

Chapter 10

6.1 Introductory Remarks

All molecules in the liquid, gas, or solution phases are in constant motion. That motion is generally divided into translational, rotational, and vibrational motions. The first two are largely absent in the solid state. Vibrational motions are observable in the infrared region of the electromagnetic spectrum via infrared and Raman spectroscopies.

Prior to taking physical chemistry, you probably thought bond vibrations occur randomly. Because the center of mass in a molecule cannot change during a vibration, vibrations occur fixed patterns and the number of possible collections of vibration is limited for each molecule. One other thing should be mentioned. The term vibration is used loosely here. It includes the back-and-forth movements, in- and out-of-plane movements (e.g. ring puckering), and bond angle changes (scissoring).

6.2 The Symmetry of Normal Vibrations

Molecules of more than two atoms display an apparently convoluted pattern of internal motion (vibration) to the observer. The apparent randomness of the motions gets worse as the molecules contain larger numbers of atoms. This can be seen for three simple molecules SO_3 , H_2O , and CO_2 at <http://jchemed.chem.wisc.edu/JCEWWW/Articles/WWW0001/index.html> which shows both individual vibrations and multiple vibrations superimposed. Another website, http://www2.ess.ucla.edu/~schauble/molecular_vibrations.htm, shows uncoupled normal mode vibrations for a number of molecules.

As you know there are $3n-6$ modes of vibration (different kinds of vibration) within a molecule, unless it is linear and then there are $3n-5$ modes. This is because with 3 vectors (x, y,

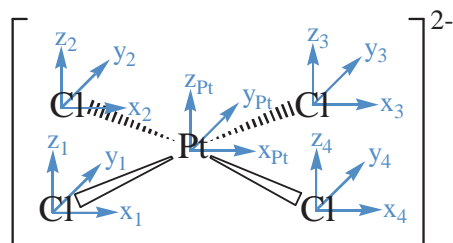
z), there are $3n$ ways each atom can move. Six modes are subtracted for translation and rotation along the x , y , and z axes.

On p. 306 the book shows the normal modes of vibration (ground state) for CO_3^{2-} . You are not expected to be able to predict these. It also provides a key explaining how to interpret the symbolism. Read over the rest of the section. It explains how to assign irreducible representations to normal modes and works through the E irreducible representation for you. You should verify that the A_1' and A_2'' modes are, in fact, correctly assigned on your own.

10.3 Determining the Types of Normal Modes

We noted earlier that there are $3n-6$ normal vibrational modes for a typical molecule, in addition to 3 translational and 3 rotational modes. The process of determining them begins with choosing a molecule, determining its point group, and placing a set of 3 vectors. The vectors should point along sets of aligned coordinate axes (see Figure 10.3 for an example).

Your book works through the carbonate ion. I'll do PtCl_4^{2-} . First draw a picture and go through the steps just described. The point group is D_{4h} .



Now apply the C_4^1 axis (clockwise looking down from $+z$) to the molecule, what happens? On the platinum, z_{Pt} remains the same, but y_{Pt} becomes x_{Pt} and x_{Pt} becomes $-y_{\text{Pt}}$. On the chlorines, z_1 becomes z_2 , y_1 becomes x_2 , and x_1 becomes $-y_2$. Similar changes occur for the other 3 atoms.

The technically proper way to solve this problem is to construct a 15 x 15 matrix and enter values that describe the movement of these vectors, but as the book demonstrates, any vector whose base moves, yields an off-diagonal element in the matrix. Since only the character (diagonal) matters, solving problems is greatly simplified by ignoring any vector that moves to another location. We only need worry about vectors that either remain in place or rotate about their base. From the last paragraph, we thus ignore the vectors on the chloride ions, but must consider all three on the platinum ion.

For the platinum vectors, we see that the x and y vectors are coupled to each other, but that the z vector remains independent. Now apply the standard matrix from p. 72 to generate the value of the character. This yields the matrix:

$$\begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \cos 90^\circ & -\sin 90^\circ & 0 \\ \sin 90^\circ & \cos 90^\circ & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Thus, the character for the matrix arising from applying C_4 is 1. For the C_2 axis, the matrix yields a character of -1.

$$\begin{bmatrix} \cos 180^\circ & -\sin 180^\circ & 0 \\ \sin 180^\circ & \cos 180^\circ & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

This process can be simplified further. As you can see a vector that remains in place generates a character of +1, one that rotates 90° a character of 0, while a 180° shift generates a -1. Thus, if you remember this, the matrices are needed only for shifts involving other angles.

With this in mind, we can generate the reducible representation for this entire molecule. We'll assume that C_2 coincides with the C_4 axis, the C_2' and σ_v lie along bonds, and C_2'' and σ_d lie between them.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{3n}	15	1	-1	-3	-1	-3	-1	5	3	1

Now go through the standard process to determine the make-up of this reducible representation.

$$\Gamma_{3n} = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

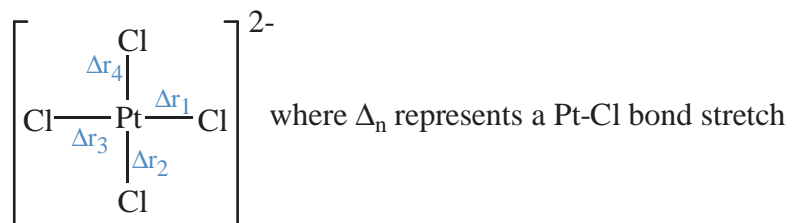
But some of the irreducible representations will be assigned to translations and rotations. From the character table you can see that the x, y, and z translations transform as A_{2u} and E_{1u} , while the rotations transform as A_{2g} and E_g . Removing these from the irreducible representations for all motion leaves:

$$\Gamma_{3n-6} = A_{1g} + B_{1g} + B_{2g} + E_g + A_{2u} + B_{2u} + 2E_u$$

Thus, we have determined the irreducible representation for all vibrations

10.4 Contributions of Particular Internal Coordinates to Normal Modes

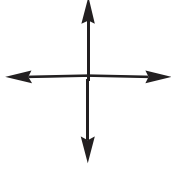
It would be nice to be able to subdivide the vibrations into their various subdivisions (e.g. stretches, bends, and plane deformations). Not surprisingly, this can be done. We'll begin with stretches and that requires us to draw a different picture than is used for generic motion.

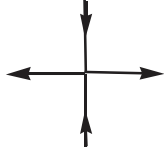


Since we're looking at specific motions (i.e. the in-out motion of a particular bond) there are only two possible values for the characters 1 and 0. If a vibration does not move it has a character of one, if it moves it is zero. So for all of the stretches we determine:

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{Pt-Cl}	4	0	0	2	0	0	0	4	2	0

Γ_{Pt-Cl} yields $A_{1g} + B_{1g} + E_u$. The results in 2 questions: What do the modes look like, and which are IR active and which Raman active? To answer the first question we need to use a projection operator.

$$\begin{aligned} \hat{P}^{A_{1g}} &= \Delta r_1 + (\Delta r_2 + \Delta r_4) + \Delta r_3 + (\Delta r_1 + \Delta r_3) + (\Delta r_2 + \Delta r_4) + \Delta r_3 + (\Delta r_2 + \Delta r_4) + \Delta r_1 + (\Delta r_1 + \Delta r_3) + \\ &\quad (\Delta r_2 + \Delta r_4) \\ &= 4\Delta r_1 + 4\Delta r_2 + 4\Delta r_3 + 4\Delta r_4 \\ &\approx \Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 \quad (\text{which is what you'd predict for something total symmetric}) \end{aligned}$$


$$\begin{aligned} \hat{P}^{B_{1g}} &= \Delta r_1 - 2(\Delta r_2 + \Delta r_4) + \Delta r_3 + (\Delta r_1 + \Delta r_3) - (\Delta r_2 + \Delta r_4) + \Delta r_3 - (\Delta r_2 + \Delta r_4) + \Delta r_1 + (\Delta r_1 + \Delta r_3) - \\ &\quad (\Delta r_2 + \Delta r_4) \\ &= 4\Delta r_1 - 4\Delta r_2 + 4\Delta r_3 - 4\Delta r_4 \\ &\approx \Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4 \end{aligned}$$


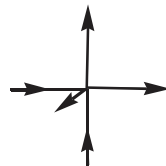
$$\begin{aligned} \hat{P}^{E_u} &= 2\Delta r_1 - 2\Delta r_3 - 2\Delta r_3 + 2\Delta r_1 \\ &= 4\Delta r_1 - 4\Delta r_3 \\ &\approx \Delta r_1 - \Delta r_3 \end{aligned}$$

There exists an equivalent projection: $\Delta r_2 - \Delta r_4$, which should seem reasonable by now. These may be added or subtracted:

$$(\Delta r_1 - \Delta r_3) + (\Delta r_2 - \Delta r_4) = \Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4$$

or

$$(\Delta r_1 - \Delta r_3) - (\Delta r_2 - \Delta r_4) = \Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4$$



Note that for the E_u representation the platinum moves. This is because the center of mass of the ion cannot change. The chlorines move the mass up and right, so the platinum must move down and left to compensate. A similar exercise can be performed for bond angles and plane deformations.

So we now know how many bond stretching modes there are and their symmetry. The next question is: Which will be IR active, which Raman active, and which will be both? Recall from Chapter 5 the Schrodinger integral for the infrared: $I \propto \int \psi_{v'} \mu \psi_{v''} d\tau$, where $\psi_{v'}$ and $\psi_{v''}$ are the wave functions for two vibrations and μ = electric dipole moment.

For almost all observed vibrations, it can be shown that $\psi_{v'}$ is the ground state vibration and $\psi_{v''}$ is the first excited state. (Most molecules are in the vibrational ground states most of the time.)

The above integral is non-zero (allowed) only if the direct product of the irreducible representations of each of the functions includes A_{1g} . The ground state vibrations of any molecule will be described by the totally symmetric representation of its point group. Therefore, the direct product of the irreducible representations of the electric dipole and the excited state must include the A_{1g} .

$$\text{Useful relation: } \Gamma_A \times \Gamma_B \text{ includes } A_1 \text{ or } A_{1g} \text{ iff } \Gamma_A = \Gamma_B .$$

Recall from Chapter 5, μ can be polarized along the x, y, and z axes, and the irreducible representations of those axes are then used. Thus, each irreducible representation determined for the molecule that corresponds to an irreducible representation for x, y, z will be IR active.

For PtCl_4^{2-} : E_u is IR active and one of the stretching modes.

The Raman bands are determined in a similar manner. The Schrodinger equation for Raman

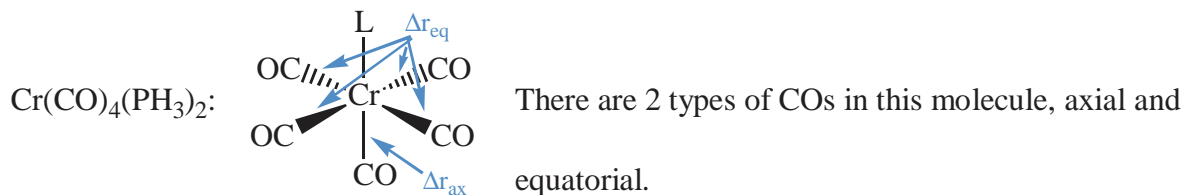
spectroscopy is $I \propto \int \psi_v' \alpha \psi_v'' d\tau$, where α is the polarizability tensor,
$$\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz} \end{pmatrix}$$
. There

are 6 different values in this matrix ($\alpha_{xx}, \alpha_{xy}, \alpha_{xz}, \alpha_{yy}, \alpha_{yz}, \alpha_{zz}$) and if any of the integrals with one of these terms is non-zero there will be observable Raman bands. The $\alpha_{xy}, \alpha_{xz}, \alpha_{yz}$, and α_{zz} transform as the respective *d*-orbitals, while α_{xx} and α_{yy} transform as either $x^2 + y^2$ or $x^2 - y^2$.

Thus for $\text{PtCl}_4^{2-} : A_{1g} + B_{1g}$ i.e. there are two Raman bands.

A few points worthy of note:

- 1) IR and Raman modes will be mutually exclusive if the molecule is centrosymmetric. (possesses the “i” element). In other molecules, some bands may be both IR and Raman active.
- 2) While uncommon, some modes may be neither IR nor Raman inactive.
- 3) It might appear from the previous discussion that a molecule can have at most 3 IR and 6 Raman x-y bands. This is not true. All equivalent atoms/groups and their respective motions are treated as a unit. If non-equivalent atoms/groups exist, they are treated separately. For example, in the case of PtCl_4^{2-} bond scissoring and plane deformation bands are also possible. Another example follows:



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
$\chi(\text{CO}_{\text{ax}})$	1	1	1	1	1
$\chi(\text{CO}_{\text{eq}})$	4	0	0	2	0

Without doing any math we can say that $\chi(\text{CO}_{\text{ax}})$ transforms as the A_1 irreducible representation.

For the equatorial set we find that $\chi(\text{CO}_{\text{eq}}) = A_1, B_1,$ and E . Now A_1 and E are IR active so there will be a total of 3 IR bands $2A_1 + E$. Also A_1, B and E are Raman active so there will be 4 Raman CO stretching bands.

Note it is commonly the case for E bands to be broader than A and B bands and T bands to be broader than E bands. In practice, resolution decreases in the order gas phase > solution phase > solid phase. Resolution is better in solution with non-interacting solvents than with ones that interact strongly with the compound.

10.5 How to Calculate Force Constants: The F and G Matrix Method

There is no real, practical reason to do this. The method is fine for small molecules (i.e. those with a handful of atoms), but the bands are generated for gas phase molecules. Band positions will change in solution or solid state and are rather complicated to calculate.

10.6 Selection Rules for Fundamental Vibrational Transitions

In Chapter 5, you were introduced to the selection rules for IR and Raman spectroscopies. We now go over them in somewhat greater depth. The vibrations of molecules may be thought of as harmonic oscillations. The wave function for a harmonic oscillator is given by the equation

$$\psi_i(n) = N_i e^{-(\alpha_i/2)\xi_i^2} H_n(\sqrt{\alpha_i} \xi_i)$$

where N_i is a normalizing constant, $\alpha_i = 2\pi\nu_i/h$ (ν_i = frequency of i^{th} normal mode), ξ_i is the normal coordinate displacement of the i^{th} vibration, and H_n is a Hermite polynomial of order n . Recall that a Hermite polynomial is an orthogonal (to $e^{-x^2/2}$) polynomial sequence. The first 3 Hermite polynomials are $H_0(x) = 1$, $H_1(x) = 2x$, $H_2(x) = 4x^2 - 2$.

Under normal conditions, all vibrations in a typical molecule are in ground state. For the ground state, $H_0(\sqrt{\alpha_i} \xi_i) = 1$ and $\psi_i(0) = N_i e^{-(\alpha_i/2)\xi_i^2}$. If ξ_i represents a nondegenerate vibration, all symmetry operations change it into ± 1 times itself (i.e. the vibration moves as normal or reverses itself). A result is that ξ_i^2 is unchanged by the symmetry operations and the whole wave function $\psi_i(0)$ is invariant. Thus, the ground state wave function for normal vibrations behaves like the totally symmetric irreducible representation.

Essentially all vibrational excitations in the infrared region occur for $v = 0 \rightarrow 1$ (i.e. from the ground state to the first excited state). This is simply a practical function of the available thermal energy at room temperature. Such excitations are called fundamental transitions and lead to much more intense IR and Raman bands than other kinds of excited state transitions. This leads us back to Chapter 5 where we find that for a fundamental transition the integral then written as $I_x \propto \int \psi_1 x \psi_0 d\tau$ becomes $I_x \propto \int \psi_0 x \psi_1 d\tau$. Since we now know ψ_0 belongs to the totally symmetric irreducible representation, then x , y , or z , and ψ_1 must belong to the same irreducible representation for a nonzero result from the integral to occur. This is why we use the x , y , and z coordinates in the character table to determine whether or not a particular representation is IR active.

10.7 Illustrative Examples – Read on your own.

10.8 Some Important Special Effects

- 1) In molecules with centers of symmetry, IR and Raman active vibrations are mutually exclusive. In other words, no irreducible representation will be valid for both IR and Raman transitions.
- 2) When you first covered infrared spectroscopy you learned about overtones. These are weak peaks found in IR (and Raman) spectra that are exact multipliers of fundamental absorptions (i.e. If a fundamental (strong) absorption occurs at 1203 cm^{-1} , the overtone would be found at 2306 cm^{-1} , but would have much lower intensity.) Now, if a second absorption occurs at about the same value as the overtone and the excited state that gives rise to that absorption has the same irreducible representation as the excited state that occurs in the overtone, a Fermi resonance may occur. It is a mixing of the states and there are two results. The first is that the two absorptions will move away from each other and the second is that the overtone intensity will increase while the fundamental intensity will decrease. This is shown pictorially on p. 341.
- 3) All of the preceding text has assumed the molecules were in the gas phase. In general, the discussion will hold for solutions as well. The solid state is somewhat different. Here the symmetry of the entire crystal governs the appearance of the absorption spectrum. The symmetry of the crystal may be lower than that of the molecule, but not higher. As a result, degeneracies (E & T bands) in the gas phase absorption spectra may be split. Likewise, IR/Raman inactive bands in the gas phase, may become visible for solid state spectra.