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ANALYSIS OF HIGHER OVERTONE VIBRATIONAL FREQUENCIES IN CYCLOHEXANE USING A LIE ALGEBRAIC APPROACH

M.V. Subba Rao[a], T. Sreenivas[a,b], J. Vijayasekhar[c]*
[a]Department of Mathematics, Anil Neerukonda Institute of Technology & Sciences (ANITS), Visakhapatnam, India
[b]Department of Mathematics, Jawaharlal Nehru Technological University, Kakinada, India
[c]Department of Mathematics, GITAM (Deemed to be University), Hyderabad, India
**Corresponding Author e-mail: vijayjaliparthi@gmail.com*

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This study contains a sophisticated computational approach to predict cyclohexane while maintaining the D3d point group symmetry higher overtone vibrational frequencies (C_6H_{12}), precisely, third, fourth, and fifth. We utilize a Lie algebraic approach within the context of the vibrational Hamiltonian. The method uses cyclohexane's carbon-hydrogen (C-H) and carbon-carbon (C-C) bonds as unitary Lie algebras, accurately modelling the molecular vibrational structure. Thus, the vibrational Hamiltonian takes Casimir and Majorana's invariant operators and parameters and successfully outlines the molecules' vibrational modes. This Lie algebraic approach clearly outlined cyclohexane's higher overtone vibrational dynamics and provided helpful information that can be applied in other fields of study and technology.

Keywords: *Lie algebraic approach; Vibrational frequencies; Vibrational Hamiltonian; Cyclohexane*
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1. INTRODUCTION

One of the essential aspects of molecular spectroscopy is the determination of the vibrational and energy distribution characteristics of the molecules within a study and, therefore, the understanding of different structures, interactions and activities of such molecules. Vibrational spectroscopy methods deal with the so-called vibrational spectra, which correspond to discrete energy levels, each of which relates to molecular vibrations. Such frequencies are also considered molecular fingerprints, essential in understanding the types of chemical bonds, structures, and interactions and identifying different molecules. Cyclohexane (C_6H_{12}), with its simple D_{3d} point group symmetry, is ideally suited for such studies since it is known to have very complex vibrational interactions even at high overtone levels [1,2]. Many of the traditional approaches taken by researchers seeking to explain the vibration of molecules have been based on the so-called harmonic oscillator model, where it is assumed that the behaviour of a vibrating molecule can be appreciated within the limits of a symmetrical parabolic potential well-located about the equilibrium position of the molecule. Remember that this modelling of the fundamental vibrational modes works well. It is well known that the anharmonicity of molecular vibrations is most apparent at higher energy levels. The simple fact is that molecular bonds show non-linearities instead of a perfect harmonic oscillation due to the atoms' stretching in a molecule. This anharmonicity becomes much more significant as I work with higher vibrational overtones where the simple picture of the potential energy curve as a parabola fails all along the sides [3-9]. The Morse oscillator model improves and provides a better geometrical description of molecules than the diatomic oscillator model because it incorporates the concept of anharmonicity into the potential energy surface. The Morse potential extends bond lengths and allows bond breaking to be considered a refinement using spherical averages of molecular vibration models. Besides, describing and analyzing the data of vibrational spectra involves working with conventional models of molecules and applying the Morse oscillator, which is necessary to assess energy distributions and vibrational transitions adequately, particularly at high overtone levels. More detailed representations of present or future molecules, like cyclohexane, should extend classical models and consider more advanced mathematical frameworks. The significant relation in this case is the vibrational Hamiltonian, which summarizes all modes of molecular vibrations and enables any rationalization of the normal modes and their couplings. Tackling the many body problems and other Hamiltonian terms by reformulating the vibrational Hamiltonian in terms of Lie algebras pretty much exhausts within the amends of the harmonic approximation in polyatomic systems. The benefit of the Lie algebraic approach is the ability to model Hamiltonians elegantly; this is essential for the calculations of complex vibrational spectra in a Lie algebra-based model. This method is well suited for polyatomic molecules because the theoretical presumption is satisfied by this formulation of Hamiltonian designed using invariant operators, such as Casimir and Majorana operators. These operators are part of the Lie algebraic representation and are indispensable in a holistic sense of molecular vibrational interactions. For example, the Casimir operator determines the number of angular momenta in the system. In contrast, the contribution of Majorana operators includes enhancing the vibrational coupling of different molecular bonds. As described in the article, Lie algebraic methods are used to create a cyclohexane vibrational Hamiltonian, capable of reproducing the higher overtones vibrational frequencies (third, fourth and fifth overtone) with more accuracy than existing methods. We construct a Hamiltonian consistent with the D_{3d} symmetry of cyclohexane and include the nonharmonic couplings present in the molecule's vibrational spectrum by viewing the chemical

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bonds C-H and C-C as unitary Lie algebras. To find the vibrational frequencies, for which the Hamiltonian matrix for the molecule will be constructed in such a way as to include all possible vibrational couplings in the account of cyclohexane. Each vibrational state corresponds to a matrix element of the Hamiltonian, and there is no need to solve the matrix directly; instead, the energy eigenvalues of the matrix through which the state associated with the vibrations is represented are evaluated [10-12]. This way of looking at matrices also aids in predicting higher overtone frequency levels. It gives a glimpse of the interaction between the various vibrational forms and the general motion of the molecule. The main conclusion of this research is that the Lie algebraic approach is a practical tool for estimating cyclohexane's higher overtone vibrational frequencies since it accounts for anharmonicity, and the interaction of active coordinates typically neglected within simple harmonic models. Regardless of the covalent bonding nature, when the kinetic energy operator is expressed as a linear combination of the Lie algebra generators, Casimir and Majorana operators, we systematically elucidate the vibrational properties of cyclohexane and other more complex polyatomic systems. One of the outcomes of this work is that these molecular vibrations are essential for spectroscopic studies and other related scientific activities. Experimentally, assigning vibrational frequencies accurately can be significant since it will help interpret experimental spectra and molecular reactivity and map out the potential energy surfaces of the molecules in question. The Lie algebraic approach provides a coherent and generalizable framework that can be applied to other polyatomic molecules to facilitate the examination of vibrational spectra for various chemical, physical, and engineering purposes [13,14]. It brings new insights into the molecular vibrations that are of great importance to material science, chemical engineering and molecular physics with respect to the design, application and enhancement of advanced spectroscopic techniques aimed at studying reaction pathways and constructing novel materials reaction mechanisms.

Concisely, this investigation proves the predictive capability of the Lie algebraic approach to extending higher overtone vibrational frequencies and confirms this method as a single-line weapon in molecular spectroscopy development. It is also worth mentioning that such a thorough incorporation of the Morse oscillator model, anharmonicity and, importantly, Lie algebraic operators within the vibrational Hamiltonian opens new technological opportunities for the polyatomic molecules vibration analysis and cyclohexane tasks.

2. LIE ALGEBRAIC APPROACH

The Lie algebraic approach has thus proved to be a very effective tool in representing the vibrational frequencies within a molecule being fashioned, such a treatment accommodating the interactions involved in both the fundamental and the overtone transitions. This approach differs in that instead of using potential energy surfaces or differential equations to outline framework, it employs the mathematical structures of Lie algebras, particularly the U(2) algebra wherein vibrational states are treated as vectors and transitions as operators acting on these states. With the aid of algebra, molecular vibrations can be described which has advantages because harmonic and non-harmonic behaviours can be dealt with in a single framework. Central to this system is the formulation of the vibrational Hamiltonian which determines the energy levels and vibrational frequencies of the molecule. The Hamiltonian is written in terms of U(2) Lie algebra generators that operate with raising, lowering and projection including projection operators, Casimir (C_i, C_{ij}) and Majorana (M_{ij}) operators bonding single vibrational mode and modes interaction. By adjusting parameters such as $A_i, A_{ij}, \lambda_{ij}$, the Hamiltonian accurately models the vibrational dynamics, capturing fundamental frequencies and overtone transitions observed in molecular spectra. This strategy is effective in the case of complex and multi-vibrational molecules as it allows the analysis of vibrational spectra systematically and flexibly for molecules of extensive diversity. The advantage of the Lie algebraic approach is that it makes it possible to describe molecular vibrations not only in harmonic systems but also in anharmonic ones, which is, to a great degree, essential in molecular spectroscopy and enables correlation with experimental [13, 14].

To determine the vibrational modes of the molecule, it is essential to have the C-H and C-C stretching leads to the so-called vibrational Hamiltonians in cyclohexane. These Hamiltonians account for stretching vibrational interactions and energy and provide an idea of how the energy levels of vibration are structured within the molecule. For the case of the C-H stretching vibrations, this Hamiltonian is prepared to describe how the C-H bonds behave when they are stretched. It includes the normal vibrational modes and other inclusions to model higher overtone frequencies. This Hamiltonian usually has terms about the harmonic oscillator basis; however, other terms are included regarding flexible coupling terms, which are more representative of the accurate molecular picture. Similarly, cyclohexane is modelled for the C-C stretching vibrations with a Hamiltonian considering the bond stretching between the carbon atoms. However, the picture is more complicated in this case because of the cyclohexane symmetry and the coupling of the neighbouring C-C bonds. It is designed to include interactions between individual C-C stretching modes and between C-H and C-C vibrations, providing a more holistic representation of the vibrational structure.

The Hamiltonian can be expressed in terms of Lie algebra generators, in particular, using the U(2) algebraic model. This method permits a thorough and systematic description of the fundamental and overtone vibrational frequencies, which ensures that the calculated frequencies are consistent with experimental data. These Hamiltonians include harmonic and anharmonic terms, which can be used in detail to analyze the vibrational dynamics of cyclohexane.

The established Hamiltonian operator which keeps in view the D_{3d} symmetry of cyclohexane is given as [15]:

$$H^{C-H} = E_0 + \sum_{i=1}^{n=12} A_i^{C-H} C_i + \sum_{i<j}^{n=12} A_{ij}^{C-H} C_{ij} + \sum_{i<j}^{n=12} \lambda_{ij}^{C-H} M_{ij} \tag{1}$$

$$H^{C-C} = E_0 + \sum_{i=1}^{n=6} A_i^{C-C} C_i + \sum_{i<j}^{n=6} A_{ij}^{C-C} C_{ij} + \sum_{i<j}^{n=6} \lambda_{ij}^{C-C} M_{ij} \tag{2}$$

The algebraic operators and dimensionless Vibron number *N* can be defined from the following expressions,

$$\langle C_i \rangle = -4(N_i v_i - v_i^2) \tag{3}$$

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

$$\left.\begin{aligned} \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle &= v_i N_j + v_j N_i - 2 v_i v_j \\ \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -[v_j (v_i + 1)(N_i - v_i)(N_j - v_j + 1]^{1/2} \\ \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -[v_i (v_j + 1)(N_j - v_j)(N_i - v_i + 1]^{1/2} \end{aligned}\right\} \tag{5}$$

The vibrational quantum numbers for the different bonds i and j are denoted by v_i and v_j, respectively. .

$$N = \frac{\omega_e}{\omega_e \chi_e} - 1 \tag{6}$$

The initial guess for the parameters A_i is obtained from the energy expression for single-oscillator fundamental mode,

$$E_i^{C-H}(v = 1) = -\,4A_i^{C-H}(N^{C-H}\text{-}1) \tag{7}$$

$$E_i^{C-H}(v = 1) = -\,4A_i^{C-C}(N^{C-C}\text{-}1) \tag{8}$$

The initial guesses for λ_{ij} are obtained by the relations,

$$\lambda_{ij}^{C-H} = \frac{E_i^{C-H} - E_j^{C-H}}{12\,N^{C-H}}, \quad \lambda_{ij}^{C-C} = \frac{E_i^{C-C} - E_j^{C-C}}{6\,N^{C-C}} \tag{9}$$

Here, $E_i^{C-H}, E_j^{C-H}, E_i^{C-C}, E_j^{C-C}$ represent the different energies corresponding to the symmetric and antisymmetric combinations of the two local vibrational modes. The initial values for A_{ij} are assumed to be zero.

3. RESULTS AND DISCUSSIONS

To predict the third, fourth, and fifth overtone frequencies for cyclohexane using the U(2) Lie algebraic approach, we utilize the established vibrational Hamiltonian parameters as outlined in the methodology [15]. The Table below summarizes the third, fourth and fifth overtone vibrational frequencies, symmetry species, and associated vibrational modes within the cyclohexane molecule. These values are also presented graphically in the accompanying figure.

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

Vibrational Mode	Symmetry Species	III overtone	IV overtone	V overtone
v_1 (CH$_2$ a-str)	a$_{1g}$	10132	13293	15881
v_2 (CH$_2$ s-str)	a$_{1g}$	10180	12780	15186
v_3 (CH$_2$ scis)	a$_{1g}$	3975	6703	7959
v_4 (CH$_2$ rock)	a$_{1g}$	3511	4551	5741
v_5 (CC str)	a$_{1g}$	2623	3297	3973
v_9 (CC str)	a$_{1u}$	3662	4598	5536
v_{12} (CH$_2$ a-str)	a$_{2u}$	9945	13815	15114
v_{13} ((CH$_2$ s-str))	a$_{2u}$	10530	12871	15721
v_{14} (CH$_2$ scis)	a$_{2u}$	5120	6651	7786
v_{15} (CH$_2$ rock)	a$_{2u}$	2975	4798	5750
v_{17} ((CH$_2$ a-str))	e$_g$	9894	13112	15210
v_{18} ((CH$_2$ s-str))	e$_g$	10604	13876	16107
v_{19} (CH$_2$ scis)	e$_g$	5040	6783	8285
v_{22} (CC Str)	e$_g$	3869	4703	5835
v_{23} (CH$_2$ rock)	e$_g$	2775	3388	4082
v_{25} (CH$_2$ a-str)	e$_u$	10602	13596	15865
v_{26} (CH$_2$ s-str)	e$_u$	10759	12842	15904
v_{27} (CH$_2$ scis)	e$_u$	5023	6693	8101
v_{30} (CH$_2$ rock)	e$_u$	3012	4209	5197
v_{31} (CC str)	e$_u$	3156	3878	4630

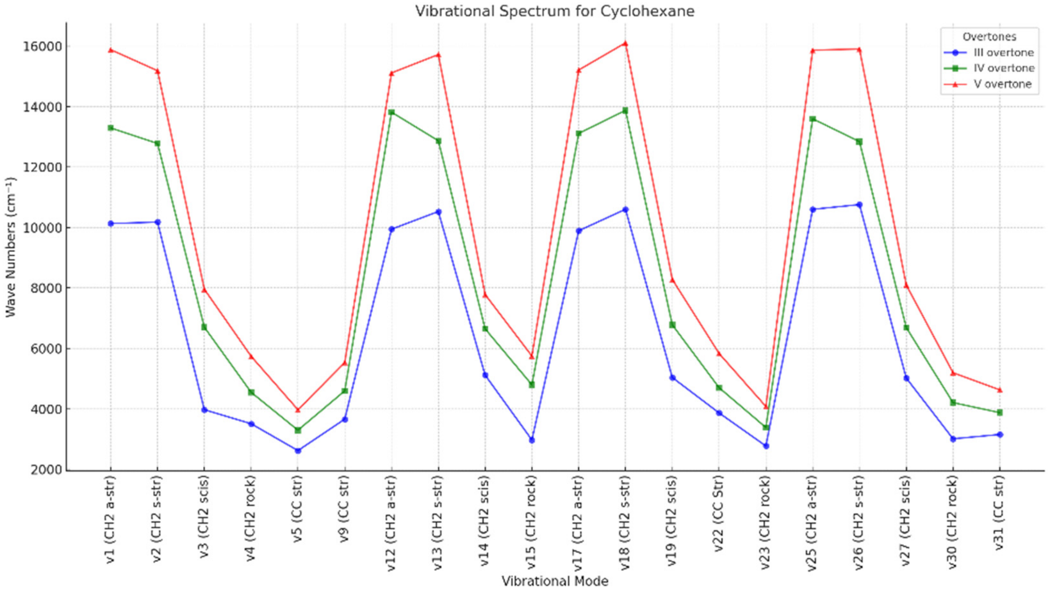

Figure. Vibrational Frequencies Representation for Cyclohexane - III, IV, and V Overtones

4. CONCLUSIONS

In this study, cyclohexane's third, fourth, and fifth overtone vibrational frequencies are predicted and analyzed using the U(2) Lie algebraic method for symmetric D_{3d} point group configurations. Applying a vibrational Hamiltonian with incorporated Casimir and Majorana operators enables one to correctly reproduce the anharmonic couplings and interactions between C−H and C−C bonds. The results prove that this method significantly gives better insight into the vibrational dynamics than the modelled systems in terms of overtones high order transitions. The results confirm the practical usefulness of the so-called Lie algebraic method for solving problems of the vibrational spectra of complex polyatomic molecules and indicate its good prospects for various studies of molecular vibrations in various other systems. The assignment of the vibration spectra is important for interpreting the experimental spectra, understanding the molecular reactivity and mapping the potential energy surfaces. This general strategy is systematic and flexible. It will help develop complex analyses with a scope that can be expanded to other molecules and provide valuable information regarding their vibrational characteristics for use in spectroscopy, materials and molecular design. In general, the findings of this research support the idea that the Lie algebraic model can predict overtone frequencies with precision while appreciably enhancing the knowledge of molecular vibrations, especially in molecules with high anharmonicity. Other studies may investigate applying this method to other polyatomic molecules and apply it to vibrational spectra of more complicated molecular systems.

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ORCID

J. Vijayasekhar, https://orcid.org/0000-0002-2745-7401

REFERENCES

[1] I.S. Butler, R.P. Kengne-Momo, G. Jaouen, C. Policar, and A. Vessières, "Recent Analytical Applications of Molecular Spectroscopy in Bioorganometallic Chemistry—Part I: Metal Carbonyls," Appl. Spectrosc. Rev. **47**(7), 531–549 (2012). https://doi.org/10.1080/05704928.2012.673189

[2] I.S. Butler, R.P. Kengne-Momo, A. Vessières, G. Jaouen, and C. Policar, "Recent Applications of Molecular Spectroscopy in Bioorganometallic Chemistry–Part 2: Ferrocenes and Other Organometallic Complexes," Appl. Spectrosc. Rev. **47**(8), 620–632 (2012). https://doi.org/10.1080/05704928.2012.697088

[3] S. Brodersen, and J.-E. Lolck, "Calculation of rotation-vibrational energies directly from an anharmonic potential function," J. Mol. Spectrosc. **126**(2), 405-426 (1987). https://doi.org/10.1016/0022-2852(87)90246-3

[4] P.T. Panek, A.A. Hoeske, and C.R. Jacob, "On the choice of coordinates in anharmonic theoretical vibrational spectroscopy: Harmonic vs. anharmonic coupling in vibrational configuration interaction," J. Chem. Phys. **150**(5), 054107 (2019). https://doi.org/10.1063/1.5083186

[5] K.B. Beć, J. Grabska, and C.W. Huck, "Current and future research directions in computer-aided near-infrared spectroscopy: A perspective," Spectrochim. Acta A. **254**, 119625 (2021). https://doi.org/10.1016/j.saa.2021.119625

[6] G. Pitsevich, and A. Malevich, "Symmetry properties, tunneling splittings of some vibrational energy levels and torsional IR spectra of the trans- and cis-conformers of hydroquinone molecule," J. Mol. Spectrosc. **404**, 111937 (2024). https://doi.org/10.1016/j.jms.2024.111937

[7] G. Pandimeena, T. Mathavan, E.J.J. Samuel, and A.M.F. Benial, "Quantum chemical, spectroscopic and molecular docking studies on methyl 2-chloro-6-methyl pyridine-4-carboxylate: A potential inhibitor for irritable bowel syndrome," Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. **294**, 122544 (2023). https://doi.org/10.1016/j.saa.2023.122544

[8] A.V. Nikitin, A. Campargue, A.E. Protasevich, M. Rey, K. Sung, and Vl.G. Tyuterev, "Analysis of experimental spectra of phosphine in the Tetradecad range near 2.3 μm using ab initio calculations," Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. **302**, 122896 (2023). https://doi.org/10.1016/j.saa.2023.122896

[9] I.M. Chandramalar, and V.P. Subhasini, "Vibrational spectroscopic analysis of 2,3:4,5-Bis-O-(1-methylethylidene)beta-D-fructopyranose Sulfamate (Topiramate) by density functional method," Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. **302**, 122997 (2023). https://doi.org/10.1016/j.saa.2023.122997

[10] V. Jaliparthi, "Vibrational Energies of Silylene, Difluorosilylene and Dichlorosilylene, Using U(2) Lie Algebraic Model," Ukr. J. Phys. Opt. **23**(3), 126-132 (2022). https://doi.org/10.3116/16091833/23/3/126/2022

[11] A.G. Rao, K. Lavanya, and J. Vijayasekhar, "Higher Overtone Vibrational Frequencies of Cyclobutane-D8 Using Lie Algebraic Framework," East Eur. J. Phys. (2), 411-415 (2024). https://doi.org/10.26565/2312-4334-2024-2-53

[12] J. Vijayasekhar, P. Suneetha, and K. Lavanya, "Vibrational spectra of cyclobutane-d8 using symmetry-adapted one-dimensional Lie algebraic framework," Ukr. J. Phys. Opt. **24**, 193-199 (2023). https://doi.org/10.3116/16091833/24/3/193/2023

[13] F. Iachello, and R.D. Levine, *Algebraic theory of molecules*, (Oxford University Press, Oxford, 1995).

[14] S. Oss, "Algebraic models in molecular spectroscopy," Adv. Chem. Phys. **93**, 455-649 (1996).

[15] T. Sreenivas, and J. Vijayasekhar, "Exploring Cyclohexane Vibrational Dynamics Through a Lie Algebraic Hamiltonian Framework," Ukr. J. Phys. Opt. **25**(3), 03093-03100 (2024). https://doi.org/10.3116/16091833/Ukr.J.Phys.Opt.2024.03093

АНАЛІЗ ВИЩИХ ОБЕРТОННИХ КОЛИВАЛЬНИХ ЧАСТОТ В ЦИКЛОГЕКСАНІ ЗА ДОПОМОГОЮ АЛГЕБРАЇЧНОГО ПІДХОДУ ЛІ

М.В. Субба Рао[a], Т. Срінівас[a,b], Дж. Віджаясекар[c]
[a]*Департамент математики, Інститут технологій і наук Аніла Нірукonди (ANITS), Вісакхапатнам, Індія*
[b]*Факультет математики, Технологічний університет Джавахарлала Неру, Какінада, Індія*
[c]*Департамент математики, GITAM (вважається університетом), Хайдарабад, Індія*

У цьому дослідженні представлено складний обчислювальний підхід до прогнозування вищих обертонних коливальних частот D3d точкової групи циклогексану (C6H12), зокрема третьої, четвертої та п'ятої. Ми використовуємо алгебраїчний метод Лі в рамках коливального гамільтоніана. У цьому підході використовуються вуглець-водневі (C-H) і вуглець-вуглецеві (C-C) зв'язки циклогексану як унітарні алгебри Лі, точно моделюючи молекулярну коливальну структуру. Як наслідок, коливальний гамільтоніан включає інваріантні оператори та параметри Казимира та Майорани, ефективно окреслюючи коливальні режими молекули. Цей алгебраїчний метод Лі пояснює вібраційну динаміку циклогексану з вищими обертонами та дає цінну інформацію для застосування в різних галузях досліджень та технологій.

Ключові слова: *алгебраїчний підхід Лі; коливальні частоти; коливальний гамільтоніан; циклогексан*