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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 Nirogen trifluoride molecules were reported in literatures. As a concrete and comple-

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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 $U_i(2)$ ($1 \le i \le 3$) algebra to describe X-Y interactions (**Figure 1**). The possible chains of molecular dynamical groups in pyramidal molecules are (see Equation (1) below)

Which corresponds to local and normal couplings respectively.

The algebraic Hamiltonian in case of stretching mode of pyramidal molecules can be constructed from two chains as

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

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 $|v_1, v_2, v_3\rangle$ are of the form

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

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 $\hat{C}_{ij}$ leads to cross-anharmonicities between pairs of distinct local oscillators which is diagonal with matrix elements given by

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

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)
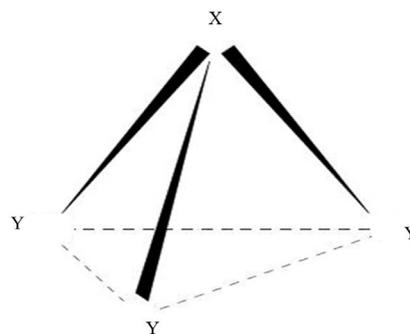

Figure 1. Schematic representation of a pyramidal XY₃ molecule.

We shall now construct the local vibrational basis which is given by

$$\left| \begin{matrix} U_1(2) \otimes U_2(2) \otimes U_3(2) \supset O_1(2) \otimes O_2(2) \otimes O_3(2) \\ N_1 \qquad N_2 \qquad N_3 \qquad v_1 \qquad v_2 \qquad v_3 \end{matrix} \right\rangle \quad (6)$$

The total vibrational quantum number is always conserved for a particular polyad. For a particular XH_3 molecule, the stretching bonds 1 to 3 are equivalent. The algebraic Hamilonian depends on 9 linear parameters. These parameters are reduced to only three parameters A_1, A_{12} and λ_{12} which give the strength of individual and coupling bonds respectively.

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, A_{12}, λ_{12} and N).

The vibron number N can be determined by the relation

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \ \ i = 1, 2, 3 \quad (7)$$

where ω_e and $\omega_e x_e$ 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

$$U_1(2) \otimes U_2(2) \otimes U_3(2) \supset O_1(2) \otimes O_2(2) \otimes O_3(2) \supset O(2)$$
$$U_1(2) \otimes U_2(2) \otimes U_3(2) \supset U(2) \supset O(2) \quad (1)$$

$$\langle N_i, v_i; N_j, v_j | \hat{M}_{ij} | N_i, v_i; N_j, v_j \rangle = v_i N_j + v_j N_i - 2v_i v_j, \left. \right\}$$
$$\langle N_i, v_i + 1; N_j, v_j - 1 | \hat{M}_{ij} | N_i, v_i; N_j, v_j \rangle = -\left[v_j (v_i + 1)(N_i - v_i)(N_j - v_j + 1) \right]^{\frac{1}{2}}, \left. \right\} \quad (5)$$
$$\langle N_i, v_i - 1; N_j, v_j + 1 | \hat{M}_{ij} | N_i, v_i; N_j, v_j \rangle = -\left[v_i (v_j + 1)(N_j - v_j)(N_i - v_i + 1) \right]^{\frac{1}{2}}, \left. \right\}$$

Table 1. Experimental and observed infrared spectra of Phosphine molecule.

v	Symmetry	v_{obs} (cm^{-1})	v_{cal} (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	4560.06	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

Δ (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}	λ_{12}
52	−11.136	−0.0617	0.0357

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

the diatomic molecules As-H and N-H are 68 and 53 respectively. From the **Figure 1**, it is noticed that some of the bonds are equivalent. It may be noted that during the calculation of the vibrational modes of XH$_3$ molecules, the value of N is kept fixed and not used as free parameter.

The next step is to obtain a guess for the second parameter A. The expression for the single-oscillator fundamental mode is

$$E\left(v=1\right)=-4A\left(N-1\right) \tag{8}$$

In the present case, we have three energies, corresponding to symmetric and antisymmetric combinations of the different local modes. A possible strategy is to use the center of gravity of these modes, so the guess for

$$\bar{A}=\frac{\bar{E}}{4\left(1-N\right)} \tag{9}$$

The third step is to obtain an initial guess for λ. Its role is to split the initially degenerate local modes, placed here at the common value E used in Equation (8). Such an estimate is obtained by considering the simple matrix

structure, we can find

$$\lambda_{12}\cong\frac{\left|E_1-E_2\right|}{3N} \tag{10}$$

With the help of numerical fitting procedure (in a least-square sense) the parameters A and λ_{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**.

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. In

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

v	Symmetry	v_{obs} (cm^{-1})	v_{cal} (cm^{-1})	
100	A$_1$	1032	1031.99	0.01
100	E	905	905	0
200	A$_1$		2047.92	
200	E	1809	1811.52	-2.52
110	A$_1$		1794.86	
110	E	1929	1921.09	7.91
300	A$_1$	2680	2669.08	10.92
300	E		2669.08	
210	A$_1$		2703.24	
210	E		2828.06	
210	A$_1$		2827.80	
210	E		2954.03	
111	A$_1$		3097.53	

Δ (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}	λ_{12}
140	−2.15	0.0655	−0.305

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

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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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