



Vibrational Frequencies of PH_3 and NF_3 : *Lie Algebraic Method*

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ABSTRACT

The subject field of vibrational frequencies of polyatomic molecules is an interesting and innovative work in the field of molecular spectroscopy. In this paper we are concerned with the vibrational frequencies of Phosphine (PH_3) and Nitrogen trifluoride (NF_3) using *Lie algebraic* method.

Keywords: Vibrational spectra, *Lie algebraic* method.

INTRODUCTION

In the last part of the 19th century, Marius Sophus Lie proposed Lie algebras. Nevertheless, these methods have been useful in the study of the problems in the beginning portion of the 20th century, after the evaluation of quantum mechanics^{1,2}. Iachello (1981) presented Lie algebraic method (vibron model) for the study of vibrational spectra of molecules. This method is based on the second quantization of the Schrodinger wave equation with a 3- Dimensional Morse potential function and is described as ro-vibration spectra of diatomic molecules. Considerable attention has been given to determining vibration spectra of molecules.

Therefore the study of molecular spectroscopy is fundamental to understanding both experimental and theoretical approaches. There are two general methods which are used to describe molecular vibrations. In the classical approach, the molecular Hamiltonian is parameterized in terms of internal coordinates and the potential energy function is represented in terms of force field constants by spectroscopic data. Although diatomic molecules have very accurate information on force fields, but not in the case of polyatomic molecules. The molecular rotation-vibration spectrum is provided by the Dunham expansion. It is a series of expansion of energy levels of rotational (J) and vibrational (v) quantum numbers. The constant coefficients y_{ij} are

called Dunham parameters. For diatomic molecules, the expansion is

$$E(v, J) = \sum_{i,j} y_{ij} \left(v + \frac{1}{2} \right)^i [J(J+1)]^j.$$

This approach is useful when the spectra can be expressed by a small number of parameters. The major drawbacks of this approach are that there is no Hamiltonian operator and it requires more number of parameters for large polyatomic molecules. The second approach is the potential approach. This approach is based on the Schrodinger wave equation. In this approach, the energy levels are computed by fitting the Schrodinger wave equation in terms of interatomic potential. The potential is expanded in terms of interatomic variable. For diatomic molecules, the possible expansion is

$$V(r) = \sum_n a_n \left(\frac{r - r_0}{b} \right)^n.$$

The potential coefficients, a's are evaluated by fitting the experimental data on energy levels. The basic drawback of this approach is that it is very difficult to fit potential coefficients if the numbers of atoms are more in the molecule⁶. To overcome the difficulties raised in analysing the vibrational spectra, we consider the third approach (Lie algebraic method).

Lie algebraic method

The Hamiltonian in the case of stretching vibrations for the polyatomic is of the form⁵

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

Here i vary from 1 to n for n stretching bonds and A_i , A_{ij} and λ_{ij} are algebraic parameters, which are determined by spectroscopic data. Where C_i is an invariant operator of the uncoupled bond with eigenvalues $-4(N_i v_i - v_i^2)$ and the operator C for coupled bonds are diagonal with matrix elements

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

while the Majorana operator M_{ij} has both diagonal and non-diagonal matrix elements

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

Where v_i ($i=1, 2, 3, \dots$) are vibrational quantum numbers. The vibron number for stretching bonds of molecule will be calculated by the following relation

$$N_i = \frac{\omega_{e_i}}{\omega_e x_{e_i}} - 1, \quad i = 1, 2. \quad \dots(2)$$

Here, ω_e and $\omega_e x_e$ are the spectroscopic constants. The initial guess value for the parameter, A_i is obtained by using the energy equation for the single-oscillator fundamental mode, which is given as,

$$E(v=1) = -4A_i(N_i - 1) \quad \dots(3)$$

Initial guess for A_{ij} may be taken as zero. The parameter λ_{ij} obtained from the relation

$$\lambda_{ij} \cong \frac{|E_i - E_j|}{3N} \quad \dots(4)$$

To have better results a numerical fitting procedure is required to obtain the parameters A_i , λ_{ij} starting from values as given by Equations (3) and (4).

RESULTS

Table 1: Vibrational spectra of PH₃ and NF₃

Vibrational mode	Vibrational frequency (cm ⁻¹)	
	PH ₃	NF ₃
(1 0 0)	2319.42356	1032.645
(2 0 0)	4564.0573	2046.936
(3 0 0)	6643.0241	2670.678

Table 2: Fitting parameters^{3,4}

PH ₃	NF ₃
N=52	N=140
Ai = -10.0456	Ai = -2.43
Aij = -0.065	Aij = 0.07
ij = -0.0123	ij = -0.332

CONCLUSION

In this paper we have reported the vibrational frequencies of PH₃ and NF₃ for three vibrational modes.

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