SPECTROSCOPY

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Chemistry Lab III

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Every honest researcher I know admits he's just a professional amateur. He's doing whatever he's doing for the first time. That makes him an amateur. He has sense enough to know that he's going to have a lot of trouble, so that makes him a professional.

— Charles F. Kettering (1876-1958) (Holder of 186 patents)

ACKNOWLEDGEMENTS

I express my sincere gratitude to our instructors, Dr. K. S. Viswanathan and Dr. K. R. Shamasundar, for bringing the subject to life and helping us discover, in depth, the science behind the procedures.

I also thank Vivek Sagar (MS11017) for his contribution to this report as my lab-partner, who made the task of performing experiments immensely comfortable and productive at the same time.

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1

INTRODUCTION TO INFRA RED AND ULTRAVIOLET - VISIBLE SPECTROSCOPY

August 9, 2012

1.1 OBJECTIVE

To

1. understand the method of Fourier Transformed Infrared and Ultraviolet spectroscopy
2. understand the preparation substances for analysis
3. handle and operate the Spectroscopes provided

1.2 THEORY

1.2.1 *Basic Concept*

To find the presence of elements and/or compounds within a given substance, we can use spectroscopy techniques, specially when their concentrations are small and they satisfy certain requirements. The essential idea behind this measurement comes from the fact that elements/compounds absorb lights of certain frequencies to get to a higher energy state. These frequencies are mostly discrete as they correspond to quantized energy levels. This energy could be absorbed for, say, changing the vibrational energy (IR Spectroscopy) or for exciting an electron in the substance to a higher energy level (UV-vis Spectroscopy). We note here that these quantized energy levels are properties of individual substances and are, for most practical purposes, unique.

How much absorption, well, the limit comes from the sensitivity of the experimental setup and concentration of substance given.

For the analysis to be possible, the first condition is that the substance must *absorb* light incident to it. Granted this, we can obtain an absorption spectrum for the given substance, which behaves like a fingerprint of the substance. This can thus be used to not only identify the compound, but also to quantify it. For identification, in the simplest case, we simply need to observe the frequency corresponding to the peaks in the absorption spectrum and match it with the known/expected substance(s). Quantification harnesses a rather "obvious" law, termed *Beer-Lambert's Law*. In the simplest form, the law

quantifies the intuitive notion; higher the concentration of the analyte, higher is the absorption. The relation is given as

$$T = \frac{I}{I_0} = 10^{-\alpha l} = 10^{-\epsilon l c} \tag{1}$$

where I is intensity of incident light, I_0 is intensity of transmitted light, ϵ is molar absorbtivity, l is the optical path length, and c is molar concentration.

1.2.2 *Infra Red Spectroscopy*

Infra Red spectroscopy usually deals with energies of the level that cause change in vibrational energies. The wavelength ranges from 2.5μm to 25μm (4000cm^{-1} to 400cm^{-1}). These energies are characteristic for different bonds which is how, using the spectrum, we can identify (and quantify) the bonds present and thus the compound.

The way the spectroscope works for Infra Red, is rather interesting and ingenious. The setup uses a Michelson interferometer.

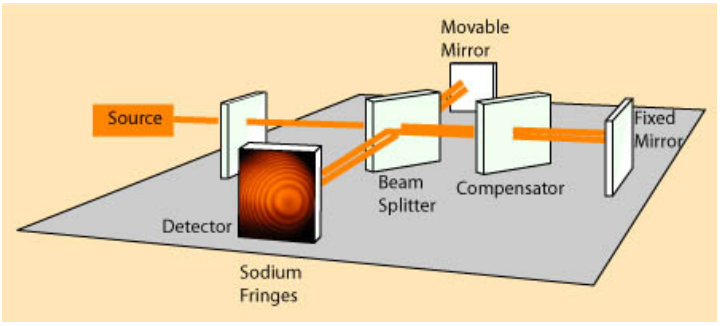


Figure 1: Michelson Interferometer [**?**]

Coherent means phase locked and Monochromatic means single frequency

Before complicating things, let us assume that the source of light is coherent and monochromatic. Now in the Figure 1, we assume the source of light to be the light transmitted through the sample to be analysed. Say the interference at the detector is, at the given configuration, constructive. If we move the movable mirror by $\lambda/4$, where λ is the wavelength of the light, then the detector will receive a dark, destructive interference. If we plot the intensity at the detector as a function of displacement of the moveable mirror, we will, in this case, receive a sine wave.

Note the fact that here, the measurement is simultaneous!

Now let us crank it up a notch. Let us consider the light to still be coherent, but not monochromatic. Let the source of light contain all the transmitted frequencies. Now if the intensity is plotted against the displacement of the moveable mirror, we will get a superposition of sine waves, and we already know how to decompose them to find individual frequencies using *Fourier Transformation*. This essentially

gives us the spectrum, with wavenumber (dimensions of one over distance) on one axis, and intensity on the other.

The source of infra-red light is a Silicon Carbide rod, that is heated to produce the desired radiations. The detector is capacitive, or so we were told.

How is SiC coherent?

1.2.3 *Ultraviolet-Visible Spectroscopy*

Here the wavelengths range from 200nm to 900nm. This range is often in the range of differences of electronic energy levels. The light source is a Tungsten-Neon lamp. In this technique, usually movable diffraction grating is used to split the transmitted light into its component frequencies, "one" of which goes to an intensity detector. Which component is detected depends on the orientation of the diffraction grating. Using this information, an intensity vs. frequency plot is generated which is the desired spectrum.

It must be noted here that the process of moving the orientation of the grating, requires time, which means that the measurement for various frequencies' intensities is not simultaneous, which in certain cases might not be suitable. One solution to such a problem is the use of multiple (arrayed) detectors. Yet it doesn't explain why a Michelson interferometer can't be used in this case. The answer to this comes from the fact that the wavelength in this case is much smaller, thereby complicating the task for preparing reflectors.

Wouldn't the ordinary mirrors for "visible light" suffice?

1.3 EXPERIMENTAL DETAILS

For this session, both IR and UV-visible spectroscopy techniques were demonstrated to us in groups of two. For IR spectroscopy, we used KBr as the base and Benzoic Acid as the analyte. For UV-vis, we used water as the base and $KMnO_4$ as the analyte.

1.3.1 *Infrared*

Procedure

The general procedure is as follows:

A. Weighed 100mg of KBr and ground it well.

B. Transferred it the dye (palletizing module).

C. Converted it into a pellet using the Hydraulic Press (about 8 tons of pressure).

D. Did IR spectroscopy.

E. Weighed 100mg of KBr and with it, 2mg of sample (in this case Benzoid Acid) and repeated from item B.

Details about the IR spectroscopy are as follows:

A. Ran the background to get rid of noise.

B. Did the accumulation 16 times (set the option).

C. Subtracted the first spectroscope from the second

Observation

Detected the carboxylic group (peaks for OH and $C = O$)

1.3.2 *UV-Vis*

Procedure

The general procedure is as follows:

A. Took a suitable amount of water.

B. Did UV-Vis spectroscopy.

C. Again took water and added a suitable amount of $KMnO_4$ and mixed it well.

D. Did UV-Vis spectroscopy.

Details about the UV-vis spectroscopy is corresponding to the previous section.

Observation

Peaks were detected in the range 520nm-550nm, complimentary to Purple as expected.

1.4 ACKNOWLEDGEMENTS

I thank the PhD students, Ms. Shruti and Ms. Shilpa, who helped us with the session and performed the experiment. They also walked us through the procedure for using the apparatus.

2

EXPERIMENT 1A: UV-VISIBLE SPECTROSCOPY

August 16, 2012

2.1 OBJECTIVE

To

1. prepare 10, 25, 50 and 75 ppm solutions of Benzoic Acid in water
2. use one of these for obtaining a spectrogram
3. use three of these for calibration and find the concentration of the third experimentally

2.2 THEORY

This section is the same as and has been covered in the previous experiment.
A few simple relations must be stated however, for clarity. Transmissivity or Transmission (T) is related to observables by Equation 2, where I is intensity of the light transmitted, I_0 is intensity of incident light, ϵ is extinction coefficient, l is the path length and c is concentration of the solution.
Relation between Absorbance (A) and intensity of light is as given by Equation 3. Clearly, A has a linear relation with ϵ as given by Equation 4 and we'll use this very relation to find the concentration of the 'unknown' sample.

$$T = \frac{I}{I_0} = 10^{-\epsilon l c} \tag{2}$$

$$A = -\log 10(\frac{I}{I_0}) \tag{3}$$

$$A = \epsilon l c \tag{4}$$

2.3 PROCEDURE

1. First calculated the mass of Benzoic Acid required for making a 25mL a 250 ppm solution in water, to be *6.25 mg*.

Just in case, $1ppm = 1uL/mL$

Mass of salt	0.0066	g
Mass of paper	0.0001	g
Mass of Benzoic Acid	6.5	mg
Concentration of Benzoid Acid Used	$\frac{6500}{25} = 260$	ppm

Table 1: For the Stock Solution of Benzoic Acid

10 ppm	$\frac{50}{260} = 0.192$	mL
25 ppm	$\frac{125}{260} = 0.480$	mL
10 ppm	$\frac{250}{260} = 0.961$	mL
10 ppm	$\frac{50}{375} = 1.442$	mL

Table 2: For varying concentrations of Benzoic Acid Solution

Used the upper meniscus consistently *for volume measurements*

But does that mean it wouldn't affect the result?

2. Weighed roughly the calculated amount of Benzoic Acid and transferred it to a volumetric flask of 25mL, and made the volume 25mL. This solution is henceforth referred to as the stock solution.
3. Calculated the volume of the stock solution required to prepare 10, 25, 50 and 75 ppm, 5 mL Benzoic Acid solutions.
4. Using a graduated pipette, measured the precise volume in accordance with the calculations and transferred it to a 5mL volumetric flask, and filled it to 5mL of water. Repeated this step for all four concentrations and labelled the flasks accordingly.
5. Calibrated the spectroscope with water first to suppress noise, if any.
6. Used one of the concentrations to generate a spectrogram.
7. Identified the maximum wavelength for use in Beer-Lambert law.
8. Used three of the concentrations to calibrate and fourth as an unknown, using the spectroscope.
9. Printed the spectrogram and noted the observations off of the screen for the known and unknown concentrations.

2.4 CALCULATIONS AND MEASUREMENTS

Refer to Table 1 for the stock solution and to Table 2 for the variants.

WAVELENGTH (λ)	ABSORBANCE
544.00nm	1.710
524.00nm	1.915

Table 3: Wavelengths Absorbed

CONCENTRATION (c)	ABSORBANCE
75ppm	1.902
50ppm	0.971
10ppm	0.237

Table 4: Absorption for various Concentrations

2.5 SPECTROSCOPIC OBSERVATIONS AND ANALYSIS

The maximum wavelength (λ_{max}) was found to be 524.00nm. Refer to Table 3. The Absorbance (A) for various concentration is given in Table 4

Absorbance of 'unknown' sample (25 ppm): 0.489

In accordance with the application, the best fit for the three points was not linear and the concentration of the unknown sample was calculated to be 30.0720 ppm which amounts to a 20% error.
In accordance with least square straight line fit, we get the slope as 0.0249395 $\pm$ 20.34 % but the intercept as -0.0856124 $\pm$ 310.2%. In accordance with these numbers, the concentration works out to be 16.174 ppm, which is 35% off. Refer to Figure 2 for details.

Expected accuracy is 2 – 3%

2.6 DISCUSSION

The accuracy of this experiment, as told by our instructor, is expected to be less than 3%. Since we clearly failed at achieving that number, we analyse in this section, what could've caused the enormous error.

The error could be caused by making errors in any of the following processes

1. Weighing
2. Volume measurement
    a) Pipetting
    b) Filling the Volumetric Flask

Despite taking sufficient care, even if one of the steps mentioned above go wrong, for even one of the samples, since the number of samples for calibration is just three, the entire experiment can, and in this case, did go wrong.

Thus for ensuring such errors do *not* crop up in the future, we can attempt the following

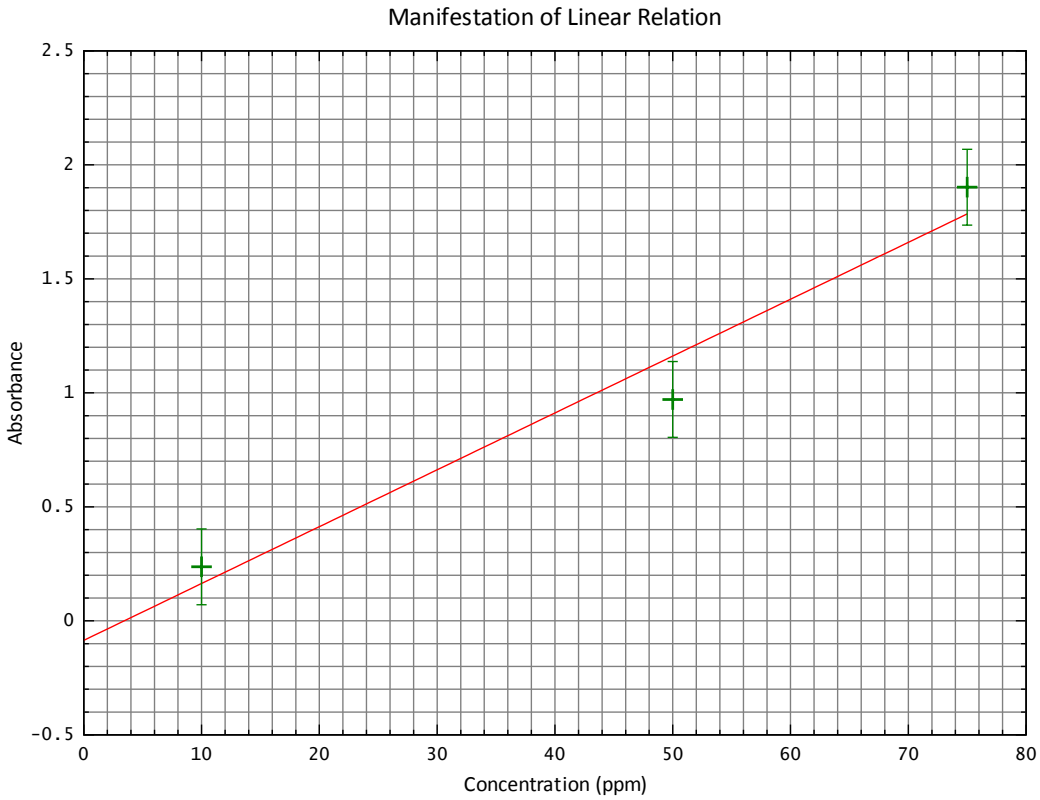
1. Weighing:
    a) Put the paper on the weighing scale and tare it
    b) Add the required amount of substance ensuring nothing gets wet
    c) Keep the container, viz. Volumetric Flask, with accessories, viz. Funnel etc. near the setup
    d) After transferring the contents, weigh the paper again to ensure everything got transferred
2. Volume Measurement
    a) Pipetting
        i. Read the upper meniscus consistently (for this experiment and in general for opaque solutions)
        ii. Use graduated pipettes that can provide sufficient precision
        iii. *Ensure the liquid doesn't stick on the walls*
    b) Filling Volumetric Flask
        i. Again, use the upper meniscus
        ii. Use a dropper to add towards the end to avoid accidentally adding extra volume

This is most likely what went wrong!

2.7 ACKNOWLEDGEMENTS

I thank Ms. Sumyra, the PhD student, who helped us with the use of the spectroscope. I also acknowledge the contribution of Ms. Athira J. Nair and Mr. Arpit Porwal for the performance of the experiment as team members.

Experiment: UV-visible Spectroscopy

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Slope of Best Fit Line          : +0.0249
Intercept of Best Fit Line      : -0.0856
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Performed on: August 16, 2012
Performed by: Athira, Arpit and Atul
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Figure 2: Least Square Fit

3

EXPERIMENT 1B: INFRA RED SPECTROSCOPY

August 23, 2012

3.1 OBJECTIVE

To study the spectroscopic characteristics of atleast three of the following compounds using an FTIR spectroscope.

1. Benzoic Acid
2. Naphthalene
3. Urea
4. Thio-Urea
5. Salicylic Acid

3.2 THEORY

This section is the same as and has been covered earlier in Chapter 1.

3.3 PROCEDURE

1. Weighed approximately 200mg of KBr and $2-4$mg of sample and ground it well using mortar and pestle. (Didn't use any sample for the first time, to use for baseline correction.)
2. Transferred the powdered contents into the palette maker and put it inside the hydraulic press
3. Applied about $6-8$ tons of pressure for $30-60$ seconds. Released the pressure after, and transferred the contents to the palette holder.
4. Placed the palette holder into the FTIR spectroscope and scanned it (in case of the first palette, background scanned it).

The process must be done quickly to avoid accumulation of moisture.

3.4 ANALYSIS

1. Urea - Table 5
2. Benzoic Acid - Table 6

$N-H$ stretching	3399.69	cm^{-1}
$C=O$ stretching	1669.64	cm^{-1}
$N-H$ bending	1625.39	cm^{-1}

Table 5: IR peaks for Urea

$C-H$ stretching	2832.14	cm^{-1}
$O-H$ stretching	2554.86	cm^{-1}
$C=O$ stretching	1694.66 and 1699.26	cm^{-1}

Table 6: IR peaks for Benzoic Acid

3. Thio Urea - Table 7
4. Naphthalene - Since there are no functional groups, according to L. G. Wade's *Organic Chemistry*, peaks are expected to be observed in the following ranges
   a) For Naphthalene in general:
      i. between 3000 and 3100
      ii. between 1570 and 1650

   Corresponding observations are given in Table 8

What does alpha mean structurally in this case?

   b) For *alpha* naphthalene, we have
      i. between 1375 and 1425
      ii. between 750 and 810

   Corresponding observations are given in Table 9
   c) For *beta* naphthalene, peaks are expected to be in the ranges:
      i. less than 700
      ii. between 800 and 860

   These were found to be absent.

3.5 DISCUSSION

For this experiment, even though we knew which compounds we're taking, after printing the spectrographs, we didn't label them to see if

NH_2 stretching	3368.14	cm^{-1}
NH_2 bending	1588.41	cm^{-1}
$C=S$ stretching	1092.87	cm^{-1}

Table 7: IR peaks for Thio-Urea

3061.97	cm^{-1}
3048.41	cm^{-1}
3029.35	cm^{-1}
1651.94	cm^{-1}
1634.25	cm^{-1}
1592.53	cm^{-1}

Table 8: IR peaks for Naphthalene

1383.98	cm^{-1}
782.47	cm^{-1}

Table 9: IR peaks for *alpha* Naphthalene

they could be identified by matching them with their expected peaks. This method does in fact work quite accurately and the fingerprint region was also observed to match, when compared with known spectrographs. I have still not been able to understand the meaning of alpha and beta structures of Naphthalene, which I so far believe to not exist. However, experimentally, in accordance with the literature, the structure seems to be alpha.

3.6 ACKNOWLEDGEMENTS

I acknowledge the contribution of Mr. Arpit Porwal for the performance of the experiment as a team member. I would also like to thank Mr. Biplob Nandy and Ms. Saumya Gupta for exchanging results to mutually provide scope for wider analysis.
I am grateful to Mr. Arjit Kant Gupta who helped me with the analysis and confirmation of the results by sharing his spectrographs of known compounds.
I also thank L. G. Wade for the book “Organic Chemistry” which was used to look up the expected IR peaks in the compounds analysed.

4

EXPERIMENT 2A: JOB'S METHOD OF CONTINUOUS VARIATION (UV-VIS)

August 30, 2012

4.1 OBJECTIVE

To find the reaction stoichiometry of the Fe^{3+}—Salicylic complex using Job's method of continuous variation.

4.2 THEORY

The idea is fairly simple. We analyse a compound which is formed by a combination of two reactant substances. The only requirement is that we should know of some way using which we can quantify the compound, given a mixture consisting of the compound along with the residual reactant substances.

Here's what we do...:

1. Decide on a total number of moles you will initially take (of both the reactant substances combined)
2. Now take the reactant substances in various ratios, such that the total number of moles is as decided
3. For each ratio, find out the quantity of the compound obtained

...and why:

A little thought will make the entire procedure appear elegantly simple. In the various combinations, one of the reactants will always be a limiting reagent. However, the highest yield will be obtained in the case when the reactants are closest to the stoichiometric ratio of the compound. Thus, a plot of the concentration of the compound against that of one of the reactants will attain a maxima. The point at which the maxima is obtained, can be used to find the concentration of both reactants, whose ratio gives us the reaction stoichiometry, with respect to the reactants!

And just to state the obvious, as the title suggests, the technique we use for quantifying is UV Visible spectroscopy.

4.3 PROCEDURE

As always, when practically performing an experiment, we have a few extra details to take care of.

Fe^{3+} SOLUTION'S VOLUME (mL)	SALICYLIC ACID'S VOLUME (mL)
0.5	4.5
2.0	3.0
2.5	2.5
3.0	2.0
4.5	0.5

Table 10: Concentrations for Job's Method

1. Make a 0.001M, 25mL solution of Iron Nitrate, $Fe(NO_3)_3$.
   a) The Molar Mass was given to be 404g.
   b) Thus, for 25mL we need 10.0mg.
2. Make a 0.001M, 25mL solution of Salicylic Acid
   a) The Molar Mass was given to be 138.12g
   b) Thus, for 25mL, we need 3.5mg.

Since the molarity of both solutions, is the same, we can use volume as a measure of number of moles.

3. We use 10mL as the total volume.
4. We used the volumes given in Table 10, of the reactants from the 0.001M solutions prepared, for creating 5mL solutions and marked the volumetric flasks with the corresponding concentrations.
   a) Used an appropriate graduated pipette for measuring the volumes
   b) Used the pipette for measuring one of the reactants only, and filled the volumetric flask with the other reactant using a dropper, to 5mL using the mark on the flask. This was done to avoid errors.
   c) Each of the flasks were ensured to be dry.
5. Recorded the spectrum of one of the samples and found the peak corresponding to the compound we're interested in, viz. Fe^{3+}—Salicylate Complex.
6. Recorded the absorbance of the frequency determined in the previous step for all concentrations.

4.4 OBSERVATIONS AND ANALYSIS

1. Characteristic wavelength was found to be 518.00.
2. Intensities for varying concentrations of Fe^{3+} have been listed in Table 11.

Fe^{3+} SOLUTION'S VOLUME (mL)	ABSORBANCE
0.5	0.350
2.0	0.682
2.5	0.801
3.0	0.740
4.5	0.282

Table 11: Absorbance for Varying Concentrations

3. From Figure 3, it's clear that the maximum concentration is obtained for the *stoichiometric ratio of 1:1*, as the maxima is obtained very close to 2.5mL, which represents equal concentrations of both reactants.

How do you know the graph will be linear on both sides?

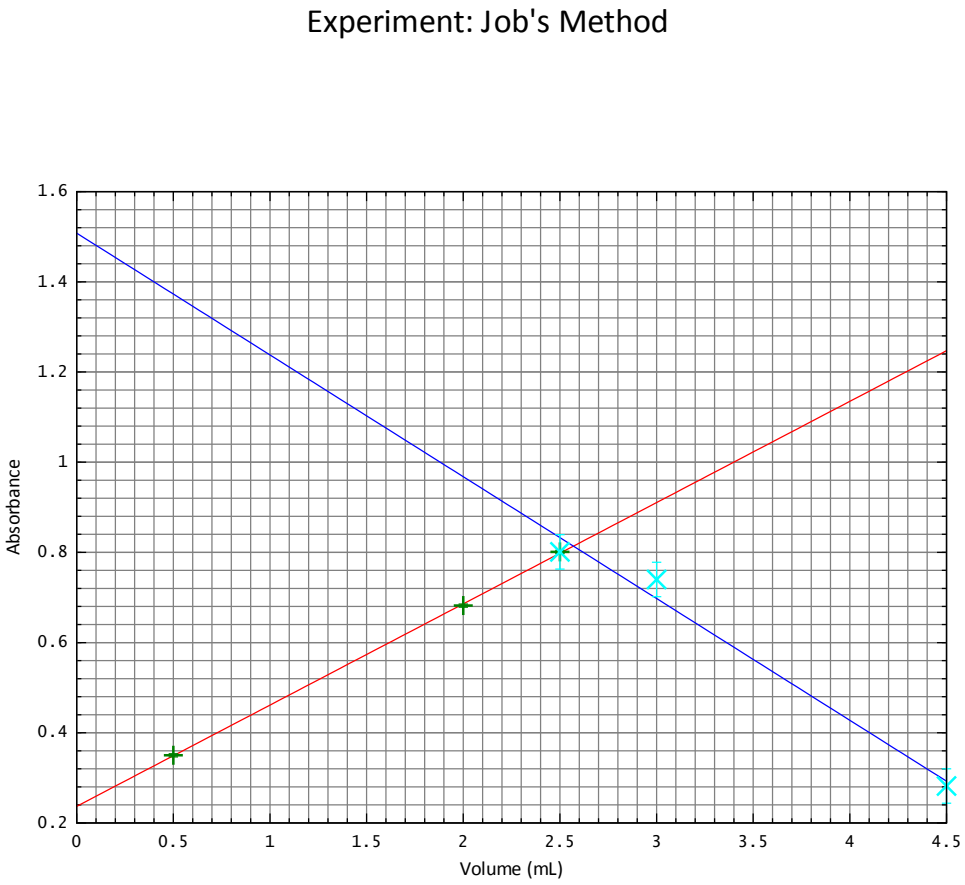
[Product] ∝ [Limiting Reactant]

4.5 DISCUSSION

Fortunately or unfortunately, the experiment returned expected results and therefore there's no real requirement of a discussion. However, it must be mentioned that by just looking at the colour of the solution, the search can be narrowed to a great extend, that is, cases in which the product and/or reactants are coloured.

4.6 ACKNOWLEDGEMENTS

I acknowledge the contribution of Mr. Arpit Porwal and Ms. Athira Nair, for the performance of the experiment as team members. I would also like to thank Ms. Ritu Roy Chowdhury for discussing the expected graph, which helped me understand the experiment better.



Slope of Best Fit Line 1 : +0.2245
Standard Deviation 1 : +0.0035
Slope of Best Fit Line 2 : -0.2701
Standard Deviation 2 : +0.0381

Performed on: September 3, 2012
Performed by: Athira, Arpit and Atul

Figure 3

5

EXPERIMENT 2B: INFRA RED SPECTROSCOPY

September 13, 2012

5.1 OBJECTIVE

To study the spectroscopic characteristics of the following compounds using an ATR-FTIR spectroscope.

1. Polymers
    a) CD Cover
    b) Teflon
2. Solids
    a) Benzaldehyde
    b) Phenol
3. Liquids
    a) Benzoic Acid
    b) Urea

5.2 THEORY

This FTIR part of this section is the same as and has been covered earlier in Chapter 1. What makes this section special is the word ATR, which stands for Attenuated Total (internal) Reflection. Total internal reflection occurs, as we know, when light travelling in an optically denser medium, is incident on a rarer surface, with an angle greater than some 'critical' value, then the light is completely reflected. What has this got to do with spectroscopy, well as it turns out, light when is reflected as aforesaid, it penetrates to about 20 micrometers into the rarer surface. Here's where the fun begins. As the wavelength approaches the absorption range of the rarer substance, the reflected ray undergoes higher attenuation. And that does it! We harness this very property to 'scan' through different wavelengths and find the spectrum of the substance.
Experimentally, we use a crystal of a substance of very high refractive index, typically Thallium Bromide/Iodide and let the incident light from the FTIR, enter the crystal as shown in Figure 4, hit the rarer surface multiple times to accumulate attenuation and then allow this light ray to pass through the same FTIR detector. (In our case however, we used $ZnSe$.)

$C-H$ stretching	2917.68	cm^{-1}
$C-H$ bending	1376.45	cm^{-1}

Table 12: IR peaks for a CD Cover

What is the immediate advantage? Aside from the ability to measure spectra of opaque substances, we can use this technique to find spectra of fluids as well. Further, since this is a surface technique, situations where bulk is not of interest, this technique comes to the rescue.

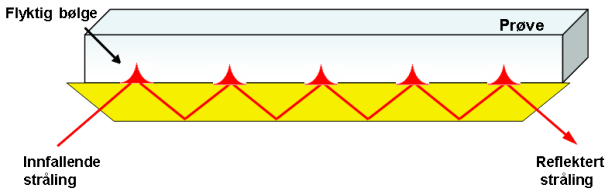


Figure 4

5.3 PROCEDURE

The procedure for ATR is rather straightforward and easily done, unlike the palette preparation requirement in the conventional FTIR.

1. Method for Liquids:
   a) Cleaned the $ZnSe$ tray with CCl_4 and wiped off its excess
   b) Liquid samples were then loaded and the tray covered
2. Method for Solids:
   a) Powdered the solid finely using Pestle and Mortar and spread evenly on the tray.
   b) The tray was placed and tightened using a screw firmly.
3. For Films and Plastics:
   a) An extra apparatus provided with the ATR crystal was used.

5.4 ANALYSIS

1. CD Cover - Table 12
2. Teflon - Table 13
3. Benzaldehyde - Table 14

$C-F$ stretching	1206.97 and 1150.19	cm^{-1}

Table 13: IR peaks for Teflon

$O-H$ due to presence of Benzoic Acid	3059.5	cm^{-1}
$H-C=O$ stretch	2738.04	cm^{-1}
Carbonyl $C=O$ stretch	1583.77	cm^{-1}

Table 14: IR peaks for Benzaldehyde

4. Phenol - Table 15
5. Benzoic Acid - Table 16
6. Urea - Table 17

5.5 REFERENCE

1. Modern Spectroscopy, Fourth Edition, by J. Michael Hollas
2. http://en.wikipedia.org/wiki/Total_internal_reflection
3. Lecture Notes from CHM211 and CHM201, 2012-13
4. Organic Chemistry by L. G. Wade

5.6 ACKNOWLEDGEMENTS

I acknowledge the contribution of Mr. Arpit Porwal and Ms. Athira Nair, for the performance of the experiment as team members. I specially thank Mr. Arpit Porwal for assisting me with the print outs.

$C-H$ stretch	3049.49	cm^{-1}
$O-H$ stretch	3324.03	cm^{-1}
$C-C$ multiple bond stretching	$1450-1600$	cm^{-1}
$C-O$ stretching vibration	1367.17	cm^{-1}
$O-H$ bending	1222.87	cm^{-1}
$C-H$ bending	748.40	cm^{-1}

Table 15: IR peaks for Phenol

$C-H$ stretch	2822.7	cm^{-1}
$O-H$ stretch	2554.7	cm^{-1}
$C=O$ stretch	1688	cm^{-1}

Table 16: IR peaks for Benzoic Acid

$C=O$ stretch	1598.07	cm^{-1}
$C-N$ stretch	1460	cm^{-1}

Table 17: IR peaks for Urea

6

QUEST FOR SYMMETRY: IR VS. RAMAN SPECTROSCOPY

September 20, 2012

6.1 OBJECTIVE

To gain an insight into the structure of the following chemicals by analysing their Raman and IR spectra:

1. Pthalic Acid
2. Pthalic Anhydrate
3. Napthalene

6.2 THEORY

6.2.1 *Raman Spectroscopy*

Idea Behind it

What's so cool about Raman Spectroscopy? Well the fact that it uses scattering of light instead of absorption. This has a remarkable consequence. Let's start from the beginning. There are various numbers of molecules in any given quantum state, frequency of which depends on Temperature amongst various other factors (ambiguity is necessary for generality). Now, when an incident beam, of a given frequency, say ν_i, strikes a molecule, it is excited from whichever allowed quantum state it was in, to an energy state, called a *virtual state*, (which in this case is higher in energy). Now the speciality of a virtual state is that it can exist anywhere in the energy scale, however its lifetime tends to zero. They are not 'physical', whatever that's supposed to mean! So immediately after jumping to the virtual state, the molecule drops to an allowed energy state, where by allowed, I mean the states allowed by the selection rules.

Stokes and Anti-Stokes

Now say the energy difference between the two energy states, viz. final minus initial, is represented by $\nu_{absorbed}$. Energy of the scattered photon is given by

$$\nu_s = \nu_i - \nu_{absorbed} \tag{5}$$

It's then obvious to note that if $\nu_{absorbed}$ is positive, then the scattered photon will have a lower energy, and when $\nu_{absorbed}$ is negative, the energy is higher. But here's something which is not immediately obvious. When the resultant energy is lower, corresponding spectroscopic lines are called stokes lines and in vibrational-raman spectroscopy, they are brighter than their counterpart, the anti-stokes lines (definition of which is implied). However in case of rotational-raman, the intensities of both the anti-stokes and stokes lines are comparable.

Vibrational Raman Spectra

Let us lose the generality and talk about, Vibrational-Raman Spectroscopy. We can borrow the expression for energy levels (expressed in wavenumbers) from the prior discussions as:

$$\epsilon = \overline{\omega}(\nu + \frac{1}{2}) - \overline{\omega}_e x_e (\nu + \frac{1}{2})^2 \text{ cm}^{-1} \tag{6}$$

where the symbols have the usual meanings. The selection rule for this reads

$$\Delta\nu = 0, \pm 1, \pm 2, ... \tag{7}$$

What about the overtones then?

Transitions from $\nu = 0 \Rightarrow \nu = 1$ are fundamental and are clearly visible on the spectra due to high population of molecules in the state defined by $\nu = 0$. Transitions from $\nu = 1 \Rightarrow \nu = 2$ (Hot Bands) and $\nu = 0 \Rightarrow \nu = 2$ (overtones) are not observable in most cases. This can be attributed to low populations. Thus, since $\nu_{absorbed} = \nu_{fundamental}$, we can expect a spectra determined by Equation 5, with Stoke's lines showing up with a frequency less than ν_i and Anti-Stokes' mirrored about ν_i with a much lower intensity.

What does Raman 'see'?

Note polarisability is distinct from the dipole moment IR is sensitive to

As Raman spectroscopy is essentially based on scattering of light, whether the scattered light will be scattered 'elastically' or 'inelastically' would depend on whether change in molecular configuration results in a change in polarisability. This is best understood by considering a two simple examples.

1. Consider a Carbon Dioxide molecule and imagine it executing a symmetric stretch. Now the polarisability of the molecule will increase as the oxygen atoms move away from the equilibrium position. Contrary to this, the polarisability will drop when the oxygen atoms congest with the carbon. This essentially means if we plot polarisability, α against displacement from equilibrium position of the oxygen atom, ζ, the slope at $\zeta = 0$ is positive. Note this. Also note, the dipole moment doesn't change in this case.

2. Again consider a Carbon Dioxide molecule but this time, imagine its bending, with the Carbon in the centre and Oxygens oscillating up and down. In this case, its easy to observe that the polarisability will be least when the molecule is its equilibrium condition. Thus, in this case, slope of the α vs ζ graph, at $\zeta = 0$ will be zero. Also observe, the dipole moment changes as a function of ζ.

Wait, what is ζ supposed to be here?

It's the angle of Carbon Oxygen bond from the equilibrium position

Thus, Raman will 'see', in this example, only the first, viz. Symmetric Stretch, which doesn't show up in IR. And as you would've guessed by now, IR will 'see' the second, but Raman won't.

Consequences of Symmetry

Clearly symmetry has a major role to play in deciding what characteristic of the molecule shows up where. Discussing that at length is not in the scope of this report. Yet the following must be stated, for the analysis relies on understanding of the principle.

"*Rule of mutual exclusion* [1]: If a molecule has a *centre of symmetry*, then Raman active vibrations are infra-red inactive and vice versa. If there is no centre of symmetry then some (but not necessarily all) vibrations may be both Raman and infra-red active."

The converse of the statement is also true, viz. if the molecule shows no common lines in Raman and infra-red, then the molecule has a centre of symmetry (although concluding this might be tricky as the peaks can be diminishingly small).

6.3 PROCEDURE

For ATR, please refer to Chapter 5. For Raman, we performed two calibration follow these simple steps

1. The sample was taken in a glass slide
2. The glass slide was placed inside the Raman apparatus
3. Using the attached computer, the point for analysis was fixed
4. Spectrum was recorded

6.4 OBSERVATIONS

1. Pthalic Acid - For Raman, refer to Table 18 and for IR, refer to Table 19
2. Pthalic Anhydride - For Raman, refer to Table 20 and for IR, refer to Table 21

1 Fundamentals of Molecular Spectroscopy, 4^{th} Edition, Banwell and McCash

PHENOMENON	EXPECTED (cm^{-1})	OBSERVED (cm^{-1})
$C-H$ Out of plane bending	$690-900$	773
$C-O$ stretching	$1000-1300$	1047, 1177
$C=C$ stretching	$1475-1600$	1644
$C-H$ stretching	$3050-3150$	3092

Table 18: Pthalic Acid Raman Spectra

PHENOMENON	EXPECTED (cm^{-1})	OBSERVED (cm^{-1})
$C-H$ Out of plane bending	$690-900$	794.16, 739.58
$C-O$ stretching	$1000-1300$	11071.27, 1279.40
$C=C$ stretching	$1475-1600$	(aprox) 1530
$C-H$ stretching (overlaps with $O-H$)	$2400-3400$	2871.26

Table 19: Pthalic Acid IR Spectra

PHENOMENON	EXPECTED (cm^{-1})	OBSERVED (cm^{-1})
$C-H$ Out of plane bending	$690-900$	773, 737
$C-O$ stretching	$1000-1300$	1047, 1009 (only strong listed)
$C=C$ stretching	$1475-1600$	1600
$C-H$ stretching	$3050-3150$	3081
$C=O$ stretching	$1800-1830$,$1740-1775$	1848, 1766

Table 20: Pthalic Anydride Raman Spectra

PHENOMENON	EXPECTED (cm^{-1})	OBSERVED (cm^{-1})
C – H Out of plane bending	690 – 900	712
C – O stretching	1000 – 1300	1282
C = C stretching	1475 – 1600	(absent)
C – H stretching	3050 – 3150	3023 (slightly out)
C = O stretching	1800 – 1830,1740 – 1775	1820, 1764

Table 21: Pthalic Anydride IR Spectra

PHENOMENON	EXPECTED (cm^{-1})	OBSERVED (cm^{-1})
C – H bend	690 – 900	764
C = C stretch	1475 – 1600	1578
C = H stretch	3050 – 3150	3062

Table 22: Napthalene Raman Spectra

3. Napthalene - For Raman, refer to Table 22 and for IR, refer to Table 23

6.5 CONCLUSIONS

1. Acid and Anhydride
   a) The energy levels split in case of Anhydride because the C – OH get very close compared to their position in the Acid. The split can be attributed to in phase and out of phase motion. Further the motions get coupled in case of Anhydride.
   b) The peaks obtained were not complimentary, therefore we could conclude both molecules lack a centre of symmetry.
2. Naphthalene
   a) It should be silent in IR, however we observed peaks. Reason is that the region is not isotropic. The crystal structure distorts the molecule and perturbations are induced, which

This however can be asserted confidently only if neighbouring molecules don't disturb

PHENOMENON	EXPECTED (cm^{-1})	OBSERVED (cm^{-1})
C – H bend	690 – 900	776
C = C stretch	1475 – 1600	1505, 1590
C = H stretch	3050 – 3150	3049

Table 23: Napthalene IR Spectra

makes the molecule visible in IR, despite having a centre of symmetry.

6.6 ACKNOWLEDGEMENTS

I thank our PhD student guide, Ms. Shruti, who helped us with the performance of the Raman experiments. I thank Ritu Roy Chaudhury, Prashansa Gupta, Athira T John and Vivek Sagar for discussing their analysis.

6.7 REFERENCES

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7

ALCOHOL ESTIMATION

September 27, 2012

7.1 OBJECTIVE

To estimate the level of alcohol in a given solution (in water).

7.2 THEORY

7.2.1 *Idea*

The objective is to measure the concentration of alcohol. So we first think of the methods by which alcohol can be recognized. One such method would be to oxidise the alcohol using a reagent that changes colour. This way we can use the UV-Vis spectrometer to quantify the concentration of the said reagent. One reagent that fits the bill is Potassium Dichromate ($K_2Cr_2O_7$).

7.2.2 *Details*

We want Potassium Dichromate in its +6 oxidation state. For this, it must have a sufficiently acidic medium for which H_2SO_4 is used. Further, $AgNO_3$ is required for speeding up the reaction. The basic reaction is give in Figure 5.

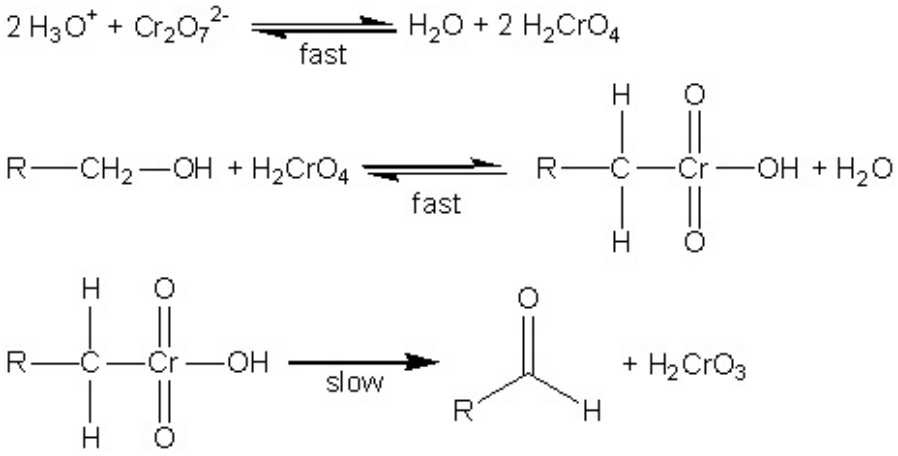

Figure 5

7.3 PROCEDURE

A 50% (v/v) solution of H_2SO_4 was provided as 'Solution A'. A 200 µL/L solution of Ethanol was provided as 'Solution B'. The following steps were then followed:

1. Weighed 20 mg of $K_2Cr_2O_7$ and 25 mg of $AgNO_3$ into a volumetric flask of 50 mL using a funnel. Solution A was used to make the volume to 50 mL. The solution thus obtained was labelled 'Solution C'.

Even if the mass is not very precise, it doesn't matter so long as the same volume of the solution is used, since the important factor here is change in concentration

2. Pipetted the following volumes in four separate 10 mL volumetric flasks.
   a) 7.5 mL of solution C and 0.5 mL of solution B
   b) 7.5 mL of solution C and 1.0 mL of solution B
   c) 7.5 mL of solution C and 1.5 mL of solution B
   d) 7.5 mL of solution C and 2.0 mL of solution B

   And in another 10 mL flask, pipetted 7.5 mL of solution C and a volume unknown to other team members between 0.5 to 2.0 mL of solution B.
   The volume was filled up using Solution A.

Take care to not accidentally include the extra 'unmarked' volume while pipetting

3. Measured the absorbance as a function of alcohol concentration and estimated the concentration of unknown alcohol sample given.

7.4 OBSERVATIONS

Our experiment failed since the trend was unacceptable. We will repeat the experiment in the make-up lab, as was advised by our Professor.

7.5 ACKNOWLEDGEMENTS

I thank our PhD student guide, Ms. Shruti, who helped us with the performance of the UV-Vis Spectroscopy. I also acknowledge the contribution of my team members, Ms. Athira and Mr. Arpit, for performance of the experiment.

7.6 REFERENCES

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Part II

THE SHOWCASE

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COLOPHON

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