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LIE ALGEBRAIC HAMILTONIAN APPROACH TO THE VIBRATIONAL SPECTRA OF XENON TETRAFLUORIDE

AMAL S. ALALI [1], VIJAYASEKHAR JALIPARTHI [2*]

[1] Department of Mathematical Sciences, College of Science, Princess Nourah bint Abdulrahman University, P.O. Box 84428, Riyadh 11671, Saudi Arabia.
[2] Department of Mathematics and Statistics, School of Science, GITAM (Deemed to be University), Hyderabad, India.
* Corresponding author: vijayjaliparthi@gmail.com

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Abstract. Xenon tetrafluoride (XeF_4), a square-planar molecule with the D4h point group, exhibits complex vibrational properties owing to anharmonicity, vibrational coupling, and symmetry-induced degeneracies. In the current study, its vibrational spectra were viewed with a symmetry-adapted U(2) Lie algebraic perspective. The vibrational frequencies of molecular vibrations are defined by the coupled local anharmonic oscillators related to the Xe–F stretching and the F–Xe–F bending modes. A symmetry-specific vibrational Hamiltonian is derived using Casimir and Majorana operators to account for anharmonic effects, bond interactions, and vibron-exchange processes that preserve the molecular symmetry D_{4h}. The Hamiltonian matrix is defined in a local basis and diagonalized to yield vibrational eigenvalues for fundamental, first, and second overtone vibrations. The predicted vibrational frequencies fit the observed values rather well, thereby validating the proposed model. The XeF_4 study findings detail vibrational delocalization, anharmonic corrections, and symmetry-induced splitting. The results indicate that the symmetry-adapted U(2) Lie algebraic framework serves as an effective tool for providing a reasonable description of the vibrational spectra of highly symmetric polyatomic molecules, while preserving the essential symmetry properties and anharmonic characteristics of the system.

Keywords: Lie Algebraic Approach, vibrational Spectra, Xenon Tetrafluoride, symmetry-adapted Hamiltonian, Casimir and Majorana operators
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1. Introduction

One of the widely known methods for assessing the structural, dynamic, and electronic properties of molecular systems at scale and across the spectrum of vibrations is vibrational spectroscopy [1]. Its work is based on the interaction between electromagnetic radiation and molecular vibrations, as observed through processes such as infrared (IR) absorption and Raman scattering, which provide complementary information about changes in molecular dipole moment and polarizability [1]. The vibrational frequencies are extremely sensitive to molecular geometry, chemical bonding, and intermolecular interactions; therefore, vibrational spectroscopy has become a versatile tool for the characterization of molecular structure and dynamics in chemical, biological, materials, and astrophysical systems [2]. Ongoing improvements in experimental equipment and theoretical approach have significantly enhanced the precision and interpretation of vibrational spectra [3,4]. The vibrational spectra of molecules are theoretically described within the framework of quantum mechanics, where the vibrational energy levels and corresponding spectra are obtained by solving the molecular Schrödinger equation. For example, the analysis of polyatomic molecules is typically impractical because exact analytical solutions are not available; instead, approximate and

numerical methods based on potential energy surfaces and variational techniques are required [5]. Symmetry-adapted formulations and analytic models of vibrational wavefunctions are particularly interesting in these systems for simplifying and improving computational efficiency [6]. Various theoretical methods for calculating vibrational frequencies (including harmonic-oscillator-based models, Dunham expansions, and quantum-chemical approaches) have been established. Density functional theory is one of them, as it offers a good trade-off between computational cost and accuracy [7]. Moreover, anharmonic corrections, including second-order vibrational perturbation theory, provide good agreement between theoretical and experimental spectra, especially for terms involving overtones, combination bands, and resonance interactions [8]. Nonetheless, the precise treatment of anharmonicity remains a significant challenge in computational spectroscopy due to its strong impact on vibrational frequencies, intensities, and temperature-dependent spectral features [9]. Lie groups and Lie algebras are mathematical structures used to describe symmetry in quantum systems and to study different classes of molecules in molecular spectroscopy techniques [10]. Their generators and commutation relations also characterize physical observables and symmetry operations for molecular dynamics [11,12]. In spectroscopy, Lie algebraic methods reduce quantum-mechanical problems to algebraic equations for eigenvalues by utilizing symmetry-adapted Hamiltonians [13]. These methods also facilitate the computation of vibrational spectra, eigenvalues, and transition amplitudes while preserving molecular symmetry properties [11]. Unitary pairwise structures, such as U(4), are well-known algebraic models in molecular spectroscopy for efficient estimation compared to direct coordinate-space solves of the Schrödinger equation [14]. They characterize molecular vibrations using bosonic operators and symmetry-adapted basis states to obtain a systematic account of anharmonicity and intermode coupling [15]. The algebraic principles of molecular dynamics, as developed by Iachello and Levine, relate distinct dynamical symmetry limits to harmonic, anharmonic, local, and normal vibrational configurations, thereby offering a comprehensive, unified framework for describing molecular dynamics [16]. Moreover, algebraic Hamiltonians based on Casimir and Majorana operators, which have efficient representations of stretching, bending, and coupling interactions with a smaller space, as they preserve their symmetry in a molecular geometry [17]. These techniques help reduce the difficulties of learning complex polyatomic systems and enable their study and comparison with the visible spectra of their vibrational transitions. The Lie algebra approach has been proposed as an excellent computational method for analyzing vibrational spectra using the data available for modeling polyatomic and highly symmetric molecules. Symmetry-adapted U(2) Lie algebraic formulations with interacting Morse oscillators have proven to suit tetrahedral silane-type molecules such as SiH_4, SiF_4, and $SiCl_4$, with accurate prediction of vibrational frequencies and higher overtones [18]. The same techniques were implemented for triatomic molecules such as SiH_2, SiF_2, and $SiCl_2$ [19], and for larger molecular systems such as cyclohexane and naphthalene, where they efficiently capture anharmonicity and intermode coupling effects [20, 21]. More recent theoretical advances prove the applicability of algebraic methods to multi-dimensional

2. Molecular Structure and Vibrational Characteristics of XeF_4

XeF_4 is a prototypical noble-gas compound that has attracted considerable attention owing to its highly symmetric molecular structure and distinctive vibrational properties. Infrared and Raman spectroscopic studies, diffraction measurements, and ab initio calculations have

established that XeF_4 possesses a square-planar geometry belonging to the D_{4h} point group [26,27]. Its high symmetry plays a crucial role in determining vibrational mode classifications, degeneracy patterns, and spectroscopic selection rules. Consequently, XeF_4 provides an excellent model system for investigating the influence of molecular symmetry on vibrational dynamics and spectroscopic behaviour. In this group theoretical analysis, the nine normal vibrational modes of XeF_4 are classified into irreducible A_{1g}, A_{2u}, B_{1g}, B_{2g}, B_{2u} and E_u in the D_{4h} point group [28], where E_u modes are doubly degenerate. The symmetric stretching vibration is wholly assigned to the A_{1g} species, but the remaining stretching and bending modes are distributed on B-type and E-type representations [26]. Because of inversion symmetry, XeF_4 follows the mutual exclusion rule, where the gerade modes are Raman active, and the ungerade modes are infrared active [29]. The experimental work indicated strong infrared bands at 123 cm^{-1}, 291 cm^{-1}, and 586 cm^{-1}, along with Raman bands in the 502–543 cm^{-1} interval, attributed to bending and stretching vibrations [26]. Infrared and Raman studies in conjunction with force constant measurements indicate the importance of bonding interactions and vibrational coupling [30]. High-resolution spectroscopy and calculations using advanced quantum-chemical methods further showed agreement between theoretical predictions and observed vibrational frequencies [27]. At condensed phases, weak intermolecular interactions marginally modify the structure without completely altering the principal vibrational features of the molecule [31]. The electronic transitions of XeF_4 can be observed in the far-ultraviolet region, providing insights into its electronic structure and demonstrating ligand-field properties, as well as spin–orbit coupling [32]. The high symmetry and well-characterised vibrational spectrum of XeF_4 make it an appropriate system for assessing theoretical approaches to molecular vibrations. Its D_{4h} symmetry and distinct vibrational features provide a suitable framework for investigating the applicability of symmetry-adapted algebraic methods to highly symmetric polyatomic molecules. In the present study, the vibrational spectra of XeF_4 are analysed within a U(2) Lie algebraic framework. Based on the bond-indexing scheme and interaction topology used to construct the vibrational Hamiltonian, Figure 1 depicts the square-planar structure of XeF_4 and the interactions considered in the model. By equilibrium geometry, XeF_4 belongs to the D_{4h} point group, where the xenon atom is symmetrically coordinated by four fluorine atoms located in the same plane. F–Xe–F bond angles are 90° between adjacent bonds and 180° between opposite bonds. Each of the four equivalent Xe–F bonds are labelled 1 (top), 2 (left), 3 (right), and 4 (bottom), which can serve as a systematic basis for defining bond interactions. XeF_4 vibration properties are defined in terms of stretching and bending interactions, categorised based on their geometric structure. The neighbouring stretching interactions exist between bond pairs separated by 90°, (1–2), (2–4), (4–3), and (3–1), while the opposite stretching interactions are between bond pairs separated by 180°, (1–4), (2–3). Adjacent interactions characterise local couplings between neighbours, and opposite interactions represent long-range correlations that provide important information for symmetric and antisymmetric stretching vibrations. Angular deformations of the F–Xe–F bond angles give rise to bending interactions. The adjacent bending interactions are due to the 90° bond-angle changes, and the opposite one in the bond pair (1–4) and (2–3) on the other side in the same direction is related to oscillatory relationships between the bonds, which result in vibrational coupling and symmetry-dependent vibrations. While all four

Xe–F bonds comply with D_{4h} symmetry, distinguishing them from each other and vice versa is crucial for generating symmetry-based vibrational Hamiltonians. Such classification is foundational to establishing Casimir and Majorana interaction operators in the U(2) Lie algebraic model, allowing for an efficient and physical modelling of stretching and bending vibrations in XeF_4.

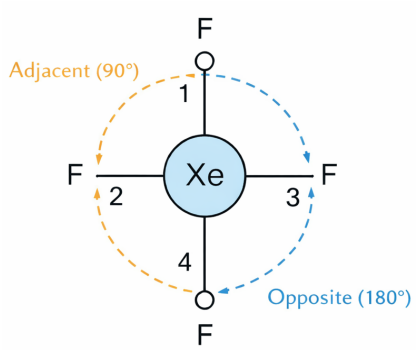

Fig. 1. Bond indexing with adjacent and opposite interactions in XeF_4.

3. Lie algebraic framework for the vibrational spectra of XeF_4

The vibrational structure of XeF_4 is analyzed by a U(2) Lie algebraic representation, making it possible to describe anharmonic oscillations in polyatomic molecules. Under this method, molecular vibrations are manifested as interacting local oscillators rather than as harmonic normal modes, so it is most appropriate for the spectra of XeF_4, in which the effects of anharmonicity, vibrational coupling, and symmetry-induced splitting are highly influential. The shape of XeF_4 is square planar, formed within the D_{4h} point group, and the four equivalent Xe–F bonds are symmetrically positioned around the central xenon atom. For this reason, the vibrational Hamiltonian must preserve D_{4h} molecular symmetry while incorporating local anharmonicity, interbond coupling, vibron exchange interactions, and vibrational delocalization. These effects are naturally captured in the Lie algebraic vibron model via Casimir and Majorana operators. The total vibrational Hamiltonian is separated into stretching and bending contributions according to $H = H^{(\mathrm{str})} + H^{(\mathrm{bend})}$, where $H^{(\mathrm{str})}$ describes the radial Xe–F stretching vibrations, and $H^{(\mathrm{bend})}$ describes the angular bending vibrations associated with the F–Xe–F bond angles. Each Xe–F bond is treated as an independent local anharmonic oscillator associated with a U(2) algebra. Therefore, the total dynamical algebra for the stretching sector becomes $U_1(2) \otimes U_2(2) \otimes U_3(2) \otimes U_4(2)$. The local stretching basis states are represented as $|v_1, v_2, v_3, v_4\rangle$, where v_i denotes the number of vibrational quanta (vibrons) associated with the i^{th} Xe–F bond. For the fundamental stretching polyad, $v_1 + v_2 + v_3 + v_4 = 1$, which generates the four basis states $|1000\rangle, |0100\rangle, |0010\rangle, |0001\rangle$. These basis states correspond to the vibrational excitation being localized on bonds 1, 2, 3, and 4, respectively. Since four basis states are obtained, the stretching Hamiltonian is represented by a 4×4 matrix. Because XeF_4 possesses square-planar symmetry, the interactions between the bonds separate naturally into two geometrically distinct classes: adjacent interactions, (1,2), (2,4), (3,4), (1,3), and opposite interactions, (1,4), (2,3). This distinction is physically important because adjacent and opposite bonds experience different interaction strengths due to their geometrical orientations.

Accordingly, the stretching Hamiltonian is written as

$$H^{(\mathrm{str})} = E_0^{(\mathrm{str})} + A^{(\mathrm{str})}\left(C_1+C_2+C_3+C_4\right) + A_1^{(\mathrm{str})}\left(C_{12}+C_{13}+C_{24}+C_{34}\right) + A_2^{(\mathrm{str})}\left(C_{14}+C_{23}\right) + \lambda_1^{(\mathrm{str})}\left(M_{12}+M_{13}+M_{24}+M_{34}\right) + \lambda_2^{(\mathrm{str})}\left(M_{14}+M_{23}\right). \quad (1)$$

In this Hamiltonian, $E_0^{(\mathrm{str})}$ represents the zero-point stretching energy, C_i are the single-mode Casimir operators, C_{ij} are the two-body Casimir interaction operators, and M_{ij} are the Majorana interaction operators. The parameter $A^{(\mathrm{str})}$ represents the local anharmonic stretching strength of an individual Xe–F bond. Physically, this parameter determinethe intrinsic vibrational energy associated with a single local oscillator. The parameters $A_1^{(\mathrm{str})}$, $A_2^{(\mathrm{str})}$ represent anharmonic interaction strengths between coupled Xe–F bonds. Specifically, $A_1^{(\mathrm{str})}$ corresponds to adjacent bond interactions, and $A_2^{(\mathrm{str})}$ corresponds to opposite bond interactions. These parameters arise from the two-body Casimir operators and capture interbond anharmonic correlations. The parameters, $A_1^{(\mathrm{str})}$, $A_2^{(\mathrm{str})}$ represent vibron exchange interaction strengths generated by the Majorana operators. Physically, $A_1^{(\mathrm{str})}$ controls vibron transfer between adjacent bonds, $A_2^{(\mathrm{str})}$ controls vibron transfer between opposite bonds. These parameters govern vibrational delocalization and the splitting between symmetric and antisymmetric vibrational modes.

The diagonal matrix elements of the single-mode Casimir operators are given by

$$\langle C_i \rangle = -4\left(N_i v_i - v_i^2\right), \quad (2)$$

where, N_i is the vibron number associated with the i^{th} oscillator, v_i is the local vibrational quantum number.

The vibron number N_i determines the dimension of the algebraic representation and controls the anharmonicity of the oscillator. Since all Xe–F bonds are equivalent, $N_i = N$. For the basis state $|1000\rangle$, the first oscillator is excited while the remaining oscillators remain unexcited: $v_1 = 1, v_2 = v_3 = v_4 = 0$. The Casimir expression gives $\langle C_1 \rangle = -4(N-1)$, while the remaining oscillators contribute zero. Therefore, the diagonal contribution arising from the single-mode Casimir operators becomes $D_{C_i} = -4A^{(\mathrm{str})}(N-1)$. This contribution represents the intrinsic local anharmonic vibrational energy of the excited Xe–F bond.

The two-body Casimir operator matrix elements are defined by

$$\langle C_{ij} \rangle = 4\left[(v_i + v_j)^2 - \left(v_i + v_j\right)\left(N_i + N_j\right)\right]. \quad (3)$$

For the interacting pair $(1,2)$, $v_1 = 1, v_2 = 0$, which gives $v_1 + v_2 = 1$, and $N_1 = N_2 = N$ The two-body Casimir expression gives $\langle C_{12} \rangle = 4(1-2N)$.

For the state $|1000\rangle$, the excited oscillator interacts with two adjacent bonds and one opposite bond. Therefore, the total two-body Casimir contribution becomes

$$D_{C_{ij}} = 8A_1^{(\mathrm{str})}\left(1-2N\right) + 4A_2^{(\mathrm{str})}\left(1-2N\right). \quad (4)$$

This term represents anharmonic interbond coupling energy arising from interactions between neighboring stretching oscillators.

The diagonal matrix elements of the Majorana operators are expressed as

$$\langle M_{ij} \rangle = N_i v_j + N_j v_i - 2v_i v_j. \quad (5)$$

For identical oscillators, $\langle M_{ij} \rangle = N\left(v_i + v_j\right) - 2v_i v_j$. For the state $|1000\rangle$, $\langle M_{12} \rangle = N$, $\langle M_{14} \rangle = N$, $\langle M_{13} \rangle = N$.

Among these terms, two correspond to adjacent interactions, and one corresponds to an opposite interaction. Consequently, the total diagonal Majorana contribution becomes

$$D_M = 2\lambda_1^{(\mathrm{str})}N + \lambda_2^{(\mathrm{str})}N. \tag{6}$$

This contribution represents vibrational coupling produced by vibron exchange between local oscillators.

The Majorana operators also generate off-diagonal matrix elements responsible for vibrational energy transfer between bonds. The general off-diagonal matrix element is given by

$$\langle v_i+1, v_j-1 \,|\, M_{ij} \,|\, v_i, v_j \rangle = -\sqrt{v_j(v_i+1)(N_i-v_i)(N_j-v_j+1)}. \tag{7}$$

Consider the transition $|1000\rangle \to |0100\rangle$, $v_i = 0, v_j = 1,$ gives

$\langle 0100|M_{12}|1000\rangle = -\sqrt{1\times 1\times N\times N} = -N.$ Therefore, $H_{12} = -\lambda_1^{(\mathrm{str})}N.$

Similarly, for opposite interactions, $H_{13} = -\lambda_2^{(\mathrm{str})}N.$

Defining $\beta_1 = -\lambda_1^{(\mathrm{str})}N, \text{and} \beta_2 = -\lambda_2^{(\mathrm{str})}N,$ the total diagonal matrix element becomes

$$D = -4A^{(\mathrm{str})}(N-1) + +8A_1^{(\mathrm{str})}(1-2N) + 4A_2^{(\mathrm{str})}(1-2N) + 2\lambda_1^{(\mathrm{str})}N + \lambda_2^{(\mathrm{str})}N. \tag{8}$$

Using the ordered basis $|1000\rangle, |0100\rangle, |0010\rangle, |0001\rangle,$ the stretching Hamiltonian matrix becomes

$$H^{(\mathrm{str})} = \begin{pmatrix} D & \beta_1 & \beta_2 & \beta_1 \\ \beta_1 & D & \beta_1 & \beta_2 \\ \beta_2 & \beta_1 & D & \beta_1 \\ \beta_1 & \beta_2 & \beta_1 & D \end{pmatrix}. \tag{9}$$

The diagonal elements contain local anharmonic energies and interaction corrections, whereas the off-diagonal elements represent vibron exchange interactions responsible for vibrational mixing and symmetry-induced mode splitting.

The diagonalization of the vibrational Hamiltonian matrix yields the eigenvalues $D+2\beta_1+\beta_2, D-2\beta_1+\beta_2, D-\beta_2,$ where the last eigenvalue is doubly degenerate. These eigenvalues correspond to the vibrational frequencies of the molecule. The degeneracy arises from the symmetry of the molecular structure, leading to two vibrational modes possessing identical energies.

The bending vibrations are described using the angular coordinates $\theta_{ij} = \angle(F_i - \mathrm{Xe} - F_j),$ which generates six independent bending coordinates:

$$\theta_{12}, \theta_{13}, \theta_{14}, \theta_{23}, \theta_{24}, \theta_{34}.$$

The bending Hamiltonian incorporates local angular anharmonicity, angular interaction terms, and bending vibron exchange interactions.

$$\begin{aligned} H^{(\mathrm{bend})} = {} & E_0^{(\mathrm{bend})} + A^{(\mathrm{bend})}\left[C(\theta_{12}) + C(\theta_{13}) + C(\theta_{14}) + C(\theta_{23}) + C(\theta_{24}) + C(\theta_{34})\right] \\ & + A'^{(\mathrm{bend})}\begin{bmatrix} C(\theta_{12},\theta_{13}) + C(\theta_{12},\theta_{14}) + C(\theta_{12},\theta_{23}) + C(\theta_{12},\theta_{24}) + C(\theta_{12},\theta_{34}) \\ + C(\theta_{13},\theta_{14}) + C(\theta_{13},\theta_{23}) + C(\theta_{13},\theta_{24}) + C(\theta_{13},\theta_{34}) + C(\theta_{14},\theta_{23}) \\ + C(\theta_{14},\theta_{24}) + C(\theta_{14},\theta_{34}) + C(\theta_{23},\theta_{24}) + C(\theta_{23},\theta_{34}) + C(\theta_{24},\theta_{34}) \end{bmatrix} \\ & + \lambda_1^{(\mathrm{bend})}[M(\theta_{12},\theta_{24}) + M(\theta_{24},\theta_{34}) + M(\theta_{34},\theta_{13}) + M(\theta_{13},\theta_{12})] + \lambda_2^{(\mathrm{bend})} M(\theta_{14},\theta_{23}). \end{aligned} \tag{10}$$

Here, $E_0^{(\mathrm{bend})}$ denotes the zero-point energy associated with the bending vibrational manifold. The operator $C(\theta_{ij})$ represents the single-mode Casimir operator, which accounts for the anharmonic contribution of an individual bending coordinate θ_{ij}. The two-body Casimir operator $C(\theta_{ij}, \theta_{kl})$ describes the anharmonic correlations between different bending coordinates, while the Majorana operator $M(\theta_{ij}, \theta_{kl})$ characterizes vibron exchange interactions and mode mixing between angular oscillators. The parameter $A^{(\mathrm{bend})}$ quantifies the intrinsic anharmonicity of each bending oscillator, whereas $A'^{(\mathrm{bend})}$ represents the coupling strength between distinct bending coordinates. The parameters $\lambda_1^{(\mathrm{bend})}$ and $\lambda_2^{(\mathrm{bend})}$ correspond to the Majorana interaction strengths associated with adjacent and opposite bending oscillators, respectively, and govern the transfer of vibrational quanta within the bending vibrational network. Together, these parameters define the anharmonic structure and intermode coupling effects of the bending vibrations within the symmetry-adapted Lie algebraic framework.

As with stretching vibrations, the vibrational Hamiltonian for bending vibrations also has the same algebraic form. The Hamiltonian is constructed using the U(2) Lie algebra generators involving Casimir and Majorana operators. As bending interactions and force constants differ for bending modes compared to stretching modes, the Hamiltonian parameters associated with them differ. Hence, while the Hamiltonian's mathematical structure remains unchanged, separate parameter sets are used for stretching and bending vibrations to reproduce the molecule's corresponding vibrational frequencies.

The vibron number N, which determines the dimension of the algebraic basis and the degree of anharmonicity in the Lie algebraic $U(2)$ vibron model, is obtained from the spectroscopic constants using the relation

$$N = \left[\omega_e / \omega_e x_e\right] - 1, \tag{10}$$

where ω_e represents the harmonic vibrational frequency and $\omega_e x_e$ denotes the anharmonicity constant. These spectroscopic constants are extracted from the experimentally observed infrared and Raman vibrational spectra of XeF_4 using standard spectroscopic analysis procedures. The harmonic vibrational frequency ω_e is determined from the observed fundamental vibrational bands, whereas the anharmonicity constant $\omega_e x_e$ is evaluated from the deviation of overtone frequencies from exact harmonic behavior using the Morse oscillator approximation. Thus, the parameter N defines the finite size of the vibron space and reflects the anharmonic character of the molecular vibrational dynamics.

The local anharmonic parameters are initially estimated using

$$A^{(\mathrm{str})} = -\frac{E^{(\mathrm{str})}}{4\left(N^{(\mathrm{str})} - 1\right)}, \text{ and } A^{(\mathrm{bend})} = -\frac{E^{(\mathrm{bend})}}{4\left(N^{(\mathrm{bend})} - 1\right)}. \tag{11}$$

Here, $E^{(\mathrm{str})}$ denotes the experimental fundamental stretching vibrational energy, and $E^{(\mathrm{bend})}$ denotes the experimental fundamental bending vibrational energy.

The Majorana interaction parameters are estimated from the experimentally observed splitting between symmetric and antisymmetric vibrational modes:

$$\lambda_i^{(\mathrm{str})} = \frac{\left| E_s^{(\mathrm{str})} - E_{as}^{(\mathrm{str})} \right|}{k_i^{(\mathrm{str})} N^{(\mathrm{str})}}, i = 1,2, \text{ and } \lambda_i^{(\mathrm{bend})} = \frac{\left| E_s^{(\mathrm{bend})} - E_{as}^{(\mathrm{bend})} \right|}{k_i^{(\mathrm{bend})} N^{(\mathrm{bend})}}, i = 1,2. \tag{12}$$

In these expressions, $E_s^{(\mathrm{str})}$ is the symmetric stretching vibrational energy, $E_{as}^{(\mathrm{str})}$ is the antisymmetric stretching vibrational energy, $E_s^{(\mathrm{bend})}$ is the symmetric bending vibrational energy, $E_{as}^{(\mathrm{bend})}$ is the antisymmetric bending vibrational energy, k_i represents the geometrical multiplicity factor associated with the interaction topology. Here, $k_1 = 4, k_2 = 2$, corresponding to adjacent and opposite interactions, respectively.

The vibrational frequencies of XeF_4 are determined using least-squares fitting, allowing all Hamiltonian parameters to be optimized. The U(2) Lie algebraic Hamiltonian we generate is also highly rigorous and physically meaningful in terms of the vibrational structure of the molecule due to the inclusion of anharmonicity, local mode interactions, vibron exchange mechanisms, vibrational delocalization, and the splitting of degenerate vibrational states. The coupling of stretching and bending dynamics of XeF_4 is successfully described accurately by a compact algebraic model.

4. Results and discussion

With a symmetry-adapted U(2) Lie algebraic framework incorporating stretching and bending vibrational interactions, the vibrational spectra of XeF_4 were explored. The vibrational Hamiltonian was constructed using Casimir and Majorana operators to account for local anharmonicity, neighboring- and opposite-bond interactions, vibron-exchange processes, and symmetry-adapted mode splitting, while preserving the D_{4h} molecular symmetry. The optimized Hamiltonian parameters derived through least-squares fitting are shown in Table 1. The stretching and bending vibrational numbers were 158 and 36, respectively, revealing additional anharmonic signatures related to radial and angular vibrations. The computed and observed frequencies are compared in Table 2. The calculated frequencies are reasonably close to the observed data and reproduce the vibrational-state symmetry ordering. The model successfully describes the Raman-active A_{1g} and B_{1g} stretching modes, the infrared-active A_{2u} and E_u modes, and the bending vibration B_{2u}.

Table 1. Optimized fitting parameters (all are in cm^{-1}, except N) for the Lie algebraic vibrational Hamiltonian.

Parameter	Type	Physical Meaning	Value
$N^{(\mathrm{str})}$	Stretching	Stretching vibron number	158
$A^{(\mathrm{str})}$	Stretching	Single-mode stretching Casimir parameter	-0.804 cm^{-1}
$A_1^{(\mathrm{str})}$	Stretching	Adjacent stretching interaction	-0.020 cm^{-1}
$A_2^{(\mathrm{str})}$	Stretching	Opposite stretching interaction	-0.015 cm^{-1}
$\lambda_1^{(\mathrm{str})}$	Stretching	Adjacent Majorana coupling	0.0475 cm^{-1}
$\lambda_2^{(\mathrm{str})}$	Stretching	Opposite Majorana coupling	0.150 cm^{-1}
$N^{(\mathrm{bend})}$	Bending	Bending vibron number	36
$A^{(\mathrm{bend})}$	Bending	Single-mode bending Casimir parameter	-1.58 cm^{-1}
$A'^{(\mathrm{bend})}$	Bending	Two-body bending Casimir interaction	-0.034 cm^{-1}
$\lambda_1^{(\mathrm{bend})}$	Bending	Adjacent bending Majorana interaction	0.507 cm^{-1}
$\lambda_2^{(\mathrm{bend})}$.	Bending	Opposite bending Majorana interaction	0.792 cm^{-1}

Table 2. Experimental and calculated fundamental, first overtone, and second overtone vibrational frequencies of XeF_4 using the symmetry-adapted Lie algebraic model.

Mode	Symmetry	Fundamental Vibrational Frequencies		Overtone Frequencies	
		Observed [26, 30]	**Calculated**	**First**	**Second**
v_1	A_{1g}	554	574.20	1164.21	1751.08
v_2	A_{2u}	291	269.50	563.02	848.84
v_3	B_{1g}	524	604.24	1206.69	1803.12
v_5	B_{2u}	216	211.00	404.96	581.44
v_6	E_u	586	636.62	1252.49	1859.20

Moreover, the doubly degenerate Eu mode is reproduced by the symmetry property of the Hamiltonian, confirming the efficiency of the symmetry-adapted algebraic formulation. These first and second overtone frequencies are also calculated to demonstrate that the U(2) Lie algebraic model can describe anharmonic vibrational excitations beyond the fundamental range. The overtone frequencies differ from the harmonic multiples of the fundamental frequencies because the intrinsic anharmonicity was incorporated through Casimir interaction terms and vibron-exchange mechanisms modeled by the Majorana operators. These results illustrate that, at its extreme, the model can consistently describe fundamental and higher vibrational excitations within an algebraic framework. The deviation of the root mean square (RMS) for the vibrational modes is 44.49 cm^{-1}. This degree of agreement implies that the symmetry-adapted Lie algebraic framework can accurately describe the vibrational dynamics of XeF_4 using a small dataset with physically meaningful dimensions. The present method works well in generating fundamental and overtone frequencies, vibrational degeneracies, and the symmetry-adapted mode-splitting dynamics. After all, the outcome indicates that the symmetry-adapted U(2) Lie algebraic model is, generally, a valid, efficient, and suitable framework for performing computational calculations on analytes with anharmonic vibrational spectra of symmetric polyatomic molecules. The comparatively large deviations observed for the ν_4 and ν_7 bending modes, with calculated frequencies of 342.50 and 363.00 cm^{-1}, respectively, relative to the experimental values of 218 and 161 cm^{-1}, are attributed to the omission of higher-order anharmonic stretch-bend coupling and resonance interactions. These effects are beyond the scope of the present symmetry-adapted U(2) Lie algebraic Hamiltonian, which incorporates only the dominant Casimir and Majorana interaction terms. The inclusion of additional symmetry-allowed higher-order coupling operators is expected to further improve the quantitative agreement with the experimental spectrum.

5. Conclusions

The vibrational spectra of XeF_4 were effectively studied using a symmetry-adapted U(2) Lie algebraic model, which integrates stretching and bending vibrational interactions. Using the Casimir and Majorana operators, the vibrational Hamiltonian can effectively accommodate local anharmonicity, adjacent and opposite-bond interactions, vibron-exchange processes, and symmetry-induced mode splitting, while preserving D_{4h} molecular symmetry. Fundamental, first- and second-overtone vibrational frequencies were derived by diagonalizing the Hamiltonian matrix and compared with observed vibrational frequencies. The calculated results were consistent with the general vibrational structure, anharmonic

behavior, degeneracy patterns, and vibrational coupling features of XeF_4. The overall RMS deviation of 44.49 cm^{-1} indicates that the proposed symmetry-adapted U(2) Lie algebraic framework provides a satisfactory description of the anharmonic vibrational structure of XeF_4. The current study demonstrates that a symmetry-adapted U(2) Lie algebraic analysis approach provides a highly compact and computationally efficient algorithm for higher overtones, along with the physical relevance of anharmonic vibrational spectra.

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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. *Тетрафторид ксенону (XeF_4), квадратно-плоска молекула з точковою групою D_{4h}, демонструє складні коливальні властивості завдяки ангармонізму, коливальному зв'язку та симетрично-індукованому виродженню. У цьому дослідженні його коливальні спектри розглядалися з симетрично-адаптованої алгебраїчної перспективи U(2) Лі. Коливальні частоти молекулярних коливань визначаються зв'язаними локальними ангармонічними осциляторами, пов'язаними з розтягуванням*

Xe–F та згинальними модами F–Xe–F. Отримано специфічний для симетрії коливальний гамільтоніан з операторами Казиміра та Майорани, щоб врахувати ангармонічні ефекти, взаємодію зв'язків та процеси вібронного обміну, які зберігають молекулярну симетрію D_{4h}. Матриця гамільтоніана визначена в локальному базисі та діагоналізована для отримання власних значень фундаментальних, першого та другого обертонних коливань. Передбачені коливальні частоти досить добре узгоджуються зі спостережуваними, тим самим підтверджуючи запропоновану модель. Результати дослідження XeF_4 детально описують коливальну делокалізацію, ангармонічні корекції та симетрично індуковане розщеплення. Завершити аналіз, щоб визначити, що, використовуючи адаптовану до симетрії алгебраїчну структуру Лі U(2) для аналізу коливальних спектрів високосиметричних багатоатомних молекул, можна точно дослідити коливальні спектри цих сполук.

Ключові слова: *алгебраїчний підхід Лі, коливальні спектри, тетрафторид ксенону, адаптований до симетрії гамільтоніан, оператори Казимира та Майорани*