IR spectroscopy

which has become so useful in identification, estimation, and structure determination of compounds draws its strength from being able to identify the various vibrational modes of a molecule. A complete description of these vibrational normal modes, their properties and their relationship with the molecular structure is the subject of this article.

Introduction

We are familiar with resolving a translational vector into its three components along the x-, y-, and z- axes. Similarly a rotational motion can also be resolved into its components. Likewise the same is true for vibrational motion. The complex vibration that a molecule is making is really a superposition of a number of much simpler basic vibrations called "normal modes". Before we take up any further description of "normal modes" it is necessary to discuss the degrees of freedom.

Normal Modes

Normal modes are used to describe the different vibrational motions in molecules. Each mode can be characterized by a different type of motion and each mode has a certain symmetry associated with it. Group theory is a useful tool in order to determine what symmetries the normal modes contain and predict if these modes are IR and/or Raman active. Consequently, IR and Raman spectroscopy is often used for vibrational spectra

In general, a normal mode is an independent motion of atoms in a molecule that occurs without causing movement to any of the other modes. Normal modes, as implied by their name, are orthogonal to each other. In order to discuss the quantum-mechanical equations that govern molecular vibrations it is convenient to convert Cartesian coordinates into so called normal coordinates. Vibrations in polyatomic molecules are represented by these normal coordinates.

There exists an important fact about normal coordinates. Each of these coordinates belongs to an irreducible representation of the point the molecule under investigation. Vibrational wavefunctions associated with vibrational energy levels share this property as well. The normal coordinates and the vibration wavefunction can be categorized further according to the point group they belong to. From the character table predictions can be made for which symmetries can exist. The irreducible representation offers insight into the IR and/or Raman activity of the molecule in question.

Degrees of Freedom

Degree of freedom is the number of variables required to describe the motion of a particle completely. For an atom moving in 3-dimensional space, three coordinates are adequate so its degree of freedom is three. 3N where N represents the number of nuclei present in the molecule is the total number of coordinates needed to describe the location of a molecule in 3D-space. 3N is most often referred to as the total number of degrees of freedom of the molecule being investigated. The total number of degrees of freedom, can be divided into:

- *3 coordinates to describe the translational motion around the center of mass; these coordinates are called the translational degrees of freedom*
- *3 coordinates to describe the rotational motion in non-linear molecules; for linear molecules only 2 coordinates are required; these coordinates are called the rotational degrees of freedom*
- *the remaining coordinates are used to describe vibrational motion; a non-linear molecule has 3N - 6 vibrational degrees of freedom whereas a linear molecule has 3N -5 degrees of freedom.*

Table 1*: Overview of degrees of freedom*

•	*Total Degree of Freedom*	*Translational degrees of freedom*	*Rotational degrees of freedom*	*Vibrational degrees of freedom*
Nonlinear Molecules	*3N*	*3*	*3*	*3N* ***-6***
Linear Molecules	*3N*	*3*	*2*	*3N - 5*

Example1: Ethane, C2H6 has eight atoms (N=8) and is a nonlinear molecule so of the 3N=24 degrees of freedom, three are translational and three are rotational. The remaining 18 degrees of freedom are internal (vibrational). This is consistent with:

$$3N-6=3(8)-6=18$$

Example2: Carbon Dioxide, CO2 has three atoms (N=3)and is a linear molecule so of the 3N=9 degrees of freedom, three are translational and two are rotational. The remaining 4 degrees of freedom are vibrational.

Summary of Vibrational modes:

1. *A normal mode is a molecular vibration where some or all atoms vibrate together with the same frequency in a defined manner.*
2. *Normal modes are basic vibrations in terms of which any other vibration is derived by superposing suitable modes in the required proportion.*
3. *On the other hand, no normal mode is expressible in terms of any other normal mode. Each one is pure and has no component of any other normal mode (i.e. they are orthogonal to each other). Mathematically, the integral is:*

   $$\int \psi A \psi B dR = 0 \int \psi \qquad \text{(integration is done over the entire space)}$$

4. *The required number of "normal modes" is equal to the vibrational degree of freedom available so the number of modes for a nonlinear molecule is (3N−6) and that for a linear molecule is (3N−5).*
5. *Each mode has a definite frequency of vibration. Sometimes 2 or 3 modes may have the same frequency but that does not change the fact that they are distinct modes; these modes are called degenerate.*

6. *Sometimes some modes are not IR active but they exist all the same. We shall revert back to the problem of IR activity and selection rules later.*

The number of vibrational normal modes can be determined for any molecule from the formula given above.

For a diatomic molecule, $N = 2$ *so the number of modes is* $3\times2-5=1$.

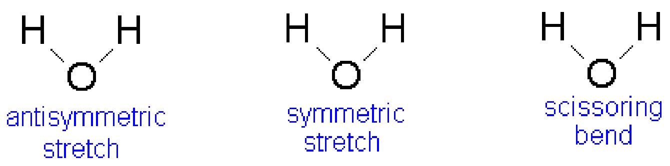
For a triatomic linear molecule (CO_2*), it is* $3\times3-5=4$

and triatomic nonlinear molecule (H_2O*), it is* $3\times3-6=3$

and so on.

To illustrate thee examples by figures as follow:

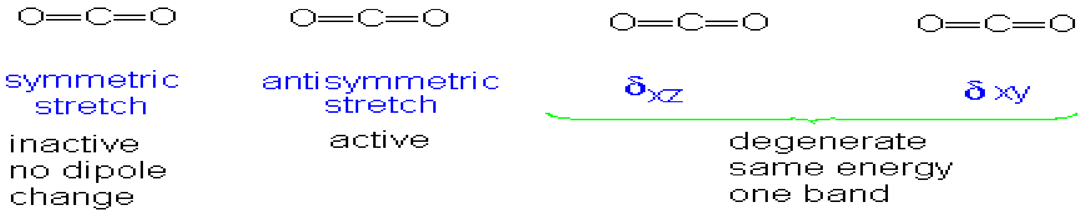
H_2O



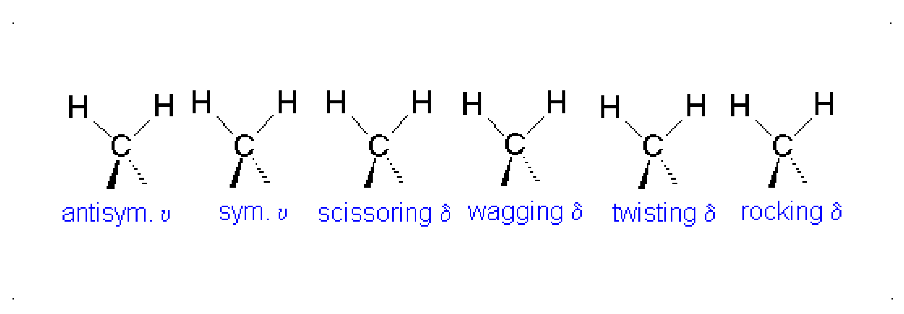
1. *The Symmetric Stretch (Example shown is an* H_2O *molecule at 3685* cm^{-1}*)*
2. *The Asymmetric Stretch (Example shown is an* H_2O *molecule at 3506* cm^{-1}*)*
3. *Bend (Example shown is an* H_2O *molecule at 1885* cm^{-1}*)*

A linear molecule will have another bend in a different plane that is degenerate or has the same energy. This accounts for the extra vibrational mode.

CO_2



METHYLENE GROUP



It is important to note that there are many different kinds of bends, but due to the limits of a 2-dimensional surface it is not possible to show the other ones.

The frequency of these vibrations depend on the inter atomic binding energy which determines the force needed to stretch or compress a bond. In the next section, We discuss this problem. The determination of the nature of the relative displacement of each atom with respect to each other is more complicated and beyond the scope of this article. However, such motion can be seen in some common molecules as shown below.

Energetics

A diatomic molecule, as seen in Figure 1, contains two atoms, which can either be composed of the same or different elements. It is easier to focus on these types of molecules when analyzing and calculating vibrational frequencies because they are simpler systems than polyatomic molecules. Whether or not the diatomic consists of the same or different elements, a diatomic molecule will have only one vibrational frequency. This singular normal mode is because of the diatomic's linear symmetry, so the only vibration possible occurs along the bond connecting the two atoms.

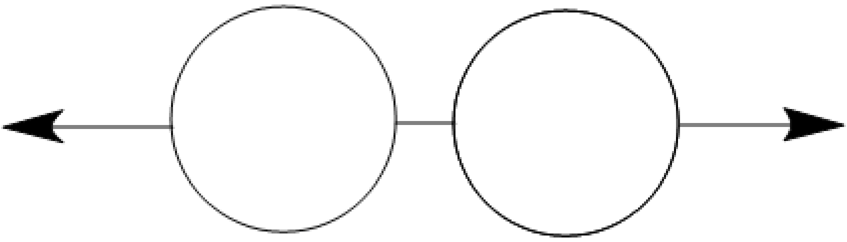


Figure 1: Diagram of a diatomic molecule with the only possible vibration it can undergo.

For studying the energetics of molecular vibration we take the simplest example, a diatomic heteronuclear molecule AB. Homonuclear molecules are not IR active so they are not a good example to select. Let the respective masses of atoms A and B be mA and mB.

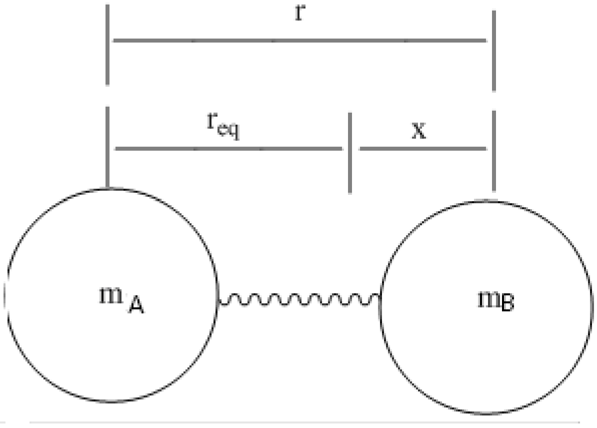


Figure 2: Representation of a diatomic molecule as masses attached by a spring separated by an equilibrium distance of r_{eq}*.*

So the reduced mass μAB *is given by:*

$$\mu_{AB}=m_A m_B/m_A+m_B \qquad (1)$$

The equilibrium internuclear distance is denoted by req. However as a result of molecular vibrations, the internuclear distance is continuously changing; let this distance be called r(t). Let $x(t)= r(t)-req$*. When x is non-zero, a restoring force F exists which tries to bring the molecule back to x=0, that is equilibrium. For small displacements this force can be taken to be proportional to x (Hook's law):*

$$F=-kx \qquad (2)$$

where k is the force constant.

The negative sign arises from the fact that the force acts in the direction opposite to x. This is indeed a case of Simple Harmonic Motion where the following well known relations hold.

$$x(t)=A\sin(2\pi vt) \qquad (3)$$

$$v=(1/2\pi)(k/\mu_{AB})^{1/2} \qquad (4)$$

The potential energy is given by

$$V(x)=\frac{1}{2}kx^2 \qquad (5)$$

The total energy E (Kinetic+Potential) is obtained by solving the Schrödinger equation.

A set of wave functions ψn *and the corresponding Eigenvalues* E_n *are obtained.* $En=(n+(1/2))hv$ *where n is an integer (-1,0,1,2 etc.). The energy is quantized, the levels are equally spaced, the lowest energy is (1/2)hv, and the spacing between adjacent levels is hv .*

Interaction with Electromagnetic Radiation

As show above, the energy difference between adjacent vibrational energy levels is $h\nu_{vibration}$. On the other hand, the photon energy is $h\nu_{photon}$. Energy conservation requires that the first condition for photon absorption be,

$H\,\nu_{vibration} = h\,\nu_{photon}$ or $\nu_{vibration} = \nu_{photon}$.

Such photons are in IR region of the electromagnetic spectrum. In addition, two more conditions must be met.

1. For absorption of electromagnetic radiation, the dipole moment of the molecule must change with increasing internuclear separation resulting from the vibration (i.e, $d\mu/dD \neq 0$).
2. The probability of a transition from one state to another is large if one of the state is odd and another even. This is possible if $n_{final} - n_{initial} = +1$ (for absorption). At room temperature, modes are predominantly in energy state $n = 0$, so this transition is from $n = 0$ to $n = 1$, and $\Delta E = h\nu$.

In diagnosis , the spectroscopy in the IR region can determine the frequency and intensity of absorption. These frequencies are generally specific for a specific bonds such as c-c, c(double bond)c, c(triple bond)c, c-o, c(double bond)o, etc. So the IR absorption data is very useful in structure determination. The intensity depends on the concentration of the resposble spec. So it is useful for quantitative estimation and for identification.

EXAMPLES:

Find the number of vibrational modes for the following molecules: NH3, C6H6, C10H8, CH4, C2H2 (linear).

1. State which of the following vibrations are IR active: N_2, CO, CO_2 (stretching), HCl.
2. Calculate the vibrational frequency of CO given the following data: mass of C = 12.01 amu, mass of O = 16 amu, the force constant $k=1.86\times10^{3} kg\cdot s^{-2}$.
3. Calculate the vibrational energy in Joules per mole of a normal mode in question 3, in its ground state of $n=0$.
4. Assuming the force constant to be the same for $H_2O$and D_2O. A normal mode for H_2O is at $3650 cm^{-1}$. Do you expect the corresponding D_2O wave number to be higher or lower?

Answers

1.) $NH_3 = 6$

$C_6H_6 = 30$

$C_{10}H_8 = 48$

$CH_4 = 9$

$C_2H_2 = 7$

2.) N_2 IR inactive

$C0$ active

$C0_2$ (stretching) – inactive

HCl active

3.) $\mu_{AB} = m_A m_B/(m_A+m_B) = 11.395x10^{-27}$

$v = (1/2\pi)(k/m_{AB})^{.5} = 2143.3\ cm^{-1}$

4.) Energy of the mode for $n = 0$

$E_0 = (1/2)hv^{\cdot} = 2.13x10^{-20}$

Energy per mole = $2.13x10^{-20}x6.022x10^{23}$ = 12.8KJ/mole

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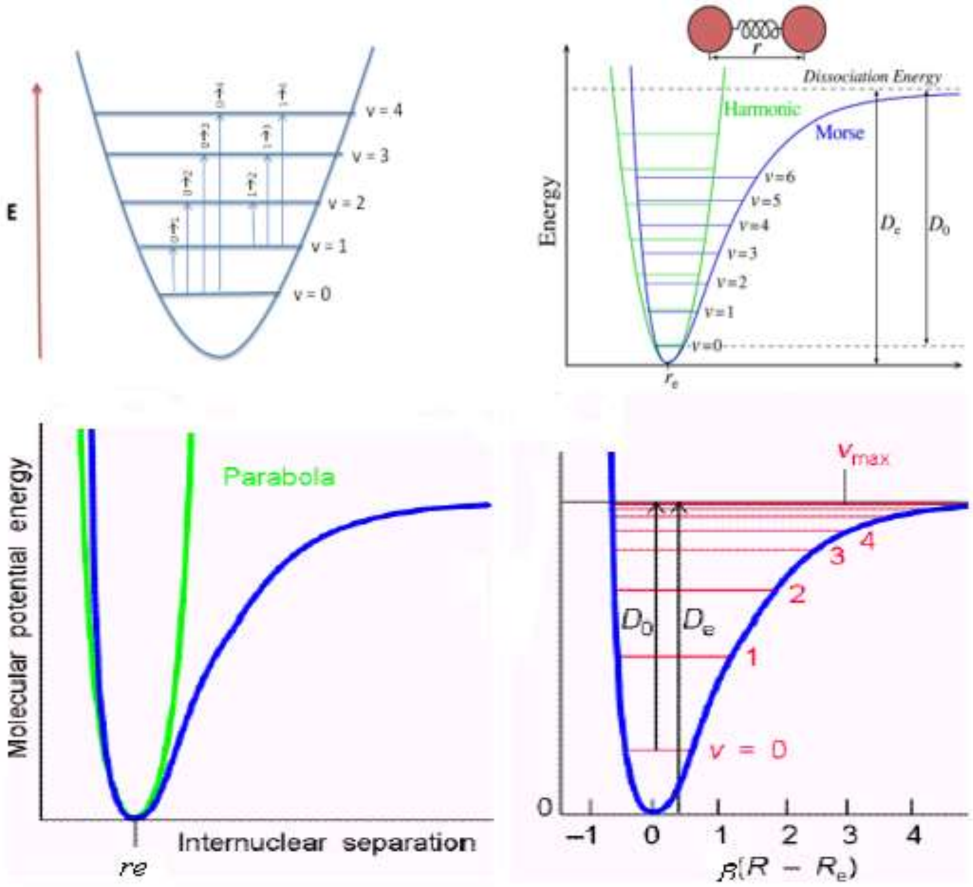
5.) v for D_2O will be lower because v is inversely proportional to $1/(\mu^{.5})$, where μ is the reduced mass.

Combination bands, overtones, and Fermi resonances

Combination bands, overtones, and Fermi resonances are used to help explain and assign peaks in vibrational spectra that do not correspond with known fundamental vibrations. Combination bands and overtones generally have lower intensities than the fundamentals, and Fermi resonance causes a spilt and shift in intensity of peaks with similar energies and identical symmetries. Hot bands will also be briefly addressed.

Fundamental vibrational frequencies of a molecule corresponds to transition from $v=0$ to $v=1$. For a non-linear molecule there will by 3N-6 (where N is the number of atoms) number vibrations. The same holds true for linear molecules, however the equations 3N-5 is used, because a linear molecule has one less rotational degrees of freedom. (There are many details and will discussed in later in Normal Modes). Figures show a diagrams for a vibrating diatomic molecule(the first model is semiquantized for many reasons and the second one is an actual model)). To explain the potential energy of diatomic molecule AB changes as a function of internuclear distance, for small displacements from equilibrium a simple approximate way expressing this mathematically iin eq. 5 ($V(x) = \frac{1}{2}kx^2$.)Where the co-ordinate x represents the change in internuclear separation relative to the equilibrium position thus the value of $x = 0$ represents the equilibrium configuration with the lowest potential energy. When $x < 0$ the two atoms are closer to each other, and for $x > 0$ the two atoms are farther apart.

k is called force constant and its value reflects the strength of the force holding the two masses to each other. Equation (1.14) is a consequence of Hook's law and referred to the harmonic potential and the application of classical mechanics. The system is commonly referred to as harmonic oscillator and the shape of potential function is parabolic with minimum at x=0.



Potential energy diagram for a vibrating diatomic molecule (potential curve) and Harmonic potential. Pictured above is the HOA (green parabola) super imposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension.

Where $\mathbf{D_0}$ *is the thermal dissociation energy and* $\mathbf{D_e}$ *is the spectroscopic dissociation energy.*

This simple picture of molecular energies predicts that the potential energy of diatomic molecule increases symmetrically with respect to bond elongation or compression and does this without limit. Physical intuition suggests that this description can not be entirely true. It is correct that as the nuclei are brought very close to each other, strong repulsion forces are brought to bear and these forces increase sharply with decreasing x. In contrast, as the nuclei are pulled apart, the chemical bond is weakened and eventually broken, and then potential energy therefore becomes constant. Thus the *harmonic potential becomes unrealistic for large internuclear distances. This inadequacy of the harmonic potential is called anharmonicity. The application of quantum mechanics to harmonic oscillator reveals that the total vibration energy of the system is constrained to certain values, it is quantized. The levels denoted by vibrational quantum numbers v represent the potenital energy for the harmonic (quadratic) oscillator. The transition 0→1 is fundamental, transitions 0→n(n>1) are called overtones, and transitions 1→n (n>1) are called hot transitions (hot bands).*

Symmetry Requirements

The symmetry requirement of vibrational transisition is given by the transition moment integral,

$$\mu=\int\psi *\mu\psi d\tau\neq 0 \qquad (6)$$

where,

$$\mu=i\mu x+j\mu y+k\mu z \qquad (7)$$

These integrals can be separated into each component: x,y, and z. Because the ground state contains the totally symmetric representation, the coordinate x, y, or z and ψ^* *must belong to the same representation so that the direct product will contain the totally symmetric representation.*

Harmonic Oscillator Breakdown

From the figures, the harmonic oscillator approximation is convenient to use for diatomic molecules with quantized vibrational energy levels given by the following equation:

$$Ev(cm^{-1})=(v+1/2)\omega e \qquad (8)$$

A more accurate description of the vibrational energies is given by the anharmonic oscillator (also called Morse potential) with energy of

$$Ev(cm^{-1})=\omega e(v+1/2)-\omega exe(v+1/2)^2+\omega eye(v+12)^3+\ldots \qquad (9)$$

where ω_e *is the vibrational frequency for the* r_e *internuclear separation and* $\omega_e >> \omega_e x_e >> \omega_e y_e$*. This accounts for the fact that as the higher vibrational states deviate from the perfectly parabolic shape, the level converge with increasing quantum numbers. It is because of this anharmoniticity that overtones can occur.*

While it may seem that the harmonic oscillator and the anharomic oscillator are closely related, this is in fact not the case. The differences in the wavefunctions lead to a breakdown of selection Rules, specifically, $\Delta v=\pm 1$ *selection rule can not be applied, and higher order terms must be accounted in the energy calculations.*

There is only a small correction from the ground state to the first excited state for the anharmonic correction, but it becomes much larger for more highly excited states which are populated as the temperature increases. The deviation from the harmonic oscillator to the anharmonic oscillator results in expanding the energy function with additional terms and treating these terms with perturbation theory. The results in the correct vibrational energies and also relaxes the selection rules. A $\Delta v=\pm 1$ is still most predominant, however, weaker overtones with $\Delta v=\pm 2, \pm 3, \ldots$ can occur. It should be noted that a $\Delta v=2$ transition does not occur at twice the frequency of the fundamental transition, but at a lower frequency. Overtone transitions are not always observed, especially in larger molecules, because the transitions become weaker with increasing Δv.

Overtones

Overtones occur when a vibrational mode is excited from $v=0$ to $v=2$, which is called the first overtone, or $v=0$ to $v=3$, the second overtone. The fundamental transitions, $v=\pm 1$, are the most commonly occurring, and the probability of overtones rapid decreases as the number of quanta ($\Delta v=\pm n$) increases. Based on the harmonic oscillator approximation, the energy of the overtone transition would be n times larger than the energy of the fundamental transition frequency, but the anharmonic oscillator calculations show that the overtones are less than a multiple of the fundamental frequency. This is demonstrated with the vibrations of the diatomic HCl in the gas phase:

Table 1: HCl vibrational spectrum.

Transition	$\tilde{\nu}_{obs}$ **[cm^{-1}]**	$\tilde{\nu}_{Harmonic}$ **[cm^{-1}]**	$\tilde{\nu}_{Anharmonic}$ **[cm^{-1}]**
0→1 (fundamental)	2,885.9	2,885.9	2,885.3
0→2 (first overtone)	5,668.0	5,771.8	5,665.0
0→3 (second overtone)	8,347.0	8,657.7	8,339.0
0→4 (third overtone)	10,923.1	11,543.6	10,907.4
0→5 (fourth overtone)	13,396.5	14,429.5	13,370

We can see from Table 1, that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase.

Special case

If one of the symmetries(the symmetry operations are an important subject in molecular spectrscopy) is doubly degenerate in the excited state a recursion formula is required to determine the symmetry of the vth wave function, given by:

$$\chi v(R)=1/2[\chi(R)\chi v-1(R)+\chi(Rv)] \qquad (10)$$

Where $\chi_v(R)$ is the character under the operation R for the vth energy level; $\chi(R)$ is the character under R for the degenerate irreducible representation; $\chi_{v-1}(R)$ is the character *of the (v-1)th energy level; and* $\chi(R^v)$ *is the character of the operation* R^v*. This is demonstrated for the* D_{3h} *point group(as said before , it is symmetry operation) .*

Combination Bands

Combination bands are observed when more than two or more fundamental vibrations are excited simultaneously. One reason a combination band might occur is if a fundamental vibration does not occur because of symmetry. This is comparable to **vibronic coupling** *in electronic transitions in which a fundamental mode can be excited and allowed as a "doubly excited state." Combination implies addition of two frequencies, but it also possible to have a difference band where the frequencies are subtracted.*

To determine if two states can be excited simultaneous the transition moment integral must be evaluated with the appropriate excited state wavefunction. For example, in the transition,

$$\psi 1(0)\psi 2(0)\psi 3(0)\rightarrow\psi 1(2)\psi 2(0)\psi 3(1) \qquad (11)$$

the symmetry of the excited state will be the direct product of the irreducible representation for $\psi_1(2)$ *and* $\psi_3(1)$*.*

In spectroscopic diagnosis*, a practical use for understanding overtones and combination bands is applied to organic solvents used in spectroscopy. Most organic liquids have strong overtone and combination bands in the mid-infrared region, therefore, acetone, DMSO, or acetonitrile should only be used in very narrow spectral regions. Solvents such at* CCl_4*,* CS_2 *and* $CDCl_3$ *can be used above 1200* cm^{-1}*.*

Hot Bands

Hot bands are observed when an already excited vibration is further excited. For example an v1 to v1' transition corresponds to a hot band in its IR spectrum. These transitions are temperature dependent, with lower signal intensity at lower temperature, and higher signal intensity at higher temperature. This is because at room temperature only the ground state is highly populated (kT ~ 200 cm^{-1} *where, k is the Boltzmann constant and T is the temperature in Kelvin), based on the Boltzmann distribution..*

In the harmonic oscillator model, hot bands are not easily distinguished from fundamental transitions because the energy levels are equally spaced. Because the spacing between energy levels in the anharmonic oscillator decrease with increasing vibrational levels, the hot bands occur at lower frequencies than the fundamentals. Also, the transition moment integrals are slightly different since the ground state will not necessarily be totally symmetric since it is not in v=0.

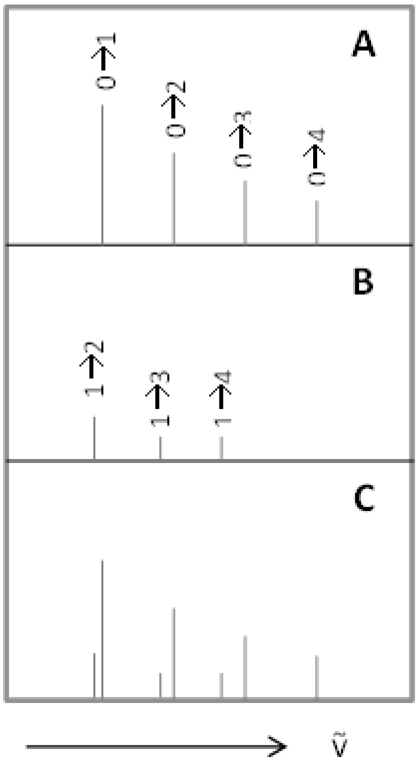


Figure 4: Example of hot bands in a vibrational line spectrum of a diatomic molecule: (A) harmonic frequencies; (B) hot band transitions; (C) combination of both spectra.

Fermi Resonances

Fermi resonance results in the splitting of two vibrational bands that have nearly the same energy and symmetry in both IR and Raman spectroscopies. Fermi resonance most often occurs between fundamental and overtone excitations, if they are nearly coincident in energy or combination band. The wavefunctions for the two resonant vibrations mix according to the harmonic oscillator approximation, and the result is a shift in frequency and a change in intensity in the spectrum. As a result, two strong bands are observed in the spectrum, instead of the expected strong and weak bands. It is not possible to determine the contribution from each vibration because of the resulting mixed wave function.

If the symmetry requirements are fulfilled and the energies of the two states are similar, the two conditions must be satisfied for the occurrence of Fermi Resonance:

- *In other words, the two vibrations must have the same symmetries (Mulliken symbols).*
- *The transitions coincidentally have very similar same energies.*

Fermi resonance leads to two effects.

1- *the high energy mode shifts to higher energy and the low energy mode shifts to still lower energy.*
2- *the weaker mode gains intensity (becomes more allowed) and the more intense band decreases in intensity.*

3- *The effect of this interaction is to increase the splitting between the engery levels. The splitting will be larger if the original energy difference is small and the coupling energy is large.*

The two transitions are describable as a linear combination of the parent modes. Fermi resonance does not lead to additional bands in the spectrum, but rather shifts in bands that would otherwise exist.

Because the vibrations have nearly the same frequency, the interaction will be affected if one mode undergoes a frequency shift from deuteration or a solvent effect while the other does not.An important molecule which most studied for this type of resonance is carbon dioxide, CO_2. Another typical example of Fermi resonance is found in the vibrational spectra of aldehydes. Also, CS_2 is an analog to this system.

NOTE: *When bands have non-negligible widths, Fermi resonance perturbation of localized levels cannot be applied. This broadening can be the result of a number of things, such as, intermolecular interaction, shortened excited state lifetimes, or interaction of vibrational modes with phonons. In place of perturbation theory, the distribution of interacting vibrational states can be approximated as a collection of discrete level. The influence from each level can be calculated.*

It is useful, in spectroscopic diagnosis , to understand Fermi resonance because it helps assign and identify peaks within vibrational spectra (ie. IR and Raman) that may not otherwise be accounted for, however it should not be used lightly when assigning spectra. It is easy to jump to the conclusion that an unidentifiable band is the result of Fermi resonance, however this explanation may not fully account for the inconsistency and further characterization may be required for the system being investigated. It is important to assign spectra before doing the normal mode (coordinate) calculations because doing these calculations beforehand often leads to incorrect assignments of the peaks in the spectra.

Solving Problems

Q1. Given $v_1 = 1151\ cm^{-1}$, $v_2 = 1361\ cm^{-1}$, $v_3 = 519\ cm^{-1}$ for SO_2, and the fact that there are 4 overtones and/or combination bands, predict the vibrational spectra and calculations.

A1.

$v\ [cm^{-1}]$	*Assignment*
519	v_2
606	$v_1 - v_2$
1151	v_1
1361	v_3
1871	$v_2 + v_3$
2305	$2v_1$
2499	$v_1 + v_3$

Q2. What are the two main effects of Fermi resonance?

A2. An overtone band can gain intensity from a nearby fundamental frequency with similiar symmetry. The energy levels of both bands are shifted away from one another.

Q3. Explain the difference between a combination band and an overtone.

A3. An overtone is the result of $\Delta v>1$ *from the ground state. A combination band is the result of a 2 fundamental frequencies being excited simultaneously so that the excitation is allowed by symmetry. The overtone is not subject to a symmetry requirement.*

Q4. Why are hot bands temperature dependent?

A4. For a hot band to occur, a state other than the ground state must already be populated, and this requires $>200 cm^{-1}$ *to over come the thermal energy of kT (Boltzmann constant times temperature). The more heat that it put into the system, the more likely a hot band is to occur, and the stronger the signal it will produce.*

Q5. Show the calculations for the values in Figure 1 for both the harmonic and anharmonic oscillators.

A5. Equations to use: $\tilde{v} = 2885.90v$*, for harmonic and* $\tilde{v} = 2990.9v - 52.82v(v+1)$ *for anharmonic.*

For $v=3$, $\tilde{v}_H = 2885.90(3) = 8657.7$ $\tilde{v}_{AH} = 2990.9(3) - 52.82(3)(3+1) = 8339.0$

Types of modes in a Molecule

The ***Heisenberg uncertainty principle*** *argues that all atoms in a molecule are constantly in motion (otherwise we would know position and momentum accurately). For molecules, they exhibit three general types of motions: translations (external), rotations (internal) and vibrations (internal). A diatomic molecule contains only a single motion., while polyatomic molecules exhibit more complex vibrations, known as* ***normal modes.***

So,. The main kinds ayr the streach and bending. They can be classified into sub-types (shapes) as follow:

the normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

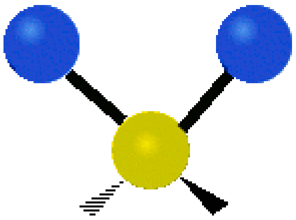
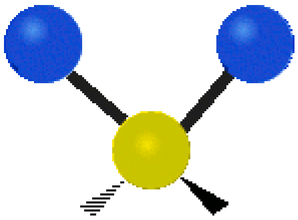
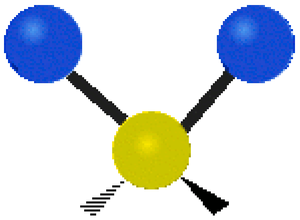
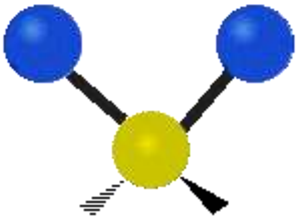
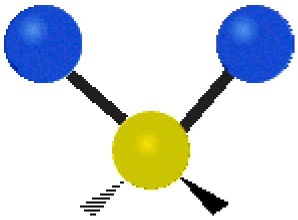
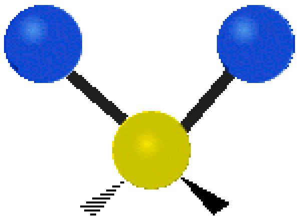
Symmetric Stretching	***Asymmetric Stretching***	***Wagging***
		
Twisting	***Scissoring***	***Rocking***
		

Figure : *Six types of Vibrational Modes.*

Description of vibrations

- *v = stretching is a change in bond length; note that the number of stretching modes is equal to the number of bonds on the molecule*
- *δ = bending is a change in bond angle*
- *ρ_r = rocking is change in angle between a group of atoms*
- *ρ_w = wagging is change in angle between the plane of a group of atoms*
- *ρ_t = twisting is change in angle between the planes of two groups of atoms*
- *π= out of plane*

In direct correlation with symmetry, subscripts s (symmetric), as (asymmetric) and d (degenerate) are used to further describe the different modes.

A normal mode corresponding to an asymmetric stretch can be best described by a harmonic oscillator: As one bond lengthens, the other bond shortens. A normal mode that corresponds can be best described by a Morse potential well: As the bond length increases the potential energy increases and levels off as the bond length gets further away from the equilibrium.

NOTE: ***The molecule has translational and rotational motion as a whole while each atom has it's own motion. The vibrational modes can be IR or Raman active. For a mode to be observed in the IR spectrum, changes must occur in the permanent dipole (i.e. not diatomic molecules). Diatomic molecules are observed in the Raman spectra but not in the IR spectra. This is due to the fact that diatomic molecules have one band and no permanent dipole, and therefore one single vibration. An example of this would be O_2 or N_2. However, unsymmetric diatomic molecules (i.e. CN) do absorb in the IR spectra. Polyatomic molecules undergo more complex vibrations that can be summed or resolved into normal modes of vibration***.

Isotope Effect In Vibrational Spectroscopy

How an isotope can affect the frequencies of the vibrational modes of a molecule?:

Isotopic substitution is a useful technique due to the fact that the normal modes of an isotopically substituted molecule are different than the normal modes of an unsubstituted molecule, leading to different corresponding vibrational frequencies for the substituted atoms.

Vibrational spectroscopy is done in the infrared region of the electromagnetic spectrum, which ranges from around 10^{-6} to 10^{3} meters. IR and Raman spectroscopy observe the vibrations of molecules, displaying the normal and local modes of the molecule in the spectra. Isotopes are atoms that share the same number of protons but differ in the number of neutrons contained in the nucleus, thus giving these atoms different mass numbers. The specific mass of each atom will affect the reduced mass of the overall molecule, therefore changing the vibrational frequencies of that molecule.

When an atom is replaced by an isotope of larger mass, μ increases, leading to a smaller veve and a downshift (smaller wavenumber) in the spectrum of the molecule. Taking the diatomic molecule HCl, if the hydrogen is replaced by its isotope deuterium, μ is doubled and therefore veve will be decreased by √2. Deuterium substitution leads to an isotopic ratio of 1.35-1.41 for the frequencies corresponding to the hydrogen/deuterium vibrations. There will also be a decrease by √2 in the band width and integrated band width for the vibrational spectra of the substituted molecule. Isotopic substitution will affect the entire molecule (to a certain extent), so it is not only the vibrational modes for the substituted atom that will change, but rather the vibrational modes of all the atoms of the molecule. The change in frequency for the atoms not directly invovled in the substitution will not display as large a change, but a downshift can still occur.

When polyaniline (Figure 4) is fully deuterated, the vibrational peaks will downshift slightly:

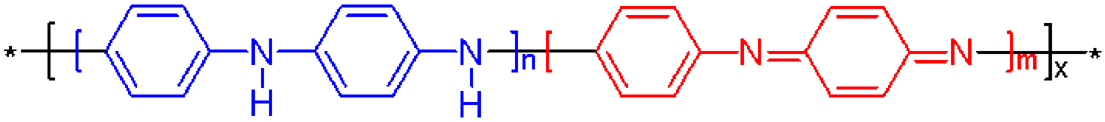


Figure 4: Structure of polyaniline.

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The following data (was summarized from Quillard et al.):

Type of vibration	***Nondeuterated (frequency, cm^{-1})***	***Deuterated (frequency, cm^{-1})***
C-C stretch	*1626*	*1599*
C-C stretch	*1581*	*1560*
C-H bend – benzenoid ring	*1192*	*876*
C-H bend – quinoid ring	*1166*	*856*
N-H bend	*1515*	*1085*

Changing hydrogen to deuterium leads to the largest effect in a vibrational spectrum since the mass is doubled. Other isotopic substitutions will also lead to a shift in the vibrational energy level, but because the mass change is not as significant, μ will not change by much, leading to a smaller change in veve. This smaller change in vibrational frequency is seen in the sulfur substitution of sulfur hexafluoride (Figure 5:), from ^{32}S to ^{34}S. The frequencies (as reported by Kolomiitsova et al.) are shown below:

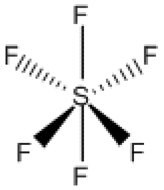

Figure 5: Structure of sulfur hexafluoride.

Vibration assignment	***$^{32}SF_6$ (frequency, cm^{-1})***	***$^{34}SF_6$ (frequency, cm^{-1})***
v3v3	*939.3*	*922.2*
v4v4	*613.0*	*610.3*

These two examples show the consistency of down shifted vibrational frequencies for atoms substituted with an isotope of higher mass.

Applications of isotpic effect results:

Substituting atoms with isotopes has been shown to be very useful in determining normal mode vibrations of organic molecules. When analyzing the spectrum of a molecule, isotopic substitution can help determine the vibrational modes specific atoms contribute to. Those normal modes can be assigned to the peaks observed in the spectrum of the molecule. There are specific CH_3 rocks and torsions, as well as CH bends that can be identified in the spectrum upon deuterium substitution. Other torsion bands from hydroxyl and amine groups can also be assigned when hydrogen is replaced with deuterium. Experimental data has also shown that using deuterium substitution can help with symmetry assignments and the identification of metal hydrides.

Isotopic substitution can also be used to determine the force constants of the molecule. Calculations can be done using the frequencies of the normal modes in determining these values, based on both calculated frequencies and experimental frequencies.

Many researchers have also attempted to contribute peak shape changes and splits in peaks of vibrational spectra to naturally occurring isotopes in molecules. It has been shown, however, that the shape of a peak is not related to the size of the atom, so substitution to an atom of larger mass will not affect the peak shape in the molecule's spectrum. As previously stated, isotopic substitution of atoms of higher mass will not have a significant enough effect on the shifts in frequencies for the corresponding vibrations, so analyzing the frequency shifts of smaller mass isotopes, like deuterium and ^{13}C *is necessary.*

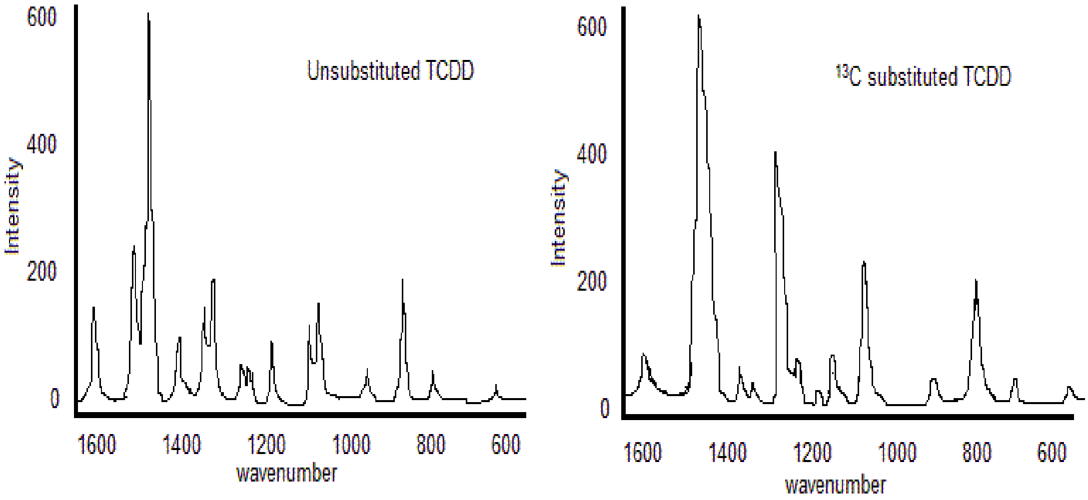

Figure 6: Spectra of unsubstituted and substituted TCDD depicting the isotopic ^{13}C *effects.*

As depicted in the rough representation of the vibrational spectra of the molecule tetrachlorinated dibenzodioxin (TCDD), the ^{13}C *substituted TCDD spectrum is slightly downshifted compared to the unsubstituted TCDD spectrum. Although the shifts and split peaks do occur in the spectra of isotopically substituted molecules, not all observed peaks can be attributed to the isotope. This is because the intensities of the peaks shown are not large enough to relate to the natural abundance of the* ^{13}C *isotope, and not all peaks can be accounted for by the substitution.*

Solving Problems

1. *How many normal modes would be found in* CO_2*? What are the different types of vibrational modes for this molecule?*
2. *If the diatomic molecule HCl, with* ^{1}H *and* ^{35}Cl *were substituted with* ^{37}Cl*, what change occurs to the reduced mass?*
3. *For a nondeuterated hydrofluoric acid diatomic, HF, the vibrational frequency of this molecule is found at 845* cm^{-1}*. If the hydrogen atom of this molecule was*

substituted with deuterium, where would you expect to now find the vibrational frequency?

Answers

1. *4; symmetric stretch, asymmetric stretch, and two degenerate bends*
2. *With ^{37}Cl the reduced mass increases from 0.97222 to 0.97368*
3. *DF would have a calculated band at 597.5 cm^{-1}*