

HIGHER OVERTONE VIBRATIONAL FREQUENCIES IN NAPHTHALENE USING THE LIE ALGEBRAIC TECHNIQUE

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Abstract. This study presents a method for predicting the vibrational frequencies of naphthalene ($C_{10}H_8$) using a vibrational Hamiltonian approach that preserves the D_{2h} symmetry of the molecule. The method incorporates linked one-dimensional Morse oscillators to replicate the behaviors of the aromatic C-H and C-C bonds and their interrelated dynamics. The outcomes of this research offer precise predictions for the fourth and fifth overtones, validating the model's effectiveness in reflecting the complex vibrational dynamics of naphthalene. Thus, this work contributes to a deeper comprehension of the vibrational characteristics of naphthalene and establishes a detailed methodological basis for analyzing the vibrational spectra of similar polycyclic aromatic hydrocarbons.

Keywords: vibrational frequencies, Lie algebraic technique, vibrational Hamiltonian, naphthalene

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1. Introduction

Vibrational spectroscopy is essential in exploring atom and molecule vibrations, significantly contributing to our understanding of molecular structures, dynamics, and surrounding environments. The vibrational spectra of naphthalene are complex, showcasing diverse atomic movements, including stretching and bending. Predominantly, infrared and Raman spectroscopies are employed within vibrational spectroscopy, each investigating distinct vibrational modes of molecules. Infrared spectroscopy measures light absorption across various wavelengths when the sample is exposed to infrared light, aiding in presenting the molecular structure and dynamics of naphthalene and its derivatives [1-4].

In theoretical chemistry and molecular physics, determining molecular vibrational frequencies is essential, demanding the application of various theoretical approaches. These methods range from quantum mechanical (QM) strategies, like ab initio methods and density functional theory, to semi-empirical and molecular mechanics (MM) approaches. Each method balances computational demand against accuracy, catering to different molecular scales and complexities. QM/MM techniques and the vibrational self-consistent field approach offer specialized solutions for extensive molecules and anharmonic effects, thus enriching our understanding of molecular vibrations [4-7].

Lie algebraic technique represents a sophisticated mathematical approach in this field, enhancing the precision and efficiency of vibrational frequency calculations. Rooted in Lie algebra theory, these methods analyze highly symmetrical molecular systems, address anharmonicity, and simplify computational constraints. By leveraging molecular symmetries,

the Lie algebraic technique provides sophisticated solutions to the vibrational Schrödinger equation, offering insights into complex, unattainable molecular systems through conventional methods [8]. Iachello and others used the Lie algebraic approach to study polyatomic molecules' vibrational frequencies [9]. This method has since improved and expanded to different molecules [10-13].

Building upon the work of Rao et al., who successfully determined naphthalene's vibrational frequencies up to the third overtone using existing computational tools [14], this research aims to pioneer the investigation of the fourth and fifth overtone frequencies. This work proposes employing the Lie algebraic method and sophisticated computational approaches to achieve this objective.

2. The Hamiltonian representation of naphthalene utilizing U(2) Lie algebra

The construction of the Lie algebraic Hamiltonian involves integrating kinetic and potential energy components with symmetry considerations, improving the basic Hamiltonian to include interactions and symmetries specific to naphthalene. This approach facilitates an in-depth examination of the molecule's vibrational energy levels and transitions, delivering profound insights into its dynamic characteristics. As the simplest polycyclic aromatic hydrocarbon (PAH), naphthalene consists of two fused benzene rings and belongs to the D_{2h} symmetry point group, which includes symmetry species such as A_{1g} , B_{1g} , B_{2g} , B_{3g} , A_{1u} , B_{1u} , B_{2u} , and B_{3u} . The molecule exhibits 48 normal modes of vibration, divided into 33 symmetric and 15 asymmetric modes.

The effective Hamiltonians for the stretching vibrations of C-H and C-C bonds in naphthalene are formulated as [14]:

$$H^{C-H} = E_0 + \sum_{i=1}^{n=8} A_i C_i + \sum_{i<j}^{n=8} A_{ij} C_{ij} + \sum_{i<j}^{n=8} \lambda_{ij} M_{ij}, \quad (1)$$

$$H^{C-C} = E'_0 + \sum_{i=1}^{n=8} A'_i C_i + \sum_{i<j}^{n=8} A'_{ij} C_{ij} + \sum_{i<j}^{n=8} \lambda'_{ij} M_{ij}. \quad (2)$$

In these expressions, E_0 represents the zero-point energy. The terms involving Casimir (C_i, C_{ij}) and Majorana (M_{ij}) invariant operators are integral within the Lie algebraic structure tied to the vibrational Hamiltonian. These operators modernize the analysis of vibrational dynamics in molecules, particularly in those exhibiting specific symmetries. In vibrational spectroscopy, Casimir operators, associated with the Lie algebra of a symmetry group, provide constants of motion for the vibrational degrees of freedom, which relate to uncoupled and coupled bonds. On the other hand, Majorana operators help form irreducible representations of the Lie algebra, which are crucial for examining vibrational modes under a specific symmetry scenario, describing local mode interactions through diagonal and off-diagonal matrix elements. Integrating Casimir and Majorana invariant operators into the vibrational Hamiltonian simplifies its algebraic structure, thus aiding in more straightforward computation and precise interpretation. These operators are essential for understanding the symmetry and vibrational dynamics of molecules. The algebraic coefficients $A_i, A'_i, A_{ij}, A'_{ij}, \lambda_{ij}$, and λ'_{ij} are determined using molecular spectroscopic data through the least squares fitting approach.

The formulas for computing the algebraic operators, C_i, C_{ij}, M_{ij} (for C-H bonds), are given as:

$$\langle C_i \rangle = -4(Nv_i - v_i^2), \quad (3)$$

$$\langle N, v_i; N, v_j | C_{ij} | N, v_i; N, v_j \rangle = 4(v_i + v_j)(v_i + v_j - 2N), \quad (4)$$

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

Here, v_i and v_j denote the vibrational quantum numbers for bonds i and j , respectively. The

Vibron number, N , is defined by $N = \frac{\omega_e}{\omega_e x_e} - 1$, where ω_e and $\omega_e x_e$ are the spectroscopic

constants for C-H and C-C bonds. Initial estimates for A_i are derived from the energy of the single-oscillator fundamental mode: $E(v=1) = -4A_i(N-1)$; here v represents the vibration level. The parameters λ_{ij} and λ'_{ij} are calculated from the energy differences between

vibrational modes: $\lambda_{ij} = \frac{|E_i - E_j|}{2N}$, $\lambda'_{ij} = \frac{|E_i - E_j|}{6N}$, where E_i and E_j are the energies associated

with vibrational modes i and j , respectively.

3. Results of calculation

In Table 1, we disclose the refined values of algebraic parameters and vibron numbers utilized within the context of the Lie algebraic approach. These parameters, adopted based on the methodologies and findings outlined in reference [14], are fundamental to the model's precision and reliability. They play a pivotal role in influencing the simulation outcomes, underlining the importance of their meticulous optimization to ensure the model's effectiveness and accuracy. Table 2 outlines the vibrational frequencies for the fourth and fifth overtones and their symmetry species and vibrational modes within the naphthalene molecule. This compilation is critical as it unveils the unique characteristics and dynamics of the studied system, highlighting the direct correlation between the vibrational frequencies and the molecule's various motions and structural symmetries.

Table 1. Optimized parameters used for our Lie algebraic technique

Algebraic parameters	
C-H	C-C
$N = 43$	$N = 135$
$A_i = 1.0157$	$A'_i = -1.9854$
$A_{ij} = -0.1105$	$A'_{ij} = 0.1773$
$\lambda_{ij} = 0.8052$	$\lambda'_{ij} = 1.9016$

Table 2. Vibrational frequencies calculated for $C_{10}H_8$ (in cm^{-1})

Symmetry species	Mode number	Frequency of Fourth overtone	Frequency of Fifth overtone	Symmetry species	Mode number	Frequency of Fourth overtone	Frequency of Fifth overtone
A_g	1	13623	16306	B_{2g}	25	4578	5217
A_g	2	13281	16172	B_{2g}	26	3908	4576
A_g	3	7532	8870	B_{2g}	27	3745	4387
A_g	4	6004	7142	B_{2g}	28	2163	2359
A_g	5	6322	7106	B_{2u}	29	14952	16257
A_g	6	5301	6324	B_{2u}	30	14300	16812
A_g	7	4874	5527	B_{2u}	31	7340	8503
A_g	8	3703	4147	B_{2u}	32	6561	7707
A_g	9	2882	2983	B_{2u}	33	5774	6561
A_u	10	5468	6205	B_{2u}	34	5483	6397
A_u	11	3829	4438	B_{2u}	35	4651	5287
A_u	12	2805	3139	B_{2u}	36	2818	3282
A_u	13	881	1017	B_{3g}	37	14745	17206
B_{1g}	14	4427	5010	B_{3g}	38	14894	17541
B_{1g}	15	3330	3872	B_{3g}	39	7958	9278
B_{1g}	16	1851	1986	B_{3g}	40	6628	7873
B_{1u}	17	14708	16441	B_{3g}	41	5832	6891
B_{1u}	18	13906	15808	B_{3g}	42	5582	6493
B_{1u}	19	7719	8827	B_{3g}	43	4473	5319
B_{1u}	20	6606	7642	B_{3g}	44	2395	2686
B_{1u}	21	5947	6991	B_{3u}	45	4530	5182
B_{1u}	22	5534	6345	B_{3u}	46	3670	4104
B_{1u}	23	3716	4271	B_{3u}	47	2284	2408
B_{1u}	24	1793	1989	B_{3u}	48	822	952

4. Conclusions

The findings of this study highlight key aspects of employing Lie algebra techniques for analyzing the vibrational frequencies of naphthalene. By implementing a vibrational Hamiltonian within the framework of Lie algebras to compute the fourth and fifth overtone vibrational frequencies of naphthalene, this research showcases the significant potential of Lie algebraic methods in examining molecular vibrations. Such an approach enhances our comprehension of naphthalene's vibrational features and notably contributes to molecular spectroscopy.

Applying these sophisticated mathematical frameworks to investigate naphthalene's properties supports existing theoretical models and lays the groundwork for studying other polycyclic aromatic hydrocarbons (PAHs). This development could foster a more profound understanding of the vibrational spectra of complex organic molecules, an essential aspect of fields like materials science, environmental chemistry, and astrochemistry. The predictive results obtained are anticipated to aid experimentalists in validating *in vivo* experimental findings.

Moreover, this research transcends the particular case of naphthalene, proposing novel experimental techniques and theoretical models, including group theory and harmonic and anharmonic approaches, suitable for various molecular systems. This is particularly pertinent for molecules with analogous symmetry properties or those requiring detailed vibrational analysis, thus broadening the prospects for future research in molecular spectroscopy and quantum chemistry.

In conclusion, the results of this investigation not only deepen our knowledge of naphthalene's vibrational behavior but also emphasize the importance of merging Lie algebraic approaches with traditional spectroscopic techniques. This interdisciplinary methodology advances our theoretical insights and provides refined tools for the detailed analysis and interpretation of molecular vibrations, setting the stage for further scientific inquiries across various disciplines.

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Анотація. У цьому дослідженні представлено метод прогнозування коливальних частот нафталіну ($C_{10}H_8$) з використанням вібраційного гамільтонівського підходу, який зберігає симетрію D_{2h} молекули. Метод включає пов'язані одновимірні осцилятори Морзе для відтворення поведінки ароматичних зв'язків C-H і C-C та їх взаємопов'язаної динаміки. Результати цього дослідження пропонують точні прогнози для четвертого та п'ятого обертонів, підтверджуючи ефективність моделі у відображенні складної вібраційної динаміки нафталіну. Таким чином, ця робота сприяє глибшому розумінню коливальних характеристик нафталіну та створює детальну методологічну основу для аналізу коливальних спектрів подібних поліциклічних ароматичних вуглеводнів.

Ключові слова: коливальні частоти, алгебраїчна техніка Лі, коливальний гамільтоніан, нафталін.