

Analysis of the Vibrational Spectra of Polyatomic Molecules Using an Algebraic Model: An Application to XH_3

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Algebraic techniques are examined as a computational tool for the analysis and interpretation of the experimental vibrational spectra of small and medium sized molecules. These techniques are based on the idea of dynamical symmetry, which in turn is expressed through the language of unitary Lie algebra. In this paper, the stretching vibrational spectra of Arsine and ammonia molecules are calculated up to $v = 4$ using $U(2)$ algebra. The model Hamiltonian so constructed seems to describe the As-H and N-H stretching modes accurately with only four numbers of parameters.

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I. INTRODUCTION

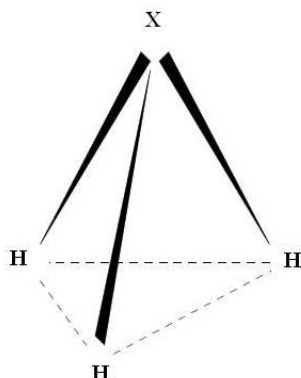
For understanding and analyzing a physical system in a befitting manner, molecular spectroscopy is an area of active interest from many scientific standpoints. Having numerous connections with many other branches, molecular spectroscopy has been playing an important role both in experimental and theoretical approaches. Before the discovery of sensitive equipment it was quite impossible to study the overtone frequencies as they are usually very weak. Therefore, most of the work in the earlier days was done on fundamentals. In order to get the higher overtones, it is necessary to develop a model of molecules which can describe the energy levels up to certain excited states after some simple calculations. The model should be based on the idea of dynamical symmetry, which is expressed through the language of Lie algebras. The algebraic method includes the lowest order anharmonicities and cross anharmonicities, and thus it is well suited for the high overtones. Applying algebraic techniques, we obtain an effective Hamiltonian operator that conveniently describes the rovibrational degrees of freedom of the physical system. The traditional theoretical approaches used to interpret the experimental data are: (i) solving the Schrödinger equation with interatomic potentials either by appropriate ab initio calculations or by more phenomenological methods; (ii) solving the Dunham like expansion [1] of energy levels in terms of rovibrational quantum numbers; (iii) the vibron model or Lie algebraic method which is a formulation of molecular spectra in terms of Lie algebra. The first approach becomes difficult as the number of atoms in the molecule increases. Similarly, the second approach contains a large number of parameters which cannot be determined from the small amount of available experimental data. The difficulties arising in analyzing the vibrational spectra by traditional methods is solved by the third approach, i.e., the vibron model based on Lie algebra [2]. This new model appears to describe the molecular spectra

successfully even in complex situations. $U(4)$ and $U(2)$ algebraic models have been used so far in the analysis of experimental data in recent years. In the $U(4)$ model, rotations and vibrations are treated simultaneously. It is to be noted here that the $U(4)$ model becomes complicated when the number of atoms in a molecule increases to more than four. The $U(2)$ model treats rotations and vibrations separately. This model has the advantage that it can be applied to any molecule, the only limitations being the size of the matrices to diagonalize for getting the excited states. Iachello, Levine, and co-workers have described the rotation-vibration spectra of diatomic and triatomic molecules [3, 4] using $U(4)$ algebra. Later on the $U(4)$ algebra was used for each bond in the case of linear and quasilinear four atomic molecules [5]. The algebraic model has been applied successfully in the study of spectra of tetrahedral molecules [6], benzene [7], and octahedral molecules [8]. Iachello and Oss presented a brief review of the development of algebraic techniques and its application to molecular spectroscopy [9] in the intervening years up to 2000. The main features and applications of Lie algebraic methods have been described in books [10, 11] and review articles [12] in the last few years. Recently we have reported the results of vibrational spectra of HCN and OCS [13], HCCF and HCCD [14], CCl_4 and SnBr_4 [15], Ni (OEP), Ni (TPP) and Ni Porphyrin [16], Propadiene [17], a comparison between OCS and HCP [18], isotopes of CF_4 [19], SO_2 , and H_2O^{18} and D_2O^{16} [20] by an algebraic approach using only a few algebraic parameters. In the recently published papers, we have derived the Schrödinger equation for the bound states of the Poschl-Teller potential [21] and also calculated the fundamental vibrational spectra of C_{50} and C_{84} fullerenes [22] using Lie algebra. The algebraic approach gives very useful results compared to experimental values in such type of molecules as we considered. In the Lie algebraic approach, there is a provision for studying the molecular vibrational energy by a normal and local Hamiltonian. Previously the local mode model has been used for the calculation of the vibrational states [23] of polyatomic molecules. In this article, we try to extend the formalism (i.e., the $U(2)$ model) to XH_3 molecules (C_{3v} point group) to check its validity. The stretching vibrational modes of AsH_3 and NH_3 are calculated up to third overtones using a one-dimensional vibron model for the first time. This is particularly nice, because the Lie algebraic approach offers a clear and simple physical picture. Of course refinements of the theory have to be made in order to understand many experimental observations in detail.

II. THEORY OF THE ALGEBRAIC MODEL

The model is based on the isomorphism of the $U(2)$ Lie algebra and the one dimensional Morse oscillator whose eigenstates may be associated with $U(2) \supset O(2)$ states [13]. For a pyramidal molecule, XH_3 , we introduce three $U_i(2)$ ($1 \leq i \leq 3$) algebras to describe the X-H interactions [Figure 1]. The possible chains of molecular dynamical groups in pyramidal molecules are

$$\begin{aligned} U_1(2) \otimes U_2(2) \otimes U_3(2) &\supset O_1(2) \otimes O_2(2) \otimes O_3(2) \supset O(2), \\ U_1(2) \otimes U_2(2) \otimes U_3(2) &\supset U(2) \supset O(2), \end{aligned} \quad (1)$$

FIG. 1: Schematic representation of a pyramidal XH_3 molecule.

which correspond to local and normal couplings, respectively.

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

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

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

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

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 with different, interacting bonds. The term \hat{C}_{ij} leads to cross-anharmonicities between pairs of distinct local oscillators which are diagonal with matrix elements given by

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

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

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

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

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

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 Hamiltonian 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 the individual and coupling bonds, respectively.

III. RESULTS AND DISCUSSIONS

Using the $U(2)$ algebraic model, the vibrational modes of XH_3 are computed using the algebraic Hamiltonian up to the third overtone and are listed in Table I and Table III with fewer algebraic parameters (i.e., A , A_{12} , λ_{12} , and N).

The vibron number N can be determined by the relation

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

where ω_e and $\omega_e x_e$ are the spectroscopic constants of diatomic molecules [12]. The value of N must be as initially guessed from Equation (7); however one can expect changes in an estimated N , which should not be larger than $\pm 20\%$ of the original value. The vibron numbers N between the diatomic molecules As-H and N-H are 68 and 53, respectively. From 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 is not used as a free parameter.

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

$$E(\nu = 1) = -4A(N - 1). \quad (8)$$

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, hence the guess for

$$\bar{A} = \frac{\bar{E}}{4(1 - N)}. \quad (9)$$

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 Eq. (8). Such an estimate is obtained by considering the simple matrix structure, we can find

$$\lambda_{12} \cong \frac{|E_1 - E_2|}{3N}. \quad (10)$$

With the help of a numerical fitting procedure (in a least-square sense) the parameters A and λ_{12} starting from the values of Eq. (9) and Eq. (10), and A_{12} (whose initial guess can be zero) were adjusted. Vibrational modes of arsine and ammonia are computed using

TABLE I: Observed and calculated stretching vibrational modes of the AsH₃ molecule.

V	Symmetry	AsH ₃	
		v_{obs} (cm ⁻¹)	v_{calc} (cm ⁻¹)
100	A ₁	2115.16	2114.88
100	E	2126.42	2126.10
200	A ₁	4166.77	4167.36
200	E	4167.94	4178.57
110	A ₁	4237.70	4251.73
110	E	4247.53	4251.73
300	A ₁	6136.34	6157.44
300	E	6136.33	6168.66
210	A ₁	6275.83	6314.85
210	E	6282.36	6314.85
210	A ₁		6314.85
210	E	6294.72	6303.85
111	A ₁	6365.97	6365.89
400	A ₁	8029.2	8085.42
400	E		8096.34
310	A ₁		8297.98
310	E		8293.57
310	E		8304.57
310	A ₂		8301.16
220	A ₁		8366.61
220	E		8374.51
211	A ₁		8439.54
211	E		8439.54
$\sigma(\text{r.m.s})$		10.14 cm ⁻¹	

Observed values are taken from reference [23].

the algebraic Hamiltonian up to the third overtone and are listed in Table I and Table III. From the group theoretical point of view, the first three equivalent stretching bonds (X-H) describe two irreducible representations: A_1 and E for $v = 1$. To get an estimation of the precession of both the observed and calculated data, we use the standard deviation (SD)

TABLE II: Values of the algebraic parameters used in the calculation of AsH₃.

N	A	A_{12}	λ_{12}
68	-7.71	-0.045	0.055

All the values are in cm^{-1} except N which is dimensionless.

denoted by σ at the bottom of the two tables:

$$\sigma^2 = \frac{1}{o-p} \sum_{i=1}^o (E_{\text{cal}}^i - E_{\text{obs}}^i)^2, \quad (11)$$

where o is the number of the observed data and p is the number of parameters used in the fitting.

The calculation of the vibrational modes of second overtones of arsine shows deviations of .08 to 39 cm^{-1} from the observed values. But the value of σ (r.m.s) comes out to be 10.14 cm^{-1} for 24 vibrational modes. In the case of ammonia, the value of σ (r.m.s) comes out to be 55.80 cm^{-1} for 24 vibrational levels with four as the number of parameters. The complete vibrational spectrum of ammonia up to $v = 4$ did not give very good agreement with the data from Halonen's work by the local mode model. The present results show a σ for the fundamentals of XH_3 ($X=\text{As}, \text{N}$) molecules which is reasonable but becomes larger for higher overtones. But we can say definitely that if the number of the observed data is more, the algebraic model could give more accurate result and less standard deviation. The local versus normal behavior of the stretching modes of XH_3 can be characterized by introducing the quantity, $\xi = 2/\pi \tan^{-1} [8\lambda_{12}/(A + A_{12})]$. Here we find $\xi = .03609$ for the As-H bond and $\xi = .1963$ for N-H, which confirms the highly local behavior of the stretching modes of arsine and ammonia. Thus, we can say that the algebraic model Hamiltonian is successful in predicting the energies in this complex molecular system. We believe that more satisfactory results will be obtained if the second order interaction is included in the algebraic Hamiltonian. The fitting parameters for arsine and ammonia are given in Table II and IV.

IV. CONCLUSIONS

Using a 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 Table I and Table III the fundamental splitting is ≈ 11.26 and 106.05 cm^{-1} respectively. The splitting pattern determines the interbond interactions ($\lambda_{ij} = \lambda_{12}$). In third overtones, we have predicted nine (eight) stretching vibrational modes for arsine (ammonia) from only one (two) observed data. To proceed further it would be necessary to record spectra of higher overtones to produce more accurate vibrational modes. In 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

TABLE III: Observed and calculated stretching vibrational modes of NH₃ molecule.

V	Symmetry	NH ₃	
		v_{obs} (cm ⁻¹)	v_{calc} (cm ⁻¹)
100	A ₁	3337	3337.80
100	E	3443	3443.85
200	A ₁		6543.46
200	E	6608	6649.52
110	A ₁	6850	6908.22
110	E	6850	6908.22
300	A ₁		9625.03
300	E	9760	9723.02
210	A ₁		10095.55
210	E	10105	10096.72
210	A ₁		10096.72
210	E		10199.11
111	A ₁		10199.11
400	A ₁	12609	12558.34
400	E	12609	12664.34
310	A ₁		13171.08
310	E		13171.08
310	E		13274.47
310	A ₂		13274.47
220	A ₁		13510.50
220	E		13510.50
211	A ₁		13542.49
211	E		13644.49
$\sigma(\text{r.m.s})$		10.14 cm ⁻¹	

Observed values are taken from reference [23].

TABLE IV: Values of the algebraic parameters used in the calculation of NH₃.

N	A	A_{12}	λ_{12}
53	-16.978	.2314	0.667

applications, it is expected that the present calculation will open new windows in the field of spectroscopy.

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