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Lie Algebraic Modeling of Higher Overtone Vibrational Frequencies in PCl_5 and $SbCl_5$

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ABSTRACT: The third and fourth overtone vibrational frequencies of Phosphorus Pentachloride (PCl_5) and Antimony Pentachloride ($SbCl_5$), belonging to the D_{3h} point group, have been studied using the symmetry-adapted Lie algebra technique. The vibrational Hamiltonian, incorporating Casimir and Majorana operators, provides both harmonic and anharmonic contributions, enabling the systematic calculation of higher-order vibrational excitations. The study demonstrates the effectiveness of the Lie algebraic method for modelling overtone structures of high-symmetry molecules. It elucidates the importance of vibrational analysis for PCl_5 and $SbCl_5$ in molecular spectroscopy and atmospheric chemistry.

Key Words: Phosphorus pentachloride, antimony pentachloride, D_{3h} symmetry, higher overtone frequencies, Lie algebraic method.

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1. Introduction

Determining all fundamental, as well as higher overtone vibrational frequencies, is crucial for understanding polyatomic molecules and their structure and spectroscopic characteristics. Investigating higher overtones, specifically the third and fourth, provides a deeper understanding of anharmonicity and vibrational couplings that fundamental transitions alone do not encompass. This type of research holds tremendous value, not only for spectroscopic studies on molecules but also for domains such as atmospheric chemistry, environmental science, and optical absorption [1,2]. The Dunham series expansion, as well as models for the vibrational potential energy functions, have been, and still are, among the first-order methods used for vibrational analysis. Although these methods are effective, a serious effort is needed to compare them to real-world data for parameter values that can make the methods more useful. This is especially true for molecules that exhibit high symmetry or when there is limited data available from empirical studies. This heavy reliance on a data set is a serious impediment to making calculations that extend to higher overtone areas [3,4,5,6,7,8,9]. Incorporating both harmonic and anharmonic contributions of the vibrational Hamiltonian using Casimir and Majorana operators reduces the reliance on a plethora of experimental data, while still allowing for systematic improvements to higher overtone orders. Within the past few years, the effectiveness and adaptability of the Lie Algebraic Method have been demonstrated on a range of polyatomic molecules, such as cyclobutane, cyclohexane, dichlorine monoxide, and naphthalene, by Vijayasekhar and associates, showcasing the method's effectiveness on a variety of molecular symmetries. Their findings indicate that within the framework outlined, vibrational spectra and higher overtone structures can be accurately reproduced and predicted, respectively [10,11,12,13,14,15,16,17]. In this paper, the Lie Algebraic method has been employed to compute the third and fourth overtone vibrational frequencies of PCl_5 and $SbCl_5$, both of which belong to the D_{3h} point group. The vibrational Hamiltonian, as referenced in [18], and the parameterisation utilised in this research have been provided by Amal Alali and Vijayasekhar. This work aims to provide a deeper

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insight into the overtone vibrational dynamics of high-symmetry molecules, emphasising the expansion of the algebraic method to the pentahalides, given the growing use of algebraic methods in contemporary molecular spectroscopy.

2. Lie Algebraic Hamiltonian Representation of PCl_5 and $SbCl_5$

The effective vibrational Hamiltonian for axial, equatorial, and bending modes can be expressed as [10,11,18]:
Axial bond vibrations:

$$H^{(\text{axial})} = E_0 + \sum_{i=1}^{3} A_i^{(\text{axial})} C_i + \sum_{i<j}^{3} A_{ij}^{(\text{axial})} C_{ij} + \sum_{i<j}^{3} k_{ij}\lambda_{ij}^{(\text{axial})} M_{ij} \tag{2.1}$$

Equatorial bond vibrations:

$$H^{(\text{equatorial})} = E_0 + \sum_{i=4}^{5} A_i^{(\text{equatorial})} C_i + A_{45}C_{45} + k_{45}\lambda_{ij}^{(\text{equatorial})} M_{45} \tag{2.2}$$

Axial–equatorial couplings:

$$H^{(\text{axial-equatorial})} = \sum_{i=1}^{3}\sum_{j=4}^{5}(A_{ij}C_{ij} + \lambda_{ij}M_{ij}) \tag{2.3}$$

Here, E_0 is the zero-point energy. Casimir operator for mode i is:

$$< C_i >= -4(N_i v_i - v_i^2) \tag{2.4}$$

where $N_i = \frac{w_e}{w_e \chi_e} - 1$ is the vibron number, with w_e $w_e\chi_e$ being harmonic and anharmonic constants. The parameter A_i is given by:

$$A_i = -\frac{E^{fundamental}}{A(N_i - 1)} \tag{2.5}$$

Two-mode interactions are represented by the Casimir operator:

$$\langle N_i, v_i; N_j, v_j \,|\, C_{ij} \,|\, N_i, v_i; N_j, v_j\rangle = 4(v_i + v_j)(v_i + v_j - N_i - N_j) \tag{2.6}$$

Anharmonic couplings are described by the Majorana operator M_{ij}:

$$\left.\begin{aligned}
\langle N_i, v_i; N_j, v_j \,|M_{ij}|\, N_i, v_i; N_j, v_j\rangle &= v_iN_j + v_jN_i - 2v_iv_j \\
\langle N_i, v_i+1; N_j, v_j-1 \,|M_{ij}|\, N_i, v_i; N_j, v_j\rangle &= -[v_j(v_i+1)(N_i - v_i)(N_j - v_j + 1]^{1/2} \\
\langle N_i, v_i-1; N_j, v_j+1 \,|M_{ij}|\, N_i, v_i; N_j, v_j\rangle &= -[v_i(v_j+1)(N_j - v_j)(N_i - v_i + 1]^{1/2}
\end{aligned}\right\} \tag{2.7}$$

with coupling strength:

$$\lambda_{ij} = \frac{|E_s - E_{as}|}{mN} \tag{2.8}$$

The bending Hamiltonian is expressed as:

$$H^{(\text{bend})} = \sum_k b_k\,\theta_k + \sum_{k<l} b_{kl}\,g_{kl} \tag{2.9}$$

where b_k and b_{kl} represent single-mode and coupling contributions. All parameters $(A_i, A_{ij}, b_k, b_{kl}, \lambda_{ij})$ are optimized through least-squares fitting with experimental data.

3. Results and Discussions

Utilising the algebraic technique, the vibrational overtone spectra of PCl_5 and $SbCl_5$ were examined with a focus on the estimation of frequencies of the third and fourth overtone. For PCl_5, the symmetric stretch of the PCl_3 unit (v_1) was seen at the third overtone 1573.39 cm^{-1}, and voila, it shifts at the fourth overtone to 1995.33cm^{-1}. PCl_2 symmetric stretch (v_2) was seen at 1472.94 cm^{-1} and 1867.05 cm^{-1}, respectively. PCl_2 unit asymmetric stretching vibration (v_3) was seen at the third overtone 1854.65 cm^{-1} and the fourth overtone 2354.53 cm^{-1}. Deformation out of the plane of the PCl_3 group (v_4) was calculated at 1201.36 cm^{-1} and 1534.29 cm^{-1}. Among the vibrational modes, the highest frequency values were seen on the degenerate stretch of PCl_3 (v_5), attaining 2364.92 cm^{-1} and 3006.22 cm^{-1} at the third and fourth overtones, respectively. Degenerate deformation mode (v_6) was seen at 1096.89 cm^{-1} and 1400.88 cm^{-1}, while bending vibration frequencies were relatively lower. Thus, v_7 was predicted at 400.68 cm^{-1} and 510.58 cm^{-1} and v_8 at 1048.68 cm^{-1} and 1339.30 cm^{-1}. These findings suggest that the overtone progression in PCl_5 is anharmonically shifted. Stretching modes of the overtone, however, were retained over the bending and deformation modes in the lower frequency region. In the case of $SbCl_5$, the overtones followed a similar distribution, although the frequencies were lower owing to the more massive center atom and the greater lengths of the Sb–Cl bonds. For the $SbCl_3$ symmetric stretch (v_1), the third and fourth overtones were recorded at 1329.75 cm^{-1} and 1645.06 cm^{-1}, while for the $SbCl_2$ symmetric stretch (v_2), the values were calculated at 1143.51 cm^{-1} and 1414.66 cm^{-1}. The asymmetric stretching vibration of $SbCl_2$ (v_3) was recorded at 1416.64 cm^{-1} and 1737.89 cm^{-1}, whereas the $SbCl_3$ out-of-plane deformation (v_4) was located at 573.62 cm^{-1} and 709.63 cm^{-1}. For the degenerate stretching vibration of $SbCl_3$ (v_5), the values were predicted at 1478.37 cm^{-1} and 1824.51 cm^{-1}, and for the degenerate deformation (v_6), the values were 659.29 cm^{-1} and 815.62 cm^{-1}. The bending modes were much lower in frequency, with v_7 at 268.19 cm^{-1} and 331.78 cm^{-1} and v_8 at 614.59 cm^{-1} and 760.32 cm^{-1} for the third and fourth overtones, respectively. These results indicate that the overtone bands of $SbCl_5$ have a greater red shift than those of PCl_5, showing the mass of Sb compared to P, and the overtone transitions' structure and bonding sensitivity. Thus, the predictive capacity of the Lie algebraic method in overdescribing high-order vibrational excitations has been corroborated through a systematic analysis conducted on the third and fourth overtones. The predominance of stretching and bending modes, along with their respective energetic scales and the expected anharmonic behaviour, also helps to separate the vibrational energy scales clearly. These results enhance the vibrational characterisation of both PCl_5 and $SbCl_5$, and also strengthen the foundation for applying the same methodology to other systems consisting of pentahalides.

4. Conclusions

Using a symmetry-adapted Lie-algebraic approach, the third and fourth overtone vibrational frequencies of PCl_5 and $SbCl_5$, which belong to the D_{3h} point group, were computed in this work. Constructed with the vibrational Hamiltonian in the form of Casimir and Majorana operators, the overtones balance the anharmonic and harmonic interactions, allowing for the precise prediction of higher-order overtones without the need for extensive fitting to experimental data. The findings support the notion that stretching vibrations always reside in the higher frequency domain, while bending and deformation modes are confined to the lower frequency domain. The systematic third and fourth overtone bands, with their progression, illustrate the anharmonic character of the vibrational spectra, which the Lie-algebraic method captures well. The work demonstrates the use of the algebraic method for polyatomic vibrational analyses, extending to higher overtones, for molecules PCl_5 and $SbCl_5$. The study correlates with the vibrational structure and energy distribution of the molecules, enhancing the available literature.

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