EAST EUROPEAN JOURNAL OF PHYSICS. 4. 512-516 (2025)
DOI:10.26565/2312-4334-2025-4-52 ISSN 2312-4334

LIE ALGEBRAIC MODELING OF VIBRATIONAL FREQUENCIES IN HEXACHLOROBENZENE: A SYMMETRY-ADAPTED APPROACH FOR THE D_{6h} POINT GROUP

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Received August 31, 2025; accepted October 16, 2025

This work uses a symmetry-adapted Lie algebraic framework to study the vibrational frequencies of hexachlorobenzene (C_6Cl_6). A U(2)-based vibrational Hamiltonian captures the fundamental modes and the first and second overtones by exploiting the molecule's D_{6h} point group symmetry. The algebraic approach considers anharmonicity and symmetry constraints to provide a compact and manageable analytical portrayal of the vibrational spectrum. The computed fundamental frequencies agree strongly with the observed values, validating the approach. Moreover, the extension to overtones underlines the algebraic model's capability to evaluate higher-order vibrational excitations in polyatomic molecules systematically. These results confirm the effectiveness of Lie algebraic methods in modelling vibrational features of highly symmetric molecules and serve as a solid basis for further work in molecular spectroscopy.

Keywords: *Hexachlorobenzene; Vibrational spectra; Lie algebraic modelling; Symmetry-adapted Hamiltonian; D_{6h} point group*
PACS: 33.20.Tp, 33.15.Mt, 03.65.Fd, 02.20.Sv, and 61.50.Ah

1. INTRODUCTION

Hexachlorobenzene (HCB) has been noted as an aromatic hydrocarbon that has been fully chlorinated, attracting much attention from scholars because of its remarkable stability, environmental longevity, and toxicity. Its diverse industrial applications and use as a fungicide were prominent in the past. However, it has become glaringly apparent that its biological consequences, alongside its long half-life in the environment, result in its classification as a persistent organic pollutant, which goes against international agreements. Reports indicate bioaccumulation of the compound in humans and animals, in which the toxin is contained within the adipose tissues. This results in neurotoxicity, hepatotoxicity, immunotoxicity, and endocrine disruption. Such results are noted as disturbing, especially in children and pregnant women, who are the most vulnerable [1].

The theory of symmetry states that a point group is associated with molecules that have planar structures, are of extreme symmetry, have angle and side counts, and cross elements of 12, like a hexagon. Thus, HCB can be derived from benzene and its six hydrogens replaced with chlorines. The high symmetry planar molecules can thus be characterised and have set vibrational modes that can be useful for modelling vibrational systems. Saeki (1962) states that there are 30 normal vibrational modes of HCB, and they can be divided into three parts: Raman modes, Infrared modes, and inactive (B_{2g}, B_{1u}, E_{2u}, A_{1u}) modes. The inactive modes can be characterised to determine structure, space location, and environmental impacts [2,3,4,].

HCB is a model used to study the vibrational states, and HCB and its depletion have many satellites and data files associated with them. Many techniques have been used to study the vibrational spectra of HCB. HCB has an abundance of data made from approaches for predicting the molecular rotational structures of HCB, like using DFT for electronic charge and spectrum analysis of HCB, and DFT and SQMFF and the DFT approaches with Raman and Infrared spectra techniques [5]. These approaches have proven helpful in many scenarios. However, the approach must be altered regarding computational symmetry, molecules, and the border set. It involves a high cost for experimental observations, resulting in a loss of molecular symmetry and anharmonicity in many systems.

The Lie algebraic approach provides an alternative method for vibrational analysis that is compact, and symmetry driven. It involves the construction of vibrational Hamiltonians in terms of U(2) Lie algebra generators and number, Casimir, and Majorana operator terms. Due to the symmetry and anharmonic effects incorporated within the approach, a more intuitive and physically more precise representation of vibrational states is obtained. In contrast to standard ab initio methods, the algebraic approach does not depend on potential energy surfaces and offers an algebraic formulation for vibrational levels [6-14].

The exceptionally well-defined vibrational characteristics of HCB and high D_{6h} symmetry make it a perfect subject for algebraic modelling. An adapted symmetry Hamiltonian readily provides analysis of overtone and combination bands with a reduced set of adjustable parameters. In this paper, we use the U(2) Lie algebraic approach to compute the fundamental vibrational frequencies of HCB and to compare these with experimental results to illustrate the usefulness of the approach [2].

Cite as: D. Rajani, T. Sreenivas, J. Vijayasekhar, East Eur. J. Phys. 4, 512 (2025), https://doi.org/10.26565/2312-4334-2025-4-52

2. MOLECULAR STRUCTURE AND SYMMETRY-BASED VIBRATIONAL MODE CLASSIFICATION

HCB comprises a benzene ring in which all its six hydrogen atoms are replaced with chlorine atoms. The molecule is fully substituted in this form, retains its planar form, and maintains D_{6h} symmetry. X-ray crystallographic and other structural studies have demonstrated that the molecule is also planar in the solid and gas phases [3]. The D_{6h} point group is one of the highest symmetries possible for a molecule, characterised by having a C_6 principal rotation axis, six C_2 perpendicular axes, horizontal and vertical mirror planes (σ_h and σ_v), dihedral planes, and an inversion centre (i) [2].

The symmetry of HCB is so high that it profoundly constrains the vibrational activity of the molecule in the Raman and infrared spectra. The molecule in question, containing 12 atoms, has 3N- 6 = 30 normal vibrational modes, all governed by the D_{6h} symmetry group. The Raman-active modes are the A_{1g}, E_{2g}, and E_{1g}, while the infrared-active modes are E_{1u} and A_{2u}. The representations B_{2g}, B_{1u}, E_{2u}, and A_{1u} are all silent in the spectrum.

Experimental investigations have assigned detailed vibrations of modes. Saeki (1962) recorded a strong A_{1g} symmetric C–Cl stretching mode at ~1225 cm^{-1} and a breathing mode close to 377 cm^{-1}. E_{2g} modes at ~692 cm^{-1} are considered in-plane deformations of C–C–C. Kopelman and Schnepp (1959) reported strong IR-active E_{1u} modes at 696 cm^{-1} and 1340 cm^{-1}, associated with asymmetric C–Cl stretching vibrations. The empirical work of Zhang et al. (2011) regarding comparative Raman studies of benzene and HCB documented how substituting chlorine with benzene alters the vibrational frequencies and symmetry assignments. The authors reported low-frequency bands in the 219-377 cm^{-1} range attributed to Cl-bending and A_{2u} and E_{1u} Cl shear vibrations [2,3,4].

Computational studies have further improved the clarity of the spectral interpretations. Castillo et al. (2015) applied DFT with SQMFF correction, using B3LYP/6-31G* and 6-311++G** with geometry optimisation and frequency calculation in DFT, and validated the results with D_{6h} symmetry possession and experimental Raman and IR spectra. Their work reinforces the remaining theoretical and experimental analyses of vibrational spectral data by supporting the' detailed assignments of their findings [5].

The classification of HCB vibrational modes under D_{6h} symmetry has been precisely defined, which makes it useful for algebraic modelling. The ease of construction of symmetry-adapted Lie algebraic Hamiltonians, because of the regularity and degeneracy of the vibrational levels, makes the anterior framework simple to calculate and valuable for an analytical approach to vibrational frequencies. These aspects make it the core of the study at hand.

3. U(2) LIE ALGEBRAIC VIBRATIONAL HAMILTONIAN OF HEXACHLOROBENZENE

The U(2) Lie algebraic approach identifies bosonic realisations of U(2) algebras with each of the vibrational modes of a molecule. For a molecule of vibrational type, the Hamiltonian is expressed through the number operators, Majorana interaction terms, and Casimir invariants [15, 16]. For polyatomic molecules, Iachello, Levine, and Oss formulated the general algebraic Hamiltonian as

$$H = E_0 + \sum_{i=1}^{n} A_i\, C_i + \sum_{i<j}^{n} A_{ij}\, C_{ij} + \sum_{i<j}^{n} \lambda_{ij}\, M_{ij} \tag{1}$$

where:

- $\langle C_i \rangle = -4(N_i v_i - v_i^2)$ is the Casimir invariant of U(2) for the i th mode,
- $\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4(v_i + v_j)(v_i + v_j - N_i - N_j)$ is the two-mode Casimir interaction term between modes i and j,
- $$\left.\begin{array}{c} \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle = v_i N_j + v_j N_i - 2 v_i v_j \\ \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -[v_j (v_i + 1)(N_i - v_i)(N_j - v_j + 1]^{1/2} \\ \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -[v_i (v_j + 1)(N_j - v_j)(N_i - v_i + 1]^{1/2} \end{array}\right\}$$ denotes the Majorana interaction operator representing dynamic coupling,
- $A_i, A_{ij}, \lambda_{ij}$ are empirical parameters,
- $N_i (= N), i = 1,2,3,4,5,6$ is the boson number associated with mode i,
- v_i is the vibrational quantum number for mode i.

The boson number N determines the basis set size for describing molecular vibrations and is defined as:

$$N = \frac{\omega_e}{\omega_e \chi_e} - 1,$$

where ω_e and $\omega_e \chi_e$ denote the harmonic and anharmonic spectroscopic constants of the C-Cl and C-C bonds, respectively, as reported by Karl K. Irikura [17].

There are three classes of non-diagonal interactions within the benzene framework of the HCB molecule. They are represented as couplings associated with various positions of the structure's hexagonal bent carbon vibrational modes [15].

First-neighbour couplings (nearest-neighbour interactions): Couplings of adjacent carbon atoms in the ring.
Examples: (1-2), (2-3), (3-4), (4-5), (5-6), (6-1).

Second-neighbour couplings (next-nearest-neighbour interactions): Couplings of carbon atoms with a spacing of one bond.
Examples: (1-3), (2-4), (3-5), (4-6), (5-1), (6-2).

Third-neighbour couplings (opposite interactions): Couplings of carbon atoms located diametrically opposite the ring.
Examples: (1-4), (2-5), (3-6)

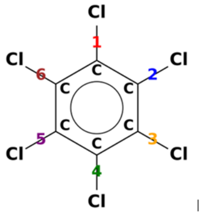

Figure 1. HCB structure with labelled C–Cl bonds

Consider S^{I} (C-H type first neighbour interactions), S^{II} (C-H type second neighbor interactions), S^{III} (C-H type third neighbor interactions) are symmetry-adapted operators. In the context of the HCB D_{6h} symmetry, the symmetry-adapted operators pertain to precisely these couplings, which are

$$S^{I} = \sum_{i<j}^{6} k'_{ij}\, M_{ij}, \quad S^{II} = \sum_{i<j}^{6} k''_{ij}\, M_{ij}, \quad S^{III} = \sum_{i<j}^{6} k'''_{ij}\, M_{ij}$$

With

$$k'_{12} = k'_{23} = k'_{34} = k'_{45} = k'_{56} = k'_{16} = 1,$$

$$k'_{13} = k'_{24} = k'_{35} = k'_{46} = k'_{15} = k'_{26} = 0,$$

$$k'_{14} = k'_{25} = k'_{36} = 0,$$

$$k''_{12} = k''_{23} = k''_{34} = k''_{45} = k''_{56} = k''_{16} = 0,$$

$$k''_{13} = k''_{24} = k''_{35} = k''_{46} = k''_{15} = k''_{26} = 1,$$

$$k''_{14} = k''_{25} = k''_{36} = 0,$$

$$k'''_{12} = k'''_{23} = k'''_{34} = k'''_{45} = k'''_{56} = k'''_{16} = 0$$

$$k'''_{13} = k'''_{24} = k'''_{35} = k'''_{46} = k'''_{15} = k'''_{26} = 0$$

$$k'''_{14} = k'''_{25} = k'''_{36} = 1$$

For the case of the HCB molecule, in which all the molecule's bonds are equivalent, the most general and most basic, as well as the lowest-order, Hamiltonian describing the C-H stretching vibrations can be formulated as follows:

$$H = E_o + A\sum_{i}^{6} C_i + A'\sum_{i<j}^{6} C_{ij} + \lambda' S^{I} + \lambda'' S^{II} + \lambda''' S^{III}$$

Given the equivalent bonds, the vibron numbers N_i must hold the same value, i.e., $N_i = N$. Consequently, the molecule's symmetry establishes specific requirements on the coefficients within equation (1), as follows:

$$N_i = N,\ A_i = A,\ \ A_{ij} = A'$$

$$\lambda_{12} = \lambda_{23} = \lambda_{34} = \lambda_{45} = \lambda_{56} = \lambda_{61} = \lambda'$$

$$\lambda_{13} = \lambda_{24} = \lambda_{35} = \lambda_{46} = \lambda_{15} = \lambda_{26} = \lambda''$$

$$\lambda_{14} = \lambda_{25} = \lambda_{36} = \lambda'''$$

The distinctive attributes of $C - H$ stretching vibrations in benzene encompass five quantities: $A, A', \lambda', \lambda'', \lambda'''$. The initial guess for the fundamental mode parameters A is obtained from the single-oscillator energy expressions:

$$A = -\frac{E}{4(N-1)}.$$

The initial values of interaction parameters $\lambda', \lambda'', \lambda'''(= 0)$ are given by:

$$\lambda' = \frac{|E_1' - E_2'|}{2N}, \lambda'' = \frac{|E_1' - E_2'|}{6N},$$

where E_1 and E_2 represent the symmetric and antisymmetric energy combinations of the two local modes. The parameters are optimised using least-square regression fitting, while A' is initially set to zero to ensure a systematic optimization procedure using the available observed data reported by Saeki (1962). The optimised parameter values are: $N^{C-Cl} = 160$, $N^{C-C} = 134, A = -3.52$, $A' = 0.73$, $\lambda' = 1.81, \lambda'' = 0.26$.

4. RESULTS AND DISCUSSION

The vibrational spectrum of HCB was successfully predicted using the symmetry-adapted U(2) Lie algebraic Hamiltonian. Table 1 presents the predicted fundamental frequencies, which align remarkably well with the corresponding experimental data. The small Deviations, encapsulated by an root mean square (RMS) error of 5.21 cm^{-1}, underscore the exceptional fit achieved by the algebraic approach across the entire vibrational region. A comprehensive study of the overtones was conducted, and the results, including both the first and second overtones, are detailed in Table 2. The remarkably low RMS value underscores the reliability of the Lie algebraic framework. Its succinct nature, in terms of the number of fitting parameters and algebraic complexity, makes it a trustworthy choice. When compared to conventional approaches at the same accuracy level, the algebraic treatment eliminates much of the nucleation and convergence uncertainty, providing a pragmatic and trustworthy route for precise vibrational modelling without the need for multiple layers of fitted functional input.

Table 1. Fundamental Vibrational frequencies (in cm^{-1}) for HCB

Vibrational Mode	Mode	Activity	Symmetry Species	Fundamental	
				Observed [2]	**Calculated**
ν_1	C-Cl stretching	Raman	A_{1g}	1225	1221.03
ν_{13}	C-Cl stretching	IR	E_{1u}	696	697.27
ν_{12}	Ring Stretching	IR	E_{1u}	1350	1346.51
ν_{15}	Ring Stretching	Raman	E_{1u}	1522	1519.55
ν_{18}	C-Cl in -plane bending	Raman	E_{2g}	322	329.90
ν_{11}	C-Cl in -plane bending	Raman	E1g	213	221.04

Table 2. First and second overtone Vibrational frequencies (in cm^{-1}) for HCB

Vibrational Mode	Mode	Symmetry Species	Vibrational Frequencies	
			I Overtone	**II Overtone**
ν_1	C-Cl stretching	A1g	2426.6	3616.72
ν_{13}	C-Cl stretching	E1u	1375.71	2055.33
ν_{12}	Ring Stretching	E1u	2665.98	3988.4
ν_{15}	Ring Stretching	E1u	3016.87	4507.95
ν_{18}	C-Cl in -plane bending	E2g	641.62	957.17
ν_{11}	C-Cl in -plane bending	E1g	430.28	644.73

5. CONCLUSIONS

The present study shows that using symmetry-adapted U(2) Lie algebra techniques leads to an accurate yet computationally efficient description of the vibrational spectrum of hexachlorobenzene. Computed fundamental frequencies align extremely well with observed values, yielding a root mean square deviation of only 5.21 cm^{-1}, which attests to the method's robustness. Extending the algebraic model to predict overtone bands underscores its ability to treat anharmonicity and symmetry constraints simultaneously and elegantly. In summary, the symmetry-adapted U(2)-algebraic engine delivers a compact formulation that rivals the precision of extensive quantum chemistry calculations while remaining straightforward. These attributes provide a solid foundation for applying the approach to other polyatomic species possessing high symmetry in forthcoming work.

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АЛГЕБРАЇЧНЕ МОДЕЛЮВАННЯ ЛІ КОЛИВАЛЬНИХ ЧАСТОТ У ГЕКСАХЛОРБЕНЗЕНІ: ПІДХІД, АДАПТОВАНИЙ ДО СИМЕТРІЇ ДЛЯ ТОЧКОВОЇ ГРУПИ D_{6h}

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У цій роботі використовується адаптована до симетрії алгебраїчна структура Лі для вивчення коливальних частот гексахлорбензолу (C_6Cl_6). Вібраційний гамільтоніан на основі U(2) фіксує фундаментальні моди та перший і другий обертони, використовуючи симетрію точкової групи D_{6h} молекули. Алгебраїчний підхід враховує обмеження ангармонізму та симетрії, щоб забезпечити компактне та кероване аналітичне зображення коливального спектру. Обчислені фундаментальні частоти добре узгоджуються зі спостережуваними значеннями, що підтверджує правильність підходу. Більше того, розширення на обертони підкреслює здатність алгебраїчної моделі систематично оцінювати коливальні збудження вищого порядку в багатоатомних молекулах. Ці результати підтверджують ефективність алгебраїчних методів Лі в моделюванні коливальних характеристик високосиметричних молекул і служать міцною основою для подальшої роботи в молекулярній спектроскопії.

Ключові слова: *гексахлорбензол; вібраційні спектри; алгебраїчне моделювання Лі; симетрійно-адаптований гамільтоніан; точкова група* D_{6h}