Group Methods for Molecular Vibrational Spectra

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Abstract. This article explores the application of group theory to molecular vibrational spectra, a key area of study in physics and chemistry, focusing on retro of early derivations understanding how group theoretical methods can simplify the analysis of molecular vibrations and the corresponding spectroscopic selection rules. It then investigates the use of point group and factor group representations to describe the symmetry properties of molecules and their normal modes of vibration. The methods employed include mathematical formulations based on group theory, such as symmetry operations, representation theory, and reduced coordinates. The results demonstrate that group theory effectively reduces the computational complexity of analysing molecular vibrational spectra, clarifying the degeneracy in normal modes and facilitating the interpretation of infrared and Raman spectra. This study provides a fundamental framework that could be expanded with advanced computational tools and experimental techniques, contributing to deeper insights into molecular dynamics and the development of new theoretical models in vibrational spectroscopy.

Keywords: Group theory; Molecular vibration; Selection rule.

1. Introduction

Some people say it is very surprising that mathematics is so useful in physics, while the author thinks it is natural because, in view mathematics is the language of precision. If the universe follows precise rules, then it will be describable by mathematics as the language. Some fundamental reasons for certain theories to succeed in levels of atoms and molecules are the symmetries provided by those physical systems that could be reflected by the theories. Approaches upon symmetry ask nothing about the details of the model, and language of group theory is central for dealing with symmetry [1].

For the energy level structures of atoms and molecules, quantum theory has given explanations on chemical bindings beyond the realm of classical theory. Regardless of whether quantum action is considered or not, the symmetric structures of molecules and their normal vibration modes possessed has already been discussed in classical physics. Group representations play a crucial role in linking group theory with the symmetry characteristics of this physical system [2]. While the primary focus is on quantum systems, much of this discussion is equally relevant to be describable through classical physics. Despite the developments in IR absorption and Raman scattering devices, newest information about the structure of molecules and their vibrational spectroscopy can only be fundamentally understood with group theory, i.e. representations of point group and factor group. The author believes that in the current context where chemical research on molecular vibrational properties predominantly concentrates on the analysis of experimental details, it is imperative to appropriately return to factor group analysis and first-principles calculations to foster the formulation of new theories, especially now that computational methods have also become mainstream [3].

This article traces the progress of mathematical analysis on molecular vibrations, from the very primitive treatments to the most recent developments, in order to showcase the role of group theory in different stages. Section 2 will first focus on symmetries possessed by molecules, covering operations and their resemblance to point group elements, including imitations of early mathematical processing, and then turning to discuss reduced coordinates methods. Following that, Section 3 will discuss how group representation simplified the computations in the early developments of normal modes and finally selection rules associated with infrared and Raman processes in the 20th century, inspired computational methods in the early 21st century, and the application of factor group analysis and first principles calculations in recent studies.

2. Methods and Theory

2.1. Background: The symmetry of a molecule

It is reasonable to assume that the nuclei in a molecule will be arranged symmetrically in equilibrium, so this article resorts to group theory, the mathematics of symmetry. Ideally, suppose some operations comprising reflections and rotations return the molecule to its original, each covering operation C can be represented by an $3\,x\,3$ orthogonal matrix Γ_C, given a set of Cartesian coordinates with the origin at the center of mass of the molecule in equilibrium, i.e. the point $(X \quad Y \quad Z)^T$ under the operation becomes $\Gamma_C(X \quad Y \quad Z)^T$. Denote $r_1, r_2, \dots, r_n$ a set of coordinates indicating the relative positions of the nuclei in the molecule such as distances between nuclei and angles between bonds. When the nuclei vibrate around their equilibrium positions, those$r$'s vary. Let $R_1, R_2, \dots, R_n$ be r's increments, and further let $x_1, y_1, z_1, x_2, \dots, x_N, y_N, z_N$ be the increments in the Cartesian coordinates of the N nuclei. For small vibrations, the R's are in linear approximations with the x's, y's and z's [4]

$$R = \begin{pmatrix} R_1 \\ R_2 \\ \vdots \\ R_n \end{pmatrix} = BA, \tag{1}$$

Where $A = (x_1 \quad y_2 \quad \cdots \quad z_N)^T$ and B being a constant $n\,x\,3N$ matrix. After performing the operation$C$, the molecule is indistinguishable from the original self, so the author writes Eq. (1) down and obtains a new equation for the new molecule:

$$R^C = BA^C \tag{2}$$

Here,R^C's represents the coordinates of the new molecule, which coincide with R through the operation C, and

$$A^C = \begin{pmatrix} \Gamma_C \begin{pmatrix} x_{C^{-1}1} \\ y_{C^{-1}1} \\ z_{C^{-1}1} \end{pmatrix} \\ \vdots \\ \Gamma_C \begin{pmatrix} x_{C^{-1}n} \\ y_{C^{-1}n} \\ z_{C^{-1}n} \end{pmatrix} \end{pmatrix} \tag{3}$$

Where $C^{-1}i$ is the nucleus which will become the nucleus i after the operation C let Z_C be a square matrix of order $3N$ with the elements $(Z_C)_{ix,jx} = \delta_{j,C^{-1}i}, (Z_C)_{ix,jy} = 0\ etc.\ i,j = 1,2,\dots,N$ and let P_C stand for $\begin{pmatrix} \Gamma_C & 0 & 0 & 0 \\ 0 & \Gamma_C & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & \Gamma_C \end{pmatrix}$, then Eqs (2) And (3) give

$$R^C = BP_CZ_CA. \tag{4}$$

This equation applies to all operations C and serves as the mathematical expression of the molecule's symmetry [5].

In certain cases, the coordinates $R_1, R_2, \dots, R_n$ are sufficient to determine $R_1^C, R_2^C, \dots, R_n^C$ for all covering operations C. This is true if (i) R contain only complete sets of equivalent coordinates; or if (ii) the R's includes all that are necessary to describe the internal structure of the molecule. In both cases, for small vibrations $R^C = A_CR$; where A_C is an orthogonal matrix with elements 0 or 1 in case (i), and a $n\,x\,n$ matrix in case (ii). By (4), $BP_CZ_CA = R^C = A_CR = A_CBA$But since A is arbitrary,

$$BP_CZ_C = A_CB. \tag{5}$$

This is the fundamental relationship on which all the following derivations are based.

To proceed further, note that the covering operations C form a group, and P_C's Z_C's, and A_C's each form a group isomorphic with it. This group is known as the "point group." In modern physics, the point group theory is so significant that the properties have been studied in detail, as demonstrated, it provides the mathematical foundation for interpreting the spectra of molecules.

2.2. Choice of Internal Coordinates

First choose the coordinates $R_1, R_2, \dots, R_n$ such that they contain only complete sets of equivalent internal coordinates and are necessary for determining the structure of the molecule. The simplest approach is to select the increments of inter-nuclear distances and bond angles as the R's. The matrix B can then be determined. Clearly, the choice falls under case (i) of §2.1, so they A_C's are orthogonal and have elements 0 or 1. It is evident that $(A_C)_{i,j} = 0$ if R_i and R_j are not equal. The author will utilize the following theorem from group theory:

If A_C constitutes a group of orthogonal matrices, and $W_C^{\alpha}(\alpha = 1,2, \dots, k)$ are the irreducible orthogonal representations of this group, then there exists an orthogonal matrix M such that $W_C = MA_CM^{-1}$ takes the form [6]

$$\begin{pmatrix} W_C^1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & W_C^1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \ddots & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & W_C^1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & W_C^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & W_C^2 \end{pmatrix} \tag{6}$$

Define real $Q = (Q_1 \quad Q_2 \quad \cdots \quad Q_n)^T = MR$ as the "reduced coordinates". Evidently $Q^C = MR^C = MA_CR = MA_CM^{-1}Q = W_CQ$. Not all Q's are independent. To select the independent ones comes the following theorem.

Theorem 1. It is always possible to omit some Q's so that (i) the remaining ones are all independent; (ii) the omitted ones are dependent on the remaining ones; and (iii) the remaining ones belong to complete blocks of the group of the matrices W_C [7].

Because of the properties (i) and (ii), the remaining coordinates is found to satisfy $R'' = (R''_1 \quad R''_2 \quad \cdots \quad R''_{3N-6})^T$ and are the "independent reduced coordinates". From (iii), $R''^C = U_CR''$ where U_C is obtained from W_C by omitting some blocks. These coordinates may also be obtained in alternate ways and have been given various names by different authors. The relation between R'' and the "symmetry coordinates" of Howard and Wilson will be discussed in §3.1.

To calculate $Spur(U_C)$, suppose that the constraints on the R's are given by $DR = 0$ where $DD' = I$.

Theorem 2. It is found that

$$Spur(U_C) = Spur(A_C)' - Spur(\mathrm{D}A_CD') \tag{7}$$

This theorem greatly simplifies the calculation of $Spur(U_C)$ (since the elements of A_C are 0 or 1) and Q can be carried out before performing the transformation from R. Additionally, it allows us to calculate the contributions of different constraints separately.

2.3. The Kinetic and the Potential Energies

Suppose that $(R_1 \quad R_2 \quad \cdots \quad R_{3N-6})^T = R$ are the increments of $3N-6$ independent internal coordinates, for small vibrations $R = BA$, where $A = (x_1 \quad \cdots \quad z_N)^T$ is defined in §2.1. Suppose that the equilibrium positions of the nuclei are, in Cartesian coordinates, (X_1, Y_1, Z_1) (X_2, Y_2, Z_2) and(X_N, Y_N, Z_N). Here, $m_1, m_2, \dots, m_N$ be their masses. Write

$$F=\begin{pmatrix} m_1 & 0 & 0 & m_2 & 0 & 0 & \cdots & 0 \\ 0 & m_1 & 0 & 0 & m_2 & 0 & \cdots & 0 \\ 0 & 0 & m_1 & 0 & 0 & m_2 & \cdots & m_N \\ 0 & m_1Z_1 & -m_1Y_1 & 0 & m_2Z_2 & -m_2Y_2 & \cdots & -m_NY_N \\ -m_1Z_1 & 0 & m_1X_1 & -m_2Z_2 & 0 & m_2X_2 & \cdots & m_NX_N \\ m_1Y_1 & -m_1X_1 & 0 & m_2Y_2 & -m_2X_2 & 0 & \cdots & 0 \end{pmatrix} \tag{8}$$

Then the first column of $B\begin{pmatrix} \frac{1}{m_1} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \frac{1}{m_N} \end{pmatrix}F'$ is the matrix $B(1 \quad 0 \quad 0 \quad 1 \quad 0 \quad 0 \quad \cdots \quad 0)^T$ which is the value of R when all the nuclei are displaced by 1 unit of length along the $X-$axis. And denote $M=\begin{pmatrix} \frac{1}{m_1} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \frac{1}{m_N} \end{pmatrix}$ from now on. But the R's are the increments of internal variables, hence $B(1 \quad 0 \quad 0 \quad 1 \quad 0 \quad 0 \quad \cdots \quad 0)^T = 0$. In the same manner it can be shown that $BMF' = 0$.

So far, the molecule in a specific Cartesian coordinate system has been described. However, when the molecule moves, rotates, and vibrates in space, there remains some arbitrariness in the choice of the axes fixed to the molecule. Nevertheless, the following method for selecting these axes is most preferable. The $3N-6$ internal variables $R_1, R_2, \ldots, R_{3N-6}$ is determined uniquely from the structure of the molecule. Define $x_1, y_1, \ldots, z_N$ by

$$A=\begin{pmatrix} x_1 \\ \vdots \\ z_N \end{pmatrix}=\begin{pmatrix} B \\ F \end{pmatrix}^{-1}\begin{pmatrix} R \\ 0 \end{pmatrix}, \tag{9}$$

So that $FA = 0$.

According to the definition of B, it can be concluded that it is possible to find a reference axis system such that the positions of the nuclei are $(X_1 + x_1, Y_1 + y_1, Z_1 + z_1), (X_2 + x_2, Y_2 + y_2, Z_2 + z_2), \ldots, (X_N + x_N, Y_N + y_N, Z_N + +z_N)$ when the molecule is not significantly distorted from its equilibrium structure. Thus, there are 6 external variables specifying the position and orientation of the axes in space, and $3N-6$ variables $R_1, R_2, \ldots, R_{3N-6}$ indicating the positions of the nuclei with respect to these axes as given by equation (9) [8].

The equation (10) indicates that the origin of the moving axes is always at the center of mass of the molecule, and the angular momentum of the molecule in this reference frame is of order $mx\dot{x}$. Therefore, if the molecule rotates in space with an angular velocity ω around the center of mass, its kinetic energy is $T_{COM} + T_{rotation} + \frac{1}{2}\sum_i m_i(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) + term \sim mx\dot{x}\omega$. But $T_{rotation} = (K.E.\ of\ rotation\ if\ A = 0) \sim m\omega^2 xX$. Now $T_{COM} + (K.E.\ of\ rotation\ if\ A = 0)$ depends on the external variables and their time derivatives only. And in a gas, due to thermal agitation,$\omega X \sim \dot{x}$ Thus in the first approximation the equation of motion is to be derived from

$$T=\frac{1}{2}\sum_i m_i(\dot{x}_i^2+\dot{y}_i^2+\dot{z}_i^2)=\frac{1}{2}(\dot{R}' \quad 0)\begin{pmatrix} B \\ F \end{pmatrix}^{-1'}\begin{pmatrix} m_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & m_N \end{pmatrix}\begin{pmatrix} B \\ F \end{pmatrix}^{-1}\begin{pmatrix} \dot{R} \\ 0 \end{pmatrix} \tag{10}$$

But $\begin{pmatrix} B \\ F \end{pmatrix}M(B' \quad F') = \begin{pmatrix} BMB' & 0 \\ 0 & FMF' \end{pmatrix}$. Hence writing

$$G = BMB', \tag{11}$$

One has

$$2T = \dot{R}'^{G^{-1}\dot{R}}. \tag{12}$$

If take the independent reduced coordinates R'' (§2.2) to be the R's, the results may be summarized

$$R'' = LA, G'' = LML', 2T = \dot{R''}'G''^{-1}\dot{R''}. \tag{13}$$

Now by (5), $LP_CZ_C = U_CL$ (U_C $stands\ for\ A_C, cf.$ §2.2) so that $G'' = LML' = U_C'LP_CZ_CMZ_C'^{P_C'}L'^{U_C}$. But M, P_C and Z_C commute with each other, hence $G'' = U_C'LML'^{U_C} = U_C'G''^{U_C}$. Suppose

$$(U_C)_{\alpha\beta,\alpha'\beta'} = \delta_{\alpha\alpha'}\delta_{\beta\beta'}W_C^{\alpha}, \alpha = 1,2,\dots,k, \beta = 1,2,\dots,n_\alpha, \tag{14}$$

Where W_C^{α} is irreducible. (cf. §2.2) Since $U_CG'' = G''^{U_C}$, one has $W_C^{\alpha}(G'')_{\alpha\beta,\alpha'\beta'} = (G'')_{\alpha\beta,\alpha'\beta'}W_C^{\alpha'}$. Hence

$$(G'')_{\alpha\beta,\alpha'\beta'} = \delta_{\alpha\alpha'}\, g_{\beta\beta'}^{\alpha} I. \tag{15}$$

If W_C^{α} is of orderd_α, this shows that the nonvanishing elements of G'' are in $\sum_{\alpha=1}^{k} d_\alpha$ diagonal blocks of which d_α are identical of dimension $n_\alpha\ x\ n_\alpha$.

The potential energy depends only on the internal coordinates. For small vibrations, it is approximately equal to$\frac{1}{2}R'''\Phi R''$, where Φ is a positive symmetric matrix, since the potential energy is minimized when the molecule is in equilibrium. The covering operations leave the potential energy unchanged: $\frac{1}{2}R'''\Phi R'' = \frac{1}{2}R''^{C}\ '\Phi R''^{C} = \frac{1}{2}R'''^{U_C'}R''$ But R'' is arbitrary, hence $\Phi = U_C'\Phi U_C$. Thus as Eq. (14) tells, one has

$$(\Phi)_{\alpha\beta,\alpha'\beta'} = \delta_{\alpha\alpha'}\, v_{\beta\beta'}^{\alpha} I, \alpha = 1,2,\dots,k, \beta = 1,2,\dots,n_\alpha \tag{16}$$

There are therefore totally $\sum_{\alpha=1}^{k} n_\alpha^2$ independent constants in the potential energy, which are usually unknowns.

3. Results and Applications

3.1. Normal Coordinates

In terms of the independent reduced coordinates R'' defined in §2.2, the kinetic energy and the potential energy are $\frac{1}{2}\dot{R''}'G''^{-1}\dot{R''}$ and $\frac{1}{2}R'''\Phi R''$, where G'' is positive definite. Let $\lambda_1, \lambda_2, \dots, \lambda_{3N-6}$ be the roots of the equation

$$\left|\lambda G''^{-1} - \Phi\right| = 0, i.e. |\lambda I - \Phi G''| = 0. \tag{17}$$

Then there exists a matrix L'' such that $L''G''L''' = I, L''^{-1'}\Phi L''^{-1} = \begin{pmatrix} \lambda_1 & 0 & & 0 & 0 \\ 0 & \lambda_2 & & 0 & 0 \\ 0 & 0 & \ddots & & 0 \\ 0 & 0 & 0 & \lambda_{3N-6} \end{pmatrix} = \Lambda$. Put $\Phi = \begin{pmatrix} \Phi_1 \\ \vdots \\ \Phi_{3N-6} \end{pmatrix} = L''\Phi$, the author immediately gets

$$2\ x\ kinetic\ energy = \dot{R''}'G''^{-1}\dot{R''} = \dot{\Phi}'\Phi = \sum_{i=1}^{3N-6} \dot{\Phi}_i^2, \tag{18}$$

$$2\ x\ potential\ energy = R'''\Phi R'' = \Phi'\Lambda\Phi = \sum_{i} \lambda_i\Phi_i^2. \tag{19}$$

These coordinates Φ_i are known as the "normal coordinate"s. They are obtained by first solving (16), thus getting λ_i; and then determining L'' from

$$L''G''\Phi = \Lambda L''. \tag{20}$$

This L'' must be normalized by

$$L''G''\mathrm{L}'' = I. \tag{21}$$

The normal coordinates are then calculated from $\Phi = \mathrm{L}''\mathrm{R}''$ [9].

Now this article shall be able to shed light on the role that symmetry plays in simplifying the calculations. Equations. (15) And (16) show that the secular equation (17) is factored into $\sum_{\alpha=1}^{k} d_\alpha$ equations of which d_α are identical and are of the n_α-th degree. The labor of solving for the Λ's is considerably saved. Moreover, the no. of unknown constants in Φ is reduced. The normal coordinates are also a special form of the "symmetry coordinates" introduced by Howard and Wilson. The most general form of the symmetry coordinates φ is given by $\Phi = \mathrm{L}\varphi$ where $L_{\alpha\beta,\alpha'\beta'} = \delta_{\alpha\alpha'}\, l^{\alpha}_{\beta\beta'} U^{\alpha}, \alpha = 1,2,\dots,k, \beta = 1,2,\dots,n_\alpha$in which U^α is orthogonal and $l^{\alpha}_{\beta\beta'}$ form an orthogonal matrix when β range over $1,2,\dots,n_\alpha$

3.2. Solution of Classical Theory

The Lagrangian is, from Eqs. (18) And (19), $\frac{1}{2}\sum_{i=1}^{3N-6}\left(\dot{\Phi}_i^2 - \Lambda_i\Phi_i^2\right)^2$. the equations of motion are therefore $\ddot{\Phi}_i + \Lambda_i\Phi_i = 0, i = 1,2,\dots,3N-6$. Hence$\Phi_i = (\Phi_i)_0 \cos\left(\sqrt{\Lambda_i}t + \phi_i\right)$. The frequencies of vibration are thus $\frac{\sqrt{\Lambda_1}}{2\pi}, \frac{\sqrt{\Lambda_2}}{2\pi}, \dots, \frac{\sqrt{\Lambda_{3N-6}}}{2\pi}$. this is correct only in the first approximation; but it serves to give almost all essential knowledge about the forces within the molecules.

3.3. Solution of Quantum Theory

Now, the author will calculate $T = \frac{1}{2}\sum_i \dot{\Phi}_i^2, V = \frac{1}{2}\sum_i \Lambda_i\Phi_i^2$. the wave equation is most easily obtained from the variational formulation of the problem: $\delta\int\left\{\sum \hbar^2 g^{ij}\frac{\partial\psi^*}{\partial\Phi_i}\frac{\partial\psi}{\partial\Phi_j} + (V - E)\psi^*\psi\sqrt{g}\, d\Phi_1 \dots d\Phi_{3N-6}\right\} = 0$, where g^{ij} is given by $T = g_{ij}\dot{x}^i\dot{x}^j$. Hence $\sum_i \frac{1}{2}\left(-\hbar^2\frac{\partial^2}{\partial\Phi_i^2} + \Lambda_i\Phi_i^2\right)\psi = E\psi$. The electric moment in any direction is, in the first approximation $D_0 + \sum_{i=1}^{3N-6} D_i\Phi_i$, where D_i is immediately calculable from (9). Thus, the wave function and selection rules, hence the frequencies in the vibrational spectra of the molecule, are the same as those of $3N-6$ independent harmonic oscillators with coordinates $\Phi_1, \Phi_2, \dots, \Phi_{3N-6}$. The frequencies are therefore exactly those obtained classically.

3.4. The Degree of Degeneracy

The author has observed that the secular equation (17) is decomposed into d_1 identical equations of the n_1-th degree, d_2 identical equations of the n_2-th degree… Therefore, there must be n_1 frequencies each corresponding to d_1 different normal modes of vibration (d_1-fold degenerate). Hence, d_1 d_2 etc., are referred to as "the degrees of degeneracy".

Interestingly, these can be determined along with n_1 n_2, etc., without the need to calculate the normal coordinates. For details, refer to (14), $\sum_\alpha n_\alpha Spur(W_C^\alpha) = Spur(U_C)$. But $\sum_c Spur(W_C^\alpha)Spur\left(W_C^\beta\right) = \delta_{\alpha\beta}h,$ where h = order of the group. Hence

$$n_\alpha = \frac{1}{h}\sum_c Spur(U_C)Spur(W_C^\alpha)\,. \tag{22}$$

Now both $Spur(W_C^\alpha)$ and d_α can be found from a table of characters of the point group, and $Spur(U_C)$ can be calculated through the theorem in §2.2, so that d_α and n_α are easily calculable from (22).

3.5. Computational Methods

Vibrational Spectroscopy has often been carried out for resolving the structure and bonds of the molecules, where incident radiation excites the molecule to a higher energy state with higher vibrational amplitude. Obtained spectra then will be analysed with techniques applying distinct physical principles, infrared and Raman spectroscopy. Infrared spectroscopy concerns with the absorption lines of the molecule, therefore it directly measures the vibrational frequencies; while Raman spectroscopy refers to the frequencies differences between the incident and the Raman-scattered light. The selection rule for vibrational transitions of infrared spectroscopy refers to the change of the electric dipole moment, but quite differently, Raman is about the change of the polarizability.

Molecular symmetry and point group are extensively utilized for the study of these vibrational spectra and their corresponding selection rules. However, in practice, the inefficient access to those group data makes it rather cumbersome to apply group theory. Insofar as the information revolution occurred, computer algebra clears the road, programs carried the game and promising ones emerged. BETHE program within MAPLE, for instance, helps determine the normal coordinates and activities in spectroscopy. Detailed basic group data including the cyclic, dihedral, the improper cyclic, the cubic and the icosahedral groups are provided. These families of point-group are crucial because in the character table, only those vibrational motions with the symmetry properties described can be allowed. Next together with the theoretical background of the BETHE program, the author tends to show little mathematical aspect of the selection process:

In infrared spectroscopy, the change in wave functions must result from the interaction between a change in the dipole moment μ and the incident radiation. For this type of transition, the probability is directly proportional to the square of the transition moment:

$$M_{if} = \int d\tau \Psi^*_{final} \mu \Psi_{initial} \tag{23}$$

In a similar manner, a vibrational transition will only take place if the polarizability α changes during the vibration. Therefore, a Raman transition necessitates a non-zero transition moment of this kind:$M_{if} = \int d\tau \Psi^*_{final} \alpha \Psi_{initial}$

3.6. Factor Group Analysis

Nowadays, researchers usually proceed factor group analysis to clarify the symmetry and the prediction of each vibrational mode in Infrared and Raman activities. Symmetry operations of, say, various space groups will be considered and to identify the representation of each mode, the corresponding character tables will be checked by directly performing the relevant symmetry operations on each displacement pattern. Using the matrix element theorem, prediction of which vibrations will be active in IR or Raman spectroscopy based on the symmetry characteristics of the normal modes will be performed. As for the internal vibration, the symmetry representations of, say, the point group shall be used. In some cases, the irreducible representations are the key. When it comes to rigid-body motion, factor group analysis also has something to Infrared intensities with those additional vibrational modes.

4. Conclusion

This article has explored the role of group theory in the study of molecular vibrations, focusing on the application of symmetry operations and group representations to understand vibrational spectra. By employing point group and factor group analysis, the author has demonstrated how group theory can simplify complex mathematical calculations related to normal modes of vibration and selection rules for infrared and Raman spectroscopy. The study covered fundamental equations such as those for the kinetic and potential energies, the secular equation, and the determination of normal coordinates, highlighting the power of symmetry in reducing computational complexity and revealing

the degeneracy in vibrational modes. The findings confirm that group theory provides a robust framework for analysing molecular vibrations, offering deeper insights into the structural properties and spectroscopic behaviour of molecules. However, there are areas for improvement, such as incorporating more advanced computational methods and integrating the latest experimental techniques to validate the theoretical models further. Future research could focus on developing more comprehensive computational tools to handle larger and more complex molecular systems, as well as extending the factor group analysis to include various molecular interactions. By doing so, people can enhance their understanding of molecular dynamics and pave the way for novel theoretical approaches in vibrational spectroscopy.

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