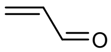
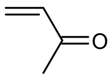
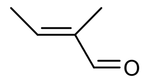
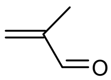
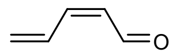
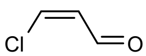
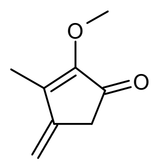
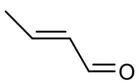
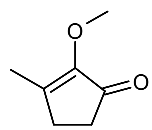
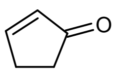
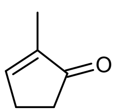
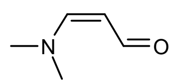
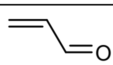
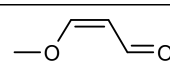
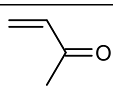
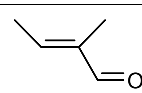
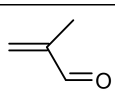
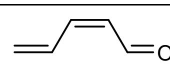
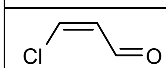
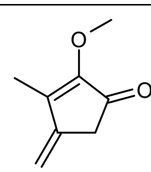
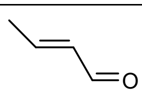
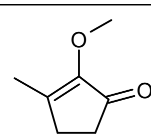
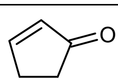
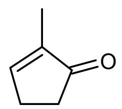
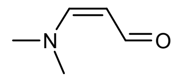
UV Spectra of Conjugated Carbonyl Compounds.[1]

Spartan: AM1-CI

	Experimental	AM1 (nm)		Experimental	AM1 (nm)
	209 nm	223.31		239 nm	263.50
	215	223.97		241	250.89
	219	236.64		251	281.22
	221	238.45		259	317.92
	221	237. 10		266	291.11
	219	239.63		294	329.09
	229	250.31		304	327.85

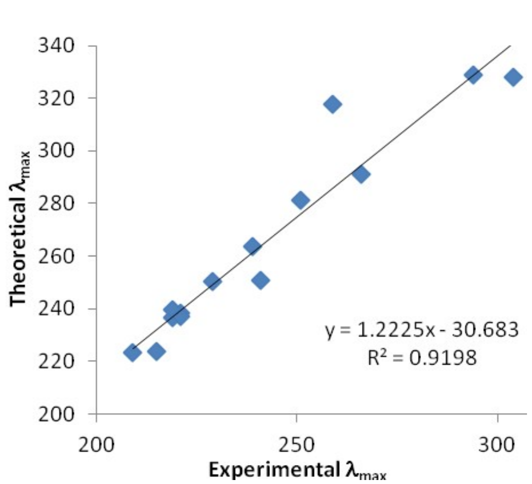
ZINDO (AM1 minimized geometry)

	Experimental	ZINDO (nm)		Experimental	ZINDO (nm)
	209 nm	212.56		239 nm	246.82
	215	210.71		241	245.55
	219	227.81		251	269.67
	221	Cl not available		259	306.46
	221	230.49		266	274.74
	219	225.62		294	254.30

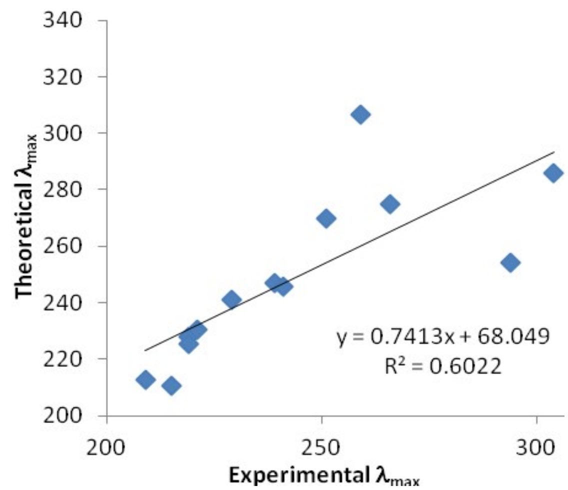
	229	240.98		304	286.03

The root-mean-squared, RMS, deviation of the AM1-CI values from the experimental is 26.1 nm, while the ZINDO RMS is slightly better at 19.6 nm. However, the overall correlation of the AM1-CI values is better, because of the better handling of heteroatoms; see the correlation plots below.

AM1-CI



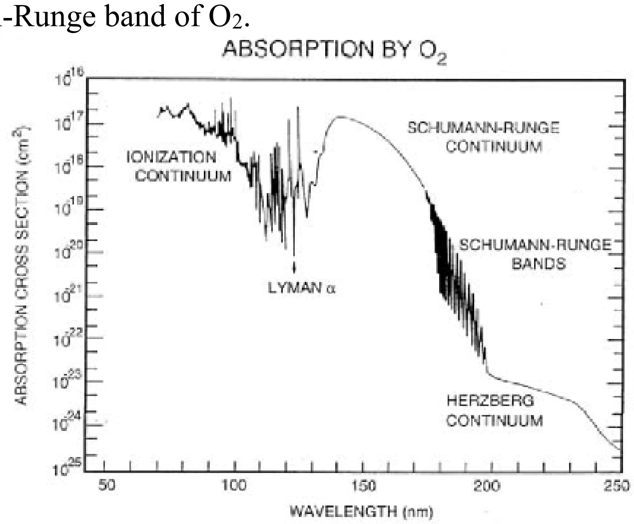
ZINDO



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 ^3P oxygen atoms, and the first excited state dissociates into a ^3P and a ^1D 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.

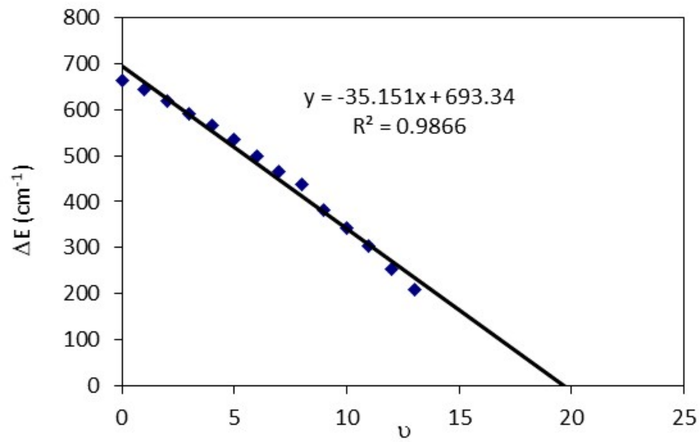
Transition energies in cm^{-1} of the Schumann-Runge band of O_2.

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



Answer: See Example 28.2.2. The curve fit is shown below.

υ	cm^{-1}	ΔE (cm^{-1})
0	50062.6	662.8
1	50725.4	643.6
2	51369.0	619.6
3	51988.6	590.4
4	52579.0	564.4
5	53143.4	536.2
6	53679.6	497.4
7	54177.0	464.8
8	54641.8	436.4
9	55078.2	381.8
10	55460.0	343.1
11	55803.1	304.2
12	56107.3	253.0
13	56360.3	210.3
	56570.6	



slope	-35.1512	693.34	b
±	1.182949	9.047817	±
r^2	0.986592	17.84254	s(y)
F	882.9758	12	df
ss_{reg}	281100.7	3820.273	$ss_{residual}$

Using Eq. 28.2.17, the slope gives the anharmonicity: $\chi_e^{ex}\,\tilde{\nu}_e^{ex} = -\tfrac{1}{2}\,\text{slope} = 17.58 \pm 0.59\ \text{cm}^{-1}$

Using Eq. 28.2.18: $\upsilon_{cl} = \dfrac{\Delta\tilde{\nu}_o}{2\chi_e^{ex}\,\tilde{\nu}_e^{ex}} = \dfrac{693.34}{35.151} = 19.72 \pm 0.71$

Using Eq. 28.2.19: area = $\tfrac{1}{2}\,\Delta\tilde{\nu}_o\,\upsilon_{cl} = \tfrac{1}{2}(693.34)(19.72) = 6837.89 \pm 261.8\ \text{cm}^{-1}$
Using Eq. 28.2.20, the transition wave number at the convergence limit is:

$$\tilde{\nu}_{\infty o} = \tilde{\nu}_{oo} + \text{area} = 50062.6\ \text{cm}^{-1} + 6837.9\ \text{cm}^{-1} = 56900.5 \pm 261.8\ \text{cm}^{-1} = 7.055 \pm 0.032\ \text{eV}$$

Using Eq. 28.2.6, the bond energy of the ground state is:

in cm^{-1}: $\tilde{D}_o = \tilde{\nu}_{\infty o} - \Delta\tilde{E}_{atomic} = (56900.5 \pm 261.8\ \text{cm}^{-1}) - 15883.\ \text{cm}^{-1} = 41018 \pm 274\ \text{cm}^{-1}$
in eV: $D_o = \Delta E(j,\infty\leftarrow i,0) - \Delta E_{atomic} = (7.055 \pm 0.032\ \text{eV}) - 1.9692\ \text{eV} = 5.086 \pm 0.034\ \text{eV}$
in kJ mol^{-1}: $= 490.7 \pm 3.3\ \text{kJ mol}^{-1}$

This bond energy is plotted in Figure 26.4.12 with the expected qualitative bond order of 2. The dissociation energy of the excited state is equal to the area calculated above:

$$\tilde{D}_o^{ex} = \text{area} = 6837.89 \pm 261.8\ \text{cm}^{-1} = 0.848 \pm 0.032\ \text{eV} = 81.8 \pm 3.1\ \text{kJ mol}^{-1}$$

The excited state bond strength is significantly smaller than the ground state, as is often the case. The O=O bond is easier to break in the excited state.

References:

1. W. J. Hehre, L. D. Burke, A. J. Shusterman, W. J. Pietro, Experiments in Computational Organic Chemistry, Wavefunction, Inc., Irvine, CA. Experiment 24