

Running rovibrational calculations in PGOPHER

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All you need to run PGOPHER on a Windows machine is the executable file sourced from [here](#).

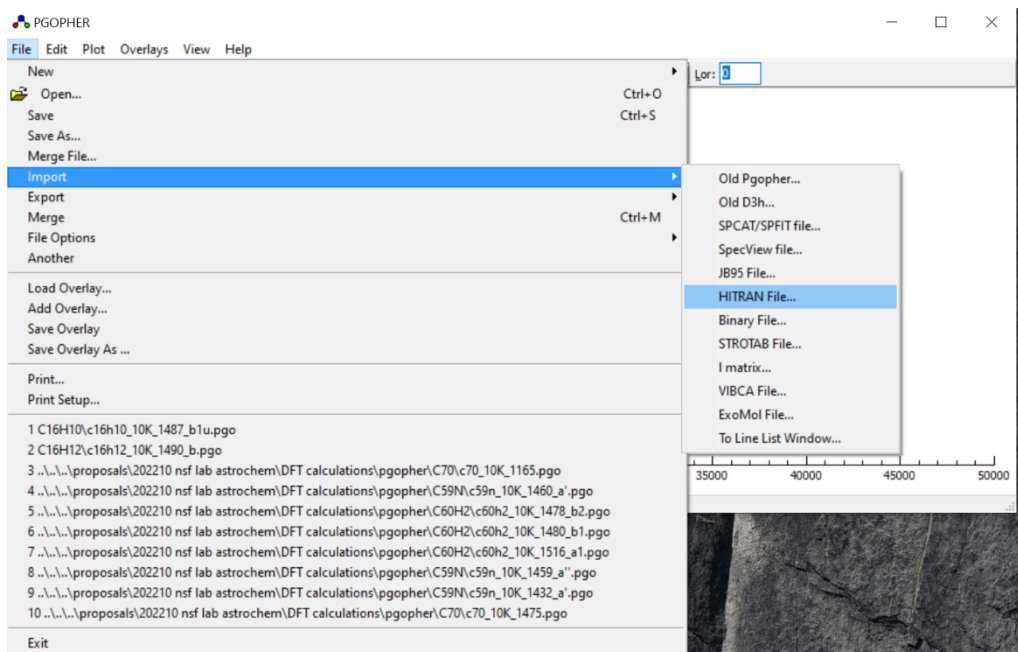
PGOPHER can do a lot of things, and there is a lot of detailed documentation available from the dedicated website [here](#), as well as various online and published resources including:

- The original PGOPHER [paper](#) in the Journal of Quantitative Spectroscopy and Radiative Transfer. More details than you could possibly want.
- Here's a [recent nice paper](#) from folks at PNNL walking through some specific examples of PGOPHER simulations for both high- and low-symmetry molecules.
- [Paper 1](#) and [Paper 2](#) on using PGOPHER to *fit* experimental spectra (MLW has not done much of this, so please share your expertise if you end up using it!)
- This useful [appendix](#) from Matt Sprague's thesis at Caltech on Gaussian inputs for PGOPHER simulation

Here I'll walk through a few basic ways to simulate rovibrational spectra with PGOPHER.

HITRAN input to PGOPHER

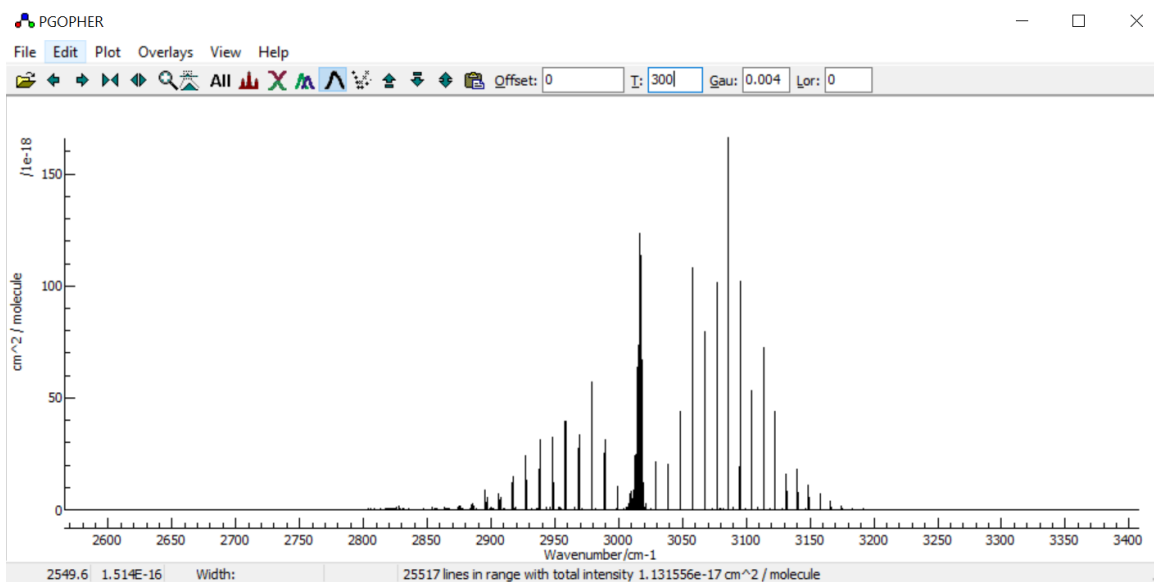
If your molecule of interest is covered in the [HITRAN line-by-line database](#), you're in great luck. All you have to do is download the relevant .par file for your desired molecule and import it in PGOPHER.



From here, pretty much your only adjustable parameters are

- T, temperature in Kelvin
- Gau, Gaussian line broadening (full width at half maximum) in cm^{-1} . Typically use expected Doppler linewidth at temperature T
- Lor, Lorentzian line broadening (full width at half maximum) in cm^{-1} . Typically use expected pressure broadening linewidth.

- More info on simulation parameters [here](#)



You can click File > Export > Main Plot to save a file with x,y values from the plot window.

Gaussian input to PGOPHER

Say we want to study an unusual molecule not documented in HITRAN. We can create rovibrational simulations from scratch using the output from Gaussian calculations. Here we'll walk through simulating the rovibrational band of a single fundamental vibrational mode.

First, run a freq calculation in Gaussian with the `iop(7/33=1)` keyword so dipole derivatives are printed for vibrational normal modes.

Here, I'll use the output from a Gaussian harmonic frequency calculation at the B3LYP/6-31g level for the D_{2h} pyrene molecule as an example.

This system is going to be an [asymmetric top](#). It's also helpful to have the character table for the relevant point group handy.

First, let's collect various pieces of information from our Gaussian output:

1. Molecular structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000000	0.000000	0.714802
2	6	0	0.000000	0.000000	-0.714802
3	6	0	0.000000	1.239197	1.432217
4	6	0	0.000000	1.239197	-1.432217
5	6	0	-0.000000	-1.239197	1.432217
6	6	0	-0.000000	-1.239197	-1.432217
7	6	0	0.000000	2.469414	0.682704

8	6	0	0.000000	2.469414	-0.682704
9	6	0	-0.000000	-2.469414	0.682704
10	6	0	-0.000000	-2.469414	-0.682704
11	6	0	0.000000	1.213769	2.839570
12	6	0	0.000000	1.213769	-2.839570
13	6	0	-0.000000	-1.213769	2.839570
14	6	0	-0.000000	-1.213769	-2.839570
15	6	0	0.000000	0.000000	3.531937
16	6	0	0.000000	0.000000	-3.531937
17	1	0	0.000000	3.405972	1.232946
18	1	0	0.000000	3.405972	-1.232946
19	1	0	-0.000000	-3.405972	1.232946
20	1	0	-0.000000	-3.405972	-1.232946
21	1	0	0.000000	2.152534	3.385882
22	1	0	0.000000	2.152534	-3.385882
23	1	0	-0.000000	-2.152534	3.385882
24	1	0	-0.000000	-2.152534	-3.385882
25	1	0	0.000000	0.000000	4.617306
26	1	0	0.000000	0.000000	-4.617306

In this orientation, the molecule is in the y-z plane, with y along the shorter axis, and z along the longer axis of the molecule; see cartoon below.

2. Rotational constants for the ground vibrational state of the molecule:

Rotational constants (GHZ): 1.0055831 0.5524280
0.3565522

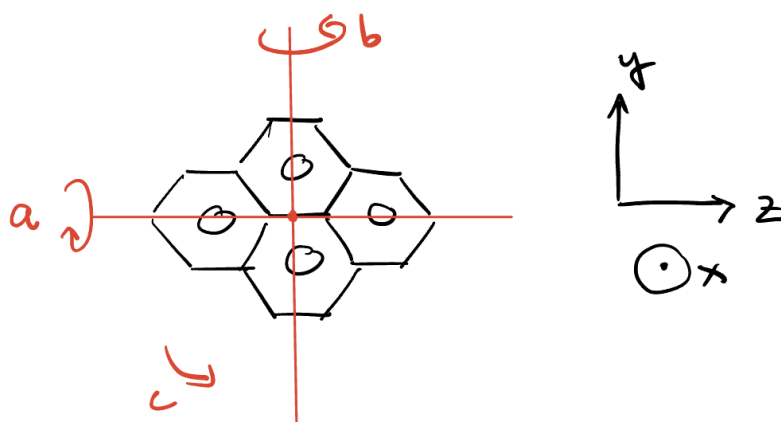
By convention, rotational constants are $A > B > C$. So here,

A = 1.0055831 GHz

B = 0.5524280 GHz

C = 0.3565522 GHz

We can correlate these rotational constants with rotation about one of the three principle axes of the molecule, which in the standard orientation are aligned to the Cartesian axes. I tend to do this by inspection: rotational constants are inversely proportional to the moment of inertia for rotation about the relevant principle axis. So the largest rotational constant A corresponds to rotation about the axis with the smallest moment of inertia, etc. See cartoon below, which correlates A \leftrightarrow rotation about z, B \leftrightarrow rotation about y, C \leftrightarrow rotation about x. For some additional info, see my [notes](#) on rotational spectroscopy in polyatomic molecules.



It will be useful at this point to determine the [asymmetric top axis system](#) that PGOPHER will want to use to represent this molecule.

A \leftrightarrow z, B \leftrightarrow y, C \leftrightarrow x corresponds to the "II" axis system. Hold onto this info!

3. Vibrational frequencies

Now look at the vibrational mode you are interested in. In this example, we'll use mode 53 of pyrene, the B1u symmetry IR-active mode near 1487 cm⁻¹:

	53
	B1U
Frequencies ---	1487.0913
Reduced masses ---	3.0672
Force constants ---	3.9964
IR Intensities ---	12.1813
Raman Activities ---	0.0000
Depol. (Plane) ---	0.0000
Depol. (Unpol) ---	0.0000

```

Coord Atom Element:
1      1      6      -0.00000
2      1      6      -0.00000
3      1      6      -0.10786
1      2      6       0.00000
2      2      6       0.00000
... etc

```

4. And finally, let's dig out the vibrational dipole derivatives for this mode:

Dipole derivative wrt mode 53: -3.63779D-12 -7.67078D-11 -3.49017D+00

Polarizability derivatives wrt mode 53

	1	2	3	
1	0.000000D+00	0.000000D+00	0.000000D+00	
2	0.000000D+00	0.000000D+00	0.000000D+00	
3	0.000000D+00	0.000000D+00	0.000000D+00	
Vibrational polarizability contributions from mode	53			0.0000000
0.0000000	0.1482352			

Vibrational hyperpolarizability contributions from mode 53
0.0000000 -0.0000000 -0.0000000

IFr= 0 A012= 0.48D-21 0.27D-14 0.46D-15 Act= 0.32D-14 DepolP= 0.00D+00
DepolU= 0.00D+00

Here, we can see the dipole derivatives along the x,y,z Cartesian axes. Note, the sum of the squares of these components should equal the total IR intensity in km/mol!

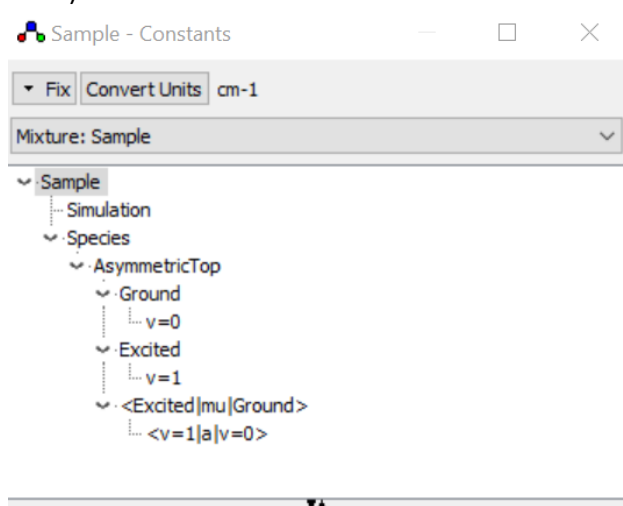
For this example, we can see the only significant dipole derivative is along the z axis. We can also validate this by looking at the vibrational normal mode displacements visualized in GaussView or Avogadro. For this high-symmetry molecule, the character table for the point group alone will also tell you that B1u vibrations change the dipole of the molecule along the z axis. (This assumes of course that the character table uses the same conventions for the Cartesian axes as the standard orientation in Gaussian- always a big assumption and good to double check).

In any event, we have convinced ourselves that mode 53 has a net stretching motion aligned along the z-axis, and therefore along the A rotational axis. This vibrational motion is therefore an *a*-type transition. Hold onto this info!

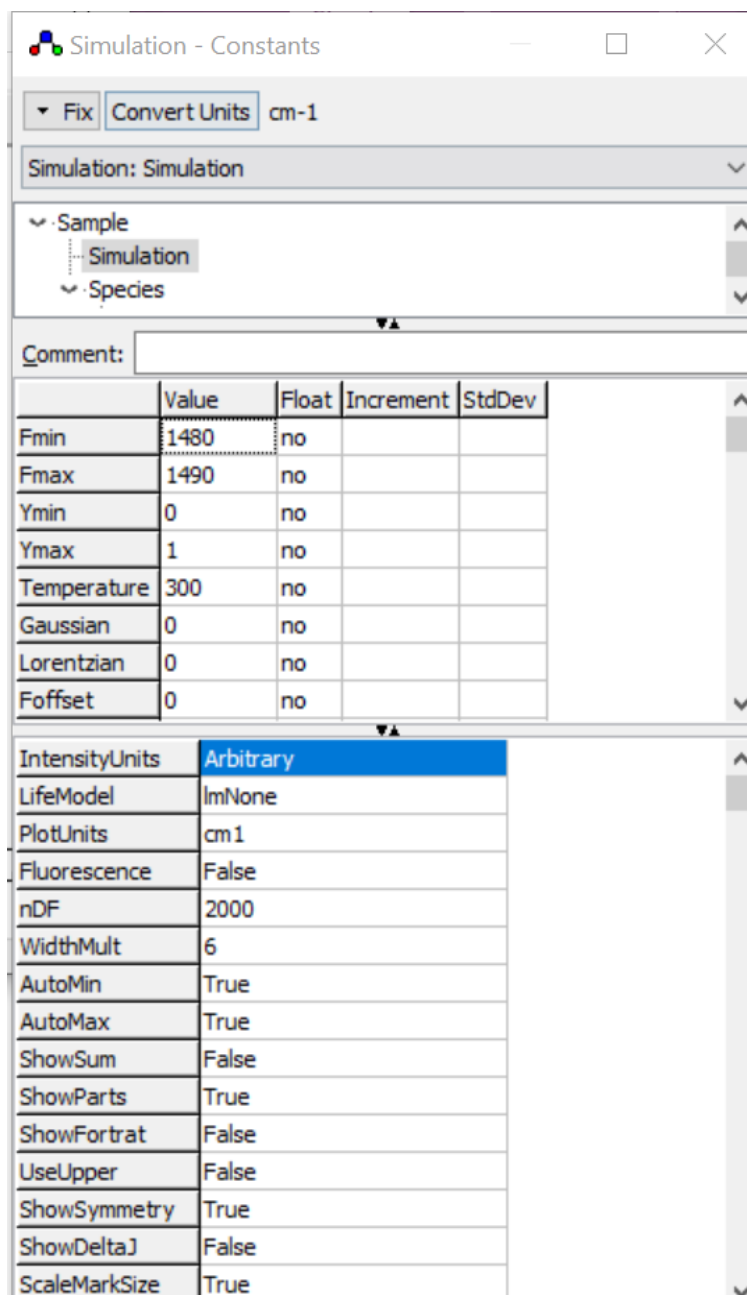
Note: *a*, *b*, and *c*-type vibrational transitions will have very different looking rotational patterns accompanying them. It's worth playing around with simulating band profiles for B1u, B2u, and B3u modes in a D2h molecule, for instance, to explore this.

Now let's get into the PGOPHER simulation.

- a. Open PGOPHER, and select File > New > Asymmetric Top
- b. Now open up the constants panel through View > Constants. Everything we'll need to do is filling in parameters in the Constants panel. There are five items to define in particular: the simulation parameters (**Simulation**), the molecular species (**Species**), the molecular symmetry (**Asymmetric Top**), the vibrational level properties (**v=0 and v=1**), and the transition moment integrals (tabs under **<Excited|mu|Ground>**)

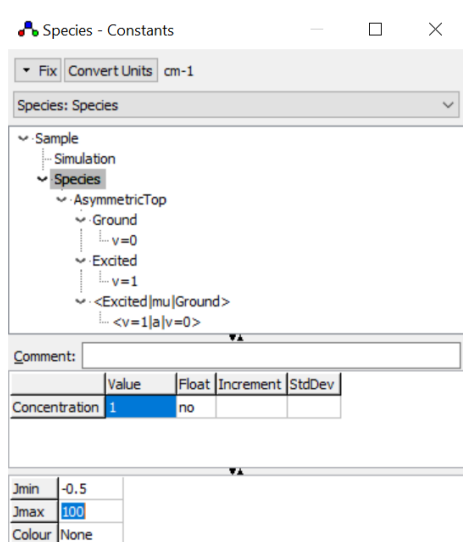


- c. Under the **Simulation** tab

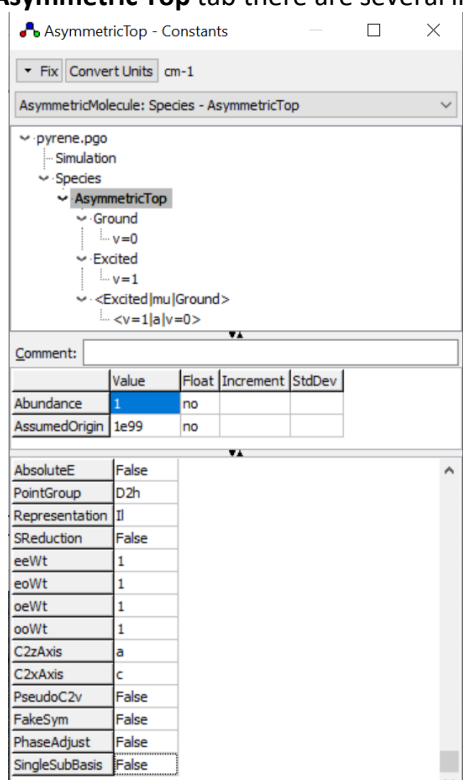


Here are the parameters to focus on here:

- Fmin, Fmax: this is the frequency window. You can set it here, but it will also update automatically when you change the plot range in the GUI.
- Temperature (Kelvin)
- Gaussian and Lorentzian fwhm (leaving 0 is ok to create a stick spectra)
- IntensityUnits: arbitrary or normalized is fine if you don't need absolute values. Otherwise, (cm^2 wavenumber/molecule) is the same as spectral line intensity S_{ij} from HITRAN data. More on this [here](#) and in the 2017 PGOPHER paper.
- nDF: number of points within spectrum; somewhat important when exporting plotted data.
- d. Under the **Species** tab, all you need to check is the value of Jmax (maximum rotational quantum number plotted), which may have to be increased for big molecules or at high temperatures



e. Under the **Asymmetric Top** tab there are several important items



The parameters to focus on here are:

- PointGroup. For pyrene we use D2h.
- Representation: again, this is what determines which inertial axis is which Cartesian axis, as detailed [here](#). For the pyrene example we put II, as detailed above.

- eeWt, eoWt, oeWt, ooWt can be used to handle nuclear spin statistics in systems with indistinguishable nuclei (like ortho- and para- states in H₂O for instance). We'll not get into this with this example.
- C2zAxis and C2xAxis relate the C2 symmetry axes for the molecule's point group with the inertial axes. See the section for the specific point group on [this page](#) for how best to define these. For our D2h system, we again use the relation between the z <> A and x <> C axes. In practice, if you get these wrong, the transitions you are looking for often become forbidden, so it's pretty easy to tell when these axes are defined incorrectly.

f. We now get into the **v=0** and **v=1** parameters

AsymmetricTop: Species - AsymmetricTop - Ground - v=0

pyrene.pgo

- Simulation
- Species
 - AsymmetricTop
 - Ground
 - v=0

Comment:

	Value	Float	Increment	StdDev
Origin	0	no		
Width	0	no		
A	.0335426	no		
B	.018427	no		
C	.0118933	no		
BBar	0	no		
BDelta	0	no		
DK	0	no		
DJK	0	no		
DJ	0	no		
deltaK	0	no		
deltaJ	0	no		
HK	0	no		
HKJ	0	no		

Colour	None
RveSelect	all
S	0
Symmetry	Ag
Kmin	all
Kmax	all

For v=0, we define parameters for the *lower* vibrational state, from which transitions derive.

- Origin: Set the origin of the ground state to 0 cm-1 (or whatever reference energy you'd like to use).
- A,B,C: Enter the rotational constants for the ground vibrational state, from our Gaussian calculations
- S: set the spin of the lower electronic state

- Symmetry: Set the symmetry of the lower state, in this case to Ag, since the vibrational ground state of a closed shell molecule is totally symmetric.
- Note there are many many constants here (DK, DJK, DJ, deltaK, deltaJ...). These are centrifugal distortion constants that come from vibration-rotation interaction. They will provide small corrections to the spectrum, and we neglect them here. You can in principle find these in an anharmonic Gaussian calculation, or sometimes in the precision spectroscopy literature.

For the vibrationally excited state, $v=1$, the parameters look much the same, but we enter the origin and symmetry of the vibrational mode of interest. Here's what we enter for pyrene:

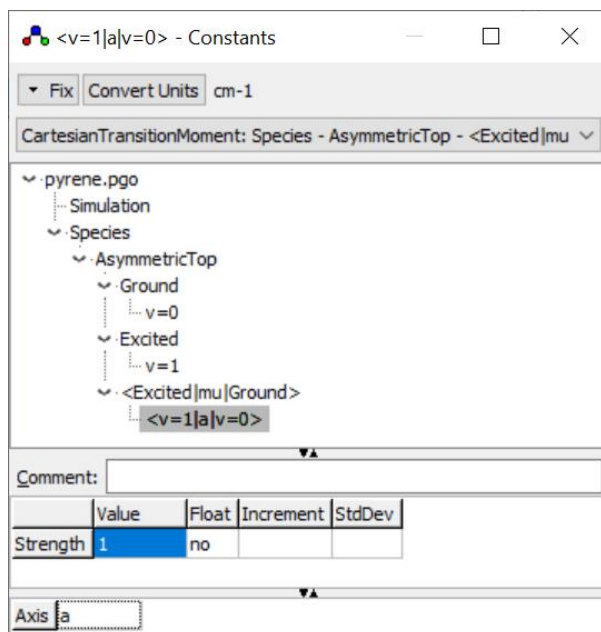
Comment:

	Value	Float	Increment	StdDev
Origin	1487	no		
Width	0	no		
A	.0335426	no		
B	.018427	no		
C	.0118933	no		
BBar	0	no		
BDelta	0	no		
DK	0	no		
DJK	0	no		
DJ	0	no		
deltaK	0	no		

Colour	None
RveSelect	all
S	0
Symmetry	B 1u
Kmin	all
Kmax	all

Note: For simplicity I've used the same rotational constants here as I did for the $v=0$ state. One should really update these with vibrational state-specific rotational constants by performing anharmonic frequency calculations. For big molecules like pyrene, anharmonic calculations are pretty expensive, so I have not taken this step in this example.

g. Finally, let's get into the **transition dipole moment** parameters:



- Axis: needs to be consistent with the direction of transition dipole and how it aligns with the inertial axes. For this B_{1u} vibration of pyrene, we had determined this to be the *a* axis.
- Strength: here left as 1, since we are using arbitrary units for the peak intensities

Note: In a low symmetry molecule, a single vibration may well have transition dipole moment components along more than one inertial axis, making it some simultaneous combination of a,b, and/or c-type transitions. To account for this, simply right-click on $\langle \text{Excited} | \mu | \text{Ground} \rangle$ then click Add New > Cartesian Transition Moment, and provide the relative strengths of the two components using the relative weighting of dipole derivatives along each axis from the Gaussian calculations. For pyrene B_{1u}-symmetry mode 53, recall that these dipole derivatives looked like:

Dipole derivative wrt mode 53: $-3.63779\text{D}-12$ $-7.67078\text{D}-11$ $-3.49017\text{D}+00$

Since the derivatives along x and y are 11 orders of magnitude smaller than that along z, we can safely ignore them in this example. More about this in [this paper](#) about C₁ symmetry (or lack thereof) molecules.

Finally, below is the produced spectrum for our pyrene rovibrational band, evaluated at 10 K.

