

## -Raman Scattering practice

Calculate the static Raman spectrum for H<sub>2</sub>CO molecule at RHF/STO-3G level of theory as follows. 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:

```
! RHF STO-3G TightSCF SmallPrint
! Opt NumFreq
%elprop Polar 1
end
* xyz 0 1
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
*
```

After the calculation is finished (at this point the cursor in windows terminal will go to the next line, also all the .tmp files in the folder of the running job will be erased), we check for the normal termination of the run and start analysing/visualizing the results:

- We can see in the output that 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 (-)>>>

```

- Under the title “RAMAN SPECTRUM” we can find the activities (in Å<sup>4</sup>/AMU) and the Raman depolarization ratios:

```

-----
RAMAN SPECTRUM
-----

```

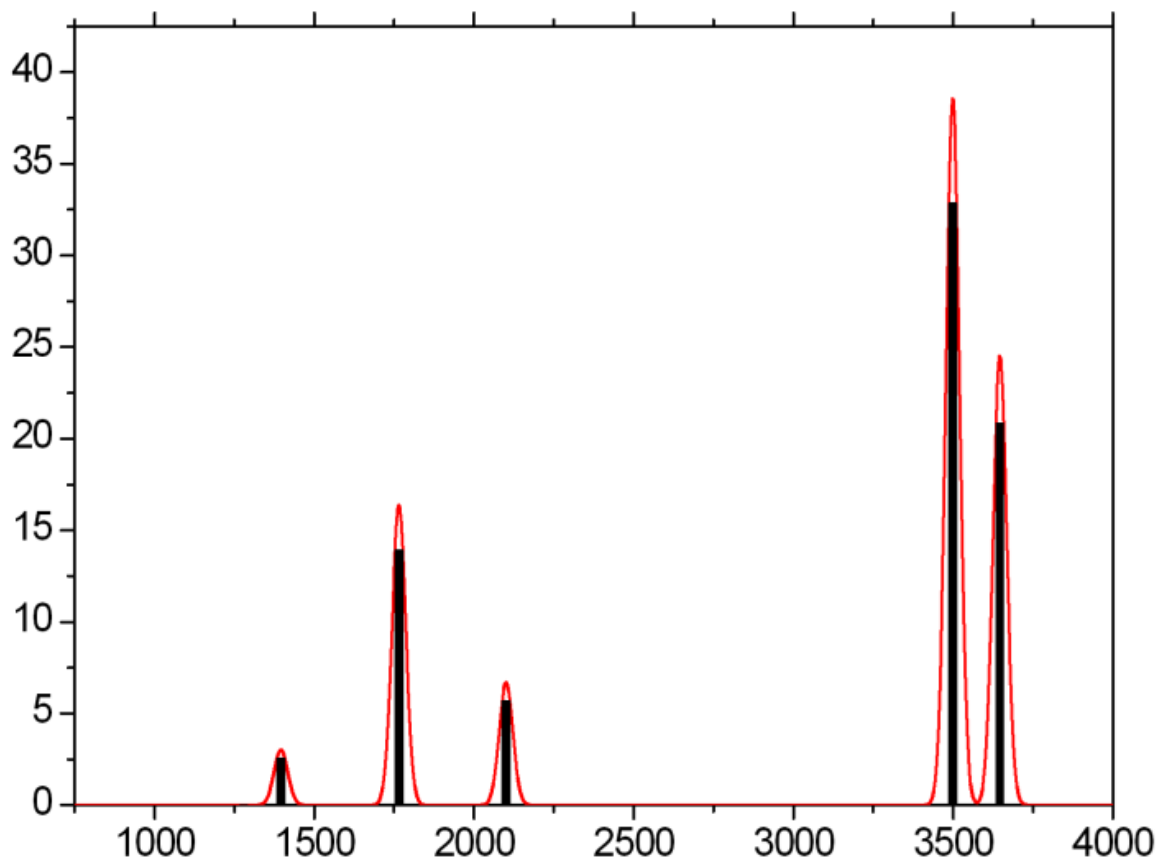
Mode	freq (cm <sup>**</sup> -1)	Activity	Depolarization
6:	1277.66	0.000000	0.000000
7:	1397.45	0.000000	0.000000
8:	1767.01	16.386770	0.707350
9:	2099.21	6.702060	0.075705
10:	3499.49	38.647287	0.186526
11:	3645.45	0.000000	0.000000

```

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

```

- We can 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).

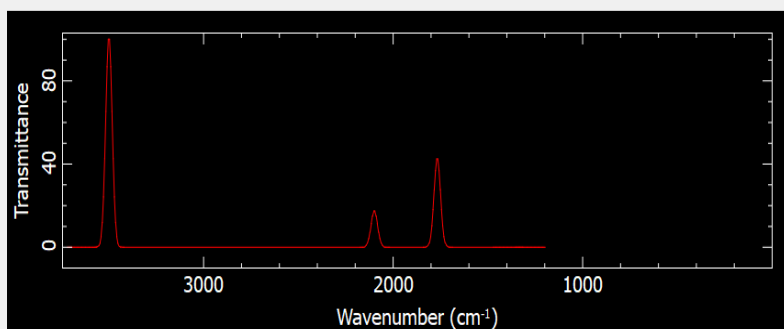


- We can also use Avogadro to visualize the Raman spectrum based on the steps below:

The screenshot shows the Avogadro software interface. On the left is a 3D ball-and-stick model of a molecule with green arrows indicating vibrational displacement. On the right is the 'Vibrations' panel, which contains a table of vibrational modes and a 'Show Spectra...' button highlighted with a red box.

$\nu$ (cm <sup>-1</sup> )	I (km/mol)	Activity
1277.66	6.411	0.000
1397.45	29.586	0.000
1767.01	4.193	16.387
2099.21	8.425	6.702
3499.49	1.793	38.647
3645.45	19.989	0.000

Animation controls include: Amplitude: [slider],  Normalize displacements,  Display force vectors,  Animation speed set by frequency, Start Animation, and Pause.



1277.66	0.000000
1397.45	0.000000
1767.01	0.424008
2099.21	0.173416
3499.49	1.000000
3645.45	0.000000

Raman Load data... **Advanced <<** 2 Close

Appearance Export Image Infrared Spectra Settings **Raman Settings** 3

Y Axis Units: Transmittance

Intensities

Temperature: 298.15 K Laser Wavenumber: 9381.50 cm<sup>-1</sup>

Scaling Type: Linear Line Shape: Gaussian

Scale Factor: 1.0000

Peak Width: 40.0

Points per Peak: 25  Label peaks Threshold: 0.00



Export Data  
Export Spectra Data

# -UV-Visible Spectroscopy Practice

predict the absorption spectrum for COH<sub>2</sub>, using the following input file, 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 calculation is finished (at this point the cursor in windows terminal will go to the next line, also all the .tmp files in the folder of the running job will be erased), we check for the normal termination of the run and start analysing/visualizing the results:

- We can find the excitation energies, the single orbital transitions involved and their contribution under “TD-DFT/TDA EXCITED STATES (SINGLET)” in the output:

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

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)

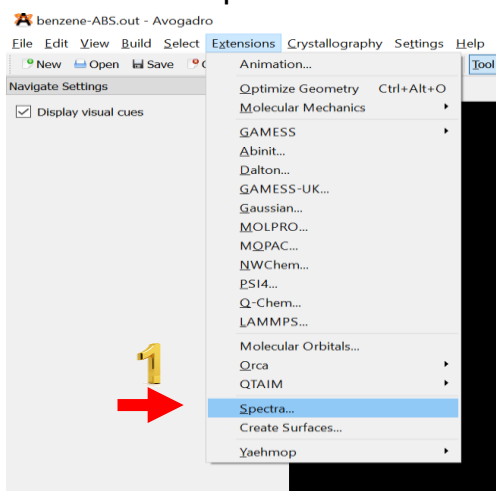
STATE 6: E= 0.408972 au     11.129 eV      89758.9 cm**1 <S**2> = 0.000000
7a -> 11a : 0.996262 (c= 0.99812904)

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 (cm <sup>-1</sup> )	Wavelength (nm)	fosc	T2 (au**2)	TX (au)	TY (au)	TZ (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:



- 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\myexercise\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)

```

```

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\myexercise\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
       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  $\rightarrow$  8a

