

Simulating Vibrationally-resolved Electronic Spectra Using Gaussian

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This is a tutorial designed to introduce users to simulating vibrationally-resolved electronic spectra utilizing the Gaussian 09 software package (1). Specifically, the simulation of vibrationally-resolved UV-Vis absorption spectra is performed on an anisole molecule. Users are expected to have a foundation in Unix/Linux. See for example our Primer (<http://pogorelov.scs.illinois.edu/tutorials/>)

Note: If time is a constraint, you may use the previously generated output and checkpoint files that accompany this tutorial.

Outline: To generate the vibrationally-resolved UV-Vis absorption spectra, three steps are generally needed:

1. Geometry optimization and calculation of frequencies for the **initial** state.
2. Geometry optimization and calculation of the frequencies for the **final** state.
3. Generation of the vibrationally-resolved UV-Vis absorption spectra.

In the first two steps, we calculate the frequencies and save the frequency information in the checkpoint files, which will be used in step 3 to generate the spectra.

1. **Software.** Available on the SCS cluster Triton: Gaussian (1), GaussView (2), and Vim. Personal computer: xserver (Xming for a Windows) or Terminal (Mac), Origin (3) or other graphing software. This tutorial can be completed on iMacs in the SCS VizLab (151 Noyes Lab) or with personal computers with Windows or Mac OS. Small modifications might be needed when used on other computers.

2. **Starting up.** Open Windows PowerShell (or Mac OS Terminal) window. Connect to Triton with the following command using your SCS login. If connecting outside of campus, connect to the VPN first.

```
> ssh -YC myscs-login@triton.scs.uiuc.edu
```

Make a directory for this tutorial:

```
> mkdir uvvis-spectra-tutorial
```

Change your directory to the new directory you just made:

```
> cd uvvis-spectra-tutorial
```

Start up a session of Gaussian with the following command (subject to the Linux shell your account uses – check by typing `> echo $SHELL`):

if bash shell use:

```
> source /share/apps/gaussian/g09_login.sh
```

if csh shell use:

```
> source /share/apps/gaussian/g09_login.csh
```

Open GaussView with the following command:

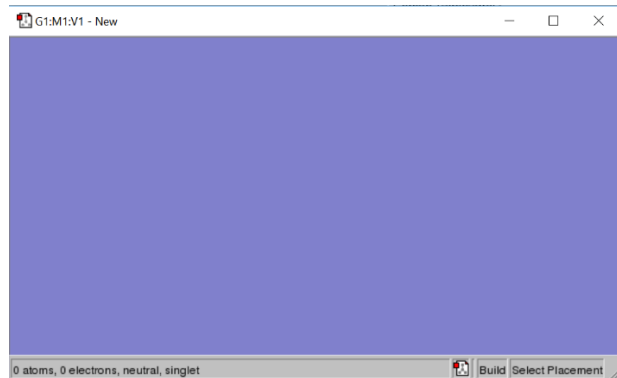
```
> gv
```

Note: You may encounter the following error message:

```
Failed to locate Gaussian scratch directory
```

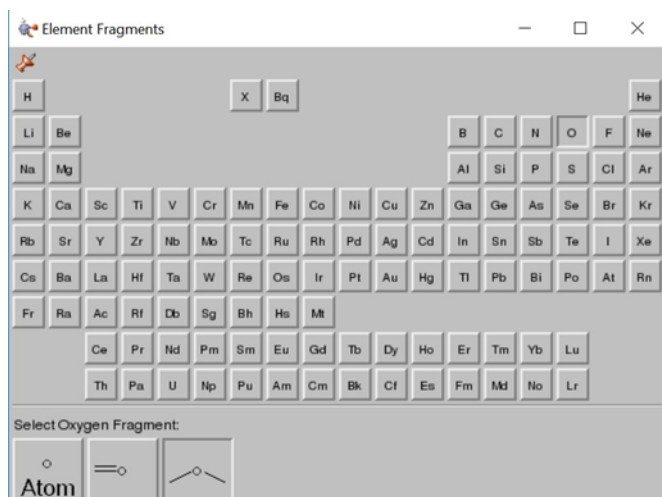
Ignore this error by simply hitting the “OK” button. GaussView should open.

3. Constructing a molecule. Construct your molecule of interest in the blue window (which should initially be blank):

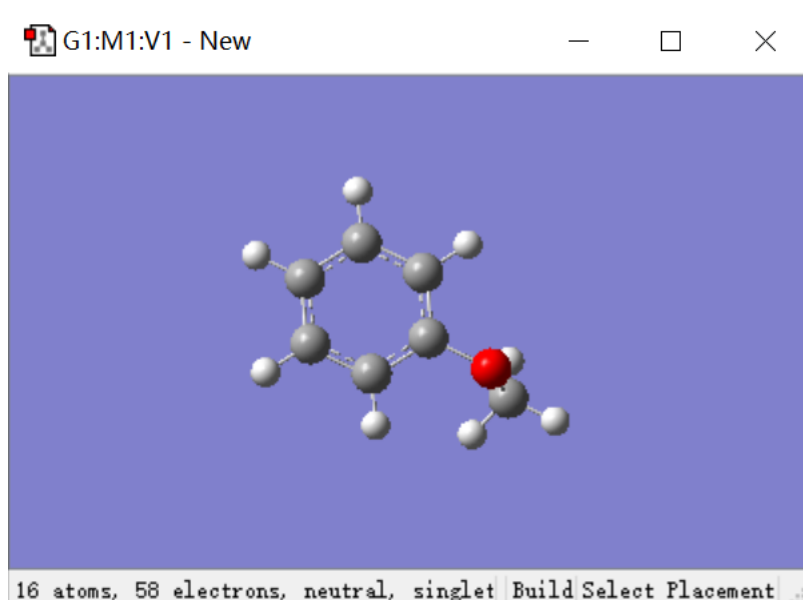


Right click anywhere on the blue window and select “Builder.” Click “Ring fragment.” Right click, select “Builder” again, and then click “Fragment” and select benzene. Click anywhere in the blue window to place the benzene ring.

Now, right click again and select “Builder”. Select “Element Fragment” which should pull up a periodic table. Select the oxygen fragment on the far right. Click on any hydrogen atom of the ring to substitute one of the hydrogens for a hydroxyl group. Then select the carbon fragment on the far right. Click on the hydrogen atom of the hydroxyl group to substitute this hydrogen atom for a methyl group.



Your anisole molecule should look like this:



Note: Anisole has a planar conformation of the methoxy group, for experimental evidence please refer to *Phys. Chem. Chem. Phys.* **2001**, 3, 1407-1410. (4)

4. Optimization and Frequency Calculations of the initial state in the gas phase. Now save the structure you just constructed as the Gaussian input file File -> Save anisole_S0.com. Then quit GaussView and go back to the terminal window.

Type the following command to edit the input file:

```
> vim anisole_S0.com
```

Replace the route section (line 2) with the keywords below.

Vim/vi refresher: move cursor to the line 2, press "dd", to delete the line, press i to enter the Insert mode of vim/vi, copy and paste the line below. Now quit Vim/vi:

press Esc to switch to the **C**ommand mode and press “:” then type wq (for write and quit) and press enter.

```
#p opt Freq=SaveNM B3LYP/6-31G(d) geom=connectivity
```

These keywords will start a Gaussian job which first optimizes the geometry for the initial state and then calculates the frequencies of the optimized geometry. By using the option freq=SaveNM, the frequency information will be saved in the checkpoint file `anisolet_S0.chk`. For this job we choose B3LYP as the functional and 6-31G(d) as the basis set, which should be sufficient to give relatively accurate results. Save the input file and quit Vim.

Submit the calculation to Gaussian with the following command:

```
> submit-g09 -n # -q ib1 anisolet_S0.com
```

Replace the “#” in the command with the number of cores desired to be utilized for the calculation. The number of cores should be consistent to what you specify in the Gaussian input file (`#nprocshared=`). Do not exceed 16.

After submission, check the progress of the calculation with

```
> qstat -u myscs-login
```

Once your SCS username no longer appears, the calculation has completed. Hint: if the command `tail *log` shows a quote then your Gaussian job finished properly.

5. Optimization and Frequency Calculations of the final state in the gas phase. Open GaussView, type “Ctrl + O” and select the Gaussian output file `anisolet_S0.log`. Click “Open” and you will see the optimized structure of the initial state. Type “Ctrl + S” and save this file as a new Gaussian input file `anisolet_S1.com`. Quit GaussView and return to the terminal window.

Type the following command to edit the input file:

```
> vim anisolet_S1.com
```

Replace the route section with the following keywords:

```
#p TD(nstates=6,root=1) B3LYP/6-31G(d) opt Freq=saveNM  
geom=connectivity
```

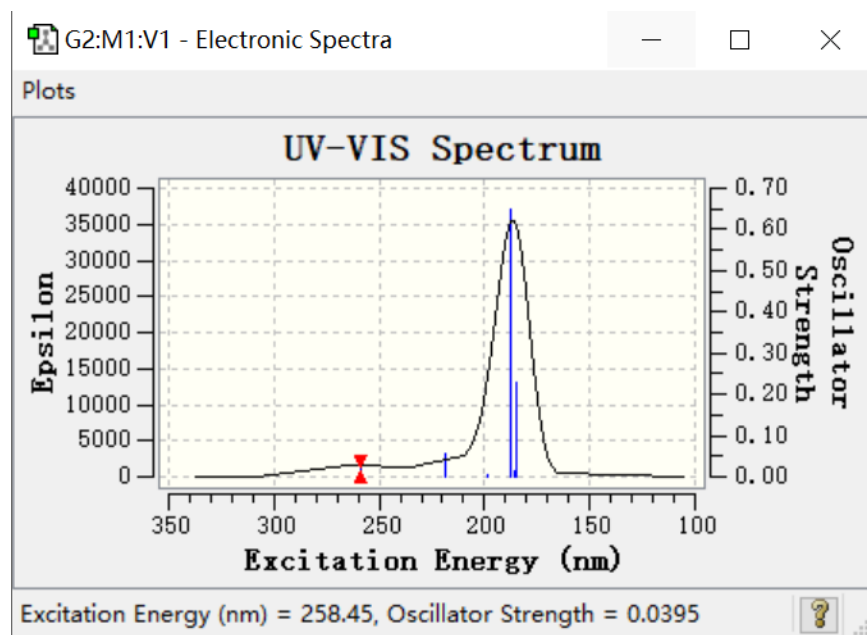
These keywords will start a Gaussian job which first optimizes the geometry for the final state (the first excited state) and then calculates the frequencies of the

optimized geometry. This job is based on the time-dependent density functional theory, which is the keyword TD. The value of root is the excited state of interest. For example, in this job root equals to 1, so the structure of molecule will be optimized for the first excited state. The value of nstates must be larger than the value of root. Generally, you can let nstates = root + 5. Again, the frequency information will be saved in the checkpoint file `anisolet_S1.chk`. We choose B3LYP as the functional and 6-31G(d) as the basis set, which is consistent to what we did for the initial state. Save the input file and quit Vim.

Submit the calculation to Gaussian with the following command:

```
> submit-g09 -n # -q ib1 anisolet_S1.com
```

Once that job is complete, open GaussView, type "Ctrl + O" and select the Gaussian output file `anisolet_S1.log`. Click "Results" and select "UV-VIS", the UV-Vis absorption spectra generated by GaussView is as follows:



The excitation energy of the first excited state is 258.45 nm, and apparently it is not the maximum absorption peak.

6. Generation of the vibrationally-resolved UV-Vis absorption spectra. Quit GaussView and return to the terminal window. Create a Gaussian input file by typing the following command:

```
> vim spectra.com
```

The input file is as follows:

Link 0 Commands

```
%chk=anisoле_S0.chk
```

```
#p geom=AllCheck Freq=(ReadFC,FC,SaveNM) NoSymm
```

```
anisoле_S1.chk
```

Copy this text into your spectra.com input file. Remember to leave a blank line at the end of the input file. The options geom=AllCheck and Freq=ReadFC are described in the Gaussian manual. Basically, they let us extract all necessary data from the checkpoint file given in the line starting by %chk= without doing the frequency calculation again. The option Freq=FC means we will utilize the Franck-Condon method to compute the amplitudes for electronic transitions between the initial and final states. Save the input file and quit Vim.

Submit the calculation to Gaussian with the following command:

```
> submit-g09 -n # -q ib1 spectra.com
```

7. Description of the output and create the spectra. Open the output file spectra.log by typing the following command:

```
> vim spectra.log
```

Search for the words "Final Spectrum", and the spectrum generated by Gaussian is printed as follows:

```
+-----+
| Final Spectrum |
+-----+

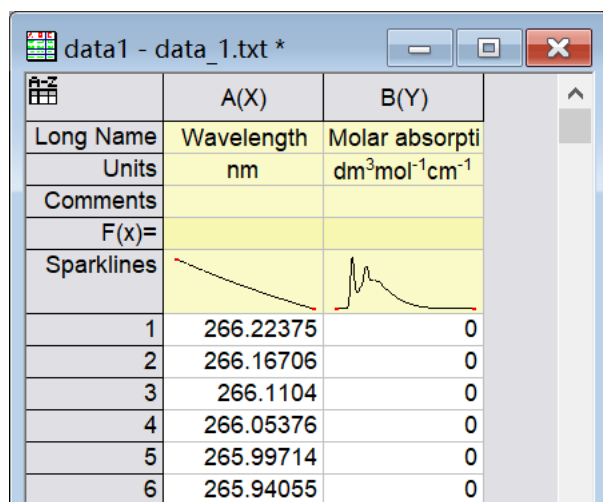
Axis X = Energy (in cm^-1)
Axis Y = Molar absorption coefficient (in dm^3.mol^-1.cm^-1)

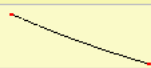
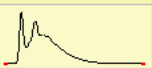
-----
37562.3887    0.000000D+00
37570.3887    0.000000D+00
37578.3887    0.000000D+00
37586.3887    0.000000D+00
37594.3887    0.000000D+00
37602.3887    0.000000D+00
```

The first column is the value of energy in cm^{-1} . The second column is corresponding molar absorption coefficient in $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. You can turn the energy (cm^{-1}) into wavelength (nm) simply by

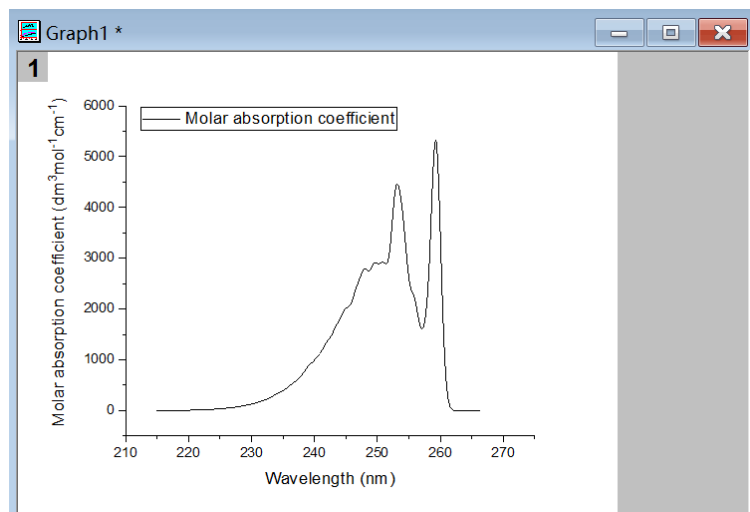
$$\text{wavelength} = \frac{10^7}{\text{energy}}$$

Then you can use Origin or any other graphing software to plot the spectra which is presented as a column in ASCII format. Take Origin for example, copy the two columns of data into Origin:



	A(X)	B(Y)
Long Name	Wavelength	Molar absorpti
Units	nm	$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$
Comments		
F(x)=		
Sparklines		
1	266.22375	0
2	266.16706	0
3	266.1104	0
4	266.05376	0
5	265.99714	0
6	265.94055	0

Type the “Long Name” and “Units” for axis X and axis Y. Then type “Ctrl + A”. Right click, select “Plot”, “Line”, “Line”. The vibrationally-resolved UV-Vis absorption spectra of anisole is as follows:



There are two main absorption peaks at 253 nm and 259 nm. Note that this time there are more details of the $S_0 \rightarrow S_1$ absorption peak which cannot be found in the spectra we generated first because here we take different vibrational states of the initial and final states into account.

Summary. We covered the three steps needed to calculate vibrationally-resolved electronic spectra.

Contact. If you find errors/typos or have suggestions or comments on the material in this tutorial, please contact us at pogorelo@illinois.edu and adelio@illinois.edu. See more tutorials at the Pogorelov Lab website is <http://pogorelov.scs.illinois.edu/>

References.

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2. GaussView, Version 5.0.9, Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, **2016**.
3. Origin, Origin 7.5, OriginLab Corp., Northampton, MA, **2003**.
4. C. G. Eisenhardt, G. Pietraprazia, M. Becucci. The High-Resolution Spectrum of the $S_1 \leftarrow S_0$ Transition of Anisole. *Phys. Chem. Chem. Phys.* **2001**, 3, 1407-1410.