



Algebraic approach to analyze the vibrational spectra of tetrahedral molecules

Joydeep Choudhury¹, Nirmal Kumar Sarkar² and Ramendu Bhattacharjee^{1*}

¹ Department of Physics, Assam University, Silchar-788 011, Assam, India

² Department of Physics, Karimganj College, Karimganj-788 710, Assam, India

E-mail choudhuryjoy@rediffmail.com

Abstract Molecular spectroscopy is undergoing a considerable attention in last few decades. There is a considerable current research interest in the study of vibrational ground and excited states of polyatomic molecules using Lie algebraic method. Both the stretch and bend fundamental vibrational modes of tetrahedral molecules are calculated by using $U(2)$ algebraic model. Its application to four molecules are presented. The result obtained by this model are the best fit with the observed data. This study will give a general approach for solving tetrahedral molecules with good accuracy.

Keywords Algebraic model, vibrational energy level, vibrational mode, tetrahedral molecules

PACS Nos. 03.65.Fd, 31.15.Hz

1. Introduction

Molecular spectroscopy has received a lot of attention in last few decades. There is considerable current research interest in the study of vibrational ground and excited states of polyatomic molecules using Lie algebraic method. $U(4)$ and $U(2)$ algebraic model have been used so far in the analysis of experimental data. The algebraic approach to molecules was first introduced by Wulfman [1] in the study of Morse oscillator. Iachello, Levine and co-workers [2,3] described the rotation-vibration spectra of molecules using $U(4)$ algebra. Later on the $U(4)$ algebra was used for each bond in case of linear triatomic and four atomic molecules [5,6]. It is to be noted that the $U(4)$ model becomes complicated when the number of atoms in a molecule increases more than four. In 1984, Van Roosmalen *et al.* proposed an algebraic model to describe stretching vibrational modes of ABA molecules [7]. This model is based on the isomorphism between one dimensional Morse potential and $SU(2)$ algebra and correspond to the algebraic version of coupled Morse

* Corresponding Author

oscillator method developed by Halonen and Child [8]. Michelot, Moret -Bailly and Leroy [9,10] proposed an algebraic approach to study the vibrational stretching mode in a polyatomic molecule using unitary group $U(n)$ with $(n-1)$ vibrational degrees of freedom. In order to study vibrational modes of medium sized molecules, one usually chooses a tetrahedral molecules as one of good samples. In 1994, Lemus and Frank proposed an algebraic $SU(2)$ model based on group theoretical ideas to calculate the stretching and bending vibrational energy levels of methane like molecules[12]. Recently, using Lie algebraic method we have reported better results [11,22] for the vibrational frequencies of HCN than those reported earlier. The $U(2)$ model was used successfully in explaining the stretching vibrations of polyatomic molecules like octahedral and benzene molecules [13,14]. Later on, Iachello and Oss has developed the algebraic model to incorporate the bending modes in case of benzene [15] and acetylene [16]. As the algebraic approach emphasizes anharmonicity (and cross anharmonicity) even in the zeroth order, higher order coupling can be introduced in a systematic and sequential fashion. As such the approach is particularly appropriate for many challenges of modern spectroscopy. This approach is important for the representation of higher accuracy spectroscopic data and especially so for larger molecules. The algebraic approach starts with a Hamiltonian and hence such a fit provides more than just a compact parametrization of the data. Rather, it determines some of the parameters in the Hamiltonian and so provides explicit predictions (including information on the potential).

In this paper, the fundamental vibrational modes of tetrahedral molecules like GeH_4 , $GeCl_4$, SiF_4 and CCl_4 are calculated by using an algebraic model Hamiltonian. The values of boson numbers N_1 and N_2 can be found out by knowing anharmonic constant ω_e and $\omega_e x_e$ of stretching and bending bonds of different diatomic molecules under study. The result obtained by this model are in good agreement with the observed data. Therefore this study will give "a general approach" to solve the vibrational energy levels accurately for tetrahedral molecules.

2. Algebraic model

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[13]. For

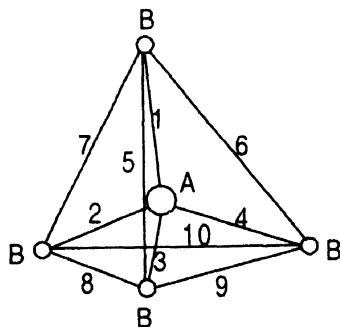


Figure 1. Assignment of the $U(2)$ algebra to tetrahedral molecule.

a tetrahedral molecule, AB_4 , we introduce four $U_i(2)$ ($1 \leq i \leq 4$) algebra to describe A-B interactions and six $U_j(2)$ algebra ($5 \leq j \leq 10$) for B-B interaction [Figure 1]

The two possible chains of molecular dynamical groups in tetrahedral molecules are given by the product

$$U^1(2) \times \dots \times U^{10}(2) \supset O^1(2) \times \dots \times O^{10}(2) \supset O(2) \tag{2.1}$$

$$U^1(2) \times \dots \times U^{10}(2) \supset U(2) \supset O(2). \tag{2.2}$$

Which corresponds to local and normal coupling respectively. For these two situations the Hamiltonian operator can be diagonalised analytically

The Hamiltonian upto two body interactions is given in terms of 10 operators, representing ten one dimensional Morse oscillator, plus two types of bond-bond interaction $C_2(O^j(2))$ and $M_j(2)$ known as Casimir and Majorana operators respectively of $O^j(2)$ group.

For tetrahedral molecules, the Hamiltonian can be written as

$$H = H^S + H^B + V^{S-B}. \tag{2.3}$$

The term H^S denotes the stretching degrees of freedom (A-B bond), H^B is the bending contribution (B-B bond) and V^{S-B} represents the stretching bending interaction which is neglected in case of first order approximation. The common algebraic model Hamiltonian in case of stretching and bending mode for tetrahedral molecules can be considered as [13,17]

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i<j}^n A_{ij} C_{ij} + \sum_{i<j}^n \lambda_{ij} M_{ij} \tag{2.4}$$

Where i runs from 1 to $n = 4$ for calculation of stretching and i runs from 5 to $n = 10$ for bending vibrational energy level. In the eq. (2.4), C_i is an invariant operator with eigen values $4(v_i^2 - N_i v_i)$ and the operator C_{ij} is diagonal with matrix elements

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4 \left[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j) \right] \tag{2.5}$$

while the operator M_{ij} has both diagonal and non-diagonal matrix element.

$$\langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle = (N_i v_i + N_j v_j - 2v_i v_j)$$

$$\langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = - \left[v_j (v_i + 1) (N_i - v_i) (N_j - v_j + 1) \right]^{1/2} \tag{2.6}$$

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

For a tetrahedral molecule AB_4 , we choose the parameters $N_i = N_1$, $A_i = A_1$ (for $i = 1$ to 4), $A_{ij} = A_{12}$ (any i and j) and λ_{12} for stretching mode and $N_j = N_2$, $A_j = A_5$ (for $j = 5$ to 10), $A_{ij} = A_{5,6}$ (any i and j) and $\lambda_{5,6}$ for bending mode respectively.

3. Results and discussion

We report in Table I the results of fundamental vibrational energies A_1 , F_2 (stretching) and E , F_2 (bending) for four tetrahedral molecules like GeH_4 , $GeCl_4$, SiF_4 and CCl_4 taken from references 18,19,20 and 21. The estimated values of six parameters (A_1 , A_{12} , λ_{12} for stretching and A_5 , $A_{5,6}$, $\lambda_{5,6}$ for bending mode) along with boson numbers N_1 and N_2 are also shown in the Table 1 for four molecules. We have reported the vibrational fundamental modes ν_1 , ν_2 , ν_3 and ν_4 for four tetrahedral molecules, but we can obviously calculate overtone and combination bands up to higher number of quanta as well. The model Hamiltonian (2.4) appears to describe the vibrational frequencies with good accuracy.

Table 1. Comparison of calculated and observed fundamental vibrational frequencies of GeH_4 , $GeCl_4$, SiF_4 and CCl_4

V	Normal mode of vibration	Γ	GeH_4		$GeCl_4$		SiF_4		CCl_4	
			ν_{obs}	ν_{cal}	ν_{obs}	ν_{cal}	ν_{obs}	ν_{cal}	ν_{obs}	ν_{cal}
1	ν_1	A_1	2106	2105.88	398	398.04	800.8	800.58	460	459.96
1	ν_2	E	930.9	930.94	132	132.35	264.2	264.20	214.2	214.5
1	ν_3	F_2	2111.78	2111.66	450	449.94	1031.39	1031.3	792	791.83
1	ν_4	F_2	819.3	819.31	172	172.33	388.44	388.45	313.5	312.9
Stretching Parameters			GeH_4		$GeCl_4$		SiF_4		CCl_4	
		N_1	55		299		100		342	
		A_1	-8.215		-0.34		-1.175		-0.155	
		A_{12}	0.2534		-0.0010		0.1404		-0.0431	
		λ_{12}	0.0263		0.0434		0.5769		0.2426	
Bending Parameters			GeH_4		$GeCl_4$		SiF_4		CCl_4	
		N_2	28		140		15		140	
		A_5	-29.475		-1		-13.94		-1	
		$A_{5,6}$	2.5595		-0.0958		1.113		-0.765	
		$\lambda_{5,6}$	-0.9968		0.0714		2.070		0.1758	

All values are in cm^{-1} , except N_1 and N_2 which are dimensionless. Observed values are taken from references 18, 19, 20 and 21.

4. Conclusions

Using model Hamiltonian, we have calculated the vibrational fundamental modes of four tetrahedral molecules, GeH_4 : $\nu_1 = 2105.88$, $\nu_2 = 930.94$, $\nu_3 = 2111.66$, $\nu_4 = 819.31 \text{ cm}^{-1}$, GeCl_4 : $\nu_1 = 398.04$, $\nu_2 = 132.35$, $\nu_3 = 449.94$, $\nu_4 = 172.33 \text{ cm}^{-1}$, SiF_4 : $\nu_1 = 800.58$, $\nu_2 = 264.2$, $\nu_3 = 1031.3$, $\nu_4 = 388.45 \text{ cm}^{-1}$ and CCl_4 : $\nu_1 = 459.96$, $\nu_2 = 214.5$, $\nu_3 = 791.83$, $\nu_4 = 312.9 \text{ cm}^{-1}$ with good accuracy. As it is already reported that AB_4 is an important member of the family of molecules. Hence, we can claim that using this model, the vibrational fundamental modes of some tetrahedral molecules can be found out accurately. It is obvious that once we calculate the vibrational fundamental modes of a molecule accurately, the overtone and combination bands can be calculated with the help of such a model Hamiltonian by fitting the experimental data with the help of computer programming.

Acknowledgment

One of us (RB) is thankful to the DST, government of India for providing research grant

References

- [1] R D Levine and C E Wulfman *Chem Phys Lett* **60** 372 (1979)
- [2] F Iachello *Chem Phys Lett* **78** 581 (1981)
- [3] F Iachello and R D Levine *J Chem Phys* **77** 3046 (1982)
- [4] F Iachello and R D Levine *Algebraic Theory of Molecules* (Oxford: Oxford University press) (1995)
- [5] S Oss *Adv Chem Phys* **93** 455 (1996)
- [6] F Iachello, S Oss and R Lemus *J Mol Spectroscopy* **146** 56 (1991) *ibid* **149** 132 (1991)
- [7] O S Van Roosmalen, I Benjamin and R D Levine *J Chem Phys* **81** 5986 (1984)
- [8] L Halonen and M S Child *Mol Physics* **46** 239 (1982)
- [9] F Michelot and J Moret-Bailly *J Phys* **48** 51 (1987)
- [10] C Leroy and F Michelot *J Mol Spectroscopy* **151** 71 (1992)
- [11] N K Sarkar, J Choudhury and R Bhattacharjee *Mol Phys* **104** 3051 (2006)
- [12] R Lemus and A Frank *J Chem Phys* **101** 8321 (1994)
- [13] F Iachello and S Oss *Phys Rev Lett* **66** 2976 (1991)
- [14] J L Ping and J Q Chen *Ann Phys (N Y)* **255** 75 (1997)
- [15] F Iachello and S Oss *J Chem Phys* **99** 7337 (1993)
- [16] F Iachello and S Oss *J Chem Phys* **104** 6956 (1996)
- [17] F Iachello and S Oss *Chem Phys Lett* **205** 285 (1993)
- [18] R S McDowell, M J Reisfeld, C W Patterson, B J Krohn, M C Vasque and G A Laguna *J Chem Phys* **77** 4337 (1982)
- [19] R J H Clark and D M Rippon *Chem Communication* 1295 (1971)
- [20] R J Clark and P D Mitchell *J Chem Soc Faraday Trans 2* **71** 515 (1975)
- [21] M Petri, U Simon, W Zimmermann, W Urban, J P Towle and M Brown *Mol Phys* **72** 315 (1991)
- [22] N K Sarkar, J Choudhury and R Bhattacharjee *First Asian Spectroscopic Conference* (II Sc, Bangalore) p 106 (2007)