

Symmetry and Group Theory for the study of vibrational spectroscopy for complex molecule

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Abstract

The application of symmetry and group theory is a powerful tool for investigating the vibrations of molecules. In this paper, we use group theory to vibrational spectroscopy and instructions on how to use them for complex molecule. First we briefly discuss the quantum mechanical nature of vibrations and the experimental methods used. Group theory is a mathematical model connecting molecular symmetry to properties such as IR-active vibrational modes. Every molecule can be classified with a point group, which describes every symmetry element present in a molecule with respect to a fixed point. We then present the principal concepts for applying group theory to molecules. Group theory provides special tables, called character tables, to predict the effect of a molecule's symmetry on its vibrational modes and other important properties. The symmetry operations which are used to comprise groups are described and then used to determine the point groups of molecules. The properties of character tables are presented and the method for obtaining a reducible representation for all the motions of a molecule is detailed. This can then be broken down to obtain the irreducible representation which contains the symmetry species of the individual vibrations. The determination of symmetry adapted linear combinations is outlined and the basis for spectroscopic selection rules is presented. The paper concludes by examining how matrix algebra along with symmetry concepts simplifies calculations.

Keywords: Irreducible representation, wave function, vibrational spectroscopy.

Introduction

Reducible representations and irreducible representations [1] will be needed for normal mode of analysis and classification of vibrational modes according to symmetry species. The direct product of the irreducible representations is utilized to obtain the selection rules for infrared [2] and Raman spectroscopy.

According to quantum mechanical rule, $\Delta v = \pm 1$ i.e. transition $v_0 \rightarrow v_1$ is allowed. The absorption of IR depends upon the transition moment integral of the type

$$\int \psi_i^* \mu \psi_j dT \quad \dots\dots(1)$$

i.e. transition occurs from vibrational ground state(initial) ψ_i to vibrationally excited state ψ_j by absorbing one quanta [3] of energy. This is called fundamental transition. The μ is molecular dipole moment vector. The probability of such transition from ψ_i (ground vibrational state) to ψ_j (ground vibrational state) is directly proportional to transition moment [4-5] given by the integral of the type given in equation (1). As ψ_i ground state wave function is always real, i.e. $\psi_i^* = \psi_i$. Equation (1) can be written as

$$\int \psi_i \mu \psi_j dT \quad \text{where } dT \text{ means integration is carried over all variables of the wave function.}$$

The spectroscopic activity of a vibrational band [6] depends upon the value of transition moment integral $\int \psi_i \mu \psi_j dT$. If this integral has zero value for a particular transition, then the probability of occurring this transition will be zero and no absorption of IR radiations will occur. Thus, the transition is forbidden and vibration will be vibrationally inactive. If the integral is non zero, then there will be of IR radiations by the molecule and the transition will be allowed. Hence it will be IR active.

Material and Method

In this paper we study vibration will be vibrationally active or inactive for complex molecule of Penta aqua phallate chromium (I) complex complex $[\text{Cr}(\text{C}_8\text{H}_5\text{O}_4)(\text{H}_2\text{O})_5]$. The character table of the group is computed. In general, solving of integrals of the type $\int \psi_i \mu \psi_j dT$ is a cumbersome process. Group theory helps and simplifies the solutions of such integrals. According to group theory and symmetry considerations, "if the direct product in this integral contains totally symmetrical representation (an irreducible representation for which $\chi = +1$ for all symmetry operations of the point group), then the integral will be non zero and there will be interaction between electric field component of electromagnetic radiation (in IR region) and electric field component of oscillating electric dipole moment of the vibrating molecule and hence absorption of IR radiation will occur and vibration will be IR active"[7,8].

Thus only difficulty left, in assigning the spectroscopic activity to vibrational modes, is to solve this integral.

Transition moment integral vector μ can be splitted up into three components along X-,Y- and Z- axes, so that component integrals of the main integral, $\int \psi_i \mu \psi_j dT$ can be written as,

$$\int \psi_i \mu_x \psi_j dT \quad \dots\dots\dots(2)$$

$$\int \psi_i \mu_y \psi_j dT \quad \dots\dots\dots(3)$$

$$\int \psi_i \mu_z \psi_j dT \quad \dots\dots\dots(4)$$

If any of these integrals, as given as equation (2),(3),(4) is non zero according to symmetry consideration, then the vibrational mode will be IR active.

So problem now is how to check the symmetries of direct product in these three component integrals. We know that vibrational ground state $v_0=0$ i.e ψ_i has mathematical similarity to that of s-orbital. Since a sphere is totally symmetrical in a point group, the ground vibrational state ψ_i will be totally symmetrical for all molecules.

Symmetries of transition moment vectors μ_x, μ_y, μ_z is the same as that of X-, Y- and Z-axes or that of translational vectors T_x, T_y, T_z . Their symmetries can be directly obtained from the character table of the point group to which the molecule belongs. The symmetry

properties of vibrationally excited states ψ_j are the same as that of the vector that describes forms the basis for the particular vibrational mode (Γ_{vib}).

So we have to evaluate the direct product of (i) ψ_i ground state (totally symmetric), (ii) the irreducible representation for which X-, Y- and Z-axes or T_x, T_y, T_z form the basis for representations and(iii) ψ_j , excited state, i.e. irreducible representation of the vibrational mode to be considered for IR activity(i.e. spectroscopic activity of which we want to determine).

To explain this procedure let us take complex $[\text{Cr}(\text{C}_8\text{H}_5\text{O}_4) (\text{H}_2\text{O})_5]$ point group molecules. We know as $\Gamma_{vib}= 2A_1 + B_1 + E$. We have to find the activity of A_1, B_1 and E modes i.e. ψ_j belongs to either A_1 or B_1 symmetries. In C_{4v} point group, the totally symmetric representation is A_1 . We have to find the irreducible representations for which X-,Y- and Z-axes or T_x, T_y, T_z form the basis for representations, i.e. symmetry species of μ_x, μ_y, μ_z components.

Character table for C_{4v} point group

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	Quadratic functions	Cubic functions
A_1	+1	+1	+1	+1	+1	z	x^2+y^2, z^2	$z^3, z(x^2+y^2)$
A_2	+1	+1	+1	-1	-1	R_z	-	-
B_1	+1	-1	+1	+1	-1	-	x^2-y^2	$z(x^2-y^2)$
B_2	+1	-1	+1	-1	+1	-	xy	xyz
E	+2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)	(xz^2, yz^2) (xy^2, x^2y) (x^3, y^3)

Using character table of C_{4v} point group symmetries of these vectors are;

$$\mu_x = T_x \quad \text{or } x \rightarrow E$$

$$\mu_y = T_y \quad \text{or } (y) \rightarrow E$$

$$\mu_z = T_z \quad \text{or } z \rightarrow A_1$$

So to check the activity of vibrational modes $\Gamma_{vib} = 2A_1 + B_1 + E$ we have to solve the integrals of the type;

$$\int \psi_i \mu_x \psi_j dT = \int A_1 \otimes E \otimes A_1 = A_1 \quad \dots\dots\dots(5)$$

$$\int \psi_i \mu_y \psi_j dT = \int A_1 \otimes E \otimes A_1 = A_1 \quad \dots\dots\dots(6)$$

$$\int \psi_i \mu_z \psi_j dT = \int A_1 \otimes A_1 \otimes A_1 = A_1 \quad \dots\dots\dots(7)$$

Here, ψ_i has A_1 symmetry; μ_x, μ_y, μ_z have E and A_1 symmetries respectively and ψ_j has the symmetries of the type A_1 . Only integral that contain totally symmetrical representation of E and A_1 in eq. (5), eq.(6) and eq. (7) will be non zero and hence this mode will be IR active. Out of these three integrals, if any of the integrals contains totally symmetric representation A_1 then that IR mode will be active. Here out of integrals given by the eq.(5), eq.(6) and eq.(7) only eq.(7) integral contains totally symmetric representation A_1 thus the overall integral $\int \psi_i \mu_z \psi_j dT$ is non zero.

So A_1 mode is IR active. Similarly E mode is also IR active.

Thus in $\Gamma_{3N} = 2 A_1 + B_1 + E$ both A_1 and E are IR active for complex $[\text{Cr}(\text{C}_8\text{H}_5\text{O}_4)(\text{H}_2\text{O})_5]$.

Conclusion

Since A_1 and E are infrared active means it must result in a periodic change in the dipole moment of the complex molecule. It absorbs infrared radiation so that the transition results in a deformation of the molecule so that the dielectric constant is different in the excited state from the ground state.

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