

Applications to Molecular Vibrational Spectra

Unlike electronic absorption spectroscopy, which occurs in the UV and visible regions, vibrational spectroscopy occurs with no electronic transitions. Electromagnetic radiations with lower energies (longer wave lengths) are therefore consumed here. Vibrational spectra involve Infra-Red (IR) and Raman Scattering (RS) spectra. In IR spectra, relatively long wave lengths (IR region) are needed to excite the bonds and cause vibrations. In RS spectra, radiations of higher energies (such as UV) are first used. The molecule is excited to a virtual excited state. Energy is then released and the molecule then reaches the ground state. If vibration occurs, there will be a difference in energy between excitation and emission radiations; i.e. the emitted wavelength is longer than the absorbed one. The small energy differences between absorbed and emitted light correspond to bond vibrations in RS spectra, which are essentially in the IR region.

To be an IR active band, a given vibration should cause a change in total dipole moment ($\Delta\mu \neq 0$) in the molecule upon excitation. Therefore the asymmetric stretching vibration in CO_2 is an IR active band, whereas the symmetric stretching vibration is not, Figure (5.1). Similarly, the stretching vibration in $\text{N}\equiv\text{N}$ molecules (essentially always symmetric) is IR inactive, since it creates no change in dipole moment between the excited and the ground state.

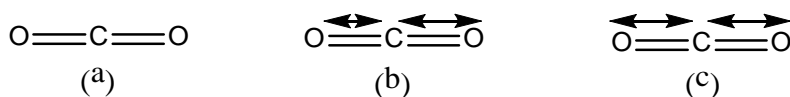


Figure (5.1): Stretching vibrations in a CO_2 molecule. (a) ground state, (b) asymmetric stretching with a change in dipole moment, and (c) symmetric stretching with no change in dipole moment.

In RS spectra, the molecular electronic cloud is polarized by the oscillating electric field vector of the incident radiation. Therefore, to be Raman active, a vibration must cause a change in the polarizability of the molecule.

Based on these discussions, the following two symmetry selection rules may now be formulated:

- IR active modes: to be an IR active band, a molecular vibration must have same symmetry as a component of dipole moment (should belong to same symmetry species x , y or z).
- Raman active modes: to be Raman active, a vibration must have same symmetry as that of one (or more) component(s) of polarizability (should belong to same symmetry species of binary products $x^2, y^2, z^2, xy, xz, yz$ or $x^2 - y^2$).

Group Theoretical Treatment of Vibrational Spectra

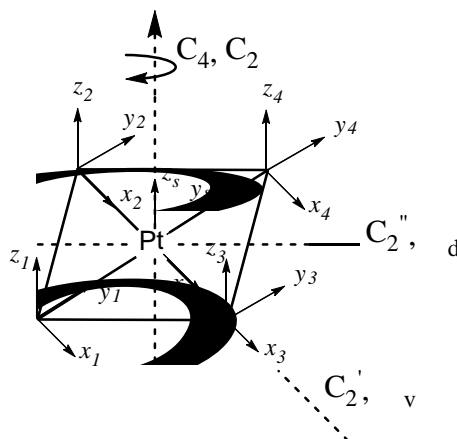
Group theory can be used to understand vibrational spectra by predicting which vibration(s) is (are) IR or Raman active in a given molecule. This can be achieved as follows:

Consider a square planar $[PtCl_4]^{2-}$ complex ion, (D_{4h}), as an example.

- Determine the total number of vibrations in the given molecule.

For a molecule of n (atoms) there will be $(3n - 6)$ vibrations for non-linear systems, or $(3n - 5)$ vibrations for linear ones. Therefore, in the case of $[PtCl_4]^{2-}$ ion (non-linear) there should be a maximum number of $3 \times 5 - 6 = 9$ vibrations.

- Choose a suitable basis on which all the symmetry operations are to be performed. In vibrational spectra, the basis is a set of $3n$ axes, three ones on each atom. For $[PtCl_4]^{2-}$ the basis is shown in structure I below:



I

- Perform all symmetry operations on the basis to generate a reducible representation. For $[PtCl_4]^{2-}$, D_{4h} , the reducible representation will be

generated using all the 15 axes. The method is as discussed in Chapter 4 earlier, where the (character of the matrix representing the effect of a given operation on the basis) is equal to number of unshifted axes by that operation. For $[PtCl_4]^{2-}$, the reducible representation is thus:

D_{4h}	E	$2C_4$	$C_2(=C_4^2)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	15	1	-1	-3	-1	-3	-1	5	3	1

And using the reduction formula, this reduces to:

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

The result accounts to exactly 15 species (equals $3 \times 5 = 15$ axes that appear in the basis).

Since the basis involved all axes of all atoms, the fifteen symmetry species include all modes of motion including translational, rotational and vibrational modes. Thus:

d) Out of the number of symmetry species, consider only the ones that are related to vibrational modes. This is achieved by excluding all symmetry species related to translational and rotational modes. In $[PtCl_4]^{2-}$, this could be done as follows:

- i) exclude all symmetry species related to translational modes. From the D_{4h} Character Table, it appears that the x - and y -axes belong to E_u (doubly degenerate) and the z -axis belongs to A_{2u} . Since x -, y - and z -axes are associated with translation, then one A_{2u} and one E_u symmetry species are excluded.
- ii) exclude all symmetry species related to rotational modes. From D_{4h} Character Table, it appears that the R_x - and R_y -rotations belong to E_g (doubly degenerate) while the R_z -rotation belongs to A_{2g} . Therefore, one E_g and one A_{2g} symmetry species are excluded.

Out of the fifteen symmetry species, we are now left with only nine vibrational modes, as:

$$\Gamma_{vibr} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$$

To check if one is on the right track, one needs to compare the number of symmetry species (nine in this case) with that of vibrational modes (nine) discussed earlier. The symmetries listed here correspond only to vibrational modes.

- e) The resulting vibrational symmetry modes may now be checked if they are IR active or not using the IR selection rule shown earlier. For $[PtCl_4]^{2-}$, it appears from D_{4h} Character Table that only A_{2u} and E_u symmetries are related to x -, y - and z -axes. Therefore the vibrations with the symmetries

$$A_{2u} + 2E_u$$

are the only ones that are IR active. These are: a singly degenerate, a doubly degenerate (two) and a doubly degenerate (two). Since the doubly degenerate vibrations are indistinguishable, the $[PtCl_4]^{2-}$ IR spectrum may have three bands, one corresponding to the A_{2u} vibration, and one corresponding to each of the two E_u vibrations. This is in accordance with experiment, since the ion $[PtCl_4]^{2-}$ is known to have three IR bands at 168, 321 and 191 cm^{-1} .

- f) To find the Raman active vibrations, use the Raman selection rule, discussed earlier, to check each of the nine vibrations. For $[PtCl_4]^{2-}$, it appears from D_{4h} Character Table that the vibrations:

$$A_{1g} + B_{1g} + B_{2g}$$

are the only Raman active ones. This is because each of them involves a combination of directional properties (z^2 , x^2-y^2 and xy in this case). This is in accordance with experimental finding where $[PtCl_4]^{2-}$ has only three Raman vibrational frequencies at 333, 196 and 306 cm^{-1} .

Note that in molecules having an inversion operation (i), such as D_{4h} , the IR bands and RS spectral bands should not coincide and should occur at different positions. Systems with no i operation, such as T_d , have coincidence between IR and RS bands.

Group Theoretical Treatment of Particular Vibrational Modes

In this section, attention will be devoted to application of group theory to specific vibrational modes, such as the **stretching** of a given class of bonds present in a given molecule. The procedure is direct, and can be performed as follows:

- Determine the symmetry point group of the molecule.
- Choose a suitable basis, using the set of bonds, in question, to vibrate as desired. The vibration of each of these bonds can be represented by an arrow.
- Generate a reducible representation by performing the symmetry operations on the basis.

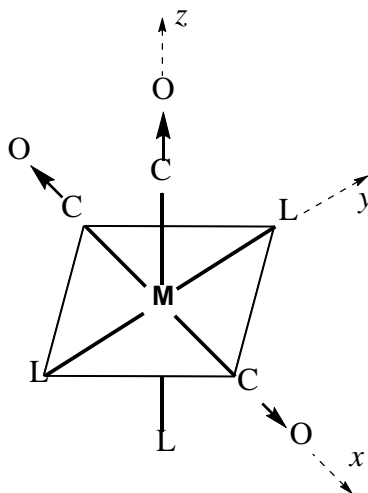
- d) Reduce the resulting reducible representation, into its irreducible representations, to find symmetries of all stretching vibrational modes possible for the given bonds.
- e) Use selection rules discussed earlier, with the aid of the proper Character Table, to find out which of these stretching vibrations are IR active and which are Raman active ones.

Example:

For the *mer*-[ML₃(CO)₃] complex, find out the IR and Raman active CO stretching vibrations.

Solution:

The symmetry point group of the molecule is C_{2v} , and the basis is a set of three arrows, as shown in structure II below. Each CO bond stretching is represented by an arrow



II

The reducible representation that results is:

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
Γ_{str}	3	1	3	1

which reduces to: $2A_1 + B_1$
that shows all C-O stretching vibrations.

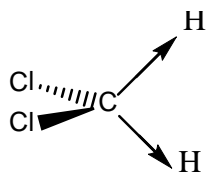
Using the C_{2v} Character Table, then:

- 1) All $2A_1 + B_1$ vibrations are IR active ones, since z -axis belongs to A_1 , and x -axis belongs to B_1 . The IR active spectra should therefore have three different IR CO stretching bands.
- 2) All $2A_1 + B_1$ vibrations are Raman active, since z^2 -binary

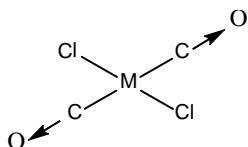
product belongs to A_1 , and xz -binary product belongs to B_1 .
 The RS spectra should therefore have three vibrational CO stretching bands.

Exercises:

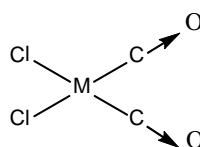
- 1) For each of the following, write down :
 - i) Symmetry species of all possible modes of vibration
 - ii) All IR and Raman active vibrations
- B_2H_6 , $[Co(L)_6]^{3+}$, *trans*- $[PtCl_2(NH_3)_2]$
 III IV V
- 2) For each of the following specific bonds shown by arrows, write down:
 - i) Symmetry species of all possible stretching vibrations
 - ii) All IR and Raman active stretching vibrations



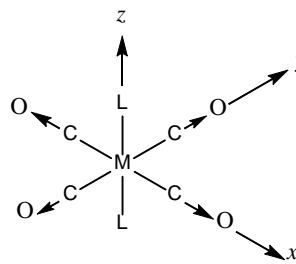
VI



VII
(With four right angles)



VIII



IX

References for Further Reading

- [1] G. M. Barrow, "Basic Principles of Spectroscopy ", Mc Graw-Hill Kogashua, (1971).
- [2] D. M. Bishop, "Group Theory and Chemistry", Dover Publications, Inc., N. Y., (1973).
- [3] R. L. Carter, "Molecular Symmetry and Group Theory", J. Wiley, N. Y., (1998).
- [4] R. Chang, "Basic Principles of Spectroscopy ", Mc Graw-Hill, Kogashua, (1971).
- [5] J. F. Cornwell, "Group Theory in Physics", Volume I, Academic Press Inc, London, (1984).
- [6] F. A. Cotton, "Chemical Applications of Group Theory", 2nd ed., J. Wiley, N.Y., (1971).
- [7] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley Interscience, NY, (1988).
- [8] J. D. Donaldson and S. D. Ross, "Symmetry and Stereochemistry", Intertext Books, London, (1972).
- [9] B. Douglas, D. H. McDaniel and J. J. Alexander, "Concepts and Models of Inorganic Chemistry", 2nd ed., J. Wiley, N.Y., (1983).
- [10] R. S. Drago, "Physical Methods in Inorganic Chemistry", Van Nostrand Reinhold, N.Y., (1965).
- [11] R. S. Drago, "Physical Methods for Chemists", 2nd ed., Saunders College Publ. Ft. Worth, (1992).
- [12] M. S. Dresselhaus, G. Dresselhaus and A Jorio, "Group Theory: Application to the Physics of Condensed Matter", Springer-Verlag, N. Y., (2008).
- [13] A. E. A. V. Ebsworth, D. W. H. Rankin and S. Cradock, "Structural Methods in Inorganic Chemistry", Blackwell Scientific Publications, Oxford, (1987).
- [14] J. N. Franklin, "Matrix Theory", Prentice-Hall, N. J., (1968).
- [15] S. Fritzsche, "Application of Point-Group Symmetries in Chemistry and Physics: A Computer-Algebraic Approach", International Journal of Quantum Chemistry 106, 98–129, (2005).
- [16] N. N. Greenwood, Chem. Brit., 6, (1970), 119.
- [17] M. Hamermesh, "Group theory and Its Application to Physical Problems", Addison - Wesley Publishing Company, Reading, Massachusetts, (1962).

- [18] J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity", 3rd ed., Harper & Row, Publ., NY (1983).
- [19] J. E. House, "Fundamentals of Quantum Chemistry", 2nd ed. Elsevier- Academic Press. (2004).
- [20] P. W. M. Jacobs, "Group Theory with Applications in Chemical Physics", Cambridge University Press, Cambridge, (2005).
- [21] H. H. Jaffe' and M. Orchin, "Symmetry in Chemistry", 3rd Printing, J. Wiley, N. Y., (1965).
- [22] A. W. Joshi, "Elements of Group Theory for Physicists", 3rd ed. Wiley Eastern Limited, New Delhi, (1982).
- [23] B. Kolman, "Introductory Linear Algebra with Applications", 6th ed., Prentice-Hall, N. J., (1997).
- [24] S. F. A. Kettle, "Symmetry and Structure: Readable Group Theory for Chemist", 3rd ed., J. Wiley, Chichester, (2007).
- [25] W. Ledermann, "Introduction to Group Characters", Cambridge University Press, Cambridge, (1977).
- [26] A. M. Lesk, "Introduction to Symmetry and Group Theory for Chemists", Kluwer Academic Publishers, Dordrecht, (2004).
- [27] I. N. Levine, "Quantum Chemistry", 3rd ed., Allyn and Bacon, Boston, (1983).
- [28] D. E. Littlewood, "The Theory of Group Characters and Matrix Representations of Groups ", 2nd ed., Clarendon Press, Oxford, (1950).
- [29] R. McWeeny, "Symmetry: An Introduction to Group Theory and Its Applications", Pergamon Press, Oxford, (1963).
- [30] R. G. Mortimer, "Mathematics for Physical Chemistry ", Macmillan, N. Y., (1981).
- [31] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compound: Part A", 5th ed., J. Wiley, N. Y., (1997).
- [32] A. D. Polyanin, and V.A. Manzhirov, "Handbook of Mathematics for Engineers and Scientists", Chapman & Hall/CRC Press, London, (2007).
- [33] K. V. Raman, "Group Theory and its Applications to Chemistry", Tata McGraw-Hill, New Delhi, (1990).
- [34] J. S. Rose, "A Course on Group Theory", Cambridge University Press, Cambridge, (1978).
- [35] J. A. Salthouse and M. J. Ware, "Point Group Character Tables and Related Data ", Cambridge University Press, London, (1971).
- [36] W. R. Scott, "Group Theory", Courier Dover, N. Y., (1987).

- [37] R. B. Shirts, "Correcting Two Long-Standing Errors in Point Group Symmetry Character Tables", *J. Chem. Ed.*, **84** (11), (2007).
- [38] M. Tinkham, and G. Mckay, "Group Theory and Quantum Mechanics", McGraw-Hill, N. Y., (1964).
- [39] W. Tung, "Group Theory in Physics", World Scientific Publishing, Singapore, (1985).
- [40] D. S. Urch, "Orbitals and Symmetry", The Macmillan Press LTD, London, (1979).
- [41] T. Veszprémi, and M. Fehér, "Quantum Chemistry: Fundamentals to Applications", Springer, N. Y., (1999).
- [42] A. Vincent, "Molecular Symmetry and Group Theory", J. Wiley, Chichester, (1977).
- [43] E. B. Wilson Jr., J.C. Decius, and P.C. Cross, "Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra", Dover, N. Y., (1955).
- [44] G. Wulfsberg, "Inorganic Chemistry", University Science Books, Sausalito, CA, (2000).
- [45] <http://symmetry.jacobs-university.de/>
- [46] <http://chemistry.umeche.maine.edu/Modeling/mulliken.html>