Texas A&M HPRC Short Course Series

Quantum Mechanics Simulations of Spectra

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High Performance
Research Computing
DIVISION OF RESEARCH

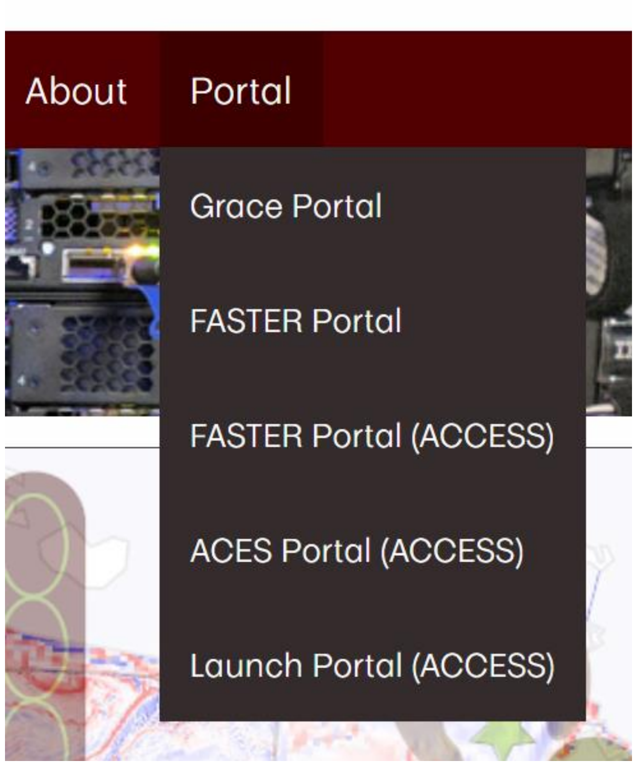
Outline

1. **Grace Basic**
    - File uploading/downloading
    - VNC: GaussView
2. **Theory and practice**
    - IR/Raman
    - UV/Vis
    - NMR
3. **Future suggestion**

Grace Portal

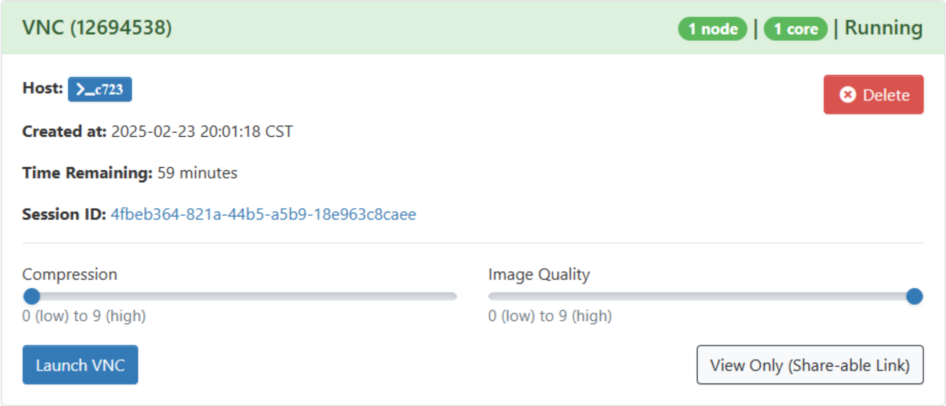
- **Grace: https://hprc.tamu.edu/**

- **OnDemand**
    - Files
    - Clusters:
      ```
      $ cd $SCRATCH
      $ cp -r /scratch/training/QM_spectra/ ./
      ```
    - Interactive Apps -> VNC



Grace Portal

- **OnDemand**
  - Interactive Apps -> VNC
  - VNC: CPU only



VNC (12694538)

1 node | 1 core | Running

Host: c723

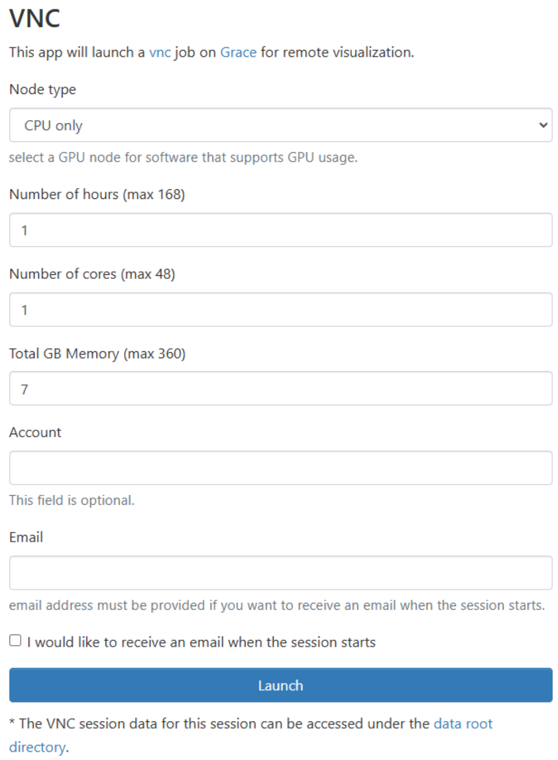
Created at: 2025-02-23 20:01:18 CST

Time Remaining: 59 minutes

Session ID: 4fbeb364-821a-44b5-a5b9-18e963c8caee

Compression: 0 (low) to 9 (high)

Image Quality: 0 (low) to 9 (high)



VNC

This app will launch a vnc job on Grace for remote visualization.

Node type: CPU only

select a GPU node for software that supports GPU usage.

Number of hours (max 168): 1

Number of cores (max 48): 1

Total GB Memory (max 360): 7

Account:

This field is optional.

Email:

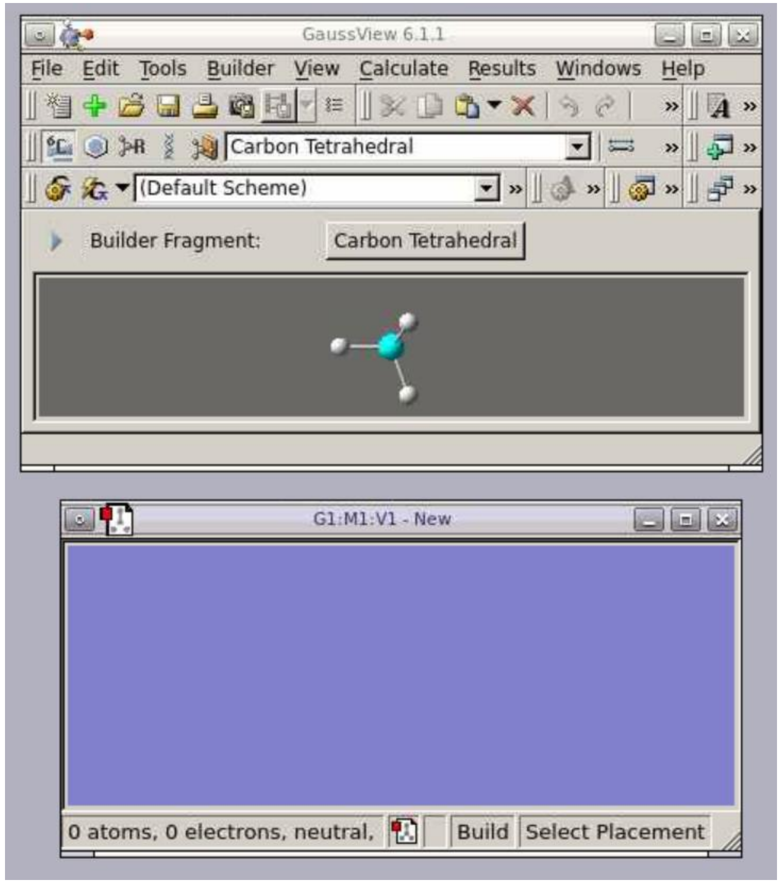
email address must be provided if you want to receive an email when the session starts.

☐ I would like to receive an email when the session starts

* The VNC session data for this session can be accessed under the data root directory.

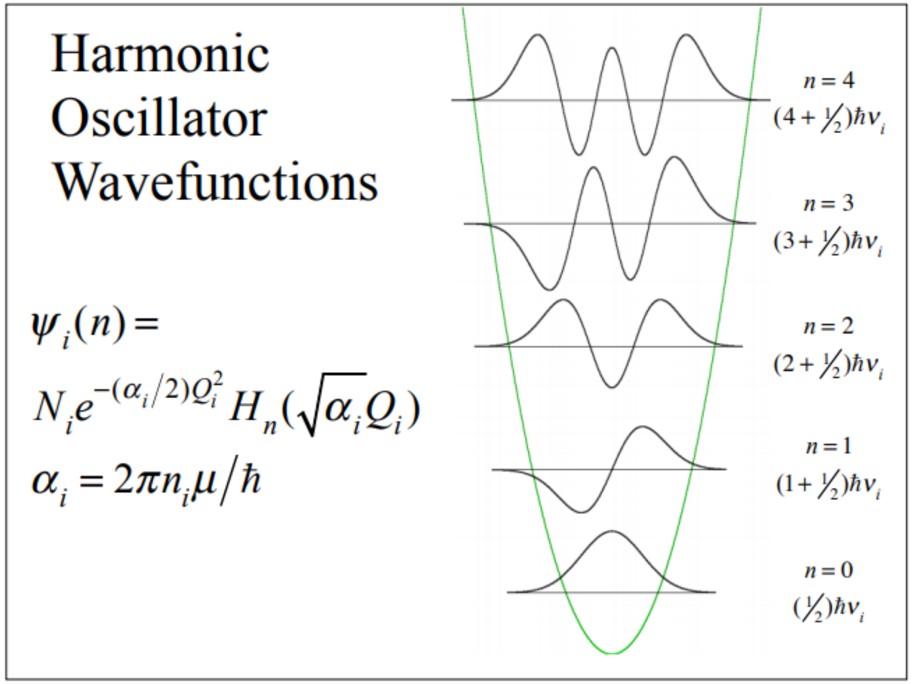
Grace Portal

- **VNC: GaussView**
  - $ ml Gaussian/g16_C01
  - $ gv &



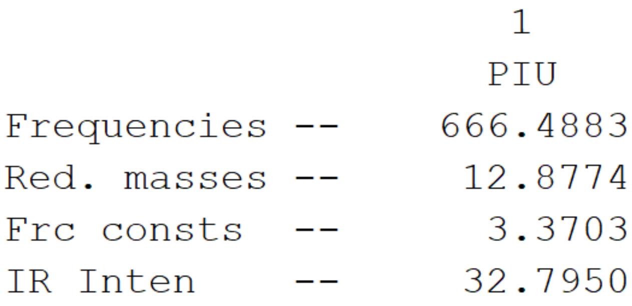
IR Spectra

- Frequency calculations are valid only at stationary points on the potential energy surface: must be performed on optimized structures.
- Must use the same method and basis set as produced the optimized geometry.
- Only fundamental transitions are predicted, so no overtones and combination bands are included.

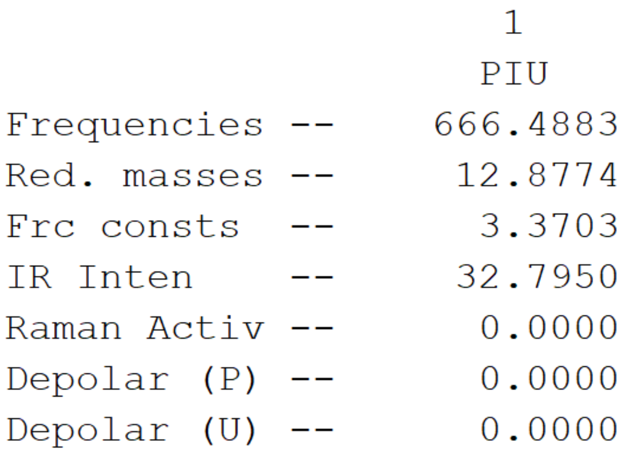


IR Spectra

- Freq calculations: Energy derivative with respect to …
  - Frequencies (Force constants): nuclear position & nuclear position
  - Infrared intensities: nuclear position & electric field
  - Raman intensities: nuclear position & electric field & electric field



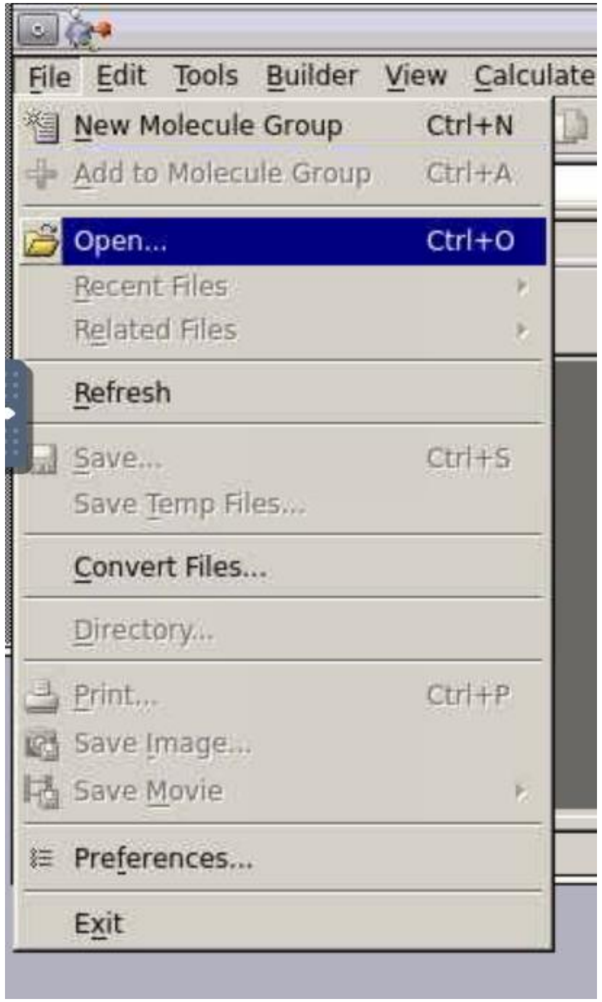
```
                              1
                             PIU
Frequencies --          666.4883
Red. masses --           12.8774
Frc consts  --            3.3703
IR Inten    --           32.7950
```



```
                              1
                             PIU
Frequencies --          666.4883
Red. masses --           12.8774
Frc consts  --            3.3703
IR Inten    --           32.7950
Raman Activ --            0.0000
Depolar (P) --            0.0000
Depolar (U) --            0.0000
```

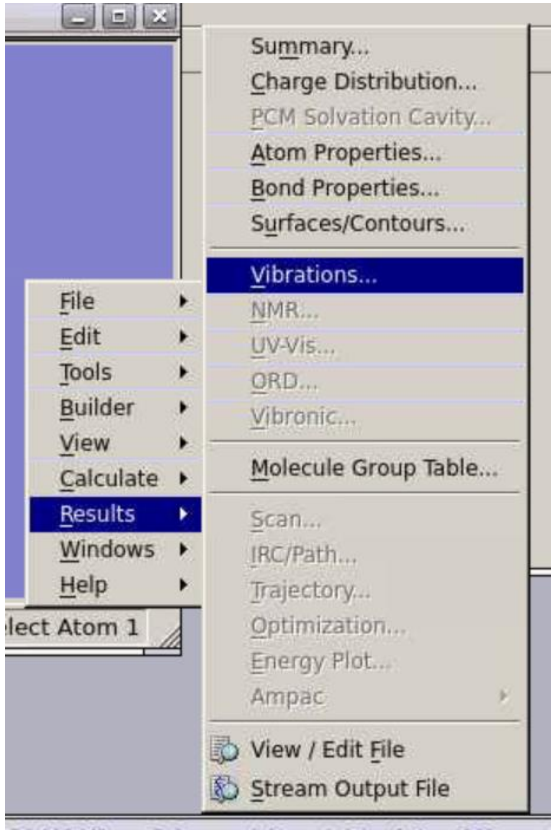
IR Spectra

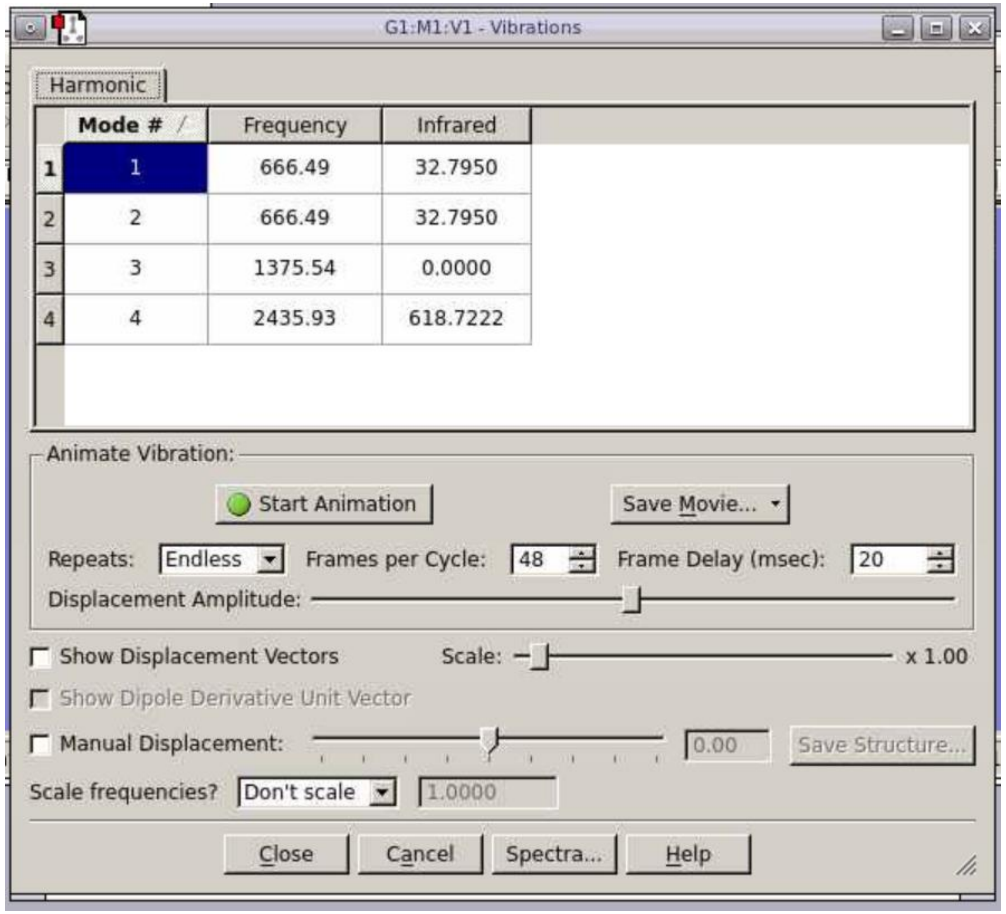
- Example: CO_2
- Submit Job
  - Modify g16.sub (“task=“)
  - $ sbatch g16.sub
- GaussView: File -> Open…



IR Spectra

- Results -> Vibrations …





	Mode #	Frequency	Infrared
1	1	666.49	32.7950
2	2	666.49	32.7950
3	3	1375.54	0.0000
4	4	2435.93	618.7222

Animate Vibration:

Repeats: Endless

Frames per Cycle: 48

Frame Delay (msec): 20

Displacement Amplitude:

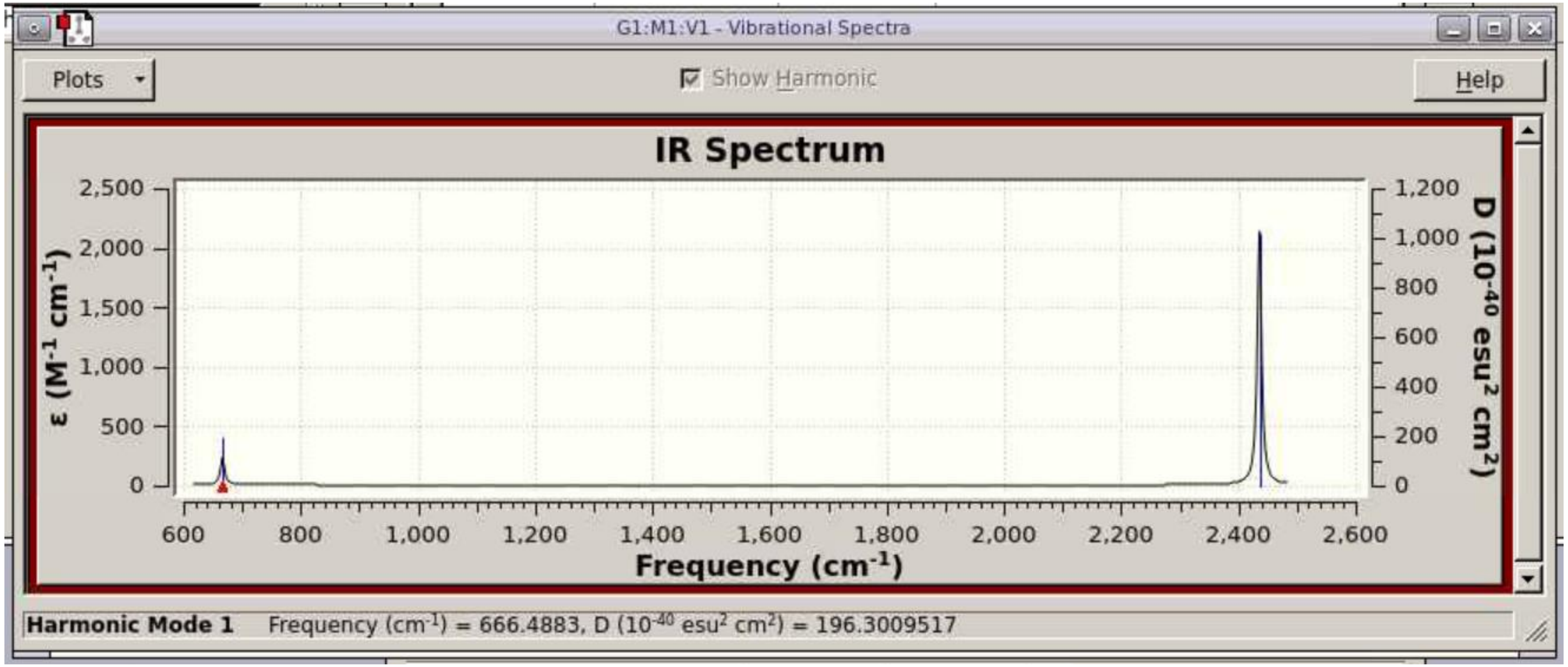
☐ Show Displacement Vectors Scale: x 1.00

☐ Show Dipole Derivative Unit Vector

☐ Manual Displacement: 0.00

Scale frequencies? Don't scale 1.0000

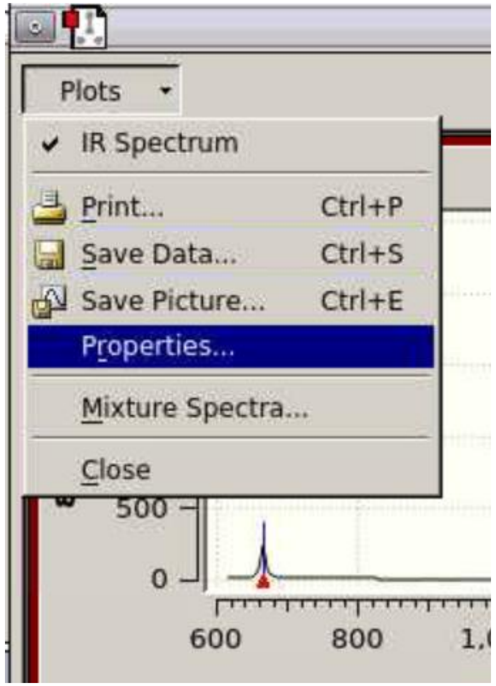
IR Spectra

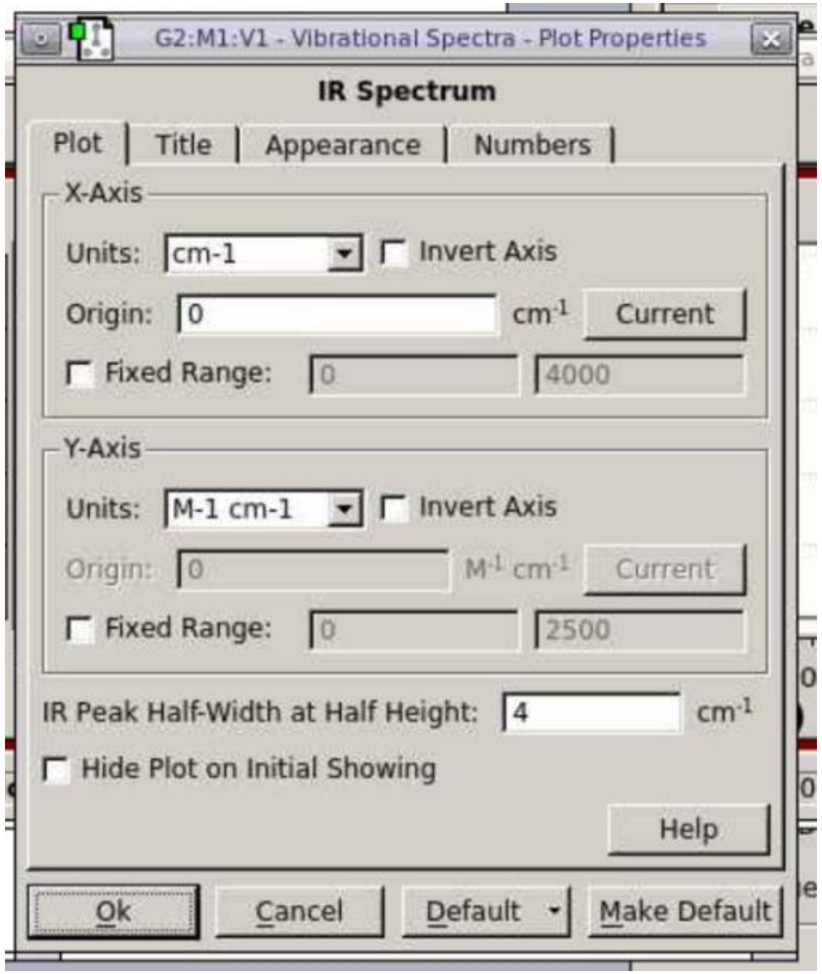


Harmonic Mode 1 Frequency (cm^{-1}) = 666.4883, D (10^{-40} esu^2 cm^2) = 196.3009517

IR Spectra

- Plots -> Properties…
- “Invert Axis”
- Half-Width: 50cm^{-1}





IR Spectrum

X-Axis

Units: cm-1 ☐ Invert Axis

Origin: 0 cm^{-1}

☐ Fixed Range: 0 4000

Y-Axis

Units: M-1 cm-1 ☐ Invert Axis

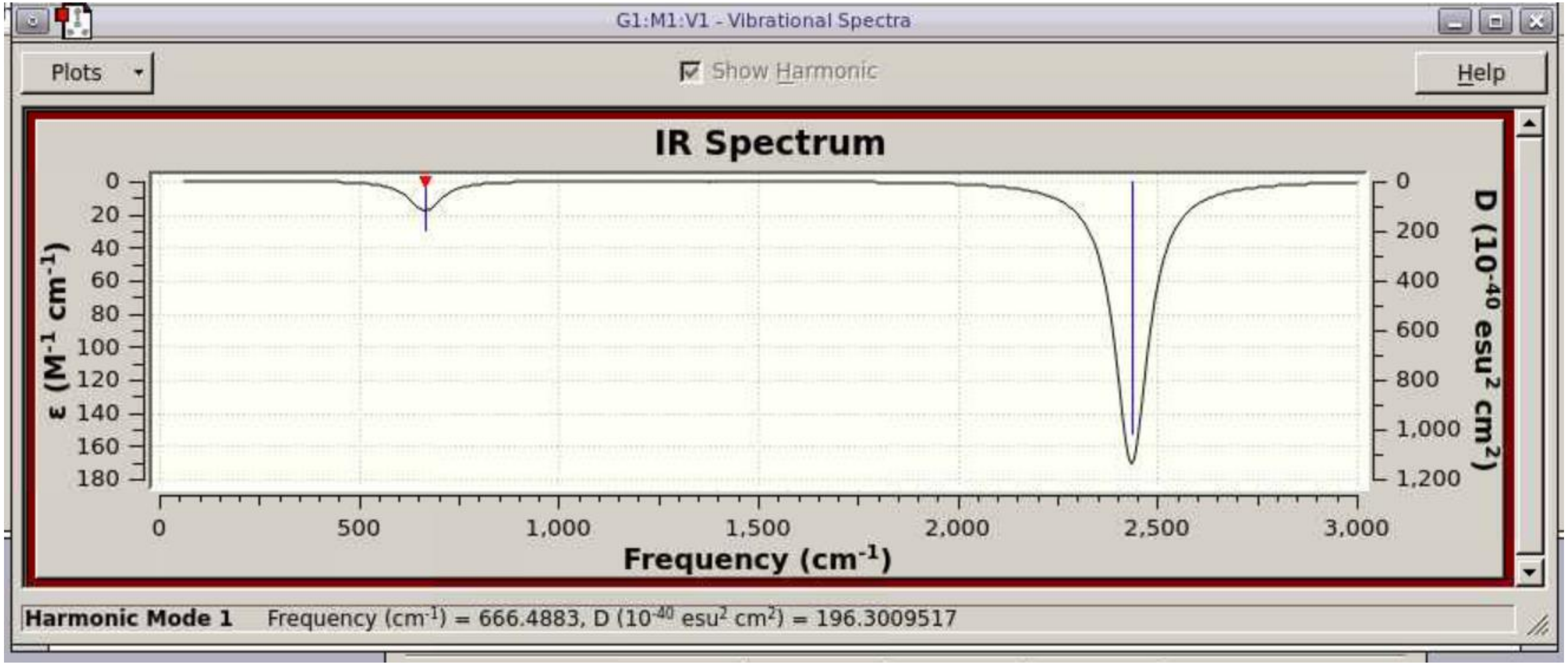
Origin: 0 M^{-1} cm^{-1}

☐ Fixed Range: 0 2500

IR Peak Half-Width at Half Height: 4 cm^{-1}

☐ Hide Plot on Initial Showing

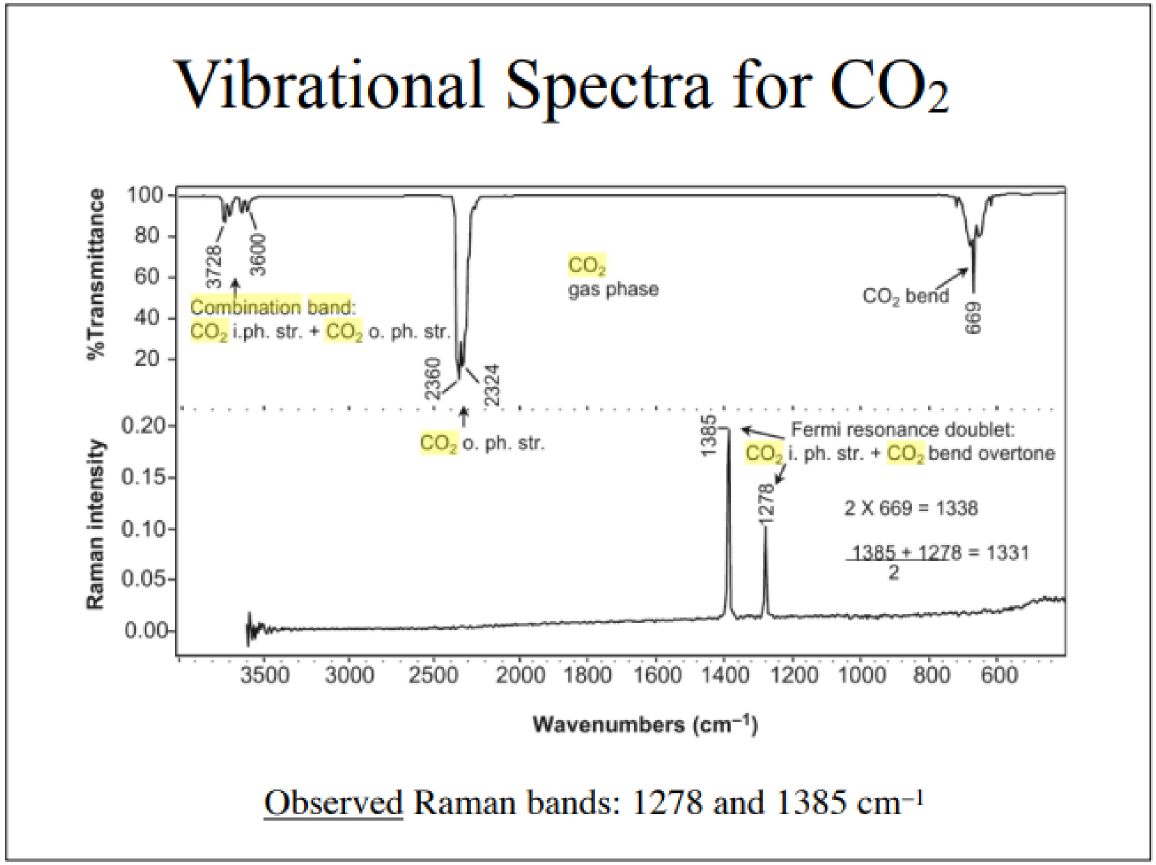
IR Spectra



Harmonic Mode 1 Frequency (cm^{-1}) = 666.4883, D (10^{-40} esu^2 cm^2) = 196.3009517

CO_2 Spectra

- IR: 669, 2324cm^{-1}, 2360cm^{-1}
- Raman: 1278cm^{-1}, 1385cm^{-1}
- Combination: 3600cm^{-1}, 3728cm^{-1}



Vibrational Spectra for CO_2

Observed Raman bands: 1278 and 1385 cm^{-1}

Freq

- The vibrational frequencies produced by ab initio programs are often multiplied by a scale factor to better match experimental vibrational frequencies
  - calculations are approximate
  - potential energy surface is not harmonic
  - https://comp.chem.umn.edu/freqscale/index.html

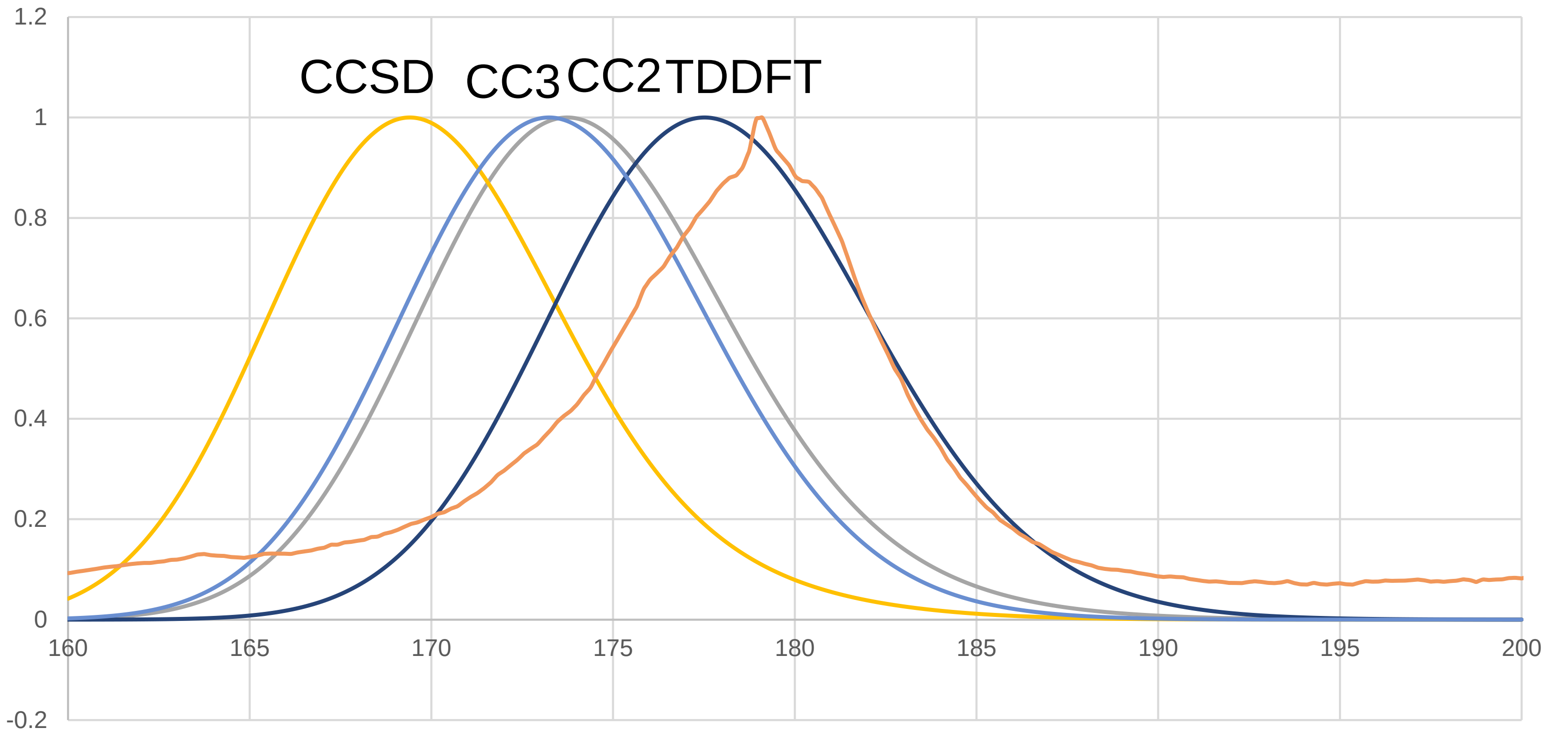
- Isotope
  - Deuterium

```
0 1
H(iso=2) -3.37789 0.83512 -0.00000
H(iso=2) -2.66989 0.83512 -0.00000
```

UV/Vis Spectra

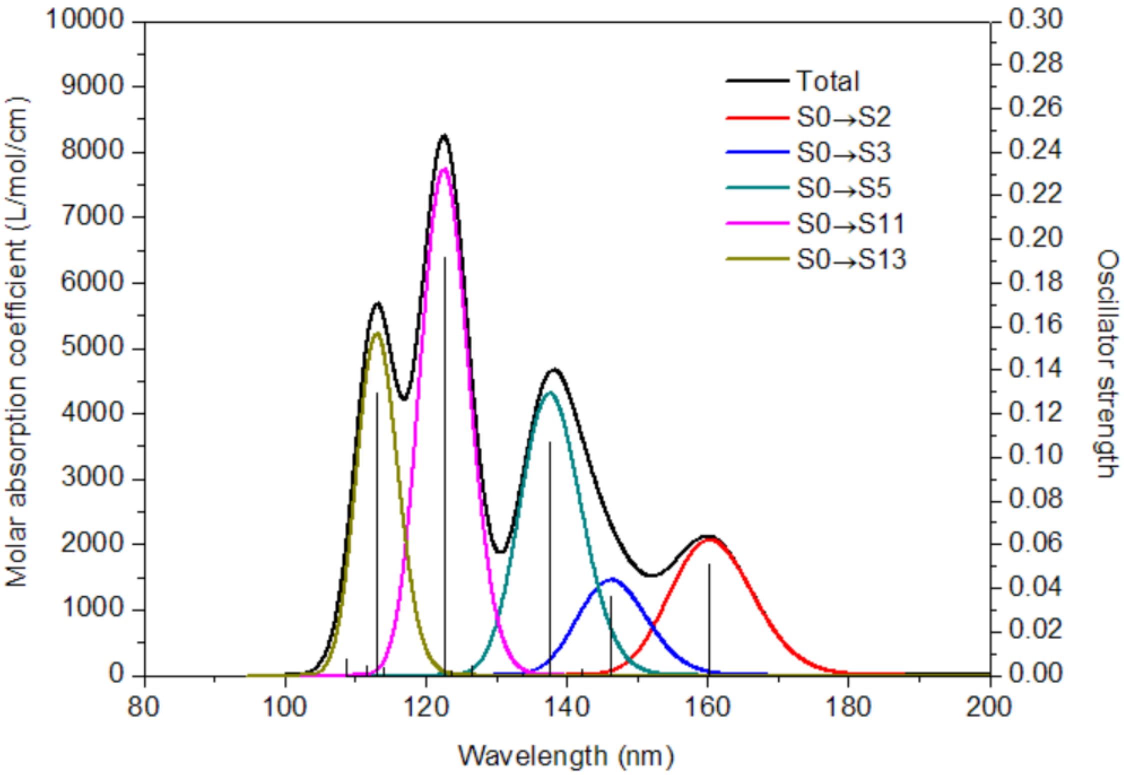
- ZINDO: semi-empirical
- TD-DFT: time-dependent DFT
- CIS: configuration interaction singles: same as TD-HF with TDA approximation
- EOM-CC (equation-of-motion coupled cluster):
  EOM-CCS, EOM-CC2, EOM-CCSD, EOM-CC3, EOM-CCSDT, …

UV/Vis Spectra



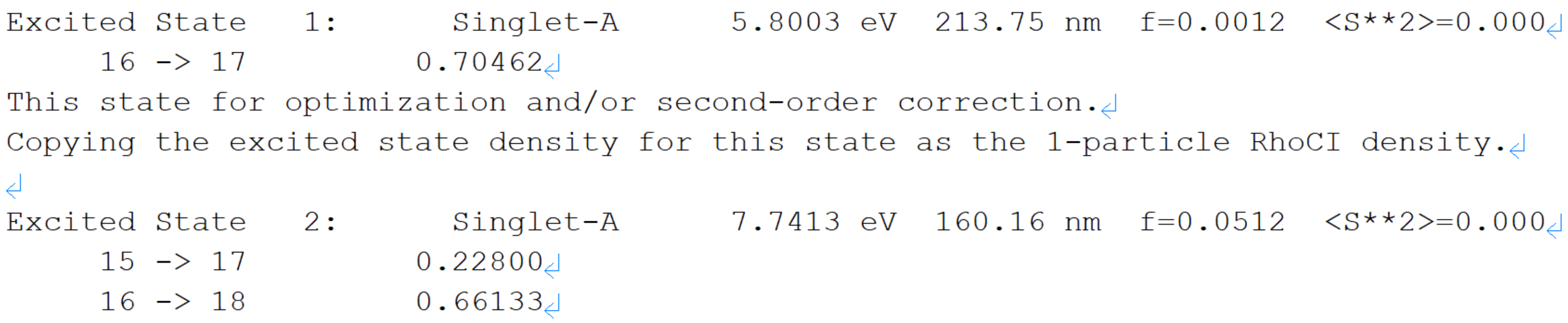
UV/Vis Spectra via TD-DFT

- Keyword: td
- Peak Position: Excitation energies
- Peak Height: Oscillator strength



UV/Vis Spectra via TD-DFT

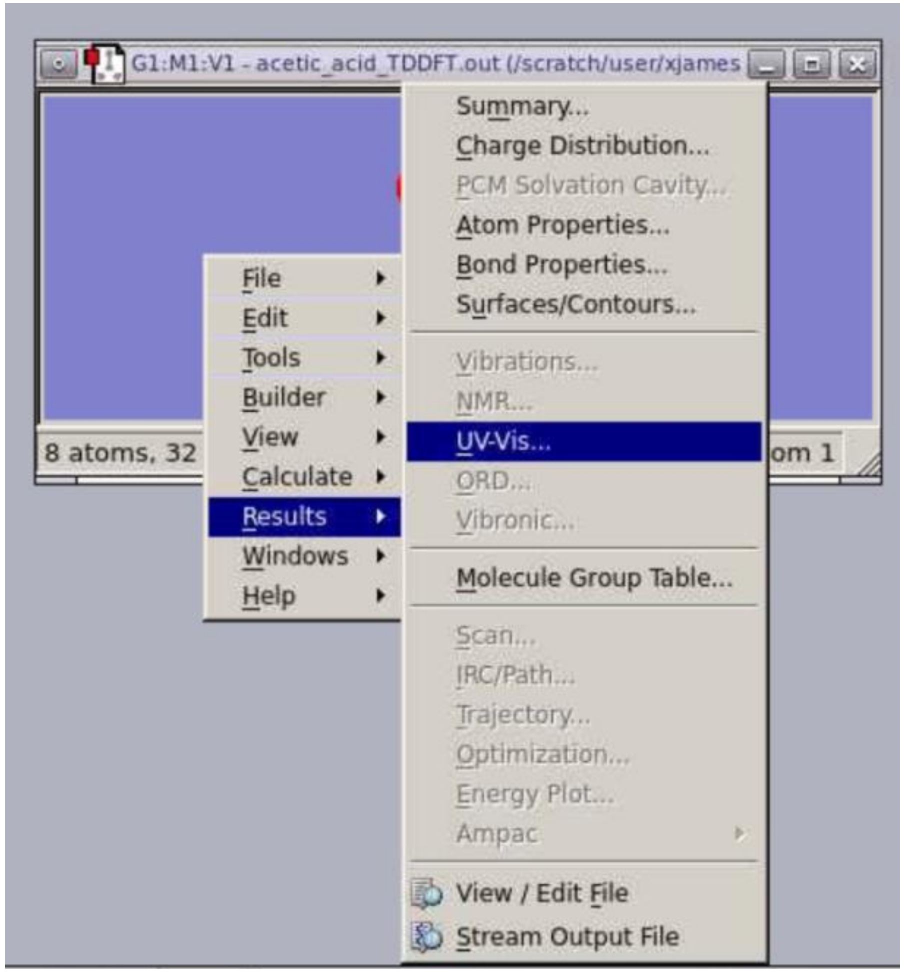
- Position:
- Height: Oscillator strength



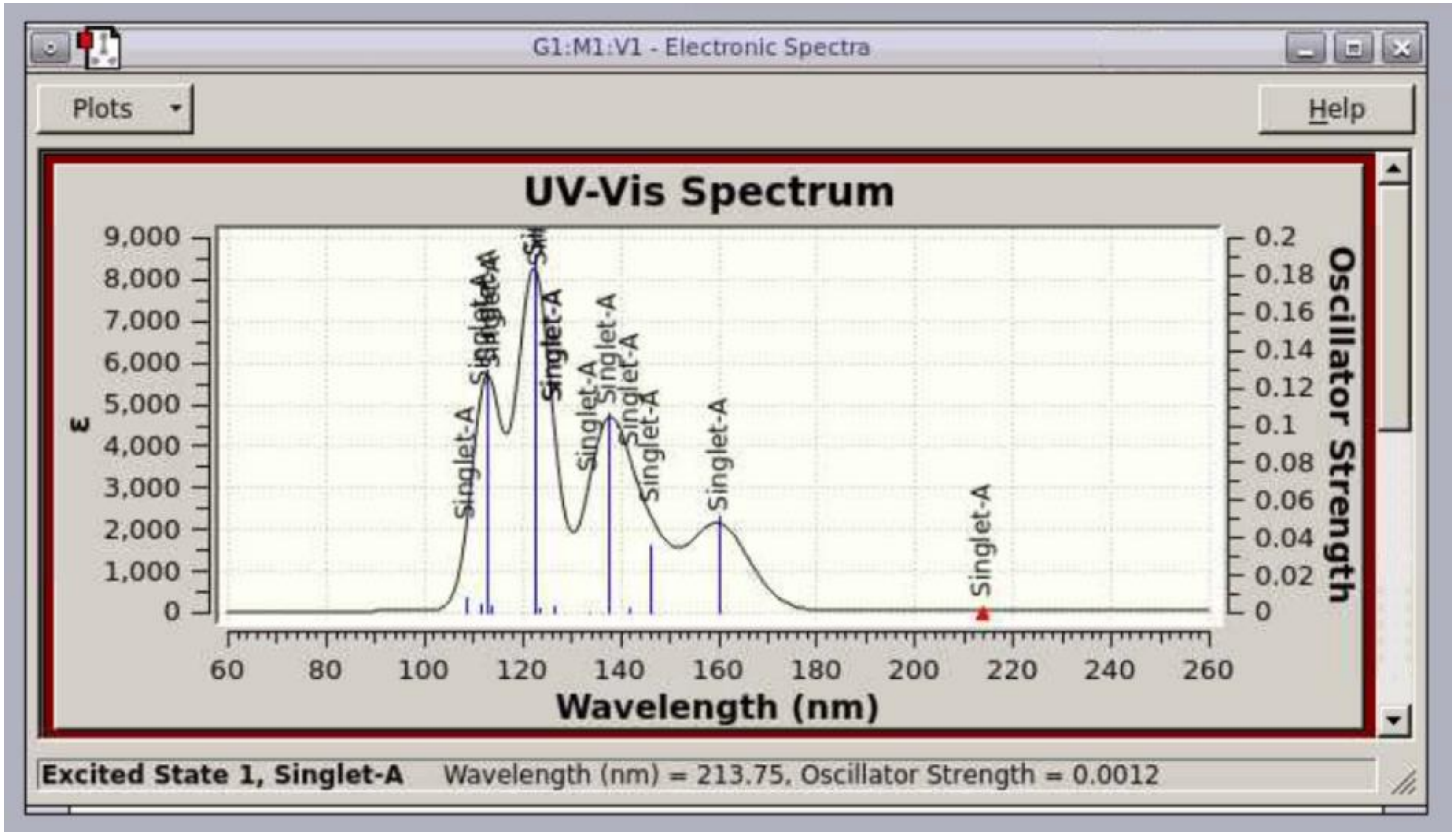
```
Excited State   1:      Singlet-A      5.8003 eV  213.75 nm  f=0.0012  <S**2>=0.000
     16 -> 17         0.70462
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   2:      Singlet-A      7.7413 eV  160.16 nm  f=0.0512  <S**2>=0.000
     15 -> 17         0.22800
     16 -> 18         0.66133
```

UV/Vis Spectra via TD-DFT

- Example: acetic acid
- File-> Open…: acetic_acid_TDDFT.out



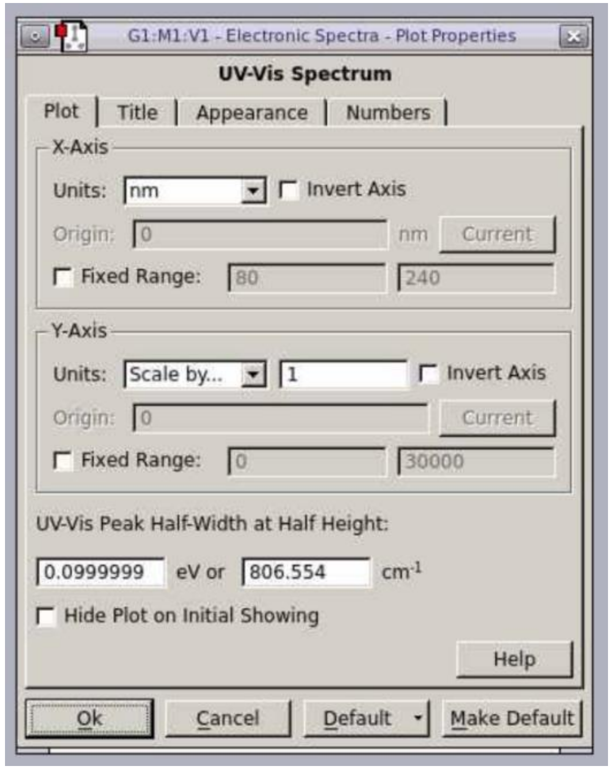
UV/Vis Spectra via TD-DFT



Excited State 1, Singlet-A Wavelength (nm) = 213.75, Oscillator Strength = 0.0012

UV/Vis Spectra via TD-DFT

- Adjust Half-Width at Half Height



X-Axis

Units: nm ☐ Invert Axis

Origin: 0 nm

☐ Fixed Range: 80 240

Y-Axis

Units: Scale by... 1 ☐ Invert Axis

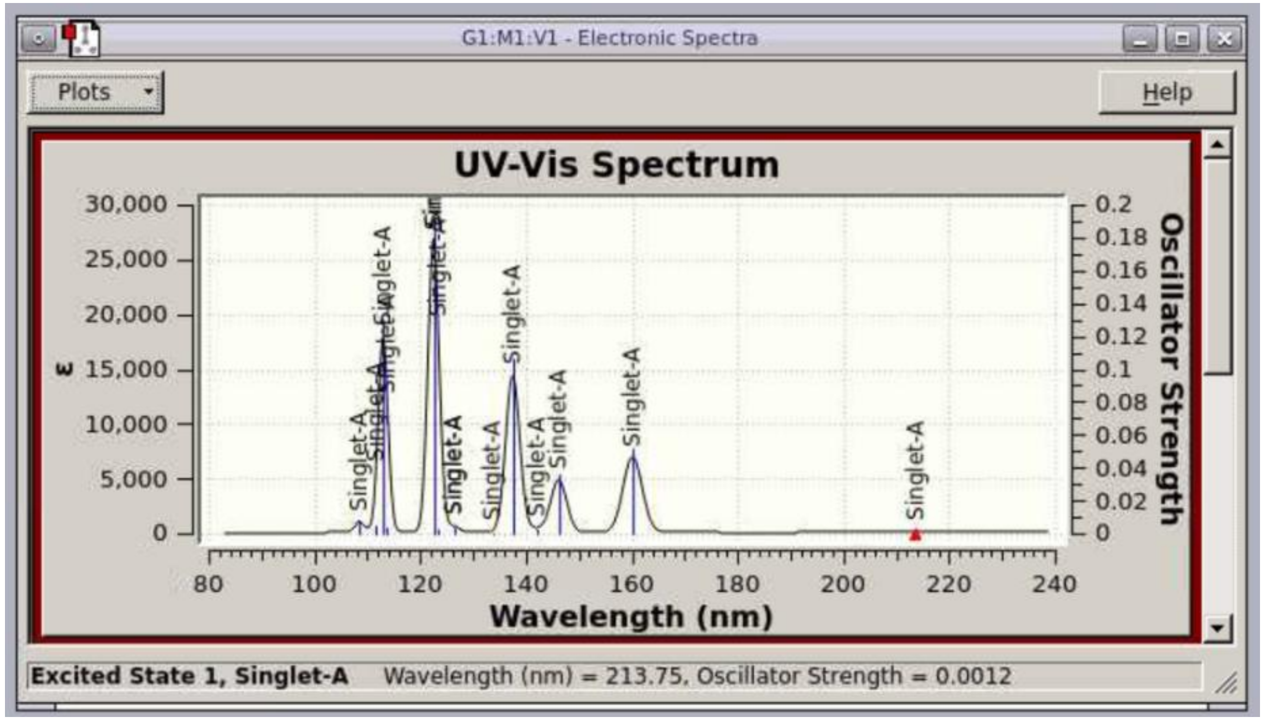
Origin: 0

☐ Fixed Range: 0 30000

UV-Vis Peak Half-Width at Half Height:

0.0999999 eV or 806.554 cm^{-1}

☐ Hide Plot on Initial Showing



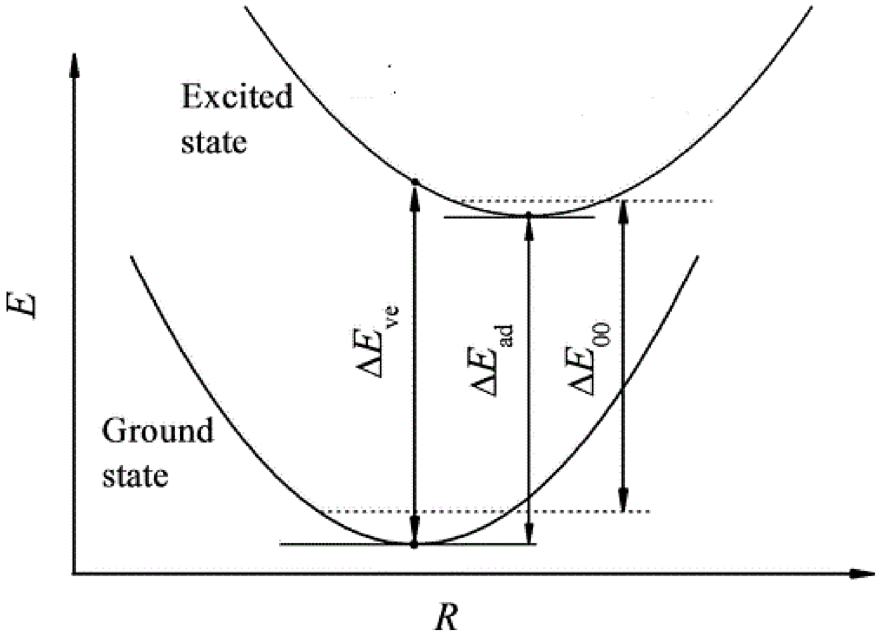
Excited State 1, Singlet-A Wavelength (nm) = 213.75, Oscillator Strength = 0.0012

UV/Vis Spectra via TD-DFT

- Vertical transition energies: the difference between excited state and ground state energies computed on a given geometry.

- Adiabatic energies: the difference of total energies of the ground state and excited state at their respective minima.

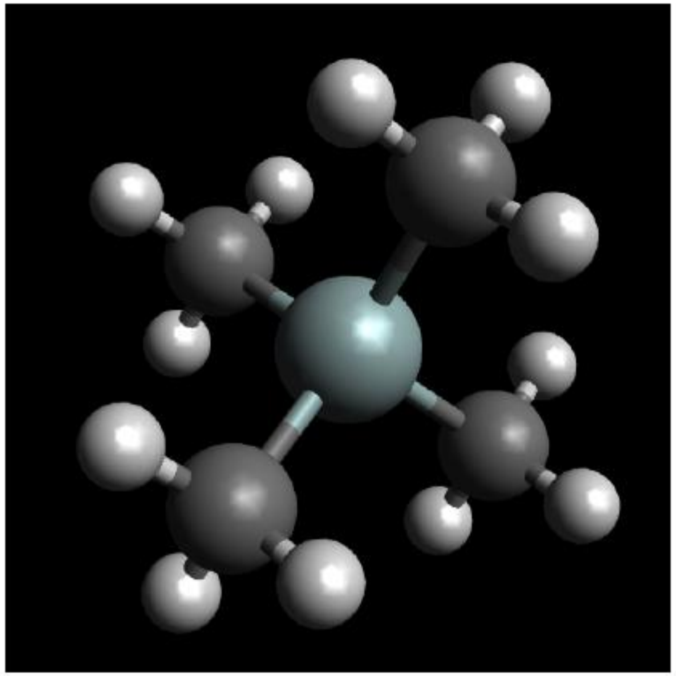
- 0-0 energies: adiabatic energies corrected for zero-point vibrational energies.



NMR Spectra

- Chemical shielding tensor
- Shielding tensor depends on gauge origin if basis set is not complete.
- Chemical (NMR) shifts

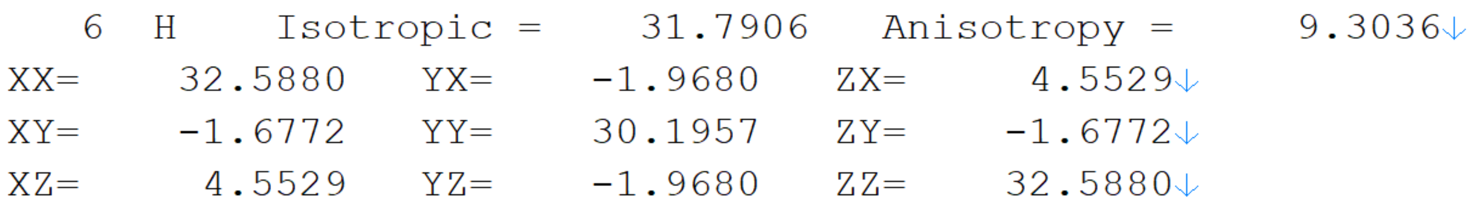
$$\delta = \frac{\sigma_{\text{iso,ref}} - \sigma_{\text{iso}}}{1 - \sigma_{\text{iso,ref}}} \approx \sigma_{\text{iso,ref}} - \sigma_{\text{iso}}$$



TMS: Tetramethylsilane

NMR Spectra

1. Geometry optimization of TMS.
2. Geometry optimization of your molecule.
3. NMR calculations for both TMS and your molecule using same method/basis set.
4. Calculate chemical shifts.



```
     6  H     Isotropic =    31.7906   Anisotropy =      9.3036↓
 XX=     32.5880    YX=     -1.9680    ZX=      4.5529↓
 XY=     -1.6772    YY=     30.1957    ZY=     -1.6772↓
 XZ=      4.5529    YZ=     -1.9680    ZZ=     32.5880↓
```

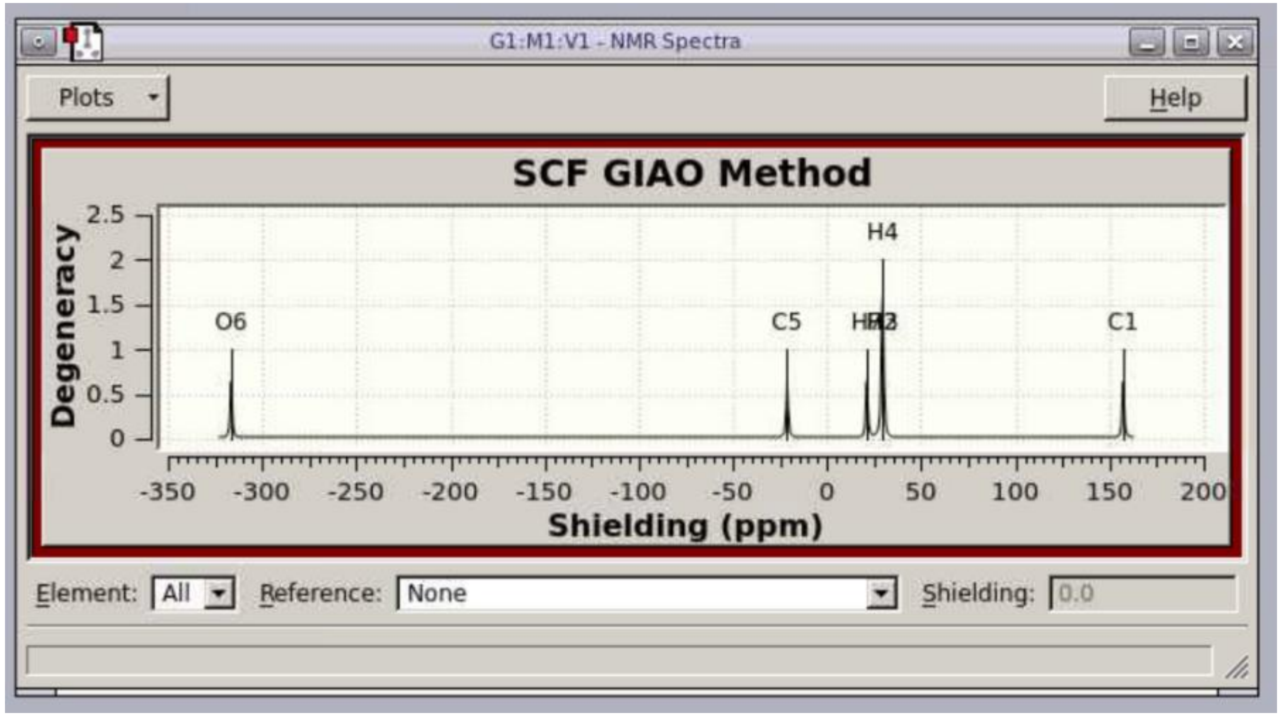
NMR Spectra

- NMR shifts are quite dependent on the conformer you choose. A conformer search and a Boltzmann weighting might be necessary!

- Solvent effect.

NMR Spectra

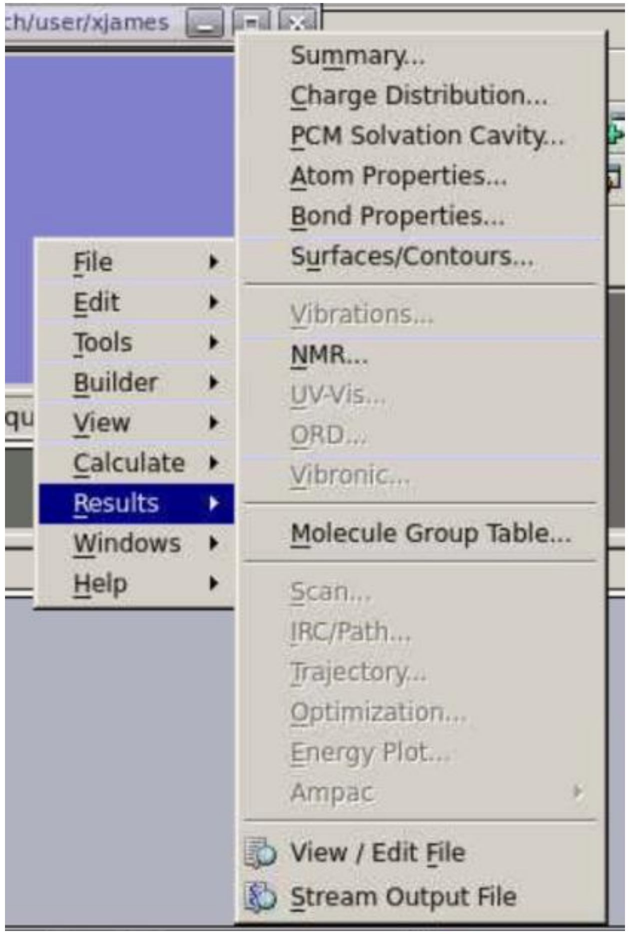
- Example: Acetaldehyde (2.2ppm, 9.8ppm)
- File-> Open…: Acetaldehyde_nmr.out



Element: All

Reference: None

Shielding: 0.0



Future QM Course: Suggestion

- Other Software: ORCA, GAMESS, Psi4, ADF, …
- Analysis:
  - Atomic charges
  - Energy decomposition analysis
  - AIM
  - NBO
  - ONIOM

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