

Experiment 8. Raman Spectroscopy

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Abstract.

Raman spectroscopy enables rapid, non-destructive measurements, and the technique is a promising tool for on-line process monitoring and analysis. Our objective is to analyze the Raman spectra for liquid substances such as Ethanol, Buthanol, Metanol, and Propanol and discuss our results based on literature. Intensity peaks were found at around 900 cm^{-1} and 1400 cm^{-1} for Ethanol, 1050 cm^{-1} and 1500 cm^{-1} for Metanol, 800 cm^{-1} for Buthanol, and 800 cm^{-1} for Propanol.

I. INTRODUCTION

Raman spectroscopy enables rapid, non-destructive measurements, and the technique is a promising tool for on-line process monitoring and analysis. Thus such a technique is studied in universities on the undergraduate level and used in research programmes[1].

Inelastic light scattering is known as Raman radiation and was first documented by Raman and Krishnan in 1928 [2]. Substances irradiated with monochromatic light scatter energy mostly by radiation of the incident frequency, this is known as Rayleigh scattering. However a small quantity (0.0001%) of photons with shifted frequency is observed. This shift may result in Stokes (scattered from molecular centres) or anti-Stokes scattering where Stokes photons have less energy than before the interaction and anti-Stokes photons have a greater energy than those of the exciting radiation[3].

Many factors determine the wavenumber shift and intensity at which each functional group's peak or peaks will be found. Some functional groups are more Raman active than others, and will produce more intense peaks. For example, the C=O bond characteristic of aldehydes is not strongly Raman-active. Alternatively, the aromatic ring breathing mode in toluene is strongly Raman-active. By assigning all of the functional groups in a Raman spectrum, the identity of a substance can be accurately determined.

Two major technologies are used to collect the Raman spectra: dispersive Raman; and, Fourier transform Raman (FT-Raman). The differences between both technologies are the laser that is used and the way the Raman scattering is detected and analysed. Dispersive Raman can use different wavelength incident lasers and is used primarily in aqueous samples, FT-Raman uses infrared wavelength light and provides limited fluorescence [3].

For this experimental session, due to lack of equipment, the basic principles of dispersive Raman were studied and those of FT-Raman spectroscopy were left for investigation. Our objective is then to plot and analyze the Raman spectra for liquid substances such as Ethanol,

Buthanol, Metanol, and Propanol and cyclohexanone and discuss our results based on literature.

II. EXPERIMENTAL PROCEDURE

Samples containing butanol, cyclohexanone, ethanol, methanol, and propanol were provided by the lab instructor and were examined in equipment from the universities chemistry department.

With samples ready to be examined the power source of the laser beam was turned on and the software application was started and set up. After defining conditions of the experiment such as wavelength (785nm) and data collection span, measurements were started.

Final steps of our experimental procedure included rescaling of graphs and saving the data collected into text files. This process was repeated by every team for their respective samples.

III. RESULTS

The spreadsheets with the data collected in the experimental session were used to generate the following scatter plots that show Raman spectra.

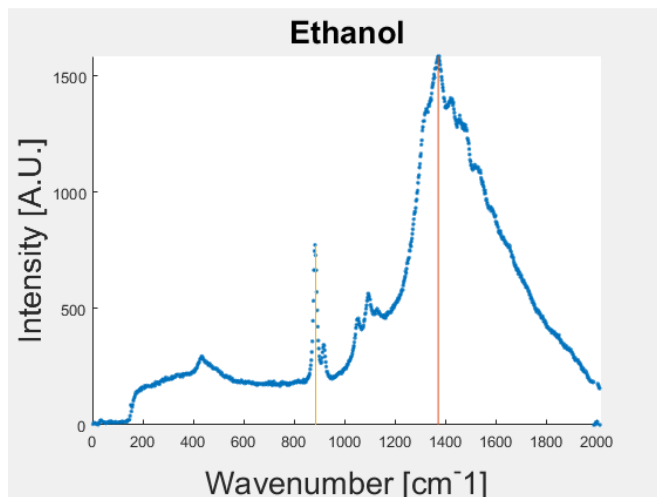


FIG. 1: Dispersive Raman spectra for Ethanol obtained using software and equipment provided by the university. Vertical lines are located at a) local maximum for the 800-950 range where CCO bend is expected [4] and b) global maximum.

For figures 1 through 4 we can observe that definition is better for those with higher intensity. This is because intensity is actually a repetition of counts of radiation detection. Thus, the greater the span of data collection the better the definition is and the more counts are detected.

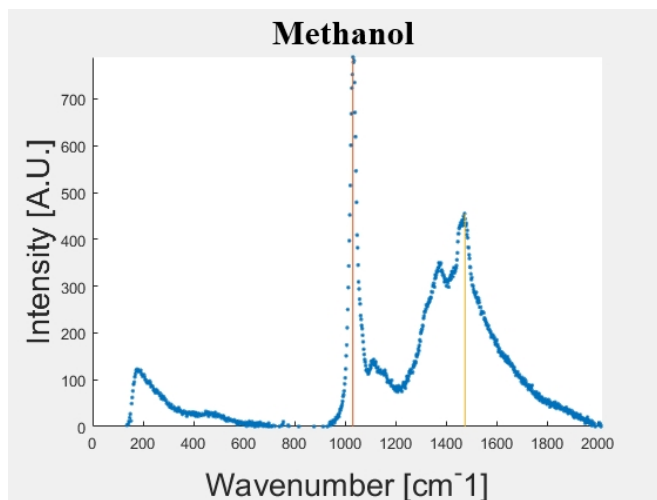


FIG. 2: Dispersive Raman spectra for metanol obtained using software and equipment provided by the university. Vertical lines are located at a) global maximum where CO stretch is expected [6] and b) local maximum for the 1400-1550 range where CH bend is expected [6].

In general peaks with several repetitions which account to a greater intensity are expected to be vibration modes. This is because the scattering of light is more common

for this specific wavenumbers.

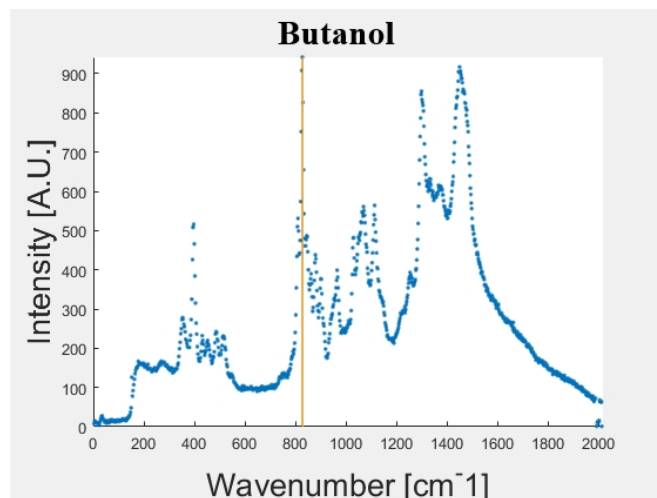


FIG. 3: Dispersive Raman spectra for Buthanol obtained using software and equipment provided by the university. Vertical lines are located at global maximum where a vibration mode is expected.

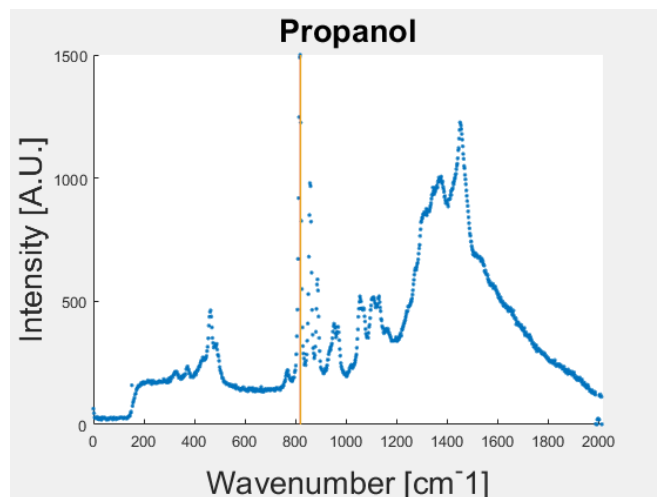


FIG. 4: Dispersive Raman spectra for Propanol obtained using software and equipment provided by the university. Vertical lines are located at global maximum where a vibration mode is expected.

It is important to mention as well that greater data collection spans would make peaks greater than the rest of the graph in proportion and this would result in more well defined peaks. The reason why the spans are not set to several seconds is the high possibility of damaging the samples and as well of causing a structural change in the sample spoiling the experiment.

IV. DISCUSSION OF RESULTS

As it can be appreciated in the previous section, in all the results presented there's a ever present "bulge" in the middle of every graph. This is a sort of "background" that pollutes the results. The team believes this may have to do with fluorescence or any other type of scattering that occurs simultaneously with the glass or some impurity within the substances or their containers (e.g. poorly washed).

Peaks around the 800-1100 cm^{-1} range for methanol, ethanol, butanol and propanol were found. These type of peaks correspond to one of the alcohol functional group vibrational modes. A functional group is a portion of a molecule that is a recognizable/classified, and that, depending on the type of bond that composes it, can be classified using this. In organic chemistry it is very common to see molecules comprised mainly of a carbon backbone with functional groups attached to the chain.[4]

Concerning methanol, according to the data tables compiled by Shimanouchi, peaks should be expected at shifts of 1464 (two modes), 1165, 1107 and 1033 cm^{-1} . Figure 2 shows very appreciable peaks at 1473 and 1031 cm^{-1} , with a smaller one at 1106 cm^{-1} and a very slight one 1157 cm^{-1} [6], showing great compliance. However, there are two unexpected peaks present at about 173 and 1372 shifts. These seem to reappear in all the other spectra presented.

Concerning butanol, Kipkemboi et al. measured frequency peaks at 1456 (strong), 1365 (weak), 1240 (medium), 1210 (medium), 1024 (weak), 915 (strong) and 752 cm^{-1} (very very strong). Figure 3 shows very strong peaks at 1450, 1299 and 827 cm^{-1} [7]. Other appreciable are 1366, 1300(?), 1254, 1215, 1113(?), 1069(?), 1029, 965(?), 836(?), 827, 397(?). As with the other figures, most of the stronger frequency peaks are readily visible. Weak ones find themselves mostly obscured by the background. Those marked with a "?" weren't mentioned by any of the references. Therefore they seem to be related to sample pollution.

A detailed table for the shifts to be expected from both ethanol and propanol couldn't be found. However, given that both substances are alcohols there are some characteristic vibrations in all of them (incl. methanol and butanol). Some of these include strong peaks inbetween 1410-1480 and 800-900 cm^{-1} [4], which can be readily appreciate in Figures 1-4.

V. CONCLUSION

During this experiment we reported Raman spectra for a group of primary alcohols and identified the char-

acteristic fingerprints (intensity peaks) that constitute them. In general, alcohol functional group peaks were detected around 800-1100 cm^{-1} for each of the samples. Stretch, deformation and wagging type of vibrations were detected more easily in bigger chain alcohols in various shift ranges according to tables found in literature [4]. Raman spectroscopy is a widely used technique since its applications and various "improvements" (such as SERS and TERS) have been proposed since its creation in 1925. All this variety illustrates the diverse nature of this technique and its extraordinary ability to solve many biological problems of interest. Applications range from drug discovery to, polymorph identification, real-time process monitoring, active pharmaceutical ingredients imaging and so on.

VI. REFERENCES

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