A Study on Vibrational Spectra of PH₃ and NF₃: An Algebraic Approach

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ABSTRACT

With the new theoretical approach i.e. lie algebraic approach, we have calculated the infrared spectra of Phosphine in the range from 3000 cm⁻¹ to 9500 cm⁻¹ and Nitrogen Trifluoride in the range from 900 cm⁻¹ to 4500 cm⁻¹. The model Hamiltonian, so constructed, seems to describe the P-H and N-F stretching modes accurately with only four numbers of parameters.

Keywords: Vibrational Spectra; Lie Algebraic Model; Hamiltonian

1. Introduction

After the recent development of new sophisticated spectroscopic instruments which allows scientists to measure vibrational states of polyatomic molecules with high accuracy and precision. The model is based on the idea of dynamical symmetry, which is expressed through the language of Lie algebras. Applying algebraic techniques, we obtain an effective Hamiltonian operator that conveniently describes the rotational vibrational degrees of freedom of the physical system. The proposed algebraic models are formulated such that they contain the same physical information for both ab initio theories (based on the solution of the Schrödinger equation) and semi empirical approaches (making use of phenomenological expansions in powers of appropriate quantum numbers). Various approaches have been used so far in the study of molecular spectra. Out of these, two important approaches are—1) Dunham expansion [1] and 2) potential approach [2]. A simple analysis of molecular ro-vibrational spectra is provided by the Dunham expansion. This is an expansion of the energy levels in terms of vibration-rotation quantum numbers. Compared to the Dunham expansion, a better analysis is provided by the potential approach in the study of molecular spectra. Energy levels are obtained by solving the Schrödinger equation with an inter-atomic potential. The potential is expanded in terms of interatomic variables. The algebraic models are successful models in the study of the vibrational spectra of small and medium-sized molecules. Some small and large molecules can be studied by using the U(4) and U(2) algebraic models. But, the U(4) model becomes complicated when the number of atoms in a molecule increases more than four. On the other hand, the U(2) model introduced by Wulfman and Levine [3] is found to be successful in explaining the stretching vibrations of polyatomic molecules such as tetrahedral, octahedral, icosahedral, and benzene-like molecules. The brief review and the research work done with the algebraic models up to the year 2000 and its outlook and perception in the first decade of the 21st century was presented by Iachello and Oss [4-7]. Recently, it is found that Lie algebraic method [8-24] is extremely successful and accurate in calculating the vibrational frequencies of polyatomic molecules compare to the other methods such as Dunham expansion and potential approach method reported earlier. So far no extensive experimental study of the infrared vibrational spectra of Phosphine and Nitrogen trifluoride molecules were reported in literatures. As a concrete and comple-
mentary technique to the conventional approaches, the algebraic approach has already proven successful in the study of molecular spectra during the last 30 years.

2. Summary of the Algebraic Theory

The model is based on the isomorphism of the $U(2)$ Lie algebra and one dimensional Morse oscillator whose eigen states may be associated with $U(2) \supset O(2)$ states [25-29]. For a pyramidal molecule, $XY_3$, we introduce three $U(2)$ ($1 \leq i \leq 3$) algebra to describe X-Y interactions (Figure 1). The possible chains of molecular dynamical groups in pyramidal molecules are (see Equation (1) below)

$$\hat{H} = E_0 + \sum_{i=1}^{3} A_i \hat{C}_i + \sum_{i<j}^{3} A_{ij} \hat{C}_{ij} + \sum_{i<j}^{3} \lambda_{ij} \hat{M}_{ij}$$ \hspace{1cm} (2)

In Equation (2), there are three types of contributions. The operators $\hat{C}_i$ are the Casimir invariant operators of $O_i(2)$ algebras, $i = 1, 2, 3$. Their diagonal matrix elements in the local basis $\{v_1, v_2, v_3\}$ are of the form

$$\langle \hat{C}_i \rangle = -4v_i (N_i - v_i), \hspace{1cm} i = 1, 2, 3$$ \hspace{1cm} (3)

with $N_1 = N_2 = N_3 = N$. Interbond couplings can be introduced in terms of operators associated with products of $U(2)$ and $O(2)$ algebras associated different, interacting bonds. The term $\hat{M}_{ij}$ leads to cross-anharmonicities between pairs of distinct local oscillators which is diagonal with matrix elements given by

$$\langle N_i, v_i; N_j, v_j | \hat{M}_{ij} | N_i, v_i; N_j, v_j \rangle = 4\left[ (v_i + v_j)^2 - (v_i + v_j) (N_i + N_j) \right]$$ \hspace{1cm} (4)

The modes of three equivalent X-H bond are now mixed, shifted and split under the action of the operator $\hat{M}_{ij}$. The Majorana operator is used to describe local mode interactions in pairs and has both diagonal and non-diagonal matrix elements given by (see Equation (5) below)

$$\langle N_i, v_i; N_j, v_j | \hat{M}_{ij} | N_i, v_i; N_j, v_j \rangle = v_i N_j + v_j N_i - 2v_i v_j ,$$

$$\langle N_i, v_i + 1; N_j, v_j - 1 | \hat{M}_{ij} | N_i, v_i; N_j, v_j \rangle = -v_j (v_i + 1)(N_i - v_i)(N_j - v_j + 1)^{\frac{1}{2}}$$ \hspace{1cm} (5)

Figure 1. Schematic representation of a pyramidal $XY_3$ molecule.

3. Results and Discussions

Using $U(2)$ algebraic model Vibrational modes of $XH_3$ are computed using algebraic Hamiltonian up to third overtone and are listed in Tables 1 and 2 with fewer algebraic parameters (i.e. $A_i, \lambda_{ij}$ and $N$).

The vibron number $N$ can be determined by the relation

$$N_i = \frac{\omega_i}{\omega_{XH}}, -1, \hspace{1cm} i = 1, 2, 3$$ \hspace{1cm} (7)

where $\omega_i$ and $\omega_{XH}$ are the spectroscopic constants of diatomic molecules [30-33]. The value of $N$ must be as initially guessed from the Equation (7); however one can expect changes in an estimated $N$, not be larger than $\pm 20\%$ of the original value. The vibron number $N$ between
Table 1. Experimental and observed infrared spectra of Phosphine molecule.

| $\nu$ | Symmetry | $\nu_{\text{obs}}$ (cm$^{-1}$) | $\nu_{\text{cal}}$ (cm$^{-1}$) | $\Delta$ (cm$^{-1}$) |
|-------|----------|------------------|-----------------|---------------|
| 100   | A$_1$    | 2321.1314        | 2322.185        | -1.0536       |
| 100   | E        | 2326.8766        | 2327.926        | -1.0494       |
| 200   | A$_1$    | 4566.26          | 4554.32         | 11.94         |
| 200   | E        | 4565.78          | 4566.06         | 5.72          |
| 110   | A$_1$    | 4644.66          | 4658.10         | -13.44        |
| 110   | E        | 4758.104         |                  |               |
| 300   | A$_1$    | 6714.60          | 6713.42         | 1.18          |
| 300   | E        |                  | 6713.42         |               |
| 210   | A$_1$    | 6881.533         | 6892.51         | -10.98        |
| 210   | E        | 6883.731         | 6886.92         | -3.189        |
| 210   | A$_1$    | 6875.51          |                  |               |
| 210   | E        | 6890.861         | 6881.25         | 9.611         |
| 111   | A$_1$    | 6971.1576        | 6976.91         | -5.75         |

$\Delta$ (rms) = 28.21 cm$^{-1}$.

Table 2. Fitting parameters used in the study of Phosphine molecule.

| Boson number | Stretching parameters |
|--------------|----------------------|
|              | $N$  | $A_1$  | $A_{12}$ | $\lambda_{12}$ |
| 52           | -11.136 | -0.0617 | 0.0357   |               |

$A_1; A_{12}; \lambda_{12}$ all are in cm$^{-1}$ whereas $N$ is dimensionless.

Table 3. Experimental and observed infrared spectra of Nitrogen Trifluoride molecule.

| $\nu$ | Symmetry | $\nu_{\text{obs}}$ (cm$^{-1}$) | $\nu_{\text{cal}}$ (cm$^{-1}$) |
|-------|----------|------------------|-----------------|
| 100   | A$_1$    | 1032             | 1031.99         |
| 100   | E        | 905              | 905             |
| 200   | A$_1$    | 2047.92          | 2047.92         |
| 200   | E        | 1809             | 1811.52         |
| 110   | A$_1$    | 1794.86          | 1794.86         |
| 110   | E        | 1929             | 1921.09         |
| 300   | A$_1$    | 2680             | 2669.08         |
| 300   | E        | 2669.08          | 2669.08         |
| 210   | A$_1$    | 2827.80          | 2828.06         |
| 210   | E        | 2827.80          | 2827.80         |
| 111   | A$_1$    | 3097.53          | 3097.53         |

$\Delta$ (rms) = 12.72 cm$^{-1}$.

Table 4. Fitting parameters used in the study of Nitrogen Trifluoride molecule.

| Boson number | Stretching parameters |
|--------------|----------------------|
|              | $N$  | $A_1$  | $A_{12}$ | $\lambda_{12}$ |
| 140          | -2.15 | 0.0655 | -0.305   |               |

$A_1; A_{12}; \lambda_{12}$ all are in cm$^{-1}$ whereas $N$ is dimensionless.

4. Conclusion

Using model Hamiltonian, we have presented an algebraic model of one dimensional Morse oscillators which can be used to describe X-H stretching vibrations quite accurately. In third overtones, we have predicted nine (eight) stretching vibrational modes for Arsine (Ammonia) from only one (two) observed data’s. To proceed further it would be necessary to record spectra of higher overtones to produce more accurate vibrational modes.

With the help of numerical fitting procedure (in a least-square sense) the parameters $A$ and $\lambda_{12}$ starting from values Equation (9) and Equation (10), and $A_{12}$ (whose initial guess can be zero) were adjusted. Vibrational modes of Arsine and Ammonia are computed using algebraic Hamiltonian up to third overtone and are listed in Tables 3 and 4.
the last twenty five years, the Lie algebraic approach was found to be successful in explaining vibrational modes of small, medium, polymers, bio-molecules and biopolymers. In view of many possible applications, it is expected that the present calculation will open new windows in the field of spectroscopy.

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