Lab Week 2 – Module β_2

Temperature and Vibration

OBJECTIVES

- ✓ Introduce normal modes of vibration
- ✓ Introduce IR and Raman spectroscopy
- ✓ Explore the relationship between temperature and vibrational spectra

Tasks

1) Obtain the Raman spectrum for Si at different temperatures
2) Determine the instrument prefactor γ
3) Compare the temperatures computed from Raman data to measured T values

Introduction

The scope of this laboratory experiment is to understand excitations in molecules and solids. It is known that solids are constantly vibrating because of the thermal energy that they possess and because of interactions with external energy fronts (e.g. electromagnetic and sound waves).

Also, remember that in quantum mechanics we have already seen that a particle in a potential cannot be at rest, thus particles are always oscillating.

All solids can be thought as a series of balls (the atoms) kept together with springs (the chemical bonds). The mass of the balls is a simple function of the chemical nature of the atoms that compose the material, while the spring constant depends simply on the bond strength. This assumption not only allows for a substantial simplification of the analysis of vibration in solids but also helps with the understanding of the results of vibrational spectroscopic methods.

This laboratory will use the difference in population of vibrational states of solids to determine temperature, employing a technique known as Raman spectroscopy.

Normal Modes of Vibration

In order to understand vibrations in solids it is important to first understand vibrations in simpler systems such as a series of masses held together with springs. In particular the concept of normal modes has central importance in the analysis of all the problems that deal with molecular dynamics.

Definition:
Normal modes: are the vibrational modes that decouple the energy problem, i.e. they diagonalize the Hamiltonian of the system

Let's see what this means by considering a system of three identical masses (m) kept together by four springs of constant *k* as shown in figure 1.

In order to solve the classical problem of the oscillations of these masses the first thing to do is to set a system of coordinates that conveniently describes the system. In this
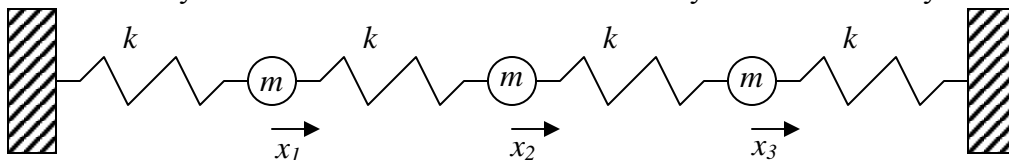

Figure 1. Schematic drawing of a series of equal masses held together by equal massless springs. The boxes at the extremes represent unmovable infinite masses.

particular case we will assume that the masses can move only along the mass-mass direction, that is, we will consider only the one dimensional problem. As shown in figure 1 the first choice that we can make is that of the "internal coordinates", a series of coordinates x_i that describes the displacement of masses from their rest position.

Classically this system can be solved by first writing its Hamiltonian as a function of the three internal coordinates (x_1, x_2, x_3) and of the three momenta of the particles (p_1, p_2, p_3)

$$H = T + V = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{p_3^2}{2m} + \frac{1}{2}kx_1^2 + \frac{1}{2}k(x_2 - x_1)^2 + \frac{1}{2}k(x_3 - x_2)^2 + \frac{1}{2}kx_3^2 \quad (1)$$

where T and V are the total kinetic and potential energy of the system.

A complete solution of the system is then determined by solving the six differential equations

$$\begin{cases} \dfrac{\partial H}{\partial p_i} = \dfrac{dx_i}{dt} \\ \dfrac{\partial H}{\partial x_i} = -\dfrac{dp_i}{dt} \end{cases} \quad with \ \ i = 1, 2, \ and \ 3 \qquad (2)$$

It should be evident that all of these equations will depend on at least 4 of the system variables.

It can be shown that there always exists a linear combination of the internal coordinates called normal coordinates that generates a Hamiltonian that is simply the sum of the three independent Hamiltonians. A consequence of this is that the solution of the vibrational problem of the system becomes the solution of three simpler and independent problems.

Each solution is a normal mode of vibration that is a vibration that happens at a given energy.

In this particular problem by introducing the following variables

$$\begin{cases} X = x_1 - x_3 \\ Y = x_1 - \sqrt{2} * x_2 + x_3 \\ Z = x_1 + \sqrt{2} * x_2 + x_3 \\ P_1 = p_1 - p_3 \\ P_2 = p_1 - \sqrt{2} * p_2 + p_3 \\ P_3 = p_1 + \sqrt{2} * p_2 + p_3 \end{cases} \qquad (3)$$

it can be shown that the Hamiltonian becomes:

$$H = \frac{P_x}{2m} + \frac{P_y}{2m} + \frac{P_z}{2m} + \frac{1}{2}kX^2 + \frac{1}{2}kY^2 + \frac{1}{2}kZ^2 =$$
$$= \left(\frac{P_x}{2m} + \frac{1}{2}kX^2\right) + \left(\frac{P_y}{2m} + \frac{1}{2}kY^2\right) + \left(\frac{P_z}{2m} + \frac{1}{2}kZ^2\right) = H_x + H_y + H_z \qquad (4)$$

Each Hamiltonian can be solved independently and indeed the whole system can be solved by solving the three independent systems.

$$\begin{cases} \dfrac{\partial H}{\partial p_x} = \dfrac{dX}{dt} \\ \dfrac{\partial H}{\partial X} = -\dfrac{dp_x}{dt} \end{cases} ; \quad \begin{cases} \dfrac{\partial H}{\partial p_y} = \dfrac{dY}{dt} \\ \dfrac{\partial H}{\partial Y} = -\dfrac{dp_y}{dt} \end{cases} ; \quad \begin{cases} \dfrac{\partial H}{\partial p_z} = \dfrac{dZ}{dt} \\ \dfrac{\partial H}{\partial Z} = -\dfrac{dp_z}{dt} \end{cases} \qquad (5)$$

Each system will be solved by an equation of the type

$$X = C\exp(i\nu t) \qquad\qquad (6)$$

where C is a real number that specifies the vibrational amplitude of the normal mode and ν is the frequency of oscillation of the normal mode.

To summarize: normal modes are those particular vibrational modes of a system that decouple the energy problem, that is, they allow the separation of the Hamiltonian into independent Hamiltonians. (This property in linear algebra can be called orthogonality).

Additionally, it can be showed that any system vibration is always a linear combination of normal modes.

This classical derivation of the normal modes can be extended trivially to quantum mechanics by simply changing the classical energy expression with the quantum mechanics operators. Even in that case it can be shown that the normal modes are the ones that allow for the separation of the Hamiltonian of the system into independent Hamiltonians.

In quantum mechanics we know that frequency and energy are related by:

$$E = h\nu = hc\omega \qquad\qquad (7)$$

where ν is the frequency (expressed in s^{-1}), while ω is the wavenumber (generally expressed in cm^{-1}), h is Planck's constant (6.626×10^{-34}J s) and c is the speed of light in vacuum (2.99792458×10^{10} cm/s).

Thus each normal mode has its own energy.

Molecular Dynamics

A molecule can be seen as an isolated system of atoms (masses) held together by forces around their equilibrium position.

Let's first look at a diatomic molecule. The energy that keeps the molecule together is shaped as illustrated in figure 2
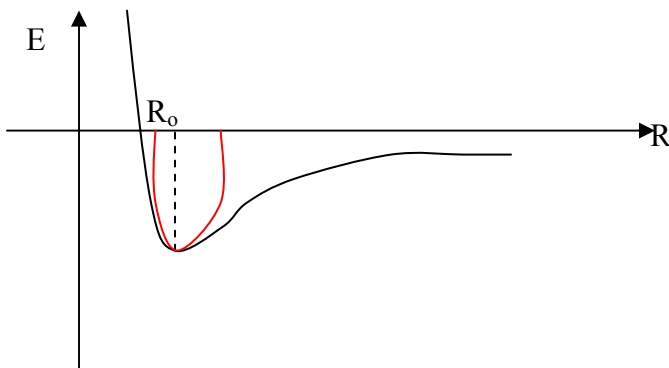

Figure 2. Schematic drawing of an energy-position plot for a diatomic molecule. R represents the distance between the atoms. As shown from the red line near the equilibrium position (R_o) the energy barrier can always be approximated by a parabola and thus the bond can be treated like a spring.

Around the equilibrium position the energy increases as the square of the displacement, that is, the energy is that of a spring (or of a system of springs) that holds the atom in place. As seen in 3.012 a particle in a square potential (linear harmonic oscillator) has quantized energy levels evenly spaced. These energy levels are the vibrational levels of the molecule. Their frequency of oscillation is determined by the difference in energy between the vibrational states as shown in figure 3.
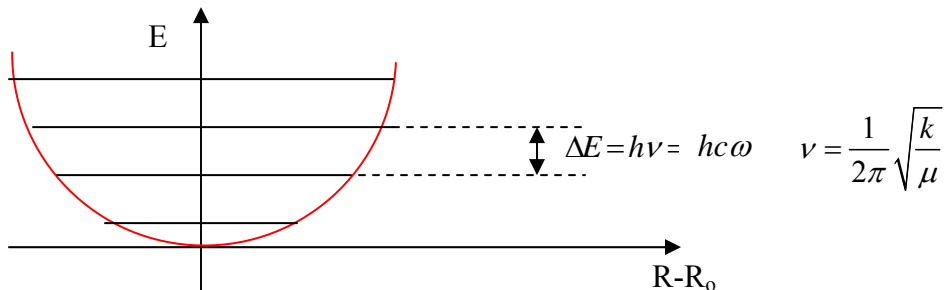

$$\Delta E = h\nu = hc\omega \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Figure 3 Distribution of the vibrational energy levels in a linear harmonic oscillator. ν is the frequency expressed in s^{-1} while ω is the wavenumber expressed in cm^{-1}. μ is the effective mass, while k is the spring constant

Table 1 Stretching frequencies for some diatomic molecules

	μ (amu)	k (mdyne/Å)	ω (cm^{-1})
H_2	0.5	5.2	4160
D_2	1.0	5.2	2940
HF	0.95	8.8	3950
HCl	0.97	4.8	2885
HBr	1.00	3.9	2559
HI	1.00	2.9	2230

A polyatomic molecule composed of N atoms has 3N degrees of freedom of which 6[1] are the 3 translations and the 3 rotations of the molecule as a whole and thus do not change the relative distances between the molecules. The other 3N-6 are vibrational degrees of freedom of the molecules. For each degree of freedom there is a normal mode of vibration. While the energy-position plot for a diatomic molecule is a two dimensional plot, the same plot for a polyatomic molecule becomes a (3N-6)+1 dimensional surface of a very complex shape. If this surface is sectioned by a plane that follows the displacement along a normal mode then (at least around the equilibrium position) the plot will look exactly like the one in fig. 3. This is the beauty of normal mode formalism.

Normal modes arise from stretching bonds between atoms (some examples are given in Table 1), as well as bending motions involving multiple atoms. Some normal modes are localized mostly on a few atoms and consequently are used to detect those chemical bonds or groups, while others are distributed along the whole molecule and thus can be used to extract information about the whole molecule.

Raman Spectroscopy

There are 2 main ways for probing the vibrations of a molecule or a solid: infrared spectroscopy and Raman spectroscopy. In the case of infrared (IR) spectroscopy an electromagnetic wave (photon) of energy comparable to that of the vibrational mode is sent to the sample and its absorption is probed. In the case of Raman spectroscopy an electro magnetic wave (photon) of energy much higher then the vibrational energy is sent to the sample. The particle that is in one of the vibrational states gets excited and goes into a virtual state from which it immediately decays back, emitting another photon. In most cases the particle goes back into its original state (known as Rayleigh or elastic scattering) but in rare cases the particles will undergo an inelastic collision with the incident photon (energy is transferred) and decay to a different vibrational state. In such cases the difference in energy between the incoming and the emitted photons equals the vibrational energy. When the particle starts from the first vibrational state and decays to the second vibrational state, gaining energy, it is known as a Stokes scattering event.

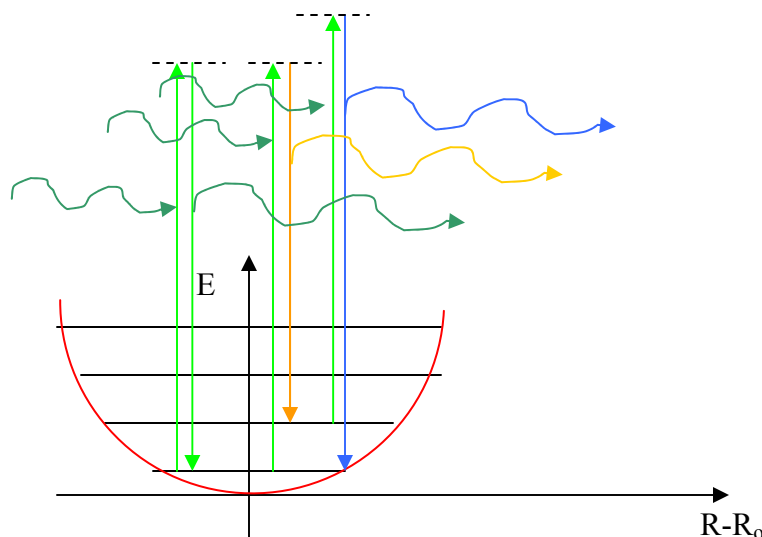[1] 5 in the case of linear molecules.

Figure 4 Schematic drawing of the three possible off-resonance interactions between an electro-magnetic wave and a molecule. In the case of Rayleigh scattering a photon gets absorbed and immediately reemitted without gaining or losing energy (left). In the case of anti-Stokes scattering a photon excites a particle that is in the second vibrational state. The particle then decays to the first vibrational state, losing energy (right). The opposite happens in Stokes scattering (middle).

When the particle starts from the second vibrational state and decays to the first vibrational state then we have an anti-Stokes scattering event.

In the case of IR spectroscopy the interaction between the molecule and the electromagnetic wave can happen only if there is a change in molecular dipole during the vibration. For example, let's consider the molecule of chlorine (Cl_2). Stretching this molecule does not change its dipole (that remains zero) thus it is not possible to excite this vibrational mode with an infrared photon. In the case of acid chloride (HCl), stretching this molecule changes its dipole. Thus, if irradiated with a photon of the right energy this molecule will absorb it.

In Raman spectroscopy the situation is more complex and a vibrational mode can be excited only if the polarizability of the molecule changes. The polarizability is *the ability of a molecule to form a dipole in the presence of an applied electro-magnetic field*. It is directly related to the ability of a molecule to freely move its electrons. If we again consider the case of a chlorine molecule, stretching the electron cloud that surrounds the molecule changes its shape and the further the two atoms are from each other, the more the electrons acquire mobility and consequently polarizability. This vibrational mode can thus be detected in Raman spectroscopy, making this a complementary technique to IR.

We can understand the origin of the Raman effect by considering the interaction of the incident radiation

$$E = E_0 \cos 2\pi \nu t \qquad\qquad (8)$$

with a bond having a characteristic vibrational frequency ν_{vib} and a bond length x given by [1]:

$$x = x_{eq} + x(t) = x_{eq} + x_{max} \cos 2\pi \nu_{vib} t \qquad (9)$$

The dipole moment induced by the incident photon is given by:

$$\mu_{ind}(t) = \alpha E \qquad (10)$$

where α, the polarizability, depends on the bond length [1]:

$$\alpha(x) = \alpha(x_{eq}) + \left(\frac{d\alpha}{dx}\right)_{x=x_{eq}} (x - x_{eq}) + \ldots \qquad (11)$$

Substituting equations 8, 9 and 11 into eq. 10, and simplifying gives [1]:

$$\mu_{ind}(t) = \alpha(x_{eq})E_0 \cos 2\pi \nu t + \frac{1}{2}\left(\frac{d\alpha}{dx}\right)_{x=x_{eq}} x_{max} E_0 [\cos 2\pi(\nu + \nu_{vib})t + \cos 2\pi(\nu - \nu_{vib})t] \quad (12)$$

The second term in this expression shows that the induced dipole moment will radiate photons of energy lower than the incident photons, with frequency (ν - ν_{vib}), corresponding to Stokes scattering, and those of energy higher than the incident photons, with frequency ($\nu + \nu_{vib}$), corresponding to anti-Stokes scattering, as long as there is a change in the polarizability, i.e., $d\alpha/dx$ is nonzero.

The anti-Stokes scattering is found to be much weaker than the Stokes scattering, because of the difference in populations of the starting vibrational states. In Raman experiments, therefore, one typically measures the Stokes scattering. The inherently weak nature of Raman scattering requires the use of a laser as the excitation source.

The Raman peak intensities are given by:

$$I^{anti-Stokes} = (\nu + \nu_{vib})^4 N_\nu^2 a(\nu) \qquad (13)$$

$$I^{Stokes} = (\nu - \nu_{vib})^4 N_\nu^1 a(\nu) \qquad (14)$$

where N_ν^i is the starting population of the ith vibrational state and a(ν) is the scattering cross-section. The ratio of the populations is given by Boltzmann statistics [1]:

$$\frac{N_\nu^2}{N_\nu^1} = \exp\left(\frac{-\Delta E}{k_B T}\right) = \exp\left(\frac{-h\nu_{vib}}{k_B T}\right) = \exp\left(\frac{-hc\omega_{vib}}{k_B T}\right) = \exp\left(\frac{-1.4388\omega_{vib}(cm^{-1})}{T(K)}\right) \qquad (15)$$

where k_B is Boltzmann's constant (1.380658×10^{-23}J K^{-1}). The intensity ratio of the anti-Stokes and Stokes lines gives:

$$\frac{I^{anti-Stokes}}{I^{Stokes}} = \frac{\left(\omega+\omega_{vib}\right)^4}{\left(\omega-\omega_{vib}\right)^4} \exp\left(\frac{-hc\omega_{vib}}{k_B T}\right) \qquad (16)$$

For an actual experiment, this expression must be modified by an instrumental prefactor γ that corrects for differences in detection efficiencies for the two photons of interest [2]:

$$\frac{I^{anti-Stokes}}{I^{Stokes}} = \gamma\frac{\left(\omega+\omega_{vib}\right)^4}{\left(\omega-\omega_{vib}\right)^4} \exp\left(\frac{-hc\omega_{vib}}{k_B T}\right) \qquad (17)$$

Taking the log of both sides of eq. 17 and rearranging gives:

$$T = \frac{-hc\omega_{vib}}{k_B}\left(\ln\left[\frac{1}{\gamma}\frac{I^{anti-Stokes}}{I^{Stokes}}\frac{\left(\omega-\omega_{vib}\right)^4}{\left(\omega+\omega_{vib}\right)^4}\right]\right)^{-1} \qquad (18)$$

Equation 18 shows how Raman spectrometers can be used as non invasive thermometers [2,3], if one measures the ratio of intensities of the anti-Stokes and Stokes lines and has knowledge of the instrument prefactor.

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