

Vibrational spectroscopy of SnBr_4 and CCl_4 using Lie algebraic approach

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Abstract. The stretching and bending vibrational energies of SnBr_4 and CCl_4 are calculated in the one-dimensional framework. The dynamical symmetry group of tetrahedral molecule was taken into consideration to construct the model Hamiltonian in this framework. Casimir and Majorana invariant operators were also determined accordingly. Using the model Hamiltonian so constructed, we reported the vibrational energy levels of SnBr_4 and CCl_4 molecules accurately.

Keywords. Algebraic model; vibrational energy level; tetrahedral molecules.

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1. Introduction

For the last few years, theoretical studies of highly excited vibrational states of polyatomic molecules have been one of the most interesting topics for theoreticians and experimentalists because of the development of new laser spectroscopic techniques. Wulfman played a great role in introducing algebraic approach to molecules. He is the pioneer to publish the first paper on the algebraic approach to molecules [1] (the algebraic approach to the Morse oscillator) in 1979. Later, in 1981, Iachello [2] used Lie algebraic methods to study the spectra of molecules (vibron model) using $U(4)$ algebra. The $U(4)$ model takes the rotation and the vibration into account simultaneously but becomes complex when the number of atoms in the molecules becomes larger than four. After 1981, there is a rapid progress in this field. Iachello *et al* [3,4] have proposed $U(4)$ algebra to calculate the stretching and bending vibrational excitations of linear triatomic and tetratomic molecules. The situation up to 1995 was reviewed in a study by Iachello and Levine [5]. Oss has presented a comprehensive and up-to-date review of mathematical concepts, physical aspects, practical applications and numerical implementation of algebraic models in molecular spectroscopy [6]. Iachello and Oss [7] presented a brief review of the work done

in this field up to 2000 and also provided perspectives for the algebraic method in the first decade of the 21st century. Recently, using Lie algebraic method we have reported better results [8] for vibrational energy levels of HCN than those reported earlier. The vibrational energy levels of HCN obtained by local Hamiltonian give better results than that by triatomic carbonyl sulphide molecule [9]. The $U(2)$ model was particularly successful in explaining stretching vibrations of polyatomic molecules such as tetrahedral, octahedral and benzene-like molecules [10–17]. In the Lie algebraic method, there is a provision to study molecular vibrational energy by a normal and a local Hamiltonian. There is a renewed interest to study the vibrational excitation of two types of tetrahedral molecules, SnBr_4 and CCl_4 , by Lie algebraic approach. In this paper, the stretching vibrational excitations of SnBr_4 and CCl_4 are predicted first time to locate theoretically the overtone energy values in one-dimensional framework. The calculated vibrational excitations of CCl_4 up to $v = 2$ is compared with observed data. However, due to lack of sufficient database, we could not compare the calculated vibrational energy levels with that of the observed data of SnBr_4 at higher overtones. This theoretical study will be useful to the experimentalists to analyse the predicted vibrational energies with the observed data.

2. The algebraic theory

The interpretation of experimental data by solving Schrödinger equation with interatomic potentials becomes increasingly difficult as the number of atoms in the molecule increases. Similarly, Dunham expansion contains large numbers of parameters which cannot be determined from the few available data. The third approach is the algebraic model in which each bond is represented by $U(4)$ algebra [2] (the vibron model). It contains information about both the rotation and vibration energy levels of molecules considered. The $U(2)$ model is very much successful in explaining the stretching and bending vibrational energies of medium size molecules. The algebraic Hamiltonian in the $U(2)$ model is constructed with the Casimir and Majorana operators of $U(2)$ [11].

In this section, we use the $U(2)$ algebraic model which was introduced as an alternative approach to the traditional Dunham expansion and Schrödinger equation for tetrahedral molecules. This model which may be called one-dimensional vibron model, starts from the observation that the eigenstates of one-dimensional Schrödinger equation with a Morse potential [13],

$$h(p, x) = \frac{p^2}{2\mu} + D [1 - \exp(-\alpha x)]^2 \quad (2.1)$$

can be put into one-to-one correspondence with the representation of the algebra $U(2) \supset O(2)$ characterized by the quantum numbers $|N_1, m\rangle$, with the provision that one takes only the positive branch of m , i.e., $m = N_1, N_1 - 1, N_1 - 2, \dots, 1$ or 0 for $N_1 = \text{odd}$ or even ($N_1 = \text{integer}$). However, to have complete description of molecular vibrations we need both stretching and bending modes. This is achieved by considering the isomorphism of $U(2)$ Lie algebra with the solution of Schrödinger equation with another potential called Poschl–Teller potential [18].

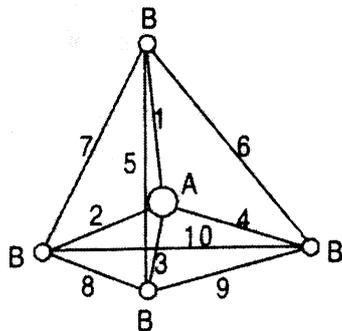


Figure 1. Assignment of the $U^i(2)$ algebra to the tetrahedral molecule.

This potential is very much applicable for calculating bending vibrations where Morse potential is not appropriate. The eigenstates of Schrödinger equation with Hamiltonian operator is

$$h(p, x) = \frac{p^2}{2\mu} - \frac{D}{\cosh^2 \alpha x}. \quad (2.2)$$

It can also be put into one-to-one correspondence with the representation of $U(2) \supset O(2)$, characterized by the quantum numbers $|N_2, m\rangle$, with the provision that one takes only the positive branch of m , i.e., $m = N_2, N_2 - 1, N_2 - 2, \dots, 1$ or 0 for $N_2 = \text{odd}$ or even ($N_2 = \text{integer}$). In the above equation, the coordinate x is the product of the radius of bender r times the bending angle θ , i.e., $x = r\theta$.

For a tetrahedral molecule like AB_4 (figure 1), we introduce four $U(2)$ Lie algebra to describe four stretching bonds (A-B) and six $U(2)$ Lie algebra to describe six bending bonds (B-B) respectively. The two possible chains [11] of molecular dynamical groups in tetrahedral molecule are

$$U^1(2) \otimes \dots \otimes U^{10}(2) \supset O^1(2) \otimes \dots \otimes O^{10}(2) \supset O(2) \quad (2.3)$$

$$U^1(2) \otimes \dots \otimes U^{10}(2) \supset U(2) \supset O(2) \quad (2.4)$$

which correspond to local and normal coupling respectively. The coupling to final $O(2)$ group in the first chain is carried out through different intermediate couplings $O^{ij}(2)$ and the second chain arises from all the possible couplings of $U^i(2)$ groups to obtain a total $U(2)$ group, which in turn contains the final $O(2)$ group [11]. For these two situations the Hamiltonian operator can be diagonalized analytically.

The common algebraic model Hamiltonian in the case of stretching and bending mode for tetrahedral molecules can be considered as [13]

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i<j}^n A_{ij} C_{ij} + \sum_{i<j}^n \lambda_{ij} M_{ij}, \quad (2.5)$$

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.

The simplest basis to diagonalize the Hamiltonian is characterized by the representation of local mode chain [10].

$$\begin{array}{cccccccc}
 |U^1(2) \times \dots \times U^4(2) \times U^5(2) \times \dots \times U^{10}(2) \supset O^1(2) \times \dots \times O^{10}(2) \supset O(2)\rangle \\
 \downarrow \qquad \qquad \qquad \downarrow \\
 [N_1] \dots \dots \dots [N_1] \quad [N_2] \dots \dots \dots [N_2] \quad v_1 \dots \dots \dots v_{10}; \quad V
 \end{array} \tag{2.6}$$

where below each group we have used quantum numbers characterizing the eigenvalues of the corresponding invariant operator. N_1 and N_2 are the number of bosons related to two sets of physical modes (stretching and bending). The quantum numbers v_i correspond to the number of quanta in each oscillator while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^{10} v_i. \tag{2.7}$$

For a particular polyad, the total vibrational quantum number is always conserved. The inclusion of M_{ij} in the local Hamiltonian operator cannot affect the $V = \sum_{i=1}^{10} v_i$ conservation rule. In eq. (2.5), C_i is an invariant operator of uncoupled bond with eigenvalues $4(v_i^2 - N_i v_i)$ and the operator C_{ij} for coupled bonds are diagonal with matrix elements [13].

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)] \tag{2.8}$$

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

$$\begin{aligned}
 \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle &= (N_i v_j + N_j v_i - 2v_i v_j), \\
 \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\
 &= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2}, \\
 \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\
 &= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2}.
 \end{aligned} \tag{2.9}$$

For a tetrahedral molecule AB_4 , we number the bonds from 1 to 10 as shown in figure 1. It is seen that all stretching bonds (A-B) from 1 to 4 are equivalent. Thus, we choose the parameters for stretching bond as $N_i = N_1$, $A_i = A_1$ (for $i = 1-4$), $A_{ij} = A_{12}$ and $\lambda_{ij} = \lambda_{12}$ (for $i = 1-3$ and $j = 2-4$). Similarly, for bending bonds (B-B) from 5 to 10, we choose the parameters as $N_j = N_2$, $A_i = A_5$ (for $i = 5-10$), $A_{ij} = A_{5,6}$ and $\lambda_{ij} = \lambda_{5,6}$ (for $i = 5-9$ and $j = 6-10$). The parameters λ_{ij} describe the interactions between stretching bonds (λ_{12}) and interactions between bending bonds ($\lambda_{5,6}$) respectively.

The values of N_1 and N_2 can be determined by the relation [6]

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \quad i = 1, 2, \tag{2.10}$$

where ω_e and $\omega_e x_e$ are the spectroscopic constants of diatomic molecules of stretching and bending interactions of molecules considered.

Table 1. Fitting parameters* used in the study of SnBr_4 .

Boson numbers		Stretching parameters			Bending parameters		
N_1	N_2	A_1	A_{12}	λ_{12}	A_5	$A_{5,6}$	$\lambda_{5,6}$
399	295	-0.155	2.23	0.0538	-0.275	-0.0272	0.0202

* $A_1, A_{12}, A_5, A_{5,6}, \lambda_{12}, \lambda_{5,6}$ all are in cm^{-1} whereas N_1 and N_2 are dimensionless.

Table 2. Experimental and calculated energies (cm^{-1}) of SnBr_4 (ref. [19]).

V	Normal level	Γ	Experimental	Calculated
1	ν_1	A_1	220	220
	ν_2	E	66.5	66.63
	ν_3	F_2	306	305.86
	ν_4	F_2	90.5	90.46
2	$2\nu_1$	A_1		385.19
	$\nu_1 + \nu_3$	F_2		543.67
	$2\nu_3$	A_1		564.5
		F_2		556.9
		E		556.86

Table 3. Fitting parameters* used in the study of CCl_4 .

Boson numbers		Stretching parameters			Bending parameters		
N_1	N_2	A_1	A_{12}	λ_{12}	A_5	$A_{5,6}$	$\lambda_{5,6}$
342	140	-0.155	-0.0303	0.2426	-1	-0.0765	0.1758

* $A_1, A_{12}, A_5, A_{5,6}, \lambda_{12}, \lambda_{5,6}$ all are in cm^{-1} whereas N_1 and N_2 are dimensionless.

From the view of group theory, the first four equivalent oscillators (A–B) describe the fundamental stretching modes ($A_1 \otimes F_2$) and the next six equivalent ones describe fundamental bending modes ($E \otimes F_2$) for $V = 1$. As is well-known, there are only five degrees of freedom for the bending vibrations, so that the six bending oscillators must contain a spurious state in local wave function (2.3). When $V = 2$, the stretching vibrational states are separated into five sets of irreps [Γ]: two A_1 , one E and two F_2 , and the bending vibrational states are separated into ten sets: three A_1 , three E , three F_2 and one F_1 . There are also five sets spurious states in $V = 2$. Thus, these spurious states can be removed from the basis by introducing the projection operators [11].

3. Results and discussion

The values of fitting parameters of SnBr_4 and CCl_4 molecules are given in tables 1 and 3 respectively. In tables 2 and 4, we report the results of stretching vibrational

Table 4. Experimental and calculated energies (cm^{-1}) of CCl_4 (refs [20–22]).

V	Normal level	Γ	Experimental	Calculated
1	ν_1	A_1	460	459.76
	ν_2	E	214.2	214.50
	ν_3	F_2	792	791.64
	ν_4	F_2	313.5	312.90
2	$2\nu_1$	A_1		917.53
	$\nu_1 + \nu_3$	F_2	1234.2	1251.37
	$2\nu_3$	A_1		1580.84
		F_2	1533	1580.83
		E		1580.82

energy of Sn–Br (C–Cl) up to first overtone and two bending fundamental vibrational energy of Br–Br (Cl–Cl) using the model Hamiltonian (2.5). With the help of model Hamiltonian, we calculate the vibrational frequencies with good accuracy. In tables 2 and 4, the irreps (Γ) for $V = 1$ corresponds to A_1 , F_2 (for stretching) and E , F_2 (for bending). There are also five stretching vibrational states separated into two A_1 , one E and two F_2 irreps (Γ) for $V = 2$. The calculated energies of two tetrahedral molecules are: for SnBr_4 : $\nu_1 = 220$ (A_1), $\nu_2 = 66.63$ (E), $\nu_3 = 305.86$ (F_2), $\nu_4 = 90.46$ (F_2); $2\nu_1 = 385.19$ (A_1), $(\nu_1 + \nu_3) = 543.67$ (F_2), $2\nu_3 = 564.5$ (A_1), 556.9 (F_2), 556.86 (E) cm^{-1} and for CCl_4 : $\nu_1 = 459.76$ (A_1), $\nu_2 = 214.5$ (E), $\nu_3 = 791.64$ (F_2), $\nu_4 = 312.9$ (F_2); $2\nu_1 = 917.53$ (A_1), $(\nu_1 + \nu_3) = 1251.37$ (F_2), $2\nu_3 = 1580.84$ (A_1), 1580.83 (F_2), 1580.82 (E) cm^{-1} . In view of the fact that there are very few available observed data, tables 2 and 4 should be considered more as a prediction of unknown states rather than a fit. The model Hamiltonian (2.5) contains up to two body interactions. It is certainly possible to include in the model Hamiltonian higher powers and products of Casimir operators. This may improve the vibrational description considerably, especially for higher vibrational excitations. The interactions included in the Hamiltonian assume the conservation of total number of quanta V . This means that the Darling–Dennison interactions have been taken into account, but like Fermi resonances, have not been included in the model Hamiltonian. The vibron number for two molecules is calculated using eq. (2.10) which gives the number of bound states in each molecule.

4. Conclusion

Using model Hamiltonian, we have presented an algebraic model of coupled one-dimensional Morse oscillators which can be used to describe A–B stretching vibrations of tetrahedral molecules with good accuracy. The model presented here describes the splitting of local Sn–Br (and C–Cl) stretching modes due to residual interbond interactions. In the fundamental, the splitting is ≈ 83 cm^{-1} (Sn–Br) and ≈ 332 cm^{-1} (C–Cl). The splitting pattern determines the nature of interaction (parameter λ_{12}). Once we get the parameter, one then predict the splitting pattern of

overtone. From the obtained parameters, we see that the interaction between the bending vibrations are weak, when compared with the stretching vibrations for two molecules. These conclusions can be drawn from algebraic Hamiltonian. It is worth pointing out that most applications of the previous algebraic models are restricted to vibrations of gas molecules. The present calculations demonstrate that $U(2)$ model can be applied successfully to solid and liquid phases as well. It is necessary to mention that we have used standard normal mode notation. However, for highly excited states, this notation may not be appropriate. More satisfactory results will be obtained if the interaction between the stretch and the bend is considered. It is believed that once we get the observed energy levels of higher overtones and combination bands, the comparison of calculated bands can be easily done with the help of model Hamiltonian using the parameters.

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