

## VIBRATIONAL FREQUENCIES OF PHOSPHORUS TRICHLORIDE WITH THE VIBRATIONAL HAMILTONIAN

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This study presents an approach for precisely determining the stretching vibrational frequencies of the P-Cl bond in phosphorus trichloride (PCl<sub>3</sub>) using a vibrational Hamiltonian framework that maintains the C<sub>3v</sub> symmetry point group. Our methodology enables the accurate prediction of vibrational frequencies up to the fifth overtone. It identifies related combination bands, marking a significant advancement in vibrational spectroscopy and molecular modelling. By enhancing the accuracy and depth of our understanding of molecular vibrations, this research paves the way for developing more sophisticated computational models, thereby significantly improving the precision of chemical analyses, and contributing to the broader field of chemical physics.

**Key words:** Molecular Physics; Vibrational frequencies; Phosphorus trichloride; Vibrational Hamiltonian; Lie algebraic method

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### 1. INTRODUCTION

The field of spectroscopy has witnessed substantial advancements, significantly refining the precision and accuracy with which the vibrational modes of polyatomic molecules are determined. This progress has spurred the development of sophisticated theoretical frameworks leveraging the principles of dynamical symmetry articulated through the intricate mathematical formalism of Lie algebras. These cutting-edge models stand at the forefront of elucidating the complex interplay of vibrational and rotational dynamics within molecular systems. Central to these models is the adept use of algebraic techniques to construct an effective Hamiltonian operator. This operator plays a pivotal role in delineating the rotational and vibrational degrees of freedom within physical systems, enriching our understanding of molecular dynamics with unprecedented precision. One of the most innovative aspects of algebraic models lies in their ability to harmonize the physical underpinnings shared with both *ab initio* and semi-empirical methodologies. While *ab initio* methods delve into the theoretical realm by solving the Schrödinger equation, semi-empirical approaches leverage observed data to predict molecular vibrations pragmatically. Historically, the analysis of molecular spectra has oscillated between two predominant methodologies: the Dunham expansion and the potential energy approach. The Dunham expansion simplifies the analytical landscape by expressing energy levels as expansions in terms of vibration-rotation quantum numbers, thus offering a foundational understanding of molecular rovibrational spectra.

In contrast, the potential energy approach embarks on a more nuanced exploration by solving the Schrödinger equation with a specific inter-atomic potential, enriching our insight into molecular interactions. In recent years, algebraic models have excelled in deciphering the vibrational spectra of small to medium-sized molecules. These models utilize various mathematical groups or symmetries, such as U(4) and U(2), to adeptly analyze diverse molecular structures. While the U(4) model caters well to smaller molecules, its complexity burgeons with larger molecules, diminishing its applicability to systems exceeding four atoms. The U(2) model emerges as a solution to this challenge, demonstrating remarkable proficiency in modeling the stretching vibrations of complex polyatomic molecules. The superiority of U(2) Lie algebraic techniques over conventional methods, such as the Dunham expansion, is particularly notable in their precision and the minimal reliance on empirical data [1]. Iachello et al. initially applied the Lie algebraic method to explore the vibrational frequencies of polyatomic molecules, introducing a novel, mathematically rigorous approach to the field [2,3]. This methodology, which draws from the complex symmetry and structures inherent in Lie algebra, offered a more refined and accurate perspective on how molecules vibrate, significantly enhancing our understanding beyond what was achievable with previous methods. Since this foundational work, the Lie algebraic technique has seen extensive refinement and broad application. Researchers have honed the method for greater precision and extended its use to analyze a broader range of molecules [4,5,6]. This growth demonstrates the method's robustness and flexibility, showcasing its utility in providing deeper insights into the vibrational characteristics of a broad spectrum of molecular configurations, from simple to highly complex structures [7,8]. The continual development of the Lie algebraic approach represents the progressive nature of scientific exploration, where initial breakthroughs lay the groundwork for ongoing advancements. As this method evolves, it opens new doors for understanding the quantum mechanics of molecular vibrations, contributing significantly to spectroscopy, material science, and chemical engineering.

In recognition of the diverse applications of phosphorus trichloride vibrational frequencies, this study calculates them up to the fifth overtone alongside their combination bands. To achieve this, we employ a Hamiltonian operator

within the framework of Lie algebra. This approach not only underpins the mathematical rigor of our methodology but also enhances our ability to accurately model and predict the complex vibrational spectra of phosphorus trichloride. Through this algebraic method, we aim to provide a comprehensive analysis that contributes to the broader understanding and application of vibrational frequencies in phosphorus trichloride, offering valuable insights for both theoretical research and practical applications in the field.

## 2. STRUCTURE OF PHOSPHORUS TRICHLORIDE

The structural configuration of phosphorus trichloride is characterized by a trigonal pyramidal arrangement, perfectly embodying the  $C_{3v}$  symmetry point group. This symmetry classification is further detailed by its symmetry species:  $A_1$  (symmetric stretch),  $A_1$  (symmetric deformation),  $E$  (degenerate stretch), and  $E$  (degenerate deformation). At the heart of this molecular geometry lies a phosphorus atom, encircled symmetrically by three chlorine atoms. These atoms are not merely adjacent but strategically placed at the vertices of a triangle, forming the pyramid's base, with each chlorine atom bonded to the phosphorus atom through single bonds.

The essence of  $PCl_3$ 's symmetry, the  $C_{3v}$  point group, is underscored by a singular  $C_3$  axis of symmetry complemented by three vertical planes of symmetry ( $\sigma_v$ ). The  $C_3$  axis, emblematic of a three-fold rotational symmetry, vertically pierces through the phosphorus atom. It stands orthogonal to the plane demarcated by the chlorine atoms, facilitating a rotation of 120 degrees around the phosphorus nucleus without altering the molecule's spatial configuration. Meanwhile, the  $\sigma_v$  planes, aligning vertically with the triangular base, dissect the P-Cl bonds so that each plane hosts the phosphorus atom and one chlorine atom. These planes enable a reflection of the molecule along them, reinforcing its trigonal pyramidal shape. This comprehensive symmetry not only bestows  $PCl_3$  with its distinct non-linear shape but also intricately influences its vibrational modes, setting it apart from molecules with linear geometries.

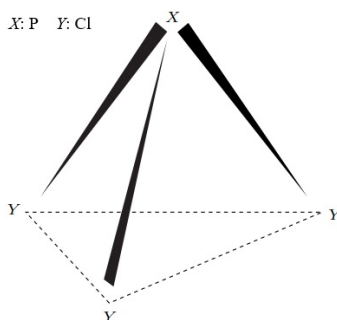


Figure 1. Structure of  $PCl_3$

## 3. THE HAMILTONIAN APPROACH OF $PCl_3$

The exploration of the stretching modes (P-Cl) in phosphorus trichloride involves a sophisticated development of a Lie algebraic vibrational Hamiltonian, which intricately blends kinetic and potential energy elements. This blending is thoughtfully executed with a strong focus on the symmetry properties intrinsic to the molecule's structure. The advanced Hamiltonian model goes beyond its basic formulation by weaving in the complex interactions and symmetries specific to  $PCl_3$ . This results in a more refined and customized examination of its vibrational features, offering a deeper and more precise insight into the P-Cl stretching modes that mirror the unique molecular dynamics and interactions characteristic of  $PCl_3$ .

For the detailed analysis of the stretching vibrations of the P-Cl bonds, the effective Hamiltonians are crafted as follows [1,2,9]:

$$H^{P-Cl} = E_0 + \sum_{i=1}^{n=3} A_i C_i + \sum_{i<j}^{n=3} A_{ij} C_{ij} + \sum_{i<j}^{n=3} \lambda_{ij} M_{ij}. \quad (1)$$

In this formula,  $E_0$  represents the zero-point energy, establishing the foundational energy level for vibrational states. The coefficients  $A_i$ ,  $A_{ij}$ , and  $\lambda_{ij}$  are algebraically tied to the Casimir ( $C_i, C_{ij}$ ) and Majorana ( $M_{ij}$ ) operators, integral to the Lie algebra framework that underpins this vibrational Hamiltonian approach [4].

The Casimir and Majorana operators introduce modern analytical dimensions to molecular vibrational dynamics, which is particularly advantageous for molecules with unique symmetries. Casimir operators, rooted in the Lie algebra of specific symmetry groups, serve as constants of motion, elucidating the vibrational autonomy of molecules and effectively delineating both independent and interrelated bond movements. On the other hand, Majorana operators are crucial for constructing irreducible representations of Lie algebra, essential for exploring vibrational modes subject to symmetry considerations, thus outlining the interactions among local modes through diagonal and off-diagonal matrix components [10].

Incorporating these operators simplifies the algebraic structure of the vibrational Hamiltonian, facilitating computational efficiency and enhancing the precision of interpretations. These operators are vital for decoding the intricate interplay between molecular symmetry and vibrational dynamics. The calculation of coefficients  $A_i$ ,  $A_{ij}$  and  $\lambda_{ij}$  employs molecular spectroscopic data, utilizing a least-squares fitting method for heightened accuracy.

For calculating algebraic operators relevant to P-Cl bonds, the expressions are:

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

$$\langle N, v_i; N, v_j | C_{ij} | N, v_i; N, v_j \rangle = 4(v_i + v_j)(v_i + v_j - 2N), \quad (3)$$

$$\left. \begin{aligned} \langle N, v_i; N, v_j | M_{ij} | N, v_i; N, v_j \rangle &= v_i N + v_j N - 2v_i v_j \\ \langle N, v_i + 1; N, v_j - 1 | M_{ij} | N, v_i; N, v_j \rangle &= -[v_j(v_i + 1)(N - v_i)(N - v_j + 1)]^{1/2} \\ \langle N, v_i - 1; N, v_j + 1 | M_{ij} | N, v_i; N, v_j \rangle &= -[v_i(v_j + 1)(N - v_j)(N - v_i + 1)]^{1/2} \end{aligned} \right\}, \quad (4)$$

with calculations rooted in the vibrational quantum numbers  $v_i$  and  $v_j$  identify the vibrational states for bonds  $i$  and  $j$ , respectively, and the vibron number,  $N = \frac{\omega_e}{\omega_e x_e} - 1$ , derived from spectroscopic constants,  $\omega_e$  and  $\omega_e x_e$  specific to the P-Cl bond [11,12]. Initial estimates for  $A_i$  stem from the energy of the fundamental mode of a single oscillator,  $E(v = 1) = -4A_i(N - 1)$  and  $\lambda_{ij} = \frac{|E_i - E_j|}{3N}$  is calculated from the energy differences between vibrational modes, further refining the model's accuracy in depicting the vibrational landscape of  $\text{PCl}_3$ .

#### 4. RESULTS

Table 1 provides a comprehensive overview of the vibrational frequencies extending to the fifth overtones and the corresponding combination bands observed in phosphorus trichloride, meticulously categorized by their symmetry species and specific vibrational modes. This detailed compilation is pivotal in shedding light on the distinctive attributes and dynamic behaviour inherent to the molecule under study. It underscores the intricate relationship between the observed vibrational frequencies, the diverse molecular motions, and the structural symmetries of phosphorus trichloride. By mapping out these frequencies and their associated modes, the table serves as a vital resource for understanding the vibrational spectrum of  $\text{PCl}_3$ . It enhances our grasp of how the molecule's geometry and symmetry influence its vibrational characteristics. This expansion into the vibrational domain of phosphorus trichloride thus provides invaluable insights into its physicochemical properties, facilitating a deeper comprehension of the molecule's internal mechanics and interaction with external stimuli.

**Table 1:** Phosphorus Trichloride Vibrational Frequencies

Vibrational mode	Vibrational frequencies (cm <sup>-1</sup> )	
	Experimental [13]	Calculated
$v_1$ (symmetric stretching, $A_1$ )	504	502.76
$v_2$ (deg stretching, E)	482	481.04
$2v_1$	-	937
$2v_2$	-	912
$3v_1$	-	1465
$3v_2$	-	1378
$4v_1$	-	1868
$4v_2$	-	1806
$5v_1$	-	2354
$5v_2$	-	2201
$v_1+v_2$	-	984
$v_1+2v_2$	-	1414
$v_1+3v_2$	-	1967
$v_1+4v_2$	-	2308
$v_1+5v_2$	-	2856
$v_2+2v_1$	-	1418
$v_2+3v_1$	-	1946
$v_2+4v_1$	-	2349
$v_2+5v_1$	-	2835

Fitted Parameters:  $N = 246$ ,  $A_i = -0.96$ ,  $A_{ij} = -1.16$ ,  $\lambda_{ij} = 0.035$

#### 5. CONCLUSIONS

In conclusion, this research has made a substantial contribution to vibrational spectroscopy and molecular modelling by developing and applying a vibrational Hamiltonian framework tailored to phosphorus trichloride. Our methodological approach, emphasizing  $C_{3v}$  symmetry point group considerations, has enabled us to precisely predict the P-Cl stretching vibrational frequencies up to the fifth overtone and to identify the corresponding combination bands. This achievement marks a significant advancement by providing a deeper and more accurate understanding of molecular vibrations within  $\text{PCl}_3$ , thus offering insights that are crucial for developing more sophisticated computational models.

Moreover, the structural analysis of  $\text{PCl}_3$ , grounded in its trigonal pyramidal geometry and  $C_{3v}$  point group symmetry, has enriched our understanding of its vibrational modes. The detailed investigation into the Hamiltonian's

algebraic structure, incorporating Casimir and Majorana operators, offers a novel perspective on the molecular vibrational dynamics specific to  $PCl_3$ . This approach not only simplifies the computational analysis but also elevates the accuracy of our interpretations, highlighting the intricate relationship between molecular symmetry and vibrational characteristics.

The comprehensive data compilation presented in Table 1, outlining the vibrational frequencies and modes, serves as a testament to the precision and reliability of our methodological approach. It underscores the importance of symmetry considerations and algebraic methods in enhancing our understanding of molecular vibrations.

Future studies can build upon our findings by exploring the application of similar vibrational Hamiltonian frameworks to other molecules with unique symmetries. Further refinement of the computational models used in this research could lead to even more precise predictions of vibrational frequencies, thereby broadening the scope of vibrational spectroscopy and molecular modelling.

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#### ВИЗНАЧЕННЯ ЧАСТОТ КОЛИВАНЬ ТРИХЛОРИДУ ФОСФОРУ З ВИКОРИСТАННЯМ ВІБРАЦІЙНОГО ГАМІЛЬТОНІАНУ

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У цьому дослідженні представлено підхід до точного визначення коливальних частот розтягування зв'язку P-Cl у трихлориді фосфору ( $PCl_3$ ) з використанням вібраційного гамільтонового підходу, який підтримує точкову групу симетрії  $C_{3v}$ . Наша методологія дозволяє точно передбачити вібраційні частоти до п'ятого обертона. Вона ідентифікує пов'язані комбіновані смуги, знаменуючи значний прогрес у вібраційній спектроскопії та молекулярному моделюванні. Підвищуючи точність і глибину нашого розуміння молекулярних коливань, це дослідження прокладає шлях до розробки складніших обчислювальних моделей, тим самим значно підвищуючи точність хімічних аналізів і вносячи внесок у ширшу область хімічної фізики.

**Ключові слова:** молекулярна фізика; вібраційні частоти; трихлорид фосфору; коливальний гамільтоніан; алгебраїчний метод Лі