Bol. Soc. Paran. Mat.
©SPM – E-ISSN-2175-1188
SPM: www.spm.uem.br/bspm

(3s.) **v. 2025 (43) 3** : 1–6.
ISSN-0037-8712
doi:10.5269/bspm.79274

Lie Algebraic Modeling of Dibromodichlorosilane Vibrational Frequencies Using Casimir and Majorana Operators

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ABSTRACT: Mathematical models used to analyse polyatomic molecule vibrational spectra must account for anharmonicity and molecular symmetry while being computationally efficient. We applied features of the Lie algebraic model relevant to the vibrational analysis of dibromodichlorosilane ($SiBr_2Cl_2$) and provided details. The vibrational Hamiltonian is explicitly formulated within the $U(2)$ algebra with its Casimir and Majorana operators. The operator approach yields an algebraic representation of stretching and bending vibrations, eliminating the need for differential equations, thereby allowing for a direct matrix representation. Fundamental vibrational frequencies are computed and carried through to the second overtone. The results confirm that vibrational frequencies, within the algebraic structure, mathematically capture anharmonic and intermode effects. Additionally, the results show that the method is highly accurate compared to more conventional techniques and requires a minimal set of parameters. This study provides evidence of the value of Casimir and Majorana operators for constitutive algebraic models of vibrational frequencies and an important step towards broadening the scope of their use in molecular spectroscopy, mathematical physics, and operator theory.

Key Words: Dibromodichlorosilane, Lie algebraic modeling, Casimir and Majorana operators, vibrational spectra, anharmonic vibrations.

Contents

1. Introduction

Molecular vibrations and their respective movements and dynamics, alongside the system's structure and bonding, can be best appreciated through a detailed understanding and study of them, particularly in the context of the complex chemical world. The methods of spectroscopy, particularly vibrational (infrared, Raman, etc.), present tangible approaches to the numerous intricacies associated with characteristic overtones, coupling, and their frequencies. The molecular structure faces a multitude of mechanical issues, with the range of molecular resonances giving rise to complex spectra. These have been invaluable in determining signals, analyzing reactions, and providing fingerprints for solutions. The experimental work and methods have shown considerable progress over the years; however, the lack of practical theoretical approaches to the spectra of vibrations remains a key challenge, especially regarding potential energy surfaces and underappreciated and neglected approaches to spectral and anharmonic effects [1]. Classical approaches, for instance, the Dunham expansion, break down the structure of vibrations and their respective movements and dynamics alongside the system's structure and bonding to derive the constructions of the entire system's complex vibration surfaces. These surface levels are then expressed as power series in quantum molecular numbers. As it is also apparent, in the simplest of molecular configurations, the rest of the molecules and structures, alongside polyatomic complex ring systems and other systems joined by interacting superposition of bonds, are unable to reveal the full potential and landmarks of polyatomic systems at higher overtones [2,3,4]. Ab initio and density functional approaches, in contrast, are DFT methods that utilise the superposition of molecular orbitals,

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2010 *Mathematics Subject Classification:* 30C45, 30C50.
Submitted September 30, 2025. Published December 20, 2025

which are mathematically solved by the nuclear Schrödinger equation for higher levels of electronic structure. Although the pure electronic and potential structures can be overlaid in the balanced systems of polyatoms, they serve as approximation methods for the rest of the large complex system of structures [5,6,7,8,9,10,11]. The Lie algebraic framework is more efficient and elegant for describing vibrational dynamics as an operator. In the $U(2)$ vibron model, every vibrational degree of freedom is associated with a separate dynamical algebra. The Hamiltonian is written in terms of Casimir operators, which account for the separate vibrational components, and Majorana operators, which separate the mode couplings. The operator formulation more naturally incorporates anharmonicity, symmetry, and vibrational interactions than formulating differential equations. The success of the algebraic method remains unsurpassed for various molecular systems. Over the last decade, the methodology has been applied to numerous polyatomic molecules, yielding striking agreement with experimental frequencies and accurate predictions of overtone transitions. The most recent applications to various polyatomic molecules, such as cyclohexane, cyclobutane-d$_s$, and higher overtones of naphthalene, provide strong support for the universality and strength of the algebraic framework for polyatomic vibrations. In comparison to Dunham expansions and ab initio methods, the Lie algebraic approach has several benefits: (i) it directly calculates and captures anharmonic effects, (ii) the molecular symmetry is incorporated automatically, and (iii) accurate predictions can be attained with fewer parameters [12,13,14,15,16,17,18].

Mathematically, the vibrational Hamiltonians for the Si–Br and Si–Cl bonds within the algebraic framework can be expressed as

$$H^{(\text{Si–Br})} = E_0 + \sum_{i=1}^{2} a_i C_i + \sum_{i<j}^{2} a_{ij} C_{ij} + \sum_{i<j}^{2} b_{ij} M_{ij}, \tag{1}$$

$$H^{(\text{Si–Cl})} = E_0' + \sum_{i=1}^{2} a_i' C_i + \sum_{i<j}^{2} a_{ij}' C_{ij} + \sum_{i<j}^{2} b_{ij}' M_{ij}. \tag{2}$$

where $C_i = -4\left(N_i v_i - v_i^2\right)$ are the Casimir operators associated with individual vibrational modes,

$$C_{ij} = 4\left(v_i + v_j\right)\left(v_i + v_j - N_i - N_j\right) \tag{3}$$

represent two-mode Casimir interactions, and M_ij are the Majorana operators that describe intermode couplings.

The matrix elements of the Majorana operators are given by

$$\begin{aligned} \prec N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \succ &= v_i N_j + v_j N_i - 2 v_i v_j, \\ \prec N_i, v_i+1; N_j, v_j-1 | M_{ij} | N_i, v_i; N_j, v_j \succ &= -\sqrt{v_j (v_i+1)(N_i - v_i)(N_j - v_j + 1)}, \\ \prec N_i, v_i-1; N_j, v_j+1 | M_{ij} | N_i, v_i; N_j, v_j \succ &= -\sqrt{v_i (v_j+1)(N_j - v_j)(N_i - v_i + 1)}. \end{aligned} \tag{4}$$

The coefficients $a_i,\ a_{ij},\ b_{ij},\ a_i',\ a_{ij}',\ b_{ij}'$ are algebraic parameters determined from experimental data compiled by Shimanouchi.

Here, $N_i (i = 1, 2)$ denotes the is the vibronn number associated with mode i, while v_i is the corresponding vibrational quantum number. The vibronn number N defines the size of the basis set used to describe molecular vibrations and is expressed as

$$N = \frac{\omega_e}{\omega_e \chi_e} - 1 \tag{5}$$

where ω_e and $\omega_e \chi_e$ represent the harmonic and anharmonic spectroscopic constants of the Si–Br $(429.58, 0.98)$ and Si–Cl $(535.59, 2.175)$ bonds, respectively, as reported by Irikura [19,20,21]. Here, N_1 and N_2 denote the vibron numbers corresponding to the Si-Br an Si-Cl bonds, respectivel

The current work employs an operator-based $U(2)$ Hamiltonian introduced in reference [22] for the study of methylene chloride and explicitly formulated in terms of Casimir and Majorana operators to investigate the vibrational spectra of dibromodichlorosilane. This mixed tetrahalosilane exhibits peculiar features in its vibrational spectra due to the presence of halogen substituents. We compute both the fundamental vibrational frequencies and overtone transitions up to the second overtone, thereby showcasing the effectiveness and predictive power of the Lie algebraic approach in modelling halogenated silane systems.

2. Structure of Dibromodichlorosilane

Belonging to the family of tetrahalosilanes, dibromodichlorosilane consists of a silicon atom bonded covalently to two chloro and two bromo atoms. As outlined in the schematic of Figure 1, the Si–Br bonds are 1 and 2, while the Si–Cl bonds are 3 and 4, aiding in the subsequent vibrational description. The molecule resides in the C_{2v} point group as a C_2 type system, possessing a central rotation axis through the silicon atom and two vertical mirror planes. As a nonlinear system with five atoms, $SiBr_2Cl_2$ has a total of nine vibrational modes, as determined by the $3N$–6 rule. The group theoretical treatment classifies the vibrational modes intoC_{2v} point group irreducible representations as $4A_1 + A_2 + 2B_1 + 2B_2$. The A_1 modes of the system are the center of both the symmetric stretching and bending vibrations of the Si–Br (bonds 1 and 2) and Si–Cl (bonds 3 and 4) group and are found in both the IR and Raman spectra. Antisymmetric bending vibrations classified as A_2 modes are Raman active but IR inactive. The B_1 and B_2 modes, asymmetrical stretching and bending with respect to the bonds, are weakly to moderately active in both IR and Raman spectra. The vibrational elements of $SiBr_2Cl_2$, including more than scissoring, bending, rocking, and twisting, have practical applications in molecular spectroscopy and structural chemistry. These applications highlight the significance of understanding the vibrational modes of $SiBr_2Cl_2$, which are all governed by the C_{2v} molecular symmetry [23,24,25,26,27].

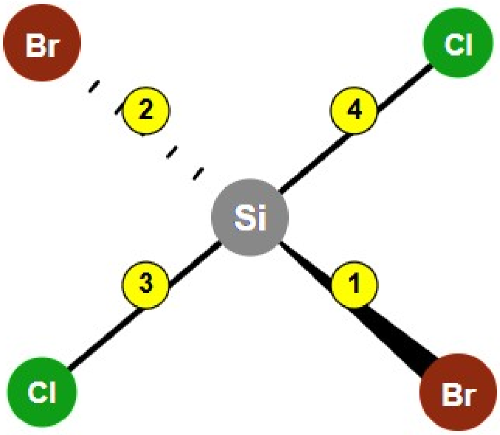

Figure 1: Molecular structure of $SiBr_2Cl_2$ with numbering scheme: Si–Br bonds labeled as 1 and 2, and Si–Cl bonds labeled as 3 and 4.

3. Results and Discussion

The initial estimates for the fundamental mode parameters a_i, a'_i, corresponding to the Si-Br and Si-Cl bonds respectively, are obtained from the single-oscillator energy expressions:

$$a_i = -\frac{E^{\text{Fundamental}}_{\text{Si-Br}}}{4(N_1 - 1)}, \quad a'_i = -\frac{E^{\text{Fundamental}}_{\text{Si-Cl}}}{4(N_2 - 1)}. \tag{6}$$

The initial values of interaction parameters b_{ij} and b'_{ij}, for the Si-Br and Si-Cl bonds respectively, are given by:

$$b_{ij} = \frac{|E_{\text{s-str}} - E_{\text{a-str}}|}{3N_1}, \quad b'_{ij} = \frac{|E'_{\text{s-str}} - E'_{\text{a-str}}|}{3N_2}. \tag{7}$$

Here, $E_{\text{s-str}}$ and $E_{\text{a-str}}$ denote the symmetric and asymmetric stretching energies of the Si-Br bond, while and $E'_{\text{s-str}}$ and $E'_{\text{a-str}}$ represent the corresponding energies for the Si-Cl bond. The initial estimates of the parameters a_{ij} and a'_{ij} corresponding to the Si-Br and Si-Cl bonds respectively, are taken to be zero. All parameters in the Hamiltonian are subsequently optimized using a least-squares fitting procedure with the fundamental mode vibrational frequencies data [28], and the final fitted values are presented in Table1.

Table 1. Optimized Lie Algebraic Parameters for the $U(2)$ Hamiltonian of $SiBr_2Cl_2$

Parameters	**Optimized Value**
N_1 (Si-Br Stretching, bending)	436, 202
N_2 (Si-Cl Stretching, bending)	244, 118
a_i (Si-Br Stretching, bending)	-0.226, -0.393
a'_i (Si-Cl Stretching, bending)	-0.575, -0.402
a_{ij} (Si-Br Stretching, bending)	-1.261, 2.398
a'_{ij} (Si-Cl Stretching, bending)	-0.507, 1.750
b_{ij} (Si-Br Stretching, bending)	0.217, 0.804
b'_{ij} (Si-Cl Stretching, bending)	0.104, 1.454

Table 2. Observed and calculated vibrational frequencies (fundamental, first overtone, and second overtone) of $SiBr_2Cl_2$

Vibrational Mode	**Symmetry Species**	**Fundamental Mode Observed [28]**	**Calculated**	**Overtone I**	**Overtone II**
$SiCl_2$ Symmetric stretching (v1)	A_1	563	559.30	1103.61	1576.07
$SiBr_2$ Symmetric stretching (v2)	A_1	326	320.75	621.26	885.86
$SiCl_2$ Scissoring (v3)	A_1	182	174.48	307.33	511.54
$SiBr_2$ Scissoring (v4)	A_1	111	107.69	188.00	284.19
$SiCl_2$ Twisting (v5)	A_2	122	116.27	219.63	317.57
$SiCl_2$ Asymmetric stretching (v6)	B_1	605	598.91	1173.06	1682.29
$SiCl_2$ Rocking (v7)	B_1	191	183.03	360.22	545.21
$SiBr_2$ Asymmetric stretching (v8)	B_2	508	501.11	971.63	1486.88
$SiBr_2$ Rocking (v9)	B_2	174	167.65	312.20	495.49

4. Conclusions

The present study completes the calculation of the vibrational spectra of $SiBr_2Cl_2$ within the framework of Lie algebra using Casimir and Majorana operators. Within the $U(2)$ algebra, the vibrational Hamiltonian was formulated in compact operator form, which permits stretching and bending vibrations to be represented without the burdens of the complications that arise in differential formulations. The optimised values showed that the algebraic Hamiltonian has the required parameters constant, and only for anharmonic intermode couplings, to obtain equilibrium results that are very close to the experimental values. Analysis of the fundamental vibrational frequencies showed an RMS deviation of 6.06 cm -1. All these underlines the authenticity of the entire approach used in the study. Moreover, the predicted systematic anharmonic first and second overtone frequencies are of great help in guiding experimenters in further exploration of the vibrational excitations of this molecule. Overall, the present work further emphasises the algebraic control over vibrational analysis of halogen-bonded silanes using Casimir and Majorana operators. While the results for $SiBr_2Cl_2$ are conclusive, the approach retains strong applicability for larger polyatomic molecules and more intricate systems, illustrating the profound relevance for molecular spectroscopy, mathematical physics and operator theory.

Acknowledgments

The author gratefully acknowledges the use of data from the NIST Standard Reference Database 69: NIST Chemistry WebBook, provided by the National Institute of Standards and Technology (NIST) https://webbook.nist.gov/cgi/inchi?ID=C13465753& Mask=80 . This resource was essential in supporting the accuracy and reliability of the present study.
The authors express their sincere thanks to the respected referee (s) and the editor for their valuable comments, which helped them to improve the presentation of the article.

Competing interests

The author declares no competing interests.

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