CHARACTERIZING MOLECULAR VIBRATIONS USING RAMAN SPECTROSCOPY

S. Garoff, B. Luokkala 1-7-2014
Last Revision, R. Schumacher: 4-14-2017 v2.3

I. INTRODUCTION

Atoms in a molecule vibrate around their equilibrium position due to thermal excitations. As in a system of masses on springs, the vibrations of the molecule are best described by the normal modes of vibrations of the molecule as a whole. The frequencies, amplitudes, and symmetries of these vibrations are determined by the strength of the interatomic bonding and the arrangements of the atoms in the molecule. In molecules, the normal modes occur at discrete frequencies; even for materials with extended lattices, a very important and large class of the normal modes also occurs at discrete frequencies. Thus, when we measure the characteristics of these vibrations, we learn about the atomic scale behavior of the material. The spectrum of vibrations of an unknown material can be used to identify that material through reference to existing libraries of vibrational spectra. In addition, vibrational spectra can be used to learn about the internal structure of materials, e.g. vibrational spectra have been instrumental in determining the mechanisms of oxygen binding in hemoglobin, the resonant bonding in benzene, and the local atomic arrangements in amorphous semiconductors. In this lab, we will explore the molecular vibrations of carbon tetrachloride (CCl₄) and benzene (C₆H₆).

The most prominent methods of studying molecular vibrations involve their interaction with electromagnetic radiation. There are two main methods: infrared (IR) absorption and Raman scattering. In infrared absorption, photons with a range of frequencies (3×10¹⁴ to 1×10¹² Hz or wavelengths from 1 to 300 microns) are incident on the sample. Those frequencies which match the vibrational frequencies of the material are absorbed; those which do not match vibrations are transmitted. Classically, this process is analogous to pumping a damped harmonic oscillator at its resonant frequency. The quantum mechanical description involves the incident radiation inducing transitions from one quantum vibrational state of the molecule to another. This is shown schematically in Fig. 1, wherein an IR photon of frequency νᵥ can induce a transition from vibrational state ν = 0 to the state ν = 1. Alternatively, such changes in molecular state can be caused by inelastic scattering of higher-energy visible photons of size ν. The energy (or frequency) shifts in the scattered radiation then give a direct measure of the vibrational frequencies of the molecule. Although the intensity of this scattered light is quite low, Sir C. V. Raman was able to observe such scattering in 1928; and the effect was later named after him. With the advent of extremely intense monochromatic laser sources, Raman spectroscopy has become much faster and more sensitive, and instrumentation for such measurements is now
reasonably common. Some of the advantages and unique features of Raman spectroscopy will be demonstrated in this experiment on liquid CCl₄ and C₆H₆.

**Exercises 1, 2, 3, 4:** After reading the handout and using supplemental references, answer the following questions in your notebook:

1. Why is the scattered light shifted in energy? How is conservation of energy involved?
2. What are the physical assumptions of the valence force, central force and group theory models? Of the isotope shift model? Note their similarities and differences in your notebook.
3. Study the formulation for finding the eigenfrequencies (from the secular equation) and the eigenmodes from the kinetic and potential energies of a system of masses. Use your text Classical Dynamics by Thornton and Marion. Read especially section 12.4 and do the part of Example 12.5 that deals with the longitudinal vibrations of CO₂ in your notebook.
4. Since we can use a classical mass-and-spring model to find the eigenstates of the CCl₄ molecule, in what way is quantum physics even relevant to Raman scattering?

**II. CLASSICAL DESCRIPTION OF THE RAMAN EFFECT**

A molecule may or may not have a permanent electric dipole moment, µ, depending on the symmetries of its charge distribution. A static or low-frequency electric field induces an additional dipole moment in a molecule because of movement of the charged electrons and nuclei. At high optical frequencies (~10ⁱ⁵ Hz), the nuclei cannot respond rapidly enough to follow the field but polarization of the electron distribution can occur. For an isolated molecule, an oscillating radiation field of intensity E will “induce” a dipole moment of magnitude

\[ \mu_{\text{ind}} = \alpha E \]  \hspace{1cm} (1)

where \( \alpha \) is called the molecular polarizability. The field E oscillates at the frequency \( \nu_0 \) of the light

\[ E = E_0 \cos(2\pi \nu_0 t) \]  \hspace{1cm} (2)

and hence the induced dipole will also oscillate at this frequency. According to classical electromagnetic theory, any oscillating dipole changing in either magnitude or direction will radiate energy; hence light of frequency \( \nu_0 \) is emitted in all directions (except that parallel to the dipole). Classical theory gives the average intensity of total radiation as

\[ I = \frac{16\pi^4 \nu^4 \mu_0^2}{3c^3} \]  \hspace{1cm} (3)

where \( \mu_0 \) is the amplitude of the net dipole moment. For this case, the scattered radiation has the same frequency as E. Radiation scattered without change in frequency (and therefore energy) is called elastic scattering; and this particular type of elastic scattering is called Rayleigh scattering. From simple molecules, typically one out of 10⁶ incident photons will be so scattered. The \( \nu \) dependence of this scattering process makes the sky blue.
Inelastic or Raman scattering of light can be understood classically as arising from modulation of the electron distribution, and hence the molecular polarizability, because of vibrations of the nuclei. For example, for a diatomic molecule, the polarizability of the molecule $\alpha$ can be represented adequately by the first two terms of a power series in the vibrational coordinate $Q$:

$$\alpha = \alpha_0 + \left(\frac{d\alpha}{dQ}\right)_0 Q.$$  \hfill (4)

Here the subscript zero indicates that the parameters $\alpha_0$ and $(d\alpha/dQ)_0$ are evaluated at the equilibrium position of the atoms. Physically, this means that as the molecule gets stretched its polarizability changes (the derivative term). In the harmonic oscillator model, $Q$ oscillates at the characteristic vibrational frequency $\nu$ according to the relation

$$Q = A \cos 2\pi \nu t$$  \hfill (5)

where $A$ is the maximum amplitude of vibration. Substitution of Eqs. 2, 4, and 5 into Eq. 1 reveals the time dependence of $\mu_{\text{ind}}$:

$$\mu_{\text{ind}} = \alpha_0 E_0 \cos 2\pi \nu_0 t + \left(\frac{d\alpha}{dQ}\right)_0 A E_0 \cos 2\pi \nu_0 t \cos 2\pi \nu_\nu t$$

$$= \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} \left(\frac{d\alpha}{dQ}\right)_0 A E_0 \left[\cos 2\pi (\nu_0 + \nu) t + \cos 2\pi (\nu_0 - \nu) t\right],$$  \hfill (6)

where the first term is responsible for Rayleigh scattering at $\nu$, while the second and third terms produce inelastic Raman scattering shifted by the frequency of the vibration, $\nu_\nu$, to frequencies which are higher (anti-Stokes) and lower (Stokes), respectively, than the incident-light frequency. The frequency $\nu_0$ usually corresponds to light in the visible region (typically the radiation from a laser), and the Raman-shifted light then occurs in the visible region but with an intensity that is $10^{-8}$ to $10^{-12}$ times that of the incident light. Recall that the vibrating molecules re-radiate energy at the three oscillation frequencies of the induced dipole moment.

This classical picture of Raman scattering only begins to describe the phenomena. It cannot account for the role of molecular symmetry, the polarization states of Raman scattered light, the selection rules predicting which vibrations will be observed, or the intensities of the scattered light. All this must be left for quantum mechanical treatments. Some of these issues are briefly discussed below.

### III. QUANTUM DESCRIPTION

The quantum mechanical treatment of light scattering predicts the same general results but more explicitly involves the quantized vibrational energy levels and wave functions of the molecule. Figure 1 shows the energy level representation of the scattering process. The virtual
states are not energy eigenstates but serve as intermediate levels from which the scattering process occurs in a time less than the period of a molecular vibration (~10⁻¹³ sec). Should the incident radiation have a frequency that causes actual absorption to an electronic eigenstate, the lifetime of the upper state is much longer (~10⁻⁸ sec) and the resultant emission at other wavelengths is termed fluorescence. In the absence of such a resonance, the ratio of the Raman intensity of the anti-Stokes and Stokes lines is predicted² to be

\[
\frac{I_A}{I_S} = \left(\frac{\nu_0 + \nu_v}{\nu_0 - \nu_v}\right)^4 \exp \left(-\frac{\hbar\nu_v}{kT}\right),
\]

where \(k\) is Boltzmann's constant and \(T\) is the absolute temperature of the molecule. Because of the \(\nu\) dependence, blue light is scattered more efficiently than red. However, the Boltzmann exponential factor is dominant in Eq. 7, and the anti-Stokes features are always much weaker than the corresponding Stokes lines. This is very different from the classical picture in which Stokes and anti-Stokes lines are predicted to be equally strong.

**Exercise 5.** Using you understanding of classical statistical mechanics, what is origin of the relative intensities between Stokes and Anti-Stokes scattering?

A word about Raman jargon: in what follows we discuss observation of energy levels of the molecules using the Raman spectrometer. These levels are described as “peaks” (in a measured spectrum) or as “lines” (in the sense of literal lines on an old-style photographic depiction of the excitations on film) or as “bands”. All three words mean essentially the same thing. Even though the word “band” often means a collection of closely-spaced lines, in the Raman spectroscopy world it refers to single discrete levels.

For polyatomic molecules, a number of Stokes Raman bands (or lines, or peaks) are observed, each corresponding to an allowed transition between two vibrational energy levels of the molecule. An allowed transition is one for which the intensity is not exactly zero due to some quantum-mechanical selection rule. For molecules with appreciable symmetry, some fundamental transitions may be absent in the Raman and/or infrared spectra. Infrared spectra are obtained with low-energy light that stimulates transitions directly from one vibrational state to the other, without the intermediate virtual states, while Raman scattering involves higher energy (visible) photons that are much more energetic than the transition that is excited.

The essential requirement is that the transition moment (“matrix element”) \(P_{ind}\), whose square determines the intensity of the light, be nonzero. For a transition from the ground state to an excited state \(0 \rightarrow 1\), the matrix element can be (very) schematically written as

\[
P_{ind}(0 \rightarrow 1) = \int \psi_0^* \mu_{ind} \psi_1 dQ = E \int \psi_0^* \alpha \psi_1 dQ \neq 0
\]

for the Raman case, and

\[
P_{ind}(0 \rightarrow 1) = \int \psi_0^* \mu \psi_1 dQ \neq 0
\]
for the infrared case. Here \( \psi_0(Q) \) and \( \psi_1(Q) \) are wave functions for states with vibrational quantum numbers \( v = 0 \) and \( v = 1 \), and the integration extends over the full range of the coordinate \( Q \). Since these two conditions are not the same, infrared and Raman spectra generally differ in the number, frequencies, and relative intensities of observed bands. For (conceptual) example, if \( \psi_0(Q) \) and \( \psi_1(Q) \) are spherically symmetric and the operator between them depends linearly on \( Q \), then the integral over all space vanishes and the transition is forbidden. The prediction of allowed transitions for both cases represents an elegant example of the role of symmetry and group theory in chemistry. Although a discussion of this topic is beyond the scope of this handout, the application of group theory to vibrational spectroscopy is presented in several standard texts (e.g., Ref. 2 and 3).

A summary of the conclusions reached for a few simple molecular structures is provided in Tables 1 and 2. Here, the general form of the vibrational coordinates is shown along with the mode-numbering nomenclature and the infrared and Raman activity for the fundamental vibrations. Each molecular type has a unique set of symmetry elements (rotation axes, reflection planes, etc.). Associated with these elements are operations (such as rotation about symmetry axes, reflections, etc.) which transform the molecule from one configuration in space to another which is indistinguishable. This set of operations defines the “point group”, which is indicated in the Table. The point group is associated with a unique set of symmetry species (denoted with names \( \Sigma_g \), \( A_1 \), \( B_1 \), \( E \), \( F_1 \), etc.), each of which behaves differently under the symmetry operations of the molecule. Every vibrational coordinate (and wave function) belongs to one of these species, as indicated in the Table; it is knowledge of this symmetry which permits the prediction of the infrared and Raman activity of a given transition.

**Exercise 6.** The selection rule for IR is a little easier to visualize. Try to rationalize the absence of IR absorption in the \( \Sigma_g \) mode of the linear \( AB_2 \) and the \( A_1' \) mode of the trigonal \( AB_3 \) molecules in Table 1. Assume that the bonding in the molecule causes the \( B \) atoms to be slightly negatively charged, while \( A \) atoms are slightly positive. Can the incident \( E \) - field cause these vibrations? Write your explanation in your notebook.

**IV. RAMAN DEPOLARIZATION RATIO**

A more realistic discussion of vibrational selection rules must take into account the vector properties of the dipole moment and the tensor character of the polarizability \( \alpha \). Thus, Eq.1 should be written

\[
\begin{align*}
&\left( \begin{array}{c} 
\mu_x \\
\mu_y \\
\mu_z 
\end{array} \right) =
\left( \begin{array}{ccc} 
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{array} \right)
\left( \begin{array}{c} 
E_x \\
E_y \\
E_z
\end{array} \right). 
\end{align*}
\]

(10)

Such considerations are of considerable importance in the study of oriented molecules, as in a crystal, but are less important for liquids and gases where the molecular orientation is random. However, in the case of Raman spectroscopy, not all information about the components of \( \alpha \) is lost by orientational averaging. Totally symmetric vibrations are those in which the symmetry of
the molecule does not change during the vibrational motion (e.g., the \( \Sigma_g^+ \), \( A' \), and \( A_1 \) vibrations of Table 1). One finds that it is possible to distinguish totally symmetric from other molecular vibrations by a measurement of the depolarization ratio

\[
\rho_i = \frac{I_\perp}{I_\parallel}
\]

of the Raman lines. Here \( I_\perp \) and \( I_\parallel \) are the intensities of scattered light with polarization perpendicular (\( \perp \)) and parallel (\( \parallel \)) to the polarization of linearly polarized exciting light. Theory shows that \( \rho_i \) is related to combinations of the tensor components of \( \alpha \), and that \( \rho_i = \frac{3}{4} \) for any vibration which is not totally symmetric and \( 0 < \rho_i < \frac{3}{4} \) for those that are totally symmetric.\(^4\) Raman bands for which \( \rho_i = \frac{3}{4} \) are called depolarized, and those with \( 0 < \rho_i < \frac{3}{4} \) are called polarized. (Note that the Raman instruments usually have different sensitivities to light polarized in different directions so the observed depolarization ratio in an experiment must be calibrated.) For totally symmetric vibrations, \( \rho_i \) values near zero are observed, such as in molecules \( \text{CO}_2 \), \( \text{SF}_6 \), and \( \text{CCl}_4 \). Thus, the measurement of \( \rho_i \) will be used in this experiment to aid in assigning the frequency of the totally symmetric \( \nu_1 \) vibration of \( \text{CCl}_4 \).

V. FORCE MODELS

With present day computers, the bonding in a small molecule can be very accurately described from quantum mechanics. Previously, models of the molecule, treating them as a set of masses on springs, were devised which could be analyzed more simply. These models cannot describe the situation exactly. But they can indicate which phenomena are most important in the bonding mechanisms and which are less important corrections. We will try to determine the force constants of these models from experimentally observed fundamental frequencies (normal modes) of the molecule. However in all except a very few cases, the number of force constants is larger than the number of normal modes so the force constants cannot all be determined. One way out of this difficulty is the investigation of molecules with a lot of structural symmetry where the force constants should be the same but the frequencies different, thus supplying the additional equations for the force constants. Another way is to make certain more specific assumptions about the forces in the molecules such that the number of force constants to be determined is reduced.\(^5\) Here, we will examine this approach to describe \( \text{CCl}_4 \). You will determine which of the three models discussed the following paragraphs best describes the vibrations of \( \text{CCl}_4 \).

In the simplest harmonic oscillator model, the valence force model, we assume that there are Hookian springs between the C and each Cl atom in the stretching coordinates and that the potential for the bond angles is also a simple harmonic potential about an equilibrium angle set by the \( \text{sp}^3 \) bonding of the C. The latter assumption is not the same as assuming a Hookian force between the chlorine atoms. Note every atom does not interact with every other atom in the molecule. Also, every force acting on each atom is zero at equilibrium, not just the net force on each atom. Under these assumptions, the potential energy of a tetrahedral molecule such as \( \text{CCL}_4 \) can be written as\(^5\)
where $r_i$ is the change in the length of C-Cl bond (whose equilibrium length is $\ell$) and $\delta_{ij}$ is the change in the angle between bonds $i$ and $j$. From classical mechanics one obtains the following relations between the vibrational frequencies and the force constants $k$ and $k_\delta/\ell^2$:

\begin{align*}
4\pi^2 c^2 \omega_c^2 &= \frac{k}{m_{Cl}} \quad (12\text{-a}) \\
4\pi^2 c^2 \omega_s^2 &= \left(\frac{3}{m_{Cl}}\right) \frac{k_\delta}{\ell^2} \quad (12\text{-b}) \\
4\pi^2 c^2 \left(\omega_3^2 + \omega_4^2\right) &= \frac{k}{m_{Cl}} \left(1 + \frac{4m_{Cl}}{3m_C}\right) + \frac{2k_\delta}{m_{Cl}\ell^2} \left(1 + \frac{8m_{Cl}}{3m_C}\right) \quad (12\text{-c}) \\
16\pi^4 c^4 \omega_3^2 \omega_4^2 &= \frac{2k_k}{m_{Cl}^2 \ell^2} \left(1 + \frac{4m_{Cl}}{m_C}\right) \quad (12\text{-d})
\end{align*}

In this expression, $\ell = 1.77\text{Å}$ is the bond length in $\text{CCl}_4$; and the masses $m_{Cl}$ and $m_C$ should be expressed in grams using $1.660531(1) \times 10^{-24}$ gr/amu. Since there are two force constants and four frequencies, one can test whether the proposed force field has captured the character of the molecular bonding by separately determining $k$ and $k_\delta/\ell^2$ from Eqs.12-a and 12-b. Then we can see if the right and left hand sides of Eq.12-c and Eq.12-d agree. For ease in error propagation, use the following high-accuracy values for the constants: $m_{Cl} = 35.4527(1)$ amu; and $m_C = 12.011(1)$ amu.

These expressions use another bit of technical jargon: all the frequencies, $\omega$, are expressed in units of “inverse centimeters” and called “Raman shifts”. This is a result of taking the conventional notion of a frequency, $\nu$, in inverse seconds and defining $\omega = \nu / c$, which has units of inverse centimeters. They are shifts in the sense that the scattered light has its frequency shifted by an amount corresponding to the vibrational excitation of the molecule.

Next we consider the central force model. In this model, we assume every atom exerts a force on every other atom along the lines of centers. We again assume a Hookian force BUT each force on an atom is no longer necessarily zero at equilibrium, only the net force on an atom is zero. See Fig.2 for the overall geometry. We assume the forces between Cl atoms have the form $F_{ClCl} = a - k_i Q_{ij}$ where $Q_{ij}$ is the displacement of the $i$th and $j$th Cl atoms distance from the equilibrium distance, $t$. The force between the C and each Cl atom has the form $F_{CCl} = b - k_2 r_i$ where $r_i$ is the displacement of the C and the $i$th Cl atom distance from its equilibrium value. A picture of the atoms and distances is shown in Fig. 2 taken from Reference 5. This leads to a
potential
\[ V = -a \sum_i \sum_j Q_{ij} + \sqrt{6}a \sum_i r_i + \frac{1}{2} k_1 \sum_i \sum_j Q_{ij}^2 + \frac{1}{2} k_2 \sum_i r_i^2 \]  

(13)

Parameters \( a \) and \( b \) are offsets that ultimately do not matter, and the secular equation leads to

\[ 4\pi^2 c^2 \omega_1^2 = \frac{k_2}{m_{cl}} + 4 \frac{k_1}{m_{cl}} \]  

(13-a)

\[ 4\pi^2 c^2 \omega_2^2 = \frac{k_1 - k'}{m_{cl}} \]  

(13-b)

\[ 4\pi^2 c^2 (\omega_3^2 + \omega_4^2) = \frac{2k_1}{m_{cl}} + \frac{4m_{cl} + 3m_C}{3m_C m_{cl}} k_2 - 2 \frac{(3m_C + 16m_{cl})}{3m_C m_{cl}} k' \]  

(13-c)

\[ 16\pi^4 c^4 \omega_3^2 \omega_4^2 = \frac{2(4m_{cl} + m_C)}{3m_C m_{cl}^2} (k_1 k_2 - 8k_1 k' - 5k_2 k' - 8k'^2) \]  

(13-d)

where

\[ k' = -\frac{a}{t} \], and \( t \) is the length of the edge of the tetrahedron in the equilibrium position. Combining equations (13-a), (13-b), and (13-c) determines \( k_1 \),

\[ 4\pi^2 c^2 (\omega_3^2 + \omega_4^2) - \frac{4m_{cl} + 3m_C}{3m_C} 4\pi^2 c^2 \omega_1^2 - 2 \frac{(3m_C + 16m_{cl})}{3m_C} 4\pi^2 c^2 \omega_2^2 = -4 \frac{(m_C + 4m_{cl})}{m_C m_{cl}} k_1 \]

\( k_2 \) and \( k' \) now follow from the first two equations, (13-a) and (13-b). (13-d) serves as a check on the model.

A more complete force field analysis based on group theory ideas\(^7\) suggests building on the valence force model by adding a constant, \( k_{rr} \), to account for bond-bond interactions. The equations for the eigenfrequencies then become:

\[ 4\pi^2 c^2 \omega_1^2 = \frac{k_r + 3k_{rr}}{m_{cl}} \]  

(14-a)

\[ 4\pi^2 c^2 \omega_2^2 = \frac{3k_\delta}{m_{cl} l^2} \]  

(14-b)

\[ 4\pi^2 c^2 (\omega_3^2 + \omega_4^2) = \frac{k_r - k_{rr}}{m_{cl}} \left( 1 + \frac{4m_{cl}}{3m_C} \right) + \frac{2k_\delta}{m_{cl} l^2} \left( 1 + \frac{8m_{cl}}{3m_C} \right) \]  

(14-c)

\[ 16\pi^4 c^4 \omega_3^2 \omega_4^2 = \frac{2(k_r - k_{rr}) k_\delta}{m_{cl} l^2} \left( 1 + \frac{4m_{cl}}{m_C} \right) \]  

(14-d)
One sees that $k_\delta / l^2$ is easily determined from (14-b). Then solving the equations, (14-a) and (14-c), one can obtain $k_r$ and $k_{rr}$. The fourth equation, (14-d) serves as a check.

VI. THE ISOTOPE EFFECT

When an atom of a molecule is replaced by an isotopic atom of the same element, it is assumed that the potential energy function and configuration of the molecule are changed by negligible amounts. The frequencies of vibration may, however, be appreciably altered because of the change in mass involved. This is especially true if hydrogen is the atom in question because of the large percentage change in mass when deuterium is substituted. This shift or isotopic effect is very useful for several purposes. In the first place it may be used to help assign spectral lines to modes of vibration. Thus, a normal mode of vibration in which the hydrogen atom in question is oscillating with a large relative amplitude will suffer a greater isotopic change in frequency than a normal mode in which this hydrogen is moving with a small relative amplitude. In the limiting case in which only hydrogen atoms are moving, replacement of all of them by deuterium atoms should decrease the corresponding fundamental frequency by the factor $1/\sqrt{2}$, this being the square root of the ratio of masses. The totally symmetric ($A_1$) vibration of methane (a molecule of the form $AB_4$ in Table 1) is an example of this situation. For CH$_4$, the frequency is 2,914.2 cm$^{-1}$, which decreases to 2,084.7 cm$^{-1}$ in the case of CD$_4$. The ratio $\omega_{CD_4} / \omega_{CH_4}$ thus has an experimental value of 0.715, compared with a theoretically expected value of 0.707. The discrepancy is attributed to the fact that the observed frequencies are influenced by cubic and quartic terms in the potential energy, so that the vibration is not strictly harmonic as has been assumed in the theoretical development.

The vibration frequencies of highly symmetric molecules are related by a rule, which is a generalization of the methane example given above. This rule may be expressed as a product over all the frequencies of the molecules

$$\prod_{i=1}^{3N-6} \frac{\omega_1'}{\omega_1} = \prod_{i=1}^{3N} \left( \frac{m_i}{m_i'} \right)^{1/2} \left( \frac{M'}{M} \right)^{3/2} \left( \frac{I_x' I_y' I_z'}{I_x I_y I_z} \right)^{1/2}$$

(15)

where the primes indicate the isotopically substituted molecule, $N$ is the number of atoms in the molecule, $m_i$ are the atomic weights, $M$ are the total masses of the molecules, and $I$ are the moments of inertia. This formula is considerably simplified when it is applied to vibrations within a specific symmetry class. We will see that simplification when we apply it to benzene and its fully deuterated analogue.

VII. EXPERIMENTAL APPARATUS

The chief components of the BaySpec Raman Spectrometer are: a polarized laser light source, optics for sample illumination and collection of scattered light, a polarization analyzer, a fiber-optic coupler, an optical element to disperse light of different wavelengths, a light detector,
and electronics for signal processing. (See Figure 3.) Our laser is a solid state laser tuned to emit light of 532nm wavelength, with a polarization ratio of 100:1. (A note: The power of this laser is more than enough to cause damage if the beam were ever to hit our eye. The apparatus is built to prevent this from happening as long as you use it just as instructed.) The optical components immediately following the laser include a collimating lens, a narrow band-pass line filter, and a second lens, which focuses the incident light into the sample vial. Another lens collects and re-collimates the scattered light at 90°, which then passes through a broader band-pass filter, a polarization analyzer, and a second band-pass filter. A fourth lens focuses the light onto a fiber-optic coupler, which carries the scattered light into the spectrometer. The light is dispersed into its spectral components by a transmission diffraction grating. The dispersed spectrum falls across a CCD linear array of solid state detectors, with each pixel of the array detecting the intensity of the light in a small wavelength range. Raman scattering does not shift the wavelength of the light much (typically <100nm) and the Rayleigh scattering from the material is much stronger than the Raman scattered light. Therefore the optics must be carefully designed so the diffraction grating keeps the unshifted Raleigh scattered light well away from the pixels detecting Raman scattered light.

The incident laser light is s-polarized (i.e. parallel to the rulings in the diffraction grating, and perpendicular to the scattering plane), with a polarization ratio of 100:1. Since the symmetric modes of vibration preserve the polarization state of the incident light, the intensity of the peaks for the symmetric modes of vibration change noticeably as you vary the angle of the polarization analyzer.

The appendix to this manual contains brief instructions for using the spectrometer. Detailed operating instructions for the BaySpec Raman Spectrometer can be found in the binder in the lab room.

VII. EXPERIMENTAL PROCEDURE, MEASUREMENTS, AND ANALYSIS

1. First, we will use the 991.6 ± 0.1cm⁻¹ line of C₆H₆ to determine the accuracy and precision of the instrument. We will use the entire C₆H₆ spectrum to learn how to locate peaks and how to optimize the signal-to-noise ratio of spectra. Take a spectrum of C₆H₆ using an acquisition time of 1sec, with the Spectrum Smoothing function turned off (unchecked in the System Settings menu window).

   a) Find the linear operating region of the instrument by repeating the scan at various acquisition times. Plot the ratio of the intensities of the more prominent the peaks to the peak at ~1000cm⁻¹ (the most intense peak) vs. the acquisition time. The acquisition time is the time each of the pixels of the detector is counting photons before it stops and reads out the number of photons it has detected (yes, it counts single photons). Determine the longest time at which the ratios are constant. At longer times, the pixels struck by photons from the most intense peak will saturate and give a count that is actually smaller than the number of photons incident on the pixel.
b) Next compare spectra with and without the Spectrum Smoothing function. What is happening? (The Spectrum Smoothing function displays a weighted average of several neighboring pixels, which reduces noise but sacrifices resolution.) Can you think of any situation in which you might want to trade off spectrum resolution in favor of noise reduction? Discuss which approach you think you should use in the experiment with the instructor.

c) Develop a method for determining peaks positions. Do not use the peak locator in the software. It is not clear exactly what algorithm the manufacturer uses to find peaks. Instead save the spectra into a spreadsheet and use a parabolic interpolation scheme to find the maximum. This method takes the highest intensity point of a peak \((\omega_2, I_2)\) and the points on either side \((\omega_1, I_1)\) and \((\omega_3, I_3)\), uses those points to determine a parabola going through all three points, and finds the position of the maximum of that parabola. The result is

\[
\omega_{\text{max}} = \omega_3 - \Delta\omega \left[ \frac{I_1^2 - I_2^2}{I_1^2 - 2I_2^2 + I_3^2} + \frac{1}{2} \right], \quad \text{where} \quad \Delta\omega = \omega_3 - \omega_2.
\]

Alternatively, fit the entire peak region with a Gaussian line shape using a fitting program (available on the lab computers).

d) With the acquisition time set somewhere in the linear regime, take the spectrum of \(C_6H_6\) 10 times. Find the average and standard deviation of the intensity in 3 fixed channel numbers within the highest peak (one near the top and two on the sides) as well as 2 or 3 channels in the background between peaks. Can you tell whether the detector is governed by Poisson statistics?

e) Now use your peak position-finding method to determine the average and standard deviation of the peak position near 1000 cm\(^{-1}\). What is the precision of your measurement? Does your value agree within error with the accepted value of 991.6 cm\(^{-1}\)? Is the uncertainty on the mean position the same as the width of the peak?

f) Finally try the multiple scan feature. Take a set of 10 spectra at the same settings as the previous single scans. What is the intensity axis showing? Has the signal-to-noise improved? How might this be useful in improving signal to noise in your spectra?

2. Next, we will investigate some of the vibrations in benzene \((C_6H_6)\) and the shift in frequencies as deuterium is substituted for the hydrogen. Take the spectrum of \(C_6D_6\) for various orientations of the polarization analyzer. The peaks near 3050 cm\(^{-1}\) may be hard to separate. Look carefully to see what is going on in this region. List all the peaks you detect and which are polarized. Look at the diagrams of the vibrations in Table 2. Which peaks should be polarized (i.e. which vibrations do not change the symmetry of the molecule)? Assign the polarized peaks to the correct diagrams in the table using the fact that it takes more energy to stretch the C-H bonds than to stretch the conjugated C=C bonds in the ring.

Now perform the same exercise with the perdeuterated benzene \((C_6D_6)\). Again identify the polarized modes and note the frequency shifts from the H compound to the D compound. You can easily see that even motions dominated by movement of only the carbons are affected by the change in mass of the H to D. Use your measured frequencies for the two polarized modes (which both belong to the same symmetry class) to test the model for the isotope effect discussed earlier. (You are testing whether, within your measurement accuracy, the only effect is a change
in effective mass of the vibrating entity or whether, contrary to the model, the force constants have changed as well.) For this set of vibrations, Eq.15 simplifies to

\[
\frac{\omega_1 \omega_2'}{\omega_1' \omega_2} = \left( \frac{m_H}{m_D} \right)^{\frac{1}{2}}
\]  

(16)

3. Now we will begin our exploration of the force models for CCl$_4$. First, identify the eigenmodes belonging to each of the eigenfrequencies (peaks) you observe in the Raman spectrum of CCl$_4$. Table 1 is a list of the eigenmodes of a tetrahedral molecule such as CCl$_4$.

a) To identify the bands, we must find their degree of polarization. Which lines are polarized and which depolarized? Assign the fundamentals of CCl$_4$ using the fact that the $\omega_1$ and $\omega_3$ CCl$_4$ stretching motions are expected to occur at higher frequencies than the $\omega_2$ and $\omega_4$ CCl$_4$ bending motions. The depolarization ratios can be used to determine which of the two high-frequency bands should be assigned as $\omega_1$. To decide on the $\omega_2$ and $\omega_4$ assignments, use the fact that the only infrared band observed below 600 cm$^{-1}$ is a feature near 300 cm$^{-1}$. See the last row of Table 1.

The $\omega_3$ vibration will be observed as a doublet due to what is known as Fermi-resonance splitting, which can occur if a higher harmonic or overtone (noi) or combination ($\omega_i + \omega_j$) energy level happens to fall near the energy level of a fundamental vibration and if both levels have the same symmetry. The $\omega_3$ frequency can be taken as the mean of the doublet peaks. From your values of $\omega_1$, $\omega_2$, and $\omega_4$, deduce which combination band is involved in the Fermi-resonance with $\omega_3$.

b) Think about the isotope shift for CCl$_4$. Since there is only one polarized mode, applying equation 15 is simple:

\[
\frac{\omega_1'}{\omega_1} = \left( \frac{m_{Cl}}{m_{Cl'}} \right)^{\frac{1}{2}}
\]  

(17)

look up the common isotopes of Cl and calculate the expected isotope shift. Is the observed linewidth in the $\omega_1$ line, large enough to account for these shifts? Why don't you see the individual peaks?

c) We now want to test the valence force model. Using your measurement of $\omega_1$ and $\omega_2$, calculate the valence force constants $k$ and $k_\delta / \ell^2$ from Eqs.12-a and 12-b. Use those constants and the measured values of $\omega_3$ and $\omega_4$ and compare the values of the left and right hand sides of Eqs.12-c and 12-d. Do they agree within uncertainties?

d) In a similar fashion, examine the central force and group theory models, each has more equations than unknowns. Which of three models best describes the data? Does the precision and accuracy of your experiments allow you to see deviations from all the models?
Appendix: BaySpec 532 Raman Spectrometer
Basic Operating Instructions
Barry B. Luokkala
7 January 2014

Laser Safety

CAUTION! Exposure to direct or specularly reflected laser light may cause serious damage to your eyes. Do not look directly into the sample holder.

Turn on the computer (if it isn’t already turned on) and logon

- Account: user
- Password: physics
- Wait for all the usual system software to load before turning on the spectrometer or opening the acquisition software

Turn on BaySpec 532 Raman Spectrometer (use the switch on the power strip)

- Wait for the spectrometer to warm up before taking spectra (about 10-15 minutes)
- Alternatively, you may wish to investigate the effect of warm-up time, to find out exactly how long it takes before repeated spectra do not change significantly.

Open Spec 20/20 data acquisition program

- Click the Spec 2020 shortcut icon on the desktop of the computer

Set the desired acquisition time

- Click “Settings” in the upper left corner of the window.
- Choose “System settings” from the drop-down menu. (Alternatively, you can just click on the camera-screwdriver icon near the upper left.)
- Type in the desired acquisition time, in units of microseconds, milliseconds or seconds.
  (Note: despite what the window says, the maximum time is 60 seconds, not 600.)

Taking a Background Spectrum

- Before acquiring a spectrum from any of the samples, you must first acquire a background spectrum. The apparatus subtracts background from the acquired spectrum before displaying the results, and will not work if a background spectrum has not already been taken.
- Gently unscrew the sample chamber cover.
- Insert a blank glass vial into the chamber and carefully replace the screw-cover (turn gently to avoid cross-threading and permanent damage to the chamber).
• Click “Acquisition” in the upper left corner of the window.
• Click “Acquire Background”
• (The progress of the acquisition of a long scan can be monitored by observing the blue bar in the lower right of the window.)
• When the scan is completed the background spectrum will be displayed. It should appear to be more-or-less random noise.

Taking Raman Spectra
• Insert the desired sample into the spectrometer sample chamber and carefully replace the screw-cover.
• Click “Acquisition”
• Click “Snapshot One Spectrum”
• Monitor progress of scan by observing the blue bar in lower right of window.
• When scan is complete, the system will subtract background and display the net spectrum.

Polarization Analysis
The polarization analyzer, located between the sample chamber and the fiber-optic coupler, can be used to determine which of the Raman-scattered peaks have preserved the polarization state of the incident laser light, and which are “depolarized.” However, the exact calibration of this polarizer is unknown. That is to say, the angle readings do not necessarily refer to the polarization direction of the laser. You can rotate the polarization analyzer through a sufficient range of angles to determine which angle most completely cuts out the polarized peaks from the spectrum.
References


4) E.B. Wilson, et. al., op cit. , pp 47ff.


6) E.B. Wilson, et. al., op cit. , pp 182.

7) E.B. Wilson, et. al., op. cit., pp 131.
Figure 1: The vibrational ground state \((v=0)\) and an excited state \((v=1)\) are separated by an energy corresponding to vibrational frequency \(\nu_v\). Infrared absorption connects the states directly, while Raman and Rayleigh scattering are indirect.

\[
\begin{align*}
\nu_{v=0} & \quad \text{IR Absorption} \\
\nu_{v=1} & \quad \text{Anti-Stokes} \\
\nu_{v=0} & \quad \text{Rayleigh} \\
\nu_{v=0} & \quad \text{Stokes} \\
\nu_v & \quad \text{Raman} \\
\end{align*}
\]

Figure 2: Tetrahedral \(XY_4\) Molecule (From Ref. 5, p165.). The length of one edge of the tetrahedron is \(t\).
Figure 3: Schematic of the BaySpec Raman spectrometer. The instrument consists of two separate pieces connected by a fiber-optic coupler (FC). The light source is a 532 nm laser, with polarization ratio 100:1. A collimating lens (L1) directs the laser light through a narrow band-pass filter (F1). The second lens (L2) focuses the incident light onto the sample (S). Scattered light from the sample is collected by another collimating lens (L3), and passed through a broad-band filter (F2), a polarization analyzer (P), and a second broad-band filter (F3). The lens L4 focuses the scattered light onto the fiber-optic coupler (FC), through which the scattered light is transmitted into the spectrometer chamber. The lens L5 directs the light through a diffraction grating (G), which resolves the light into a Raman spectrum, recorded on a CCD array.
Table 1: (From Ref. [1].) Read the caption carefully to see which types of vibrations are found in the various categories of molecules, and by which means (IR and/or Raman transitions) they can be excited.

| Type | Point group | Vibrational modes, symmetries, infrared-Raman activities, and Raman polarizations
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>B—A—B</td>
<td>$D_{oh}$</td>
<td>$\nu_1$ $\Sigma_g^+$ (IR), $\Sigma_u^+$ (IR) $\Pi_u$ (IR), $\Sigma_u^+$ (IR)</td>
</tr>
<tr>
<td>B—A—B</td>
<td>$C_{2v}$</td>
<td>$\nu_1$ $A_1$ (IR, Rp) $\nu_2$ $A_1$ (IR, Rp) $\nu_3$ $B_1$ (IR, Rd $p$)</td>
</tr>
<tr>
<td>B—A—B</td>
<td>$D_{3h}$</td>
<td>$\nu_1$ $A_1^+$ (IR) $\nu_2$ $A_2^+$ (IR) $\nu_3$ $E'$ (IR, Rp) $\nu_4$ $E'$ (IR, Rp)</td>
</tr>
<tr>
<td>B—B</td>
<td>$C_{3v}$</td>
<td>$\nu_1$ $A_1$ (IR, Rp) $\nu_2$ $A_1$ (IR, Rp) $\nu_3$ $E$ (IR, Rp) $\nu_4$ $E$ (IR, Rp)</td>
</tr>
<tr>
<td>B—B</td>
<td>$T_d$</td>
<td>$\nu_1$ $A_1$ (Rp) $\nu_2$ $E$ (Rdp) $\nu_3$ $F_2$ (IR, Rdp) $\nu_4$ $F_2$ (IR, Rdp)</td>
</tr>
</tbody>
</table>

*a) Only one of two $E$ or three $F$ modes in the respective degenerate sets is shown for the $\text{AB}_2$ and $\text{AB}_4$ cases. Each mode of a degenerate set oscillates at the same frequency, and the description of the nuclear motion associated with each component of a degenerate mode is somewhat arbitrary.*

*b) Rp indicates an allowed Raman band that is polarized; Rdp indicates an allowed depolarized Raman band.*
Table 2: The modes of vibration of the benzene molecule. The notation refers to the so-called points groups to which the various vibrations belong.