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# SYMMETRY-ADAPTED LIE ALGEBRAIC FRAMEWORK FOR MODELING THE VIBRATIONAL MODES OF SULFUR HEXAFLUORIDE

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**Abstract.** The vibrational modes of sulfur hexafluoride ($SF_6$) are analyzed using a symmetry-adapted U(2) Lie algebraic approach. In the context of $O_h$ point group symmetry, the Hamiltonian constructed with Casimir and Majorana operators includes anharmonicity and intermode coupling. The fundamental modes, measured with high precision, show a very close match, with RMS deviations of less than 1 $cm^{-1}$, aligning well with experimental data. The model also predicts the positions of combination bands and overtones to demonstrate its capabilities further. This method greatly enhances spectroscopic studies of atmospheric science compared to traditional approaches for modeling high-symmetry polyatomic molecules.

**Keywords:** Sulfur hexafluoride, vibrational modes, Hamiltonian, Casimir and Majorana operators
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## 1. Introduction

Theorists and experimentalists have recently become interested in molecular spectroscopy, which is helpful to researchers in several fields, including analytical chemistry, biophysics, environmental science, and astrophysics. Both quantitatively and qualitatively, molecular spectroscopy is undergoing dramatic changes. Spectroscopic studies that include the emission, absorption, and scattering of energy radiation in conjunction with transitions between molecular energy levels can provide information about molecular structure. Absorption and emission of energy by molecules are closely related to bands of vibrational and rotational energies that augment a molecule's electronic states. Recent advances in spectroscopy enable us to understand molecular energy and structure through vibrational and rotational energies. However, experimentalists face a problem with lower intensities, which drives them to seek newer, more sensitive experimental tools.

On the other hand, theorists face significant challenges in developing accurate models to understand the observed energy spectrum of molecules. Over the years, several theoretical approaches have been employed to model and predict vibrational spectra of higher symmetric molecules, such as polyatomic octahedral molecules with an $O_h$ point group. Conventional techniques such as density functional theory (DFT), potential energy surface methods, ab initio quantum-mechanical calculations, and semi-empirical approaches such as the Dunham expansion have been extensively used [1-3]. All these approaches compute

energy values using the differential (or wave) formulation of the Schrodinger equation in quantum mechanics. The equation's potential function optimization parameters will match the observed spectrum. Although these traditional techniques have substantially contributed to vibrational spectroscopy, they have several important drawbacks. For example, ab initio methods are computationally intensive, empirical dependencies limit the Dunham expansion, and potential-energy-based approaches have problems with functional dependencies, particularly for anharmonic and highly correlated systems. Thus, traditional approaches struggle to model higher-order anharmonicity, frequently necessitating additional impractical empirical corrections and limiting their predictive power for polyatomic molecules [4-9].

The algebraic (or matrix) formulation of quantum mechanics, a significant breakthrough, was employed to overcome the drawbacks of conventional methods. The symmetry-adapted Lie-algebraic approach offers a systematic and computationally efficient framework for modelling the vibrational spectrum. This approach, which uses algebraic operators to control the interactions of vibrational states in polyatomic structures, is a U(2) description of the Lie algebraic approach [10-11]. Its independence from empirical corrections or predefined potential energy surfaces makes it suitable for polyatomic systems, unlike ab initio methods. Higher-order anharmonic effects improve the accuracy of overtone computations and exploit molecular symmetry to enable organized vibrational analysis across various point groups. This method significantly reduces computational complexity and provides a unified theoretical framework that accurately handles large polyatomic molecules. Applying the Lie algebraic approach with symmetry adaptation to understand the vibrational modes of the $SF_6$ molecule is a testament to its potential.

Applications of $SF_6$ include tracer gas, gas-insulated substations, high-voltage electrical systems, and plasma-based semiconductor fabrication. Due to its non-flammability and thermal stability, $SF_6$ can be used safely and easily in technological applications. Despite its industrial significance, $SF_6$ poses serious environmental concerns. It is classified as one of the most potent greenhouse gases, characterised by an exceptionally long atmospheric lifetime of over 3,200 years and a global warming potential approximately 23,500 times higher than that of carbon dioxide over a 100-year assessment period [12]. Reliable and accurate spectroscopic/molecular models that enable precise climate detection and monitoring are necessary, given the unprecedented long-term environmental consequences. We can predict and lessen the hazardous properties of $SF_6$ molecules with modelling and computational studies. It is crucial to examine the $SF_6$ molecule's vibrational spectrum to characterize it. For example, the $SF_6$ molecule's infrared active modes are of fundamental spectroscopic interest and are crucial for optical diagnostics, climate science, and environmental monitoring [13-14]. Therefore, vibrational studies are pertinent when they can aid in developing sophisticated spectroscopic techniques and improving the accuracy of radiative transfer simulations. Quantum chemical techniques, such as DFT, have been used to model the vibrational properties of $SF_6$. Dincer et al. demonstrated the usefulness of the B3LYP/6-311+G(d,p) method for predicting isotopic shifts and fundamental frequencies, with substantial experimental support [2]. Ke et al. continued this work by adding combination-band and hot-band transitions to the model [15]. It is still tricky to layer higher-order anharmonicity and intermodal couplings because traditional methods typically require

substantial computational power and provide little concise, clear analytical interpretation. As more accurate radiative transfer simulations with laser-based platforms for trace gas spectroscopy become available, the accuracy of these modes indirectly affects the efficiency of these models [16]. Accurate overtone anharmonic frequency shifts, intermodal coupling, and a symmetry-adapted algebraic framework that captures these processes are the foundations of even sophisticated nonlinear spectroscopic techniques, such as ultrafast laser-induced detection of high-energy molecular transitions [17].

Algebraic approaches offer an alternative perspective by expressing molecular vibrations in terms of Lie algebraic structures. Both diatomic and polyatomic substances' vibrational spectra can be successfully analysed using the U(2) and U(4) frameworks in the literature [18-25]. High-symmetry molecules like $SF_6$ benefit significantly from their methodical application of symmetry, boundary conditions, and anharmonic terms while maintaining computational efficiency. For linear triatomic and tetratomic molecules, the rotational and vibrational modes are computed using the U(4) algebraic model. The more atoms in this U(4) model, the more complicated it becomes. Thus, to calculate the vibrational spectra of $SF_6$, we use a Lie-algebraic model based on U(2). Anharmonic and intermode coupling effects are described by Majorana operators in the vibrational Hamiltonian, while Casimir operators describe unperturbed vibrational energy levels. The $O_h$ symmetry of the $SF_6$ molecule plays a crucial role in the algebraic model, as it helps preserve the molecule's unique characteristics and simplify the computational process.

## 2. Lie algebraic framework for the vibrational spectra of $SF_6$

Infrared (IR) and Raman active modes are present in the vibrating spectrum of $SF_6$, an octahedral molecule of the $O_h$ point group with high symmetry. Understanding how vibrational modes are arranged into symmetry species depends critically on the vibrational spectrum established by spectroscopic selection rules. With its six bonded atoms and non-linear geometry, $SF_6$ exhibits 15 normal vibrational modes that give rise to sets of bending and stretching motions, providing a clear picture of its structure. Fig. 1 illustrates the molecular structure of $SF_6$, which adopts a highly symmetric octahedral geometry.

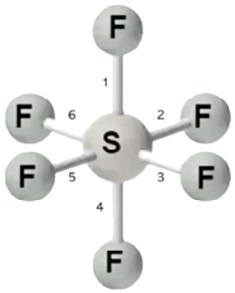


**Fig. 1.** Bond assignments in $SF_6$ illustrating S–F bond interactions.

In this structure, the central sulfur atom is surrounded by six equivalent fluorine atoms. The figure also includes bond assignments, clearly depicting the S–F bond interactions that determine the molecule's geometric and spectroscopic characteristics. The irreducible representations of these modes under the symmetry group $O_h$ are termed.

The following are some unique characteristics of each $SF_6$ vibrational mode:

• Raman active non-degenerate symmetric stretching mode $v_1$, which changes into $A_{1g}$.

• The double-degenerating symmetric stretching mode. Moreover, $v_2$ has $E_g$ symmetry and is Raman active.

• The infrared-active triply degenerate asymmetric stretching modes $v_3$ and bending modes $v_4$ are members of the $F_{1u}$ symmetry Species.
• The Raman-active, triply degenerate symmetric bending mode $v_5$ is associated with $F_{2g}$.
• Under harmonic approximations, the triply degenerate asymmetric bending mode, $v_6$, a member of $F_{2u}$, is not active in IR and Raman spectra. However, its nature is made even more intriguing by the possibility that $v_6$ could become weakly active under stronger effects, such as Coriolis or anharmonic couplings.

Thus, the vibrational activity of $SF_6$ involves Raman-active modes ($A_{1g}$, $\underline{E}_g$, $F_{2g}$), IR-active modes ($F_{1u}$), and one inactive mode ($F_{2u}$). These are represented by four stretching and eight bending modes, for a total of 15 normal modes. These 'normal modes' refer to the independent vibrational motions that a molecule can undergo, each associated with a specific frequency and energy [26-29]. They are determined by the molecule's symmetry and structure. Using Casimir and Majorana operators within U(2) Lie algebra allows previously neglected anharmonic contributions and intermode couplings to be included in the predictions of the vibrational Hamiltonian's accuracy [18-19] The vibrational system's fundamental energy contributions and two body interactions are captured by the Casimir operators $C_i$ and $C_{ij}$, alongside the $M_{ij}$ Majorana operators, enabling the systematic formulation of quantum states within a vibrational system, enabling a structured representation of vibrational excitations. On the other hand, the Majorana operators $M_{ij}$ capture anharmonic effects and intermode coupling, making thecrucial for detecting deviations from harmonic motion and higher-order vibrational interactions.

The Hamiltonian governing the S-F stretching vibrations is expressed as:

$$H^{S-F} = E_0^{S-F} + \sum_{i=1}^{6} A_i^{S-F} C_i + \sum_{1\le i<j\le 6} A_{ij}^{S-F} C_{ij} + \sum_{1\le i<j\le 6} \sum_{t=1}^{3} k_{ij}^t \lambda_{ij}^{S-F} M_{ij}^t . \tag{1}$$

Explicit analytical form for six S–F local modes:

$$\begin{aligned} H^{S-F} = {} & E_0^{S-F} + \left(A_1^{S-F}C_1 + A_2^{S-F}C_2 + A_3^{S-F}C_3 + A_4^{S-F}C_4 + A_5^{S-F}C_5 + A_6^{S-F}C_6\right) + \\ & \left(A_{12}^{S-F}C_{12} + A_{13}^{S-F}C_{13} + A_{14}^{S-F}C_{14} + A_{15}^{S-F}C_{15} + A_{16}^{S-F}C_{16} + A_{23}^{S-F}C_{23} + A_{24}^{S-F}C_{24} + A_{25}^{S-F}C_{25}\right. \\ & \left. + A_{26}^{S-F}C_{26} + A_{34}^{S-F}C_{34} + A_{35}^{S-F}C_{35} + A_{36}^{S-F}C_{36} + A_{45}^{S-F}C_{45} + A_{46}^{S-F}C_{46} + A_{56}^{S-F}C_{56}\right) + \\ & \sum_{t=1}^{3}\Big[k_{12}^t\lambda_{12}^{S-F}M_{12}^t + k_{13}^t\lambda_{13}^{S-F}M_{13}^t + k_{14}^t\lambda_{14}^{S-F}M_{14}^t + k_{15}^t\lambda_{15}^{S-F}M_{15}^t + k_{16}^t\lambda_{16}^{S-F}M_{16}^t \\ & + k_{24}^t\lambda_{24}^{S-F}M_{24}^t + k_{25}^t\lambda_{25}^{S-F}M_{25}^t + k_{26}^t\lambda_{26}^{S-F}M_{26}^t + k_{34}\lambda_{34}^{S-F}M_{34}^t + k_{35}\lambda_{35}^{S-F}M_{35}^t \\ & + k_{36}\lambda_{36}^{S-F}M_{36}^t + k_{45}^t\lambda_{45}^{S-F}M_{45}^t + k_{46}^t\lambda_{46}^{S-F}M_{46}^t + k_{56}^t\lambda_{56}^{S-F}M_{56}^t\Big]. \end{aligned} \tag{2}$$

The term $k_{ij}^t$ represents symmetry-adapted coefficients that incorporate first-, second-, and third-neighbour interactions, while preserving molecular symmetry constraints.

$$k_{ij}^1 = \begin{vmatrix} 1, (i,j) = (1,2),(2,3),(3,4),(4,5),(5,6) \\ 0, otherwise \end{vmatrix}, \tag{3}$$

$$k_{ij}^2 = \begin{vmatrix} 1, (i,j) = (1,3),(2,4),(3,5),(4,6),(1,5),(2,6) \\ 0, otherwise \end{vmatrix}, \tag{4}$$

$$k_{ij}^3 = \begin{vmatrix} 1, (i,j) = (1,4),(2,5),(3,6) \\ 0, otherwise \end{vmatrix}. \tag{5}$$

Similarly, the bending vibrational modes are governed by a Hamiltonian that incorporates Casimir and Majorana operators:

$$H^{bend} = E_0^{bend} + \sum_{j=1}^{8} A_j^{bend} C_j + \sum_{j<m}^{8} A_{jm}^{bend} C_{mj} + \sum_{j<m}^{8} g_{jm} \lambda_{jm}^{bend} M_{jm} \ . \tag{6}$$

Explicit analytical form of the Hamiltonian for eight bending local modes:

$$\begin{aligned} H^{bend} = {} & E_0^{bend} + (A_1^{bend} C_1 + A_2^{bend} C_2 + A_3^{bend} C_3 + A_4^{bend} C_4 + A_5^{bend} C_5 \\ & + A_6^{bend} C_6 + A_7^{bend} C_7 + A_8^{bend} C_8) + (A_{12}^{bend} C_{12} + A_{13}^{bend} C_{13} + A_{14}^{bend} C_{14} + A_{15}^{bend} C_{15} \\ & + A_{16}^{bend} C_{16} + A_{17}^{bend} C_{17} + A_{18}^{bend} C_{18} + A_{23}^{bend} C_{23} + A_{24}^{bend} C_{24} + A_{25}^{bend} C_{25} + A_{26}^{bend} C_{26} \\ & + A_{27}^{bend} C_{27} + A_{28}^{bend} C_{28} + A_{34}^{bend} C_{34} + A_{35}^{bend} C_{35} + A_{36}^{bend} C_{36} + A_{37}^{bend} C_{37} + A_{38}^{bend} C_{38} \\ & + A_{45}^{bend} C_{45} + A_{46}^{bend} C_{46} + A_{47}^{bend} C_{47} + A_{48}^{bend} C_{48} + A_{56}^{bend} C_{56} + A_{57}^{bend} C_{57} + A_{58}^{bend} C_{58} \\ & + A_{67}^{bend} C_{67} + A_{68}^{bend} C_{68} + A_{78}^{bend} C_{78}) \\ & + (g_{12} \lambda_{12}^{bend} M_{12} + g_{13} \lambda_{13}^{bend} M_{13} + g_{14} \lambda_{14}^{bend} M_{14} + g_{15} \lambda_{15}^{bend} M_{15} + g_{16} \lambda_{16}^{bend} M_{16} \\ & + g_{17} \lambda_{17}^{bend} M_{17} + g_{18} \lambda_{18}^{bend} M_{18} + + g_{23} \lambda_{23}^{bend} M_{23} + g_{24} \lambda_{24}^{bend} M_{24} + g_{25} \lambda_{25}^{bend} M_{25} \\ & + g_{26} \lambda_{26}^{bend} M_{26} + g_{27} \lambda_{27}^{bend} M_{27} + g_{28} \lambda_{28}^{bend} M_{28} + g_{34} \lambda_{34}^{bend} M_{34} + g_{35} \lambda_{35}^{bend} M_{35} \\ & + g_{36} \lambda_{36}^{bend} M_{36} + g_{37} \lambda_{37}^{bend} M_{37} + g_{38} \lambda_{38}^{bend} M_{38} + g_{45} \lambda_{45}^{bend} M_{45} + g_{46} \lambda_{46}^{bend} M_{46} \\ & + g_{47} \lambda_{47}^{bend} M_{47} g_{48} \lambda_{48}^{bend} M_{48} g_{56} \lambda_{56}^{bend} M_{56} g_{57} \lambda_{57}^{bend} M_{57} g_{58} \lambda_{58}^{bend} M_{58} \\ & + g_{67} \lambda_{67}^{bend} M_{67} + g_{68} \lambda_{68}^{bend} M_{68} + g_{78} \lambda_{78}^{bend} M_{78}). \end{aligned} \tag{7}$$

The coefficients $g_{jm}$ define the symmetry-adapted strength of mode-mode interactions:

$$g_{jm} = \begin{cases} 1, (i,j) = (1,2),(1,3),(1,5),(1,6),(4,2),(4,3),(4,5),(4,6) \\ 0, otherwise \end{cases} . \tag{8}$$

These operators dictate the quantum mechanical characteristics of the system by governing energy distributions, vibrational couplin and transition probabilities between quantum states [18-19]

$$\langle C_i \rangle = -4\left(N_i v_i - v_i^2\right), \tag{9}$$

$$\left\langle N_i, v_i; N_j, v_j \middle| C_{ij} \middle| N_i, v_i; N_j, v_j \right\rangle = 4\left(v_i + v_j\right)\left(v_i + v_j - N_i - N_j\right), \tag{10}$$

$$\left.\begin{aligned} \left\langle N_i, v_i; N_j, v_j \middle| M_{ij} \middle| N_i, v_i; N_j, v_j \right\rangle &= v_i N_j + v_j N_i - 2 v_i v_j \\ \left\langle N_i, v_i + 1; N_j, v_j - 1 \middle| M_{ij} \middle| N_i, v_i; N_j, v_j \right\rangle &= -\left[ v_j \left(v_i + 1\right)\left(N_i - v_i\right)\left(N_i - v_i + 1\right)\right]^{1/2} \\ \left\langle N_i, v_i - 1; N_j, v_j + 1 \middle| M_{ij} \middle| N_i, v_i; N_j, v_j \right\rangle &= -\left[ v_i \left(v_j + 1\right)\left(N_j - v_j\right)\left(N_i - v_i + 1\right)\right]^{1/2} \end{aligned}\right\} . \tag{11}$$

where $v_i, v_j$ are the vibrational quantum numbers that define excitation levels of individual vibrational modes.

The vibron number *N* determines the basis set size for describing molecular vibrations and is given by:

$$N = \frac{\omega_e}{\omega_e \chi_e} - 1 \ , \tag{12}$$

where $\omega_e$ =837.6418$(\mathrm{S-F})$ and $\chi_e = 4.46953(\mathrm{S-F})$ are the spectroscopic constants of the S-F bond, determined from experimental data [30].

The initial guess for the fundamental mode parameters $A_i^{S-F}$, $A_j^{bend}$ are obtained from the single-oscillator energy expressions:

$$A_i^{S-F} = -\frac{E^{S-F}}{4\left(N^{S-F}-1\right)}, \quad A_j^{bend} = -\frac{E^{bend}}{4\left(N^{bend}-1\right)}. \tag{13}$$

The initial estimates for the interaction parameters $\lambda_{ij}^{S-F}$,$\lambda_{jm}^{bend}$ are given by:

$$\lambda_{ij}^{S-F} = \frac{\left|E_s^{S-F} - E_{as}^{S-F}\right|}{6N^{S-F}}, \ \lambda_{jm}^{bend} = \frac{\left|E_s^{bend} - E_{as}^{bend}\right|}{2N^{bend}}, \tag{14}$$

where $E_s$ and $E_{as}$ represent the symmetric and antisymmetric energy combinations of the two local modes. The parameters $A_i^{S-F}$, $A_j^{bend}$, $\lambda_{ij}^{S-F}$ and $\lambda_{jm}^{bend}$ are optimised using least-square regression fitting, while $A_{ij}^{S-F}$ and $A_{jm}^{bend}$ is initially set to zero to ensure a systematic optimization approach.

## 3. Results and discussion

The harmonic and anharmonic contributions to molecular vibrational spectra are treated by using Casimir and Majorana operators. The model ensures that the molecule's symmetry properties are not altered, with symmetry-related interactions and transitions incorporating the group selection rules for interactions and transitions. The parameters of the vibrational Hamiltonian were calibrated within the limits shown in Table 1.

**Table 1.** Optimized fitting parameters (all in $cm^{-1}$, except $N$) for the U(2) Lie algebraic vibrational Hamiltonian of $SF_6$ with $O_h$ symmetry [27].

| Parameters | Value |
|---|---|
| $N^{S-F}$ | 186 |
| $A_i^{S-F}$ | -0.7218 |
| $A_{ij}^{S-F}$ | -1.6481 |
| $\lambda_{ij}^{S-F}$ | 0.2587 |
| $N^{bend}$ | 92 |
| $A_j^{bend}$ | -2.1153 |
| $A_{jm}^{bend}$ | 0.9310 |
| $\lambda_{jm}^{bend}$ | 0.1914 |

The listed parameters include the algebraic parameters defining single-mode energies and inter-mode coupling interaction, and N, the vibron number determining the dimension of the Hilbert space. These values were obtained by fitting the algebraic expressions to the experimental frequencies using the least-squares minimization technique, which guarantees consistent and stable parameter estimates. The form of these parameters, constrained by symmetry principles, significantly reduces computational scaling relative to quantum-chemistry calculations while maintaining high fidelity. Table 2 lists the calculated vibrational frequencies and their degeneracies, symmetry classifications, and activity types (IR, Raman, or inactive) for the six $SF_6$ fundamental modes ($\nu_1$, $\nu_2$, $\nu_3$, $\nu_4$, $\nu_5$, and $\nu_6$). The model achieves remarkable reproduction of experimental values across numerous datasets, yielding low RMS deviations of 1.06 $cm^{-1}$ [27], 0.86 $cm^{-1}$ [26], 0.49 $cm^{-1}$ [17], and 0.79 $cm^{-1}$ [31]. The accuracy of these results suggests that the physical reality of the Lie-algebra-based model is

striking in capturing the collective vibrational modes of system constituents with symmetry constraints. In particular, the spectroscopically inactive $\nu_6$ mode ($F_{2u}$ symmetry) in this model is due to higher-order Coriolis coupling [28], which exemplifies how models can be altered to account for discrete phenomena in nonlinear frameworks. A graphical representation of the correlation between computed and experimental fundamental frequencies is shown in Fig. 2. The results demonstrate nearly perfect overlap, confirming an almost exact linear dependency and proving that the Lie algebraic model quantitatively preserves the energetic hierarchy and the distance between the vibrational modes.

**Table 2.** The calculated and experimental vibrational frequencies (in $cm^{-1}$) for $SF_6$ with $O_h$ symmetry.

| Mode | Symmetry | Degeneracy | Observed | Calculated | Activity |
|---|---|---|---|---|---|
| $\nu_1$ | $A_{1g}$ | 1 | 774.55 | 774.29 | Raman |
| $\nu_2$ | $E_g$ | 2 | 643.35 | 642.33 | Raman |
| $\nu_3$ | $F_{1u}$ | 3 | 947.98 | 948.42 | IR |
| $\nu_4$ | $F_{1u}$ | 3 | 615.02 | 616.51 | IR |
| $\nu_5$ | $F_{2g}$ | 3 | 523.56 | 525.07 | Raman |
| $\nu_6$ | $F_{2u}$ | 3 | 348.08 | 347.11 | Inactive |
| **Combination bands** | | | | | |
| $\nu_1 + \nu_4$ | | | | 1385.37 | |
| $\nu_2 + \nu_6$ | | | | 987.70 | |
| $\nu_5 + \nu_6$ | | | | 871.45 | |
| $\nu_3 + \nu_4$ | | | | 1562.62 | |
| $\nu_1 + \nu_5$ | | | | 1294.91 | |

| I Overtone | | II Overtone | | III Overtone | |
|---|---|---|---|---|---|
| **Mode** | **Calculated** | **Mode** | **Calculated** | **Mode** | **Calculated** |
| $2\nu_1$ | 1548 | $3\nu_1$ | 2322 | $4\nu_1$ | 3096 |
| $2\nu_2$ | 1286 | $3\nu_2$ | 1929 | $4\nu_2$ | 2572 |
| $2\nu_3$ | 1896 | $3\nu_3$ | 2844 | $4\nu_3$ | 3792 |
| $2\nu_4$ | 1230 | $3\nu_4$ | 1845 | $4\nu_4$ | 2460 |
| $2\nu_5$ | 1048 | $3\nu_5$ | 1572 | $4\nu_5$ | 2096 |
| $2\nu_6$ | 692 | $2\nu_6$ | 1038 | $4\nu_6$ | 1384 |

The vibrational frequencies computed using the Lie-algebraic framework were compared with the corresponding scaled DFT results, as summarised in Table 3. Six fundamental vibrational modes ($\nu_1$–$\nu_6$) were examined, and the frequency deviations for each mode were evaluated. The comparison shows that both approaches exhibit strong numerical consistency, with only minor variations across all modes. The RMS deviation obtained for the complete set of vibrational levels is 15.01 $cm^{-1}$, indicating that the Lie-algebraic model provides an accurate reproduction of the DFT-predicted frequencies. This close agreement demonstrates the reliability of the algebraic approach for modelling vibrational spectra and validates its use as an efficient alternative technique.

**Table 3.** Comparison of vibrational frequencies ($cm^{-1}$) obtained from scaled DFT calculations [16] and the Lie-algebraic framework for modes.

| Mode | DFT (I) | Lie Algebraic Method (II) | Difference (I-II) |
|---|---|---|---|
| $\nu_1$ | 771.20 | 774.55 | -3.35 |
| $\nu_2$ | 662.40 | 643.35 | 19.05 |
| $\nu_3$ | 978.40 | 947.98 | 30.42 |
| $\nu_4$ | 611.30 | 615.02 | -3.72 |
| $\nu_5$ | 517.50 | 523.56 | -6.06 |
| $\nu_6$ | 346.90 | 348.08 | -1.18 |

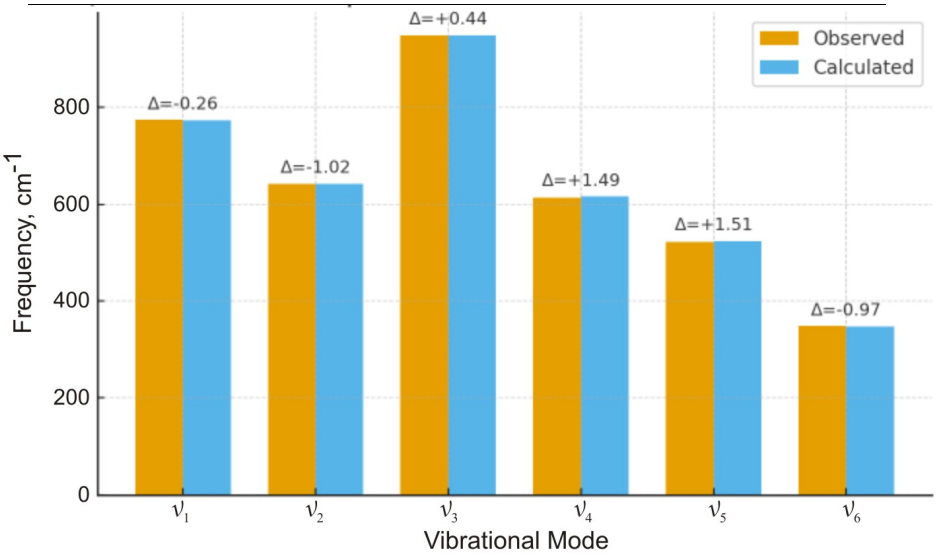


**Fig. 2.** Comparison of observed and calculated vibrational frequencies of $SF_6$ across its fundamental modes.

The model captures vibrational combination bands with high precision, as depicted in Fig. 3, in addition to fundamental modes.

These include mixed excitations such as $\nu_1 + \nu_4$, $\nu_2 + \nu_6$, $\nu_5 + \nu_6$, $\nu_3 + \nu_4$, and $\nu_1 + \nu_5$, which are symmetry-allowed because of intermode couplings. These results suggest that the model adequately accounts for vibrational-state mixing while capturing intricate resonant interactions within high-symmetry frameworks. Such couplings are embedded in the algebraic formulation via the symmetry-adapted coefficients of the Majorana interaction terms, which preserve the full molecular character in multi-mode transitions. Fig. 4 depicts the model's ability to predict overtones, showing first-, second-, and third-overtone spectra for different modes. The deviations from exact integer multiples of the fundamental frequency reveal the significance of anharmonicity for higher levels of vibrational states, where the potential energy surface is increasingly anharmonic. This thoroughness in predicting overtones is appreciated in the field. These deviations can be accurately accounted for by applying Majorana operators, which capture nonlinear shifts in energy and the coupling between different vibrational quanta. However, as previously indicated, the algebraic approach offers greater benefits than traditional techniques based on the Schrödinger equation.

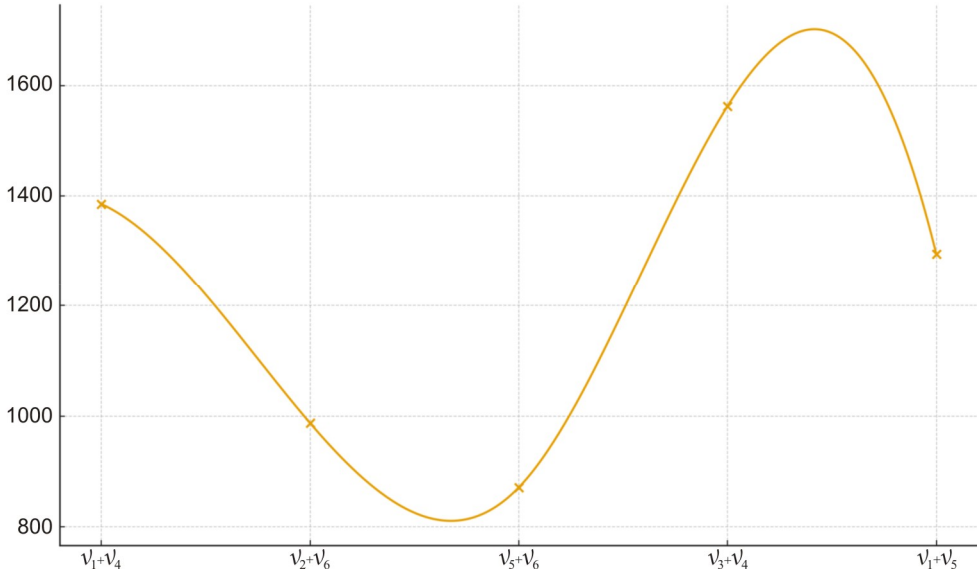


**Fig. 3.** Calculated combination band frequencies of $SF_6$ using the U(2) Lie algebraic model.

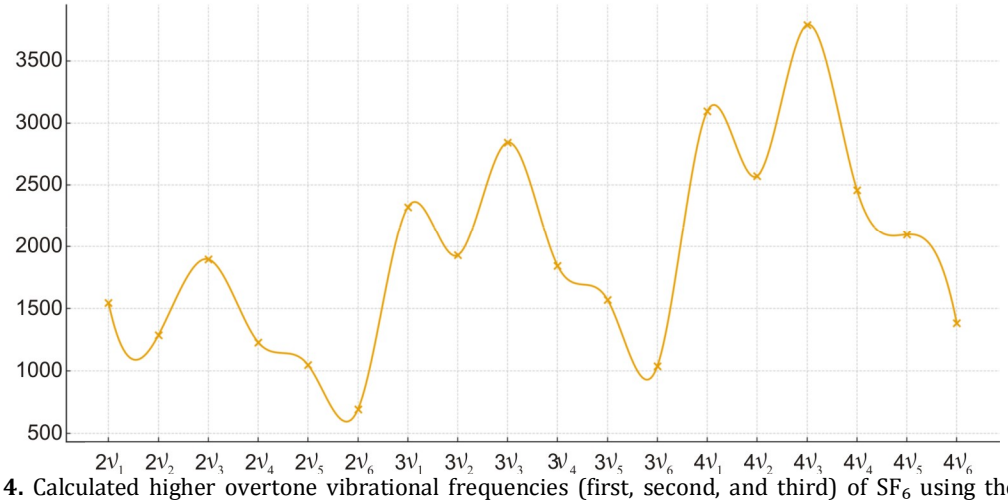


**Fig. 4.** Calculated higher overtone vibrational frequencies (first, second, and third) of $SF_6$ using the U(2) Lie algebraic model.

The consequences of this investigation are striking. For $SF_6$, accurate determination of vibrational frequencies is paramount for spectroscopic diagnostics in atmospheric and environmental physics, where $SF_6$ is used as a tracer gas and monitored as a greenhouse gas. Its intense IR-active modes, $\nu_3$ and $\nu_4$ ($F_{1u}$), contribute substantially to radiative forcing, and their precise modelling enables improved detection and remote sensing [32]. Also, the accuracy achieved with this algebraic method enables extending the application to other high-symmetry greenhouse gases, such as $CF_4$, and even to some perfluorinated compounds with similar vibrations.

## 4. Conclusions

This study presents a symmetry-adapted Lie-algebraic technique for modelling the vibrational spectra of $SF_6$, an octahedral molecule of environmental and industrial importance. By constructing the U(2) Lie algebraic framework vibrational Hamiltonian and including Casimir and Majorana operators, the model captures the harmonic and anharmonic contributions to the vibrational structure while maintaining molecular symmetry under the $O_h$ point group.

Vibrational frequencies calculated in the model, including fundamental modes, overtones up to third order, and several combination bands, show strong agreement with experimental spectroscopic data, with root-mean-square deviations near or below 1 $cm^{-1}$ across multiple reference datasets. Significantly, the model captures weakly allowed and spectrally active modes, the $F_{2u}$ mode ($\nu_6$), by higher-order interaction terms. The technique detailed in this study is not only beneficial for $SF_6$ but also has the potential to be applied to other high-symmetry polyatomic molecules, such as $CF_4$ and perfluorocarbons.

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**Data Availability.** The author declares that the data supporting the findings of this study are available within the paper.

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***Анотація.*** *В роботі досліджені коливальні моди гексафториду сірки ($SF_6$) за допомогою симетрично адаптованого алгебраїчного підходу Лі U(2). У контексті симетрії точкової групи $O_h$, гамільтоніан, сформований за допомогою операторів Казиміра та Майорани, включає ангармонізм та міжмодовий зв'язок. Фундаментальні моди демонструють високий рівень точності, зі середньоквадратичними відхиленнями менше одного $см^{-1}$, що відмінно узгоджується з експериментальними значеннями. Модель також прогнозує розташування комбінаційних смуг та обертонів, щоб*

*додатково продемонструвати її можливості. Цей метод робить значний внесок у спектроскопічні дослідження атмосферної науки, на відміну від традиційних підходів до моделювання поліатомних молекул з високою симетрією.*

***Ключові слова:*** *гексафторид сірки, коливальні моди, гамільтоніан, оператори Казиміра та Майорани*