# Raman Spectroscopy

## Session #1: Theoretical background and computer simulations of molecular vibrations.

Goals:

- Understand the origin of the Raman effect.
- Understand the vibrational normal modes of molecules.
- Learn how to operate a Raman spectrometer.

> *You will be using a class IIIb laser. Do not disconnect the optical fibers from the laser; do not disconnect the optical fibers from the Raman probe; do not defeat the safety interlock of the enclosure; and do not remove the Raman probe from the laser enclosure. The laser should always be turned off when you open the enclosure. Never look directly at the beam of any laser.*

## I. Theoretical background

When light is traveling through a material, the electric field $\vec{E}$ induces a local electric dipole

$$\vec{p} = \alpha \vec{E}, \qquad (1)$$

where $\alpha$ is the polarizability of the material. $\alpha$ is not a constant, but depends on strain u

$$\alpha(u) = \alpha_0 + \alpha_1 u + \alpha_2 u^2 + \dots \quad (2)$$

If both a strain field $u(t) = u_0 \cos(\Omega t)$ and an electric field $E(t) = E_0 \cos(\omega t)$ are present in the material, the induced electric field has a component

$$\alpha_1 E_0 u_0 \cos(\omega t) \cos(\Omega t) = \frac{1}{2} \alpha_1 E_0 u_0 \left[ \cos\left((\omega+\Omega)t\right) + \cos\left((\omega-\Omega)t\right) \right]. \qquad (3)$$

Thus photons at frequencies $\omega \pm \Omega$ can be emitted, accompanied by excitation or de-excitation of a vibration of frequency $\Omega$.

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In isolated molecules, these vibrations are associated with the interatomic bonds and the molecular geometry. In the simplest case of one mass and one spring, the kinetic T and potential V energies of the system are

$$T = \frac{1}{2}m\dot{x}^2, \quad V = \frac{1}{2}kx^2, \quad (4)$$

where k is the spring constant of the bond and x and $\dot{x}$ are, respectively, the displacement from the equilibrium position and its time derivative. The resonant frequency of this simple system is obtained solving the secular equation

$$k - m\omega^2 = 0. \quad (5)$$

Consider now a molecule formed by a set of masses (atoms) linked by springs (bonds), specified by a set of *generalized* coordinates $q_j$ (e.g., bond lengths and angles). For small oscillations around the equilibrium positions, the kinetic and potential energy of the system can be expressed as

$$T = \frac{1}{2}\sum_{j,k} m_{jk}\dot{q}_j\dot{q}_k, \quad V = \frac{1}{2}\sum_{j,k} k_{jk}q_jq_k. \quad (6)$$

These equations are formally equivalent to eqns. (4), the only difference being that the mass $M = (m_{ij})$ and spring constant $K = (k_{ij})$ are now matrixes.

The secular equation (5) becomes

$$K - \omega^2 M = 0, (7)$$

which has nontrivial solutions only for

$$\text{Det}\left(K - \omega^2 M\right) = 0. \quad (8)$$

The solutions $\omega^2$ to eqn. (8) are the eigenvalues that simultaneously diagonalize K and M, and thus correspond to the resonant frequencies of the molecule.

Let's consider the $CO_2$ molecule (O=C=O) as an example. For simplicity, we'll limit the analysis to the linear vibration modes. Consider the C atom as the origin of the coordinates; the generalized coordinates describing the molecule are the positions of the two O atoms ($x_1$ and $x_2$). The center of mass of the molecule lies at

$$x_{CM} = \frac{m_O x_1 + m_O x_2}{M}, \quad M = 2m_O + m_C. \quad (9)$$

And has a velocity

$$\dot{x}_{CM} = \frac{m_O}{M}\left(\dot{x}_1 + \dot{x}_2\right). \qquad (10)$$

The kinetic and potential energy of the system are

$$T = \frac{1}{2}m_O\dot{x}_1^2 + \frac{1}{2}m_O\dot{x}_2^2 + \frac{1}{2}M\dot{x}_{CM}^2 = \frac{1}{2}\left(m_O + \frac{m_O^2}{M}\right)\dot{x}_1^2 + \frac{1}{2}\left(m_O + \frac{m_O^2}{M}\right)\dot{x}_2^2 + \frac{m_O^2}{M}\dot{x}_1\dot{x}_2,$$

$$V = \frac{1}{2}kx_1^2 + \frac{1}{2}kx_2^2.$$

(11)

Thus,

$$\left(m_{ij}\right) = \begin{pmatrix} \left(m_O + \dfrac{m_O^2}{M}\right) & 2\dfrac{m_O^2}{M} \\ 2\dfrac{m_O^2}{M} & \left(m_O + \dfrac{m_O^2}{M}\right) \end{pmatrix}, \qquad \left(k_{ij}\right) = \begin{pmatrix} k & 0 \\ 0 & k \end{pmatrix}. \qquad (12)$$

Solving eqn. (8) yields the resonant frequencies of the molecule

$$\omega_1^2 = \frac{k}{m_O},$$

$$\omega_2^2 = \frac{2m_O + m_C}{m_O m_C}k. \qquad (13)$$

Mode 1 is the *symmetric mode*, in which both O atoms move toward the center or away from it at the same time, i.e. both O are oscillating with frequency $\omega_1$ and a 180° phase shift. Mode 2 is the *antisymmetric mode*, in which both O atoms lie still while the C atom oscillates between the O atoms with frequency $\omega_2$.

Larger molecules have many more vibrational modes but the mode frequencies and displacements can be calculated in the same way. In general, an N-atom molecule has 3N degrees of freedom of which 3 correspond to solid translation of the whole molecule and 3 (or 2, for linear molecules) correspond to solid rotations. Thus the number of vibrational modes is

$$n = 3\left(N - 2\right). \quad (14)$$

In solids, the number N is very large, on the order of $10^{20}$ cm$^{-3}$, which results in the appearance of bands of allowed vibrational frequencies ω (phonons) in the same way as coupling electronic states in atoms give rise to electron bands and gaps. These allowed frequencies, both in molecules and solids, are characteristic of each material, and can be used to fingerprint the components of a sample; and characterize microstructure and composition.

In Raman spectroscopy, we shine monochromatic light onto a sample (in this case a $\lambda_0$ = 785 nm fiber-coupled diode laser) and measure the intensity of the inelastically scattered light at a different frequency λ. The frequency difference between the incident and scattered light corresponds to that of the mode (vibration or phonon) excited. It is usually expressed in terms of the wave number ν of the *line shift*

$$\nu = \frac{1}{\lambda_0} - \frac{1}{\lambda} \,. \quad (15)$$

A related technique, infrared spectroscopy (IR), employs a white source of light in the infrared spectrum and monitors the intensity transmitted through the sample as a function of λ. The wavelengths that resonate (i.e., have the same frequency) as vibrational states are absorbed and the transmitted intensity shows a dip.

## II. Simulations

In this part of the lab you will take advantage of available computational resources to gain insight into the vibrational states of simple molecules. Go to the *WebMO* website:

http://www.webmo.net/demo/index.html

Log on to the demo server and follow the tutorial for sketching molecules ($CO_2$ to start with) until you reach step 6. In step 7, instead of selecting *Geometry Optimization*, select *Vibrational Frequencies* from the calculations options list. Click on the finished job, scroll down and observe the frequencies of each vibrational mode and the 3D animated vibrations corresponding to each mode.

Identify the *symmetric* and *antisymmetric* C=O stretching modes. What are their frequencies? Use eqns. (13) to predict the ratio of these frequencies and compare ratio to the simulation result.

Now create a $H_2O$ molecule and use the simulation to calculate the normal modes. Identify the *symmetric* and *antisymmetric* O-H stretching modes, report their frequencies and compare their ratio to that predicted by eqns. (13). What would be the frequency of oscillation of a single H atom bonded to a fixed O? Why is it that $CO_2$ has two degenerate angular vibration modes and $H_2O$ has only one?

Create a methane molecule CH$_4$ and use the simulation to calculate the normal modes. You will see three distinct modes, two of them nearly degenerate. Describe each mode and comment on the number of degeneracy of each mode.

Consider the *symmetric* C-H stretching mode in CH$_4$. You can analyze it as 4 H atoms tied to a fixed C atom and oscillating in phase (all four displacements from equilibrium are the same). Write down the kinetic and potential energy for this mode, considering the center of mass fixed on the C atom. Can you consider this mode equivalent to a single oscillating spring? Of which mass and spring constant? Use this result to estimate the spring constant of the C-H bond.

Consider now CH$_3$OH (methanol) and compare it to CH$_4$. Can you see the O-H stretching mode? How does it compare to H$_2$O? Look for this mode in C$_2$H$_5$OH (propanol) and in CH$_3$-CHOH-CH$_3$ (isopropanol) to check that similar vibration modes have similar frequencies in different molecules. This property is used to look for known functional groups in unknown molecules.

Consider now CH$_3$-CHOH-CH$_3$ (isopropanol) and CH$_3$-CO-CH$_3$ (acetone). Explore the C-H modes close to 3000 cm$^{-1}$ and the C-C bonds from 1250 to 1400 cm$^{-1}$ and close to 900 cm$^{-1}$. Where is the frequency of the C=O mode in acetone? Compare it to that in CO$_2$.

For next week's lab (Session #2) bring your own "unknown" sample with you. Completely opaque materials (e.g., metals) will not produce good spectra but many other materials will. Consider: paint pigment, makeup, jewels, minerals, bio-minerals, plastics, ceramics and glasses.

## Session#2. Acquisition of Raman spectra and data analysis

### I. Experimental procedure

### A. Raman spectrometer

The Raman spectrometer has three main components: a high power diode laser (the medium-sized tan box), a Raman probe (mounted inside the large black enclosure), and a spectrograph (the small black box). Light is carried from the laser to the Raman probe, and from the probe to the spectrograph by optical fibers. The Raman probe is a fairly sophisticated optical instrument that filters the diode laser light; delivers and focuses the laser light on the sample; collects the scattered light from the sample; and filters the scattered light to pass only the red-shifted light on to the spectrograph.

## B. Procedure for Loading Samples

1. Wear gloves when handling samples. This is to protect you as well as to avoid contaminating the samples with skin oils.
2. Make sure that the laser source is turned off. If it is on, turn it off.
3. Open the door to the laser enclosure (the large black box with the latch on the right hand side).  Place the sample under the Raman probe. If you are having trouble positioning the circular glass vial, use two glass slides on the sides to prevent the vial from rolling.
4. Adjust the probe-to-sample distance by unlocking the Raman probe and sliding the probe up or down on the vertical track.  Relock the Raman probe to the track.  The focal length of the lens at the output of the Raman probe is $\simeq$ 8 mm. There is a black plastic ruler in the instrument you can use to estimate the distance. (You will adjust the distance more accurately while observing the Raman spectra as described in the steps below.)
5. Close the door to the laser enclosure and turn on the laser.

## C. Data acquisition procedure

6. Click on the Ocean Optics icon.  While watching the Raman spectrum on the computer screen, use the knob at the top of the laser enclosure to adjust the sample-probe distance until you get an optimal signal.  Be careful not to crash the Raman probe into the sample. As the signal levels change, you may need to change the acquisition time or change the vertical scale of the plot.
7. The spectrograph disperses the different wavelengths of the scattered light using a diffraction grating and then focuses the dispersed light on a charge-coupled device (CCD) detector.  The CCD is cooled by a Peltier device to suppress signals generated by thermally excited electron-hole pairs in Si.  The *acquisition time* is the time that the CCD collects photons before the CCD is read-out by the analog-to-digital converter in the device.  The *number of scans* is the number of times the CCD detector is exposed and read-out.   Adjust the *acquisition time* and *number of scans* to get a clear data for your sample. The read-out process introduces some noise so increasing the *number of scans* is not always equivalent to increasing the *acquisition time*.  And the CCD detector has a finite dynamic range so, for intense peaks, increasing the *acquisition time* can lead to a saturation of the detector when increasing *number of scans* does not.
8. Save the Raman spectrum you have acquired as a *Sample* file. The acquisition information will be in the file's header. Make sure to use a descriptive name. *Remember to power off the laser before switching samples.*
9. Open *MatLab* and change the working directory. Call the m-file *Raman* and follow instructions as prompted by the program. This m-file takes the Sample file as its input and plots Intensity vs. wave-number.

### D. Acquire data on a well-known sample and perform background subtractions

10. First, acquire a Raman spectrum for isopropanol.

11. Acquire a background spectrum using the same experimental parameters except that the glass vial is empty.  The background comes from several sources: the analog-to-digital converters in most CCD detectors produce a an offset signal that varies from pixel to pixel; there will be some (but not much) real background from stray light collected by the probe and thermally generated carriers in the detector; and, often the most important, the amorphous structure of the glass container produces a broad Raman spectrum itself and impurities in the glass fluoresce. (Fluorescence is many, many orders of magnitude stronger on a per-atom basis than Raman scattering.)

12. Subtract the background from the data.

13. Plot this spectrum for your report.

### E. Data analysis

14. For your report, for each peak in the spectrum, plot the measured peak positions for isopropanol on the y-axis vs. the accepted peak positions (see the Raman spectra library for organics) on the x-axis.  For your report, discuss if the error in the calibration of the spectrograph is a simple constant shift or is better described by a more complicated linear dependence that varies with wave-number.

15. Make the same type of comparison between the frequencies of the vibrational modes of isopropanol calculated in Session #1 (on the y-axis) plotted as a function of the accepted peak positions (on the x-axis).

### F. Other organic liquids

16. Acquire Raman spectra for chloroform and acetone.  Using the same background spectrum and the same experimental parameters.   For your report discuss the strengths and positions of the peaks, drawing from the insights you gained from the computer simulations of Session #1.

### G. Inorganic crystals and unknowns

17. Acquire Raman spectra on SiC and ZnS SiC and ZnS have more than one crystal structure. Use the Raman spectra library for minerals to identify the phase of your sample.

18.  Acquire the Raman spectra on the  unknown samples you brought with you to the lab.  Try to identify the material using the web-based Raman libraries.   (Here is a Raman spectra library for pigments )

| Vial # | Contents |
| --- | --- |
| 01 | Chloroform |
| 02 | Acetone |
| 03 | Isopropanol |
| 04 | Ethanol |
| 05 | $ZrO_2$ |
| 07 | SiC |
| 08 | ZnS |

## H.  References

See C. Kittel, *Introduction to Solid State Physics* for more information on the RAMAN effect (chapter 11) and on phonons in solids (chapter 4).

See Thornton & Marion, *Classical Dynamics of Particles and Systems*, chapter 12 for more information on coupled oscillators and normal modes. Example 12.5 treats the $CO_2$ molecule geometry.