

## Vibrational spectrum of $\text{CF}_4$ isotopes in an algebraic model

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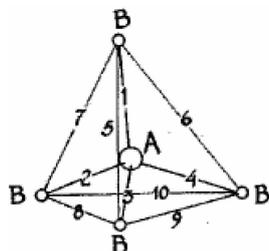
**Abstract.** In this paper the stretching vibrational modes of  $\text{CF}_4$  isotopes are calculated up to first overtone using the one-dimensional vibron model for the first time. The model Hamiltonian so constructed seems to describe the C–F stretching modes accurately using a relatively small set of well-defined parameters.

**Keywords.** Vibron model; vibrational energy level; tetrahedral molecules.

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### 1. Introduction

In the last few decades, the spectroscopy of medium and large molecules has received considerable attention as a result of new experimental techniques. On the other hand, theoretical approaches are also pushed towards their intrinsic limit, in order to provide reliable answers to the hitherto unresolved questions in complex situations. The first theoretical approach of interpreting the experimental data by solving the Schrödinger equation with interatomic potentials become difficult as the number of atoms in the molecule increases. The second approach, Dunham expansion [1], contains a large number of parameters which cannot be determined from the few available experimental data. To overcome the difficulties in analysing the vibrational spectra by traditional methods, a third approach, i.e. the vibron model (the algebraic models) based on Lie algebra [2] was developed in the second half of the 20th century. This new model appears to describe the molecular spectra successfully even in complex situations. The use of Lie algebra did not develop fully until 1970s when it was introduced in a systematic fashion by Iachello and Arima to study the spectra of atomic nuclei (interacting boson model) [3]. The algebraic model which was originally developed for diatomic and triatomic molecules [4,5]



**Figure 1.** Schematic representation of an  $AB_4$  tetrahedral molecule.

was extended to study the spectra of linear and quasilinear tetratomic molecules [6], tetrahedral molecules [7], benzene [8] and octahedral molecules [9]. Iachello and Oss presented a brief review of the development of algebraic techniques and their application to molecular spectroscopy [10] in the intervening years up to 2000. The main features and applications of Lie algebraic methods have been described in [11–13] in the last few years. Using one-dimensional vibron model the infrared spectra of CH bonds in n-paraffin molecular chain [14], CH stretching modes of n-alkane [15] and polyethylene [16] molecules were computed. Recently, we have reported the results of vibrational spectra of HCN, OCS [17–19]; HCCF, HCCD [20];  $CCl_4$ ,  $SnBr_4$  [21]; Ni(OEP), Ni(TPP), Ni porphyrin [22]; propadiene [23] and comparison between OCS and HCP [24] by an algebraic approach using only a few algebraic parameters. The algebraic approach gives very useful results compared to experimental values in such types of molecules we considered. In Lie algebraic approach, there is a provision to study molecular vibrational energy by a normal and local Hamiltonian. Carbon tetrafluoride is one of the most extensively studied molecule belonging to the tetrahedral family with point group  $T_d$ . Due to its wide-ranging industrial and environmental applications, there is once again a renewed interest to study the vibrational excitation of isotopes of  $CF_4$  molecules by algebraic approach. For carbon tetrafluoride molecules, higher excited vibrational levels are obtained for the first time using  $U(2)$  algebraic approach. Our analysis suggests some reassignments of levels and predicts location of states which are not yet observed.

## 2. Theory: The algebraic model

For more than 20 years, one-dimensional vibron model is being used in molecular spectroscopy. Here, we start with the most important feature of algebraic technique, i.e. replacement of molecular interatomic bond coordinates with boson creation/annihilation operators and their quadratic combinations. Such operators produce anharmonic sequences of vibrational states associated with Morse or Poschl–Teller potential functions (for stretching or bending modes respectively). These operators can be put in close correspondence with unitary algebraic structure which is then combined to provide the so-called spectrum generating algebra of the physical system.

For a tetrahedral molecule like  $AB_4$  (figure 1), four  $U(2)$  Lie algebra are considered to describe four stretching bonds (A–B) and six  $U(2)$  Lie algebras to describe six bending bonds (B–B) respectively. In this study, we mostly focussed on

A–B stretching vibrations of tetrahedral molecules. The two possible chains [7] of molecular dynamical groups in tetrahedral molecules are

$$U_1(2) \otimes U_2(2) \otimes U_3(2) \otimes U_4(2) \supset O_1(2) \otimes O_2(2) \otimes O_3(2) \otimes O_4(2) \supset O(2) \quad (1)$$

$$U_1(2) \otimes U_2(2) \otimes U_3(2) \otimes U_4(2) \supset U(2) \supset O(2) \quad (2)$$

which correspond to local and normal couplings respectively. In the first chain, the final  $O(2)$  group is obtained through different intermediate couplings  $O_{ij}(2)$  and the second chain arises from all possible couplings of  $U_i(2)$  groups to obtain a total  $U(2)$  group which in turn gives the  $O(2)$  group [7]. For these two chains the Hamiltonian operator can be diagonalized analytically. The algebraic Hamiltonian in the case of stretching mode of tetrahedral molecules can be constructed from the two chains (1) and (2) as

$$\widehat{H} = E_0 + \sum_{i=1}^4 A_i \widehat{C}_i + \sum_{i<j=1}^4 A_{ij} \widehat{C}_{ij} + \sum_{i<j=1}^4 \lambda_{ij} \widehat{M}_{ij}. \quad (3)$$

In the above expression, there are three types of effective contributions. The first one,  $\sum_{i=1}^4 A_i \widehat{C}_i$ , describes the four independent anharmonic sequences of vibrational levels associated with four independent local oscillators (C–F bond) in terms of operators  $\widehat{C}_i$ . The second term,  $\sum_{i<j=1}^4 A_{ij} \widehat{C}_{ij}$ , describes cross-anharmonicities between pairs of local oscillators (C–F/C–F) in terms of the operators  $\widehat{C}_{ij}$ . The third term,  $\sum_{i<j=1}^4 \lambda_{ij} \widehat{M}_{ij}$ , leads to anharmonic, non-diagonal interactions between pairs of local oscillators in terms of the operators  $\widehat{M}_{ij}$ . The term  $\widehat{C}_i$  represents an invariant operator of uncoupled bond with eigenvalues  $-4v_i(N_i - v_i)$ ,  $i = 1, 2, 3, 4$  and the term  $\widehat{C}_{ij}$  leads to anharmonicities between a pair of distinct local oscillators which is diagonal with matrix elements given by [9]

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

The modes of four equivalent C–F bonds are now mixed, shifted and split under the action of the operator  $\widehat{M}_{ij}$ . The Majorana operator is used to describe local mode interactions in pairs and has both diagonal and non-diagonal matrix elements given by [9]

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

Then we construct the local vibrational basis given by

$$\left| \begin{array}{cccccccc} U_1(2) \otimes U_2(2) \otimes U_3(2) \otimes U_4(2) \supset O_1(2) \otimes O_2(2) \otimes O_3(2) \otimes O_4(2) \supset O(2) \\ N \quad N \quad N \quad N \quad v_1 \quad v_2 \quad v_3 \quad v_4 \quad V \end{array} \right\rangle. \quad (6)$$

In the above basis, we introduce the vibron number  $N$  which is directly related to the anharmonicity of four local C–F stretching bonds. The quantum numbers  $v_i$  ( $i=1, 2, 3, 4$ ) correspond to the number of quanta in each oscillator while  $V$  is the total vibrational quantum number given by

$$V = \sum_{i=1}^4 v_i. \quad (7)$$

For a particular polyad, the total vibrational quantum number is always conserved. For a tetrahedral molecule  $AB_4$ , stretching bonds numbered from 1 to 4 are equivalent. The algebraic Hamiltonian (eq. (3)) depends on 16 linear parameters ( $A_i, A_{ij}, \lambda_{ij}$ ). The 16 independent parameters are now reduced to 3 ( $A_1, A_{12}, \lambda_{12}$ ) depending on the four equivalent stretching bonds. The parameters determine the strength of individual and coupling stretching bonds respectively. The value of vibron number  $N$  can be determined by the relation [13]

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \quad i = 1, 2, 3, 4, \quad (8)$$

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

### 3. Results and discussion

Vibrational energy levels of  $CF_4$  isotopes are calculated using algebraic Hamiltonian and are listed in table 1. From the view of group theory, the first four equivalent oscillators (C–F) describe the fundamental stretching modes separated into two sets of irreps: one  $A_1$  and one  $F_2$  for  $V = 1$ . In the case of  $V = 2$ , the stretching vibrational states are separated into five sets of irreps: two  $A_1$ , one  $E$  and two  $F_2$ . In this paper, we concentrate only on the stretching vibrations of C–F bonds. Due to lack of data of harmonic and anharmonic constants of F–F (bending) in literatures we could not predict the bending vibrations. In table 1, we have predicted states like  $2\nu_1(1795.96)$  for  $^{12}CF_4$ ;  $\nu_1(905.59)$ ,  $2\nu_1(1789.85)$  for  $^{13}CF_4$  and  $\nu_1(902.5)$ ,  $2\nu_1(1783.79)$  for  $^{14}CF_4$  using algebraic approach. It is seen from table 2 that the fitting parameters are changing from one isotope to the other. The vibron number  $N$  for C–F bond gives the number of bound states of the molecules which also varies for isotopes. As one can see from table 1 that the calculated vibrational energies are in good agreement with experiments, we think that the estimated parameters in table 2 can be used reliably to compute energies of highly excited overtones.

### 4. Conclusion

In the study of vibrational spectra of  $CF_4$  isotopes, we have applied one-dimensional algebraic model. The stretching vibrational energy levels up to first overtone are presented using algebraic Hamiltonian. In table 1, the fundamental splitting

**Table 1.** Vibrational energy levels (in  $cm^{-1}$ ) of isotopes of carbon tetrafluoride.

$v$	Vibrational level	Symmetry	$^{12}CF_4$		$^{13}CF_4$		$^{14}CF_4$	
			Exp.	Calc.	Exp.	Calc.	Exp.	Cal.
1	$\nu_1$	$A_1$	908.5	908.56		905.59	902.5	
	$\nu_3$	$F_2$	1283.2	1283.24	1241.7	1241.79	1208.7	1208.77
2	$2\nu_1$	$A_1$		1795.96		1789.85	1783.79	
	$\nu_1 + \nu_3$	$F_2$	2186.1	2193.58	2145	2148.94	2112	2125.23
	$2\nu_3$	$A_1$	2561.2	2543.71	2477.5	2460.72	2412	2394.68
		$F_2$		2543.71		2460.73		2394.68
	$E$		2543.71		2460.73		2394.68	
$\sigma$ (rms)			4.75 $cm^{-1}$		5.74 $cm^{-1}$		7.26 $cm^{-1}$	

Observed values are taken from ref. [25].

**Table 2.** Fitting parameters of isotopes of carbon tetrafluoride.

$^{12}\text{CF}_4$	$^{13}\text{CF}_4$	$^{14}\text{CF}_4$
$N = 116$	$N = 110$	$N = 104$
$A_1 = -3.30$	$A_1 = -3.25$	$A_1 = -3.15$
$A_{12} = 0.2211$	$A_{12} = 0.1946$	$A_{12} = 0.1591$
$\lambda_{12} = 0.8075$	$\lambda_{12} = 0.7641$	$\lambda_{12} = 0.7360$

The fitting parameters  $A_1$ ,  $A_{12}$ ,  $\lambda_{12}$  are in  $\text{cm}^{-1}$  and  $N$  is dimensionless.

is  $\approx 374.68$  (for  $^{12}\text{CF}_4$ ),  $\approx 336.2$  (for  $^{13}\text{CF}_4$ ) and  $\approx 306.27$  (for  $^{14}\text{CF}_4$ ) respectively. The splitting pattern determines the nature of interbond interaction ( $\lambda_{ij} = \lambda_{12}$ ). In the present study  $\sigma$ (rms) is reported as 4.75, 5.74 and 7.26  $\text{cm}^{-1}$  for  $^{12}\text{CF}_4$ ,  $^{13}\text{CF}_4$  and  $^{14}\text{CF}_4$  isotopes respectively. We also believe that more accurate results will be predicted if the higher powers and products of Casimir operators are included in model Hamiltonian. We also hope that this work will stimulate further research in analysing vibrational spectra of isotopes of other tetrahedral molecules where algebraic approach has not been applied so far. This study will be useful to the experimentalist to analyse the predicted vibrational frequencies with the observed data. We can also discuss the spectroscopic properties, isotope effects and the characteristics of potential energy surface with this algebraic Hamiltonian. The research work concerned is in progress.

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