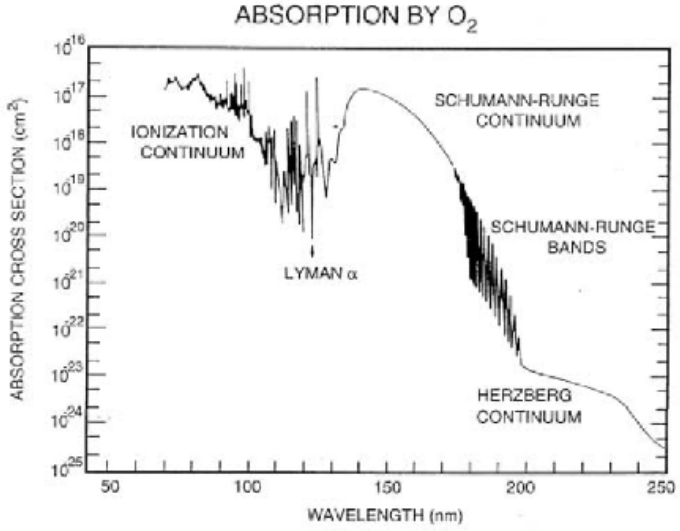
Homework 10: IR Spectroscopy

1. For NaI, $\tilde{\nu}_e$ = 286.0 cm $^{-1}$ and $\chi_e\tilde{\nu}_e$ = 0.750 cm^{-1}. Calculate the force constant, zero-point energy, and dissociation energy, D_o.

2. The Schumann-Runge band for molecular oxygen is in the UV region of the spectrum. The wavenumbers for the transitions from the ground state to the vibrational levels of the first excited state are given in the table below. The ground state dissociates into two ground state ^{3}P oxygen atoms, and the first excited state dissociates into a ^{3}P and a ^{1}D oxygen atom. Calculate (a) the dissociation energy of the excited state, (b) the dissociation energy of the ground state (the "bond strength"). The atomic excitation energy, $^3P \rightarrow {}^1D$ is 190 kJ/mol. A spreadsheet containing this data is on the Homework page or you can cut and paste this table into EXCEL.

Transition energies in cm^{-1} of the Schumann-Runge band of O_2.

50062.6
50725.4
51369.0
51988.6
52579.0
53143.4
53679.6
54177.0
54641.8
55078.2
55460.0
55803.1
56107.3
56360.3
56570.6



IR Spectrum of Formaldehyde[1]

Purpose: Illustrate the calculation of vibrational frequencies, animation of the resulting vibrational motions, and calculation of thermodynamic parameters.

In Spartan, build formaldehyde. Vibrational frequencies need to be calculated using optimized geometries. From the Setup menu choose Calculations and setup an Equilibrium Geometry calculation at the Hartree-Fock/3-21G* level. Make sure "IR," Thermodynamics, and Vibrational Modes are checked in the Setup. Click on Submit.

After the job has completed, vibrational frequencies in cm^{-1}, the symmetry species of the vibration, and the IR intensities can be listed by selecting Spectra under the Display menu. If the IR frequencies are not shown, click on the IR tab.

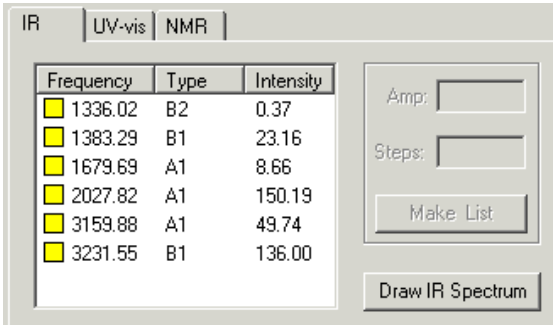


Figure 1. Vibrational frequencies at the HF/6-31G* level

Compare the listed frequencies with the experimental frequencies, Table 1.

Table 1. Experimental Frequencies for the Normal Modes of Formaldehyde.

Symmetry of mode	Description of mode	Experimental frequency (cm^{-1})
a1	CH_2 symmetric-stretch CO stretch CH_2 scissor	2783 strong 1746 very strong 1500 strong
b_1	CH_2 asymmetric-stretch CH_2 rock	2843 very strong 1249 strong
b_2	CH_2wag	1167 strong

Report the vibration frequencies: how well do experiment and calculations agree? The b_1 and b_2 designations may be switched; they are arbitrary. The totally symmetric group, a_1, contains the very symmetrical vibrations. The b_1 and b_2-groups are less symmetrical in the atom movements. The mode descriptions are the best way of understanding the symmetry differences. Frequencies from *ab initio* calculations are normally multiplied by 0.9 to compare with experimental frequencies. This factor adjusts for anharmonicity. Multiply your frequencies by 0.9; does it help?

To animate an individual vibrational mode, click on its yellow check box. To stop the animation, click on the yellow check box again. Are the motions you observe consistent with the experimental assignments given in Table 1? The default amplitude of the vibration is highly exaggerated. The amplitude can be changed using the value inside the box to the right of "Amp:"

in the Vibrations dialog. You can superimpose a plot of the theoretical IR spectrum with your molecule by clicking on the Draw IR Spectrum button.

To list the normal mode displacements and the thermodynamic calculations pull down the Display menu and choose Output. The normal mode section is at the bottom of the output. To print the text output file from the calculations pull down the File menu and choose Print while the Output window is active. The animations are generated using these normal mode displacements.

The thermodynamic calculations, Table 2, are corrections to the electronic energy needed to find the total enthalpy, entropy, and Gibbs Free Energy of formation of the molecule. We will discuss these thermodynamic calculations later in the course. For example, the “Ideal Gas” entry is equal to RT, and is necessary to convert from internal energy to enthalpy, $\Delta H = \Delta U + RT$. The Translation contribution to the enthalpy is 3/2RT, which is the equipartition contribution. The zero point energy, ZPE, is needed to adjust the energy reference to the first vibrational level, instead of the minimum of the electronic energy curve. Report the ZPE correction. Report the vibration, “Ideal Gas”, translation, rotational, and total contributions to the enthalpy and entropy of formation for formaldehyde. Also include the final Gibbs Free Energy (H-TS)total correction. You can just hand in a copy of your printout for these results.

Please give the **name of your Spartan File and the computer that you did your work on**.

Table 2. Thermodynamic correction for the electronic energy at HF/6-31G*.

Standard Thermodynamic quantities at 298.15 K and 1.00 atm

	Term	ZPE	Enthalpy	Entropy	Cv	% in	
	cm-1	kJ/mol	kJ/mol	J/mol.K	J/mol.K	Ground	IR Int.
1 B2	1336.022	7.9912	0.0254	0.0983	0.5495	99.84	0.37
2 B1	1383.295	8.2739	0.0209	0.0806	0.4686	99.87	23.16
3 A1	1679.693	10.0468	0.0061	0.0229	0.1650	99.97	8.66
4 A1	2027.820	12.1291	0.0014	0.0050	0.0448	99.99	150.19
5 A1	3159.884	18.9003	0.0000	0.0000	0.0005	100.00	49.74
6 B1	3231.546	19.3289	0.0000	0.0000	0.0003	100.00	136.00
Total Vibrations		76.6702	0.0537	0.2068	1.2286		
Ideal Gas			2.4789				
Translation			3.7184	151.1685	12.4716		
Rotation			3.7184	66.6098	12.4716		
Totals			86.6397	217.9852	26.1719		
Gibb's Free Energy (H - TS)			21.6474				

References:

1. W. J. Hehre, L. D. Burke, A. J. Shusterman, "A PC Spartan Pro Tutorial," Wavefunction, Inc., Irvine, CA., 1999, pp. 23-24.