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Determination of "Octane" in Gasoline using Raman Spectroscopy

Purpose

This experiment illustrates the ability of Raman spectroscopy to determine the octane level of gasoline. The knocking characteristics in an engine are related to the vapor pressure of fuel, and in the past were controlled with isooctane. This is the origin of the term octane rating. Recently, aromatics compounds such as toluene have replaced the very expensive isooctane as an anti-knock additive.

Traditionally, a microphone was used to listen to a standard engine running on gasolines containing different concentrations of additives to determine the octane rating. This lab demonstrates the ability of Raman spectroscopy to determine the octane rating of gasoline. The lab also demonstrates and discusses the polarization properties of Raman spectroscopy.

References

1 Ferraro, John R.; Nakamoto, Kazuo. Introductory Raman Spectroscopy, Academic Press Inc: San Diego **1994**
2 Skoog, Douglas A.; Holler, James F.; Nieman, Timothy A. Principles of Instrumental Analysis 5th ed, Saunders College Publishing, **1998**
3 Cooper, John B.; Wise, Kent L.; Welch, William T.; Bledsoe, Roy R.; Sumner, Michael B. "Determination of Weight Percent Oxygen in Commercial Gasoline: A Comparison between FT-Raman, FT-IR, and Dispersive Near-IR Spectroscopies." *App. Spec.* Vol. 50, No. 4, **1996**, p. 917-921
4 Susanne Brunsgaard Hansen, Raman Spectroscopic Studies of Gasoline http://www.kemi.dtu.dk/~ajo/rolf/susoil.pdf

Apparatus

Advantage 200A Raman spectrometer and accessories
  1 mL glass vials
  Disposable glass pipettes

Chemicals

Gasoline (approximately 1 liter, collected from local gas station, note: not all modern refineries use toluene to boost their octane)

Theory

Raman measurements not only provide intensity and frequency information, but also can determine structural properties of molecules using the *depolarization ratio.* When a molecule is excited by plane-polarized light, the scattered radiation is polarized to various degrees depending on the type of vibration excited. The symmetry of a particular molecule may be determined through the polarization properties of the Raman spectrum.

Figure 1 shows the resulting induced dipole from a molecule's interaction with perpendicular and parallel-polarized light. If you were to observe the scattered radiation orthogonal from the direction of excitation, the Raman peaks that are observed are those from an induced dipole aligned perpendicular to the direction of observation, (Figure 1A). The rule of thumb for radiation emitted by a dipole is that it radiates orthogonal to the direction of the dipole. In the case of perpendicular excitation it is emitted along the axis of observation. When the light is rotated and parallel-polarized light irradiates the sample, scattered radiation from the induced dipole will produce a node along the direction of observation. This greatly diminishes all totally symmetric vibrations and the Raman spectrum produced is that of Figure 1B. The Advantage 200A is designed to accentuate the polarization differences in a sample. To do this it subtracts spectrum A from spectrum B to provide spectrum C. The Advantage spectrum is easy to interpret, negative peaks are totally symmetric modes and positive peaks are non-totally symmetric.

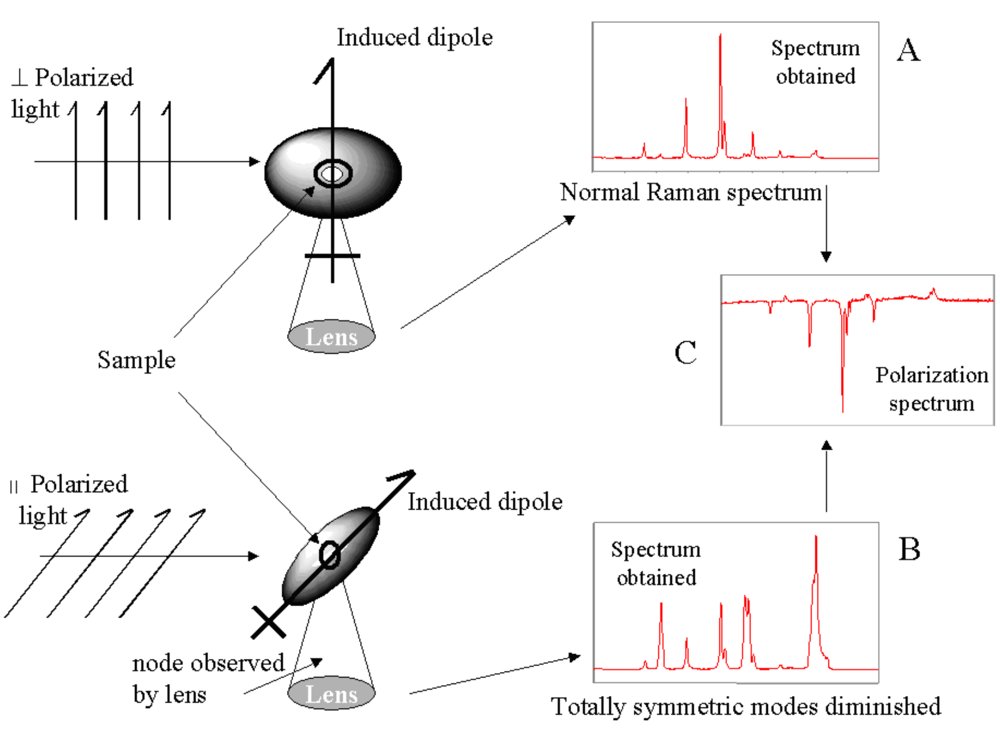

Figure 1. Induced dipole moments from perpendicular and parallel-polarized light.

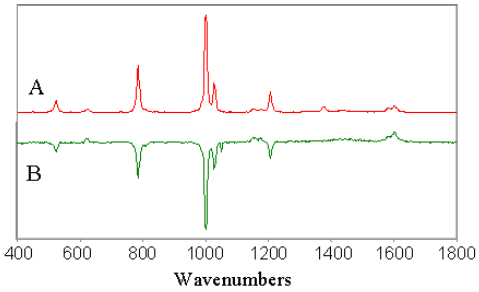

Figure 2. A Normal Raman spectrum (A) and polarized normal Raman spectrum (B) of toluene.

The depolarization ratio ($\rho = I_{\perp}/I_{\parallel}$) can be calculated from the above information by measuring the resulting intensities from both the perpendicular, ($I_{\perp}$) and parallel, ($I_{\parallel}$) polarized light. If we look at a normal Raman spectrum of toluene, (Figure 2a) and a polarized spectrum (Figure 2b) this can be explained more clearly. The 1000 cm^{-1} peak for toluene arises from a totally symmetric carbon-carbon skeletal stretch or ring stretching vibration. These vibrations interact with polarized light and induce a dipole oscillation in the same plane. The degree of polarization or amount of induced dipole is called a polarizability ellipsoid. The polarizability ellipsoid is a three-dimensional representation of the strength of the dipole oscillation emitting in all directions. The ellipsoid is sphere in the case of totally symmetrical vibrations and under such a circumstance $I_\perp = 0$, thus $\rho = 0$. Therefore, the 1000 cm^{-1} peak in toluene is said to be *polarized*. In contrast, a non-totally symmetric vibration in a molecule, for example, in toluene's case 1582 and 1601 cm^{-1}, produces a polarizability ellipsoid that is no longer sphere like. Therefore, ρ is no longer zero and the vibrations are now labeled as being *depolarized*. The final equation for the depolarization ratio can be written as follows.

$$\rho = \frac{I_\perp}{I_{\text{II}}} = \frac{3\beta}{10\alpha + 4\beta}$$

Where α represents the isotropic polarizability component of a molecule and β represents the anisotropic polarizability component of a molecule.

Procedure:

Collect approximately one liter each, of three different grades of gasoline. Gas collecting will vary depending on your location in the country. At high altitude, fuel runs from 85 to 91 octane and at low altitudes it varies from 87 to 93. This is because at high altitudes the 20% thinner air reduces the engines effective compression ratio, so high-octane fuels simply are not efficient.

Once you have your three samples, pipette approximately 1 mL of each gasoline sample into a labeled 1 mL glass vial. Repeat this step so that you have two vials of each octane rating (6 samples total).

On the instrument, set the resolution to **high**, and click the baseline to be set at **on**. Set the integration time on the Raman system to 1 second and select the **continuous** button. Focus the instrument on the sample until you see the best spectrum you can obtain with minimal noise. Once focused, stop taking spectra continuously, and change the integration time to 2 or 4 seconds. There will be fluorescence to contend with in some gasoline samples. In order not to saturate the CCD, keep the integration time low. Take a reference spectrum, and then take a spectrum of each of the six vials. Lastly, take a polarized spectrum of pure toluene and save the result. Store the spectra as an ASCII file such that data analysis can be performed in EXCEL.

Treatment of data

The vibrational mode seen in gasoline spectra at 1000 cm^{-1} is the ring breathing vibration of toluene. To quantify the octane level of the gasoline samples, the area under the target peak shown in Figure 3 must be determined. In EXCEL the data can be read as: column a, being the wavenumbers of the different peaks in the spectrum and column b the respective intensities. Create a plot of wavelength vs. intensity for the data using **XY SCATTER PLOT** type. This will display the spectrum. An area under the peak is useful as it averages out the rapid ups and downs in the spectrum due to noise in the detector. Use the spectrum to determine area under the 1000 cm^{-1} peak; to find the total area of the

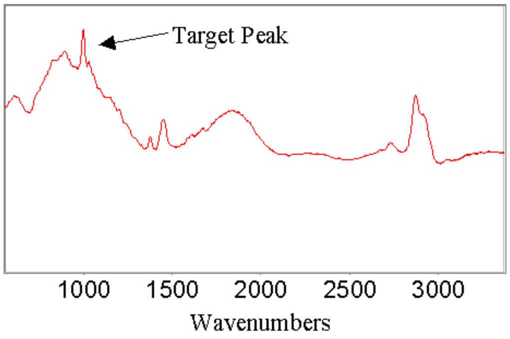

Figure 3. Sample spectrum of gasoline.

toluene peak should use roughly 959-1015 cm^{-1}. Use the SUM feature of EXCEL to find the sum of intensities (area) under the peak. Most likely there will be some fluorescence producing a "hump" under the peak. A better measure of the intensity juts due to Raman scattering would be to subtract out the area due to background. See if you can figure out a quick way to subtract this out using EXCEL. Repeat this for all of the collected spectra. Finally, create a plot of octane rating vs. area of the toluene peaks and display the coefficient of determination (R^2) on the graph.

Questions

1) What is the meaning of the R^2 calculated by EXCEL?

2) Identify at least two other vibrational modes from toluene in the spectra.

3) Figure 4 shows a spectrum of benzene. The peak at 991 cm^{-1} is the ring breathing vibration. Comparing it to the polarization spectrum of toluene, what do you think would happen to the 991 cm^{-1} mode if the polarization was rotated from perpendicular to parallel? Explain your answer.

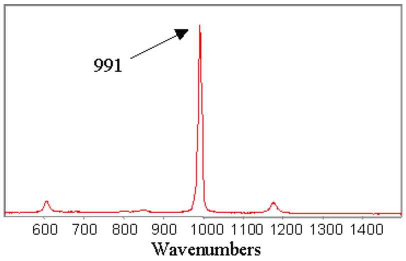

Figure 4. Spectrum of Benzene