Appendix D—Simulating Spectroscopic Bands Using Gaussian and PGopher

This appendix contains methods for using Gaussian 09[121] and PGopher[120] to simulate vibrational and electronic bands of molecules. These methods are useful for confirming spectroscopic band assignments based on band width, shape, and strength. The examples provided in this appendix are for simple molecules: the ν_1 vibrational spectrum of methanol and the A-X electronic spectrum of $HOCH_2OO\bullet$ (HMP) from Chapter 4.

Sections in this appendix:

1) Calculation of Vibrational Dipole Derivatives
2) Estimation of the A-X Dipole Derivative
3) Calculation of Anharmonic Rotational Constants
4) Simulation of the Spectroscopic band

1) Calculation of Vibrational Dipole Derivatives

By default, Gaussian 03 or 09 will not print the dipole derivatives associated with vibrational modes. However, adding the command `iop(7/33=1)` to the route line will request the dipole derivatives to be printed. The command is entered as follows:

```
#p freq rb3lyp/6-31+g(d,p) geom=connectivity iop(7/33=1)
```

Note that `iop(7/33=1)` will not work if you request an optimization and a frequency job in the same file (i.e., `opt freq`), because it will not be passed correctly to the frequency calculation. Only specify `iop(7/33=1)` with “frequency only” calculations.

Also, `iop(7/33=1)` makes use of normal modes only; anharmonic corrections are irrelevant. Running an anharmonic frequency calculation will not yield different or more accurate dipole derivatives.

Below is an excerpt from the relevant output from a frequency calculation on methanol using the `iop(7/33=1)` command.

```
Dipole derivatives wrt mode   1:  1.81379D-08  2.40612D-08 -1.18744D+01
 Vibrational polarizability contributions from mode    1         0.0000000
0.0000000      38.0275286
 Vibrational   hyperpolarizability   contributions   from   mode          1
0.0000000       0.0000000       0.0000000
 Dipole derivatives wrt mode   2: -5.06359D-01  1.15450D+01 -1.96119D-08
 Vibrational polarizability contributions from mode    2         0.0063052
3.2777142       0.0000000
 Vibrational   hyperpolarizability   contributions   from   mode          2
0.0000000       0.0000000       0.0000000
…
Dipole derivatives wrt mode  12: -4.09757D+00 -3.36931D+00 -6.58556D-08
 Vibrational polarizability contributions from mode   12         0.0306689
0.0207361       0.0000000
 Vibrational    hyperpolarizability    contributions    from    mode       12
0.0000000       0.0000000       0.0000000
```

Of interest to us are the lines marked `Dipole derivatives wrt mode xxx`, where xxx is the normal mode number. The modes are numbered from lowest to highest frequency (same listings as in the harmonic frequency output, but NOT the anharmonic frequency output). For methanol, mode 12 is the OH stretch. Presumably, the components listed are (a, b, c) (although with little documentation on this command, I am not sure if this generally holds true). As a check, the sum of the squares of the three components should equal the IR intensity (in this case, 28.1 km mol^{-1}) for the normal mode of interest.

2) Estimation of the A-X Dipole Derivative

There are two problems with calculating the A-X dipole derivatives. First, the A-X bands of peroxy radicals are weak (oscillator strengths less than 0.0001), so the magnitude of the transition moment cannot be estimated from a CIS calculation (see Appendix C). Second, our higher-level calculations on the X and A states are performed separately, and Gaussian will not report a transition dipole moment from the independent calculations.

Instead, we estimate the dipole derivative on the basis of the visualized molecular orbitals in GaussView 5.0. In Figure D.1, we show the relevant molecular orbitals involved in the A-X transition of $HOCH_2OO$• (HMP, Chapters 4–6). These orbitals were generated using the unrestricted canonical wavefunction with a 6-31+G(d,p) basis set. HMP has 33 electrons (17 α, 16 β); therefore, the A-X transition involves promotion of an electron from the 16β orbital to the 17β orbital.

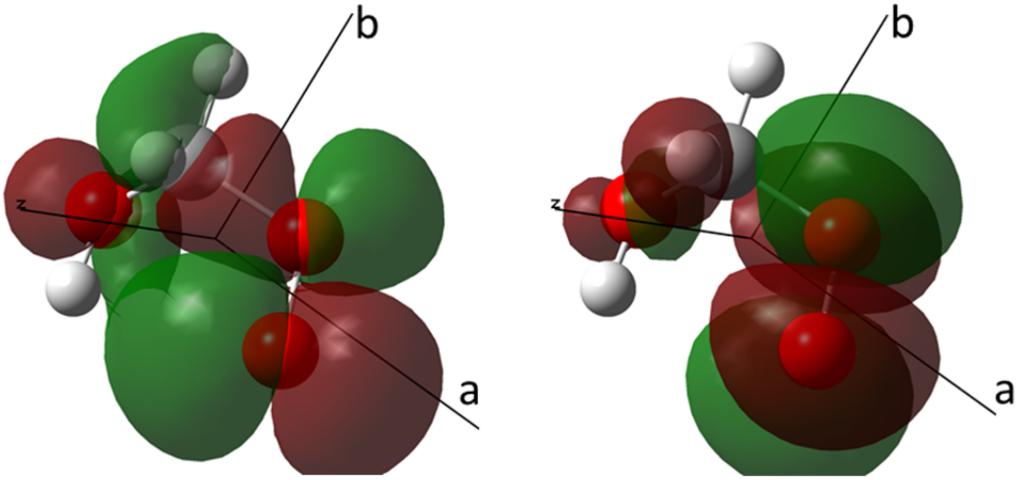


Figure D.1. Molecular orbitals involved in the A-X transition of HMP: 16β (left) and 17β (right). The c-axis is out of the plane of the paper. Unrestricted canonical orbitals were generated using the 6-31+G(d,p) basis set.

We already know that the electron density is located on the peroxy group (if we did not, we would have to generate a surface plot of electron density). We can simply look at the change in the π* orbital on the OO group to determine the dipole derivative direction. In this case, the dipole change is nearly all on the a- and c-axes, with a small contribution along the b-axis. To a first approximation, we only enter a and c components into our transition dipole moment. (To a second approximation, we can add in a small contribution from the b component. However, since the transition intensity is proportional to the square of the dipole derivative, we do not expect the small b component to make an appreciable difference in the spectrum)

3) Calculation of Anharmonic Rotational Constants

A major component to accurate spectrum simulations is to use the appropriate rotational constant for each state. This is absolutely crucial when modeling electronic transitions, as the excited states may have significantly different geometries than the ground state. Differences in rotational constants between vibrationally excited states and the ground state are much smaller; however, these differences will have a small yet observable effect on the simulated spectrum.

In general, Gaussian will only report the rotational constants for the equilibrium geometry. By requesting an anharmonic frequency calculation, Gaussian will determine zero point energies, anharmonicities, and the average geometry/rotational constants in the ground state and all vibrational states (including the first overtones and combination bands). This is requested by entering `freq=anharmonic`. Note that anharmonic frequencies are only available for HF, DFT, CIS, and MP2.[121] Calculation of anharmonic frequencies requires multiple energy evaluations along the normal mode coordinates, and therefore is much more expensive than the corresponding harmonic frequency calculation.

Below is an excerpt of the relevant information from an anharmonic frequency calculation on methanol (B3LYP/6-31+G(d,p)):

```
Vibrational Energies and Rotational Constants (cm-1)
 Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
 Equilibrium Geometry                     4.254177    0.820152    0.791998
 Ground State   11243.115    11068.551    4.201436    0.810130    0.783960
 Fundamental Bands (DE w.r.t. Ground State)
  1(1)           3838.340     3657.078    4.166657    0.809317    0.782149
  2(1)           3132.414     2987.700    4.179411    0.810602    0.784141
  3(1)           3002.706     2868.339    4.167406    0.810395    0.784668
  4(1)           1511.279     1419.780    4.723076    0.812129    0.817227
  5(1)           1484.215     1509.763    4.209302    0.752017    0.751135
  6(1)           1354.473     1310.191    4.254842    0.808235    0.780542
  7(1)           1071.906     1053.427    4.195495    0.805186    0.779969
  8(1)           1046.125     1018.149    4.199339    0.803309    0.775287
  9(1)           3055.148     2917.619    4.177511    0.811408    0.784924
 10(1)           1500.580     1463.053    3.633543    0.867621    0.785489
 11(1)           1173.087     1146.559    4.209320    0.807503    0.780678
 12(1)            315.958      308.510    4.195842    0.803800    0.785240
```

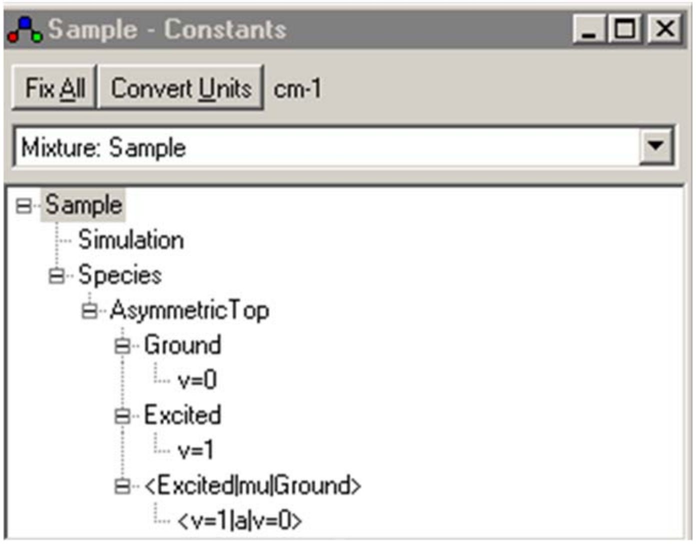
The rotational constants for each mode are listed on the right in cm^{-1}. Note that the modes are listed from highest frequency to lowest frequency, in opposite order than in the harmonic frequency listing. The OH stretch now corresponds to mode 1, not mode 12. Note also that for molecules with symmetry (such as CH_3OH, C_s), the modes are separated by symmetry. Modes 1–8 have A’ symmetry, modes 9–12 have A’’ symmetry.

In the absence of any other band position information, the anharmonic frequencies can be used in the spectrum simulations. However, these frequencies may have errors of up to 10% in the hydroxyalkylperoxy systems that we have studied (Chapter 5). When possible, experimental data or explicit modeling of the potential energy surface (Chapter 3) will give much more accurate results.

4) Simulation of the Spectroscopic Band

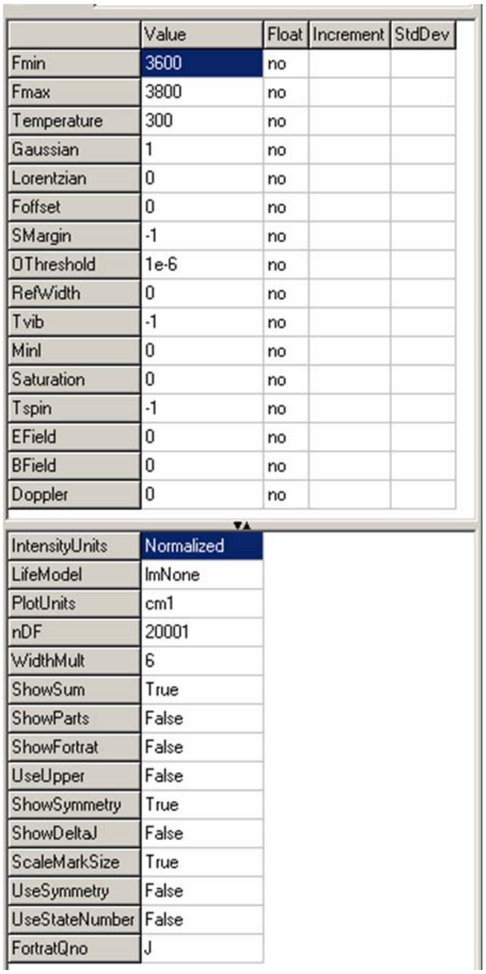
With the (absolute or relative) dipole derivatives (a, b, and c components) and rotational constants in hand, it is straightforward to simulate the bands using PGopher.[120] We have already seen the excellent agreement between simulation and CRD spectrum of the HMP A-X bands (Chapter 4); here, we compare the simulated CH_3OH ν_1 band to our CRD spectrum.

To begin our simulation, we open the PGopher program, create a new asymmetric top (File-New-Asymmetric Top), and open the list of constants (View-Constants). For now, we ignore the spectrum window and focus on entering our parameters in the Constants list.



There are four items to define before we can simulate our band: the simulation parameters (Simulation), the molecular symmetry (Asymmetric Top), the vibrational or electronic level properties (v=0 and v=1), and the transition moment integrals (listed under <Excited|mu|Ground>.

Clicking on Simulation brings up the following options:

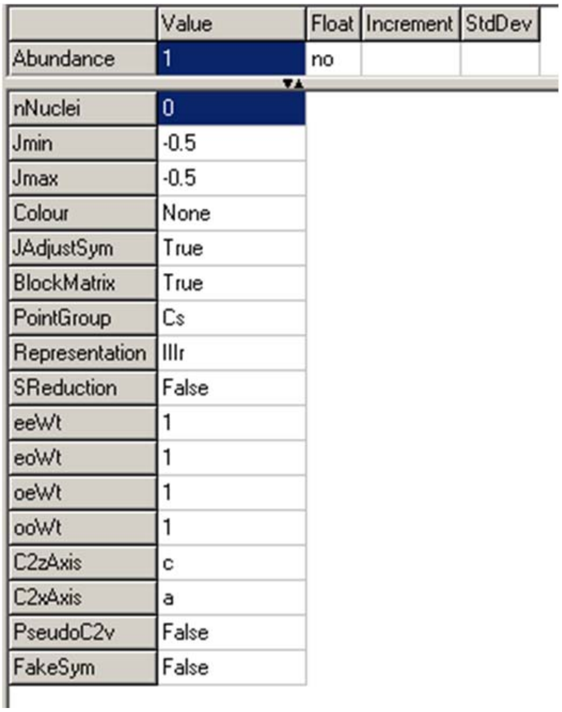


	Value	Float	Increment	StdDev
Fmin	3600	no		
Fmax	3800	no		
Temperature	300	no		
Gaussian	1	no		
Lorentzian	0	no		
Foffset	0	no		
SMargin	-1	no		
OThreshold	1e-6	no		
RefWidth	0	no		
Tvib	-1	no		
MinI	0	no		
Saturation	0	no		
Tspin	-1	no		
EField	0	no		
BField	0	no		
Doppler	0	no		

IntensityUnits	Normalized
LifeModel	lmNone
PlotUnits	cm1
nDF	20001
WidthMult	6
ShowSum	True
ShowParts	False
ShowFortrat	False
UseUpper	False
ShowSymmetry	True
ShowDeltaJ	False
ScaleMarkSize	True
UseSymmetry	False
UseStateNumber	False
FortratQno	J

The only items that need to be set are $F_{\min}$ and $F_{\max}$ (the frequency range), Temperature (K), Gaussian and Lorentzian (cm^{-1}, convolution of spectrum with these functions), and nDF (number of points within spectrum). For ease of exporting the plot, nDF should be set to $\frac{F_{\max}-F_{\min}}{\Delta\bar{\nu}}+1$. For example, if the range is 200 cm^{-1} and the desired step size is 0.1 cm^{-1}, nDF should be set to 2001. The frequencies (cm^{-1}) calculated for the main plot will be 0, 0.1, 0.2, …, 200.

Clicking on Asymmetric Top brings up the following options:

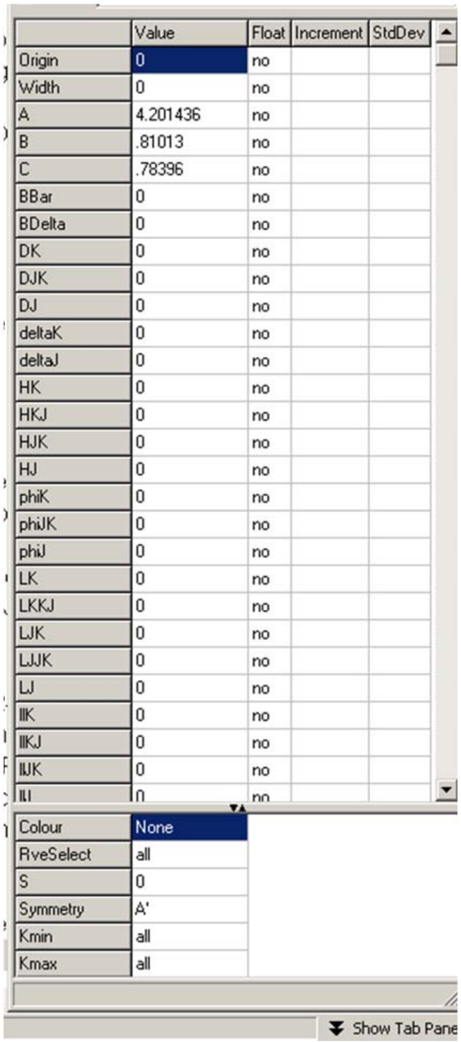


	Value	Float	Increment	StdDev
Abundance	1	no		

nNuclei	0
Jmin	-0.5
Jmax	-0.5
Colour	None
JAdjustSym	True
BlockMatrix	True
PointGroup	Cs
Representation	IIIr
SReduction	False
eeWt	1
eoWt	1
oeWt	1
ooWt	1
C2zAxis	c
C2xAxis	a
PseudoC2v	False
FakeSym	False

The options that need to be set are Point Group, Representation, C2zAxis, and C2aAxis. The Representation describes how a, b, c are related to x, y, z. In general, this will be set to IIIr (x = a, y = b, z = c), though this can be changed if necessary. C2zAxis and C2aAxis define the symmetry axes for C2/C2$_v$ molecules. For C$_s$ molecules, C2z defines the axis through which the mirror plane passes through. C2aAxis is irrelevant for C$_s$ molecules.

Clicking on either v=0 or v=1 will bring up similar options:

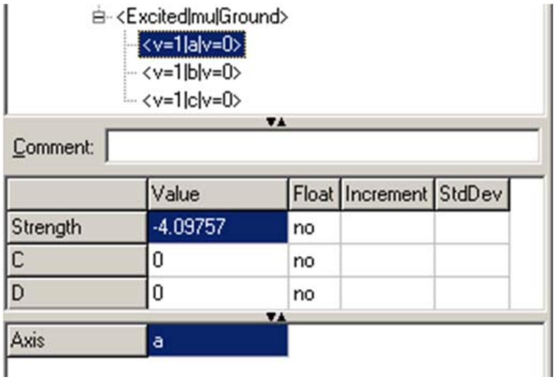


	Value	Float	Increment	StdDev
Origin	0	no		
Width	0	no		
A	4.201436	no		
B	.81013	no		
C	.78396	no		
BBar	0	no		
BDelta	0	no		
DK	0	no		
DJK	0	no		
DJ	0	no		
deltaK	0	no		
deltaJ	0	no		
HK	0	no		
HKJ	0	no		
HJK	0	no		
HJ	0	no		
phiK	0	no		
phiJK	0	no		
phiJ	0	no		
LK	0	no		
LKKJ	0	no		
LJK	0	no		
LJJK	0	no		
LJ	0	no		
llK	0	no		
llKJ	0	no		
llJK	0	no		
llJ	0	no		

Colour	None
RveSelect	all
S	0
Symmetry	A'
Kmin	all
Kmax	all

Origin should be set to 0 in the ground state (v=0), and the transition frequency in the excited state (v=1). A, B, and C should be set individually for each state to the rotational constants calculated from Gaussian. The remaining parameters are distortion constants. These are reported in any anharmonic frequency calculation and can be entered, but I have found that they make very little difference in my spectrum simulations. At the bottom, S and Symmetry should be entered to be the electron spin and overall symmetry of the state (ground, vibrational, etc.)

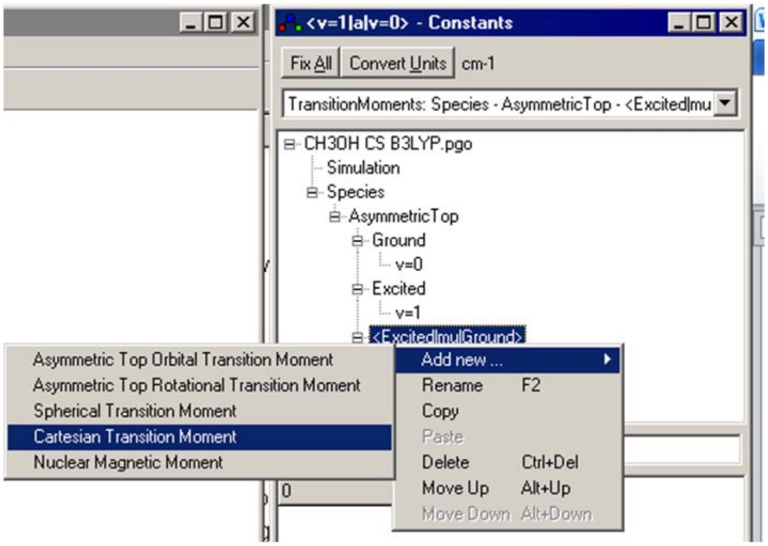
Clicking on an individual transition moment brings up the following options:



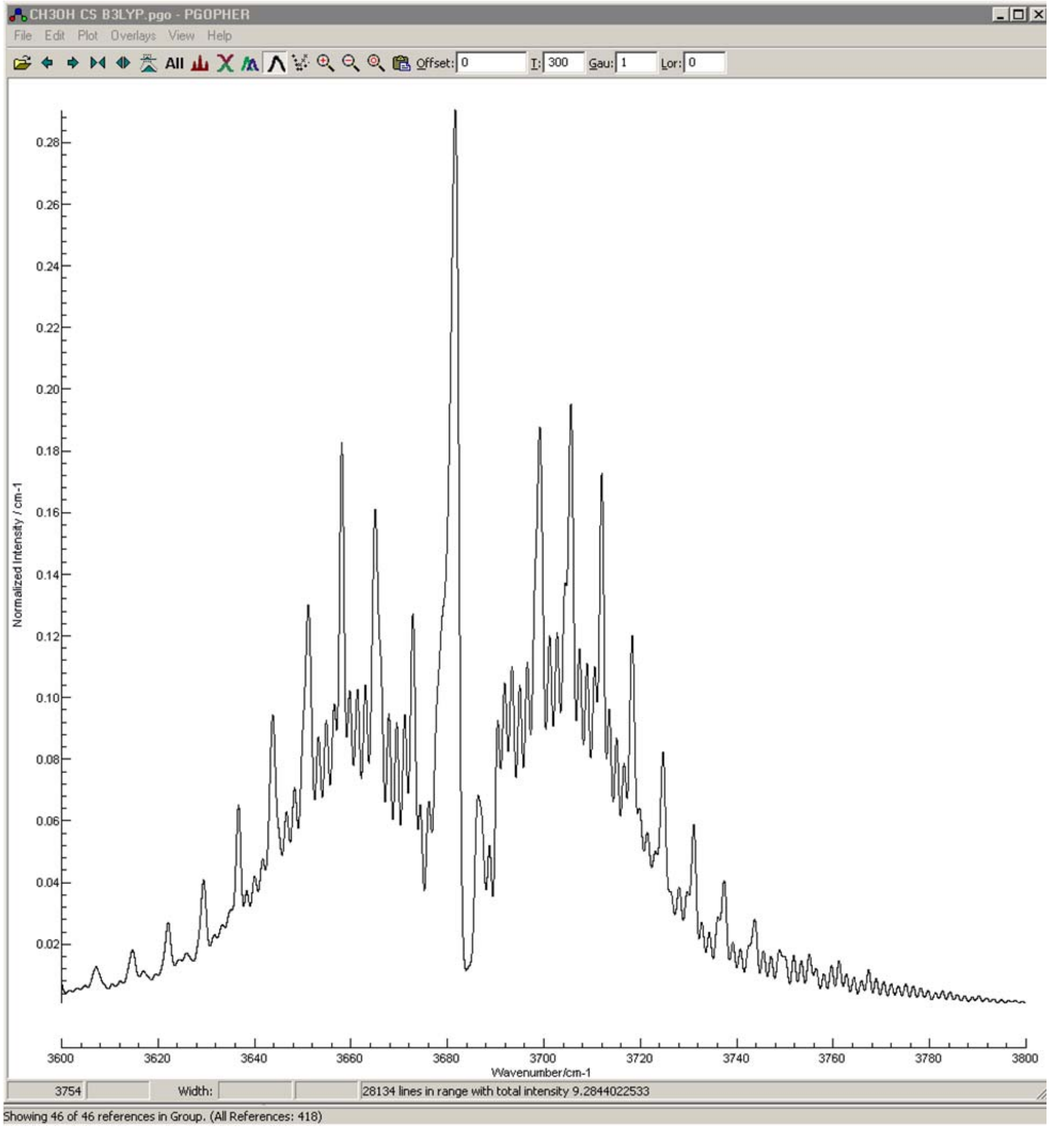
	Value	Float	Increment	StdDev
Strength	-4.09757	no		
C	0	no		
D	0	no		

Axis	a

Strength should be set to the value of the absolute dipole derivative calculated from Gaussian (vibrational spectra) or the relative dipole derivative from visual analysis of the molecular orbitals (electronic spectra). Axis defines the transition as a, b, or c type. In general, a given spectrum will contain contributions from more than one type, and multiple transition moments should be included. To add additional transition moments, right click <Excited|mu|Ground> and select Add new – Cartesian Transition Moment. This will add a second (or third, or more) transition that can be edited. In this way, a single spectrum can contain contributions from a, b, and c transitions.



Once all of the parameters have been entered, click Plot-Simulate to generate the spectrum. Figure D.2 shows the simulation of the ν_1 band of methanol.



Offset: 0 T: 300 Gau: 1 Lor: 0

28134 lines in range with total intensity 9.2844022533

Showing 46 of 46 references in Group. (All References: 418)

Figure D.2. Simulated ν_1 band of CH_3OH, B3LYP/6-31+G(d,p), anharmonic rotational constants. Screenshot directly out of the PGopher program.

We can export this plot to a text file (File-Export-Main Plot) for use in Excel or other graphing programs. This allows us to compare to an experimental spectrum. Figure D.3 compares our simulated CH_3OH band to one measured on our cavity ringdown spectrometer. We observe good agreement between the two spectra, although in general, the very sharp spikes in the simulation are washed out in the cavity ringdown spectrum.

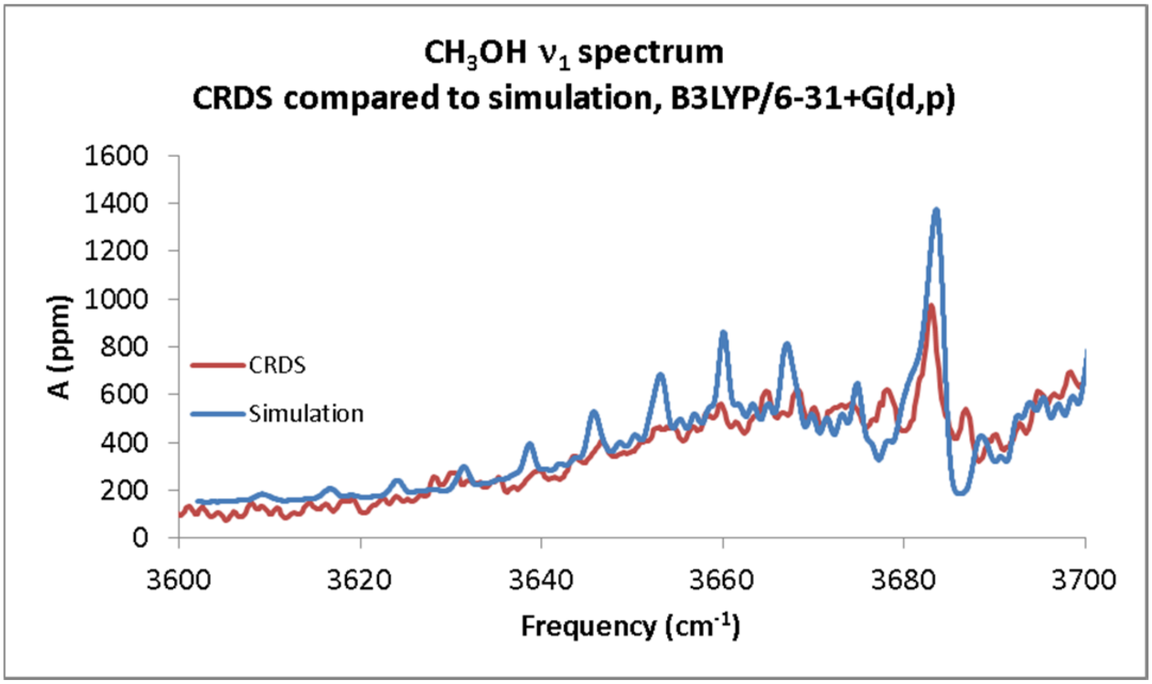


Figure D.3. Comparison of experimental (red, CRDS) and simulated (blue) ν_1 bands of CH_3OH.