Experiment 4.
Atomic and Molecular Structure

Experimental Procedure

- Objectives
- Introduction
- Experimental Procedure

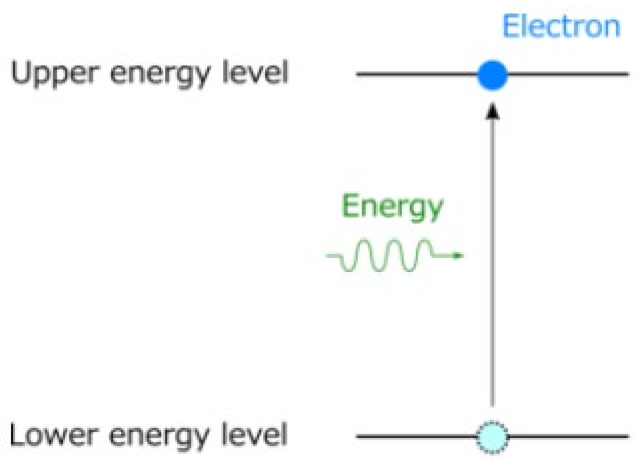
OBJECTIVES

- To view and calibrate visible line spectra
- To identify an element from via visible line spectra
- To identify a compound from its infrared spectrum
- To predict the three-dimensional structure of molecules and molecular ions

Introduction

According to quantum mechanics, energies of electrons in an atom are quantized, which means all the electrons can possess only the particularly allowed energies.

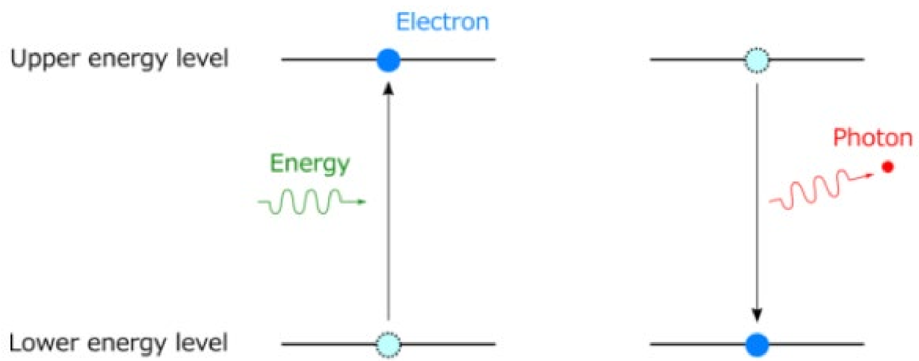
When an atom of an element absorbs a certain amount of energy, (which has the exactly same amount with the difference between energies of two different states) the electrons within it absorb the energy and reach excited states.



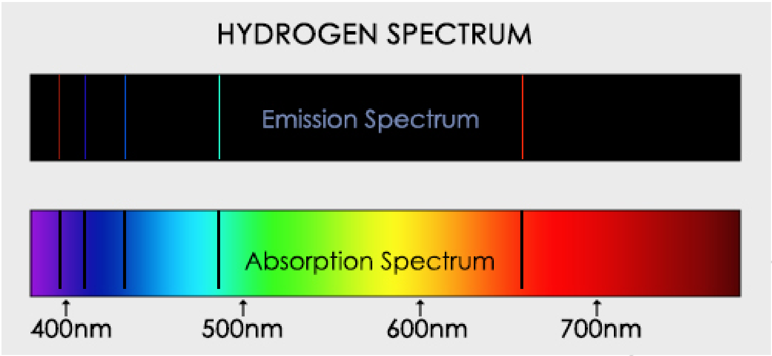
Electrons can acquire a certain amount of energy because the energies of allowed states are quantized.

Image From: https://www.fiberlabs.com/glossary/stimulated-emission/

After an electron reach an excited state, the electron returns to the ground sate by various pathways. One of the most frequent ways is fluorescence, a radiative procedure where a photon possessing a certain amount of energy comes out.



These photons can have only the allowed energies (due to the energy quantization). The energies are different according to the elements, which makes emission spectrums of various elements much different.



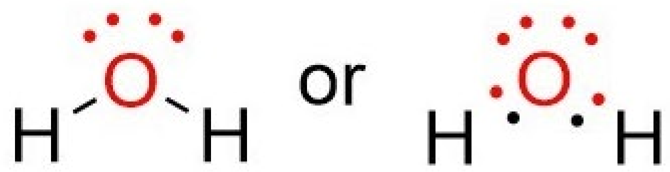
IR spectroscopy is a tool to identify what bonds a target molecule possesses. This analysis method utilizes a concept of molecular vibration. (You will learn this concept in GenChem 2)

The only thing you have to remember is that each bond has its own characteristic vibrational frequency. You may refer to Table D3.2 in the experiment manual.

Bond	Stretching Frequency (cm^{-1})	Intensity
O—H	3200–3650	Weak to strong (strongest when H-bonded)
N—H	3100–3550	Medium
C—H	2700–3300	Weak to medium
C=C	1600–1680	Weak to medium
C=O	1630–1820	Strong
C—O	1000–1250	Strong
C—C	1670 – 1640	Not interested

Image From: https://slideplayer.com/slide/4763625/

Lewis structure is a powerful tool to represent molecules into 2-D diagrams. It explains basic information about molecules such as bond order, lone pairs, hybrid orbitals, and so on.

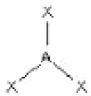
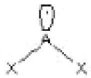
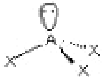
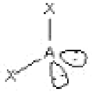
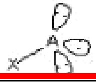


However, one of its weakness is that it lacks information about 3-D geometry, which defines many features of chemicals. Chemists needed to identify the 3-D structure, so they invented a new model called Valence Shell Electron Pair Repulsion, or VSEPR theory.

VSEPR Theory (Molecular Shapes)

A = the central atom, X = an atom bonded to A, E = a lone pair on A

Note: There are lone pairs on X or other atoms, but we don't care. We are interested in only the electron densities or domains around atom A.

Total Domains	Generic Formula	Picture	Bonded Atoms	Lone Pairs	Molecular Shape	Electron Geometry	Example	Hybridi -zation	Bond Angles
1	AX		1	0	Linear	Linear	H_2	s	180
2	AX_2		2	0	Linear	Linear	CO_2	sp	180
	AXE		1	1	Linear	Linear	CN^-		
3	AX_3		3	0	Trigonal planar	Trigonal planar	$AlBr_3$	sp^2	120
	AX_2E		2	1	Bent	Trigonal planar	$SnCl_2$		
	AXE_2		1	2	Linear	Trigonal planar	O_2		
4	AX_4		4	0	Tetrahedral	Tetrahedral	$SiCl_4$	sp^3	109.5
	AX_3E		3	1	Trigonal pyramid	Tetrahedral	PH_3		
	AX_2E_2		2	2	Bent	Tetrahedral	$SeBr_2$		
	AXE_3		1	3	Linear	Tetrahedral	Cl_2		

Total domains (or Steric number): Groups of atoms / Lone pairs

Image From: https://www.yumpu.com/en/document/view/19404788/vsepr-theory-molecular-shapes

EXPERIMENTAL PROCEDURE & RESULT VIDEOS

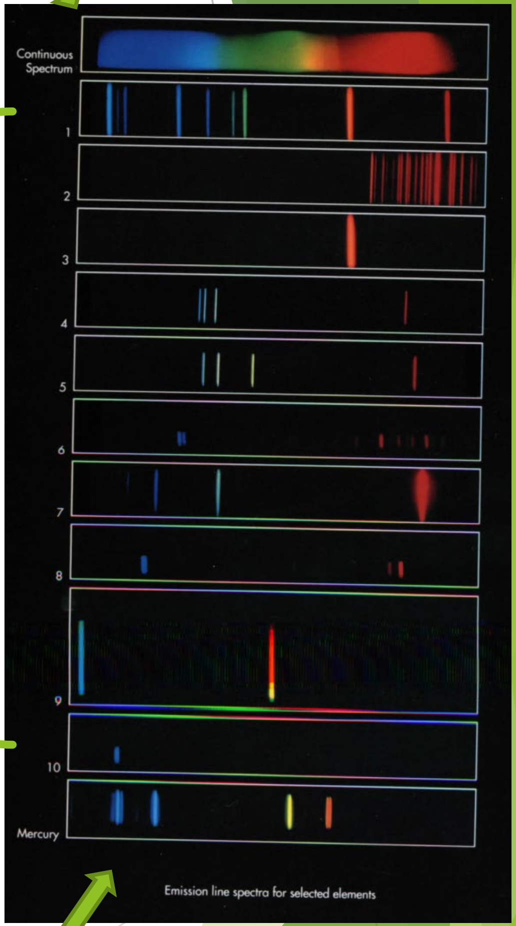
A. The mercury spectrum

1. The color plate

Notice the various experimental emission line spectra on the color plate (It is on the back cover of the book).

A continuous spectrum appears at the top, the line spectra for various elements appear in the middle (unknown elements, 1~10), and the Hg spectrum appears at the bottom.

Continuous spectrum



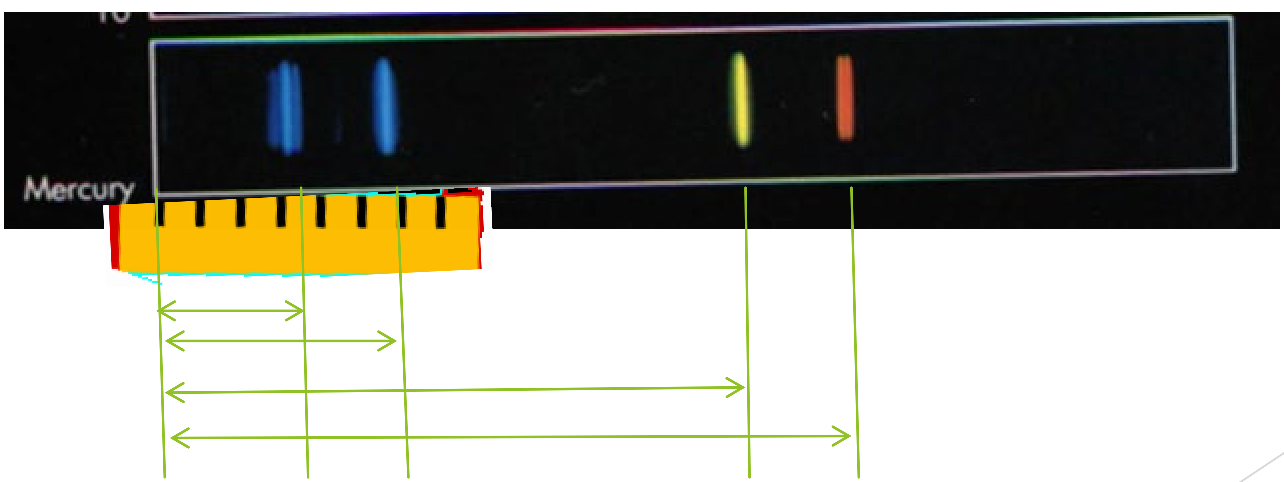
Unknown elements (1~10)

Hg spectrum

2. Calibrate the spectra of the color plate

Match the lines of Hg spectrum on the color plate with the wavelengths in Table D3.4.

Use a ruler to measure where the lines of Hg spectrum are located.



The distances between two lines of spectrum is proportional to the differences between the wavelengths of themselves.

So using the lengths we measured and the wavelengths in **Table D 3.4**, we can know wavelengths of any lines on the color plate by measuring their locations.

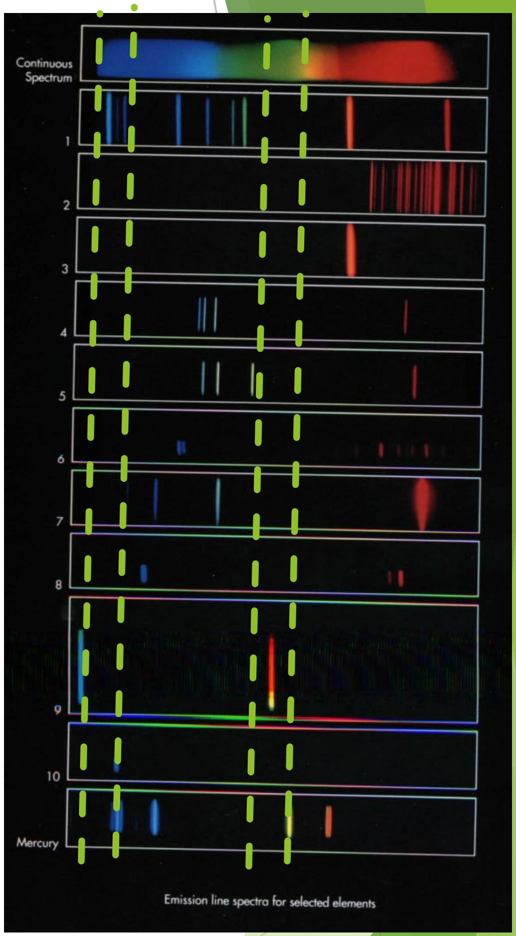


Table D3.4 Wavelengths of the Visible Lines in the Mercury Spectrum	
Violet	404.7 nm
violet	407.8 nm
Blue	435.8 nm
Yellow	546.1 nm
Orange	577.0 nm
Orange	579.1 nm

B. The spectra of elements

1. Hydrogen spectrum

Use **Figure D3.3**, page 158, to identify which of the emission spectra on the back cover is that of hydrogen. Justify your selection.

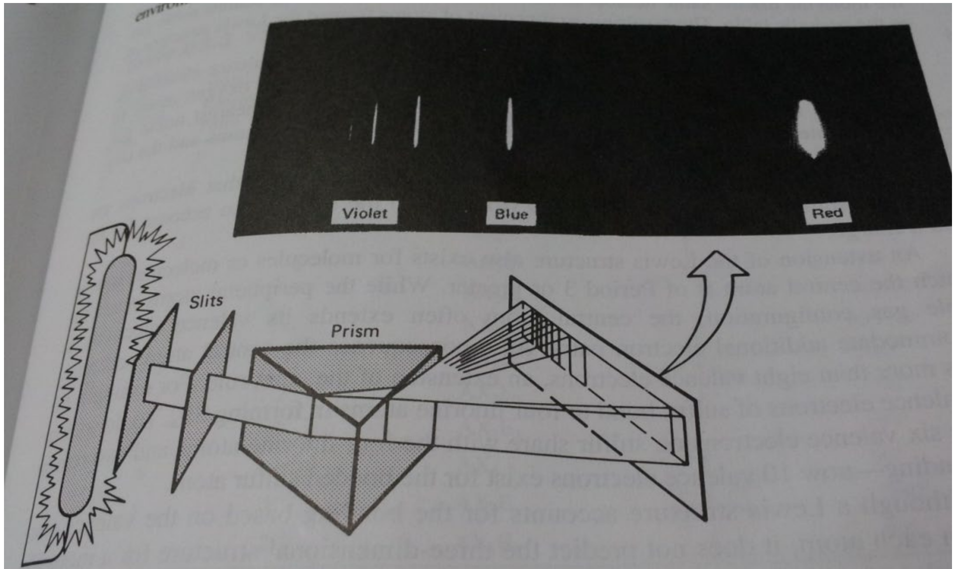
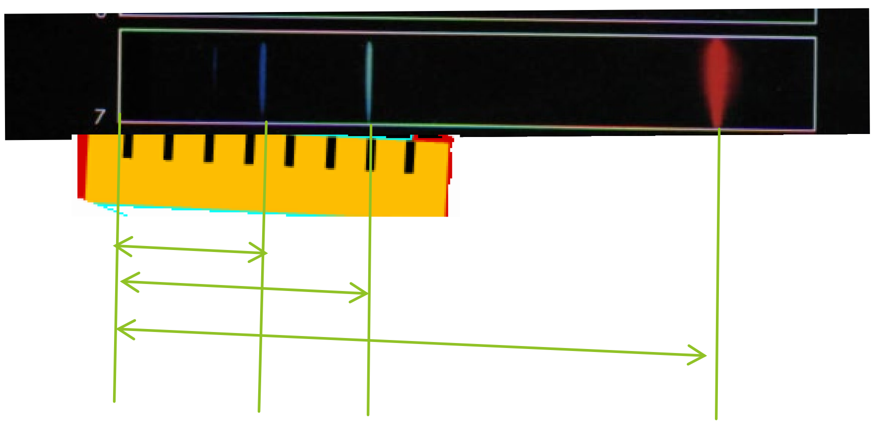


Figure **D3.3** Formation of the line spectrum for hydrogen

2. Unknown spectra

Your TA will assign to you one or two emission spectra from the color plate (1~10).

Use a ruler to measure where the lines of spectra are located.



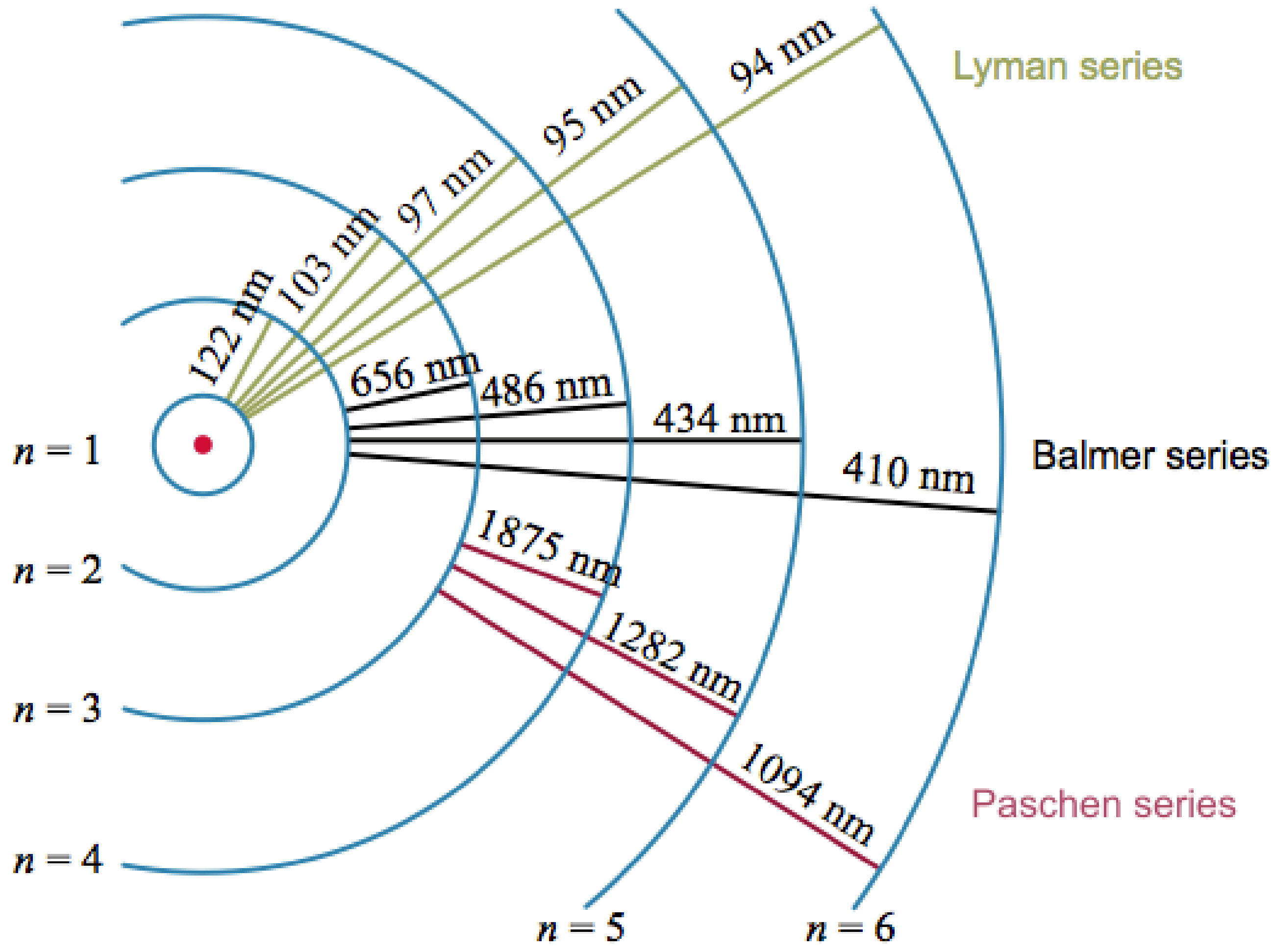
Calculate the wavelengths of them by using the data from Hg spectrum and **Table D 3.4**.

Compare the wavelengths of the most intense lines with the data in **Table D.3.5**. Identify the elements having the assigned spectra.

Additional Experiment
: Observing Real Spectra

Spectrum Tubes contain one or more elements as gaseous atoms or molecules. Energy is supplied through an electric field applied between electrodes at the ends of the tubes. Ions and electrons formed by the field are accelerated; collisions convert the increased Kinetic energy to other types, one being electronic. Electrons in energetic or excited atoms occupy one of many well-defined states. An electron with high energy E_3 will return to a lower energy state E_2 simultaneously emitting a photon of energy E_3-E_2 =ΔE= hc/λ; where $h = 6.63 \times 10^{-30}$ J-s is Planck's constant, $c = 3 \times 10^{8}$ m/s is the speed of light and λ is the wavelength of light (in meters) in the emitted photon.

Each excited atom type emits characteristic wavelength determined by energy level differences ΔE present in that species. One may observe a particular color with the eyes; analysis with a spectrometer will reveal a series of sharp (monochromatic) emission lines.



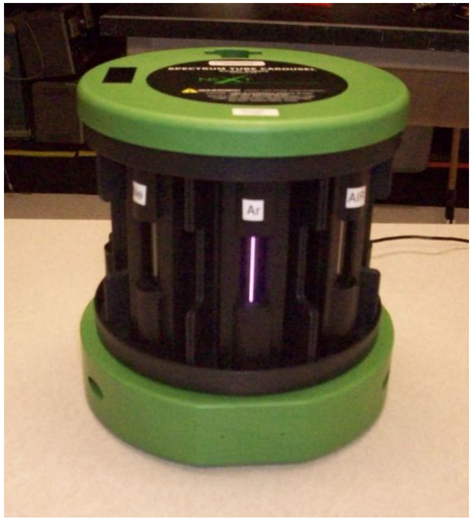
Lyman series
Balmer series
Paschen series
122 nm
103 nm
97 nm
95 nm
94 nm
656 nm
486 nm
434 nm
410 nm
1875 nm
1282 nm
1094 nm
n = 1
n = 2
n = 3
n = 4
n = 5
n = 6

In this part of the lab, you will look at the emission spectra produced by samples of hot gas. The samples are installed in the Vernier spectrum tube carousel power supply, which is shown in the picture to the right. Spectra can be measured using the Logger Pro software. The fiber optic cable of the spectrometer can be mounted in the plastic holder attached to the carousel.

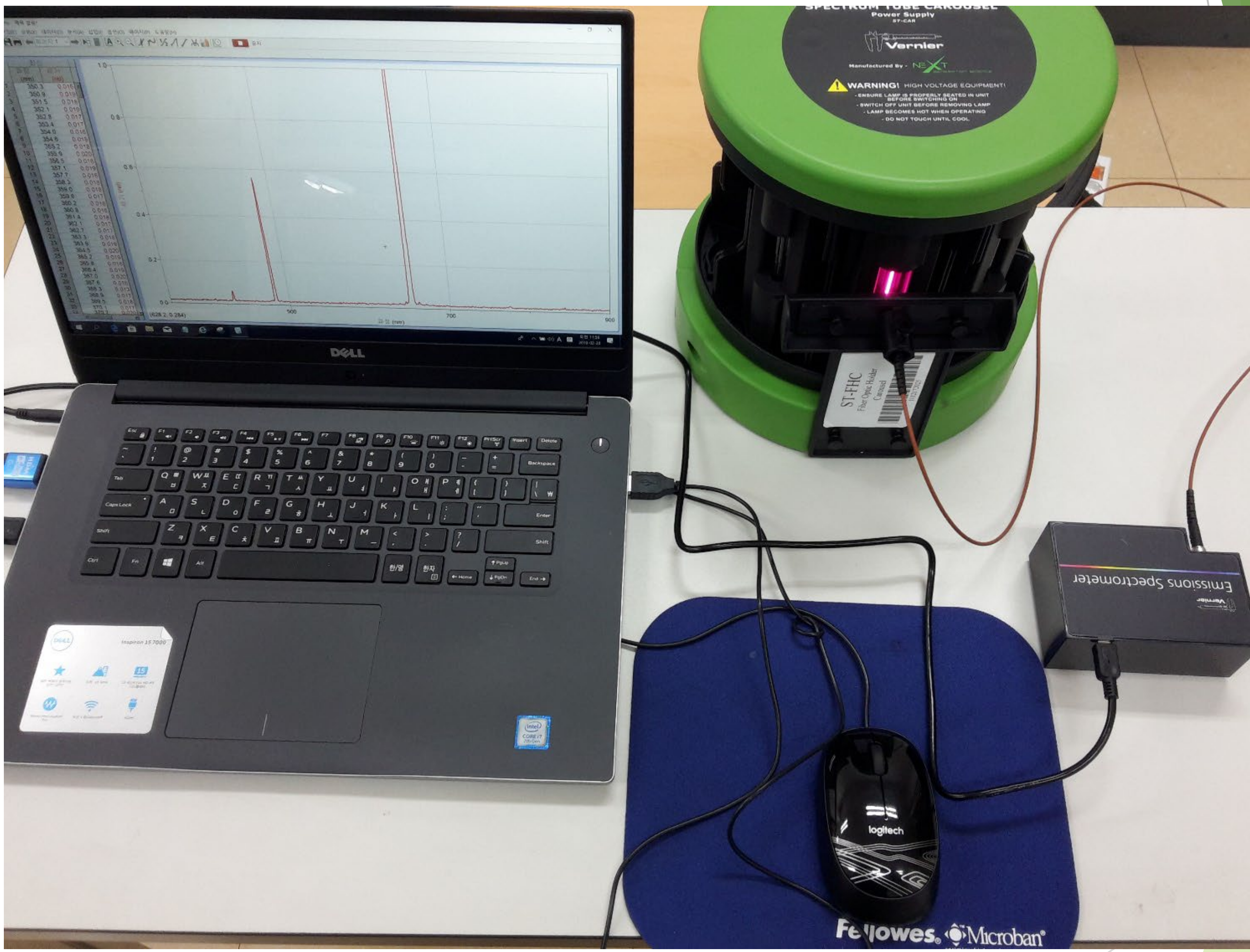
There should be seven gas samples in the carousel: hydrogen, helium, nitrogen, neon, argon, carbon dioxide, and air. To move from one sample to the next, carefully rotate the middle part of the carousel until the next sample clicks into position.

Emissions spectrometer

Emissions fiber



Spectrum Tube Carousel Power Supply

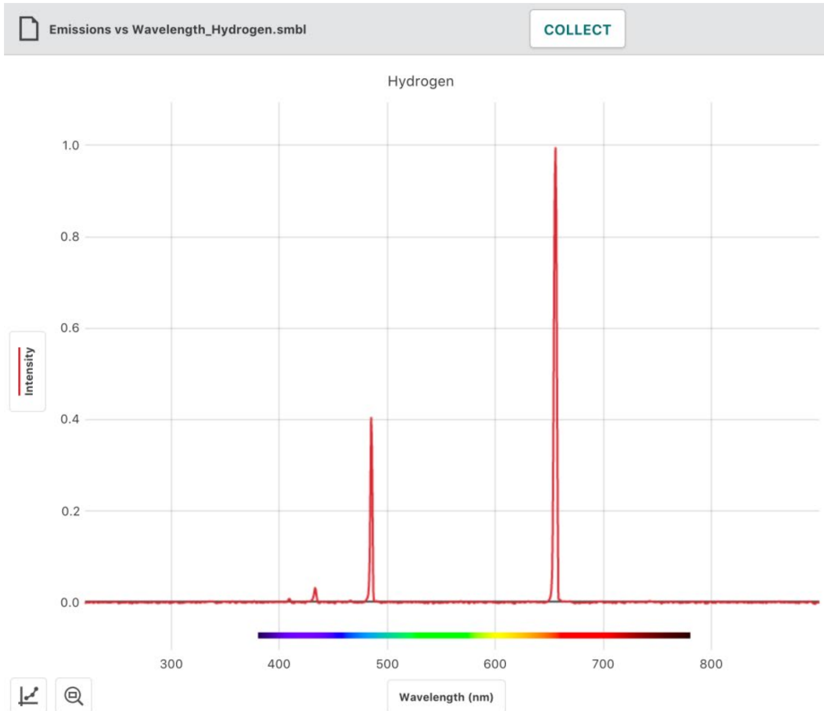

Vernier
WARNING! HIGH VOLTAGE EQUIPMENT!
DELL
ST-FHC
Emissions Spectrometer
logitech
Fellowes
Microban

NOTE: Turn off the spectrum carousel when you are not actively viewing a gas sample. The gas samples will burn out after extended use, particularly the hydrogen sample, which has a useful lifetime of approximately 40 hours.

1. Begin by observing the spectra of hydrogen and helium. Note the wavelength and intensity of the emission lines in each spectrum in your worksheet. You will need to devise a way of describing the intensity, or strength, of the individual lines.

2. Measure the spectra of neon and argon and observe the colors they make when discharging. Can you explain why these two gases glow with the colors they do?

Sample Data



	Hydrogen	
	Wavelength (nm)	Intensity
1	220.3	-0.003
2	221.0	-0.001
3	221.6	0.000
4	222.3	0.001
5	222.9	0.000
6	223.5	-0.001
7	224.2	-0.001
8	224.8	-0.001
9	225.4	-0.001
10	226.1	0.001
11	226.7	0.001
12	227.4	0.001
13	228.0	-0.002
14	228.6	-0.001
15	229.3	-0.001
16	229.9	0.001
17	230.5	0.001
18	231.2	0.000

Video: Vernier Emissions Spectrometer - Tech Tips

Also let's observe it through a Direct-Reading Spectroscope that is a replica diffraction grating instrument with an internal scale that shows students the wavelength in nanometers.

It is used for the detection and identification of elements by their characteristic spectral emission lines. The light source may be from salts in a flame or from electrically excited tubes filled with elemental gases, such as helium or nitrogen. The grating has 600 lines per mm. The scale reads from 380 to 720nm and has an actual length of approximately 35mm. The entire spectrum can be seen at once. The slit is adjustable and a reflector is provided to back-light the scale. The housing is a one-piece aluminum casting, finished with light gray polyurethane paint, mounted on a stainless steel post and supported on a cast iron tripod base.

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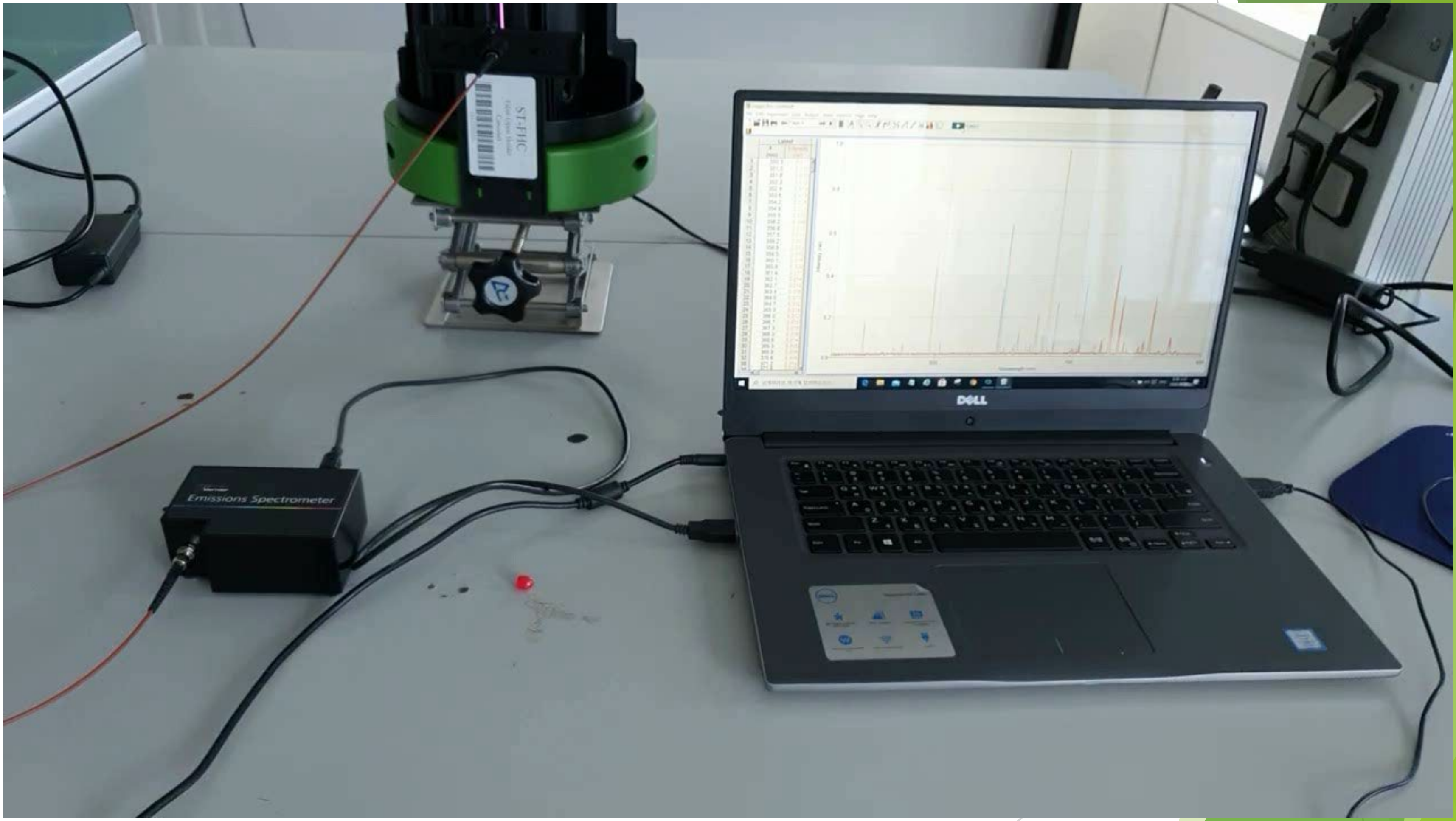
SPECTRUM TUBE CAROUSEL
Power Supply
Vernier
WARNING! HIGH VOLTAGE EQUIPMENT!
- SWITCH OFF UNIT BEFORE REMOVING LAMP
- LAMP BECOMES HOT WHEN OPERATING
- DO NOT TOUCH UNTIL COOL

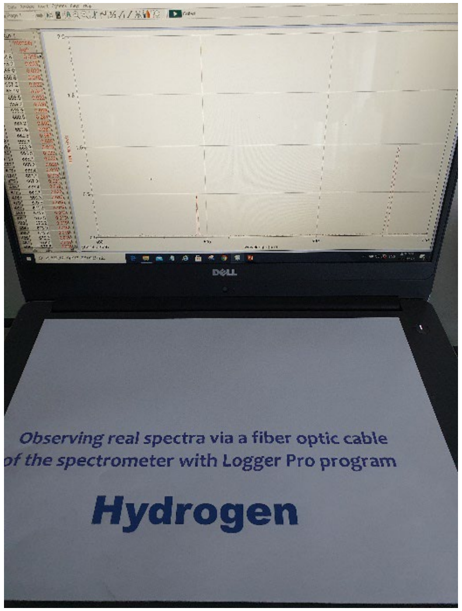
Experimental Results

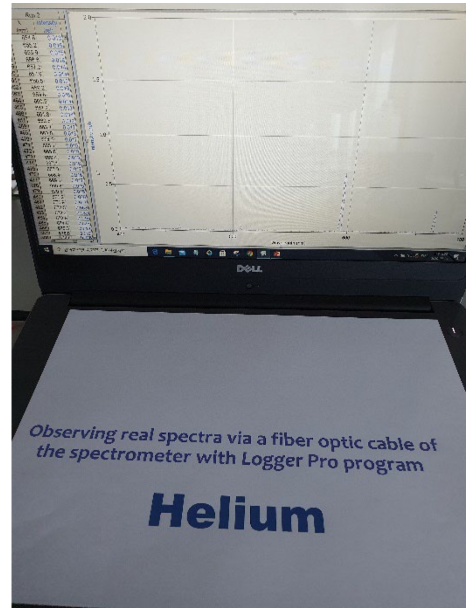
You indirectly can obtain some results and data sets from the experimental video clips and pictures conducted by TA. Both qualitative and quantitative data must be included in your lab report.

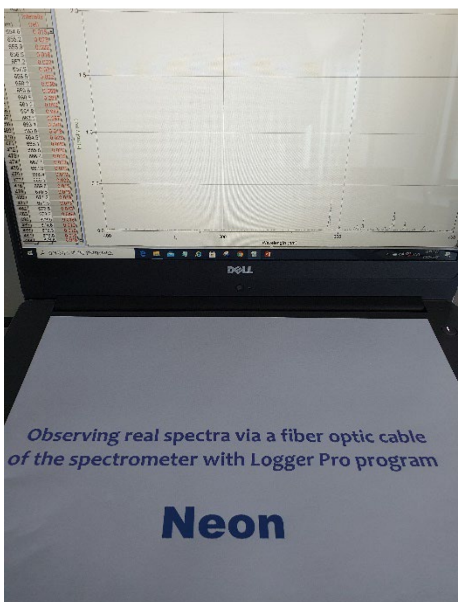
1. **Observing real spectra via the fiber optic cable of the spectrometer with *Logger Pro* program**

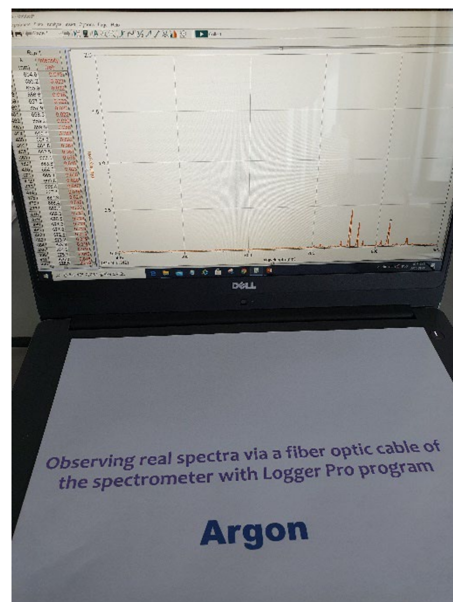


In-screen Recording

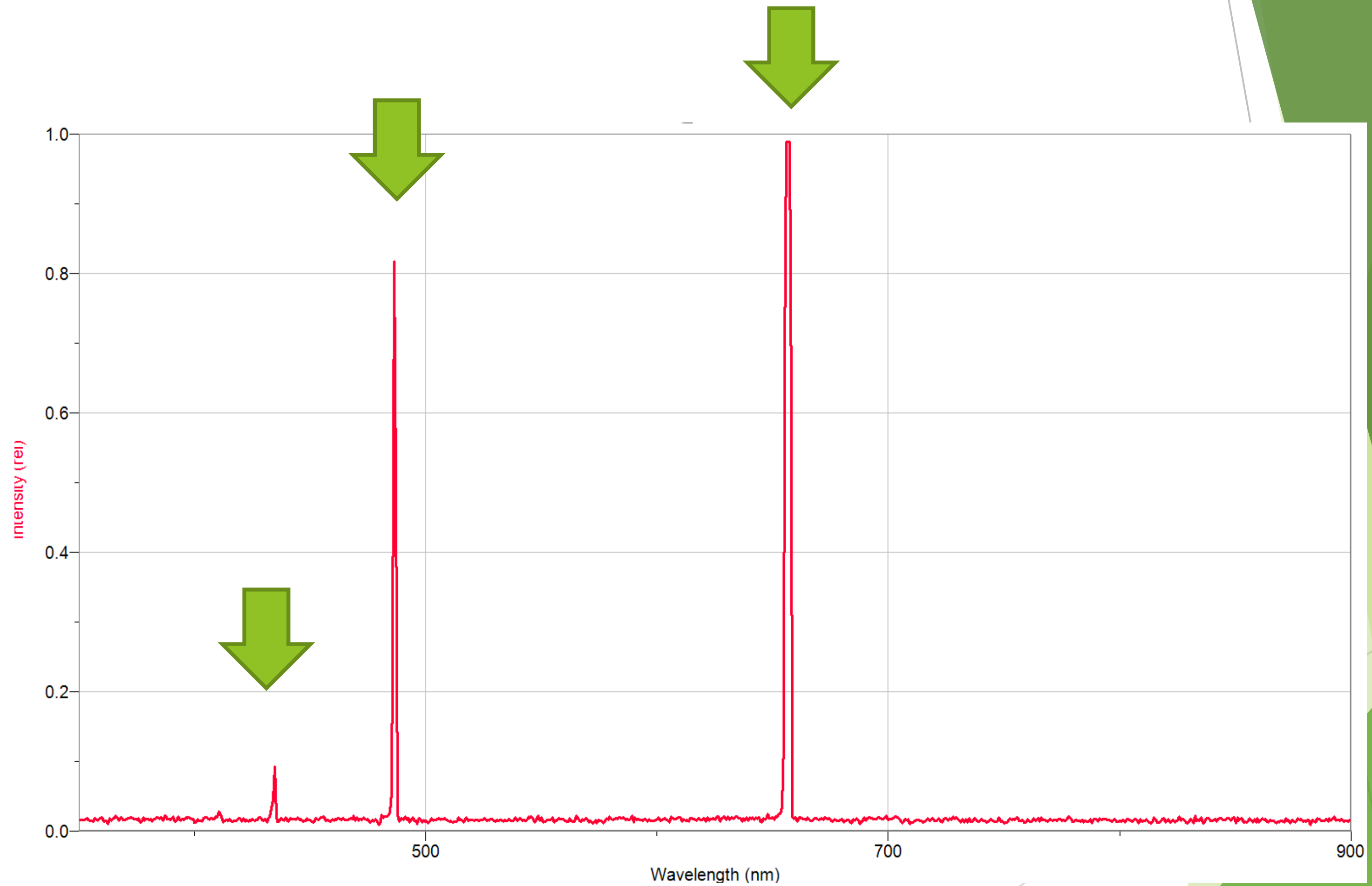

Observing real spectra via a fiber optic cable
of the spectrometer with Logger Pro program
Hydrogen


Observing real spectra via a fiber optic cable of
the spectrometer with Logger Pro program
Helium


Observing real spectra via a fiber optic cable
of the spectrometer with Logger Pro program
Neon


Observing real spectra via a fiber optic cable of
the spectrometer with Logger Pro program
Argon

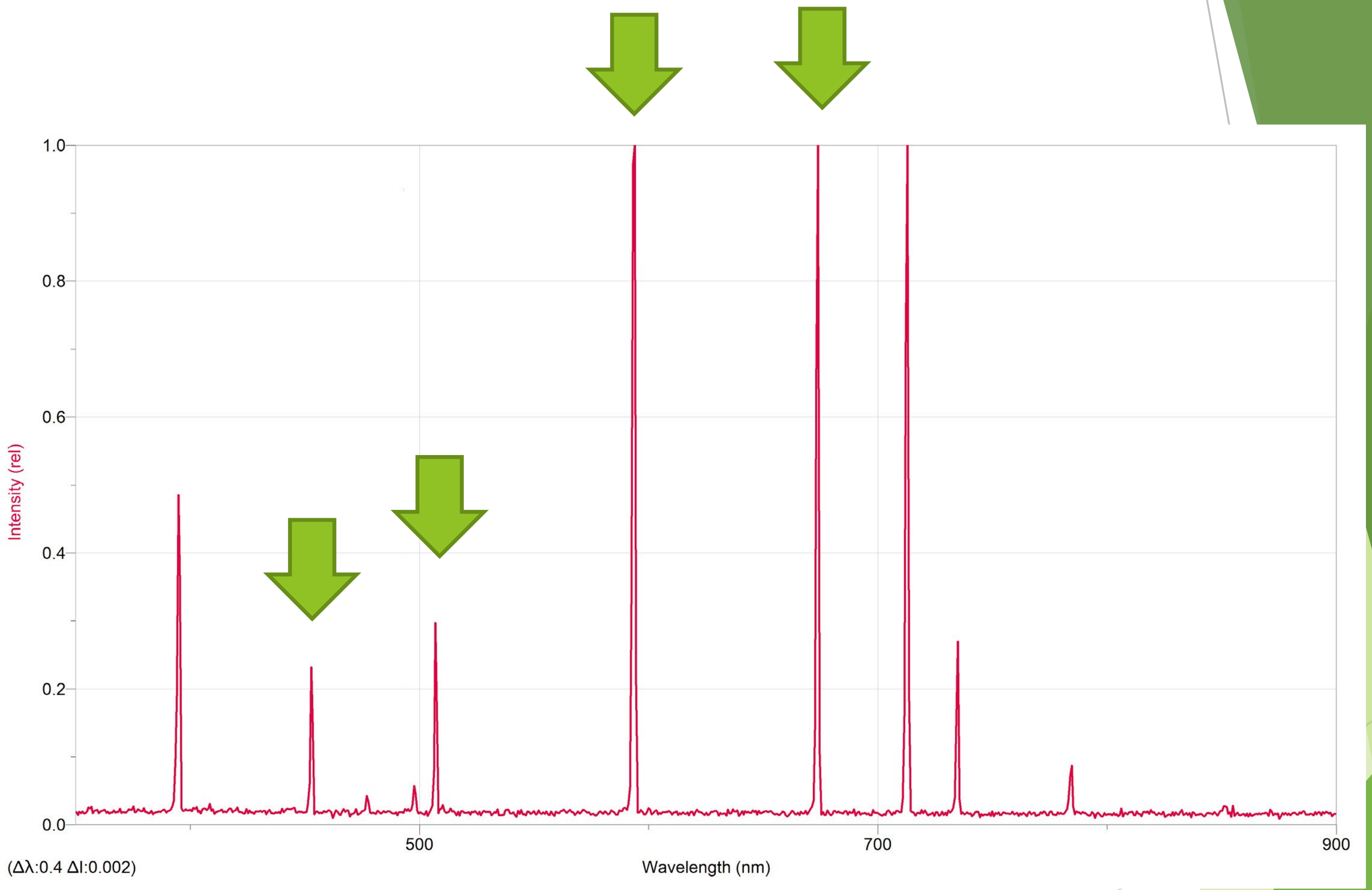
1) Hydrogen



Wavelength and Intensity of the Hydrogen

wavelength	intensity	wavelength	intensity	wavelength	intensity
431.2	0.012819867	481.7	0.01869459	652.6	0.02536278
431.9	0.017367056	482.4	0.020663	653.3	0.02537804
432.6	0.020495155	483.1	0.02131914	653.9	0.03523537
433.2	0.033205921	483.7	0.02224994	654.6	0.12710994
433.9	0.044161898	484.4	0.02783474	655.2	0.6725742
434.6	0.092594034	485.1	0.05581979	655.9	0.98925994
435.3	0.022890822	485.7	0.25339361	656.6	0.98925994
435.9	0.014055848	486.4	0.8178706	657.2	0.98925994
436.6	0.014116884	487.1	0.49747692	657.9	0.59836957
437.3	0.018252079	487.7	0.02391318	658.5	0.0213344
438	0.017107652	488.4	0.0138117		
438.6	0.014620432	489.1	0.01874037		
		489.7	0.01881666		
		490.4	0.01588693		
		491	0.02058671		

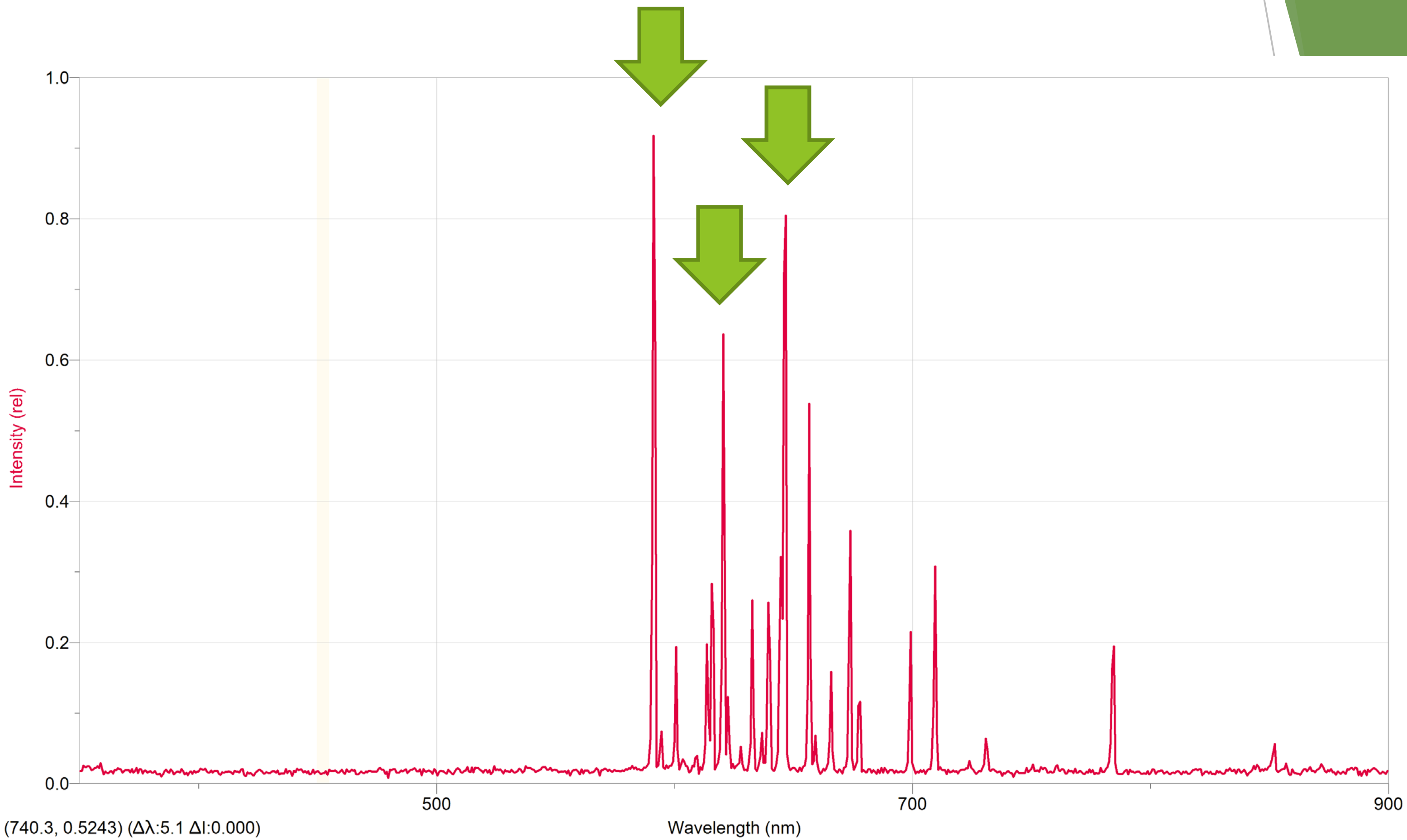
2) Helium


1.0
0.8
0.6
0.4
0.2
0.0
Intensity (rel)
500
700
900
(Δλ:0.4 ΔI:0.002)
Wavelength (nm)

Wavelength and Intensity of the Helium

wavelength	intensity	wavelength	intensity	wavelength	intensity	wavelength	intensity
450.1	0.018238	503.6	0.013233	589.1	0.024876	668.4	0.020771
450.8	0.019001	504.3	0.01807	589.8	0.025105	669.1	0.015537
451.4	0.031529	504.9	0.021977	590.5	0.022007	669.8	0.018284
452.1	0.06017	505.6	0.028202	591.1	0.030232	670.5	0.022755
452.8	0.231865	506.3	0.079915	591.8	0.055119	671.2	0.02689
453.4	0.150946	506.9	0.297295	592.5	0.324578	671.9	0.035878
454.1	0.015553	507.6	0.152716	593.2	0.972965	672.5	0.140021
454.8	0.019306	508.3	0.017094	593.9	1.000263	673.2	0.670989
		508.9	0.022648	594.5	0.206046	673.9	1.000263
		509.6	0.023823	595.2	0.018116	674.6	0.103399
				595.9	0.018208	675.3	0.01511

3) Neon



1.0
0.8
0.6
0.4
0.2
0.0
Intensity (rel)
500
700
900
Wavelength (nm)
(740.3, 0.5243) (Δλ:5.1 ΔI:0.000)

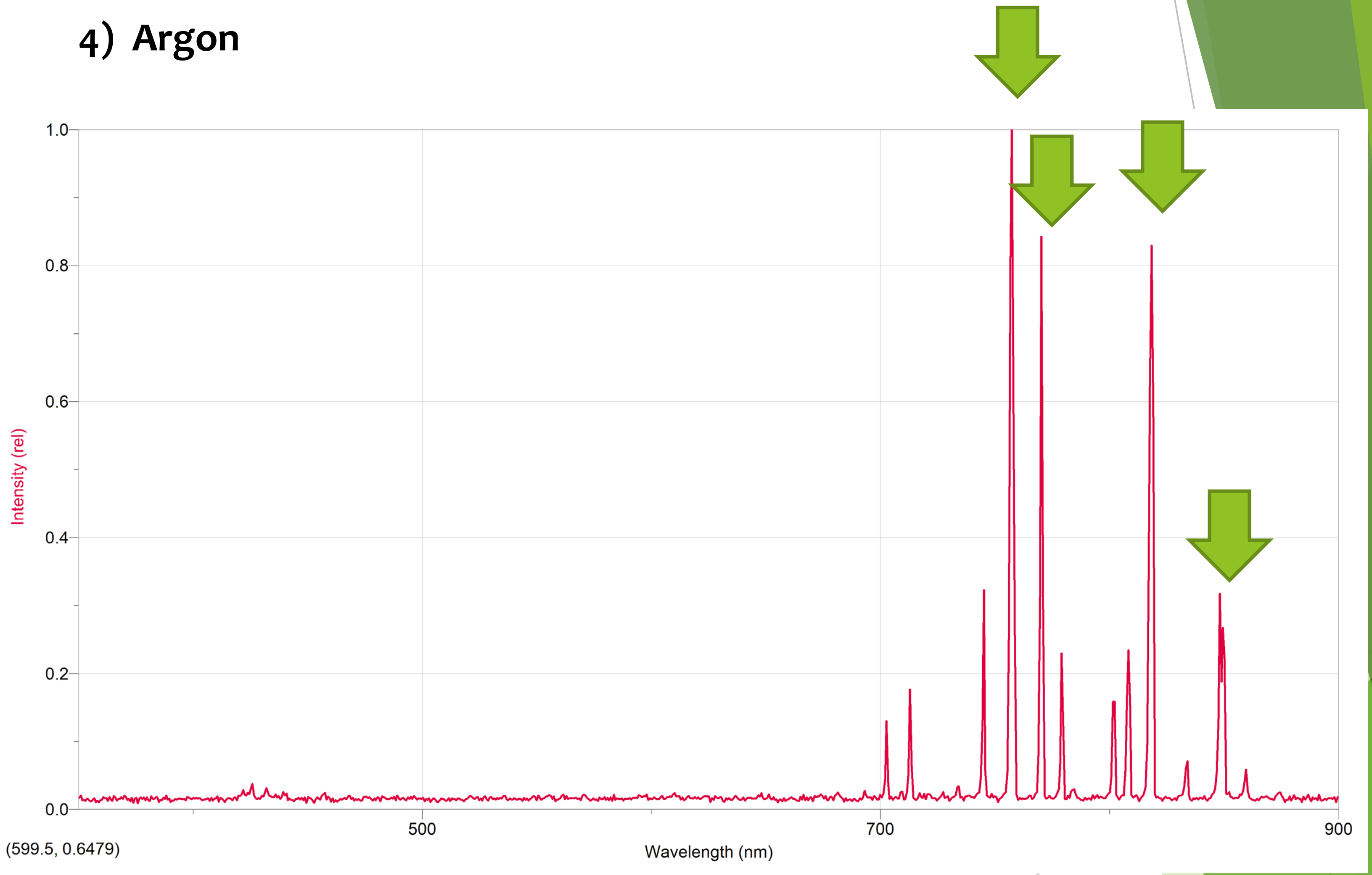
Wavelength and Intensity of the Neon

wavelength	intensity
588.4	0.024872
589.1	0.028885
589.8	0.061845
590.5	0.309834
591.1	0.917723
591.8	0.626291
592.5	0.02356
593.2	0.026352

wavelength	intensity
618.3	0.029938
619	0.047623
619.7	0.162341
620.4	0.636423
621	0.316045
621.7	0.041245
622.4	0.123339

wavelength	intensity
642.1	0.019089
642.7	0.028214
643.4	0.044663
644	0.174502
644.7	0.321431
645.4	0.233539
646	0.723934
646.7	0.804547
647.3	0.040848
648	0.024063
648.7	0.018921

4) Argon


1.0
0.8
0.6
0.4
0.2
0.0
Intensity (rel)
500
700
900
Wavelength (nm)
(599.5, 0.6479)

Wavelength and Intensity of the Argon

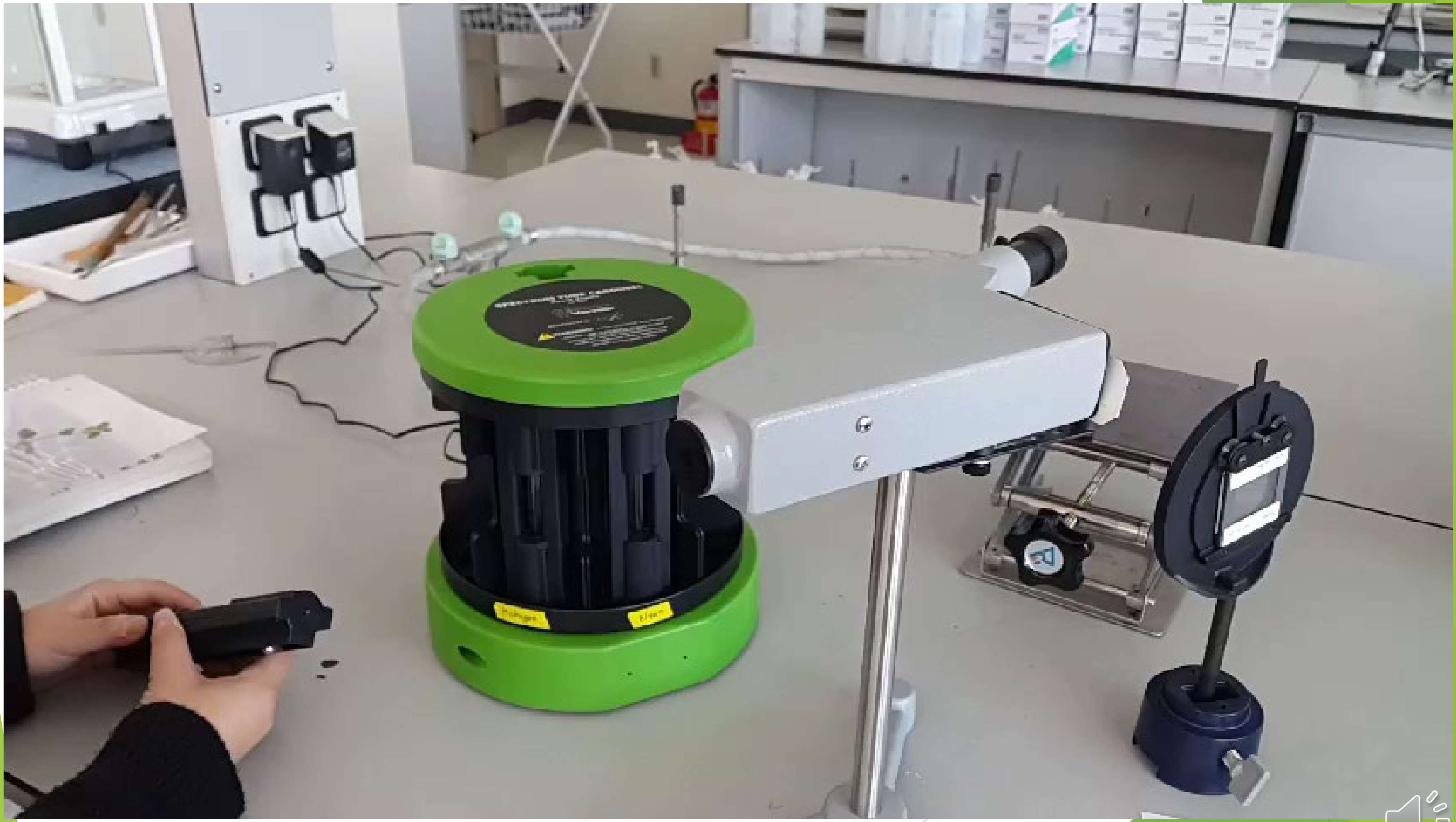
wavelength	intensity
754	0.023522
754.7	0.025185
755.4	0.055795
756	0.249935
756.7	0.813146
757.4	1.008354
758.1	0.58159
758.7	0.256435
759.4	0.021767
760.1	0.013909

wavelength	intensity
767.6	0.022805
768.3	0.025994
768.9	0.07847
769.6	0.312924
770.3	0.842626
771	0.294644
771.7	0.019768
772.3	0.015724
773	0.016869

wavelength	intensity
813	0.012169
813.7	0.017144
814.4	0.019524
815	0.023613
815.7	0.033349
816.4	0.095682
817.1	0.337232
817.7	0.622026
818.4	0.829564
819.1	0.577546
819.8	0.022179

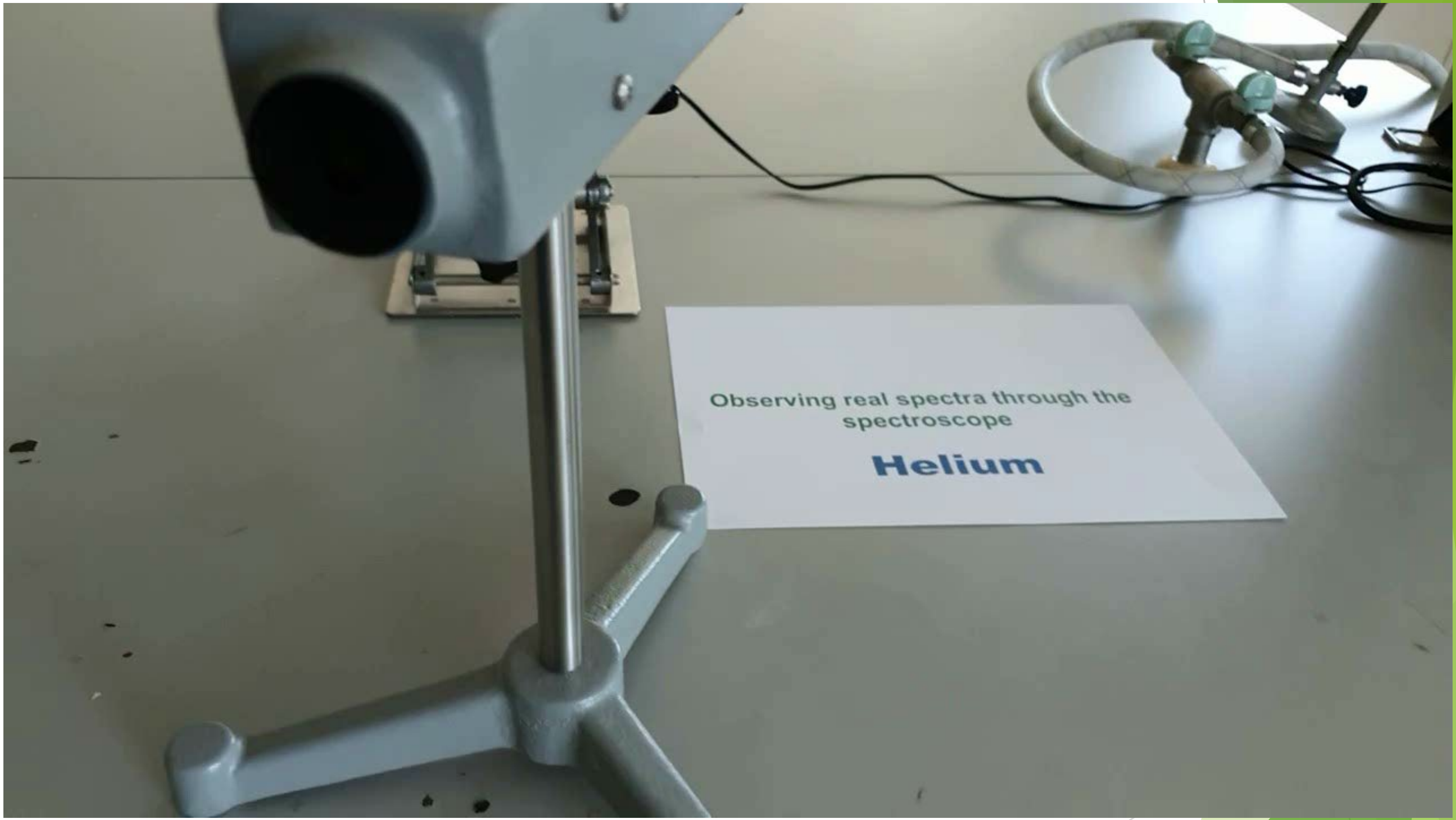
wavelength	intensity
844.1	0.01667
844.8	0.021965
845.5	0.025109
846.1	0.030694
846.8	0.05552
847.5	0.133478
848.2	0.317273
848.8	0.187739
849.5	0.267727
850.2	0.221828
850.9	0.023552
851.5	0.023033

2. Observing real spectra through the spectroscope



Spectrum Carousel

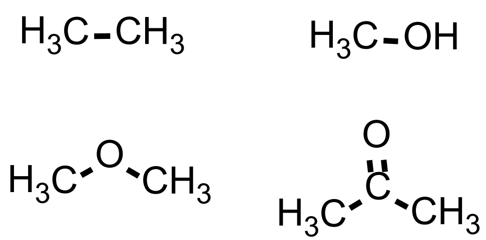

Observing real spectra through the spectroscope
Hydrogen


Observing real spectra through the spectroscope
Helium


Observing real spectra through the spectroscope
Argon

C. Infrared Spectra of Compounds (Homework)

Match of molecules with infrared spectrum (Figure D3.5A~5D). The absorption bands characteristic of atoms in bonds are listed in **Table D3.2**, page 158, to assist in the match.



Molecules

Table D3.2 Infrared Absorption Bands for specific Atoms in Bond Arrangements in Molecules

Atoms in Bonds	Wavenumbers (cm^{-1})	Wavelengths (μm)
O-H	3,700 to 3,500	2.7 to 2.9
C-H	3,000 to 2,800	3.3 to 3.6
C=O	1,800 to 1,600	5.6 to 6.2
C-O	1,200 to 1,050	8.3 to 9.5
C-C	1,670 to 1,640	6.0 to 6.1

■ Video clip

About molecular structures

- VSEPR Theory
- Polarity
- Hybrid orbitals
- Molecular orbitals

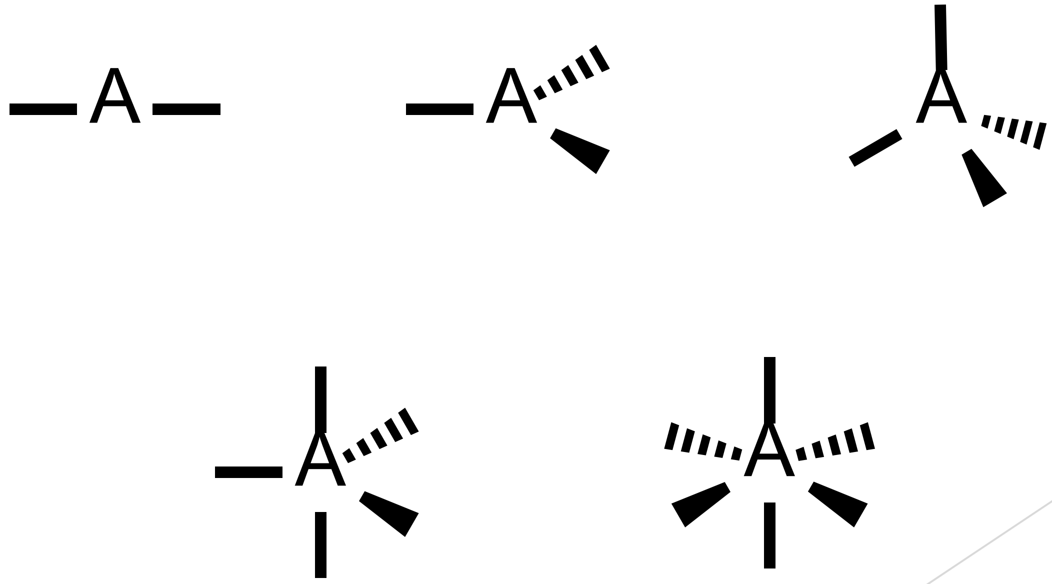
(From Standard Deviants, DVD, Learn CHEMISTRY 3)

D. Structure of Molecules and Molecular Ions

1. Five basic structures

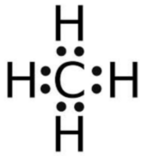
By using molecular model set provided by TA, construct the five basic three-dimensional structures shown in **Table D3.3**, page 159.

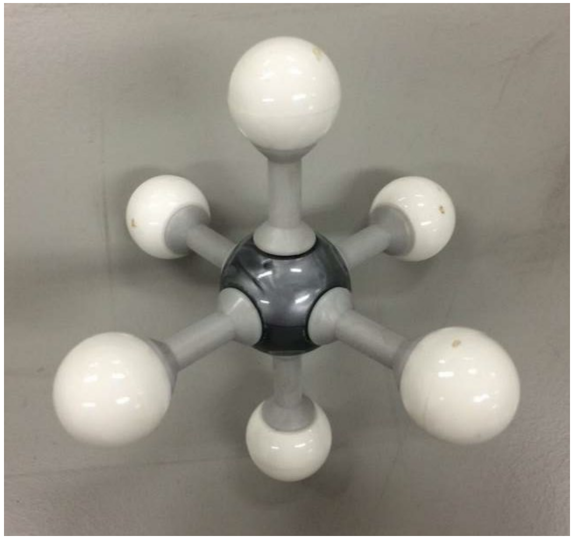
Five Basic three-dimensional structures from Table D3.3

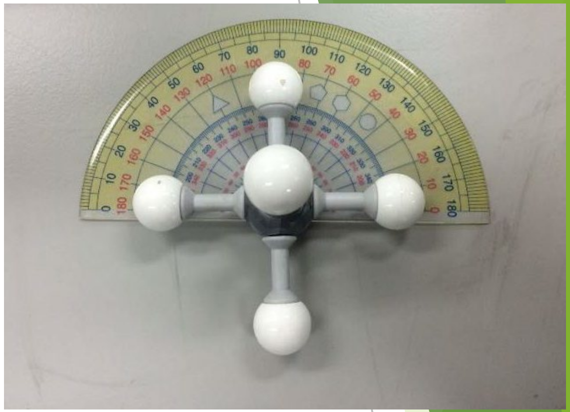


2. Determine three dimensional structures

On a separate sheet of paper, set up the following table (with eight columns) for each of the molecules/molecular ions in 'D. Structure of Molecules and Molecular ions' on the ***Report Sheet*** (164p.) that are assigned to your group. Determine their geometric shapes and approximate angles by using the molecular model set and a protractor.

molecule or molecular Ion	Lewis Structure	Valence Shell Electron Pairs	Bonding Electron Pairs	Nonbonding Electron Pairs	VSEPR Formula	Approx. Bond Angle	Geometric Shape
CH_4		4	4	0	AX_4	109.5°	tetrahedral





Experimental Results

You indirectly can obtain some results and data sets from the experimental video clips and pictures conducted by TA. Both qualitative and quantitative data must be included in your lab report.

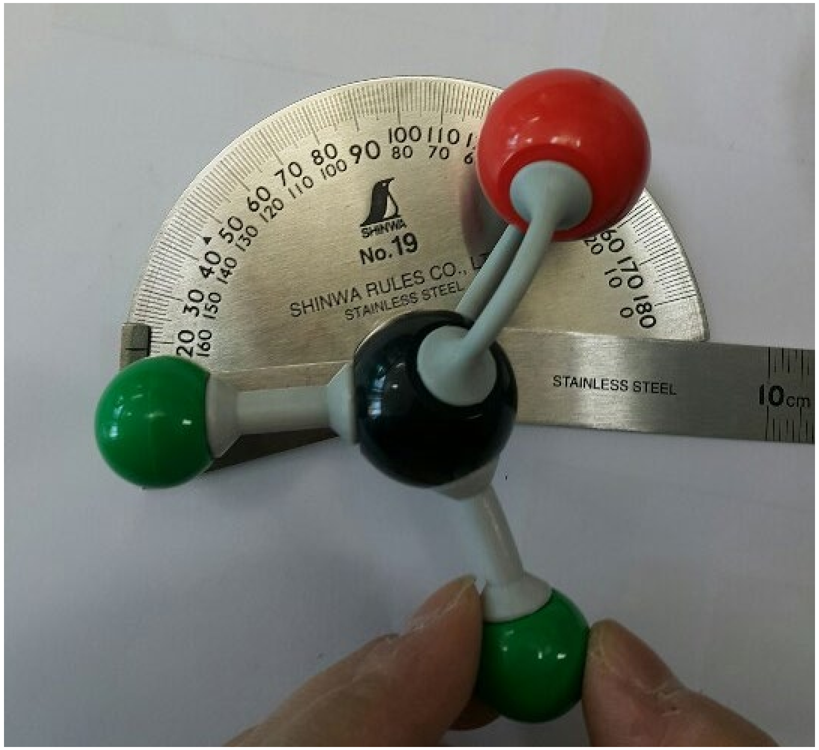
1. Molecular structure and bond angle

- How to make molecular structure model

1) CO_2

O—C—O : 180°

2) $COCl_2$

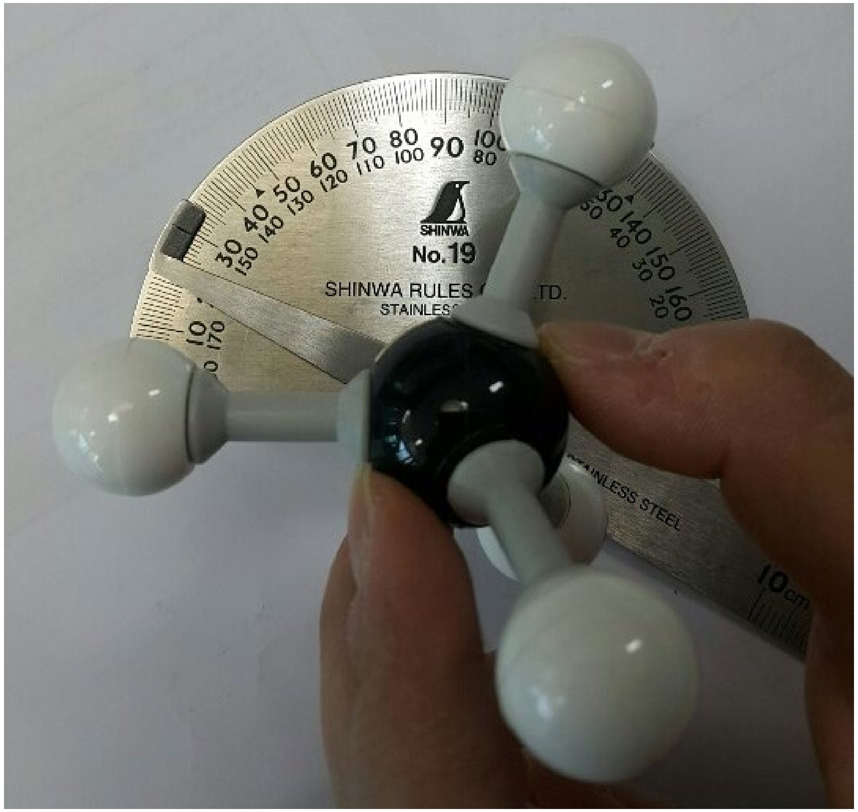


Cl—C—O : 125°

Cl—C—Cl : 109°

3) CH_4

H—C—H : 109°

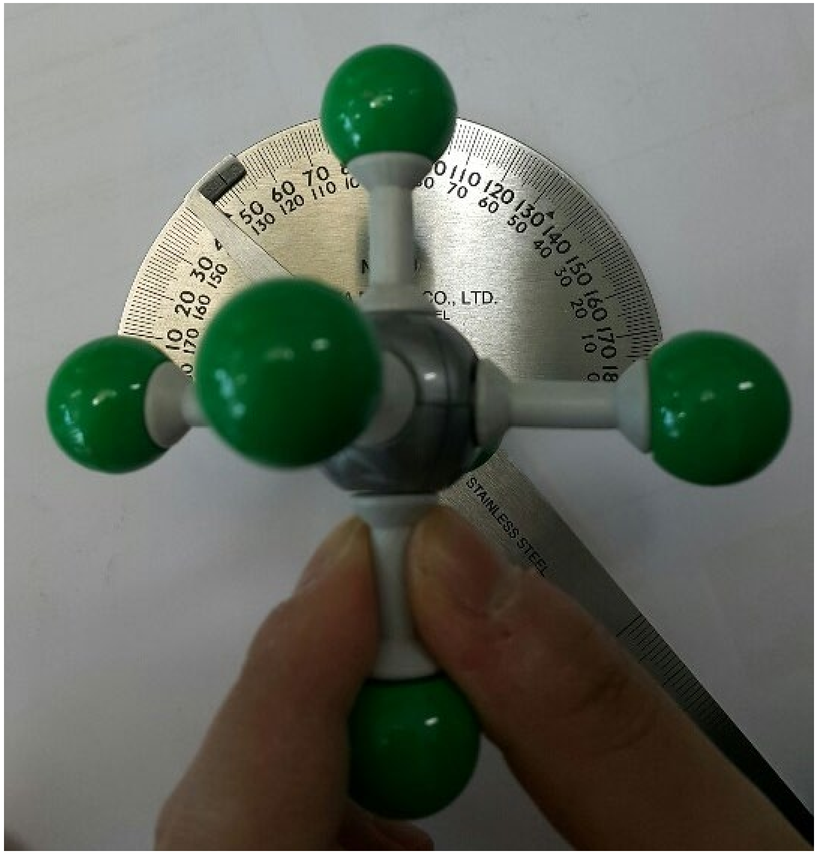


4) PCl_5

Cl—P—Cl (vertically) : 90°

Cl—P—Cl (horizontally) : 120°

5) SF_6



F—S—F (vertically)：90°

F—S—F (horizontally)：90°

REPORT SHEET

A. The Mercury Spectrum

TA's approval of the wavelength grid of the spectra on the color plate (back cover)

B. *The Spectra of Elements*

1. Spectrum number ( ) is the emission line spectrum for hydrogen on the color plate.
   What are the wavelengths and colors of the emission lines of the visible spectrum of hydrogen?

2*. **Identification of Spectra***

a. Spectrum number (   )
Intense lines in the spectrum: (   )nm; (   )nm; (   )nm; (   )nm; (   )nm; (   )nm;

b. Spectrum number (   )
Intense lines in the spectrum: (   )nm; (   )nm; (   )nm; (   )nm; (   )nm; (   )nm;

C. Match of Molecule with Infrared Spectrum

Complete the following table.

Molecule Assigned	*Atom-in-Bond Arrangements*	*Absorption Bands (cm^{-1})*	*Infrared spectrum Figure No.*

Observing Real Spectra through the spectroscope

Spectrum of Hydrogen

Intense lines in the spectrum: (   )nm; (   )nm; (   )nm; (   )nm; (   )nm; (   )nm;

Spectrum of Helium

Intense lines in the spectrum: (   )nm; (   )nm; (   )nm; (   )nm; (   )nm; (   )nm;

Spectrum of Neon

Intense lines in the spectrum: (   )nm; (   )nm; (   )nm; (   )nm; (   )nm; (   )nm;

Spectrum of Argon

Intense lines in the spectrum: (   )nm; (   )nm; (   )nm; (   )nm; (   )nm; (   )nm;

Observing real spectra *via* the fiber optic cable of the spectrometer with *Logger Pro* program

Spectrum of Hydrogen

Intense lines in the spectrum: ( )nm; ( )nm; ( )nm; ( )nm; ( )nm; ( )nm;

Spectrum of Helium

Intense lines in the spectrum: ( )nm; ( )nm; ( )nm; ( )nm; ( )nm; ( )nm;

Spectrum of Neon

Intense lines in the spectrum: ( )nm; ( )nm; ( )nm; ( )nm; ( )nm; ( )nm;

Spectrum of Argon

Intense lines in the spectrum: ( )nm; ( )nm; ( )nm; ( )nm; ( )nm; ( )nm;

D. Structure of Molecules and Molecular Ions

On a separate sheet of paper, set up the following table (with eight columns) for the molecules/molecular ions that are assigned to you/your group. The central atom of the molecule/molecular ion is italicized.

Molecular or Molecular Ions	*Lewis Structure*	*Valence Shell Electron Pairs*	*Bonding Electron Pairs*	*Nonbonding Electron Pairs*	*VSEPR Formula*	*Approx. Bond Angle*	*Geometric Shape*
1. CH_4							

D-1. *Complete the table (as outlined above) for the following molecular/molecular ions, all of which obey the Lewis octet rule. Complete 4 ones that are assigned by your TA.*

D-2. *Complete the table (as outlined above) for the following molecular/molecular ions, none of which obey the Lewis octet rule. Complete 5 molecular/molecular ions that are assigned by your TA.*

D-3. *Complete the table (as outlined above) for the following molecular/molecular ions. No adherence to the Lewis octet rule is indicated. Complete 5 molecular/molecular ions that are assigned by your TA.*

D-4. *Complete the table (as outlined above) for the following molecular/molecular ions. For molecules of molecular ions with two or more atoms considered as central atoms, consider each atom separately in the analysis according to Table D3.3. Complete 5 molecular/molecular ions that are assigned by your TA.*