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Using Forensics to Introduce IR Spectroscopy & Molecular Modeling

Joe Golab (jgolab@imsa.edu)

Illinois Mathematics & Science Academy

Illinois Mathematics & Science Academy

- IMSA is a pubic residential STEM school in Aurora for about 650 diverse 10th – 12th grade students
- Part of the higher education budget, admission is highly competitive (average SAT is 1350)
- 100% of students matriculate to top tier universities
- Classes are Inquiry-Based: *Perform activities that allow students to apply the scientific method to LEARN new concepts in a SEMI-guided way*

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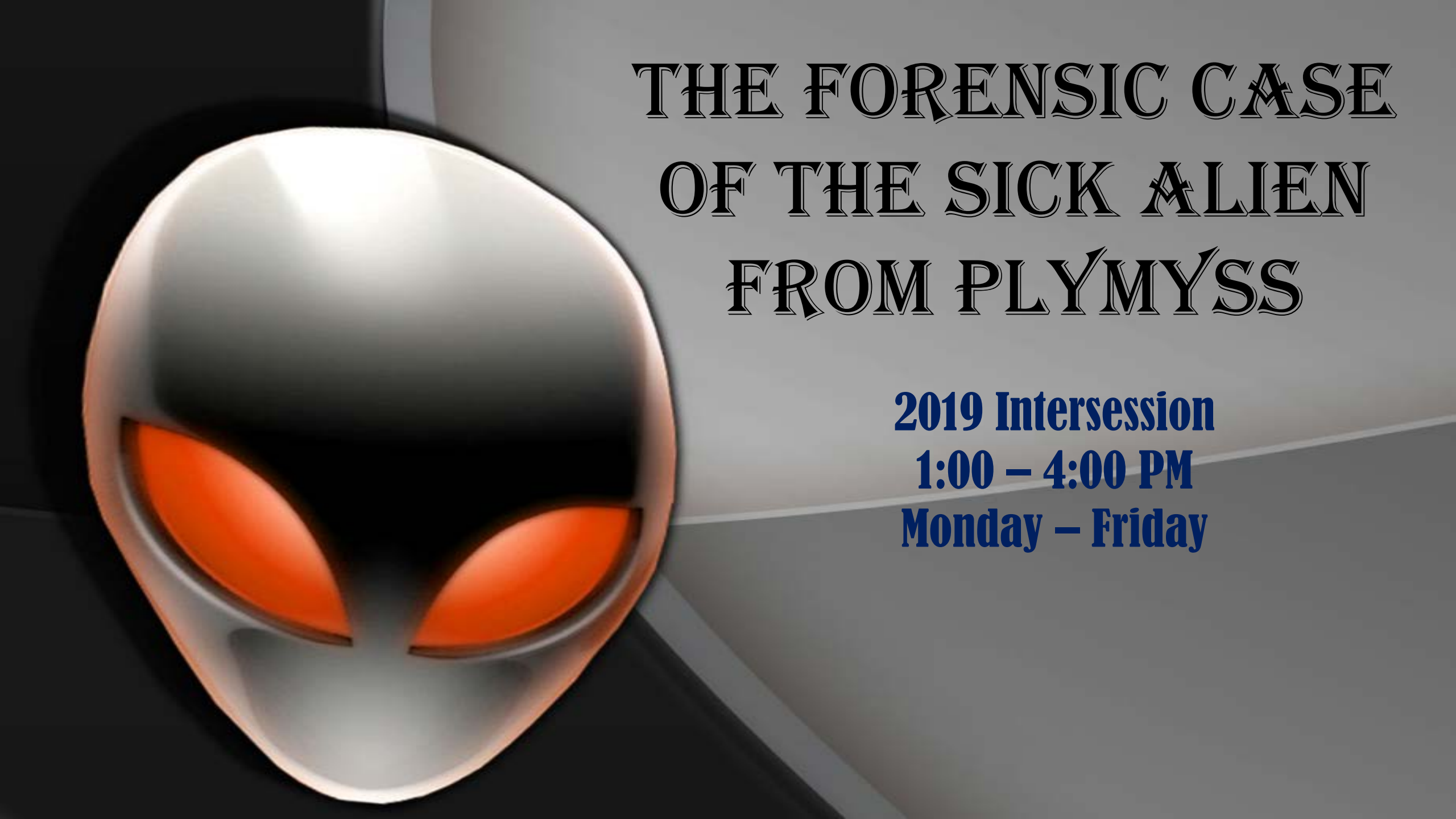
THE FORENSIC CASE
OF THE SICK ALIEN
FROM PLYMYSS
2019 Intersession
1:00 – 4:00 PM
Monday – Friday

Intersession (?)

- Intersession is offered the week before the start of the Spring semester, i.e. January
- Intersession is a week long learning opportunity offered by faculty, staff, students, alumni, and outside guests.
- Courses range from special math and science topics to cultural studies to off-campus educational trips and everything in between.
- The idea is to allow students to explore areas of interest outside the typical IMSA curriculum.

< Student attendance is mandatory >

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Intersession Syllabus

- Monday
  - Introduction - Meet/Greet
  - Software - Install & Review Use
- Tuesday
  - Review Problem
  - Review Molecular Motion
  - Calculate water vibrational spectrum
  - Review Functional Groups & Absorption
  - Show FTIR
- Wednesday
  - Work on Evidence
  - 1-2 hour window for FTIR
- Thursday
  - Work on Evidence
  - 1-2 hour window for FTIR
- Friday
  - Teams Present Conclusions
  - Feedback

Intersession S

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  - Software - Install & Use
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  - Review Molecular M
  - Calculate water vib spectrum
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sday

on Evidence

hour window for FTIR

ay

on Evidence

hour window for FTIR

s Present Conclusions

back

SCRIPT

Day 1
Introduction – Meet/Greet
Review Problem
Day 1 Lecture
Split into Teams of 4 (6 unknowns)
Pick Team Names
Install SPARTAN Software
Day 1 Software Install
Review Use of SPARTAN
Exercise 1. – Ethanol Part 1
Exercise 2. – SPARTAN Skills
Exercise 3. – Ethanol Part 2 & Conformations

Day 2
Review Molecular Motions & Introduction to IR Spectroscopy
Review Functional Groups & Absorption
Day 2 Intro to IR Spectroscopy
Continue Use of SPARTAN
Exercise 1. – Calculating IR Spectra of Simple Organics
Exercise 2. – Calculating IR Spectra of Formic & Acetic Acid
Exercise 3. – Analyzing IR Spectra

Day 3
Review IR Spectroscopy
Day 3 Lecture
Tips for Analyzing IR Spectra
Discuss Problem Solution Strategy
Suspect Compounds & Glossary
Show FTIR
Work on Evidence

Day 4
Work on Evidence
1-2 hour window for FTIR

Day 5
Teams Present Conclusions
Feedback

What the Goal? (Teacher's View)

- Draw molecules, Determine properties, and Calculate IR spectra Using Molecular Modeling Software
- Collect experimental IR spectrum
- Characterize molecular functional groups and identify them in an IR spectrum
- Present the learning as a practical activity, e.g. medical investigation

Emphasize the benefits of integrating modeling and experimental methods to solve practical problems

What's The Goal? (Student's View)

- Working in teams, analyze unknown secretions gathered by medical personnel attending to Ind. Martin.
- Using an infrared (IR) spectrometer, "take a spectrum" of your unknown.
- Using SPARTAN, a molecular modeling software, calculate the IR spectra of a list of potential chemicals.
- Identify your unknown compound by comparing your experimental spectrum with the calculational IR spectra.
- Your team will make a short presentation on the complete structural and chemical evaluation of the evidence based on your work.
- The goal is to crack the case with this information – and a few clues – so you can propose a solution that allows the citizens of Plymyss to visit Earth safely.

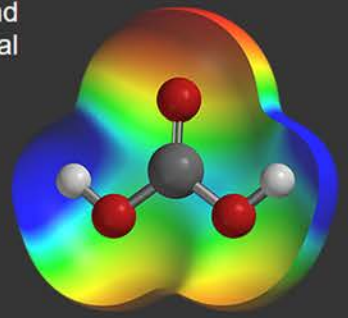
SPARTAN Software

Spartan Student V7 for Windows and Macintosh

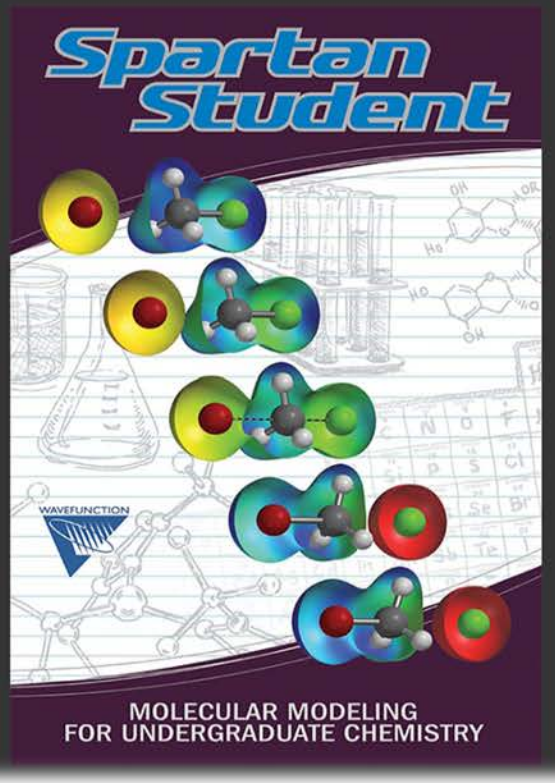
Molecular Modeling for the Undergraduate Chemistry Curriculum

***Spartan* Student Edition** provides affordable molecular modeling software and modern computational methods to explore general, organic, physical, and inorganic chemistry topics in undergraduate chemistry.

A targeted subset of features provides a highly flexible and functional interface with a streamlined set of computational models including MMFF (molecular mechanics), PM3 (semi-empirical), Hartree Fock, B3LYP and EDF2 (density functional theory), and MP2. Available licensing for schools, or as student purchases, this application is an ideal tool for both utilizing molecular modeling in the undergraduate curriculum and introducing future chemists to molecular modeling and computational chemistry.



***Spartan* Student Edition** supports chemistry education! With 3D molecule builders including organic, inorganic, peptide and nucleotide as well as a fully integrated 2D sketching environment, students can easily build almost any molecule or system. Computational models allow for elucidation of structure, properties, and energies. Tools for constructing and isolating transition states allow for exploration of reactions



SEE - https://www.wavefun.com/education

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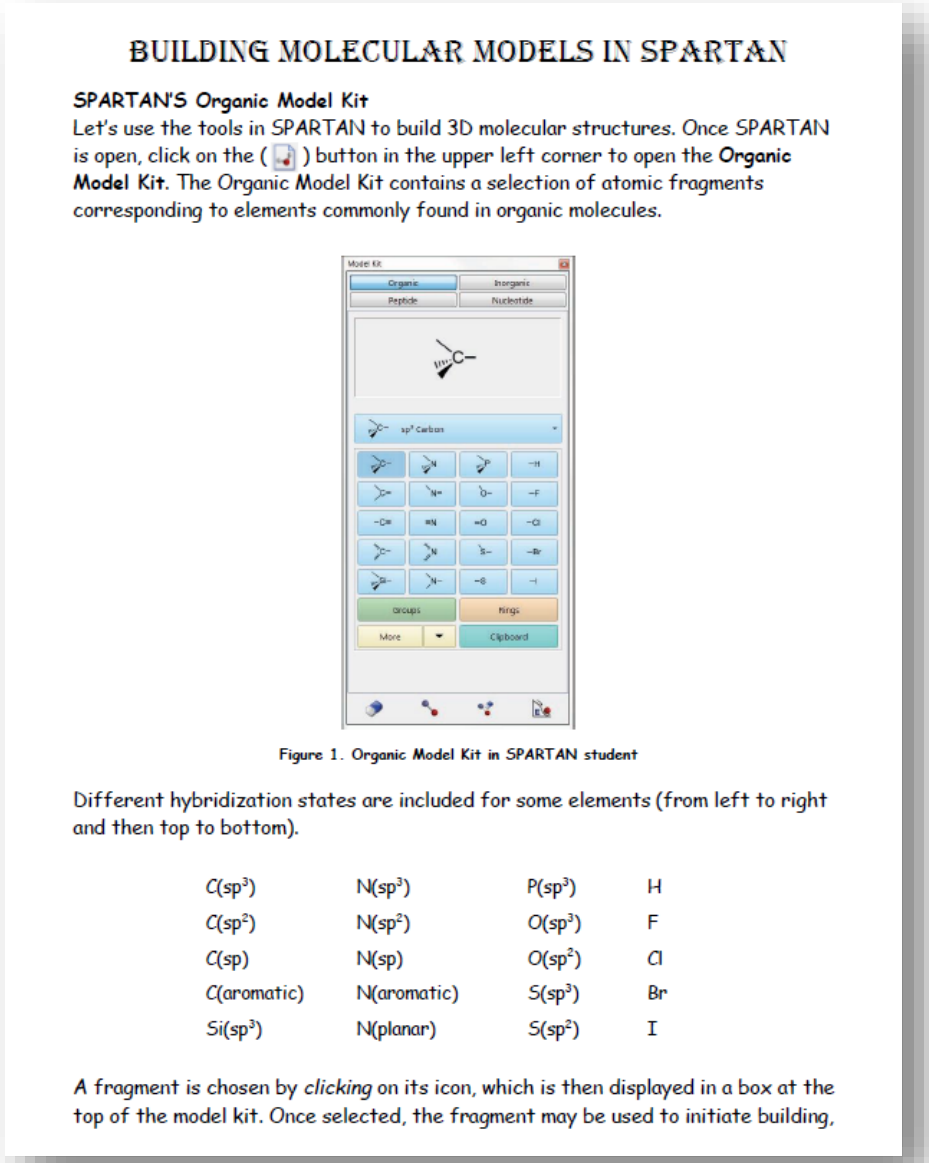
Learning SPARTAN

- Building
- Rotating & Zooming
- Viewing Options
- Measuring
- Molecules
  - Acrylonitrile (bonds)
  - Cyclohexanone (3-D)
  - Nicotine (enantiomer)
  - Lewis Structures



BUILDING MOLECULAR MODELS IN SPARTAN

SPARTAN'S Organic Model Kit

Let's use the tools in SPARTAN to build 3D molecular structures. Once SPARTAN is open, click on the ( ) button in the upper left corner to open the **Organic Model Kit**. The Organic Model Kit contains a selection of atomic fragments corresponding to elements commonly found in organic molecules.

Figure 1. Organic Model Kit in SPARTAN student

Different hybridization states are included for some elements (from left to right and then top to bottom).

$C(sp^3)$	$N(sp^3)$	$P(sp^3)$	H
$C(sp^2)$	$N(sp^2)$	$O(sp^3)$	F
$C(sp)$	$N(sp)$	$O(sp^2)$	Cl
C(aromatic)	N(aromatic)	$S(sp^3)$	Br
$Si(sp^3)$	N(planar)	$S(sp^2)$	I

A fragment is chosen by *clicking* on its icon, which is then displayed in a box at the top of the model kit. Once selected, the fragment may be used to initiate building,

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Learning SPARTAN

- Hartree-Fock Energy
- Dipole Moment (vector)
- Atomic Charge
- Molecular Orbitals
- Molecular Surface
  - Electrostatic
- Conformations
  - Acetic Acid using dipole

SPARTAN MOLECULAR PROPERTIES

So far we've examined the building, moving, viewing, and measuring tools in SPARTAN. Let's keep exploring the SPARTAN GUI by calculating a few molecular properties using the compounds ethanol and acetic acid.

Model 1. The Energy and Other Properties of Ethanol

Click (left button) on the File menu and select (*click* on) New Build. Alternatively, *click* on if it appears at the top of the screen. The organic model kit appears. Build ethanol (CH_3CH_2OH).

Click on the C—O bond. A red arrow will encircle the bond and will also appear at the top of a narrow shaded band at the left of the screen. Move the cursor up and down **inside this band** to rotate about the bond until the hydrogen atom on the hydroxyl group is in a staggered Newman Projection position (see Figure 1). Changing the torsion angle in this way leads to a molecular model structure for ethanol that has low strain. **Why?**

Figure 1. Ethanol Model Showing the Hydroxyl Hydrogen Atom in a Staggered Position
Oxygen is red, Carbon is grey, Hydrogen is yellow

Click on at the bottom of the model kit to clean up your structure. The name window should indicate ethanol.

Select Calculations... from the Setup menu ( ). Specify **Equilibrium Geometry** in **Gas** with **Hartree-Fock 6-31G*** in the Calculations box (see Figure 2).

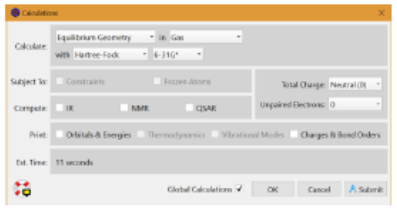

Figure 2. Calculations Box for Ethanol

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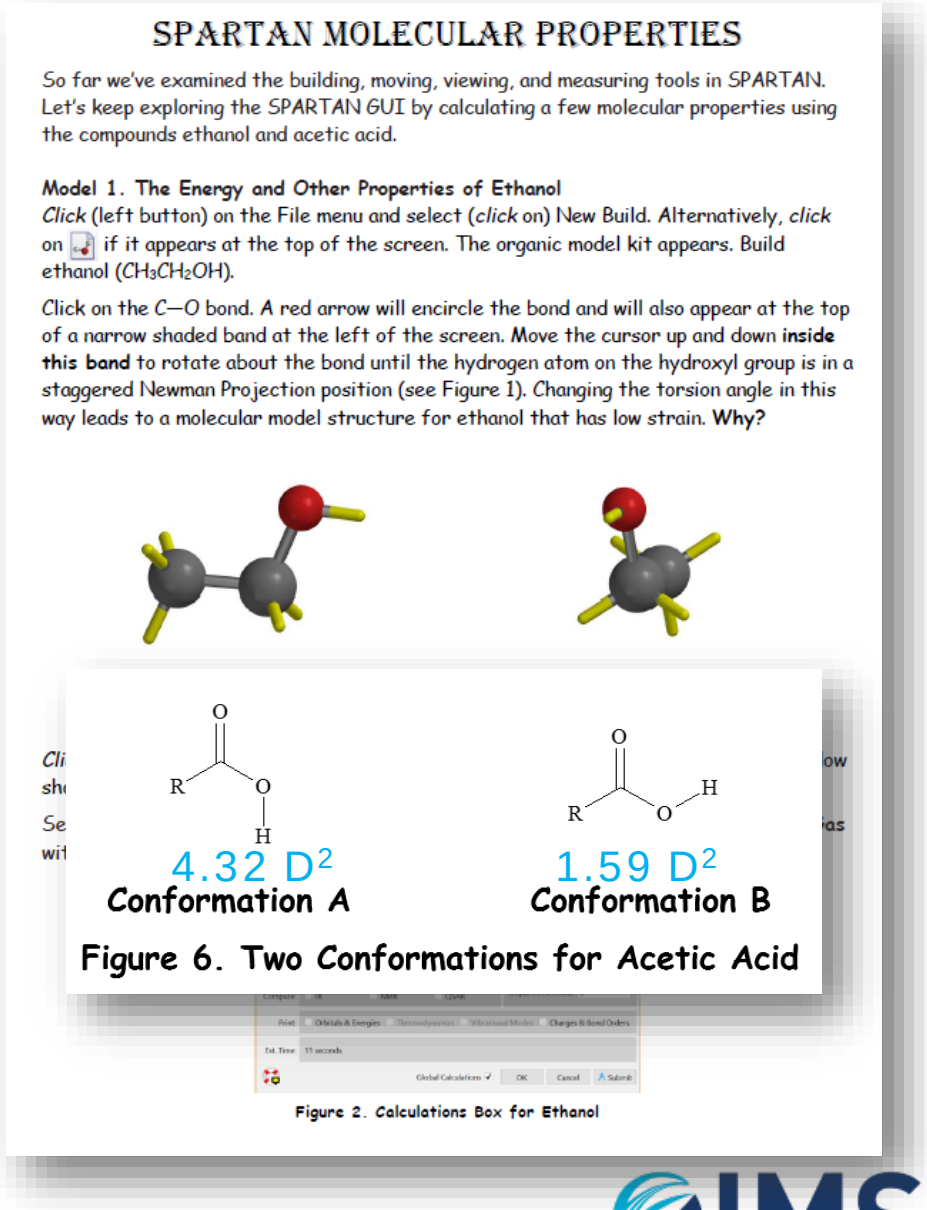

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4.32 D^2 Conformation A

1.59 D^2 Conformation B

Figure 6. Two Conformations for Acetic Acid

Figure 2. Calculations Box for Ethanol

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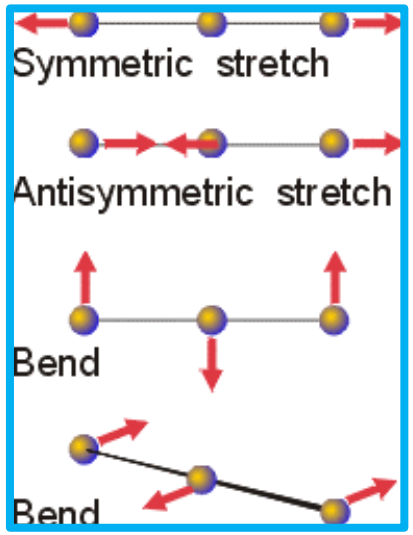
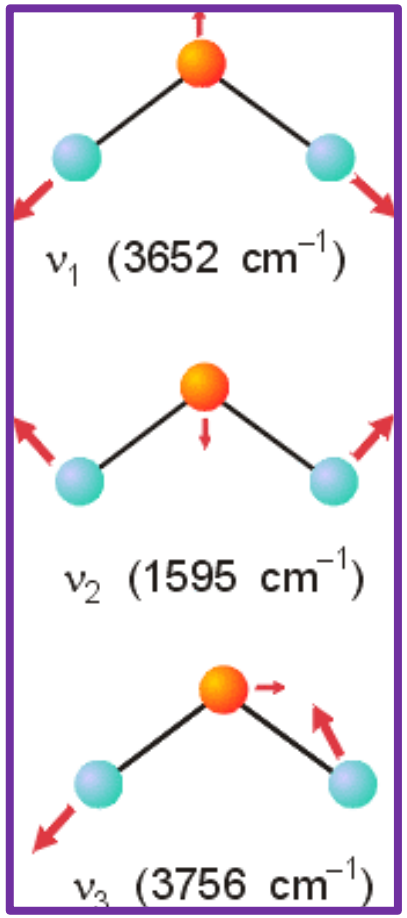
Vibrational Spectroscopy

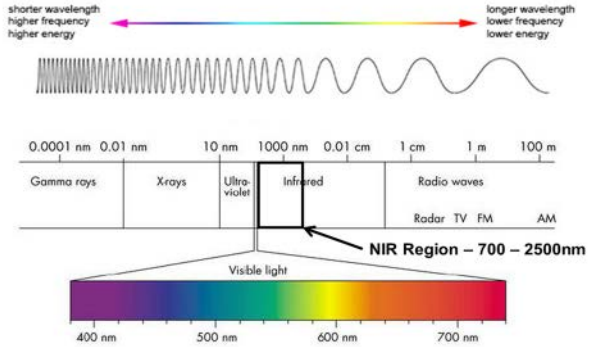
- Go Over the Basics …
- Molecules Studied
  - O_2
  - HCl
  - H_2O
  - CO_2

CO_2

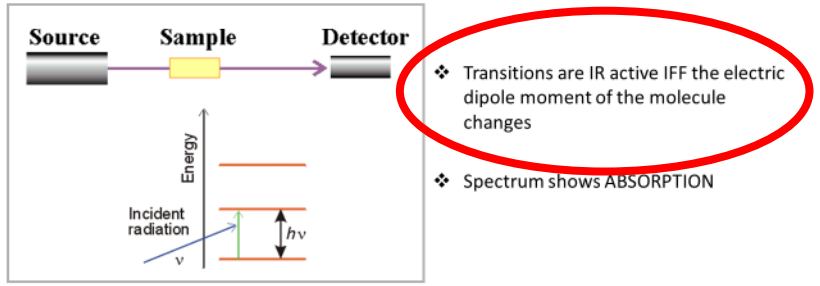


H_2O





The Electromagnetic Spectrum



Vibrational Spectroscopy - IR

Molecular Motions

- Each atom in a molecule occupies a point in 3-d space, so a molecule that contains N atoms can be described by 3N coordinates.
- Each molecule can move by translating in 3-d space (3 degrees of freedom)
- Each molecule can move by rotating in 3-d space (3 or 2 degrees of freedom)
  - Linear molecules have one less rotational degree of freedom than nonlinear molecules
- Each molecule can move by vibrating in 3-d space. (3N-6 or 3N-5 dof)
- Vibrational motions are along the bonds that make up the molecule. If that particular motion changes the molecule's dipole moment then it is also "IR active". NOTE - A permanent dipole is not necessary, only a change in dipole moment.
- Vibrational (or Infrared) Spectroscopy exploits the fact that molecules absorb frequencies of light that are characteristic of their structure.

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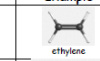
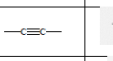
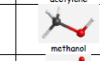
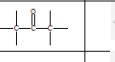
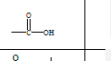
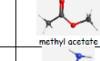
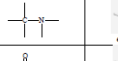
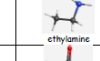
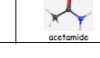
Vibrational Spectroscopy

- Review typical functional group IR absorptions
  - Compare C=O stretch for Acetone →

    Acetophenone → 2,6 dimethylacetophenone
  - 1-octyne
    - C—H, C—C, C≡C stretch
    - H—C—H and C—C—C bend
- Calculate IR spectra for Formic Acid & Acetic Acid
  - Practice identifying peaks
  - Finding similarity and difference

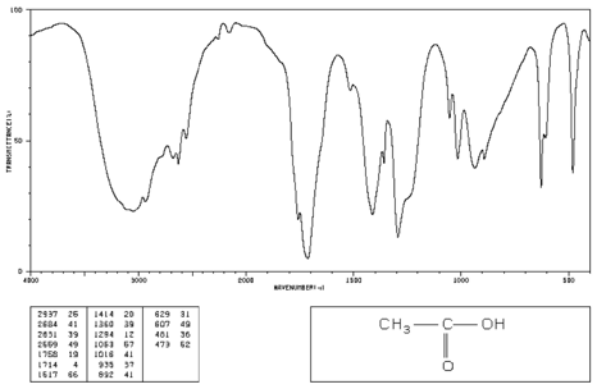
Table 1. Some Common Functional Groups and Their Characteristic Absorption

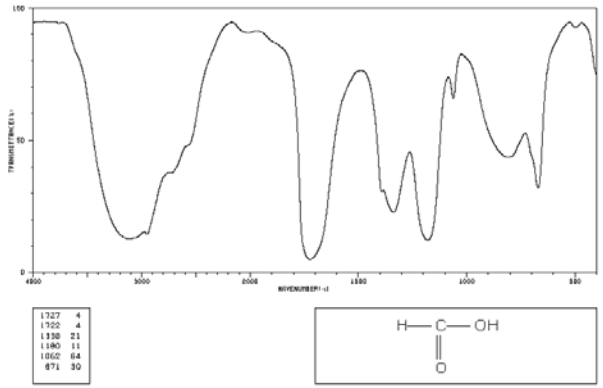
Compound Type	Functional Group	Example	Streching Frequency (cm^{-1})[1,2]	Intensity & Shape
alkene		 ethylene	3100-3000 (=C-H) 1680-1620 (C=C)	Variable Variable
alkyne		 acetylene	3340-3250 (≡C—H) 2260-2000 (C≡C)	Strong/Sharp Variable/Sharp
alcohol		 methanol	3650-3200 (O—H)	Strong/Broad
aldehyde		 acetaldehyde	2900/2700 1740-1720 (C=O)	Medium/2 peaks Strong
ketone		 acetone	1750-1700 (C=O)	Strong
carboxylic acid		 acetic acid	3000-2500 (O—H) 1725-1700 (C=O)	Strong/Very Broad Strong
ester		 methyl acetate	1750-1735 (C=O)	Strong
amine		 ethylamine	3500-3200 (N—H)	Medium/Broad
amide		 acetamide	3500-3200 (N—H) 1690-1650 (C=O)	Medium/Broad Strong

References

1. IR Spectroscopy - https://www.khanacademy.org/science/organic-chemistry/spectroscopy-jay/infrared-spectroscopy-theory/v/introduction-to-infrared-spectroscopy
2. https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/infrared/infrared.htm

[1] Note that these values are dependent on other functional groups present in the molecule.
[2] The frequency is given in units of reciprocal centimeters (cm^{-1}) rather than Hertz (Hz) because the numbers are more manageable. The reciprocal centimeter is the number of wave cycles in one centimeter (cycles/cm); whereas, frequency in cycles per second or Hz is equal to the number of wave cycles in 3E+10 cm (!) - the distance covered by light in one second.





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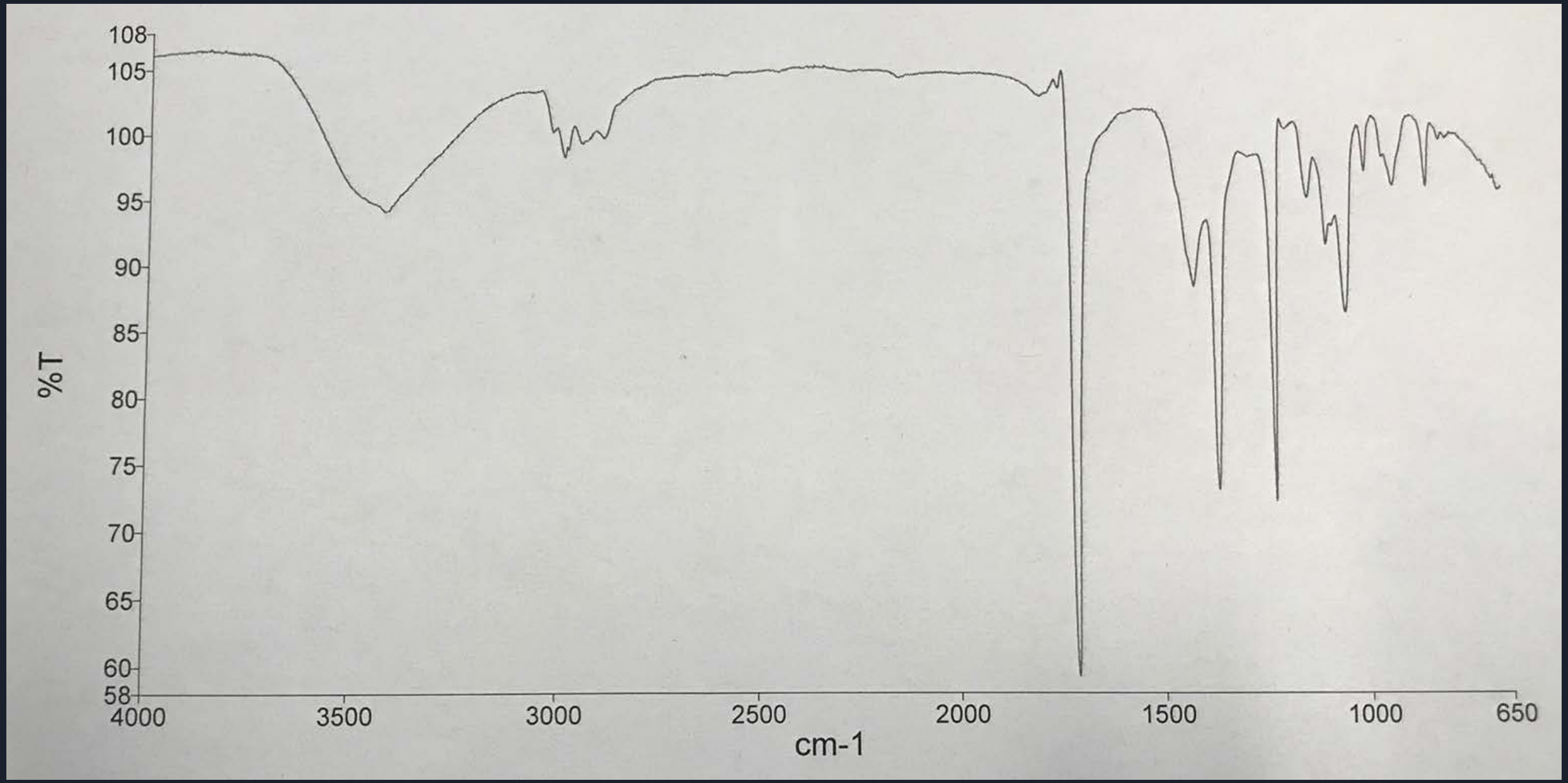
Student Presentations

Oh no, what happened to Belldoor Zip Martin?!?!

By: Team Jacks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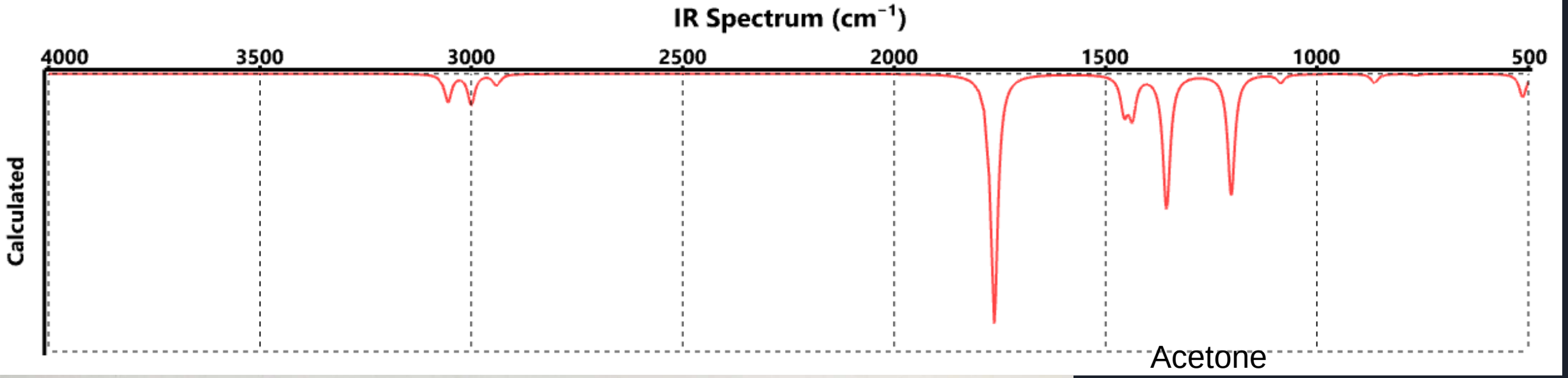
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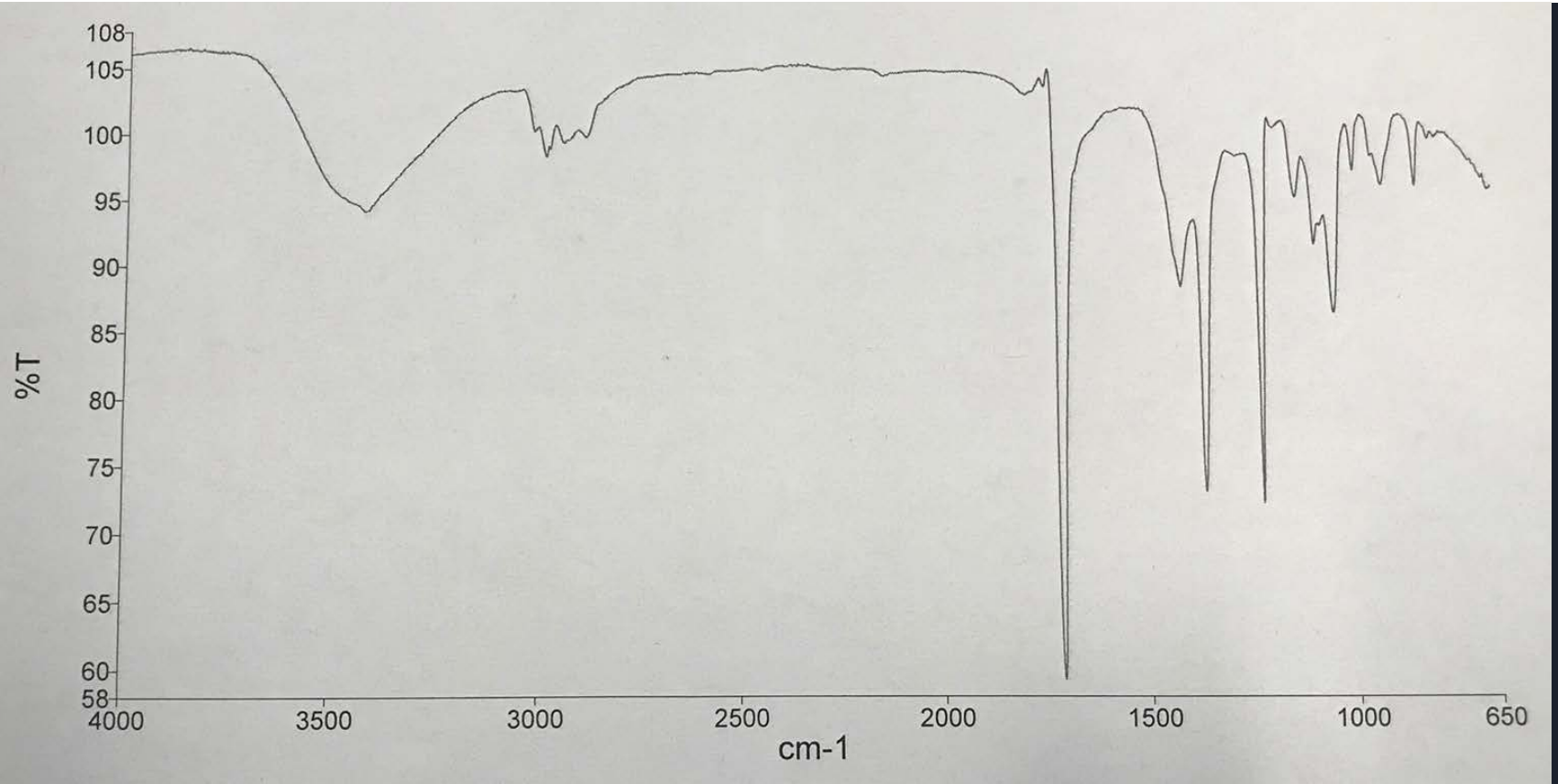
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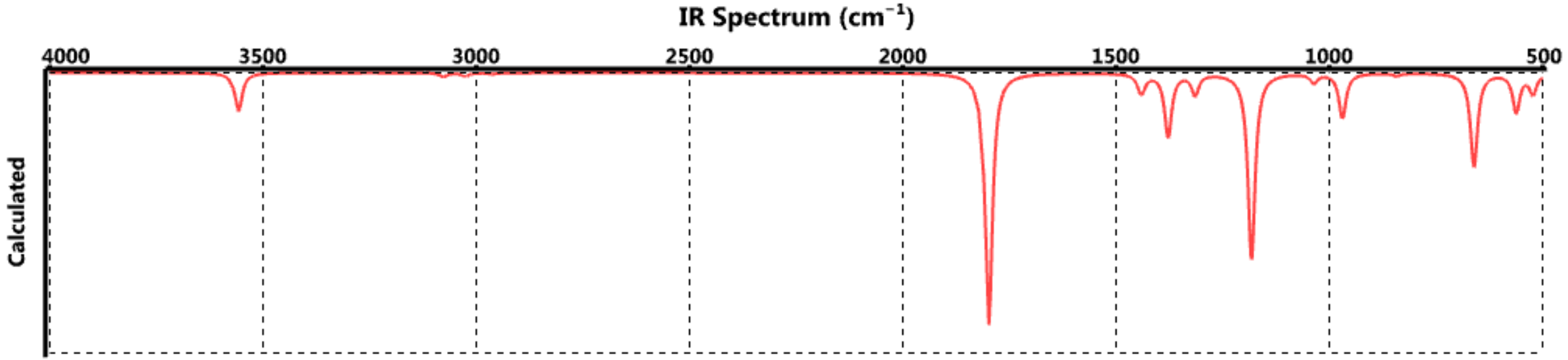
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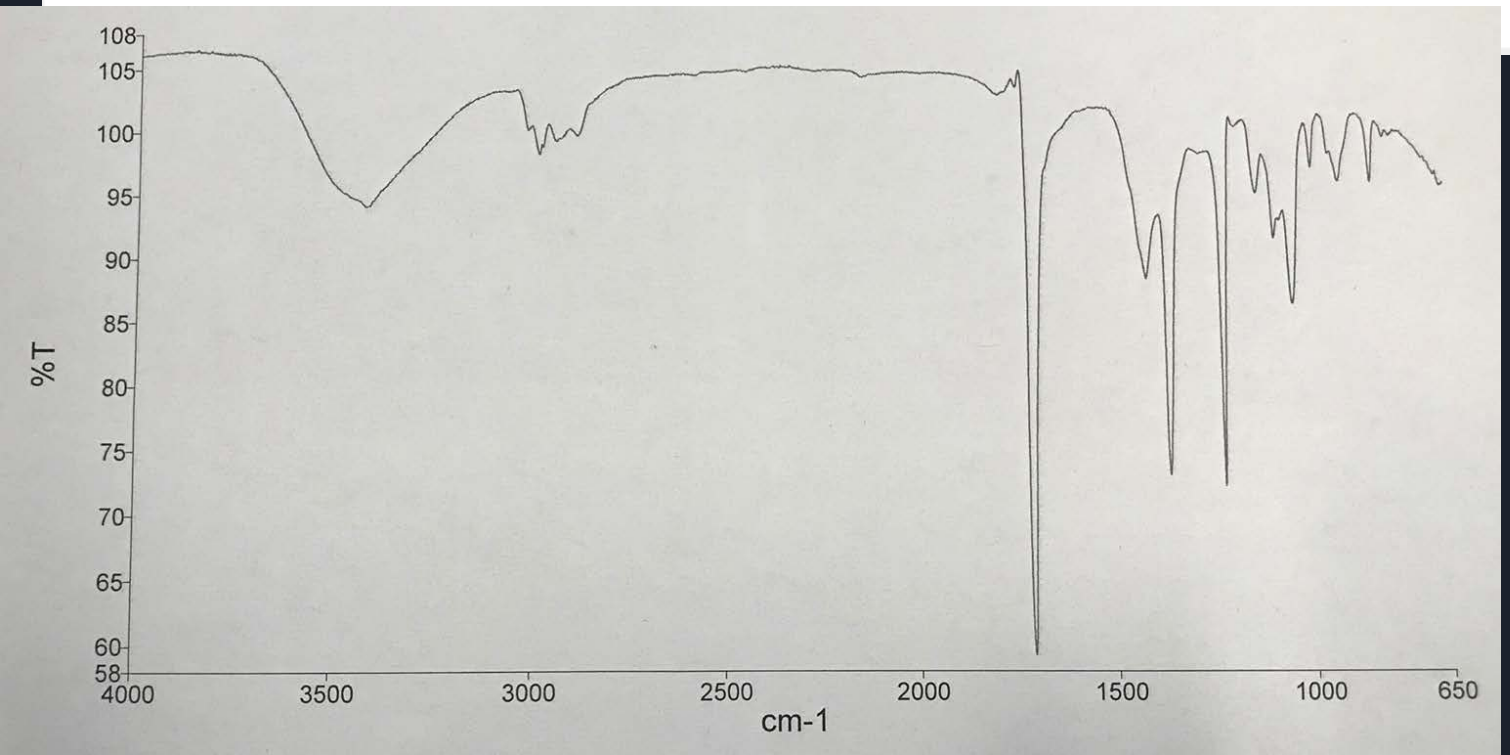
Acetic Acid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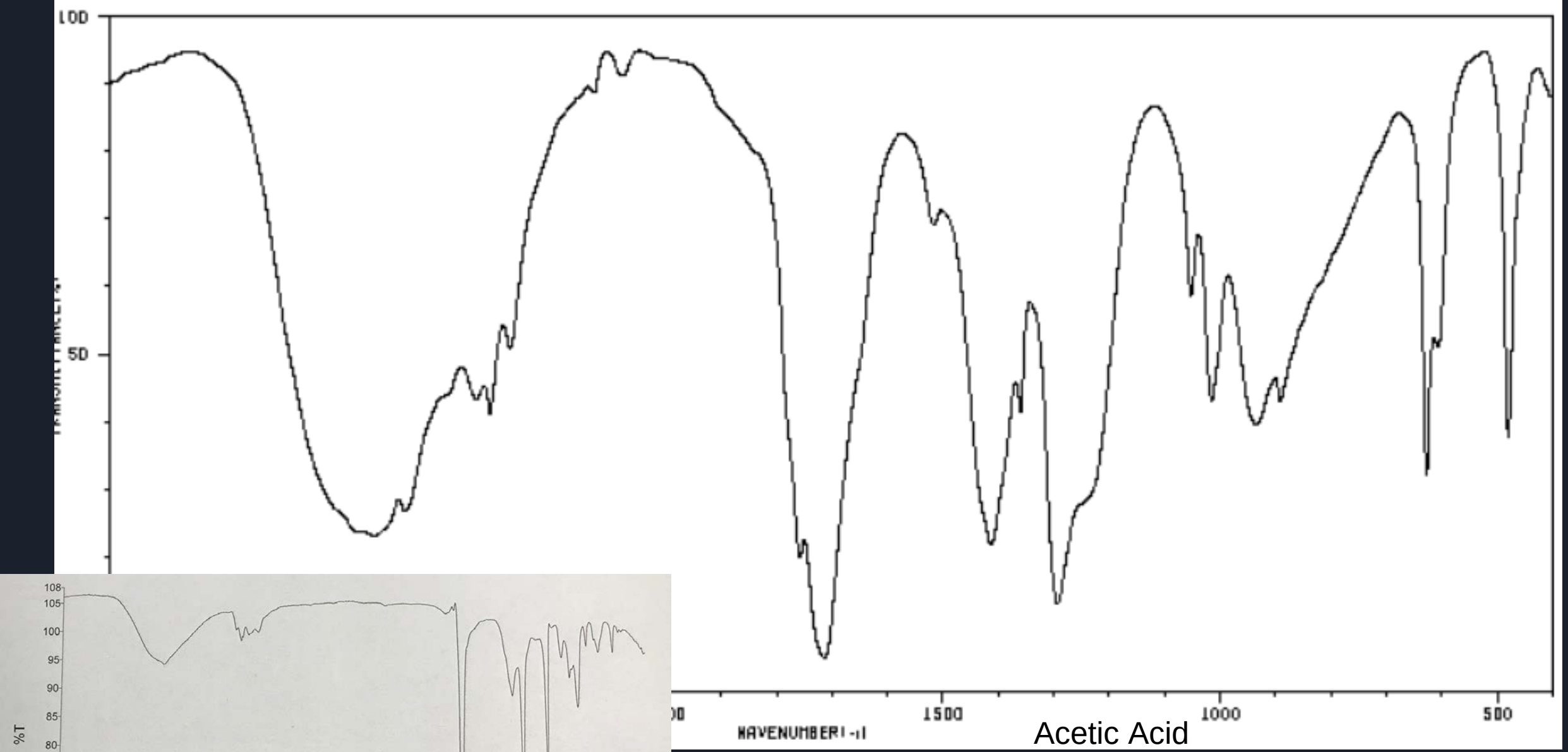
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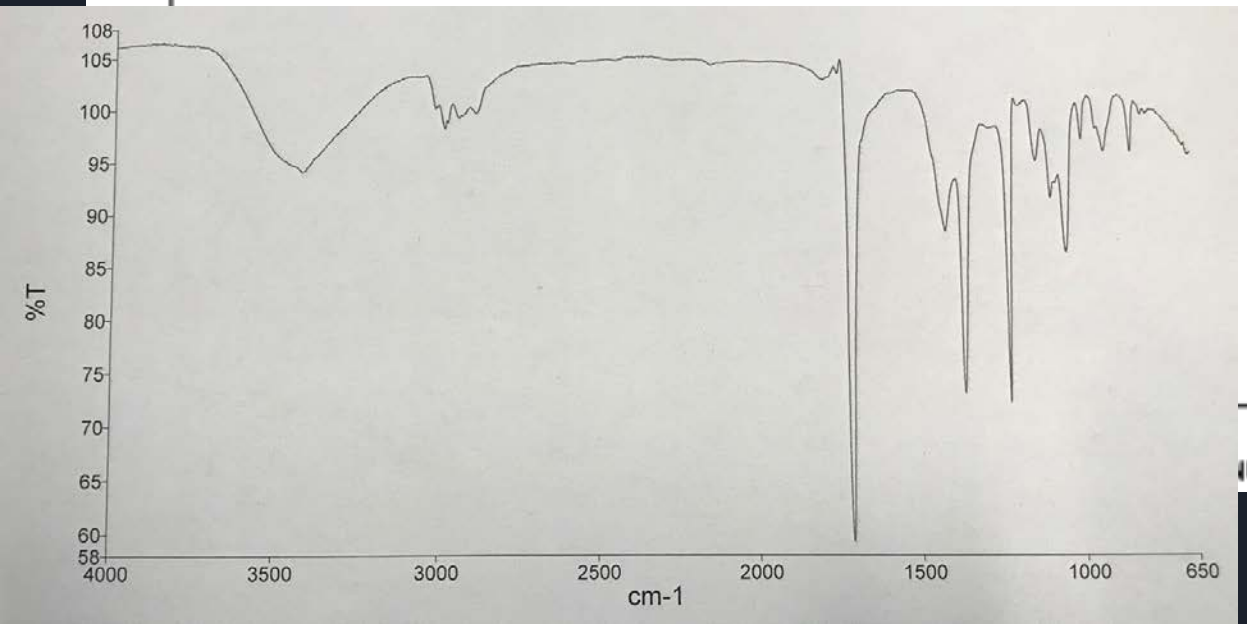
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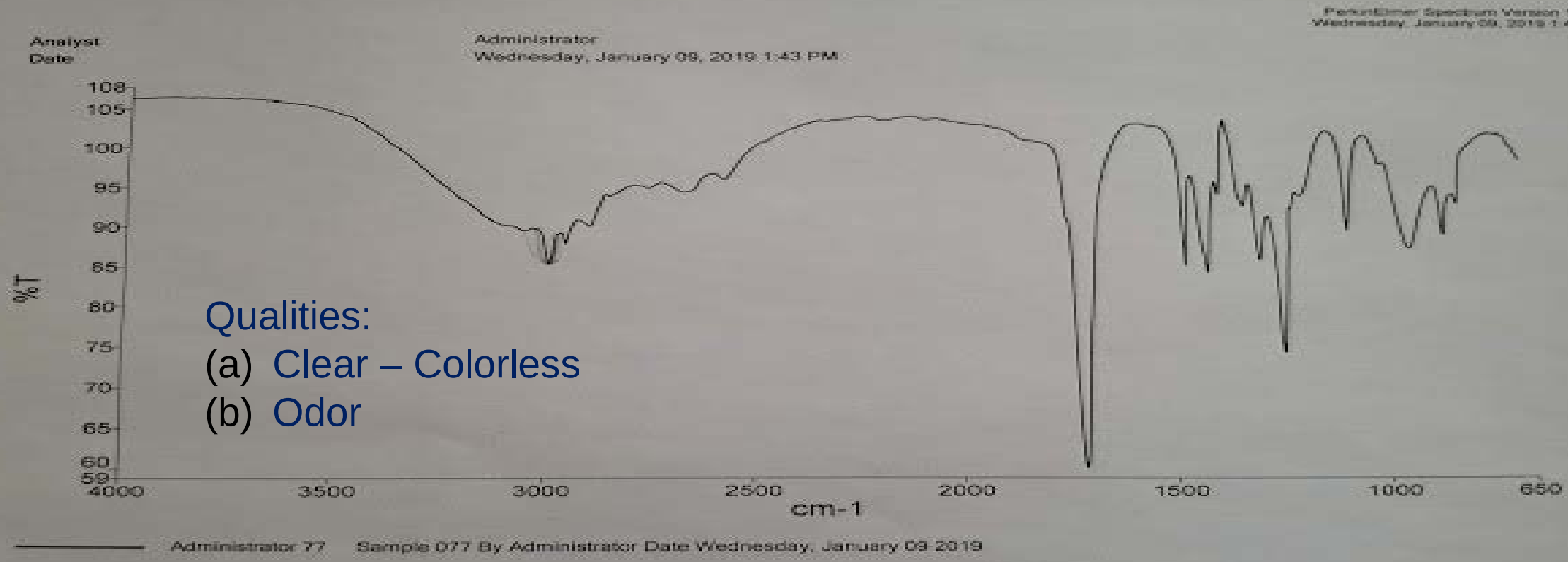
Acetone

He drank acetone :(

IR Spectra - Unknown 3

Team Aces

Experimental Spectra

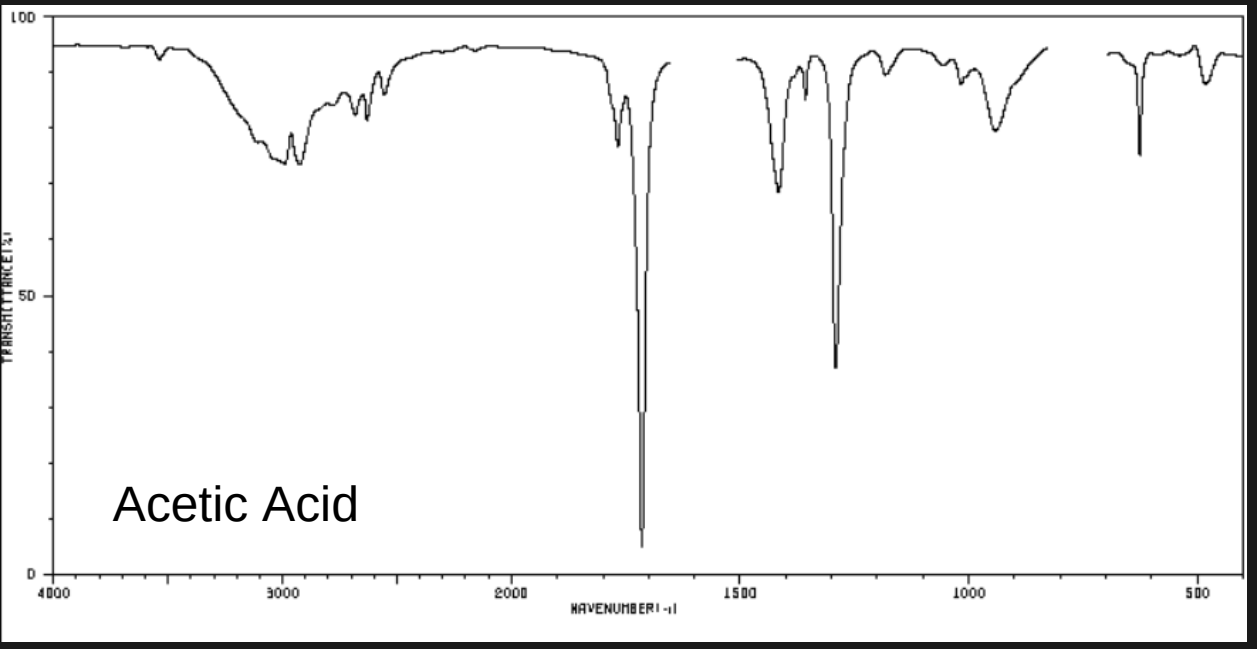


Qualities:

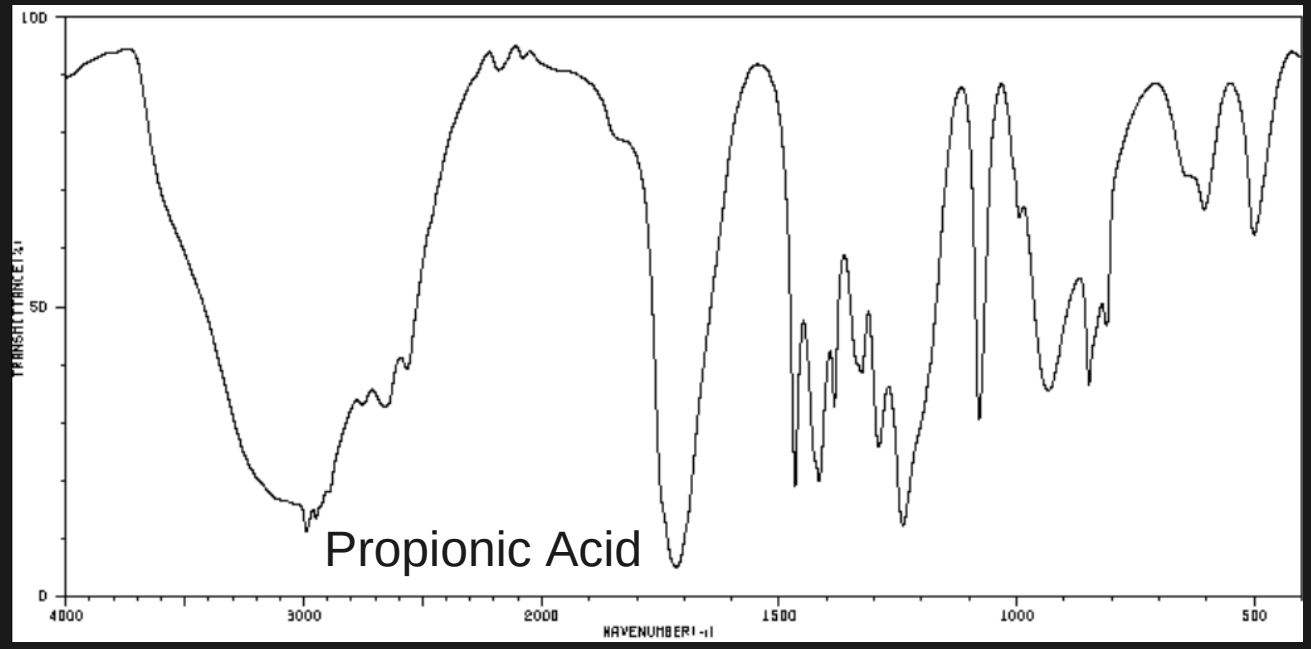
(a) Clear – Colorless

(b) Odor

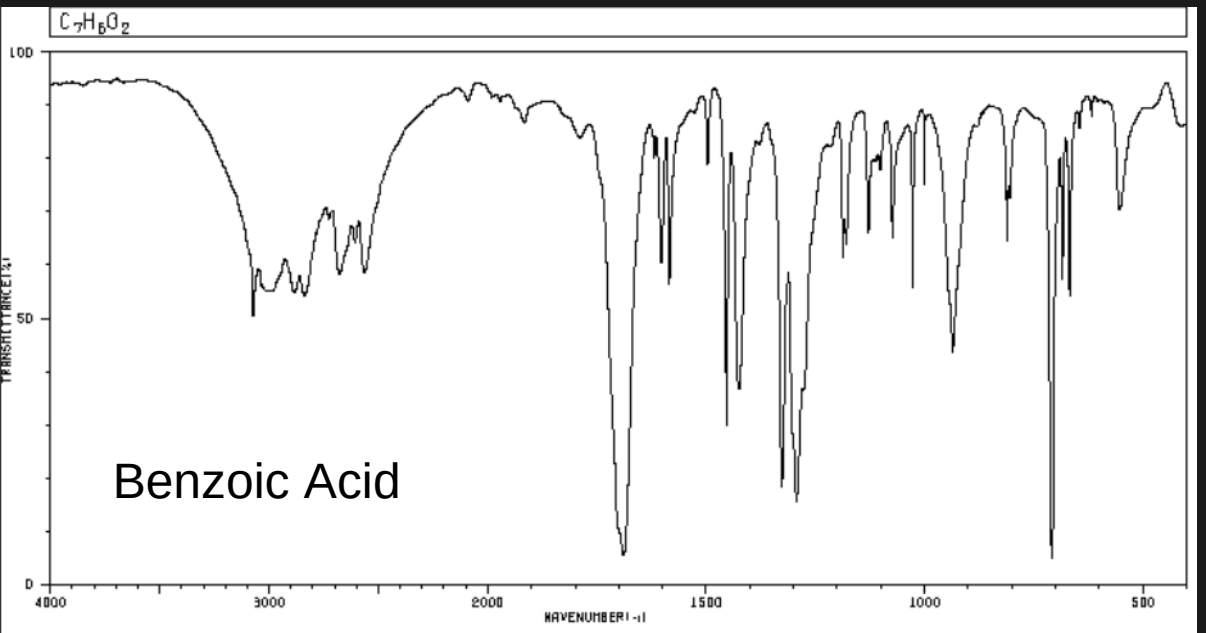
Other suspect compounds



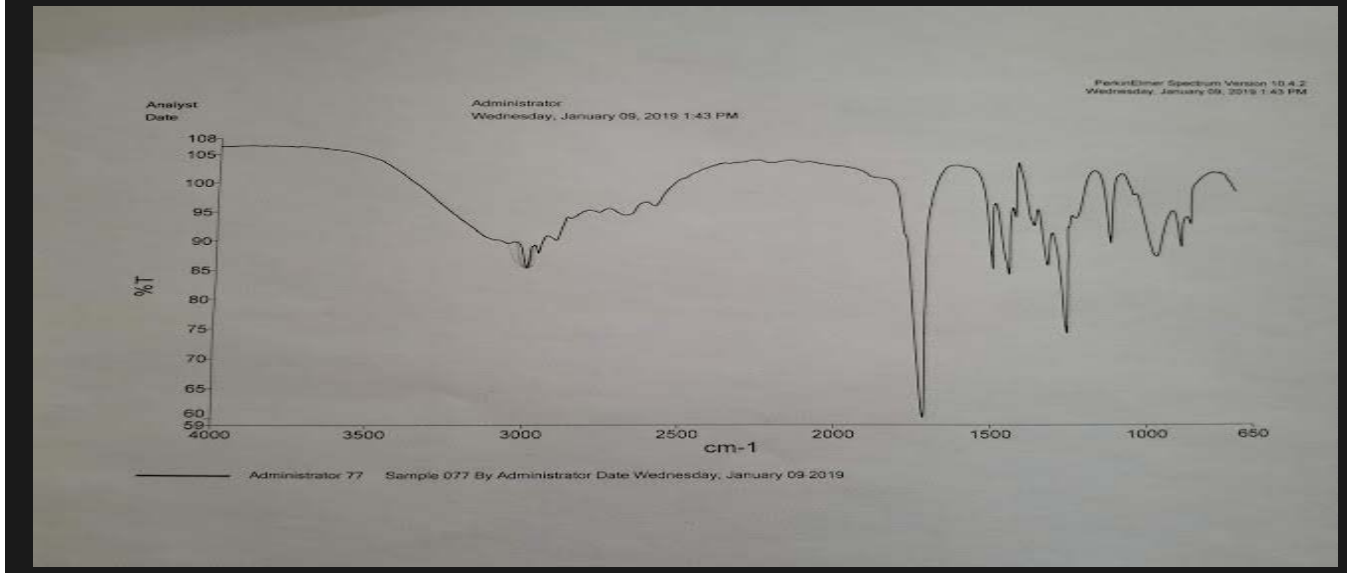
Acetic Acid



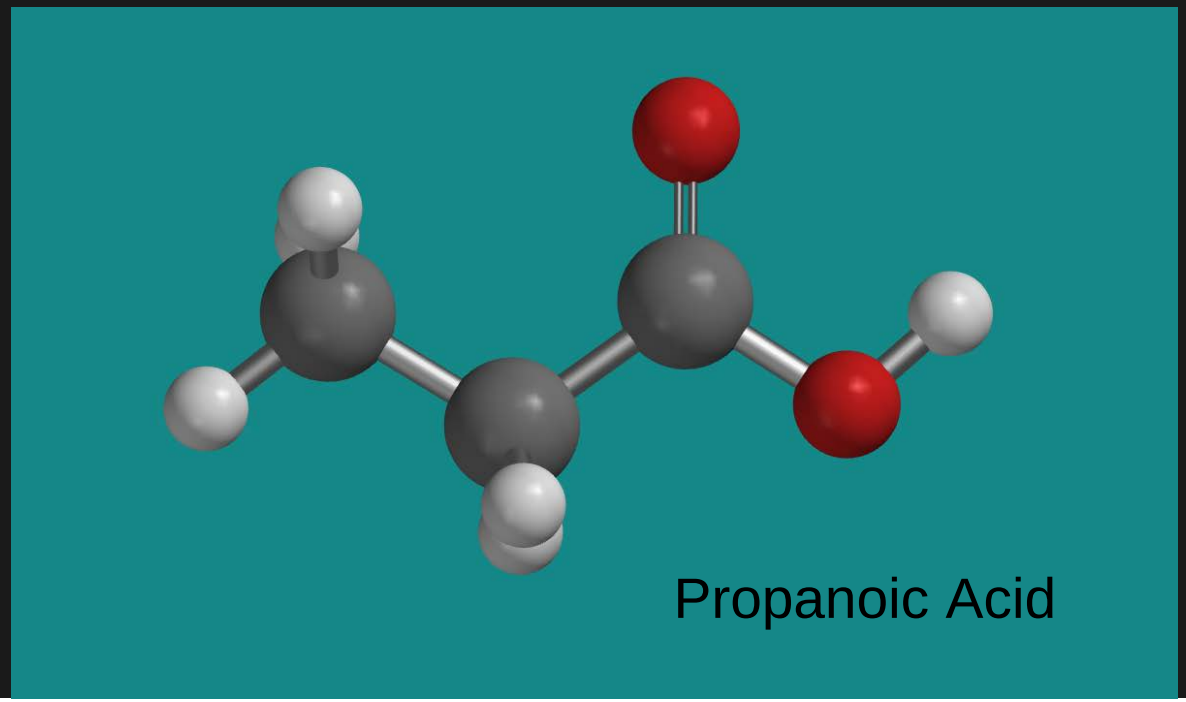
Propionic Acid



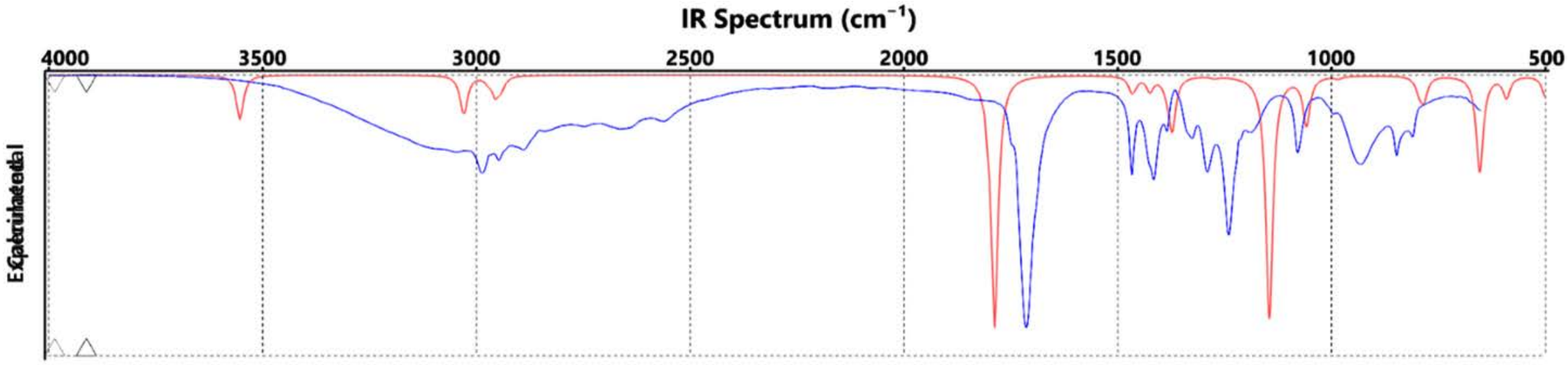
Benzoic Acid



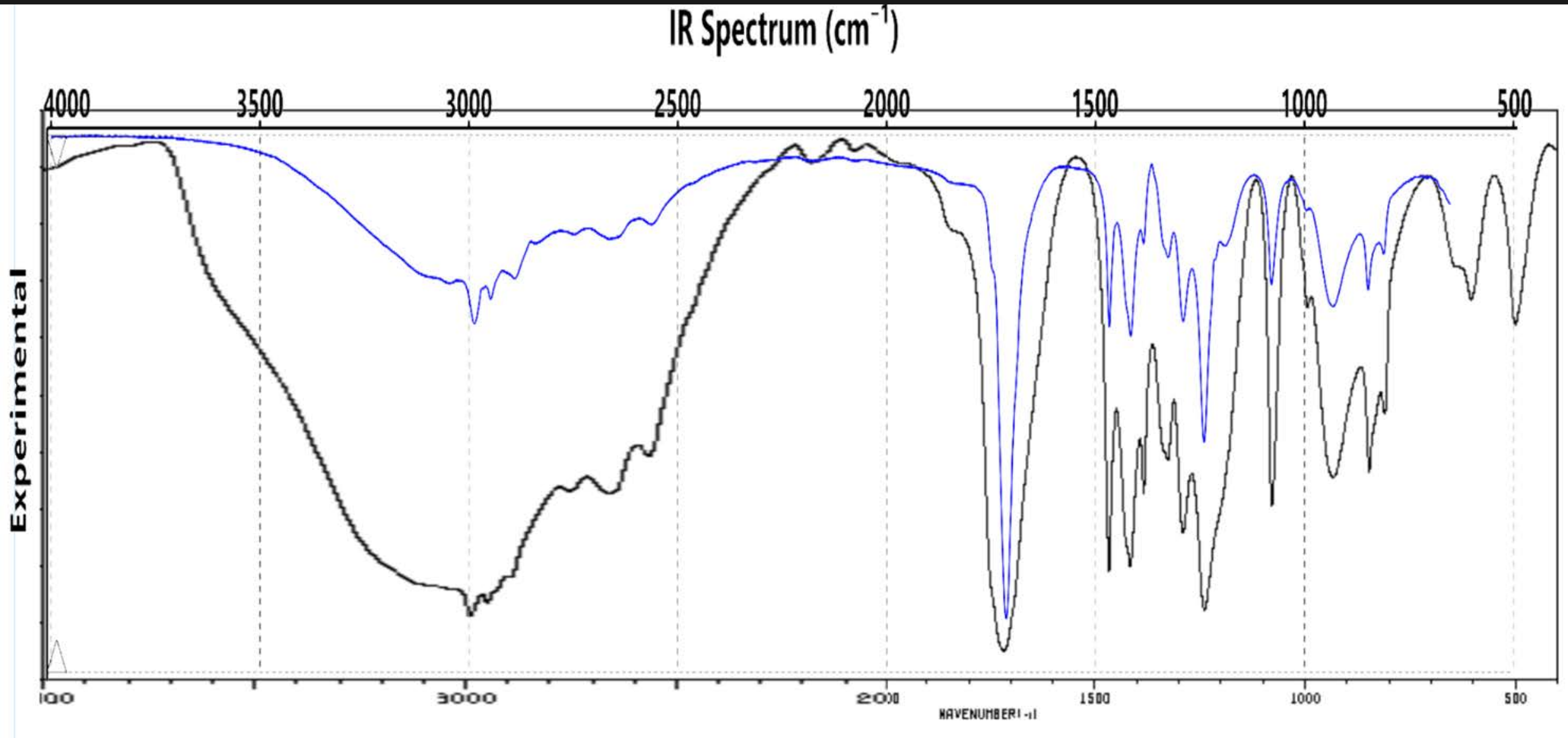
Spartan Modeling and Calculations



Propanoic Acid



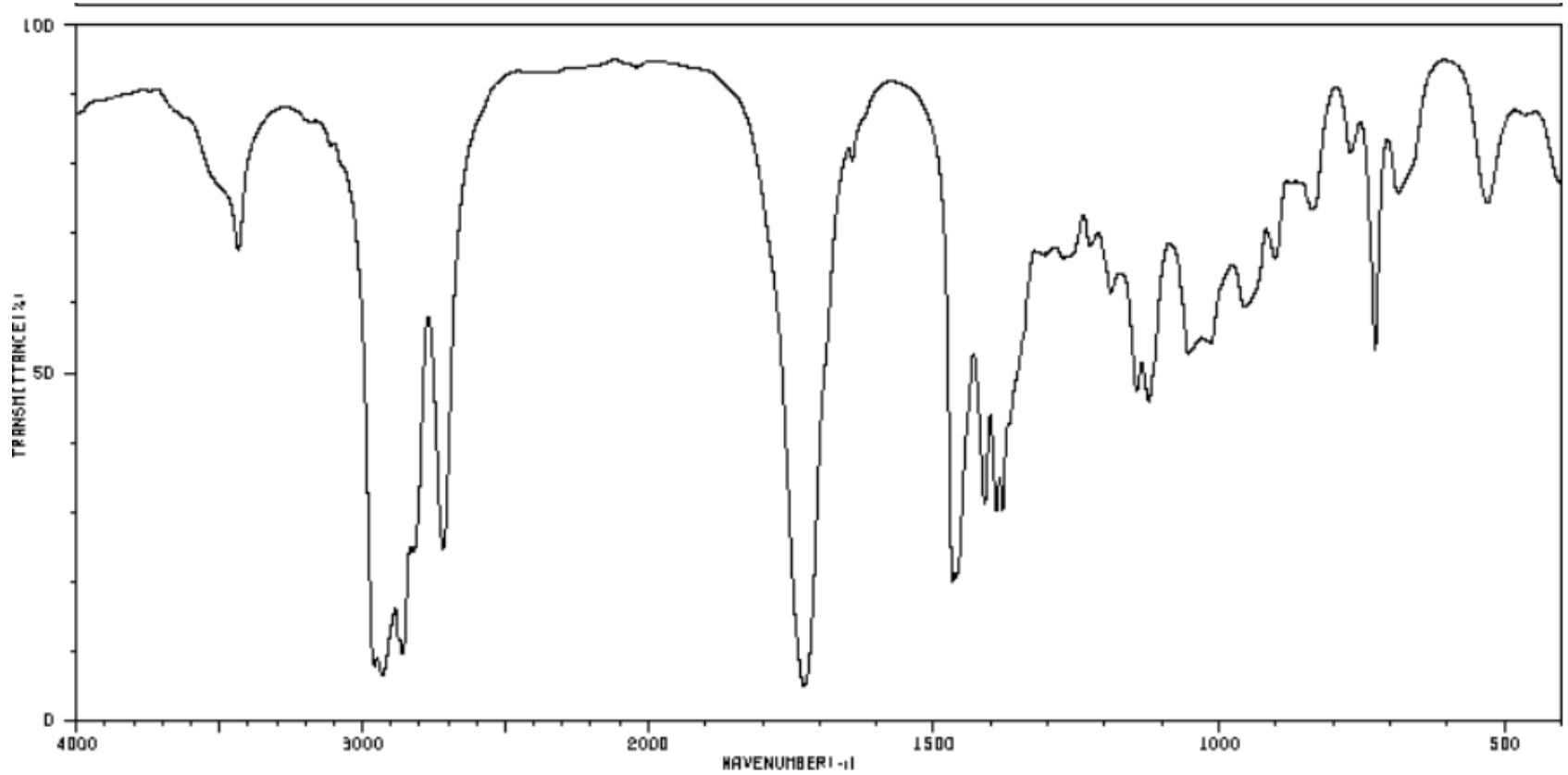
Japanese Graph vs Experimental Graph



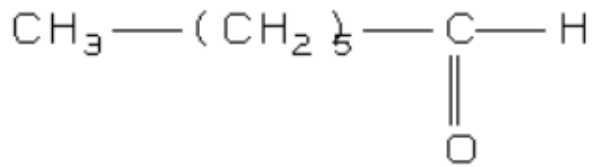
Unknown #5

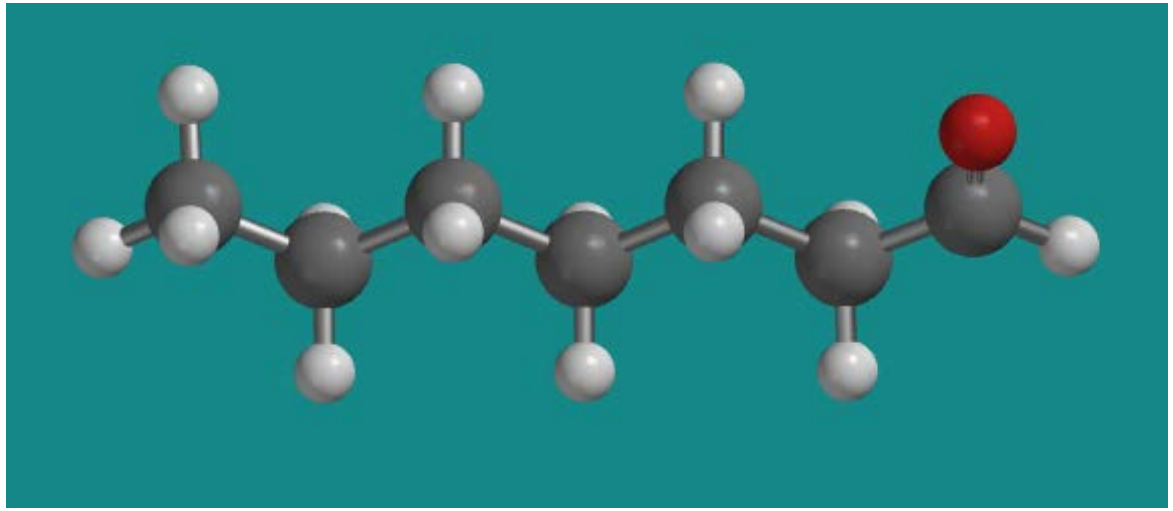
Team “Unknown 5”

Vidhi Singh, Gloria Huang, Ruchi Patel, Prarthana Prashanth



3434	66	1642	77	1268	64	1047	60	687	72
2958	7	1468	19	1262	64	956	57	673	74
2931	6	1460	20	1228	66	901	64	531	72
2873	10	1411	30	1190	68	846	72		
2859	9	1390	29	1145	46	835	70		
2717	23	1380	29	1123	43	770	79		
1727	4	1273	64	1054	60	727	62		



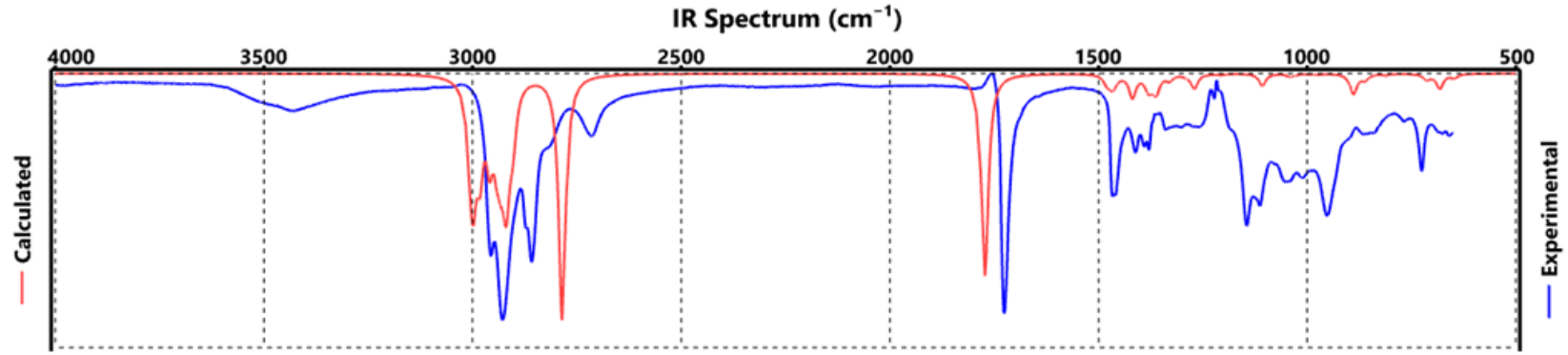


Calculated:

ν	I
648	0.02
682	0.06
713	0.02
737	0.00
812	0.01
862	0.02
889	0.08
900	0.00
975	0.00
991	0.00
1026	0.00

Experimental:

ν	I
654	0.20
673	0.09
688	0.11
726	0.35
775	0.15
831	0.20
866	0.20
910	0.21
948	0.60
977	0.27
1011	0.35

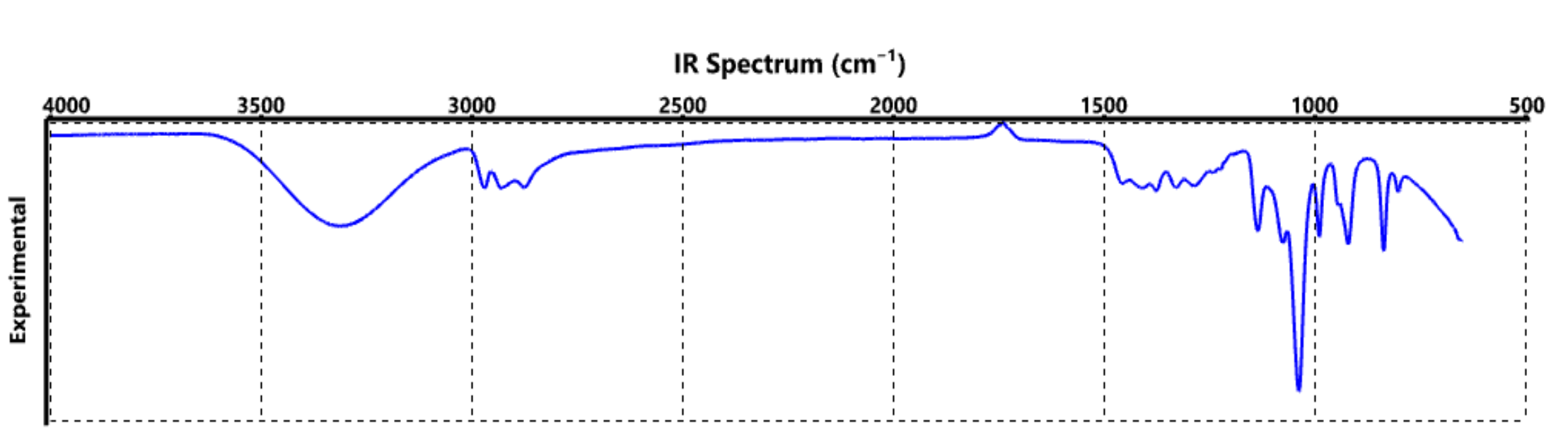


Diagnosis: Heptaldehyde

Unknown 8

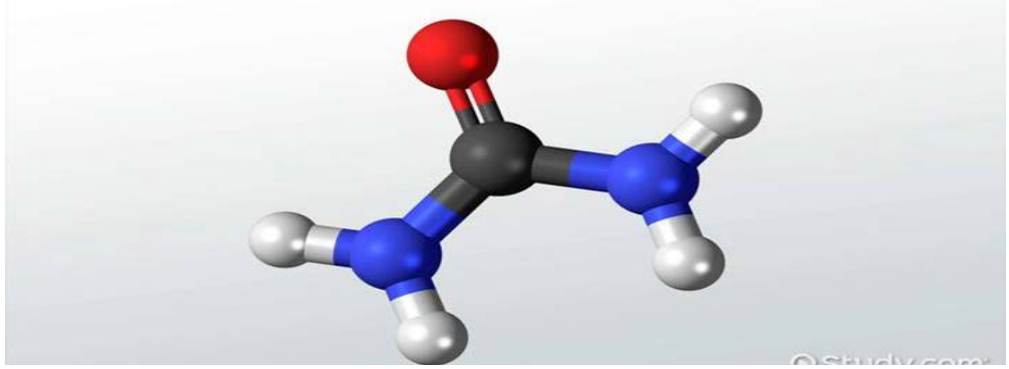
BY: The Kings

Unknown 8 IR Spectra

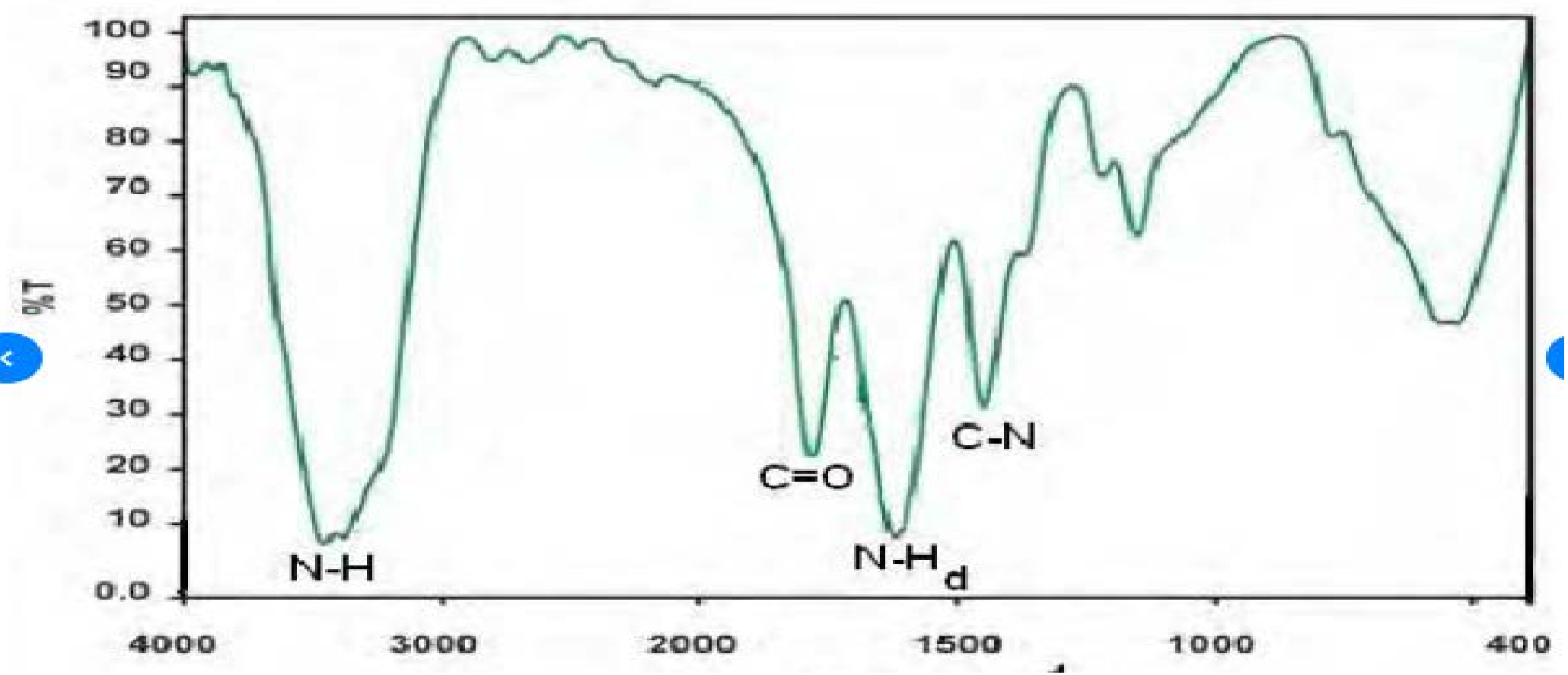


Option 1 - Urea

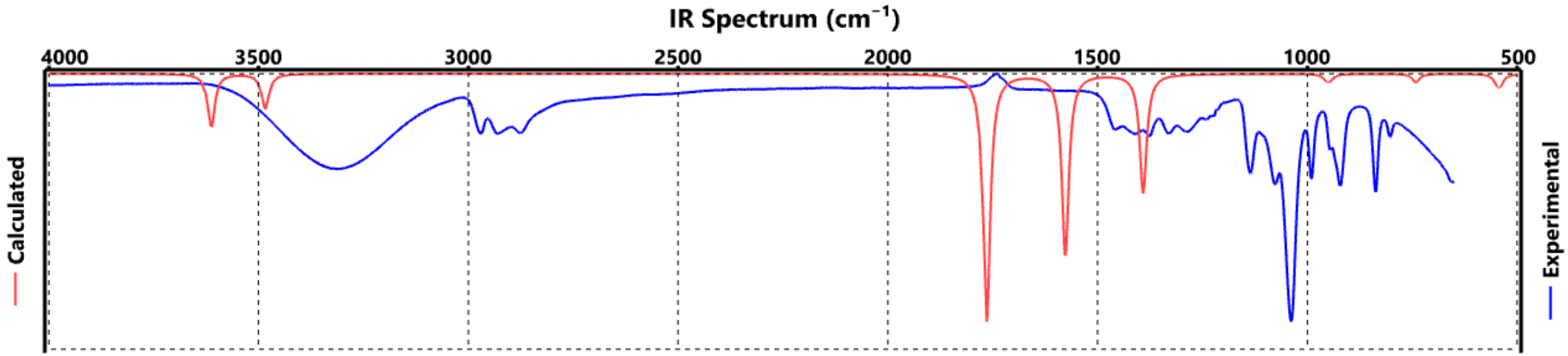
- a colorless crystalline compound which is the main nitrogenous breakdown product of protein metabolism in mammals and is excreted in urine
- If your kidneys cannot remove Urea from the blood normally.
- Can raise Blood Urea Nitrogen (BUN) indicating liver disease, malnutrition, and overhydration



Urea IR Spectra

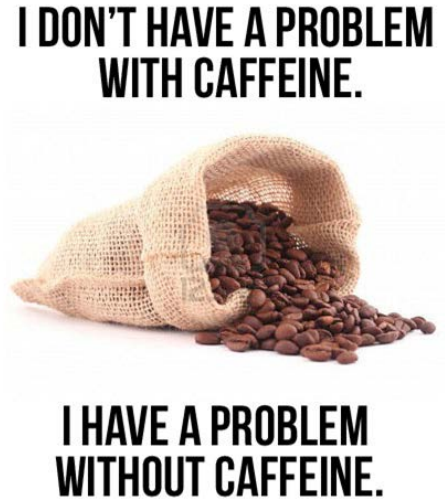


Superimposed IR Spectra

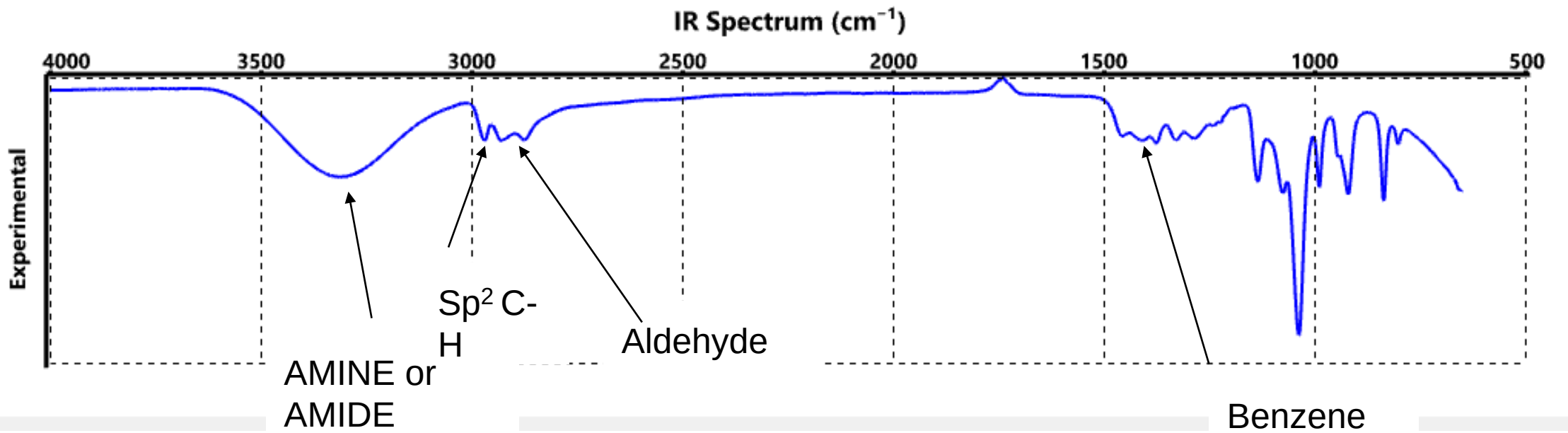


Option 2 - Caffeine Background

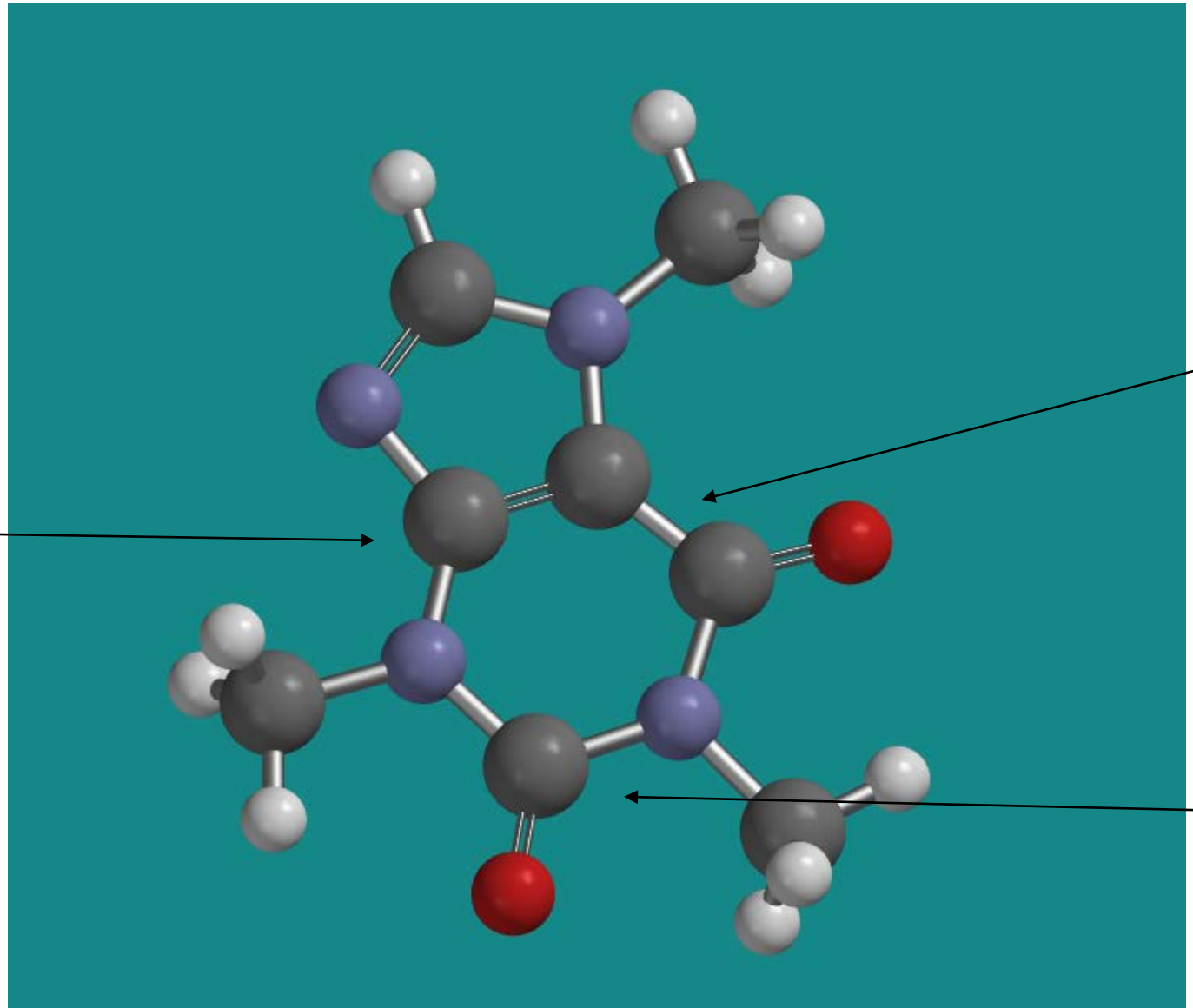
- Mainly used to improve mental alertness
- If drank for a long period of time or in fairly high amounts, it can cause side effects like insomnia, restlessness, anxiety, stomach irritation, increased heart rates, nausea, vomiting, chest pain, and ringing in the ears
- If drank in extremely high amounts, it can cause irregular heartbeats and potentially death



Why Caffeine?



Why Caffeine - Part 2

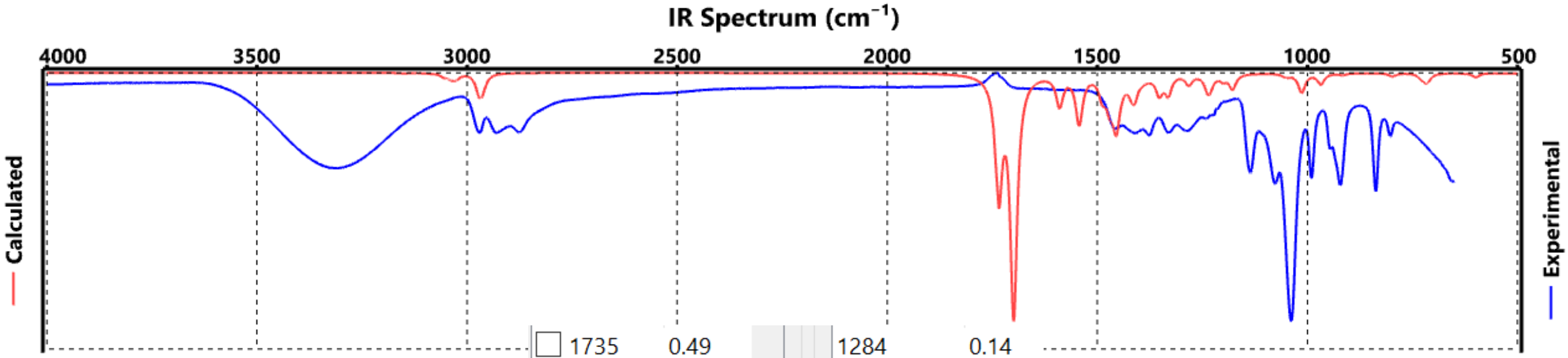


Benzene Ring

Sp2 carbon

Amide

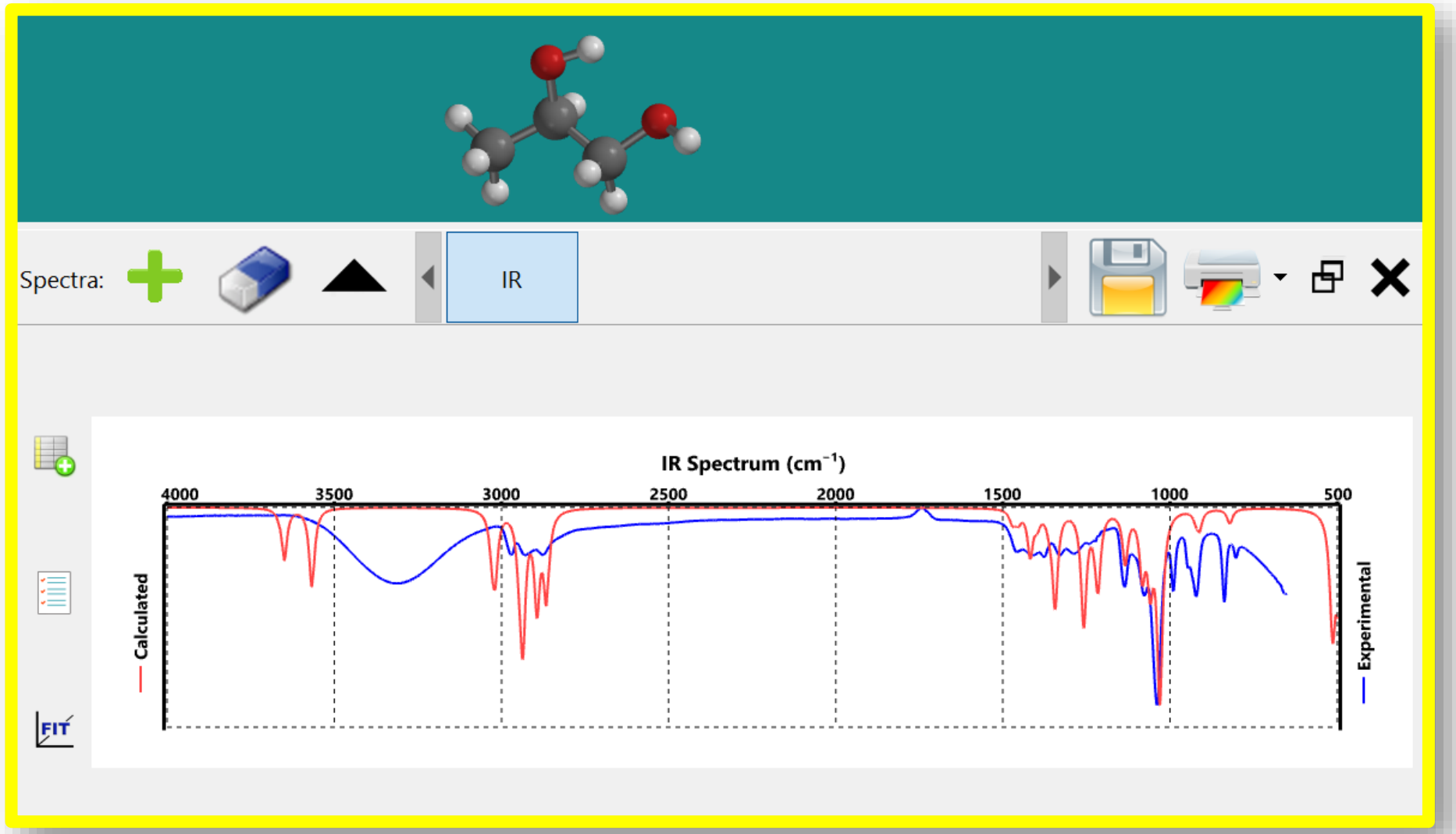
Why Caffeine? - Part 3



Near-perfect amide matches

☐	1735	0.49		1284	0.14
☐	2963	0.05		1327	0.13
☐	2970	0.04		1382	0.13
☐	2972	0.04		1414	0.11
☑	3025	0.02		1454	0.15
☐	3037	0.02		2862	0.20
☐	3048	0.01		2919	0.17
☐	3057	0.01		2969	0.14
☐	3087	0.00		3223	0.40
☐	3088	0.00		3309	0.48
☐	3150	0.00		3393	0.41

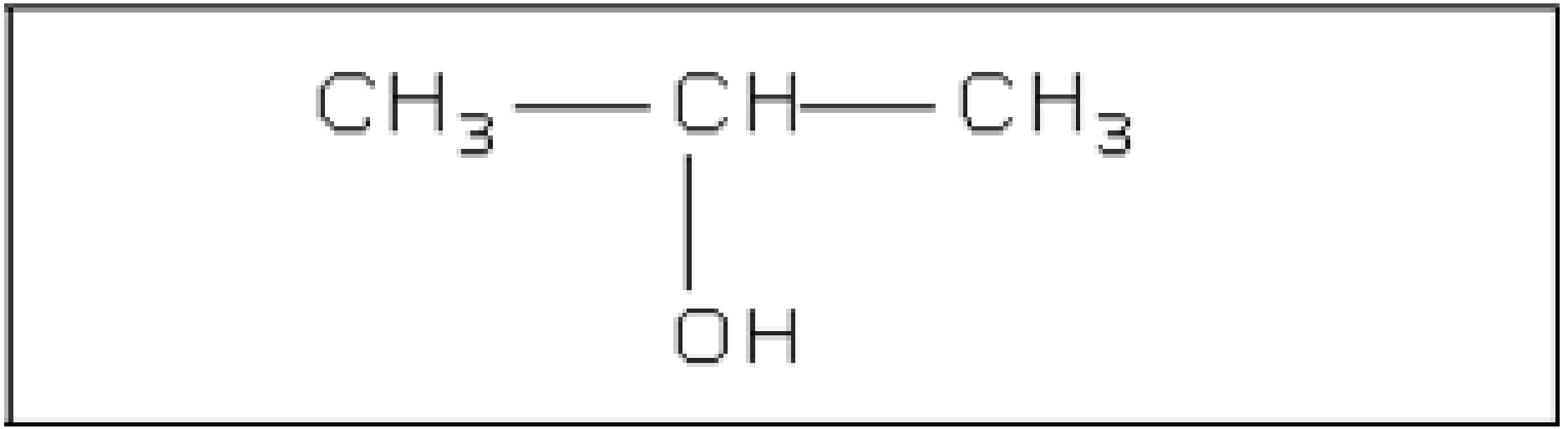
In Reality the unknown is 1,2 propanediol

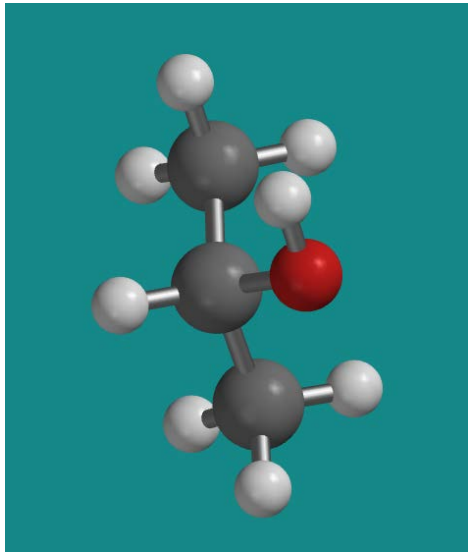


THE END

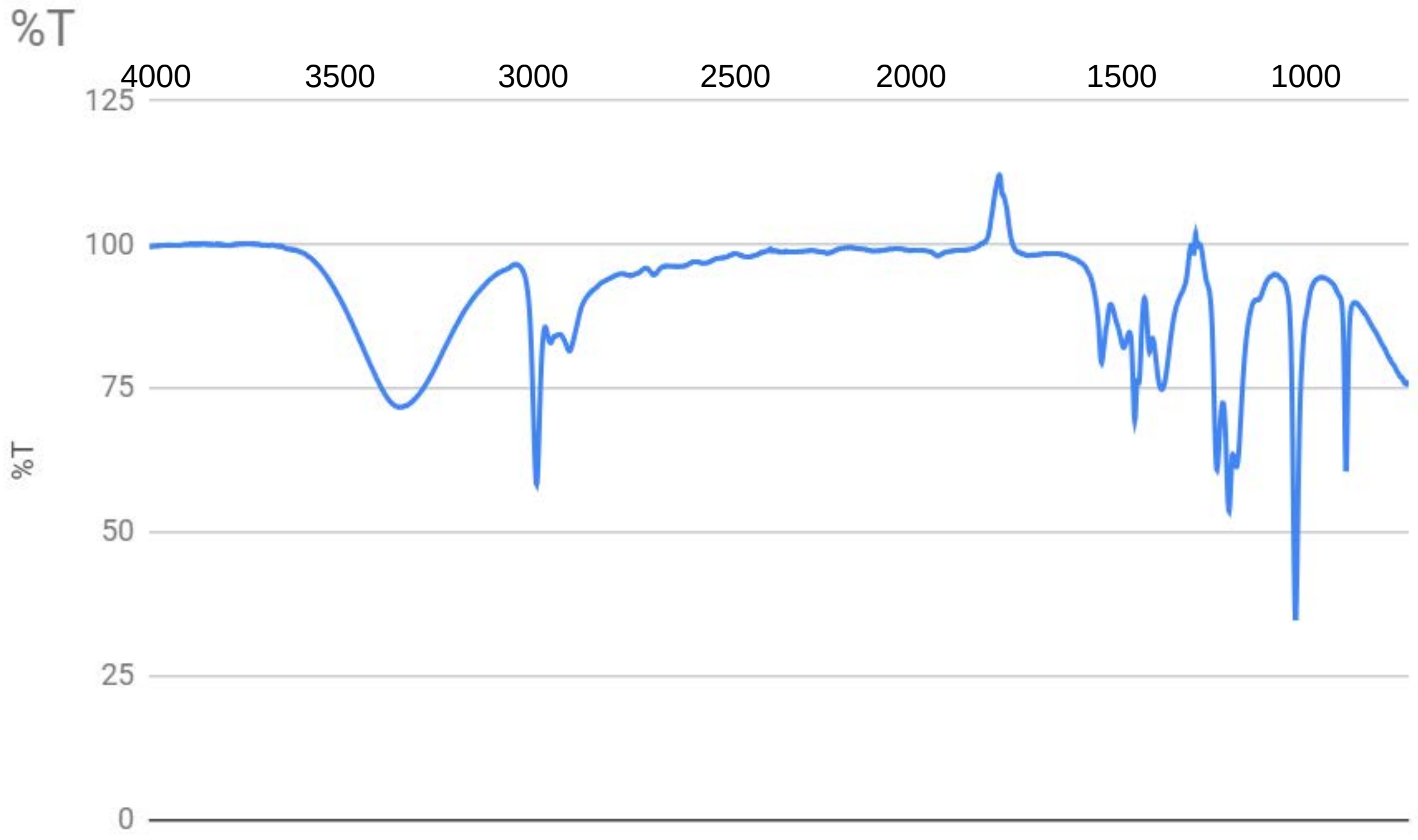
Thank You

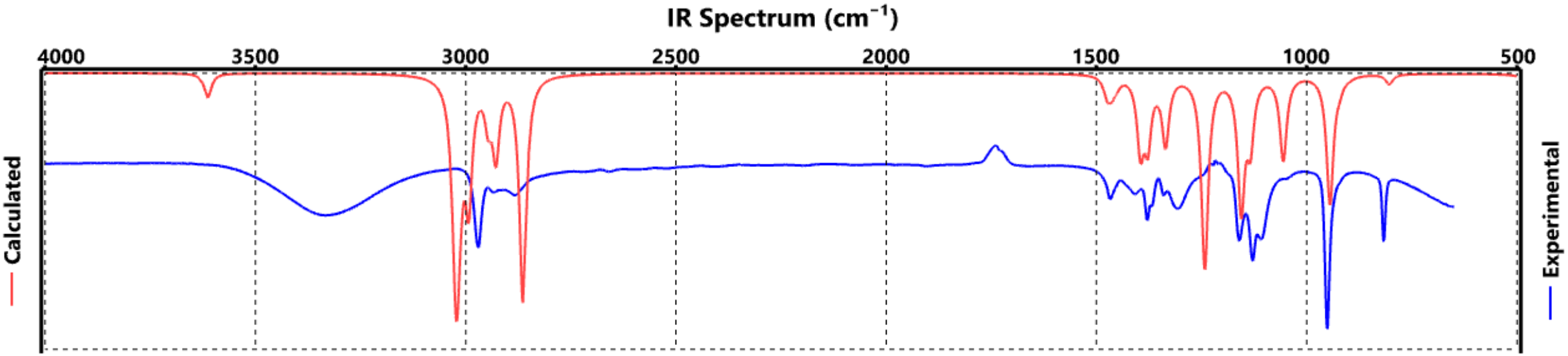
Unknown 6 - 2-propanol

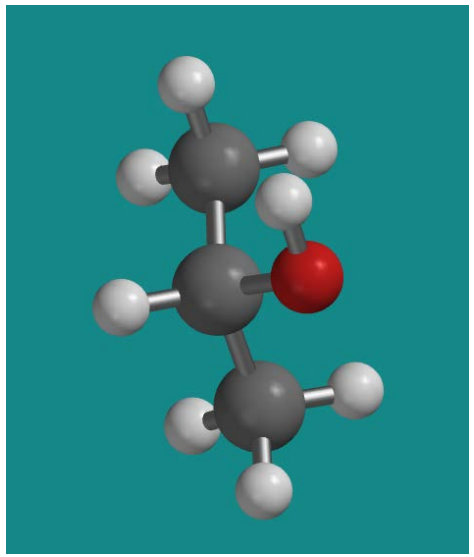


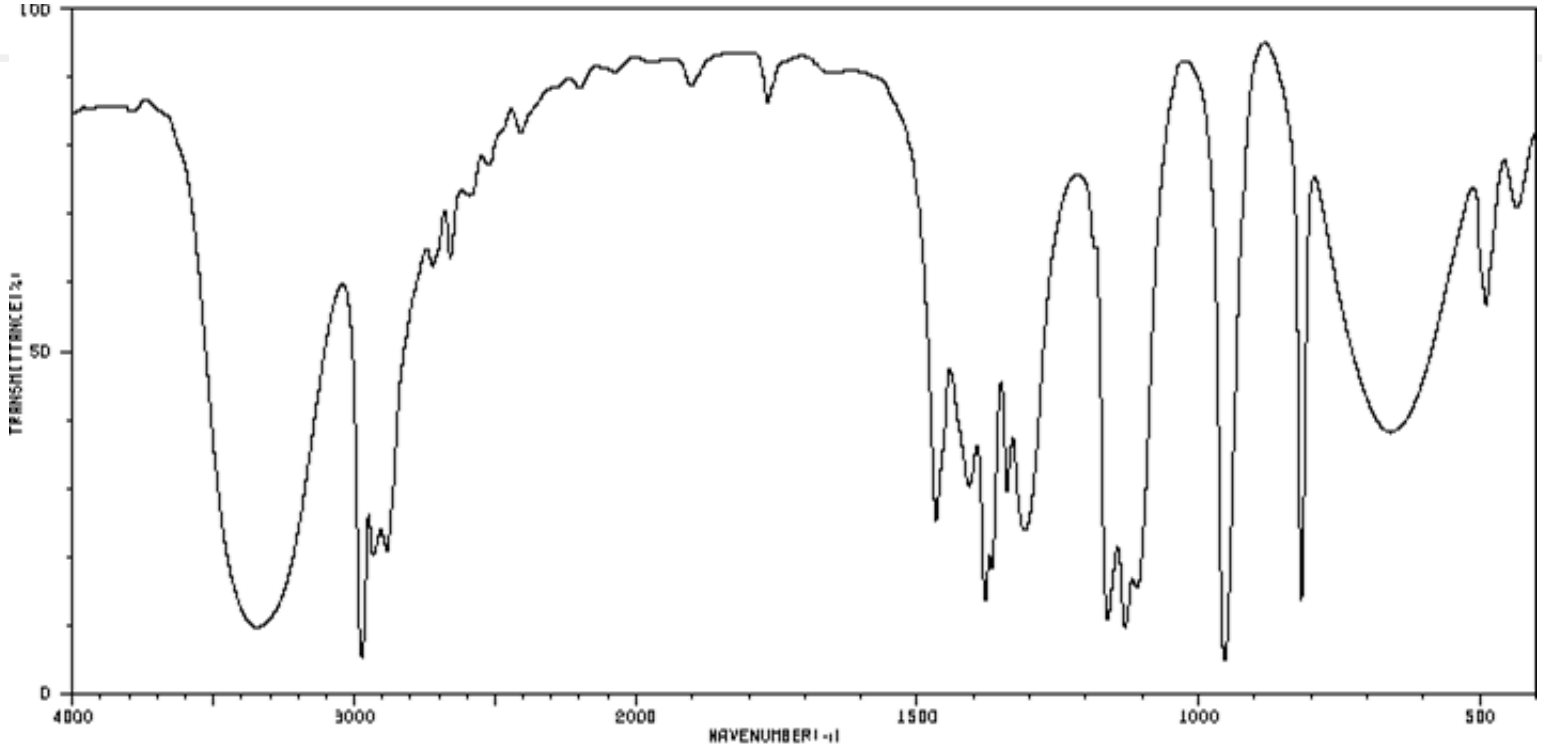


TEAM "NINES"


%T
4000
3500
3000
2500
2000
1500
1000
125
100
75
50
25
0
%T


IR Spectrum (cm⁻¹)
4000
3500
3000
2500
2000
1500
1000
500
Calculated
Experimental




100
50
0
4000
3000
2000
1500
1000
500

Reflection

- Exposure to modern experimental and calculational methods
- Student comments generally good…
  - "liked working with molecules on screen"; "enjoyed interacting with the IR spectra in SPARTAN"; "HARD to learn how to build molecules"; "Let's use the IR machine more"
- Really an INTRO to IR spectroscopy … you'd need more time to really analyze general IR spectra
- Presentation of Solution to Class
- Apply Experimental and Calculational data to problem solve

References

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4. NIST Webbook (https://webbook.nist.gov/)
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