

Vibrational Frequencies of Tetrachloroethylene using Lie Algebraic Framework

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ABSTRACT

This study employs a sophisticated computational approach to predict tetrachloroethylene's higher overtone vibrational frequencies (C_2Cl_4) up to the fourth overtone. We utilize a Lie algebraic framework within the context of the vibrational Hamiltonian. The method involves replacing tetrachloroethylene's carbon-chlorine (C-Cl) bonds with unitary Lie algebras. The resulting Hamiltonian is written in terms of Casimir and Majorana's invariant operators and parameters. The derived Hamiltonian operator effectively characterizes the stretching vibrations inherent to the molecular structure. This approach enhances our understanding of the vibrational dynamics of tetrachloroethylene at higher overtones, offering valuable insights for applications in diverse scientific and technological fields.

Keywords: Vibrational frequencies, Lie algebraic framework, Vibrational Hamiltonian, Tetrachloroethylene.

1. INTRODUCTION

Vibrational spectroscopy is a robust analytical technique that investigates the vibrational motions of atoms within molecules, which is crucial for characterizing structural and chemical properties. Infrared (IR) and Raman spectroscopy are the primary methods in this field. In IR spectroscopy, molecules interact with infrared radiation, which causes changes in vibrational energy levels and creates a molecular fingerprint that can be used to find functional groups and determine the structure of molecules. Raman spectroscopy scatters monochromatic light by molecules and offers non-destructive complementary information. Applications include identifying functional groups, quantitative analysis, chemical imaging (e.g., FTIR microscopy), real-time monitoring of chemical reactions, studying biomolecules in biochemistry, and material characterization in materials science (Barone et al., 2021; Tiernan et al., 2020; Tanwar et al., 2021). Various theoretical and computational approaches decode and predict vibrational properties in molecular vibrational spectroscopy. Molecular Dynamics, Coupled Cluster Theory, Vibrational Configuration Interaction, Semi-Empirical Methods, and Hybrid Quantum Mechanics/Molecular Mechanics are some of the most essential methods used in quantum chemistry. These approaches enhance our understanding of vibrational

Momona Ethiopian Journal of Science (MEJS), V16(2): 281-288, 2024 ©CNCS, Mekelle University, ISSN:2220-184X

Submitted :26th March 2024

Accepted : 7th April 2024

Published : 14th September 2024



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spectroscopy, guiding interpretation based on the molecule's size, complexity, and the desired balance between computational accuracy and efficiency (Mroginski, 2013; Gardner et al., 2021; Lubner, 2018; Mardirossian and Head Gordon, 2017).

Two traditional methods extensively used in vibrational spectroscopy are Dunham expansion and the potential energy approach, which embark on a more nuanced exploration by solving the Schrödinger equation with a specific inter-atomic potential. These methodologies have significantly contributed to our understanding of molecular vibrations by providing detailed insights into molecular energetics and dynamics. However, they are not without their limitations. While useful for small vibrations near the molecule's equilibrium geometry, the Dunham expansion becomes increasingly complex and less accurate for describing higher vibrational states where anharmonic effects are significant. This method's reliance on a series expansion means that incorporating higher-order corrections to improve accuracy can quickly become mathematically cumbersome, especially for molecules with many vibrational modes. On the other hand, the potential energy surface approach requires substantial computational resources, although capable of capturing anharmonic vibrations and providing a comprehensive view of the molecule's potential energy landscape. This can limit its practicality for larger molecules or systems where detailed potential energy surfaces are difficult to calculate accurately (Oss, 1996). In contrast, the Lie algebraic method introduces a novel approach to vibrational spectroscopy that addresses these limitations through its unique algebraic framework. This has successfully analyzed the vibrational spectra of molecules (Jaliparthi and Balla, 2022; Balla and Jalaparthi, 2021, 2022; Vijayasekhar et al., 2023). In vibrational spectroscopy, this framework, linked to the vibrational Hamiltonian and shown using Casimir and Majorana invariant operators, has clear benefits. Its algebraic simplicity streamlines the mathematical representation of vibrational dynamics, thereby enhancing computational ease and interpretation. The introduction of dynamic symmetry is particularly advantageous for intricate molecular systems. The Lie algebraic method addresses vibrational degrees of freedom, potentially providing computational efficiency (Iachello and Levine, 1995; Oss, 1996). Its focus on Casimir and Majorana operators makes it easier to add anharmonic effects, which is essential for accurately showing how molecules behave. The versatility of this approach extends to various molecular systems, making it a valuable tool for studying vibrational dynamics. As a bridge between experimental observations and theoretical predictions, the Lie algebraic framework contributes to a more unified understanding and provides valuable insights into the symmetry properties of molecular vibrations. The study of

tetrachloroethylene's vibrational frequencies explores its roles in diverse industries and scientific research (Orkington, 1949; Bernstein, 1950). Widely used as a solvent, it serves in industrial cleaning, degreasing, dry cleaning, chemical manufacturing, metalworking, textile processing, and laboratory applications. In vibrational spectroscopy research, tetrachloroethylene advances molecular techniques. Despite widespread use, environmental and health concerns drive ongoing research for alternative solutions. The study integrates experimental insights and emphasizes theoretical approaches to bridge the gap between observation and exploration in vibrational dynamics.

2. METHODOLOGY

2.1. Lie Algebraic Framework of Tetrachloroethylene With D_{2h} Symmetry

The vibrational Hamiltonian, constructed from the Lie algebraic framework, describes the quantized energy levels of a molecule's vibrations. It considers the essential symmetries present in the molecule's structure. In molecular vibrations, each vibrational mode corresponds to a specific symmetry species within the point group to which the molecule belongs. Symmetry species represent vibrational modes that transform according to certain irreducible representations of the molecule's point group. When expressed with symmetry considerations, the vibrational Hamiltonian helps understand the allowed vibrational transitions based on the selection rules directed by molecular symmetry. As vibrational Hamiltonian of a tetrachloroethylene belonging to the D_{2h} point group, various vibrational modes can be associated with symmetry species such as A_g , A_u , B_{1g} , B_{1u} , B_{2g} , B_{2u} , and B_{3u} . Each symmetry species represents specific vibrational motions that exhibit particular symmetry properties under the operations of the point group. When incorporating symmetry species, the vibrational Hamiltonian becomes a powerful tool for predicting and interpreting vibrational spectra. It allows us to identify which vibrational modes are active or allowed in a particular spectroscopic transition, providing a more refined understanding of the molecule's vibrational dynamics.

The vibrational Hamiltonian for tetrachloroethylene is constructed with precision, employing the Morse anharmonic oscillator and the $U(2)$ algebra for each coordinate (Vijayasekhar and Devi, 2019; Jaliparthi and Balla, 2022). The resulting mathematical expression yields a comprehensive algebraic Hamiltonian, effectively capturing the intricacies of the coupled oscillators within the molecular structure of Tetrachloroethylene. The Hamiltonian describing vibrations related to carbon-chlorine bonds is expressed as follows:

$$H = E_0 + \sum_{i=1}^4 A_i C_i + \sum_{i<j}^4 A_{ij} C_{ij} + \sum_{i<1}^4 \lambda_{ij} M_{ij} \quad \text{-----(1)}$$

Here, E_0 denotes the zero-point energy. Casimir (C_i, C_{ij}) and Majorana (M_{ij}) invariant operators are pivotal in the Lie algebraic framework associated with the vibrational Hamiltonian. These operators significantly simplify and analyze the vibrational dynamics within a molecule, especially in systems with specific symmetries. In vibrational spectroscopy, Casimir operators are connected to the Lie algebra of a symmetry group, furnishing constants of motion for the vibrational degrees of freedom, specifically for uncoupled and coupled bonds. Conversely, Majorana operators are employed to construct irreducible representations of the Lie algebra, aiding in studying vibrational modes within the given symmetry context. These operators describe local mode interactions in pairs and encompass diagonal and non-diagonal matrix elements. Incorporating Casimir and Majorana invariant operators into the vibrational Hamiltonian enhances its algebraic simplicity, facilitating more straightforward computation and interpretation. These operators are valuable tools for comprehending molecules' symmetry properties and vibrational dynamics. The parameters A_i, A_{ij} and λ_{ij} are algebraic coefficients that can be determined utilizing spectroscopic data of molecules through the Least Squares Fitting method.

The expressions for determining the algebraic operators, C_i, C_{ij}, M_{ij} are as follows

$$\langle C_i \rangle = -4(N_i v_i - v_i^2) \quad \text{-----(2)}$$

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4(v_i + v_j)(v_i + v_j - N_i - N_j) \quad \text{-----(3)}$$

$$\left. \begin{aligned} \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle &= v_i N_j + v_j N_i - 2v_i v_j \\ \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2} \\ \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2} \end{aligned} \right\} \quad \text{-----(4)}$$

Where, v_i, v_j represent the vibrational quantum numbers of bonds i and j , respectively. The Vibron number N is calculated using the formula $N_i = \frac{\omega_e}{\omega_e x_e} - 1$, where $\omega_e, \omega_e x_e$ are the spectroscopic constants (Nakamoto, 2009; Huber and Herzberg, 1979). The starting estimate for the parameter A_i is obtained by utilizing the energy equation for the single-oscillator fundamental mode: $E(v = 1) = -4A_i(N_i - 1)$. The parameter λ_{ij} can be computed from the relation: $\lambda_{ij} = \frac{|E_i - E_j|}{2N}$, where E_i and E_j are the energies associated with vibrational modes i and j , respectively.

In equation (1), the terms A_i and C_i represent the anharmonic constants and coordinates for each vibrational mode, respectively. The summation of A_i and C_i accounts for the

independent local oscillators. The summation involving A_{ij} and C_{ij} describes the anharmonic coupling between different vibrational modes, specifically addressing cross-anharmonicities between pairs of distinct local oscillators. Conversely, the summation of λ_{ij} and M_{ij} expresses the anharmonic, non-diagonal interactions involving pairs of local oscillators. This detailed Hamiltonian provides a robust foundation for comprehending the vibrational dynamics of Tetrachloroethylene, offering insights into the quantized energy levels and coupling effects among its vibrational modes.

3. RESULTS

In the vibrational analysis of tetrachloroethylene, a comprehensive range of vibrational modes is discernible, each mapped to distinct symmetry species within its specific point group. These symmetry species, A_g , A_u , B_{1g} , B_{1u} , B_{2g} , B_{2u} , and B_{3u} categorize the vibrational motions, encompassing stretching, bending, and twisting, all of which are intricately tied to the molecule's inherent symmetry. The A_g species, for instance, is linked with symmetric stretching and bending (scissoring) of carbon-chlorine (C-Cl) bonds, in addition to the stretching vibrations of carbon-carbon (C=C) bonds. Conversely, the A_u species typifies bending vibrations, notably through twisting motions of C-Cl bonds. B_{1g} emphasizes the asymmetrical stretching of C-Cl bonds, contrasting with B_{1u} and B_{2g} , which are noted for bending movements, particularly wagging of C-Cl bonds. B_{2u} is distinguished by its asymmetrical stretching and bending (rocking) of C-Cl bonds and the stretching vibrations of C=C bonds. At the same time, B_{3u} corresponds to symmetric stretching and bending (scissoring) of C-Cl bonds. This classification elucidates the diverse vibrational dynamics of tetrachloroethylene, from the A_g species illustrating uniform stretching and shortening of both C-Cl and C=C bonds to the A_u species depicting out-of-plane twisting of C-Cl bonds without inversion. B_{1g} showcases a unique asymmetrical stretching, with C-Cl bonds elongating in divergent directions. B_{1u} and B_{2g} describe wagging and scissoring, respectively, highlighting movements within the molecular plane, whereas B_{2u} extends this with rocking movements across the molecule. This detailed symmetry species framework vividly shows tetrachloroethylene's complex vibrational behavior, underscoring the intricate interplay of molecular motions crucial for a nuanced understanding of its vibrational properties. A systematic understanding of the symmetry species associated with vibrational modes is essential for a detailed interpretation of vibrational spectroscopy results, providing deep

insights into tetrachloroethylene's molecular symmetry and dynamics. Table 1 presents the calculated vibrational frequencies corresponding to the first to fourth overtone alongside their respective symmetry species and vibrational modes.

Table 1. Higher overtone vibrational frequencies (in cm^{-1}) of C_2Cl_4 .

Symmetry Species	Mode (Shimanouchi, 1972)	Overtone			
		I	II	III	IV
A_g	CCl_2 s-str	735	1129	1409	1975
A_g	CCl_2 scis	420	653	874	982
A_u	CCl_2 twist	184	270	362	402
B_{1g}	CCl_2 a-str	1765	2632	3475	4460
B_{1g}	CCl_2 rock	587	979	1133	1405
B_{1u}	CCl_2 wag	446	782	986	1275
B_{2g}	CCl_2 wag	908	1244	1736	2287
B_{2u}	CCl_2 a-str	1561	2420	3313	4110
B_{2u}	CCl_2 rock	312	482	576	810
B_{3u}	CCl_2 s-str	1357	1978	2882	3398
B_{3u}	CCl_2 scis	578	864	993	1240
Fitted Parameters (Vijayasekhar and Devi, 2019) : $N_1 = N_2 = N_3 = N_4 = 132$, $A_1 = A_2 = A_3 = A_4 = 8.27$, $A_{12} = A_{23} = A_{34} = A_{14} = -1.35$, $\lambda_{12} = \lambda_{23} = \lambda_{34} = \lambda_{14} = -1.35$.					

4. CONCLUSION

This study employed a sophisticated computational approach to predict tetrachloroethylene's higher overtone vibrational frequencies up to the fourth overtone. Utilizing a Lie algebraic framework within the vibrational Hamiltonian, we deciphered the complex vibrational dynamics of this molecule. Our results highlight the effectiveness of this approach in understanding the stretching vibrations within tetrachloroethylene's molecular structure. Integrating experimental data with theoretical advancements bridged the gap between observation and exploration in vibrational dynamics, paving the way for new possibilities in diverse scientific and technological fields. In conclusion, our study significantly advances the exploration of vibrational dynamics and offers new avenues for studying and applying molecular vibrations across various disciplines. The insights gained promise to promote our understanding of molecular behavior and facilitate the development of innovative technologies with widespread practical implications.

5. ACKNOWLEDGMENTS

Vijayasekhar is deeply grateful for the Research Seed Grants (RSG) offered by Gandhi Institute of Technology and Management (GITAM), Deemed to be University, Hyderabad, India, as

mentioned in the Sanction Letter Ref: F.No. 2021/0114, dated 26-09-2022. Furthermore, we thank the NIST Standard Reference Database 69: NIST Chemistry WebBook [webbook.nist.gov] for generously providing the experimental database utilized in this research.

6. CONFLICT OF INTERESTS

No conflict of interests.

7. REFERENCE

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