



Lie Algebraic Approach to the Stretching Vibrational Spectra of Bent H_2O Molecule

Joydeep Choudhury^{*1}, Srinivasa Rao Karumuri¹, Rupali sinha¹, Nirmal Kumar Sarkar² and Ramendu Bhattacharjee¹

¹ Department of Physics, Assam University, Silchar-788011, India

² Department of Physics, Karimganj College, Karimgang-788710, India

Correspondence; *e-mail : choudhuryjoy@rediffmail.com

Abstract

The most interesting areas of current research in Molecular physics is the study of the vibrational excited states of medium and large molecules using Lie algebra. The highly stretching vibrational energy levels of H_2O molecule are calculated using $U(2)$ algebraic approach. The model Hamiltonian so constructed appears to describe the vibrational energy levels accurately.

Key words : Algebraic Model, Vibrational Spectra, H_2O .

Introduction

The algebraic methods have been found to be very much useful in the study of vibrational spectra of medium and large molecules using Lie algebra, especially after the development of quantum mechanics in the first part of 20th century. The interesting area of current research in molecular physics is to interpret the experimental data with the help of theoretical models. Two traditional approaches like Dunham like expansion of energy levels in terms of rotation-vibration quantum number and the solution of Schrödinger equation with potentials have been used so far in the analysis of experimental data. The new theoretical concept-vibron model (based on Lie algebra) to study molecular spectra was built in the last part of the 20th century (Levine and Wulfman, 1979; Iachello, 1981). This new model seems to offer a concrete and complementary technique to the traditional approaches used in molecular spectroscopy. The algebraic model (vibron model) was originally developed for diatomic and tri-atomic molecules (Iachello and Levine, 1982; Roosmalen et al., 1983). $U(4)$ and $U(2)$ algebraic model been used so far in the analysis of experimental data. It is to be pointed out that the $U(4)$ model becomes complicated when the number of atoms in a

molecule increases more than four. The vibron model was applied successfully in describing the overtone frequencies of linear and bent X_2Y molecules (Child and Lawton, 1982; Iachello et al., 1981; Iachello and Oss, 1990; Piliva, 2000). Later, it was extended to linear and quasi-linear tetratomic molecules (Iachello et al., 1991, 1993; Iachello and Oss, 1993) and could prove itself to be a competitive one to the traditional analysis. The main features and basic applications of these methods have been described by Iachello and Levine (Iachello and Levine, 1995) and Oss. The brief review of the research work done in this field up to 2000 and its perspectives in the first part of 21st century was presented by Iachello and Oss (Iachello and Oss, 2002). Lie algebraic approach was found to be successful in our study of vibrational frequencies of HCN (Sarkar et al., 2006), HCCF, HCCD (Sarkar et al., 2008), tetrahedral (Choudhury et al, 2008) and Nickel metalloporphyrins (Karumuri et al., 2008). The stretching vibrations of some polyatomic molecules like octahedral, benzene, pyrrole, n-paraffin molecules, n-alkane molecules and polyethylene (Iachello and Oss, 1991a, 1991b, 1992, 1993; Lubich and Oss 1997; Marinkovic and Oss,

2002,2003; Oss, 2006) have been described using $U(2)$ algebra. There is a renewed interest to study the vibrational excitations of bent triatomic molecule H_2O due to its importance not only in human life but also in scientific research. In this paper we use the $U(2)$ algebraic model to calculate the highly excited vibrational states of H_2O .

$$U_1(2) \otimes U_2(2) \supset O_1(2) \otimes O_2(2) \supset O_{12}(2)$$

$$\text{quantum numbers : } N_1 \quad N_2 \quad n \quad m \quad n+m \quad (1)$$

$$U_1(2) \otimes U_2(2) \supset U_{12}(2) \supset O_{12}(2)$$

$$\text{quantum numbers : } N_1 \quad N_2 \quad v_1 + v_2 \quad (2)$$

Where the equation (1) and (2) correspond to local and normal coupling respectively. The quantum numbers corresponding to various algebras are indicated by n, m in equation (1) and v_1, v_2 in equation (2). N_1 and N_2 are vibron numbers corresponding to the number of bound states of two oscillators and are constant for the system. It is to be noted here that $n + m = v_1 + v_2$ is a conserved quantity.

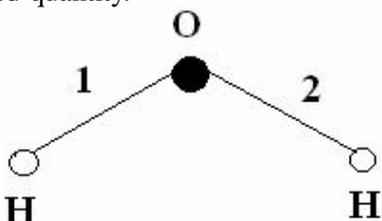


Fig. 1 : Schematic representation of a H_2O molecule.

Theory of Algebraic Model

In case of a tri-atomic molecule like X_2Y (figure 1), we introduce two $U(2)$ Lie algebra to describe two stretching bonds (X-Y) respectively. Two possible chains of molecular dynamical groups in tri-atomic molecules are described by

The generalized algebraic model Hamiltonian for H_2O molecule can be constructed from the bilinear Casimir invariants \mathcal{C} of all algebras in the two chains (Levine and Wulfman, 1979; Iachello, 1981):

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

where i runs from 1 to 2 for two stretching bonds and A_1, A_2, A_{12} and λ_{12} are algebraic parameters can be determined by spectroscopic data. Here, v_1 and v_2 denote the local stretching vibrations while v_3 denotes bending vibrations. The Hamiltonian (3) can be diagonalized to get the predicted energy values.

In equation (3), \mathcal{C}_i is an invariant operator of uncoupled bond with eigenvalues $4(v_i^2 - N_i v_i)$ and

the operator \mathcal{C}_{ij} for coupled bonds are diagonal with matrix elements

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

while the operator \mathcal{M}_{ij} has both diagonal and non-diagonal matrix element

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

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

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

For a tri-atomic molecule X_2Y , we choose the parameters for stretching bond as $N_i = N_1, A_i = A_1$ (for $i=1$ to 2), $A_{ij} = A_{12}$ and $\lambda_{ij} = \lambda_{12}$ (for $i, j=1, 2$). The parameters λ_{ij} describes the interactions between stretching bonds (λ_{12}).

The values of N can be determined by the relation

$$N = \frac{\omega_e}{\omega_e x_e} - 1 \quad (6)$$

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

Results and Discussions

Using the algebraic Hamiltonian, 44 vibrational energy levels of H_2O were calculated and shown in table 1. Using equation (6), vibron number N is found out. The values of algebraic parameters $N, A, A_{12}, \lambda_{12}$ are listed in table 2. The local behaviour

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of stretching modes of polyatomic molecule can be characterized by the quantity

$$\xi = \frac{2}{\pi} \tan^{-1} \left[\frac{8\lambda_{12}}{(A + A_{12})} \right]$$

We find $\xi = 0.2455$ for the O-H stretching bond which confirms the local behaviour of the stretching modes of water molecule. Four parameters are chosen to fit 20 observed data. Here, we have predicted the vibrational energy levels up to $v = 8$. The algebraic Hamiltonian preserves the total quantum number in a particular polyad. The vibrational energy level goes on increasing as we move to higher polyad. In our calculation lowest and highest energy values are $3,657.80 \text{ cm}^{-1}$ and $27,696.32 \text{ cm}^{-1}$ respectively. The model appears to describe the vibrational energy accurately except few excited energy levels.

Table 1 : Vibrational energy levels (in cm^{-1}) of water.

$(v_1 v_2 v_3)$	observed	calculated	(obs-cal)
(1 0 0)	3657.05	3657.80	-0.75
(0 0 1)	3755.93	3747.56	8.37
(2 0 0)	7201.54	7155.08	46.46
(1 0 1)	7249.82	7244.48	5.34
(0 0 2)	7445.05	7484.04	-38.99
(3 0 0)	10599.66	10580.76	18.90
(2 0 1)	10613.41	10668.24	-54.83
(1 0 2)	10868.86	10794.43	74.43
(0 0 3)	11032.40	11057.60	-25.20
(2 0 2)	13828.30	13665.93	162.37
(3 0 1)	13830.92	13843.40	-12.48
(4 0 0)	14221.14	14211.45	9.69
(1 0 3)	14318.80	14468.23	-149.43
(0 0 4)	14536.87	14536.44	.44
(3 0 2)	16898.40	16857.69	40.71
(4 0 1)	16898.83	16943.36	-44.53
(5 0 0)	17458.20	17377.32	80.88
(2 0 3)	17495.52	17591.24	-95.72
(1 0 4)	17748.07	17715.95	32.12
(0 0 5)	17970.90	17938.03	32.87
(4 0 2)		19880.40	
(5 0 1)		19962	
(6 0 0)		20292.79	
(3 0 3)		20555.96	
(2 0 4)		20833.07	
(1 0 5)		21077.64	
(0 0 6)		21256.28	

(5 0 2)	22315.87
(6 0 1)	22572.92
(7 0 0)	23400.32
(4 0 3)	23645.13
(3 0 4)	23922
(2 0 5)	24048.19
(1 0 6)	24330.01
(0 0 7)	24476.60
(6 0 2)	25186.15
(7 0 1)	25265.72
(8 0 0)	26083.80
(5 0 3)	26167.44
(4 0 4)	26757.32
(3 0 5)	27187.19
(2 0 6)	27276.94
(1 0 7)	27620.84
(0 0 8)	27696.32

Table 2 : Algebraic parameters in the Hamiltonians for H_2O .

$N_1 = N_2 = N$	44
$A_1 = A_2 = A$	-18.98
A_{12}	1.13
λ_{12}	1.02

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

Conclusion

On the basis of local model the highly excited vibrational energy levels are predicted for H_2O molecule with few numbers of parameters. We believe that more satisfactory results will be obtained if quadratic terms of interactions are taken in to account. In last twenty five years Lie algebraic approach was found to be successful in explaining vibrational energy levels of small, medium, polymers, biomolecules and biopolymers. In view of many possible applications, it is hoped that present calculation will open new windows in the field of spectroscopy.

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