Vibrational Spectra of Carbonyl Sulphide by U(2) Lie Algebraic Method

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Authors' contributions

Article Information

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Abstract

In this paper, we have calculated vibrational frequencies of Carbonyl sulphide (OCS) in fundamental level and at higher overtones by Hamiltonian expression, which is in terms of invariant and Majorana operators, describe stretching vibrations. The Hamiltonian is an algebraic one and so far all the operations in this method, unlike the more well-known differential operators of wave mechanics.

Keywords: Vibrational spectra; carbonyl sulphide; U(2) Lie algebraic method.

AMS classification: 81Q05, 81Q35, 81V45.

1 Introduction

U(2) Lie algebraic method has been used to trace the Heisenberg formulation of quantum mechanics [1,2,3,4]. The step up of Lie algebraic method to physical systems was introduced by Iachello and Arima in their initiate work of spectra of atomic nuclei [5-11]. Iachello (1981) presented Lie algebraic method for the study of vibrational spectra of molecules [12]. This method is based on the quantization of the Schrodinger

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wave equation with a three dimensional Morse potential function and is described as ro-vibration spectra of diatomic molecules [13]. The essential idea of the Lie algebraic method is that series expansion of the Hamiltonian in terms of a set of operators characterizes the local and normal modes of the system. The Lie algebraic method allows us to analyse experimental ro-vibrational spectra of polyatomic molecules based on the idea of dynamical symmetry. This Lie algebraic method is used to obtain Hamiltonian operator that provides the description of ro-vibrational degrees of freedom of the physical system [14].

2 Structure of Carbonyl Sulphide

Carbonyl sulphide (OCS) is a linear molecule consisting of a carbonyl group double bonded to a sulphur atom. This consists of two bonds O-C and C-S. The symmetry point group is $D_{\infty h}$.

$$O=C=S$$
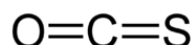
3 U(2) Lie Algebraic Method

The Hamiltonian [15,16] for the molecule (stretching vibrations for n bonds) is of the form

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

The eigenvalues of the Hamiltonian can be evaluated and give a description of n coupled anharmonic vibrations. The couplings in the Hamiltonian are only first order, in the sense that the Majorana operators M_{ij} annihilate one quantum of vibration in bond j and create one in bond i (or vice versa).

Here i vary from 1 to 2 for two stretching bonds (O-C and C-S) and $(A_i, A_{ij}, \lambda_{ij})$ are algebraic parameters, which are calculated by spectroscopic data. Where C_i is an invariant operator of the uncoupled bond with eigenvalues $-4(N_i v_i - v_i^2)$ and the operator C_{ij} for coupled bonds are diagonal with matrix elements

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

while the Majorana operator M_{ij} has both diagonal and non-diagonal matrix elements

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

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

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

$$\ldots \tag{3}$$

Where v_i (i = 1, 2, ...) are vibrational quantum numbers. The vibron number N_i (i =1, 2) for stretching bonds (O-C and C-S) of molecule will be calculated by the following relation

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, i = 1, 2 \quad ... \tag{4}$$

Here ω_e and $\omega_e x_e$ are the spectroscopic constants. The initial guess value for the parameter A_i (i =1, 2) is obtained by using the energy equation for the single-oscillator fundamental mode, which is given as,

$$E(v = 1) = -4A_i(N_i - 1) \quad ... \tag{5}.$$

Initial guess for A_{ij} taken as zero. The parameter λ_{ij} determined from the relation.

$$\lambda_{ij} \cong \frac{|E_i - E_j|}{3N}. \quad ... \tag{6}$$

To get accurate results a numerical fitting procedure is essential to obtain the parameters A_i, λ_{ij} (i, j =1, 2, i≠j) starting from values as given by equations (5) and (6).

4 Results

Calculated vibrational frequencies and fitted parameters by Lie algebraic method are as follows:

Table 1. Fitting parameters

Parameters [17]	OCS
N_1	190
N_2	159
A_1	-1.13 cm^{-1}
A_2	-3.26 cm^{-1}
A_{ij} (O-C bond)	-0.25 cm^{-1}
A_{ij} (C-S bond)	-1.29 cm^{-1}

Table 2. Vibrational frequencies of carbonyl sulphide

Vibrational mode	Vibrational frequencies (cm^{-1})	
	Experimental [18]	U(2) Lie algebraic method
(1 0 0)	859	859.0317
(0 0 1)	2062.2	2061.323
(2 0 0)	1711.1	1712.021
(0 0 2)	4101.4	4100.232
(1 0 1)	2918.1	2918.031
(3 0 0)	2556	2557.934
(0 0 3)	6117.6	6118.469
(2 0 1)	3768.5	3767.008
(1 0 2)	4953.9	4953.156

5 Conclusion

In this paper, vibrational frequencies of Carbonyl sulphide upto second overtone by U(2) Lie algebraic method calculated and also compared with available experimental data. It has been observed that results from the Lie algebraic method make known near to the exact, consistent with the experimental results.

Competing Interests

Authors have declared that no competing interests exist.

References

[1] Born M, Heisenberg W, Jordan P. Quantum mechanics II, Z. Phys. 1926;35:557-615.

[2] Born M, Jordan J. A vibrational principle for invariant-tori of fixed frequency. Z. Phys. 1925;34(1): 858-888.

[3] Dirac PAM. The fundamental equations of quantum mechanics. Proc. Roy. Soc. A. 1925;109:642-653.

[4] Heisenberg W. Quantum theoretical re-interpretation of kinematic and mechanical relations. Z. Phys. 1925;33:879-893.

[5] Arima A, Iachello F. Collective nuclear states representations of a SU(6) group. Phys. Rev. Lett. 1975;35(16):1069-1072.

[6] Arima A, Iachello F. Interacting Boson model of collective nuclear states IV. The O(6) limit, Ann. Phys. (NY). 1979;123(2):468-492.

[7] Arima A, Iachello F. Interacting Boson model of collective states I: The vibrational limit, Ann. Phys. (NY). 1976;99(2):253-317.

[8] Arima A, Iachello F. Interacting Boson model of collective states II: The rotational limit, Ann. Phys. (NY). 1978;111(1):201-238.

[9] Chen JQ, Klein A, Ping JL. Point-group symmetrised Boson representation. Algebraic solution for symmetry-adapted bases of O_h, J. Math. Phys. 1996;37:2400-2421.

[10] Iachello F, Arima A. Boson symmetries in vibron nuclei. Phys. Lett. B. 1974;53(4):309-312.

[11] Iachello F, Arima AA. The interacting Boson model. Cambridge: Cambridge University Press; 1987.

[12] Iachello F. Algebraic methods for molecular rotation-vibration spectra. Chem. Phys. Lett. 1981;78(3): 581-585.

[13] Iachello F, Levine RD. Algebraic approach to rotation-vibration spectra. I-diatomic molecules, J. Chem. Phys. 1982;77:3046-3055.

[14] Iachello F, Levine RD. Algebraic theory of molecules. Oxford University Press, Oxford; 1995.

[15] Oss S. Algebraic models in molecular spectroscopy. Adv. Chem. Phys. 1996;93:455-649.

[16] Vijayasekhar J, Rao KS, Prasad BVSNH. Vibrational frequencies of PH_3 and NF_3: Lie algebraic method. Orien. J. Chem. 2016;32:1717-1719.

[17] Sarkar NK, Choudhury AJ, Karumuri SR, Bhattacharjee R. A comparative study of the vibrational spectra of OCS and HCP using the Lie algebraic method. Eur. Phys. J. D. 2009;53:163–171.

[18] Aubanel EE, Wardlaw DM. Application of adiabatic switching to vibrational energies of three dimensional HCO, H_2O, and H_2CO. J. Chem. Phys. 1987;88:495-517.