Vibrational Frequencies of Phosphorus Trichloride (PCl₃): A Mathematical Study

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ABSTRACT

In this paper, Lie algebraic method is applied to study the stretching vibrational frequencies of Phosphorus Trichloride (PCl₃). This method provides good fits to the experimental data with less percentage of error.

Keywords: Vibrational spectra, Phosphorus trichloride, Lie algebraic method

INTRODUCTION

In 1981, Iachello applied Lie method to study the vibrational spectra of some molecules [1-3]. This method is an expansion of the Hamiltonian, which is in terms of invariant operators, characterizes the local and normal modes of the system [4-6]. Based on symmetry of molecules, one can study the rotational and vibrational spectra of polyatomic molecules using Lie algebraic method [2,4]. This method is also provides the description of vibrational degrees of freedom of the physical system [7-10].

Lie algebraic method (polyatomic molecules)

The Hamiltonian [11,12] for stretching vibrations of polyatomic molecule is:

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

For n stretching vibrations, i=1, 2, 3,.., n. Algebraic parameters A_i, A_{ij}, λ_{ij} are determined by using spectroscopic results. Here, i varies from 1-3, since the phosphorus trichloride contains three P-Cl bonds. Where, C_i is an invariant operator of the uncoupled bond with Eigen values $-4(N_i v_i - v_i^2)$. The operator, C_{ij} for coupled bonds (diagonal elements) is given by:

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

While, the Majorana operator M_{ij} has both diagonal and non-diagonal matrix elements:

$$\left\langle N_i, v_i; N_j, v_j \left| M_{ij} \right| N_i, v_i; N_j, v_j \right\rangle$$
$$= \left(N_i v_j + N_j v_i - 2 v_i v_j \right)$$
$$\left\langle N_i, v_i + 1; N_j, v_j - 1 \left| M_{ij} \right| N_i, v_i; N_j, v_j \right\rangle$$
$$= -\left[v_j \left(v_i + 1 \right) \left(N_i - v_i \right) \left(N_j - v_j + 1 \right) \right]^{1/2}$$
$$\left\langle N_i, v_i - 1; N_j, v_j + 1 \left| M_{ij} \right| N_i, v_i; N_j, v_j \right\rangle$$
$$= -\left[v_i \left(v_j + 1 \right) \left(N_j - v_j \right) \left(N_i - v_i + 1 \right) \right]^{1/2}.$$
$$\dots (3)$$

Where, v_i (i=1, 2, 3) are vibrational quantum numbers. The Vibron number N_i (i=1, 2, 3) for stretching bonds of molecule is calculated by the equation:

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \, i = 1, 2, 3 \, ... \, (4)$$

Here $\omega_e = 551.384$ and $\omega_e x_e = 2.22594$ [cccbdb.nist.gov/expdiatomics.asp] are spectroscopic constants. The parameter A_i, estimated by using the energy equation for the single-oscillator fundamental mode, which is:

$$E(v = 1) = -4A_i(N_i - 1) \, ... \, (5).$$

Initial value for A_{ij}, taken as zero. The parameter λ_{ij}, obtained from the equation:

$$\lambda_{ij} = \frac{|E_i - E_j|}{3N}. \, ... \, (6)$$

A numerical fitting procedure is used to find the parameters A_i, λ_{ij}, starting from values as given by equations (5) and (6) [4,5]. Since, PCl_3 contains three identical oscillators, $A_1 = A_2 = A_3 = A$, $N_1 = N_2 = N_3 = N$. All parameters are in cm^{-1}, but N is dimensionless (Table 1).

RESULTS

Table 1: Vibrational frequencies of PCl₃

Symmetry species	Experimental*	Calculated (cm⁻¹)	Per. of err.
A₁ (Symmetric)	504	500.3333	0.72
E (Deg.)	482	478.3333	0.76
N=247, *A*=-0.501, *A*ᵢⱼ=0.005, *λ*ᵢⱼ=0.029			

*http://cccbdb.nist.gov/intro.asp

CONCLUSION

We have calculated the fundamental vibrational frequencies of PCl_3 using Lie algebraic method and also compared with experimental data. These values can be utilised to find the vibrational frequencies in higher overtones. In this study we observed that the root mean square deviation is 2.31.

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