PROJECT NUMBER: REC0036

A Comparison of Quantum Mechanical Models Applied to α,β Unsaturated Carbonyl Compounds

---

A Major Qualifying Project
By:

William Henri Neve IV
4/28/2011

Approved By:

Professor Robert E. Connors, Ph.D.
Project Advisor

Abstract

Popular quantum mechanical methods that predict the geometries, vibrational spectra, and electronic spectra of organic molecules were investigated. Theoretical predictions were compared to experimental data and the accuracies of the predictions were determined. Methods studied include Hyperchem (semi-empirical, *ab initio*), WebMO (Gaussian B3LYP/6-311+G(d,p)) and the empirical Woodward-Fieser rules. From these comparisons the most accurate techniques were found to be the Woodward-Fieser rules (calculating the electronic spectrum λ max) and B3LYP/6-311+G(d,p) (calculating peaks in the vibrational spectrum).

Acknowledgements

I would like to thank Professor Robert E. Connors for his guidance, advice, and use of his laboratory throughout this year. I would also like to thank Christopher Zoto for always being there to help and take time out of his research to assist myself and others. Finally, I would like to thank Librarian Laura R. Hanlan for her help with literature research and dedication to learn about Chemistry in order to help find what I needed.

Table of Contents

Table of Figures

List of Tables

Introduction

With the rise of powerful computers, the scientific community has been able to run experiments using quantum mechanical methods to efficiently and quickly predict valuable structural and spectral data. Yet, there are numerous quantum mechanical programs and methods available to carry out these computations. Therefore, the question arises as to which are the most accurate and efficient? In this study, the programs Hyperchem and WebMO as well as the empirical Woodward-Fieser Rules are compared with known infrared and ultraviolet spectra for the test case of α,β unsaturated carbonyl compounds. This MQP focuses on fourteen specific carbonyl

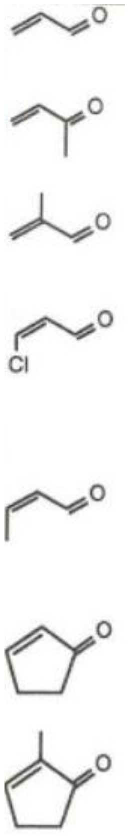


Figure 1: List of carbonyl compounds (part one). Names are listed in Table 1 for compounds one through seven.

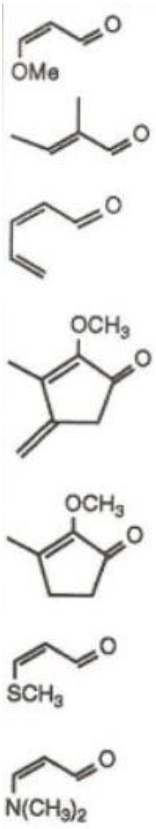


Figure 2: List of carbonyl compounds (part two). Names are listed in Table 1 for compounds eight through fourteen.

compounds which have various α and β substituents which test the methodologies of each by increasing the size and altering the type of compound. With this range of compounds, each method would be tested thoroughly for their efficiency and accuracy.

The methods that were studied in this project covered four different levels of calculations: empirical, semi-empirical, *ab initio*, and density functional theory. Semi-empirical and *ab initio* were studied in the program package known as *Hyperchem*. *Hyperchem* allows for a user to draw compounds in a three dimensions and optimize the geometry of the structure and generate vibrational and electronic data from these calculations.

The semi-empirical methods in the *Hyperchem* package that were studied are PM3 and ZINDO/S. The semi-empirical methods make approximations to make these calculations much faster than more sophisticated methods. An example of an approximation made is the two electron model of the Hamiltonian in Schrodinger’s equation being parameterized and calculations carried out normally otherwise.

The *ab initio* method in the *Hyperchem* package used was 6-31G* and is on a level of theory higher than that of semi-empirical. This level makes many less approximations than semi-empirical; however, still approximates calculations to make the Schrodinger’s equation into a “simple” eigenvalue problem, which is much easier for a computer to calculate than a full complex problem, as will be discussed a little with density functional theory. The 6-31G* method was used to calculate the geometry optimization and vibrational spectral data.

The final quantum mechanical method that was studied, was operated through the program package of *WebMO*. This is an online system that is fairly similar to *Hyperchem*; however, the use of large servers rather than just the computational power of a laptop or desktop serves for much faster calculations to be done at a higher level of calculation. *WebMO*, much like

Hyperchem, can calculate optimized geometries, vibrational spectra, and electronic spectra; however, *WebMO* allows for much easier exporting and transformation of raw data into vibrational and electronic spectra and gives the user a much nicer interface which is simpler to use.

The density functional theory (DFT) method used through *WebMO* functions on a much higher level than that of semi-empirical and *ab initio* even. The DFT level followed a Gaussian B3LYP/6-311+G(d,p) set of calculations where the calculations have become much less about approximations and much more intricate in the mathematical operations performed.

The final method studied was an empirical method known as the Woodward-Fieser Rules. This method is named for Robert Burns Woodward and Louis Fieser whom studied empirical data of many compounds to find trends in how specific bonds in certain areas in a compound would affect the peak value in the UV/Vis spectrum. These rules allow one to find the λ max absorption value, which is also the π->π* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

Experiments

I. Hyperchem Experiments

As mentioned before, *Hyperchem* was used to test the semi-empirical and *ab initio* levels of calculation in this study. Each compound shown before was created in *Hyperchem* and then their geometries were optimized. These optimized geometries in the semi-empirical method of PM3 were computed for all fourteen compounds. Afterwards, a vibrational spectrum of each compound was generated by use of the PM3 method as well. This gave the theoretical infrared spectral data for the semi-empirical method.

	Name	vinyl CH	formyl CH	C=O Stretch	C=C Stretch	formyl CH rock	vinyl CH rock
1	acrylaldehyde	3122.4	2925.81	1977.95	1847.22	1244.76	1203.33
2	Methyl Vinyl Ketone	3130.22	X	1975.45	1853.35	X	1285.91
3	methacrylaldehyde	X	2921.23	1980.11	1865.2	1353.22	X
4	(Z)-3-chloroacrylaldehyde	3058.47	2925.89	1973.12	1824.98	1286.45	1204.56
5	crotonaldehyde	3049.04	2926.47	1973.86	1874.55	1319.39	1205.4
6	2-cyclopenten-1-one	3112.95	X	2012.64	1811.43	X	1275.1
7	2-methyl-2-cyclopenten-1-one	X	X	2010.1	1866.96	X	X
8	3-methoxy-2-propenal	3144.62	2993.33	1963.79	1840.95	1378.53	1235.72
9	(2E)-2-methyl- 2-butenal	X	2916.73	1977.87	1875.56	1338.52	X
10	2,4-pentadienal	3132.67	2993	1975.2	1873.76	1335.85	1236.81
11	2-methoxy-3methyl-4methylene-cyclopent-2-enone	X	X	2015.97	1868.29	X	X
12	2-methoxy-3-methyl-2-cyclopenten-1-enone	X	X	2007.1	1874.22	X	X
13	(Z)- (9CI)-3-(methylthio)-2-propenal	3199.11	3023.3	1968.62	1817.83	1380.19	1282.21
14	(2Z)-3-(dimethylamino)-2-propenal	3133.44	2985.56	1965.67	1815.82	1344.31	1294.8

Table 1: Semi-Empirical Infrared Spectral Data

The optimized geometries were then used to calculate the UV spectral data through the use of the ZINDO/S semi-empirical method. The λ max absorption value (the π->π* transition) was focused on for this project.

Name	Semi-Empirical(in nm)
acrylaldehyde	206.2
Methyl Vinyl Ketone	206.6
methacrylaldehyde	216.9
(Z)-3-chloroacrylaldehyde	220.95
(Z)-but-2-enal	221.02
2-cyclopenten-1-one	211.69
2-methyl-2-cyclopenten-1-one	225.42
3-methoxy-2-propenal	232.14
(2E)-2-methyl- 2-butenal	229.77
2,4-pentadienal	255.21
2-methoxy-3methyl-4methylene-cyclopent-2-enone	277.9
2-methoxy-3-methyl-2-cyclopenten-1-enone	242.27
(Z)- (9CI)-3-(methylthio)-2-propenal	234.55
(2Z)-3-(dimethylamino)-2-propenal	249.22

Table 2: Semi-empirical ultraviolet spectral data

The same procedure was repeated at the *ab initio* level excluding the UV/Vis calculations. The geometries were optimized and the vibrational spectrum was calculated.

	Name (Numbers in cm^{-1})	vinyl CH	formyl CH	C=O Stretch	C=C Stretch	formyl CH rock	vinyl CH rock
1	acrylaldehyde	3382.75	3157.65	2012.78	1851.32	1414.2	1270.36
2	Methyl Vinyl Ketone	3346.05	X	1998.06	1855.84	X	1386.83
3	methacrylaldehyde	X	3165.31	2003.56	1869.78	1448.3	X
4	(Z)-3-chloroacrylaldehyde	3410.99	3169.32	2012.52	1837.03	1442.2	1347.8
6	2-cyclopenten-1-one	3383.64	X	2020.58	1816.8	X	1309.1
7	2-methyl-2-cyclopenten-1-one	X	X	2011.49	1870.28	X	X
8	3-methoxy-2-propenal	3344.77	3122	1995.71	1874.33	1402.5	1287.18
9	(2E)-2-methyl- 2-butenal	X	3155.77	1996.94	1889.47	1364.5	X
10	2,4-pentadienal	3342.95	3200.89	1995.43	1804.93	1375	1276.28
11	2-methoxy-3methyl-4methylene-cyclopent-2-enone	X	X	2010.21	1855.7	X	X
12	2-methoxy-3-methyl-2-cyclopenten-1-enone	X	X	1998.48	1891.39	X	X
13	(Z)- (9CI)-3-(methylthio)-2-propenal	3327.8	3207.24	1997.49	1809.29	1489.6	1333.12
14	(2Z)-3-(dimethylamino)-2-propenal	3273.76	3108.23	1978.01	1827.53	1340.2	1246.05

Table 3: Ab Initio Infrared Spectral Data

II. WebMO Experiments

Through the program package *WebMO* the density functional theory was tested at the Gaussian B3LYP/6-311+G(d,p) level of theory for the first ten compounds. First a geometry optimization was performed on the structures along with the vibrational spectrum. This procedure, much like the semi-empirical level, was followed by using that same geometry to determine the electronic spectrum for each compound.

	Name (Numbers in cm^{-1})	vinyl CH	formyl CH	C=O Stretch	C=C Stretch	formyl CH rock	vinyl CH rock
1	acrylaldehyde	3170.78	2882.31	1770.47	1673.92	1387.3	1297.58
2	Methyl Vinyl Ketone	3165.4	X	1744.57	1677.66	X	1307.31
3	methacrylaldehyde	X	2888.44	1765.81	1688.33	1389.8	X
4	(Z)-3-chloroacrylaldehyde	3169.63	2958.23	1754.92	1642.49	1420.3	1217
5	crotonaldehyde	3166.9	2918.11	1750.05	1685.73	1381.7	1264.77
6	2-cyclopenten-1-one	3217.7	X	1778.1	1640.59	X	1366.12
7	2-methyl-2-cyclopenten-1-one	X	X	1770.4	1686.92	X	X
8	3-methoxy-2-propenal	3196.39	2936.11	1738.4	1675.13	1387	1208.72
9	(2E)-2-methyl- 2-butenal	X	2880.88	1756.77	1700.96	1408.5	X
10	2,4-pentadienal	3167.58	2940.18	1744.07	1650.73	1383.8	1238.49

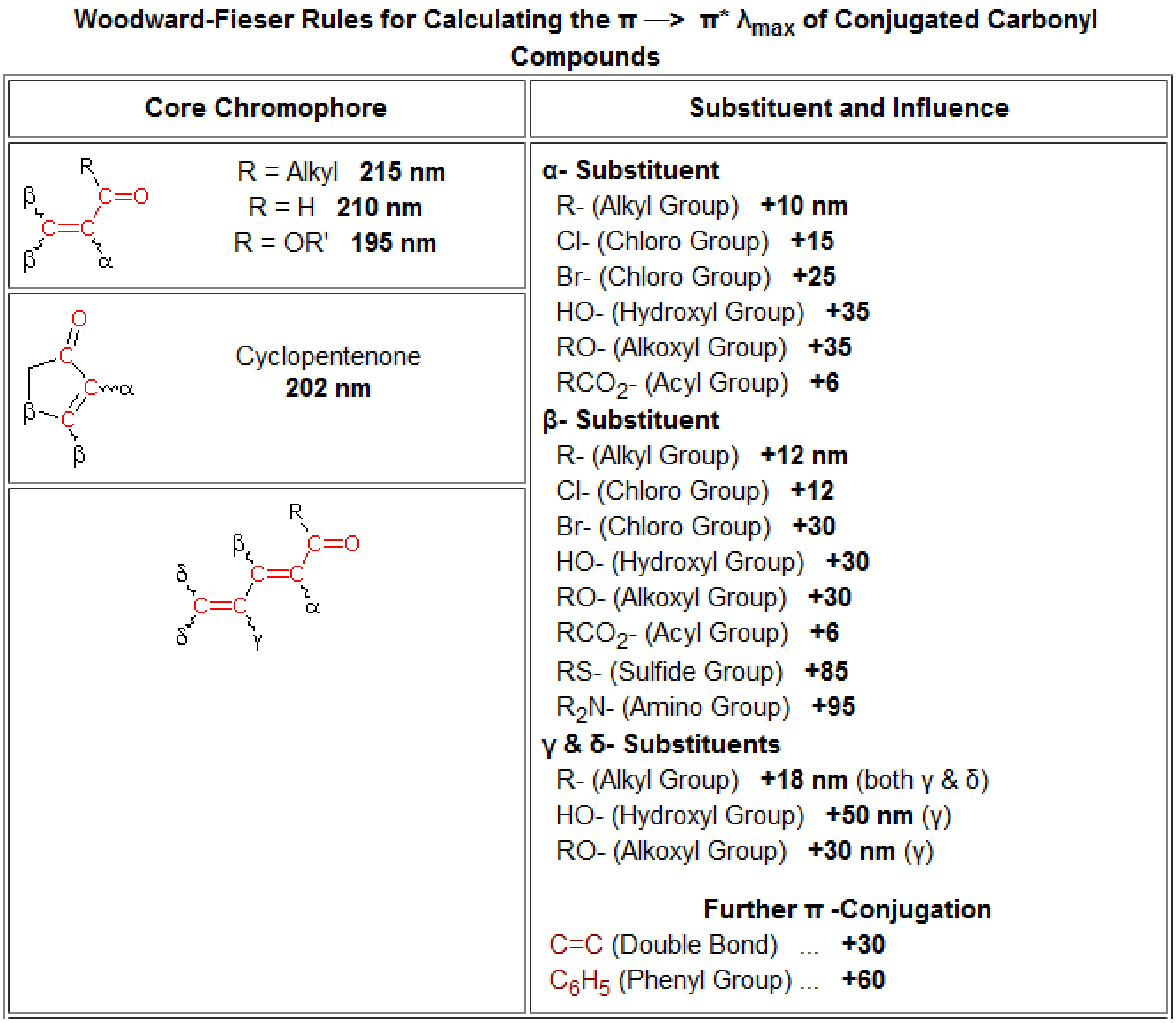
Table 4: Density Functional Theory Infrared Spectral Data

Name	DFT (in nm)
acrylaldehyde	199.52
Methyl Vinyl Ketone	203.87
methacrylaldehyde	212.48
(Z)-3-chloroacrylaldehyde	234.11
(Z)-but-2-enal	213.66
2-cyclopenten-1-one	206.78
2-methyl-2-cyclopenten-1-one	217.58
3-methoxy-2-propenal	238.17
(2E)-2-methyl- 2-butenal	217.83
2,4-pentadienal	257.26

Table 5: Density Functional Theory Ultraviolet Spectral Data

III. Woodward-Fieser Rules

Unlike the other methods, the empirical Woodward-Fieser Rules is not a quantum mechanical method and does not require complex calculations. The process to determining the λ max absorption for any carbonyl compound is a simple addition problem that can be calculated in seconds. By using observations of how substituents affect the absorption peak in the UV spectrum the Woodward-Fieser rules are able to quickly estimate the peak value for absorption.



Woodward-Fieser Rules for Calculating the π —> π* λ_{max} of Conjugated Carbonyl Compounds

Core Chromophore	Substituent and Influence
R = Alkyl **215 nm** R = H **210 nm** R = OR' **195 nm**	**α- Substituent** R- (Alkyl Group) **+10 nm** Cl- (Chloro Group) **+15** Br- (Chloro Group) **+25** HO- (Hydroxyl Group) **+35** RO- (Alkoxyl Group) **+35** RCO_2- (Acyl Group) **+6** **β- Substituent** R- (Alkyl Group) **+12 nm** Cl- (Chloro Group) **+12** Br- (Chloro Group) **+30** HO- (Hydroxyl Group) **+30** RO- (Alkoxyl Group) **+30** RCO_2- (Acyl Group) **+6** RS- (Sulfide Group) **+85** R_2N- (Amino Group) **+95** **γ & δ- Substituents** R- (Alkyl Group) **+18 nm** (both γ & δ) HO- (Hydroxyl Group) **+50 nm** (γ) RO- (Alkoxyl Group) **+30 nm** (γ) **Further π -Conjugation** C=C (Double Bond) ... **+30** C_6H_5 (Phenyl Group) ... **+60**
Cyclopentenone **202 nm**	

(2011). Retrieved March 6, 2011, 2011, from http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/UV-Vis/uvspec.htm

Figure 3: Woodward-Fieser Rules

With these rules in hand, the λ max absorption value could be calculated for each compound.

Name	Woodward (in nm)
acrylaldehyde	210
Methyl Vinyl Ketone	215
methacrylaldehyde	220
(Z)-3-chloroacrylaldehyde	222
(Z)-but-2-enal	222
2-cyclopenten-1-one	202
2-methyl-2-cyclopenten-1-one	212
3-methoxy-2-propenal	240
(2E)-2-methyl- 2-butenal	232
2,4-pentadienal	252
2-methoxy-3methyl-4methylene-cyclopent-2-enone	279
2-methoxy-3-methyl-2-cyclopenten-1-enone	261
(Z)- (9CI)-3-(methylthio)-2-propenal	295
(2Z)-3-(dimethylamino)-2-propenal	305

Table 6: Woodward-Fieser Rules Predicted UV Peak Data

Comparisons & Discussion

With the experiments concluded and a lot of information to analyze, the best course of action would be a direct comparison between the literature values and the values determined by the experiments.

I. Semi-Empirical Comparison

		Numbers in 1/cm		
Normal Mode	Literature	Semi Empirical	Corresponding To	Difference
1	3102	3142.63	vinyl CH	40.63
2	X	3122.43	X	X
3	3000	3050.66	vinyl CH	50.66
4	2800	2925.81	formyl CH	125.81
5	1723	1977.95	C=O	254.95
6	1625	1847.22	C=C	222.22
7	1422	1339.5	CH2 Bend	82.5
8	1361	1244.76	formyl CH rock	116.24
9	1276	1203.33	vinyl CH rock	72.67
10	1159	1168.3	vinyl CH2 rock	9.3
11	993	1057.4	C=C Torsion	64.4
12	980	983.02	formyl CH wag	3.02
13	959	925.25	vinyl CH2 wag	33.75
14	913	909.85	C-C	3.15
15	589	569.7	vinyl CH wag	19.3
16	564	567.56	C-C=O bend	3.56
17	340	359.15	C-C=C bend	19.15
18	158	75.14	skeletal torsion	82.86

Table 7: Acrylaldehyde Comparison of Semi-Empirical and Literature IR Peaks

		Numbers in 1/cm		
Normal Mode	Literature	Semi Empirical	Corresponding to	Difference
1	3105	3178.26	CH2	73.26
2	3027	3144.3	CH	117.3
3	2997	3130.22	CH2	133.22
4	2978	3090.93	CH3	112.93
5	2966	3078.82	CH3	112.82
6	2947	3046.52	CH3	99.52
7	1712	1975.45	C=O	263.45
8	1624	1853.35	C=C	229.35
9	1440	1405.64	δ(CH3)	34.36
10	1440	1391.78	δ(CH3)	48.22
11	1400	1383.85	δ(CH2)	16.15
12	1365	1345.86	δ(CH3)	19.14
13	1285	1285.91	(C-C), (C-CH3)	0.91
14	1248	1193.4	ρ(CH)	54.6
15	1055	1050.02	ρ(C2)	4.98
16	1022	1035.16	τ(C=C), γ(C-H)	13.16
17	998	993.07	γ(CH2)	4.93
18	965	969.64	ρ(CH3)	4.64
19	951	925.77	ρ(CH3)	25.23
20	765	873.07	(C-C-C)	108.07
21	598	677.17	τ(C=C), γ(C-H)	79.17
22	538	594.55	δ(C-C=O)	56.55
23	494	499.42	δ(C-C-CH3), δ(C-C=O)	5.42
24	432	365	γ(C=O)	67
25	280	285.04	δ(C-C-CH3), δ(C-C=O)	5.04
26	175	101.5	τ(CH3)	73.5
27	101	46.55	τ(C-C)	54.45

Table 8: Methyl Vinyl Ketone comparison of Semi-Empirical and Literature IR Peaks

		Numbers in 1/cm		
Normal Mode	Literature	Semi Empirical	Corresponding To	Difference
1	3096	3169.45	CH2	73.45
2	2998	3135.27	CH2	137.27
3	2975	3129.15	CH3	154.15
4	2960	3077.48	CH3	117.48
5	2940	3071.7	CH3	131.7
6	2830	2921.23	CHald	91.23
7	1718	1980.11	C=O	262.11
8	1648	1865.2	C=C	217.2
9	1453	1452.55	δ(CH3)	0.45
10	1453	1396.69	δ(CH3)	56.31
11	1425	1389.7	δ(CH2)	35.3
12	1390	1353.22	δ(CH3)	36.78
13	1360	1328.47	δ(CHald)	31.53
14	1310	1221.94	(C-C), (C-CH3)	88.06
15	1050	1054.84	ρ(CH3)	4.84
16	995	1008.02	ρ(CH3)	13.02
17	970	989.62	ρ(CH2)	19.62
18	948	957.75	γ(CHald)	9.75
19	932	942.28	γ(CH2)	10.28
20	813	931.6	(C-C), (C-CH3) in phase	118.6
21	695	614.46	τ(C=C)	80.54
22	628	603.18	δ(C-C=O)	24.82
23	422	452.71	γ(CH3)	30.71
24	410	437.32	δ(C=C-C), δ(C=C-CH3)	27.32
25	266	284.25	δ(C=C-C), δ(C=C-CH3)	18.25
26	X	92.01	τ(C-CH3)	X
27	169	35.95	τ(C-C)	133.05

Table 9: Methacrylaldehyde comparison of Semi-Empirical and Literature IR Peaks

		Numbers in 1/cm		
Normal Mode	Literature	Semi Empirical	Corresponding To	Difference
1	3058	3175.04	CH	117.04
2	2995	3079.36	CH	84.36
3	2980	3068.76	CH3	88.76
4	2963	3049.04	CH3	86.04
5	2938	3027.33	CH3	89.33
6	2805	2926.47	CHald	121.47
7	1720	1973.86	C=O	253.86
8	1649	1874.55	C=C	225.55
9	1455	1429.05	δ(CH3)	25.95
10	1455	1401.93	δ(CH3)	53.07
11	1391	1388.08	δ(CH3), ρ(CHald)	2.92
12	1375	1319.39	δ(CH3), ρ(CHald)	55.61
13	1304	1220.41	δ(CH)	83.59
14	1253	1205.4	δ(CH)	47.6
15	1147	1127.03	C-C	19.97
16	1074	1069.04	C-CH3	4.96
17	1042	1054.22	ρ(CH3)	12.22
18	973	1005.89	ρ(CH3)	32.89
19	973	986.76	τ(C=C), γ(C-H)	13.76
20	928	910.18	γ(CHald)	17.82
21	780	724.85	γ(C-H)	55.15
22	539	630.18	δ(C-C=O)	91.18
23	464	466.53	δ(C=C-C), δ(C=C-CH3)	2.53
24	295	363.93	τ(C=C), γ(CH3)	68.93
25	230	238.04	δ(C=C-C), δ(C=C-CH3)	8.04
26	173	58.1	τ(C-CH3), τ(C-C)	114.9
27	122	38.89	τ(C-CH3), τ(C-C)	83.11

Table 10: Crotonaldehyde comparison of Semi-Empirical and Literature IR Peaks

As one can see from the full spectral comparisons of four of the compounds above, the semi-empirical data (from the PM3 method) is varied in accuracy. Some of the peak values are fairly accurate and point towards a good comparison; however, due to the inconsistency of the peaks being above or below the value it is trying to replicate (with a standard deviation of 67.7) and there being no pattern one can decipher there is no possible way to make a scale factor for the semi-empirical data. A scale factor would multiply the experimental values by a decimal to try and have their accuracy increase compared to the literature values.

Since these values are so far off in some places and so close in others, it seems impossible to replicate the literature values from the given semi-empirical data. The double bond stretches (C=O, C=C) both have PM3 peak values that are around 200-250 cm^{-1} increased from the literature values so it would be easy to make a scale factor that is around 85-87% of those values (or multiply the PM3 values by .860 or so) as it would scale them to a value much closer to that of the literature ones. Yet, a good scale factor should be able to apply to every value and this is not the case here. Therefore, it is easy to conclude that the PM3 method is not accurate enough to be of use for a full infrared spectrum.

Where the PM3 method may have failed, the ZINDO/S method did somewhat succeed.

Pi -> Pi*	Numbers	in nm
Name	Literature	Semi-Empirical
acrylaldehyde	209	206.2
Methyl Vinyl Ketone	215	206.6
methacrylaldehyde	219	216.9
(Z)-3-chloroacrylaldehyde	221	220.95
(Z)-but-2-enal	221	221.02
2-cyclopenten-1-one	219	211.69
2-methyl-2-cyclopenten-1-one	229	225.42
3-methoxy-2-propenal	239	232.14
(2E)-2-methyl- 2-butenal	241	229.77
2,4-pentadienal	251	255.21
2-methoxy-3methyl-4methylene-cyclopent-2-enone	259	277.9
2-methoxy-3-methyl-2-cyclopenten-1-enone	266	242.27
(Z)- (9CI)-3-(methylthio)-2-propenal	294	234.55
(2Z)-3-(dimethylamino)-2-propenal	304	249.22

Table 11: Comparison of Semi-Empirical and Literature UV λ Max Peak Values

The ZINDO/S method, with the compounds that were smaller and had smaller peak values (less substituents as well) produced fairly accurate data and nearly perfect data in many instances. Yet, as the compounds increased in size, the ZINDO/S method seemed to vary as much as the PM3 method did with the IR spectrum. This observation is not too surprising as the ZINDO/S method has empirical data that these approximations are based off of and having an abundance of smaller molecules to refer from makes sense as other compounds can be based off of them. With these bases the programs are then able to use some simple calculations to try and assume the larger molecules. The data, however, shows that this method is not perfect in any way (with a standard deviation of 19.3) and cannot be considered reliable for anything other than smaller molecules.

Overall, the semi-empirical method is fast and that is about all it is. The PM3 method is far too inaccurate for anyone to use any of that data as a close approximation when they do not know the actual spectral data. The ZINDO/S is also a fast method; however, it is somewhat accurate where PM3 is not. The trouble with both are the inaccuracies due to the empirical aspect of these methods.

II. Ab initio Comparison

		Numbers in 1/cm		
Normal Mode	Literature	*Ab initio*	Corresponding To	Difference
1	3102	3423.84	vinyl CH	321.84
2	X	3382.75	X	X
3	3000	3336.61	vinyl CH	336.61
4	2800	3157.65	formyl CH	357.65
5	1723	2012.78	C=O	289.78
6	1625	1851.32	C=C	226.32
7	1422	1593.99	CH2 Bend	171.99
8	1361	1522.97	formyl CH rock	161.97
9	1276	1414.24	vinyl CH rock	138.24
10	1159	1270.36	vinyl CH2 rock	111.36
11	993	1145.78	C=C Torsion	152.78
12	980	1133.26	formyl CH wag	153.26
13	959	1122.58	vinyl CH2 wag	163.58
14	913	996.37	C-C	83.37
15	589	660.3	vinyl CH wag	71.3
16	564	611.61	C-C=O bend	47.61
17	340	346.01	C-C=C bend	6.01
18	158	173.96	skeletal torsion	15.96

Table 12: Acrylaldehyde comparison of ab initio and literature IR peak values

		Numbers in 1/cm		
Normal Mode	Literature	*Ab initio*	Corresponding to	Difference
1	3105	3426.54	CH2	321.54
2	3027	3376.92	CH	349.92
3	2997	3346.05	CH2	349.05
4	2978	3322.63	CH3	344.63
5	2966	3272.66	CH3	306.66
6	2947	3212.1	CH3	265.1
7	1712	1998.06	C=O	286.06
8	1624	1855.84	C=C	231.84
9	1440	1623.81	δ(CH3)	183.81
10	1440	1618.11	δ(CH3)	178.11
11	1400	1581.39	δ(CH2)	181.39
12	1365	1550.19	δ(CH3)	185.19
13	1285	1425.56	(C-C), (C-CH3)	140.56
14	1248	1386.83	ρ(CH)	138.83
15	1055	1174.5	ρ(C2)	119.5
16	1022	1158.56	τ(C=C), γ(C-H)	136.56
17	998	1141.8	γ(CH2)	143.8
18	965	1119.96	ρ(CH3)	154.96
19	951	1037.51	ρ(CH3)	86.51
20	765	818.64	(C-C-C)	53.64
21	598	761.18	τ(C=C), γ(C-H)	163.18
22	538	578.6	δ(C-C=O)	40.6
23	494	525.23	δ(C-C-CH3), δ(C-C=O)	31.23
24	432	470.41	γ(C=O)	38.41
25	280	295.58	δ(C-C-CH3), δ(C-C=O)	15.58
26	175	154.59	τ(CH3)	20.41
27	101	126.09	τ(C-C)	25.09

Table 13: Methyl Vinyl Ketone comparison of ab initio and literature IR peak values

		Numbers in 1/cm		
Normal Mode	Literature	*Ab initio*	Corresponding To	Difference
1	3096	3414.41	CH2	318.41
2	2998	3333.41	CH2	335.41
3	2975	3290.84	CH3	315.84
4	2960	3274.55	CH3	314.55
5	2940	3214.67	CH3	274.67
6	2830	3165.31	CHald	335.31
7	1718	2003.56	C=O	285.56
8	1648	1869.78	C=C	221.78
9	1453	1637.67	δ(CH3)	184.67
10	1453	1621.07	δ(CH3)	168.07
11	1425	1599.52	δ(CH2)	174.52
12	1390	1566.59	δ(CH3)	176.59
13	1360	1528.52	δ(CHald)	168.52
14	1310	1448.29	(C-C), (C-CH3)	138.29
15	1050	1186.25	ρ(CH3)	136.25
16	995	1136.67	ρ(CH3)	141.67
17	970	1124.61	ρ(CH2)	154.61
18	948	1103.01	γ(CHald)	155.01
19	932	1056.77	γ(CH2)	124.77
20	813	879.33	(C-C), (C-CH3) in phase	66.33
21	695	775.46	τ(C=C)	80.46
22	628	670.36	δ(C-C=O)	42.36
23	422	465.23	γ(CH3)	43.23
24	410	432.67	δ(C=C-C), δ(C=C-CH3)	22.67
25	266	281.26	δ(C=C-C), δ(C=C-CH3)	15.26
26	X	186.55	τ(C-CH3)	X
27	169	155.98	τ(C-C)	13.02

Table 14: Methacrylaldehyde comparison of ab initio and literature IR peak values

The *ab initio* data, compared to the PM3 data in the semi-empirical level of theory, seems to be equal in inaccuracy. There is, however, a big difference between these spectra above and the semi-empirical data and that is the ability for these values to be scaled. Where the semi-empirical was inconsistent as well as inaccurate the *ab initio* level is inaccurate as well (with a standard deviation of 107.7) but has a bit of consistency in how it is inaccurate (especially when compared to the PM3 method). Almost every value is greater than that of the literature value given and when they are greater they seem to be off by a similar percentage. Later on in the conclusion sections the scale factors will be covered for each level of theory.

III. Density Functional Theory Comparison

		Numbers in 1/cm		
Normal Mode	Literature	Density Functional Theory	Corresponding To	Difference
1	3102	3222.96	vinyl CH	120.96
2	X	3170.78	X	X
3	3000	3131.11	vinyl CH	131.11
4	2800	2882.31	formyl CH	82.31
5	1723	1770.47	C=O	47.47
6	1625	1673.92	C=C	48.92
7	1422	1454.7	CH2 Bend	32.7
8	1361	1387.35	formyl CH rock	26.35
9	1276	1297.58	vinyl CH rock	21.58
10	1159	1171.38	vinyl CH2 rock	12.38
11	993	1032.71	C=C Torsion	39.71
12	980	1025.02	formyl CH wag	45.02
13	959	997.75	vinyl CH2 wag	38.75
14	913	921.64	C-C	8.64
15	589	609.29	vinyl CH wag	20.29
16	564	572.72	C-C=O bend	8.72
17	340	324.36	C-C=C bend	15.64
18	158	166.82	skeletal torsion	8.82

Table 15: Acrylaldehyde comparison of density functional theory and literature IR peak values

		Numbers in 1/cm		
Normal Mode	Literature	Density Functional Theory	Corresponding to	Difference
1	3105	3223.44	CH2	118.44
2	3027	3165.4	CH	138.4
3	2997	3143.27	CH2	146.27
4	2978	3140.44	CH3	162.44
5	2966	3093.55	CH3	127.55
6	2947	3035.54	CH3	88.54
7	1712	1744.57	C=O	32.57
8	1624	1677.66	C=C	53.66
9	1440	1478.96	δ(CH3)	38.96
10	1440	1474.54	δ(CH3)	34.54
11	1400	1444.04	δ(CH2)	44.04
12	1365	1388.85	δ(CH3)	23.85
13	1285	1307.31	(C-C), (C-CH3)	22.31
14	1248	1268.44	ρ(CH)	20.44
15	1055	1072.22	ρ(C2)	17.22
16	1022	1046.99	τ(C=C), γ(C-H)	24.99
17	998	1036.87	γ(CH2)	38.87
18	965	990.65	ρ(CH3)	25.65
19	951	945.22	ρ(CH3)	5.78
20	765	760.56	(C-C-C)	4.44
21	598	694.88	τ(C=C), γ(C-H)	96.88
22	538	538.14	δ(C-C=O)	0.14
23	494	492.31	δ(C-C-CH3), δ(C-C=O)	1.69
24	432	431.52	γ(C=O)	0.48
25	280	281.1	δ(C-C-CH3), δ(C-C=O)	1.1
26	175	123.94	τ(CH3)	51.06
27	101	119.33	τ(C-C)	18.33

Table 16: Methyl Vinyl Ketone comparison of density functional theory and literature IR peak values

		Numbers in 1/cm		
Normal Mode	Literature	Density Functional Theory	Corresponding To	Difference
1	3096	3216.88	CH2	120.88
2	2998	3131.09	CH2	133.09
3	2975	3116.86	CH3	141.86
4	2960	3088.26	CH3	128.26
5	2940	3035.95	CH3	95.95
6	2830	2888.44	CHald	58.44
7	1718	1765.81	C=O	47.81
8	1648	1688.33	C=C	40.33
9	1453	1490.88	δ(CH3)	37.88
10	1453	1473.12	δ(CH3)	20.12
11	1425	1450.44	δ(CH2)	25.44
12	1390	1413.97	δ(CH3)	23.97
13	1360	1389.75	δ(CHald)	29.75
14	1310	1322.6	(C-C), (C-CH3)	12.6
15	1050	1073.83	ρ(CH3)	23.83
16	995	1035.72	ρ(CH3)	40.72
17	970	1012.8	ρ(CH2)	42.8
18	948	973.26	γ(CHald)	25.26
19	932	971.3	γ(CH2)	39.3
20	813	826.12	(C-C), (C-CH3) in phase	13.12
21	695	704.65	τ(C=C)	9.65
22	628	625.28	δ(C-C=O)	2.72
23	422	435.76	γ(CH3)	13.76
24	410	404.3	δ(C=C-C), δ(C=C-CH3)	5.7
25	266	261.06	δ(C=C-C), δ(C=C-CH3)	4.94
26	X	178.65	τ(C-CH3)	X
27	169	132.52	τ(C-C)	36.48

Table 17: Methacrylaldehyde comparison of density functional theory and literature IR peak values

		Numbers in 1/cm		
Normal Mode	Literature	Density Functional Theory	Corresponding To	Difference
1	3058	3166.9	CH	108.9
2	2995	3138.87	CH	143.87
3	2980	3119.6	CH3	139.6
4	2963	3062.61	CH3	99.61
5	2938	3023.31	CH3	85.31
6	2805	2918.11	CHald	113.11
7	1720	1750.05	C=O	30.05
8	1649	1685.73	C=C	36.73
9	1455	1483.99	δ(CH3)	28.99
10	1455	1479.82	δ(CH3)	24.82
11	1391	1450.18	δ(CH3), ρ(CHald)	59.18
12	1375	1417.69	δ(CH3), ρ(CHald)	42.69
13	1304	1381.71	δ(CH)	77.71
14	1253	1264.77	δ(CH)	11.77
15	1147	1164.17	C-C	17.17
16	1074	1072.6	C-CH3	1.4
17	1042	1026.12	ρ(CH3)	15.88
18	973	1022.32	ρ(CH3)	49.32
19	973	1012.14	τ(C=C), γ(C-H)	39.14
20	928	922.15	γ(CHald)	5.85
21	780	740.83	γ(C-H)	39.17
22	539	617.99	δ(C-C=O)	78.99
23	464	445.7	δ(C=C-C), δ(C=C-CH3)	18.3
24	295	346.25	τ(C=C), γ(CH3)	51.25
25	230	233.63	δ(C=C-C), δ(C=C-CH3)	3.63
26	173	161.58	τ(C-CH3), τ(C-C)	11.42
27	122	120.4	τ(C-CH3), τ(C-C)	1.6

Table 18: crotonaldehyde comparison of density functional theory and literature IR peak values

This method is the superior one in terms of calculation complexity and, therefore, near completion of what calculations would need to be done to exactly approximate the infrared spectrum. By looking at the comparisons above this is the superior method for estimating an infrared spectrum. The values are not only closer to the literature values (with a standard deviation of 42.8) but are also more consistently inaccurate in the same direction (as in greater or less than the literature values) compared to the semi-empirical and *ab initio* levels of theory. This seemingly is close enough to use as an approximation as it is now; however, we shall see how a scale factor improves or decreases upon the accuracy of the entire spectrum.

Just as it was with the semi-empirical method, there is also the ultraviolet spectrum to review. As it also was with the semi-empirical, emphasis was put on the accuracy of the λ max absorption peak value.

Pi -> Pi*	Numbers	in nm
Name	Literature	DFT
acrylaldehyde	209	200
Methyl Vinyl Ketone	215	204
methacrylaldehyde	219	212
(Z)-3-chloroacrylaldehyde	221	234
(Z)-but-2-enal	221	214
2-cyclopenten-1-one	219	207
2-methyl-2-cyclopenten-1-one	229	216
3-methoxy-2-propenal	239	238
(2E)-2-methyl- 2-butenal	241	218
2,4-pentadienal	251	257

Table 19: Comparison of density functional theory and literature UV λ max peak values

Where density functional theory provides fairly accurate peak values here, they are still inconsistent. There are some values which are near perfect, as has been experienced before with the semi-empirical data; however, there are also values that are inaccurate and, therefore, are not very helpful. Density functional theory may end up having a very low percent difference compared to the literature values but this is due to inconsistencies of highly accurate values and fairly inaccurate values both appearing throughout. Yet, the standard deviation was only 5.9, much better than the semi-empirical method and the Woodward-Fieser Rules.

IV. Woodward-Fieser Rules Comparison

As explained before in Figure 3 on page 15, the Woodward-Fieser Rules are simply empirical rules that are based off compounds much like the ones being studied in this project. By following them closely based on what substituents are added where on the base carbonyl structure one can quickly predict an approximate peak value for the λ max absorption.

Pi -> Pi*	Numbers	in nm
Name	Literature	Woodward
acrylaldehyde	209	210
Methyl Vinyl Ketone	215	215
methacrylaldehyde	219	220
(Z)-3-chloroacrylaldehyde	221	222
(Z)-but-2-enal	221	222
2-cyclopenten-1-one	219	202
2-methyl-2-cyclopenten-1-one	229	212
3-methoxy-2-propenal	239	240
(2E)-2-methyl- 2-butenal	241	232
2,4-pentadienal	251	252
2-methoxy-3methyl-4methylene-cyclopent-2-enone	259	279
2-methoxy-3-methyl-2-cyclopenten-1-enone	266	261
(Z)- (9CI)-3-(methylthio)-2-propenal	294	295
(2Z)-3-(dimethylamino)-2-propenal	304	305

Table 20: Comparison of Woodward-Fieser Rules and literature UV λ max peak values

As expected from empirical rules that were based on many structures, including the ones that are being studied in this project, the predicted values are extremely accurate and, in fact, are the best of the three predictions for the absorption peaks (although the standard deviation of 7.2 was higher than the density functional theory). This is much easier to see when these are all compared together.

V. Discussion

The quantum mechanical programs were tested for accuracy, speed, and consistency. For the infrared spectral data, the C=O and C=C bonds were highlighted due to their intensity in the spectrum for any compound and since they were easier to determine as the actual values they were representing, as fingerprint region data (under 1200 cm^{-1}) is inaccurate for all. By doing this, a scale factor was able to be created by dividing the literature values for each C=O and C=C stretches that were given by the experimental values. By averaging these all together, this scale factor should apply to the entire spectrum.

C=O Stretches Numbers in cm^{-1}				
Name	Lit.	S.E.	A.I	D.F.T
acrylaldehyde	1723	1977.95	2012.78	1770.47
Methyl Vinyl Ketone	1712	1975.45	1998.06	1744.57
methacrylaldehyde	1718	1980.11	2003.56	1765.81
crotonaldehyde	1720	1973.86	N/A	1750.05

Name	Diff. (S.E)	%Diff (S.E)	Diff. (A.I)	%Diff(A.I)	Diff (D.F.T)	%Diff(D.F.T)
acrylaldehyde	254.95	13.78	289.78	15.51	47.47	2.72
Methyl Vinyl Ketone	263.45	14.29	286.06	15.42	32.57	1.88
methacrylaldehyde	262.11	14.18	285.56	15.35	47.81	2.74
crotonaldehyde	253.86	13.74	X	X	30.05	1.73
Average =>	258.59	**14.00**	287.13	**15.43**	39.47	**2.27**

Table 21: C=O stretches and calculations

C=C Stretches Numbers in cm^{-1}				
Name	Lit.	S.E.	A.I.	D.F.T
acrylaldehyde	1625	1847.22	1851.32	1673.92
Methyl Vinyl Ketone	1624	1853.35	1855.84	1677.66
methacrylaldehyde	1648	1865.20	1869.78	1688.33
crotonaldehyde	1649	1874.55	N/A	1685.73

Name	Diff. (S.E)	%Diff (S.E)	Diff. (A.I)	%Diff(A.I)	Diff (MO)	%Diff(D.F.T)
acrylaldehyde	222.22	12.80	226.32	13.02	48.92	2.97
Methyl Vinyl Ketone	229.35	13.19	231.84	13.32	53.66	3.25
methacrylaldehyde	217.2	12.36	221.78	12.61	40.33	2.42
crotonaldehyde	225.55	12.80	X	X	36.73	2.20
Average =>	223.58	**12.79**	226.65	**12.98**	44.91	**2.71**

Table 22: C=C stretches and calculations

The calculations show that the most accurate of the three is density functional theory by a significant margin. With only 2.27% and 2.71% difference on average for the C=O and C=C stretches respectively the density functional theory seemingly can estimate, within very acceptable standards, these two important stretches consistently. This is a slight positive but, as we saw before, the entire spectrum follows pretty closely to the results we see here.

The semi-empirical and *ab initio* both are off around 13.50% on average which is poor for either one. As we saw before, the semi-empirical seemingly cannot provide reliable scale factors due to the inconsistency that it shows compared to the literature values but the *ab initio* possibly could. Using the scale factors created by the use of only these C=O and C=C bands, we should see an improvement in the percent difference and generally in the full spectrum.

Name (C=O)	Scale Factor	Scaled (S.E)	Scale Factor	Scaled (A.I)	Scale Factor	Scaled (D.F.T)
acrylaldehyde	0.871	1729.70	0.856	1745.94	0.973	1726.96
Methyl Vinyl Ketone	0.867	1727.52	0.857	1733.17	0.981	1701.69
methacrylaldehyde	0.868	1731.59	0.857	1737.94	0.973	1722.41
crotonaldehyde	0.871	1726.13	X	X	0.983	1707.04
Average =>	0.869		0.857		0.978	
Name (C=C)	Scale Factor	Scaled (S.E)	Scale Factor	Scaled (A.I)	Scale Factor	Scaled (D.F.T)
acrylaldehyde	0.880	1615.38	0.878	1605.88	0.971	1632.78
Methyl Vinyl Ketone	0.876	1620.74	0.875	1609.80	0.968	1636.43
methacrylaldehyde	0.884	1631.10	0.881	1621.89	0.976	1646.84
crotonaldehyde	0.880	1639.28	X		0.978	1644.30
Average =>	0.880		0.878		0.973	
Scale Factor (S.E)	**0.874**	**Scale Factor (A.I)**	**0.867**	**Scale Factor (M.O)**	**0.975**	

Table 23: Scale factor calculations for C=O and C=C stretches with averages

C=O Stretches (numbers in cm-1)				
Name	Literature	Scaled (S.E)	Scaled (A.I)	Scaled (D.F.T)
acrylaldehyde	1723	1729.70	1745.94	1726.96
Methyl Vinyl Ketone	1712	1727.52	1733.17	1701.69
methacrylaldehyde	1718	1731.59	1737.94	1722.41
crotonaldehyde	1720	1726.13	X	1707.04

Name	Diff. (S.E)	%Diff (S.E)	Diff. (A.I)	%Diff(A.I)	Diff (D.F.T)	%Diff(D.F.T)
acrylaldehyde	6.70	0.39	22.94	1.32	3.96	0.23
Methyl Vinyl Ketone	15.52	0.90	21.17	1.23	10.31	0.60
methacrylaldehyde	13.59	0.79	19.94	1.15	4.41	0.26
crotonaldehyde	6.13	0.36	X	X	12.96	0.76
Average =>	10.48	**0.61**	21.35	**1.23**	7.91	**0.46**

Table 24: C=O Scaled Stretches and calculations

C=C Stretches (numbers in cm-1)				
Name	Literature	Scaled (S.E)	Scaled (A.I)	Scaled (D.F.T)
acrylaldehyde	1625	1615.38	1605.88	1632.78
Methyl Vinyl Ketone	1624	1620.74	1609.80	1636.43
methacrylaldehyde	1648	1631.10	1621.89	1646.84
crotonaldehyde	1649	1639.28	X	1644.30

Name	Diff. (S.E)	%Diff (S.E)	Diff. (A.I)	%Diff(A.I)	Diff (MO)	%Diff(D.F.T)
acrylaldehyde	9.62	0.59	19.12	1.18	7.78	0.48
Methyl Vinyl Ketone	3.26	0.20	14.20	0.88	12.43	0.76
methacrylaldehyde	16.90	1.03	26.11	1.60	1.16	0.07
crotonaldehyde	9.72	0.59	X	X	4.70	0.29
Average =>	9.87	**0.60**	19.81	**1.22**	6.52	**0.40**

Table 25: C=C Scaled Stretches and calculations

By scaling the C=O and C=C bonds by the scale factors mentioned before, the average percent difference becomes even smaller than it already was. We can decipher that the density functional theory still has the best accuracy. The best way to see which becomes the most accurate when the scale factor is introduced is to compare a full spectrum between the literature and the three methods.

		Numbers in 1/cm			
Normal Mode	Literature	Scaled S.E	Scaled A.I	Scaled D.F.T	Corresponding To
1	3102	2746.66	2968.47	3142.39	vinyl CH
2	X	2729.00	2932.84	3091.51	X
3	3000	2666.28	2892.84	3052.83	vinyl CH
4	2800	2557.16	2737.68	2810.25	formyl CH
5	1723	1728.73	1745.08	1726.21	C=O
6	1625	1614.47	1605.09	1632.07	C=C
7	1422	1170.72	1381.99	1418.33	CH2 Bend
8	1361	1087.92	1320.41	1352.67	formyl CH rock
9	1276	1051.71	1226.15	1265.14	vinyl CH rock
10	1159	1021.09	1101.40	1142.10	vinyl CH2 rock
11	993	924.17	993.39	1006.89	C=C Torsion
12	980	859.16	982.54	999.39	formyl CH wag
13	959	808.67	973.28	972.81	vinyl CH2 wag
14	913	795.21	863.85	898.60	C-C
15	589	497.92	572.48	594.06	vinyl CH wag
16	564	496.05	530.27	558.40	C-C=O bend
17	340	313.90	299.99	316.25	C-C=C bend
18	158	65.67	150.82	162.65	skeletal torsion

Table 26: Acrylaldehyde IR spectrum comparison (scaled values)

Normal Mode	Diff (S.E)	% Diff (S.E)	Diff (A.I)	% Diff (A.I)	Diff (D.F.T)	% Diff (D.F.T)
1	355.34	12.15	133.53	4.40	40.39	1.29
2	X	X	X	X	X	X
3	333.72	11.78	107.16	3.64	52.83	1.75
4	242.84	9.07	62.32	2.25	10.25	0.37
5	5.73	0.33	22.08	1.27	3.21	0.19
6	10.53	0.65	19.91	1.23	7.07	0.43
7	251.28	19.38	40.01	2.85	3.67	0.26
8	273.08	22.30	40.59	3.03	8.33	0.61
9	224.29	19.27	49.85	3.98	10.86	0.85
10	137.91	12.65	57.60	5.10	16.90	1.47
11	68.83	7.18	0.39	0.04	13.89	1.39
12	120.84	13.14	2.54	0.26	19.39	1.96
13	150.33	17.01	14.28	1.48	13.81	1.43
14	117.79	13.79	49.15	5.53	14.40	1.59
15	91.08	16.76	16.52	2.84	5.06	0.86
16	67.95	12.82	33.73	6.17	5.60	1.00
17	26.10	7.98	40.01	12.50	23.75	7.24
18	92.33	82.56	7.18	4.65	4.65	2.90
Average =>	151.18	**16.40**	40.99	**3.60**	14.94	**1.50**

Table 27: Acrylaldehyde Differences and Percent Differences

As expected, the density functional theory method is fairly accurate to begin with; however, with the scale factor created from the double bond stretches the method performs even better and becomes significantly accurate for the entire spectrum. The semi-empirical method fails to improve due to the inconsistency of the approximation to begin with. This was expected as it is impossible to correct data that oscillates between being greater than or less than the literature values. The *ab initio* values, however, became increasingly accurate when a scale factor was applied. It went from about a 13-15% difference to a 3.60% difference which is accurate enough to be used as a good approximation of a spectrum. Be that as it may, the density functional theory is still the best even though the *ab initio* level became better than expected with the scale factor mentioned before (.867).

For the ultraviolet spectral data, the λ max peak absorption was highlighted due to it being the main peak in the absorption spectrum.

Pi -> Pi*	Numbers	in nm		
Name	Literature	Semi-Empirical	Woodward	D.F.T
acrylaldehyde	209	206.2	210	199.52
Methyl Vinyl Ketone	215	206.6	215	203.87
methacrylaldehyde	219	216.9	220	212.48
(Z)-3-chloroacrylaldehyde	221	220.95	222	234.11
(Z)-but-2-enal	221	221.02	222	213.66
2-cyclopenten-1-one	219	211.69	202	206.78
2-methyl-2-cyclopenten-1-one	229	225.42	212	217.58
3-methoxy-2-propenal	239	232.14	240	238.17
(2E)-2-methyl- 2-butenal	241	229.77	232	217.83
2,4-pentadienal	251	255.21	252	257.26
2-methoxy-3methyl-4methylene-cyclopent-2-enone	259	277.9	279	X
2-methoxy-3-methyl-2-cyclopenten-1-enone	266	242.27	261	X
(Z)- (9CI)-3-(methylthio)-2-propenal	294	234.55	295	X
(2Z)-3-(dimethylamino)-2-propenal	304	249.22	305	X

Table 28: UV λ max peak values comparison

Difference (S.E)	% Diff. (S.E)	Difference (W)	% Diff. (W)	Difference (D.F.T)	% Diff. (D.F.T)
2.80	1.35	1.00	0.48	9.48	4.64
8.40	3.98	0.00	0.00	11.13	5.31
2.10	0.96	1.00	0.46	6.52	3.02
0.05	0.02	1.00	0.45	13.11	5.76
0.02	0.01	1.00	0.45	7.34	3.38
7.31	3.39	17.00	8.08	12.22	5.74
3.58	1.58	17.00	7.71	11.42	5.11
6.86	2.91	1.00	0.42	0.83	0.35
11.23	4.77	9.00	3.81	23.17	10.10
4.21	1.66	1.00	0.40	6.26	2.46
18.90	7.04	20.00	7.43	X	X
23.73	9.34	5.00	1.90	X	X
59.45	22.50	1.00	0.34	X	X
54.78	19.80	1.00	0.33	X	X
14.53	**5.67**	5.43	**2.30**	10.15	**4.59**

Table 29: UV λ max differences and percent differences

When the data is analyzed it is clear that the most accurate (also the fastest) is the empirical Woodward-Fieser Rules. This makes sense as it is based on the empirical data from various carbonyl compounds including the ones being studied in this project. The interesting thing is that none of the methods do poorly in this study. Each one is still in single digit percent differences, which is fairly good accuracy overall. Yet, of the two non-empirical methods, the superior of these is the density functional theory method. The only issue is that is has very low consistency with the values it calculates and, therefore, is not very reliable. The semi-empirical method performed well but had some issues with consistency as well, although it was more due to the inability for the method to calculate for larger compounds.

Conclusions

From the results we can make the conclusion that the density functional theory method is the superior method overall and is fairly accurate for both infrared and ultraviolet spectral data. With that said, the superior ultraviolet predictor was the Woodward-Fieser Rules; however, they are very conditional as they will only work for compounds that are within the rules that exist (i.e. carbonyl and diene compounds). Otherwise it is a bit of a split decision as both semi-empirical (the ZINDO/S method) and the density functional theory (Gaussian B3LYP/6-311+G(d,p)) have similarities in their predictions, as they are inconsistent; however, semi-empirical is only good for smaller compounds. Since that is so, semi-empirical is the superior method for small compounds as it is quick and fairly accurate.

For the infrared spectrum the density functional theory is by far the superior method. The other two methods are very inaccurate without a scale factor and the DFT method has a percent difference of only 5% and that accuracy increased when the scale factor was applied. Therefore, DFT is the superior method for infrared spectral data.

References

(2011). Retrieved March 6, 2011, 2011, from http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/UV-Vis/uvspec.htm

Brand, J. C. D., & Williamson, D. G. (1963). Near-ultra-violet spectrum of propenal. The University, Glasgow, Department of Chemistry). , 184-191.

Oelichmann, H. J. (1981). Coupled calculation of vibrational frequencies and intensities:: Part VI. IR and raman spectra of crotonaldehyde, methacrolein and methyl-vinylketone. *Journal of Molecular Structure, 77*(3-4), 179.

SciFinder. (2011). *IR absorption spectra (acrylaldehyde).* Retrieved February 9, 2011, from https://scifinder.cas.org/scifinder/view/scifinder/scifinderExplore.jsf

Talrose, V., et al. (2009). *2-propenal: UV/Visible spectrum.* Retrieved February 15, 2011, from http://webbook.nist.gov/cgi/cbook.cgi?ID=C107028&Mask=400#Refs

Baer, T. (2002). Ultraviolet spectroscopy and UV lasers. practical spectroscopy series. volume 30 edited by prabhakar misra (howard university) and mark A. dubinskii (magnon, inc., reisterstown, MD). Marcel Dekker. *Journal of the American Chemical Society, 124*(40), 12054.

Appendix

I. Semi-Empirical Singlet and Triplet State Transitions

Acrylaldehyde

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	522.8	19127.3	0
S->T	n->π*	473.5	21118.3	0
S->S	n->π*	406.3	24612.2	0
S->S	π->π*	206.2	48487.3	0.6614

Methacrylaldehyde

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	572.6	17462.7	0
S->T	n->π*	467.2	21402.5	0
S->S	n->π*	401.8	24888.3	0
S->S	π->π*	216.9	46104.8	0.5262

(Z)-3-chloroacrylaldehyde

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	563.2	17755.8	0
S->T	n->π*	481.8	20755.1	0
S->S	n->π*	412.9	24217.4	0
S->S	π->π*	220.9	45271.6	0.6259

Crotonaldehyde

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	567	17636.5	0
S->T	n->π*	472.9	21148	0
S->S	n->π*	406.8	24581	0
S->S	π->π*	220.9	45261.1	0.6198

2-cyclopenten-1-one

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	540.2	18510.4	0
S->T	n->π*	443.5	22547	0
S->S	n->π*	389.1	25700.4	0
S->S	π->π*	211.7	47239.9	0.5848

2-methyl-2-cyclopenten-1-one

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	582.3	17172.8	0
S->T	n->π*	442.6	22593.6	0
S->S	n->π*	388.4	25743.7	0
S->S	π->π*	225.4	44360.9	0.4946

3-methoxy-2-propenal

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	591.7	16900	0
S->T	n->π*	468.1	21363.9	0
S->S	n->π*	404.1	24747.4	0
S->S	π->π*	232.4	43027.3	0.6042

(2E)-2-methyl- 2-butenal

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	635.7	15730.8	0
S->T	n->π*	459.4	21766.4	0
S->S	n->π*	397.5	25157	0
S->S	π->π*	229.8	43520.9	0.5816

2,4-pentadienal

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	746.3	13399.2	0
S->T	n->π*	479.6	20849.7	0
S->S	n->π*	412.9	24219.2	0
S->S	π->π*	255.2	39184	0.9053

2-methoxy-methyl-4methylene-cyclopent-2-enone

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	824.6	12127.2	0
S->T	n->π*	456.5	21907.1	0
S->S	n->π*	399.3	25046.3	0
S->S	π->π*	277.9	35983.6	0.6553

2-methoxy-3-methyl-2-cyclopenten-1-enone

Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	606.1	16498.3	0
S->T	n->π*	440.9	22679.4	0
S->S	n->π*	389.2	25697	0
S->S	π->π*	242.3	41275.9	0.4959

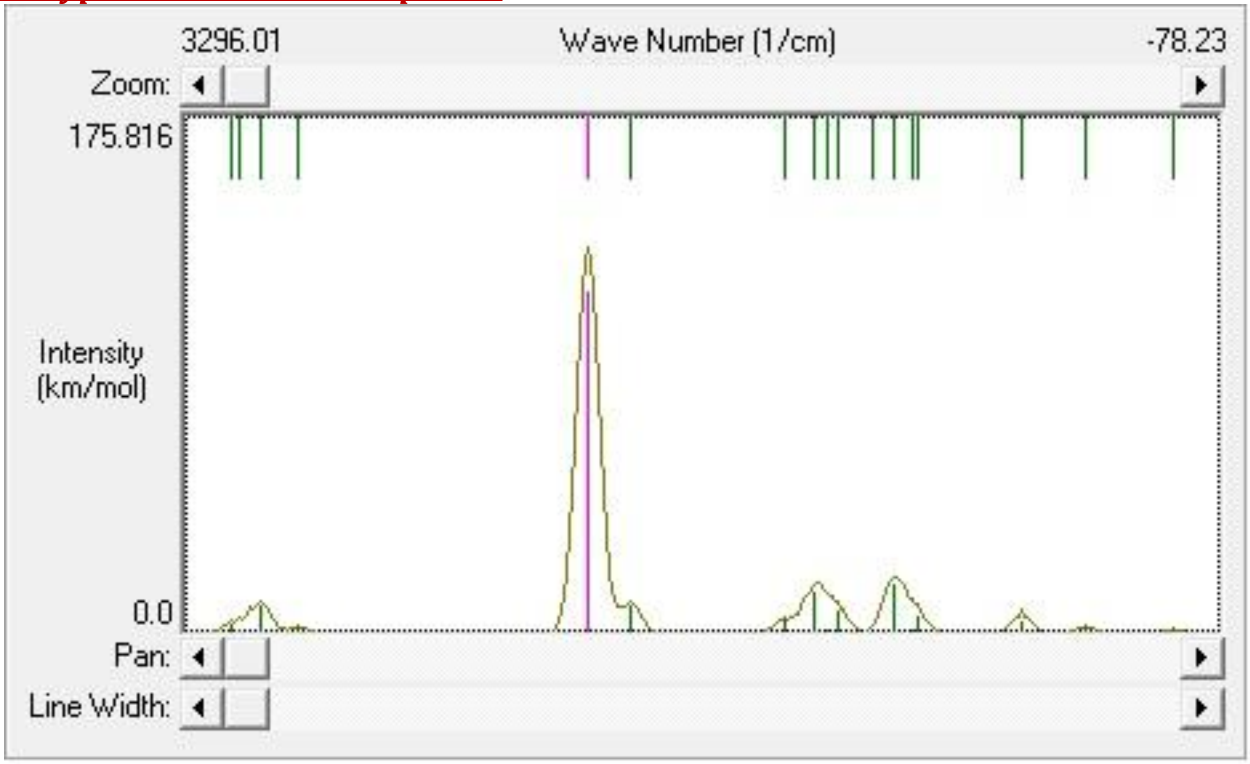
(Z)- (9CI)-3-(methylthio)-2-propenal

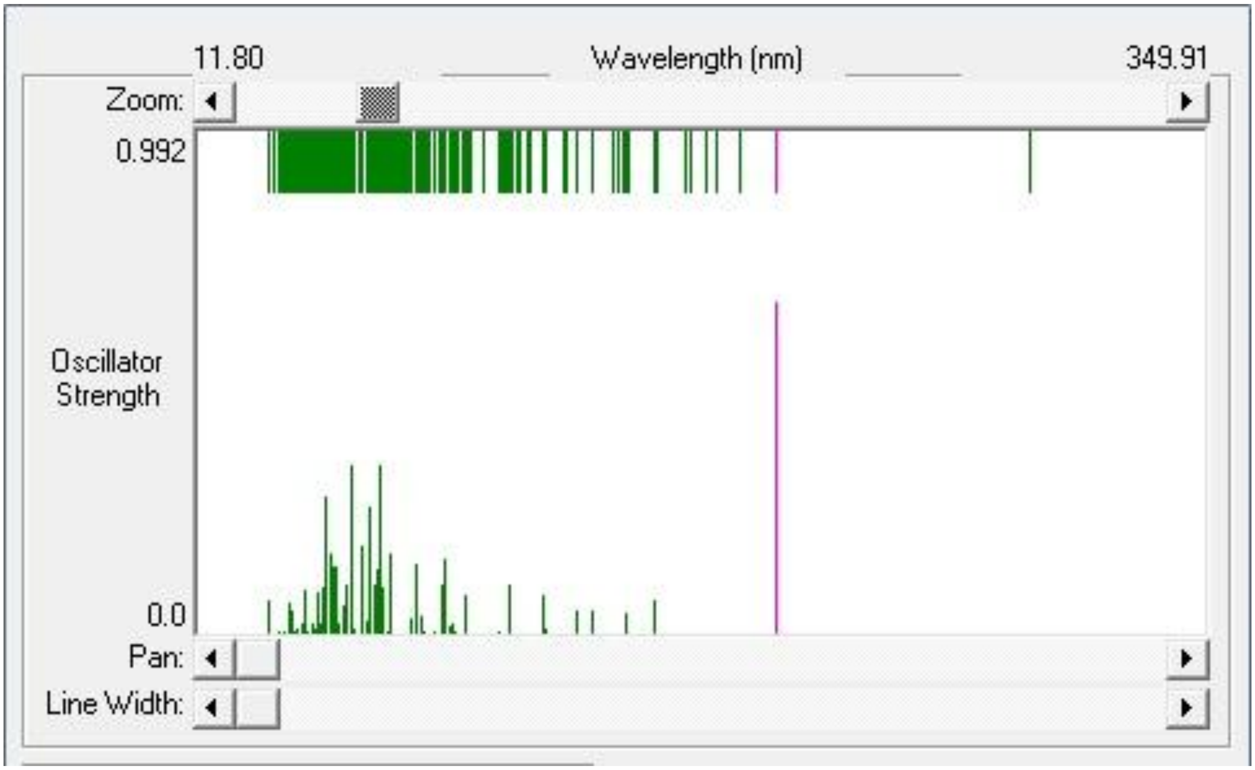
Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	569	17574.6	0
S->T	n->π*	470.1	21270.2	0
S->S	n->π*	405.3	24673.3	0
S->S	π->π*	234.6	42634.8	0.5662

(2Z)-3-(dimethylamino)-2-propenal

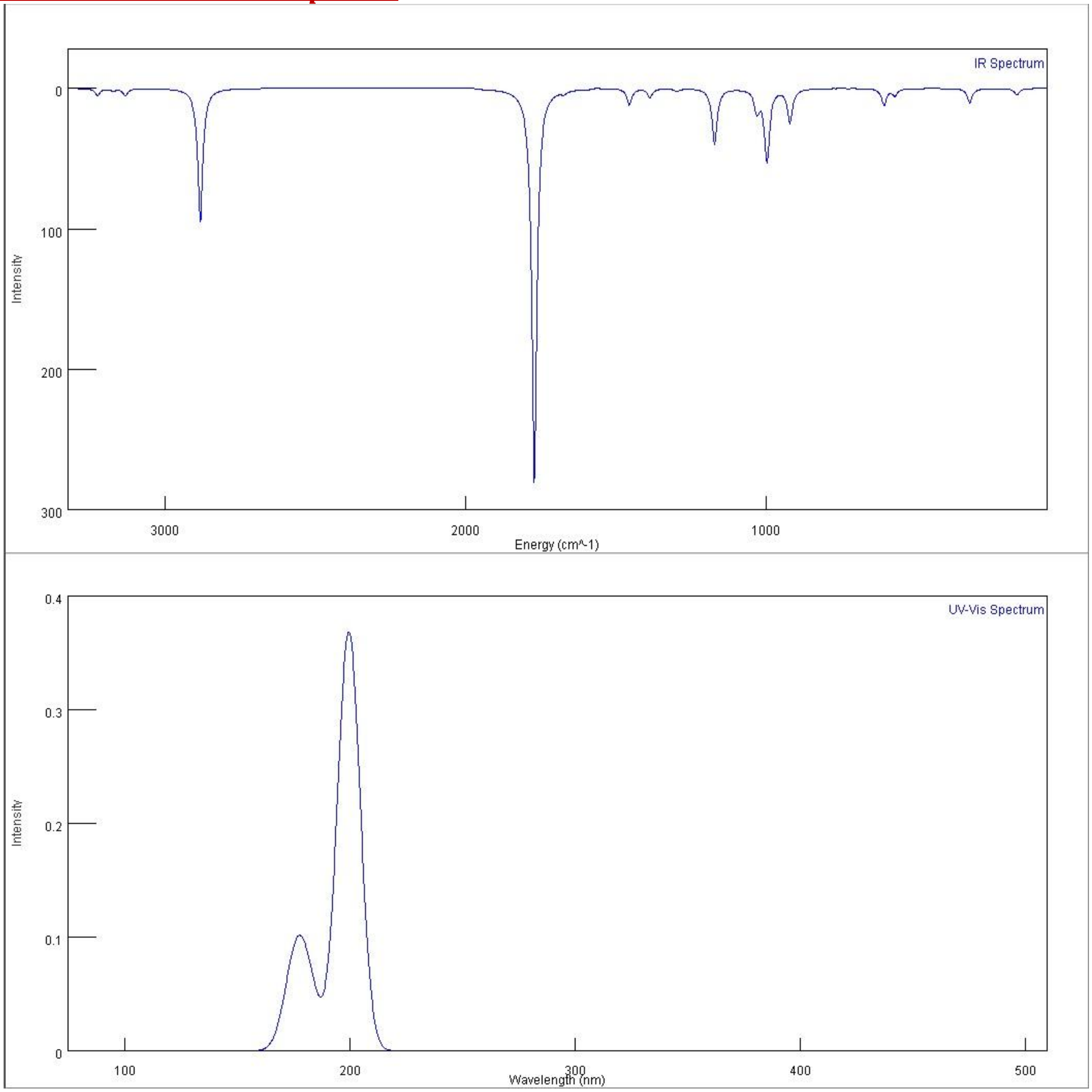
Spin	Transition	λ(nm)	1/cm	f
S->T	π->π*	587.7	17016.3	0
S->T	n->π*	455.6	21947.5	0
S->S	n->π*	395.6	25276.5	0
S->S	π->π*	249.2	40124.6	0.6948

II. Hyperchem IR and UV Spectra

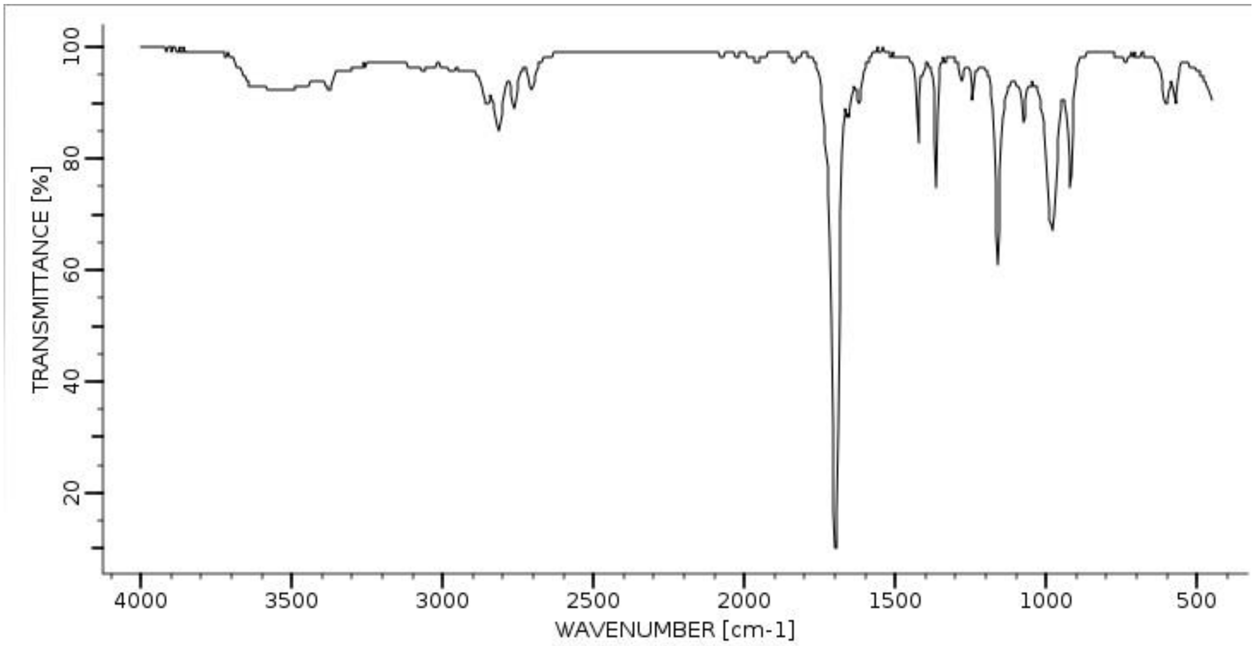


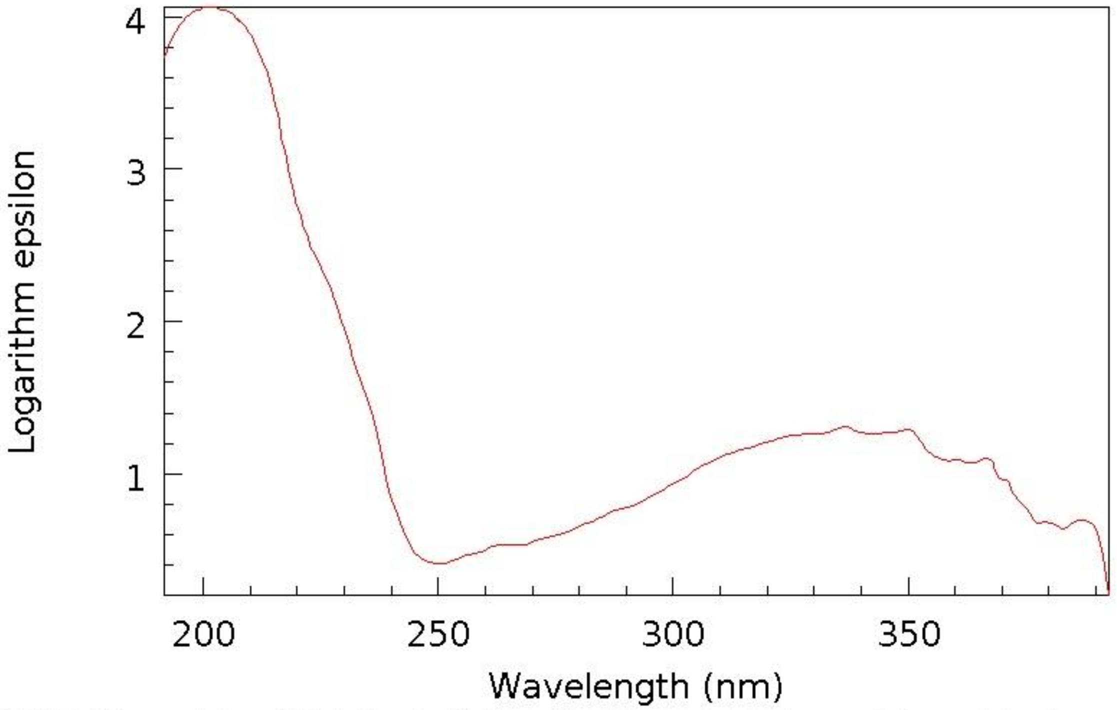

11.80
Wavelength (nm)
349.91
Zoom:
0.992
Oscillator Strength
0.0
Pan:
Line Width:

III. WebMO IR and UV Spectra



IV. Literature IR and UV Spectra





NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)