Format           ... Grid3D/Binary
Resolution       ... 40 40 40
Boundaries       ...     -8.020452      9.267671 (x direction)
                        -8.767475      8.767475 (y direction)
                        -7.000000      7.000000 (z direction)


     1 - Enter type of plot
     2 - Enter no of orbital to plot
     3 - Enter operator of orbital (0=alpha,1=beta)
     4 - Enter number of grid intervals
     5 - Select output file format
     6 - Plot CIS/TD-DFT difference densities
     7 - Plot CIS/TD-DFT transition densities
     8 - Set AO(=1) vs MO(=0) to plot
     9 - List all available densities


    10 - Generate the plot
    11 - exit this program
Enter a number: 6
The default name of the CIS-File would be: C:\Users\Admin\Desktop\TCCW2024\myexcercise\TDDFT\uv-s.cis
Is this the one you want (y/n)?y
Number of Vectors found: 10
Orbital Window: 2...7 -> 8...37
Below you have to enter the states to compute the difference/transition densities for
Their generation may take some time and therefore you may want to enter several
states that should be used for this computation and then go for a beer.
Give a list like: 1 5 12 26 (just blanks to separate state numbers)
NOTE: a. the first excited state will be state 1 as in the program output and
      the ground state cannot be given
      b. if you did a TDA FALSE calculation, the states should be given as
      2 * state - 1, for these correspond to the X+Y vectors, while the 2 * state
      correspond to the X-Y vectors. E.g. the first three states should be 1, 3 and 5.
      while 2, 4 and 6 would refer to the X-Y components of these.
Enter states: 1 2 3 4 5 6 7 8 9 10
```

We can then visualize the CDD cubes using GaussView > results > surfaces/contours > surface actions > new surface.

St1: 7a ⟶ 8a
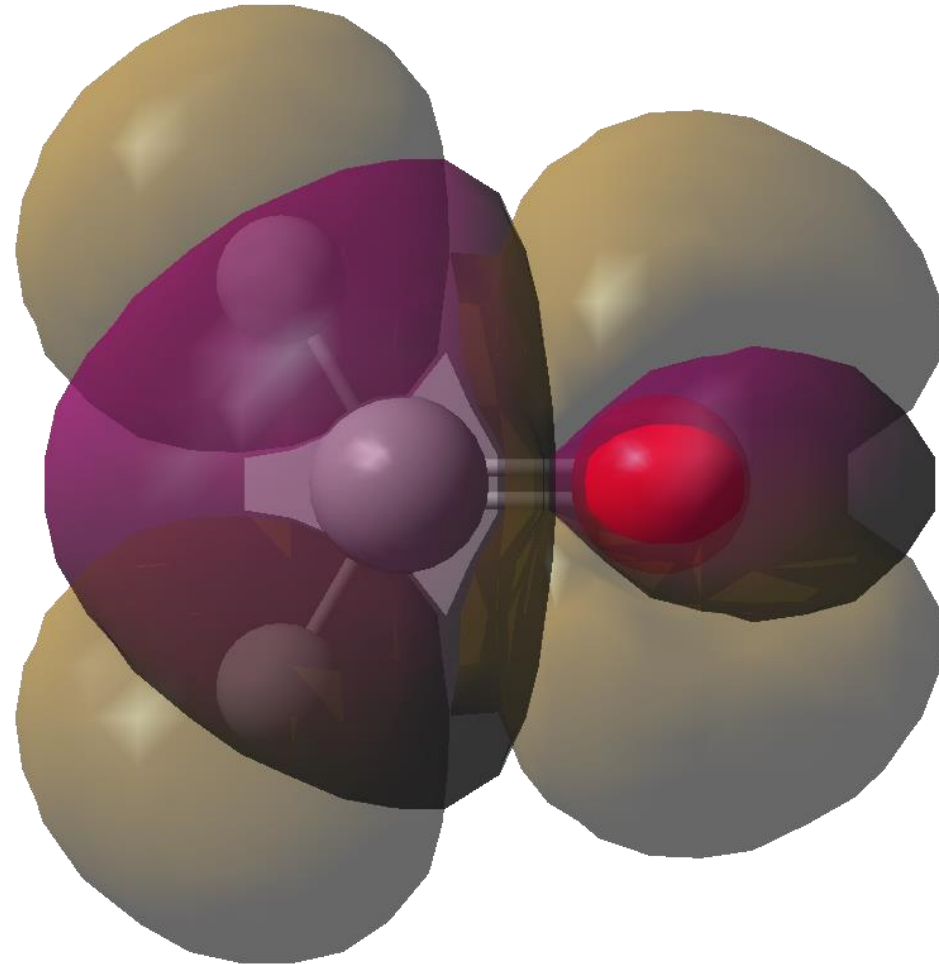
Absorption spectroscopy

The absorption rates between an initial and final electronic states under the Born-Oppenheimer and harmonic approximations, converted to the time domain are as follows:

$$k(\omega) = \frac{2\omega^3}{3\pi c^3 Z} \sum_{if} e^{-\frac{\epsilon_i}{k_B T}} \langle \Theta_i | \vec{\mu}^e | \bar{\Theta}_f \rangle \langle \bar{\Theta}_f | \vec{\mu}^e | \Theta_i \rangle \int e^{i(E_i - E_f - \omega)t} dt,$$

With ω being the incident photon frequency,
$\vec{\mu^e}$ being the electronic transition dipole,
$|\Theta\rangle$ the vibrational wavefunction of the initial or final state,
$e^{\frac{-\epsilon_i}{k_B T}}$ is the Boltzmann population of a given initial state at temperature T,
E_i and E_f are the initial and final vibronic energies,
and ϵ_i is the total vibrational energy of state I.

Absorption calculations with ORCA_ESD

The Excited State Dynamics (**ESD)** module of ORCA solves an analytic solution to the path integral of the Multidimensional Harmonic Oscillator absorption rate. **(keyword ESD(ABS))**

If one considers that the electronic part of the transition dipole varies with nuclear displacements and we allow for it to depend on the normal coordinates (**Q**), such as:

$$\vec{\mu}^e(\mathbf{Q}) = \vec{\mu}_0^e + \sum_i \frac{\partial \vec{\mu}^e}{\partial Q_i}\bigg|_{\mathbf{Q}=0} Q_i + \ldots,$$

we can even include vibronic coupling or the so-called Herzberg-Teller (HT) effect. **(block %ESD DOHT TRUE END)**

Excited state (ES) geometry and Hessian in ORCA_ESD

In order to predict absorption or emission rates, one needs both the ground state (GS) and excited state (ES) geometries and Hessians.

Adiabatic Hessian (AH) method

- When you optimize the ES geometry and input the Hessian.
- No keyword must be given on the input.
- Although the ideal model, it is challenging and time consuming!

In ORCA, we have seven different ways to approximate this ES PES: AHAS, VH, VG, HHBS, HHAS, UFBS and UFAS (only available for Absorption, Fluorescence and resonant Raman).

The idea behind these approximations is to do a geometry update step ($\Delta q_c = -gB^{-1}$ for Quasi-Newton and $\Delta q_c = -g(B + S)^{-1}$ for Augmented Hessian) to obtain the ES structure and somehow approximate the ES Hessian.

Method	Step	ES Hessian
AHAS	ES grad + GS Hessian	calculated on the ES geometry
VH	ES grad + ES Hessian at GS geometry	calculated on the GS geometry
VG (default)	ES grad + GS Hessian	equal to GS Hessian
VGFC	ES grad + GS Hessian	equal to GS Hessian (+ APPROXADEN TRUE)
HHBS	ES grad + Hybrid ES Hessian on GS geometry	Hybrid Hessian on GS geometry
HHAS	ES grad + GS Hessian	Hybrid Hessian on ES geometry
UFBS	ES grad + Updated frequencies ES Hessian on GS geometry	Updated frequencies ES Hessian on GS geometry
UFAS	ES grad + GS Hessian	Updated frequencies ES Hessian on ES geometry

Vertical Gradient (VG) model, the minimal approximation

- The excited state (ES) Hessian is equal to the GS, from which we extrapolate the ES geometry from the ES gradient and that Hessian using some step (Quasi-Newton or Augmented Hessian, which is the default here).
- The default method in ORCA.

Adiabatic Hessian After a Step (AHAS) model

- A reasonable compromise between a full geometry optimization and a simple step with the same Hessian is to do a step and then recalculate the ES Hessian at that geometry.
- Highly recommended by ORCA developers in general.

Absorption using ESD module practice:

predict the absorption spectrum for benzene, which has one band above 220 nm corresponding to a symmetry forbidden excitation to the S1 state, using the following coordinates, at B3LYP/DEF2-SVP level of theory. Use VG, AHAS and AH methods and compare the results.

First step: the GS information is obtained through an optimization and frequency calculation.

```
!B3LYP DEF2-SVP OPT FREQ
* XYZFILE 0 1 BEN.xyz
```

Second step: Using the optimized geometry, the absorption spectrum with the VG method can be done by calling the ESD module with the VG method in %ESD block with Herzberg-Teller approximation.

```
!B3LYP DEF2-SVP TIGHTSCF ESD(ABS)
%TDDFT   NROOTS   5
         IROOT    1
END
%ESD     GSHESSIAN        "BEN.hess"
         DOHT             TRUE
         HESSFLAG         VG #DEFAULT
END
* XYZFILE 0 1 BEN.xyz
```

Third step: Using the optimized geometry, the absorption spectrum can be done by calling the ESD module with the AHAS method in %ESD block with Herzberg-Teller approximation:

```
!B3LYP DEF2-SVP TIGHTSCF ESD(ABS)
%TDDFT   NROOTS   5
         IROOT    1
END
%ESD     GSHESSIAN        "BEN.hess"
         DOHT             TRUE
         HESSFLAG         AHAS
END
* XYZFILE 0 1 BEN.xyz
```

Fourth step: For the AH method, the ES S1 information is obtained through an optimization and frequency calculation for the desired excited state (**IROOT in %TDDFT**).

```
!B3LYP DEF2-SVP OPT FREQ
%TDDFT   NROOTS   5
         IROOT    1
END
*  XYZFILE 0 1 BEN_S1.xyz
```

Fifth step: Having both Hessians, we call the ESD module and specify the desired excited state number, ground and excited Hessians and performance of Herzberg-Teller calculations:

```
!B3LYP DEF2-SVP TIGHTSCF ESD(ABS)
%TDDFT   NROOTS   5
         IROOT    1
END
%ESD     GSHESSIAN          "BEN.hess"
         ESHESSIAN          "BEN_S1.hess"
         DOHT               TRUE
END
* XYZFILE 0 1 BEN.xyz
```

As you can see the FC intensity is less than 1% of the HT intensity here, so the need to include HT effect.

Energy	TotalSpectrum	IntensityFC	IntensityHT
10807.078728	2.545915e-02	2.067393e-07	2.545894e-02
10828.022679	2.550974e-02	2.071508e-07	2.550954e-02
10848.966630	2.556034e-02	2.075624e-07	2.556013e-02
...			

It is important to say that, in theory, the absorbance intensity values correspond to the experimental ε (in L mol cm^{-1}), and they are dependent on the spectral lineshape.

As we see, even the defaults produce a close spectrum to experiment and it can become much better using better approximations.
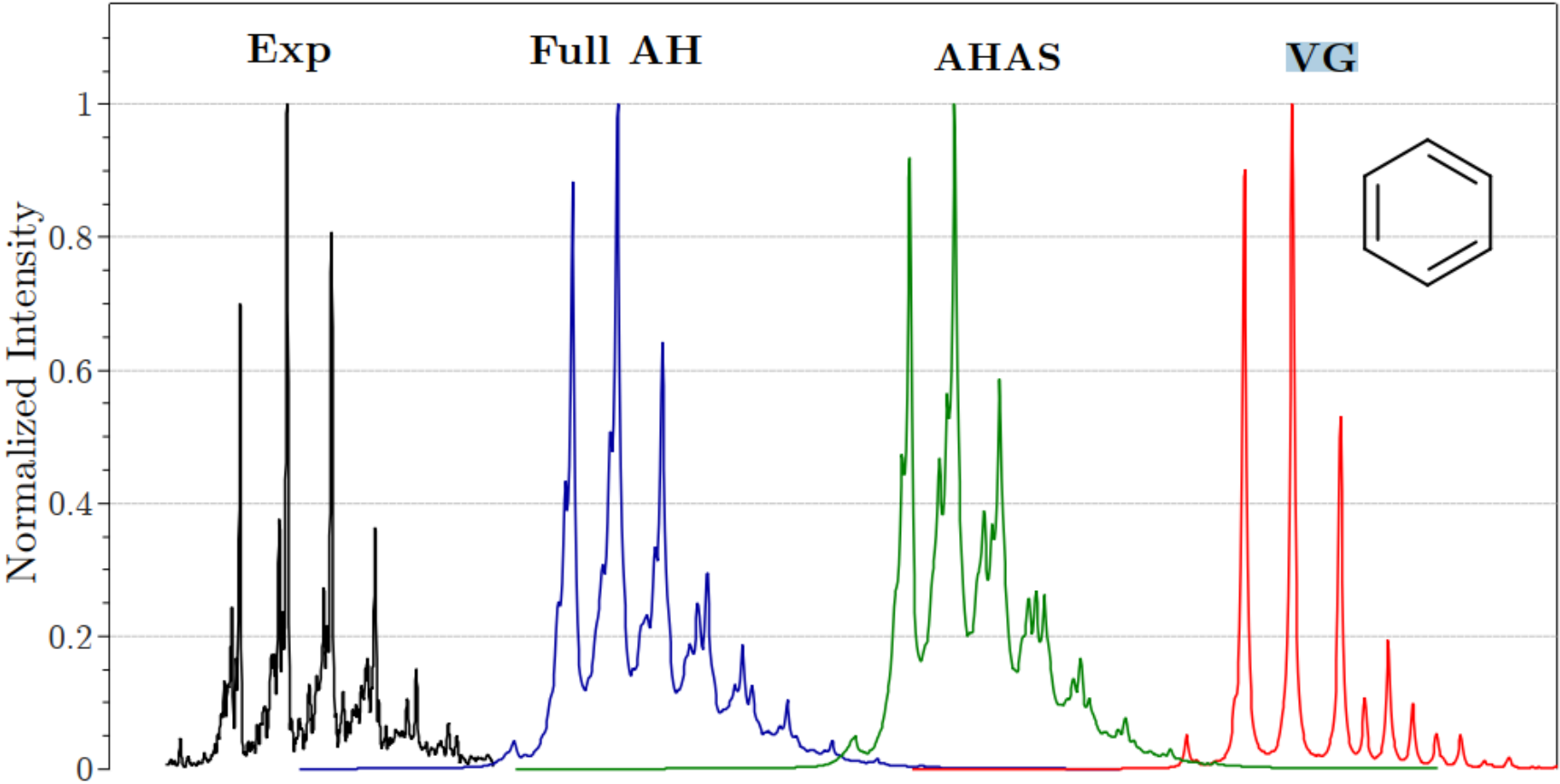

Figure 8.39: Experimental absorption spectrum for benzene (black on the left) and some predicted using **ORCA_ESD** at various PES approximations.

34

Thank you for your attention