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Group Theoretical Vibrational Analysis of 4-Chlorobenzaldehyde

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Abstract: ***In this paper, vibrational analysis of 4-chlorobenzaldehyde is been carried out using the principles of group theory in chemistry. At first the symmetry elements were analysed and point group was derived to be Cs. Based on the character values and number of unshifted atoms for each symmetry operation, its reducible representation was obtained which later converted into irreducible representations. Using the character table, the IR active and Raman active vibrations were found out. Finally, the IR spectra of 4-chlorobenzaldehyde was also discussed.***

Keywords: 4-chlorobenzaldehyde, Vibrational analysis, Reducible and irreducible representations, Point group, IR and Raman spectral analysis, Group theory in chemistry.

1. Introduction

4-chlorobenzaldehyde is a volatile aromatic compound widely used in food, pharmaceuticals, and chemical industries. It consists of an aromatic ring linked to formyl group[1-3]. Molecular aggregation plays a pivotal role in biological systems, as it underpins essential processes, gives rise to emergent properties absent in individual molecules, and serves as a cornerstone in the design of advanced functional materials[4, 5]. Its molecular structure allows it to participate in non-covalent interactions such as hydrogen bonding and π–π stacking, which can lead to aggregation phenomena[6]. These aggregation properties are significant because they can alter solubility, bioavailability, and biological activity of benzaldehyde derivatives, especially when incorporated into larger molecular frameworks or drug candidates. Benzaldehyde and its derivatives have been reported to exhibit broad-spectrum antibacterial activity[2,3]. Mechanistic studies suggest that they act through disruption of bacterial cell membranes and interference with enzyme activity, leading to oxidative stress and bacterial cell death. Modified benzaldehyde derivatives, have shown enhanced antibacterial potency in both in-vitro and computational studies[5]. These derivatives exploit benzaldehyde's aggregation tendencies to form stable complexes that interact more effectively with bacterial targets.

The dual role of benzaldehyde—its ability to aggregate and its antibacterial activity—makes it an attractive candidate for designing novel antimicrobial agents, developing food preservatives with antibacterial properties and exploring nanomaterial applications, where aggregation behaviour can be harnessed for controlled drug delivery. In the present work, vibrational analysis of benzaldehyde is been studied using group theory. Such type of study may support to study aggregation of larger peptide[7-11] or polymer moieties too[12-19].

2. Methodology

The methodology for group theory vibrational analysis involves identifying the molecule's point group, generating a reducible representation from the molecule's vibrational motions, and then reducing this representation into a set of irreducible representations that correspond to the normal vibrational modes. The final step is to use selection rules, based on the symmetry of the irreducible representations and how they transform with cartesian coordinates (x,y,z) and binary functions (x^2, y^2, z^2, xy, xz, yz), to determine which modes are active in infrared (IR) and Raman spectroscopy.

The first step involves determination of point group based on symmetry elements such as symmetry axes, symmetry planes and symmetry center present in it. The second step is to arrive the reducible representation Γ_{red} which represent the molecule's 3N vibrational degrees of freedom (where N is the number of atoms) using a set of cartesian coordinates (x, y, z) centered on each atom. For each symmetry operation in the point group, determine how many atoms are "unshifted" and the character is been assigned correspondingly for respective operations. Multiplying the characters of number of unshifted atoms with its symmetry operation character, reducible representation (Γ_{red}) may be obtained from the resulting row of characters. The third step is to reduce the representation to irreducible representations using the reduction formulae. These irreducible representations classify the molecule's 3N total degrees of freedom. The fourth step is subtracting translational and rotational modes from the 3N total degrees of freedom. The rotational modes correspond to the symmetry of the rotations R_x, R_y and R_z. The total number of vibrational modes is computed using the formula $3N-6$ being 4-chlorobenzaldehyde is non-linear molecule. The final step is determining IR activity using the cartesian coordinates x,y,z as it involves change in dipole moment and Raman activity using tensor components $(x^2, y^2, z^2, xy, xz$ or $yz)$ as it involves change in polarizability.

3. Results and Discussion

The 4-chlorobenzaldehyde molecule has 14 atoms and its structure is shown in Figure 1. It has the symmetry element identity (E) and a single plane of symmetry which bisects the molecule (σ). This plane passes through the carbon atom of the aldehyde group, the carbon atom of the benzene ring to which the aldehyde is attached, and the para-chlorine atom.

The plane also contains the carbonyl oxygen and aldehyde hydrogen atom, as shown in Figure 1 and there is neither rotation axes nor an inversion centre. The combination of only the E and σ results in the *Cs* point group. As the molecule possess 14 atoms, it should exhibit 3 x 14 – 6 = 36 fundamental modes of vibrations as per the formula *3N-6*.

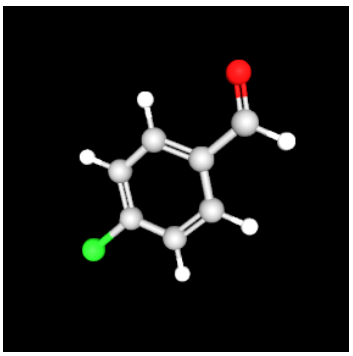

Figure 1: Molecular structure of 4-chlorobenzaldehyde

Vibrational spectroscopic techniques such as infrared (IR) and Raman spectroscopy reveal how different functional groups, particularly the aldehyde carbonyl and aromatic ring, contribute to the overall vibrational spectrum of 4-chlorobenzaldehyde. To start vibrational analysis of 4-chlorobenzaldehyde, first reducible representations were derived which are depicted in Table 1. The symmetry operation '*E*' represents do nothing operation; hence the number of unshifted atoms (USA) are 14 and the symmetry operation 'σ' represents reflection along the molecular plane. As the molecule is planar, all the atoms are unshifted during reflection operation; hence the number of USA are again 14 for reflection operation. In the second row the character values for '*E*' and 'σ' are given as 3 and 1 which were obtained from the principles of group theory. Multiplying the above two rows gives the reducible representation for the 4-chlorobenzaldehyde.

Table 1: Irreducible representations of 4-chlorobenzaldehyde

Cs	*E*	σ
No. of USA	14	14
χ value	3	1
χ_{red}	42	14

Table 2. Character table for the point group *Cs*

Irreducible Representation	E	σ	Linear Functions/ Rotations	Quadratic Functions
A′	1	1	x, y, Rz	x^2, y^2, z^2, xy
A″	1	-1	z, Rx, Ry	xz, yz

This reducible representation is converted into irreversible representation using the character table corresponding to '*Cs*' using the following reduction formula:

$$n_\Gamma = \frac{1}{h}\sum_i g_i \chi_\Gamma \chi_{red}$$

The term 'n_Γ' represents the number of times an irreducible representation appears in the reducible representation; 'h' represents the order of the group i.e., the total number of symmetry operations; $\sum_i$ represents summation over all the classes of the group; 'gi' represents the number of symmetry elements in each class; 'χ_Γ' represents the character of the irreducible representation for a symmetry operation in class (Table 2) and finally the term 'χ_{red}' represents the character of the reducible representation for a symmetry operation in class. Thus, the total irreducible represents which is the collection of translational, rotational and vibrational are obtained to be as:

Number of A′ = ½ [42+14] = 28;
and number of A″ = ½ [42-14] = 14.
$\Rightarrow \Gamma_{trans} + \Gamma_{vib} + \Gamma_{rot} = 28\ A' + 14\ A''$

From the Table 2, for translational motion, A′ transforms as x, y and A″ transforms as z; hence the Γ_{trans} are 2A′ + A″ while for rotational motion, A′ transforms as Rz and A″ transforms as Rx , Ry; hence the Γ_{rot} are A′ + 2A″. subtracting translational and rotational motions from the total value will give vibrational degrees of freedom for 4-chlorobenzaldehyde.

Γ_{vib} = 25 A′ + 11 A″ $\Rightarrow$ 25 A′ vibrations that are symmetric with respect to the plane of symmetry. These involve motions of the atoms within the plane, such as C-H stretches, C=O stretches, and ring deformations and 11 A″ vibrations that are antisymmetric with respect to the plane of symmetry. These include torsions and "wagging" motions of atoms out of the plane.

From the character table, the A′ transforms as (x,y) in the linear function suggesting that all the 25 A′ vibrations are IR active. Similarly, A′ also transforms as (x^2, y^2, z^2, xy) in the quadratic function suggesting all the all the 25 A′ vibrations are also Raman active. In a similar manner 11 A″ vibrations transform as (z) in linear function and (xz, yz) in quadratic function, indicating all the 11 A″ vibrations are both IR and Raman active. The total 36 vibrations (25 A′+11 A″) are found to be in agreement with the formula *3N-6,* which gives the number of vibrational degrees of freedom for a non-linear molecule.

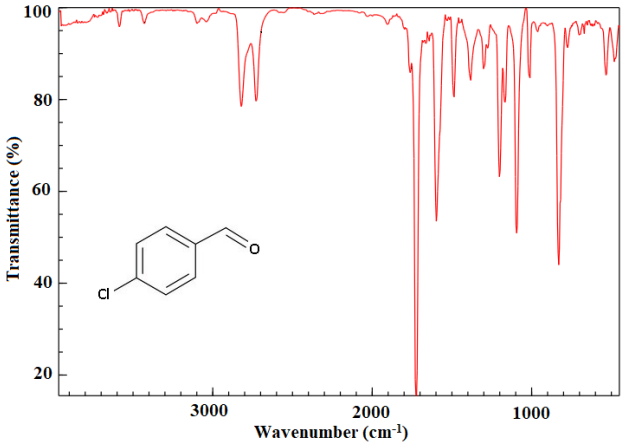

Figure 2: IR spectrum of 4-chlorobenzaldehyde

The infrared absorption spectrum of 4-chlorobenzaldeyde is given Figure 2. It is inferred from the above Figure 2 that it exhibited strong peak at 1720 cm^{-1} which is due to carbonyl stretching vibration of aldehyde group. The peak at 1600 cm^{-1} is due to -C=C- stretching vibrations. The peaks at 2720–2820 cm^{-1} is due to -C-H of aldehyde group. The -C-Cl stretching is observed in the finger print region at around 800 cm^{-1}.

4. Conclusion

The vibrational analysis of 4-chlorobenzaldehyde through group theoretical methods provides a systematic understanding of its molecular symmetry and characteristic IR/Raman active modes. By assigning the molecule to the appropriate point group (Cs), the symmetry elements guide the classification of normal modes into irreducible representations. This analysis demonstrates how theoretical tools complement experimental vibrational data, offering an insight into the structural characteristics of substituted aromatic aldehydes.

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