

Chapter 18 -lite Raman Spectroscopy

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How to do IR spectroscopy with visible light.

In our discussion of light and matter we have focused on light being absorbed by matter. For this to happen the photon of the light must collide with an atom, and the energy of the light photon must closely match some quantum change of states within the molecule. If they match, then the molecule can accept this energy for a few brief nanoseconds of time, and then the molecule changes states in a number of different ways to get rid of the energy so it can drop back into its ground state.

Today I want to focus on what happens when a photon of light collides with a molecule, but the E of the light does NOT match the E of a change of quantum states within the molecule. When this happens the electric field of the light still interacts with the dipole moment of the molecule, but since the energies don't match, the energy can't be absorbed, and the energy is sent back to the universe as photon of light energy again. This interaction, where no energy is gained or lost by the light, is called an elastic collision.

The first consequence of elastic collisions between photons and molecules, where molecules re-emit photons of light of the same energy, is light scattering. The new photon can be re-emitted in a different direction from the original photon. A study of the angle of the scattered light can tell us many things about the electronic dipole of the molecule from which the light was scattered. One everyday example of light scattering is the blue sky. If you are on the moon, and you look at the sky, you see the sun or the stars with a black sky in between. Since there is no air on the moon, the light from the sun or the stars travels directly to your eye, and you see either the light or no light. On the earth (during daylight) the light from the sun is interacting with molecules in the atmosphere and is being scattered by these molecules, so this appears that blue light is coming from all directions, hence you perceive a blue sky.

In studying scattered light it was found that sometimes the collisions between the photon and the molecule are not perfectly elastic, but that the photon has a slightly different energy than expected. The reason for this is that sometimes in kicking back the energy, the molecule doesn't return to its true electronic and vibrational ground state, but it returns to a vibrationally excited ground state. (See fig 18-2) This light has a slightly lower energy than you expected.

Let's take a stab at the math.

Use figure 18-1 as an example

We are going to look at CCl_4 with visible light of 488.0 nm
 CCl_4 has 4 IR bands at 218, 314, and 459 cm^{-1}

First remember that cm^{-1} is an alternate measure of frequency that counts the number of waves in a centimeter, rather than the number of waves that pass a point in 1 second.

If I gave you a wavelength, how would you calculate a wavenumber?

λ = wavelength

if I wanted to know how many waves were in 1 cm, I would simple take .01m (a centimeter) and divide it by the length of the wave (λ)

Thus

Wavenumber (the number of waves per cm) = $.01\text{m}/\lambda(\text{in meters})$
 $\bar{\nu} = .01 / \lambda(m)$

(Note: the way I have set this up units here cancel out, technically the wavenumber is a pure number, the number of wave in a cm. but we keep the unit cm^{-1} to remind us that this is the number of wave per centimeter)

Let's use this to calculate the frequency of the visible light at 488.0 nm

$$.01/488 \times 10^{-9} = 20,491.8 \text{ cm}^{-1}$$

If the excited molecule drops down to its vibrational excited state that correspond to the 218 cm^{-1} vibration state, then the resulting photon of light has a slightly lower frequency, reflecting the energy that when to kink the molecule up to an excited state. Remembering that frequency is directly proportional to energy, we can shortcut some math by saying that

$E = E_{\text{original}} - E_{\text{vibration}}$

$$\begin{aligned} \text{Frequency} &= \text{Frequency}_{\text{original}} - \text{frequency}_{\text{vibration}} \\ &= 20491.8 - 218 = 20273.8 \end{aligned}$$

Similarly for the other 2 vibrations

$$= 20491.8 - 314 = 20177.8$$

$$= 20,491.8 - 459 = 20032.8$$

These wavenumbers don't mean much to me, so let's change them back to wavelengths

$$\lambda(\text{in } m) = .01 / \bar{\nu}$$

$$.01/20273.8 = 493.25 \text{ nm}$$

$$.01/20177.8 = 495.59 \text{ nm}$$

$$.01/20032.8 = 499.18 \text{ nm}$$

Bottom line. If we shine a laser that has a frequency of 488.0 nm into a solution of CCl_4 , most of the scattered light will be at 488.0 nm, (perfectly elastic scattering also called Rayleigh scattering) but, if we look very carefully we will see a little light at 493.25, 495.59, and 499.18 that represents Raman spectrum - Stokes line) that represent inelastic scattering.

This is Raman Spectroscopy. With the proper machine we can measure this light of slightly different wavelengths, interpret it as changes in frequency, and these changes in frequency can be attributed to vibrational changes in state of a molecule similar to the IR.