

6.05 Computational Raman Spectroscopy

(5 points)

Raman spectra are obtained by irradiating a sample with very intense monochromatic radiation, generally produced by a laser, and examining the scattered radiation. A very high proportion of the scattered photons are at the same wavelength as the incident light, but a small fraction - typically 0.01 % or less - have frequencies different from that of the incident light; it is the frequency and intensity of these photons which we record to obtain a Raman spectrum.

The differences in frequency between the incident and scattered radiation correspond to transitions in the molecule, generally (but not exclusively) transitions involving vibrational and rotational energy levels. This relationship with a difference in frequencies, rather than the frequency itself, makes Raman spectroscopy rather different from most other spectroscopic techniques, in which there is a direct correspondence between the energy of the light that is incident upon the molecule and an energy gap within the set of molecular energy levels.

Background Information

This computational experiment deals with the principles and analysis of Raman spectra. You should have covered the principles of molecular vibrational and rotational energy levels in lectures or tutorials before starting the experiment if you are to get the maximum benefit from it.

Relevant lecture courses: Molecular Energy Levels (2nd year, Michaelmas term), Principles of Quantum Mechanics (2nd year, Michaelmas term), Molecular Spectroscopy (2nd year, Hilary term).

Experiment URL:

<http://physchem.ox.ac.uk/~hmc/tlab/605/html/605.htm>

Theory

Figure 1 shows part of the Raman spectrum of carbon tetrachloride. The exciting beam, at 15800 cm^{-1} , appears unchanged in the spectrum because of Rayleigh scattering from the sample. In addition, lines appear on both the short and the long wavelength sides of the laser line. Those at higher energies are termed *anti-Stokes* lines, while those at lower energies are called *Stokes* lines; quite generally, anti-Stokes lines are weaker than the corresponding Stokes lines. The spectra are generally plotted in terms of the energy shift with respect to the exciting line rather than in terms of the absolute wavelength, since it is the energy of this shift which is significant. Thus, the spectrum in Figure 1 reveals Raman peaks at around 203 , 301 and 425 cm^{-1} . Since Raman spectra are very weak, their detection and measurement is difficult.

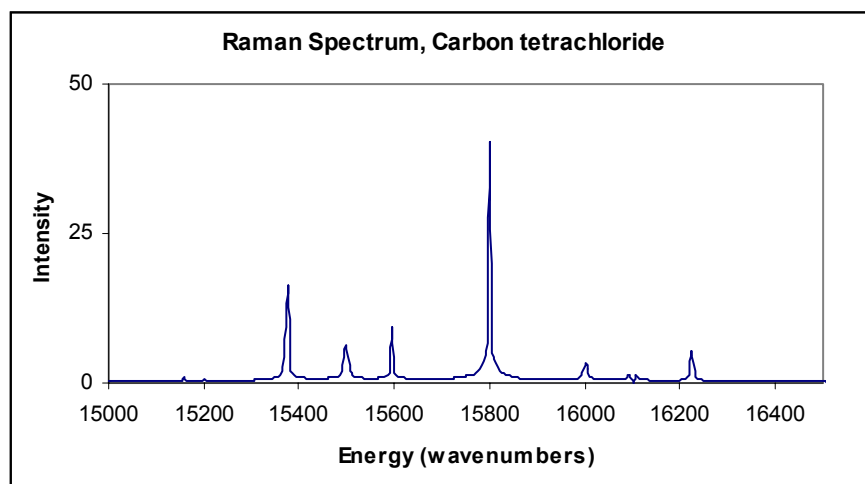


Fig. 1. The Raman spectrum of carbon tetrachloride.

Transitions responsible for Raman peaks

The energy shifts that we record in Raman spectra indicate quantized transitions between molecular energy levels. While absorption spectra arise from a transition from a lower level to an excited state, in Raman spectroscopy the transition is to a "virtual" level. Within a period of about 10^{-15} to 10^{-14} sec, a molecule excited to this virtual state by interaction with radiation generally

returns to its ground state, releasing a photon in a random direction with the same energy as the source. A few molecules, however, return from this distorted virtual state to a state which is different from the starting state. An amount of energy equal to the difference in energy between the initial and final states is therefore absorbed or released by removing or adding it to the energy of the exciting photon.

For example, if the final state is higher in energy than the initial state, the molecule has been excited and the frequency of the light it emits is lower than that it absorbed by an amount corresponding to the difference in energies between the ground and final state, ΔE . That is,

$$\nu = E_{\text{laser}} - \Delta E$$

where ν and E_{laser} are the frequencies of the Raman peak and the incident radiation, respectively.

As shown to the right of the exciting line in Figure 1, anti-Stokes spectra arise when a molecule which is already in an excited state interacts with radiation. If the molecule returns from the virtual state to the ground state, the resulting photon carries away the unwanted energy, so is *increased* in energy by the excitation energy ΔE . Since at any finite temperature fewer molecules are in an excited state than in the ground state, anti-Stokes spectra are weaker than Stokes spectra (to the left in Figure 1), which arise when an initially unexcited molecule is left in an excited state.

Vibrational modes associated with Raman spectra

The transitions responsible for Raman spectra involve the same types of molecular energy levels as those responsible for infrared spectra, in other words rotational and vibrational levels.

For a given molecule the energy shifts observed in a Raman experiment should equal the energies of its infrared absorption bands, provided that the vibrational modes involved are active in both types of spectroscopy. Often peaks appear at identical values in the two spectra. However, the relative sizes of the corresponding peaks are frequently quite different because both transition moments and selection rules differ for the two techniques, and peaks may occur in one spectrum and be absent in the other.

The differences between a Raman and an infrared spectrum are not surprising since the basic mechanisms are quite different. Infrared absorption requires that a vibrational mode of the molecule have associated with it a change in dipole. Only then can radiation interact with the molecule and promote it to an excited vibrational state. In contrast, Raman scattering involves a momentary, elastic distortion of the bonding electrons, followed by emission of radiation as the bond returns to its normal state. In its distorted form the molecule is temporarily polarised; so it has, momentarily, an induced dipole which disappears upon relaxation and photon emission.

The susceptibility of a bond to Raman scattering depends on the ease with which the electrons can be distorted from their normal positions, the so-called bond polarisability. If we are to be able to observe a Raman spectrum, there must be a change in polarisability associated with the vibration, rather than a change in dipole; this requirement of a change in polarisability is the gross selection rule for Raman spectroscopy. (Compare this with the gross selection rule for IR spectroscopy, which is that there be a change in dipole moment during the vibration.)

As a consequence, the Raman activity of a given mode may differ markedly from its infrared activity. For example, homonuclear diatomics have no dipole moment and therefore have no IR spectrum. However, bond polarisability varies in phase with the stretching vibration in a diatomic molecule, reaching a maximum at the greatest separation and a minimum at the closest approach. A Raman band corresponding in frequency to that of the vibrational mode thus results.

Raman and infrared spectra often complement each other, and are associated with different vibrational modes if the molecule possesses a centre of symmetry. In the absence of a centre of symmetry, vibrations may be (but need not be) both Raman and infrared active, and the two spectra show peaks at the same energies.

Intensity of Raman bands

The intensity of a Raman band depends upon the polarisability of the molecule, the intensity of the source, and the concentration of molecules, as well as other factors such as whether the molecule is bound to a surface. Raman emission increases with the fourth power of the frequency of the incident light, but it is hard to take advantage of this to increase the sensitivity of the method, as high energy radiation may cause photodecomposition.

As one would anticipate, Raman intensities are proportional to the number of molecules in the energy level from which the transition occurs. While in most small molecules only the ground vibrational state is appreciably populated, the situation is rather different for rotational levels. Several factors influence the population in these levels:

- a) Degeneracy of the energy level from which the transition starts. The degeneracy of rotational energy levels is $(2J+1)$, where J is the rotational quantum number.
- b) A Boltzmann factor: $e^{-\Delta\varepsilon/kT}$ where $\Delta\varepsilon$ is the difference in energy between the level of interest and the ground state
- c) The effects of nuclear spin statistics. This topic will be explored latter in the experiment.

The combination of the first two factors gives rise to the characteristic "double-wing" appearance of the IR spectra of diatomics, with which you may be familiar, while the third factor may lead to alternations in intensity of successive lines in spectra, or some lines being completely absent. The effect of all three factors will be investigated during the experiment.

The Experiment

Start a web browser and open the URL:

<http://physchem.ox.ac.uk/~hmc/tlab/605/html/605.htm>

A short section introduces Raman Spectroscopy and briefly covers experimental aspects. Read through the sections "Introduction", "The Raman effect" and "Experimental Techniques". Once you have done this, you will arrive at a page headed "Interpreting the Spectrum".

1 Preliminaries

In the first part of the experiment you will investigate the properties of an unidentified homonuclear diatomic X_2 , using the rigid rotor model. Throughout the experiment, you should record your calculations and observations in your data book. There is no need to prepare a screen dump of any of the graphics displayed by the applets, though if you do wish to print out some of the displays to help in your explanations you are welcome to do so.

Spectroscopists have an unfortunate habit of using different types of units for the various forms of spectroscopy. (This is because the different forms of spectroscopy cover huge ranges of the electromagnetic spectrum, so while an absorption in one region of the spectrum may give convenient energy values, such as 450 nm, using a particular unit, the same unit in other regions of the spectrum may give rise to very large or hopelessly small values. Thus, units are chosen so that the numerical values quoted by spectroscopists are generally conveniently-sized numbers.)

In Raman or IR spectroscopy, most measurements are made in units of wavenumber, so it is important that you be familiar with these units. We start with a little practice handling these units.

Q 1.1 Calculate the energy of the laser in wavenumber units, cm^{-1} . (The wavelength of the laser is given on the first page of "Interpreting the spectrum".)

Comment: Notice that the value you obtained is very much larger than the energy of infrared transitions (which are typically in the range $200\text{--}4,000\text{ cm}^{-1}$). Recall that it is the energy *difference* between the exciting line and the Raman line which is of significance, not the absolute energy of the band. It follows that Raman spectroscopy can - in principle - be performed using monochromatic radiation of any energy provided that this energy exceeds the energy gaps in the molecule in which one is interested.

Q 1.2 What is the energy of the laser in Joules?

Q 1.3 Calculate the moment of inertia for X_2 .

Comment: Before starting the simulation, you will do a few simple calculations based on the rigid rotor model of diatomic molecules. This will familiarise you with (or remind you of!) the relevant equations, which you can discover in any standard text on IR and Raman spectroscopy (or in texts such as Atkins). Do not forget that the reduced mass must be calculated in kg, not atomic units. This is because reduced mass has units, and it is essential that the units in all your calculations agree!

Q 1.4 Locate and write down the equation for the rotational constant B .

Comment: You'll find this, and the other relevant equations, in texts such as Banwell. It is very useful, unless you are entirely familiar with this sort of spectroscopy, to have a copy of some suitable textbook with you as you do the experiment.

Q 1.5 Calculate the value of the rotational constant, B , for this molecule.

Comment: Be careful again with the units!

Q 1.6 What is the equation for the rotational energy levels of a rigid rotor in terms of the rotational quantum number J ?

Comment: For the present, you can ignore the parameter D - we shall come to that later.

Q 1.7 Calculate the energy in wavenumber units for the first 5 rotational energy levels in X_2 .

Q 1.8 Calculate the position of the first three Stokes and Anti-Stokes lines in wavenumbers, measured from the exciting line. Also quote these in absolute wavelength.

Comment: The spectrum shown in Figure 1 shows several spectral features. The reason is that carbon tetrachloride has several vibrations that are Raman-active. A diatomic molecule of course has only one.

Now start Applet 1 and check your answers for Q1.8. By right-clicking the mouse on a spectral line you can display its energy. The rotational energy levels are shown above the spectrum, and an arrow shows the Raman transition between the rotational levels that produces a specific spectral line.

2 Bond length

In this section you will investigate how changes in bond length affect Raman spectra.

Q 2.1 Starting from the equation you gave for Q1.4, derive a relationship between the bond length and the energy of the rotational levels.

Q 2.2 Record values for a single Stokes or Anti-Stokes line at a range of bond lengths. You can change the bond length by clicking and dragging the right hand atom in Applet 1. Plot an appropriate straight line graph to demonstrate the relationship between rotational energy level and bond length.

Q 2.3 Does the graph confirm the relationship you derived?

3 Centrifugal Distortion

We move now to the non-rigid rotor model and the Centrifugal Distortion constant D . Questions Q 3.1 - Q 3.4 deal with the mechanics of circular motion. We assume a classical picture in which the bond length of a rotating molecule increases as the extent of rotation increases because of the centrifugal forces.

Q 3.1 What is the centrifugal force on a particle rotating in a circular path?

Q 3.2 In which direction is the force?

- Q 3.3 How is equilibrium maintained in a rotating molecule?
- Q 3.4 How would you expect this to affect the energy of the rotational energy levels?
- Q 3.5 Given the formula for the rotational energy levels of a non-rigid rotor, shown in the web pages, derive equations for the positions of Stokes and anti-Stokes lines.

To the left of the spectrum window in Applet 1 is a button labelled **Centrifugal Distortion**. Click on this to reveal a slider which allows you to vary the value of the parameter D . The value of D is initially zero as in the Rigid Rotor Model.

Moving the slider to the right makes D increasingly positive. Move the slider slowly to increase D and note the effect this has on both the energy levels and the spectrum.

- Q 3.6 Explain the effect of gradually increasing D . Why, for positive values of D , do the Stokes lines move closer together and the Anti-Stokes lines move further apart?

Comment: In some molecules the centrifugal constant is large enough that spectral lines appear on top of each other. Ultimately a sequence of lines can reach a "band head" and then reverse direction. Applet 2 shows an example of this.

- Q 3.7 Describe carefully what has happened to the energy levels to produce two overlapping spectral lines.

Close Applet 1 and start Applet 2.

- Q 3.8 Determine the J values for the two lines that occur on top of each other.

The first section should have clarified your understanding of the factors that affect the position of spectral lines in a rotational Raman spectrum. The next section deals with the line intensities, still using the simulation of X_2 .

4 Intensity of Spectral Lines

- Q 4.1 The intrinsic probability for a transition of a single molecule from $J = 0$ to $J = 2$ is virtually the same as that for a transition from $J = 1$ to $J = 3$. Why are not all spectral lines equally intense?
- Q 4.2 What is the relationship between the intensities of the Stokes and Anti-Stokes lines? Explain this in terms of the population of the energy levels.

- Q 4.3 The reason that the intensity of the spectral lines tail to zero is the influence on populations of an exponential term. Briefly explain the origin of this term.
- Q 4.4 What is the degeneracy of a rotational energy level? How does this affect the intensity of the lines?

Close Applet 2 and restart Applet 1

Line intensity in a Raman spectrum is related directly to the population of each energy level. Although equivalent Stokes and Anti-Stokes lines may involve the same pair of energy levels, they do not have the same intensity because it is the energy level *from which* the transition is taking place from that dictates the intensity of the spectral line.

In homonuclear diatomics, the nuclear spin can lead to the alternation in intensity of successive lines. This effect is particularly relevant to this experiment since it deals with homonuclear diatomics. To appreciate the influence that nuclear spin has on the spectrum you need to understand how the nuclear spin wave function appears in the total molecular wave function and also have a grasp of the Born Oppenheimer approximation.

Interaction of identical nuclei equidistant from the centre of the molecule can produce intensity alternations of sequential spectral lines.

- Q 4.5 Explain the difference between a Boson and a Fermion
- Q 4.6 Write down the total wave function of a diatomic molecule, in terms its constituent wave functions: electronic, rotational and nuclear spin.
- Q 4.7 Explain what approximations have been made to get to this result.

Comment: Think Born-Oppenheimer!

If the nuclear spin $I = \frac{1}{2}$, space quantisation of nuclear spin angular momentum results in the quantum number M_I taking values $\frac{1}{2}$ or $-\frac{1}{2}$. The nuclear spin wave function ψ_{ns} is usually written as α or β , corresponding to $M_I = \frac{1}{2}$ or $-\frac{1}{2}$. X nuclei, labelled 1 and 2, can have either α or β spin wave functions.

$$\psi_{ns} = \alpha(1)\alpha(2) \quad \text{or} \quad \beta(1)\beta(2) \quad \text{or} \quad \alpha(1)\beta(2) \quad \text{or} \quad \beta(1)\alpha(2)$$

The first of these wavefunctions is interpreted as nucleus 1 having an α spin, and nucleus 2 having an α spin, and so on. The *total* wavefunction of the molecule must be antisymmetric if two fermions, such as the X nuclei, are exchanged, but there is no requirement that each individual part of the wavefunction follow this rule.

The spin wavefunction can be either symmetric or antisymmetric with respect to the interchange of the nuclei. (If it is symmetric, then some other part of the wavefunction must be antisymmetric for this exchange so that the Pauli Principle is not violated.) It is evident that the first two spin functions shown above are symmetric but the latter two are neither symmetric nor antisymmetric, since a change of label does not yield the original wavefunction multiplied by $(-1)^n$

but instead yields a different wavefunction. These last two wavefunctions are therefore on their own not suitable.

From these 2 wavefunctions, linear combinations can be made that are either symmetric or anti symmetric to exchange of the labels.

Q 4.9 Write down the 4 normalised spin wave functions for the X_2 molecule.

Q 4.10 Explain the meaning of the words -ortho and -para in this context.

Q 4.11 How do these spin wave functions affect the appearance of the spectrum for X_2 ?

Comment: You need here to consider what effect the various possibilities for the spin wavefunctions will have upon the number of molecules in each state. This is well explained in many books in discussions of ortho- and para-hydrogen.

5 The Spectrum of Nitrogen

In this part of the experiment you will look in greater depth at some of the topics introduced earlier. There is a different applet to accompany each set of questions and the simulations apply to real molecules. Sometimes information taken from the applet will allow you to identify the molecule in question.

You should be familiar with the Boltzmann factor and how it influences the population of the rotational energy levels from the previous section. The appearance of the spectrum is very sensitive to temperature because of the exponential nature of the Boltzmann factor.

Start Applet 3.

Q 5.1 Why are more spectral lines visible at higher temperatures?

Q 5.2 How would you expect the intensity of the first Anti-Stokes line to vary with temperature?

Q 5.3 How does the intensity of the first Stokes line vary with temperature? Why is this the case?

Q 5.4 Using the applet, record the value of J for which line intensity is a maximum for ten different temperatures.

Q 5.5 Why are maximum intensities at higher temperatures more intense than at lower temperatures?

Q 5.6 Write down an expression for the intensity of a spectral line. Derive a formula for the J value associated with the most intense line.

Q 5.7 From a suitable graph find the value of the rotational constant for this homonuclear molecule.

Q 5.8 Hence calculate the atomic mass and identify the diatomic.

Q 5.9 What is the nuclear spin of this nucleus? Does the spectrum confirm your view?

6 The Spectrum of Nitrogen

Start Applet 4. This shows the spectrum of Nitrogen at an elevated temperature. A value for the rotational constant B and the centrifugal constant D are calculated from the spectrum of N_2 in this section.

Q 6.1 Rearrange $F(J+2) - F(J) = 2B(2J+3) - 4D(2J+3)(J+3J+3)$ into the form $y = mx + c$, so that m is a function of D only.

Q 6.2 By plotting a suitable graph, calculate the values of B and D .

Q 6.3 What is the ortho:para intensity ratio for the spectrum?

Q 6.4 What is the nuclear spin of a N nucleus as determined from the spectrum?

Q 6.5 How would the spectrum of $^{14}N-^{15}N$ differ from that of a sample of $^{14}N_2$ gas? Explain your answer. Would you expect $N^{14}N-^{15}N$ to give rise to a pure rotational spectrum?

Comment: It is important to realise that interaction of nuclear spin can only occur for identical nuclei so there would be no intensity alternation of the lines for $^{14}N-^{15}N$.

7 Isotopic Substitution

The next section compares the rotational Raman spectra of the three isotopes of Hydrogen.

Q 7.1 Deuterium is twice as massive as hydrogen. How would you expect this to affect the spectrum?

Q 7.2 Use the appropriate Applet to calculate the bond length of molecular hydrogen.

Q 7.3 Assuming that the H-H and D-D bond lengths are equal, derive a relationship between the positions of the corresponding lines in the spectra of hydrogen and deuterium.

Comment: You've assumed that the bond lengths in deuterium and hydrogen are the same. Is this realistic? Why or why not?

Q 7.4 Use the applet to test the validity of the relationship that you derived. Try and give an explanation for this finding.

Q 7.5 Calculate the bond length for deuterium.

Comment: A breakdown in the Born Oppenheimer approximation leads to the difference in the bond length of the isotopes.

Earlier you derived the four normalised nuclear spin wave functions for an $I = \frac{1}{2}$ nucleus. Now we turn to the $I = 1$ deuterium nucleus and rationalise the 2:1 ortho:para ratio for D_2 .

Q 7.5 What is the nuclear spin of the 2H nucleus?

Q 7.6 What is the possible space quantisation of this nuclear spin?

Q 7.7 How many possible spin wave functions does this produce?

Q 7.8 Write these down, labelling them either symmetric or antisymmetric.

Q 7.9 Use your findings to explain the difference in appearance of the spectra of H_2 and D_2 .

Q 7.10 How will nuclear spin affect the rotational spectrum at very low temperatures?

Q 7.11 What is the maximum intensity in the hydrogen spectrum, at 2500K?

Q 7.12 What is the maximum intensity in the deuterium spectrum, at 2500K?

Q 7.13 At what value of J do these maxima occur?

Q 7.14 Explain why the maximum intensities are different and why they occur for different J values.

Comment: Tritium is a Fermion with relative atomic mass 3.03.

8 Further Nuclear Spin

Although there is an alternation in intensity of consecutive lines, the ortho: para ratio cannot be determined merely by comparing the intensities of successive lines on the spectrum, as the population of the energy levels complicates intensity ratios. In this exercise you need to factor out the degeneracy and Boltzmann factor for a number of intensities and reveal the ortho:para spin ratio.

9 Predict the Spectrum of Oxygen

Your final task is to construct a rotational Raman spectrum of O_2 , given its physical properties.

Q 9.1 Using knowledge gained so far, sketch the rotational Raman spectrum of O_2 excited with monochromatic 336.732nm laser light, from an N_2 laser. Include the Stokes and Anti-Stokes lines arising from transitions up to the $J=10$ rotational energy level. Label each line with its rotational quantum number, position in wavenumber units and intensity.