Brief communication

Vibrational Frequencies of Dichlorine Monoxide: A Mathematical Model

N. SRINIVAS[1] and J. VIJAYASEKHAR[2]*

[1]Research Scholar, Department of Mathematics, GITAM Deemed to be University, Hyderabad, India.
[2]Department of Mathematics, GITAM Deemed to be University, Hyderabad, India.
*Corresponding author E-mail: vijayjaliparthi@gmail.com

ABSTRACT

We have determined stretching vibrational frequencies of a triatomic molecule, i.e. Dichlorine monoxide (Cl_2O) upto third overtone by Lie algebraic method. Fundamental vibrational wavenumbers calculated by Lie algebraic model are compared with available experimental values.

Keywords: Vibrational spectra, Lie algebraic method, Dichlorine monoxide (Cl_2O).

INTRODUCTION

Calculation of fundamental and higher overtones of molecule is useful to understand molecular structure. We applied Lie algebraic method to calculate vibrational frequencies (wavenumbers) of molecule. This mathematical approach helps to calculate vibrational frequencies in higher overtones and moreover useful to compare in-vivo experimental results. The vibrational wavenumbers of the molecule are analyzed by means of traditional approaches, Dunham series expansion and Potential function approach. The noticable demerit of these approaches are, requirement of huge experimental data to fit the parameters. We choose this method, as it overcomes this difficulty. In this method, vibrational frequencies are calculated using Hamiltonian operator[1-6].

Lie algebraic method for Cl_2O

Dichlorine monoxide (Cl_2O) contains two chlorine (Cl) atoms and one oxygen atom with two Cl-O bonds. Symmetry point group is C_{2v} with symmetry species A_1 (Cl-O symmetric stretching),. B_2 (Cl-O asymmetric stretching) and A_1 (Cl-O-Cl bending). This framework explains the stretching bonds in Cl_2O molecule using two Lie algebras i.e.

Below mentioned two chains, explains the molecular dynamical group.

$$\text{Chain(I):} \quad U_1(2) \otimes U_2(2) \supset O_1(2) \otimes O_2(2) \supset O_{12}(2)$$
$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$
$$N_1 \quad N_2 \quad n \quad m \quad n+m$$

$$\text{Chain(II):} \quad U_1(2) \otimes U_2(2) \supset U_{12}(2) \supset O_{12}(2)$$
$$\downarrow \quad \downarrow \quad \downarrow$$
$$N_1 \quad N_2 \quad v_1 + v_2$$

Chain (I) represents the local and chain (II) represents the normal couplings. Quantum numbers in the chain (I) related to algebras,

indicated by n, m and in the chain (II) are v_1, v_2. Vibron numbers N_1 and N_2 are taken to be constants and are related to the maximum number of bound states of two Morse oscillators. Bending vibrations can be represented with the algebra $U_3(2)$ and combined with the algebra associates with the $U_1(2) \otimes U_2(2)$ coupled stretching vibrations. Hamiltonian operator.[9,10] (stretching vibrations) of this molecule:

$$H = E_0 + A_1 C_1 + A_2 C_2 + A_{12} C_{12} + \lambda_{12} M_{12} \qquad (1)$$

In equation (1), A_1, A_2, A_{12} are λ_{12} the algebraic parameters, which are calculated from experimental spectra. The local stretching vibrations are denoted by (v_1) and (v_3), whereas (v_2) representing bending vibrations for Cl_2O. The Hamiltonian in the equation (1) can be diagonalized to get vibrational frequencies. Where in the equation (1), C_1, C_2 are invariant operators of the uncoupled bonds with eigenvalues $-4(N_i v_i - v_i^2)$ (i = 1,2) and C_{ij} (i = 1, 2) operator for coupled bonds is diagonal with matrix elements.

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

The Majorana operator M_{ij} (i =1,2) in the equation (1), describes local mode interactions in pairs and provide diagonal and non-diagonal matrix elements.

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

$$\langle N_i, v_i+1; N_j, v_j-1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -\sqrt{v_j(v_i+1)(N_i - v_i)(N_j - v_j + 1)} \qquad (3)$$

$$\langle N_i, v_i-1; N_j, v_j+1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -\sqrt{v_i(v_j+1)(N_j - v_j)(N_i - v_i + 1)}$$

The Hamiltonian matrix for the local modes is given by

$$H = \begin{bmatrix} -4\bar{A}(N-1) - 4A_{12}(2N-1) + \lambda_{12}N & \lambda_{12}N \\ \lambda_{12}N & -4\bar{A}(N-1) - 4A_{12}(2N-1) + \lambda_{12}N \end{bmatrix}$$

RESULTS AND DISCUSSION

The parameters for stretching bonds of the water molecule in equations (1), (2) and (3) as $N_i = N$, $A_i = A$, $A_{ij} = A_{12}$, $\lambda_{ij} = \lambda_{12}$ (i = 1, 2) . The vibron number N_i (i = 1, 2) calculated from the relation.[9]

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1$$

Here ω_e and $\omega_e x_e$ are the spectroscopic constants[11]. The value of the parameter A is obtained by using the energy equation[9,10] for the single-oscillator fundamental mode, which can be calculated from

$$E(v = 1) = 4A(1 - N) \qquad (4)$$

Using the equation (4), can be evaluated as,

$$\bar{A} = \frac{\bar{E}}{(4N - 4)} \qquad (5)$$

In equation (5), $\bar{A}$ and $\bar{E}$ are the average values of the algebraic parameters A's and E's.

The initial value of λ_{12}, estimate by the relation[10],

$$\lambda_{12} \cong \frac{|E_1 - E_2|}{3N} \qquad (6)$$

In order to calculate accurate results, a numerical regression fitting method is used to fit the algebraic parameters A, λ_{12} starting from the values as given by equations (5) and (6). The initial value of A_{12} assumming as zero.

Table 1: Stretching vibrational frequencies (in cm⁻¹) of Cl₂O

vib. quantum no.	observed[11]	calculated
(1 0 0)	639	638.274
(0 0 1)	686	686.932
(2 0 0)	-	1245.407
(0 0 2)	-	1357.652
(3 0 0)	-	1911.094
(0 0 3)	-	2043.086
(4 0 0)	-	2537.335
(0 0 4)	-	2687.320

N= 154, A= -1.9091, A_{12} = 0.9328, λ_{12} = 0.1863

CONCLUSION

Stretching vibrational frequencies of Cl_2O upto third overtone are calculated and compared with experimental data in fundamental mode. Vibrational frequencies (stretching) of Cl_2O are

in close agreement with experimental values in fundamental mode.

ACKNOWLEDGMENT

Conflicts of Interest

The authors declare no conflict of interest.

REFERENCES

1. Iachello, F. *Chem. Phys. Lett.*, **1981**, *78*(3), 581-585.

2. Iachello, F. ; Levine, R. D. *J. Chem. Phys.*, **1982**, *77*, 3046-3055.

3. Frank, A.; Iachello, F.; Lemus, R. *Chem. Phys. Lett.*, **1986**, *131*(4-5), 380-383.

4. Karumuri, S. R.; Vijayasekhar, J.; Sreeram, V.; Uma Maheswara Rao, V.; Basaveswara Rao, M. V. *J. Mol. Spectrosc.*, **2011**, *269*, 119-123.

5. Karumuri, S. R.; Srinivas, G.; Vijayasekhar, J.; Rao, V. U. M.; Srinivas, Y.; Sunil Babu, K.; Kumar, V. S. S.; Hanumaiah, A. *Chin. Phy.* B., **2013**, *22*(9), 090304(1-8).

6. Karumuri, S.R.; Sravani, K.G.; Vijayasekhar, J.; Reddy, L.S.S. *Acta Phys. Pol.* A., **2012**, *122*(1), 49-52.

7. Balla, M.R.; Jaliparthi, V.S. *Mol. Phys.*, **2020**. DOI: 10.1080/00268976.2020.1828634.

8. Frank, A.; Lemus, R.; Bijker, R. *Ann. Phys.*, **1996**, *252*, 211-238.

9. Iachello, F.; Oss, S. *J. Mol. Spectrosc.*, **1990**, *142*(1), 85-107.

10. FENG, Zhaochi.; XIONG, Guang.; YANG, Qihua.; XIN, Qin.; LI, Can. *Chin. Sci. Bull.*, **1999**, *44*(21), 1961-1964.

11. Irikura, K.K. *J. Phys. Chem. Ref. Data.*, **2007**, *36*(2), 389-398.

12. Shimanouchi, T. Tables of Molecular Vibrational Frequencies Consolidated Volume I, *National Bureau of Standards.*, **1972**, 1-160.