

VIBRATIONAL HAMILTONIAN OF CARBONYL SULPHIDE AND HYDROGEN CYANIDE

K. Lavanya^{a,c}, A. Ganapathi Rao^b,  J. Vijayasekhar^{c*}

^aDepartment of Mathematics, St. Francis College for Women, Begumpet, Hyderabad, India

^bDepartment of Basic Sciences and Humanities, GMR Institute of Technology, Rajam, India

^cDepartment of Mathematics, GITAM (Deemed to be University), Hyderabad, India

*Corresponding Author e-mail: vijayjaliparthi@gmail.com

Received January 6, 2023; revised January 21, 2024; accepted February 18, 2024

This study thoroughly investigates the vibrational frequencies of carbonyl sulphide (12C16O32S) and hydrogen cyanide (HCN) up to the fifth harmonic level. It offers comprehensive insights into vibrational modes by using the Hamiltonian operator formalism and concentrating on invariant operators and algebraic parameters with a one-dimensional Lie algebraic method. The findings are significant for atmospheric chemistry, spectroscopy, and quantum chemistry, contributing to a deeper understanding of molecular dynamics. This research sets the groundwork for future studies in comparable compounds and applications.

Keywords: Hamiltonian operator; Lie algebraic method; Carbonyl sulphide; Hydrogen cyanide; Morse Oscillator

PACS: 33.20.-t, 33.20.Ea, 82.80.Gk, 63.50.-x, 45.20. Jj, 47.10.Df, 02.20.Sv

1. INTRODUCTION

The vibrational frequencies of molecules have immense significance in various scientific and practical disciplines. They are essential for understanding atoms interconnectedness and spatial arrangement within a molecule. This knowledge proves essential for precisely identifying molecular structures, especially when addressing complex organic compounds. The motivation behind studying the vibrational frequencies of carbonyl sulphide and hydrogen cyanide is to represent the molecular vibrations precisely, encompassing crucial quantum mechanical complexities. Precision is essential for understanding the molecular dynamics within complex structures. These molecules play a significant role in atmospheric chemistry, and analysing their vibrational frequencies under realistic conditions helps to understand their behaviour, providing valuable insights for atmospheric studies. By studying vibrational frequencies up to the fifth harmonic level, the accuracy of predictions for spectroscopic experiments is improved, facilitating the understanding and analysis of data. This study provides a strong basis for future research and creates opportunities for investigating similar molecules, thereby expanding the knowledge of molecular dynamics.

Essentially, the acquired vibrational frequencies provide an essential understanding of the molecule's behaviour in the atmosphere, offering valuable data for atmospheric monitoring. Moreover, precise data on vibrational frequency play a crucial role in developing and analysing spectroscopic experiments, particularly in environmental monitoring and industrial processes. The results further the development and creation of materials by enhancing our comprehension of their vibrational characteristics concerning desired properties. Moreover, knowing the vibrational frequencies helps evaluate the environmental impact, offering crucial data for assessing potential hazards and implementing measures to minimize negative consequences.

The U(2) Lie algebraic method has been recognized as an effective and widely utilized tool for understanding the complexities of the Heisenberg formulation of quantum mechanics, as evidenced by an essential and expanding body of research. Iachello and Arima are renowned for their systematic application of this method to various physical systems, particularly in their pioneering studies on the spectra of atomic nuclei. Iachello's pioneering work in 1981 expanded the utilization of the Lie algebraic approach to examine vibrational spectra in molecules [1]. The present method focuses on discretizing the Schrödinger wave equation by utilizing a three-dimensional Morse potential function to describe the rovibrational spectra of diatomic molecules precisely. The Lie algebraic method systematically expresses the Hamiltonian using a series expansion that involves a set of operators. This approach illustrates the local and normal modes of the system, offering a systematic framework for analysing experimental rovibrational spectra in polyatomic molecules. By utilizing the concept of dynamical symmetry, it improves our understanding of molecular structure [2, 3, 4].

Furthermore, the Lie algebraic method helps systematically analyse experimental data and allows for generating a Hamiltonian operator. This operator completely encapsulates the rovibrational degrees of freedom within the physical system, improving our ability to comprehend and forecast molecular structure. The Hamiltonian operator, a fundamental component of quantum mechanics, represents the combined effects of the particles' kinetic energy and the potential energy resulting from their interactions [2,3]. When used in vibrational analysis, the Hamiltonian operator provides the most accurate mathematical framework for calculating the quantized energy levels of a molecule. It operates on the system's wave function, producing the corresponding energy eigenvalues. The basic principle governing our ability to analyse and predict the vibrational frequencies of molecules is of the utmost significance in various disciplines, including spectroscopy and chemical kinetics [5,6,7].

This survey highlights a gap in exploring vibrational frequencies for selected molecules, particularly in higher overtones and combination bands. Given the current relevance of this research and the absence of attempts in this direction, the study aims to fill this gap by computing the vibrational frequencies of carbonyl sulphide and hydrogen cyanide up to the fifth harmonic level. To achieve this, a symmetry-adapted one-dimensional Lie algebraic framework will be employed. The anticipated outcome is the generation of accurate vibrational results for the specified molecules, accompanied by high-quality vibrational assignments. Importantly, these calculations are expected to offer a cost-effective alternative to other theoretical methods, such as ab initio approaches, ensuring computational efficiency.

2. LIE ALGEBRAIC METHOD FOR XYZ LINEAR TRIATOMIC MOLECULE OF $C_{\infty v}$ POINT GROUP

The Lie algebraic method is a robust mathematical framework used in quantum mechanics, particularly in studying symmetries and their consequences for physical systems. It involves the application of concepts from the theory of Lie algebras to quantum mechanics. A Lie algebra is a mathematical structure that describes the algebraic properties of certain types of symmetries. In the context of quantum mechanics, symmetries are transformations that leave the physical properties of a system unchanged. The Lie algebraic method is advantageous in studying quantum systems with continuous symmetries. It allows a systematic way to analyse and understand systems' behavior under symmetry operations. The Hamiltonian operator is a central concept in quantum mechanics. It corresponds to the total energy operator of a quantum system. The eigenstates (wavefunctions) of the Hamiltonian operator correspond to the allowed energy states of the system, and the corresponding eigenvalues represent the energies associated with those states. In the Lie algebraic method, one often seeks to find operators that commute with the Hamiltonian. These operators, known as conserved quantities or constants of motion, correspond to the observables associated with the symmetries of the system. The fact that they commute with the Hamiltonian implies that these quantities do not change over time, which is a consequence of Noether's theorem.

By employing the Lie algebraic approach, one can often find a set of operators that form a representation of the Lie algebra associated with the symmetries of the system. These operators can then be used to construct a complete set of commuting observables, which provides a set of compatible measurements that can be simultaneously determined with arbitrary precision.

The Hamiltonian operator (H) associated with the Lie algebraic method for XYZ linear triatomic molecule (involving two stretching bonds, X-Y and Y-Z) is expressed as follows [8, 9, 10, 11, 12]:

$$H = E_0 + \sum_{i=1}^2 A_i C_i + \sum_{i<j}^2 A_{ij} C_{ij} + \sum_{i<j}^2 \lambda_{ij} M_{ij}. \quad (1)$$

A_i, A_{ij} , and λ_{ij} are algebraic parameters (in cm^{-1}) determined based on spectroscopic data. The operator C_i represents an invariant operator of the uncoupled bond, with eigenvalues given by $-4(N_i v_i - v_i^2)$, $i = 1$ (for X - Y), 2 (for Y - Z). For coupled bonds, the operator C_{ij} is diagonal, with matrix elements defined as:

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

The Majorana operator M_{ij} exhibits both diagonal and non-diagonal matrix elements:

$$\begin{aligned} \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle &= (N_i v_j + N_j v_i - 2 v_i v_j) \\ \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{\frac{1}{2}} \\ \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{\frac{1}{2}}. \end{aligned} \quad (3)$$

Where, v_i, v_j represent the vibrational quantum numbers. The vibron numbers N_{X-Y} and N_{Y-Z} for the stretching bonds (X-Y and Y-Z) of the molecule can be calculated using the relation:

$$N_{X-Y} = \frac{(\omega_e)^{X-Y}}{(\omega_e x_e)^{X-Y}} - 1, \quad N_{Y-Z} = \frac{(\omega_e)^{Y-Z}}{(\omega_e x_e)^{Y-Z}} - 1. \quad (4)$$

Here, $\omega_e, \omega_e x_e$ are the spectroscopic constants of diatomic molecules [13, 14]. The initial guess values for the parameters A_{X-Y}, A_{Y-Z} can be obtained using the energy equation for the single-oscillator fundamental mode, given by:

$$E(v = 1) = -4A_i(N_i - 1), \quad i = 1 \text{ (for X - Y)}, 2 \text{ (for Y - Z)}. \quad (5)$$

The initial guess for A_{ij} may be taken as zero. The parameter λ_{ij} can be obtained from the relation:

$$\lambda_{ij}^{X-Y} = \frac{|E_i - E_j|}{3N_{X-Y}}, \quad \lambda_{ij}^{Y-Z} = \frac{|E_i - E_j|}{3N_{Y-Z}} \quad (6)$$

Where, E_i, E_j are vibrational energies of X-Y and Y-Z stretching bonding. A numerical fitting procedure is required to obtain the parameters, starting from the values provided by equations (5) and (6), for more accurate results.

3. RESULTS

Tables (1) and (2) provide a comprehensive analysis of the fundamental experimental vibrational frequencies of carbonyl sulphide (X: O-C, Y: C-S) and hydrogen cyanide (X: C-H, Y: C-N), offering a detailed comparison with their calculated counterparts. These tables go beyond experimental observations, including the predicted vibrational frequencies up to the fifth harmonic level. Additionally, the stretching combinational bands are intricately detailed, enhancing our understanding of the molecular dynamics of both carbonyl sulphide and hydrogen cyanide. Table 3 compiles optimized values for algebraic parameters and dimensionless vibron numbers utilized in our model. All parameters are expressed in cm^{-1} , except unitless vibron numbers.

Table 1. Carbonyl Sulphide Vibrational Frequencies

Vibrational mode	Vibrational frequencies (cm^{-1})	
	Experimental [15,16]	Calculated
ν_1 (CO stretching)	2062.22	2062.22
ν_2 (Bending)	520.41	520.41
ν_3 (CS stretching)	858.95	858.95
$2\nu_1$	-	3807
$2\nu_2$	-	963
$2\nu_3$	-	1614
$3\nu_1$	-	5781
$3\nu_2$	-	1417
$3\nu_3$	-	2320
$4\nu_1$	-	7702
$4\nu_2$	-	1889
$4\nu_3$	-	3196
$5\nu_1$	-	9336
$5\nu_2$	-	2371
$5\nu_3$	-	3884
$\nu_1+2\nu_1$	-	5869.22
$\nu_1+3\nu_1$	-	7843.22
$\nu_1+4\nu_1$	-	9764.22
$\nu_1+5\nu_1$	-	11398.22
$\nu_3+2\nu_3$	-	2472.95
$\nu_3+3\nu_3$	-	3178.95
$\nu_3+4\nu_3$	-	4054.95
$\nu_3+5\nu_3$	-	4742.95

Table 2. Hydrogen Cyanide Vibrational Frequencies

Vibrational mode	Vibrational frequencies (cm^{-1})	
	Experimental [15,16]	Calculated
ν_1 (CH Str)	3311.47	3311.47
ν_2 (Bend)	711.98	711.98
ν_3 (CN str)	2096.85	2096.85
$2\nu_1$	-	6320
$2\nu_2$	-	1324
$2\nu_3$	-	3867
$3\nu_1$	-	9290
$3\nu_2$	-	1983
$3\nu_3$	-	5832
$4\nu_1$	-	12422
$4\nu_2$	-	2729
$4\nu_3$	-	7650
$5\nu_1$	-	14924
$5\nu_2$	-	3224
$5\nu_3$	-	9344
$\nu_1+2\nu_1$	-	9631.47
$\nu_1+3\nu_1$	-	12601.47
$\nu_1+4\nu_1$	-	15733.47
$\nu_1+5\nu_1$	-	18235.47
$\nu_3+2\nu_3$	-	5963.85
$\nu_3+3\nu_3$	-	7928.85
$\nu_3+4\nu_3$	-	9746.85
$\nu_3+5\nu_3$	-	11440.85

Table 3. Fitted Algebraic Parameters in the Vibrational Hamiltonian Operator

Parameters	carbonyl sulphide	hydrogen cyanide
N_{X-Y}	44	162
N_{Y-Z}	156	178
A_1	-11.98	-5.14
A_2	-1.38	-2.96
A_{12}	-0.23	-1.21
λ_{12}	2.91	1.84

4. CONCLUSION

This study uses the symmetry-adapted one-dimensional U(2) Lie algebras framework for precisely calculating the vibrational frequencies of carbonyl sulphide and hydrogen cyanide up to the fifth harmonic level. This comprises the stretching and combinational bands. Our results are compared with experimental data at the first harmonic level, demonstrating a close approximation to the exact values and strongly agreeing with the results of experiments. The constructed vibrational Hamiltonian, which preserves the $C_{\infty v}$ point group, includes the spectra of interacting bound states of Morse oscillators. Furthermore, to the fundamental mode vibrations, the U(2) Lie algebraic Hamiltonian can be applied to higher overtones and combination bands up to the fifth harmonic level. This approach may offer a more cost-effective computational solution than other theoretical methods. The reliability and accuracy of the U(2) Lie algebraic method in predicting vibrational frequencies is emphasized by this observation. The significant durability of this shows its appropriateness for future research and practical uses, emphasizing its ability to contribute to progress in vibrational spectroscopy and related areas.

ORCID

© Jaliparthi Vijayasekhar, <https://orcid.org/0000-0002-2745-7401>

REFERENCES

- [1] F. Iachello, "Algebraic methods for molecular rotation-vibration spectra," *Chem. Phys. Lett.* **78**(3), 581-585 (1981). [https://doi.org/10.1016/0009-2614\(81\)85262-1](https://doi.org/10.1016/0009-2614(81)85262-1)
- [2] F. Iachello, and R.D. Levine, *Algebraic theory of molecules*, (Oxford University Press, Oxford, 1995).
- [3] S. Oss, "Algebraic models in molecular spectroscopy," in: *Advances in Chemical Physics: New Methods in Computational Quantum Mechanics*, edited by I. Prigogine, and S.A. Rice, vol. 93, (John Wiley & Sons, Inc., 1996). pp. 455-649. <https://doi.org/10.1002/9780470141526.ch8>
- [4] F. Iachello, and A. Arima, *The interacting Boson model*, (Cambridge University Press, Cambridge, 1987).
- [5] M.R. Balla, and V. Jaliparthi, "Vibrational Hamiltonian of Methylene Chloride Using U(2) Lie Algebra," *Mol. Phys.* **115**, e1828634 (2021). <https://doi.org/10.1080/00268976.2020.1828634>
- [6] M.R. Balla, S. Venigalla, V. Jaliparthi, "Calculation of Vibrational Frequencies of Sulfur Dioxide by Lie Algebraic Framework," *Acta Phys. Pol. A*, **140**(2), 138-140 (2021). <https://doi.org/10.12693/APhysPolA.140.138>
- [7] V. Jaliparthi, "Vibrational Energies of Silylene, Difluorosilylene and Dichlorosilylene, Using U(2) Lie Algebraic Model," *Ukr. J. Phys. Opt.* **23**(3), 126-132 (2022). <https://doi.org/10.3116/16091833/23/3/126/2022>
- [8] N.K. Sarkar, J. Choudhury, S.R. Karumuri, and R. Bhattacharjee, "A comparative study of the vibrational spectra of OCS and HCP using the Lie algebraic method," *Eur. Phys. J. D*, **53**, 163-171 (2009). <https://doi.org/10.1140/epjd/e2009-00094-8>
- [9] N.K. Sarkar, J. Choudhury, and R. Bhattacharjee, "An algebraic approach to the study of the vibrational spectra of HCN," *Molecular Physics*, **104**(19), 3051-3055 (2006). <https://doi.org/10.1080/00268970600954235>
- [10] A. Mengoni, and T. Shirai, "Vibron Model Description of Vibrational Spectra of the HCO and DCO Molecules," *J. Mol. Spectrosc.* **162**(1), 246-256 (1993). <https://doi.org/10.1006/jmsp.1993.1281>
- [11] M.R. Balla, and V. Jaliparthi, "Vibrational Hamiltonian of Naphthalene (C₁₀H₈) Using Dynamical U(2) Lie Algebras," *Polycycl. Aromat. Compd.* **42**(7), 4684-4699 (2022). <https://doi.org/10.1080/10406638.2021.1901126>
- [12] V. Jaliparthi, and M.R. Balla, "Vibrational Hamiltonian of Tetrachloro-, Tetrafluoro-, and Mono- Silanes Using U(2) Lie Algebras," *Spectrochim. Acta A*, **264**, 120289 (2022). <https://doi.org/10.1016/j.saa.2021.120289>
- [13] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry*, (Wiley, New York, 2009).
- [14] K.P. Huber, and G. Herzberg, *Molecular Spectra and Molecular Structure. IV: Constants of Diatomic Molecules*, (Van Nostrand Reinhold, New York, 1979).
- [15] K.K. Irikura, "Experimental Vibrational Zero-Point Energies: Diatomic Molecules," *J. Phys. Chem. Ref. Data*, **36**(2), 389-397 (2007). <https://doi.org/10.1063/1.3167794>
- [16] T. Shimanouchi, *Tables of Molecular Vibrational Frequencies Consolidated*, vol. I, National Bureau of Standards, **39**, 1-160 (U.S. Government Printing Office, 1972). <https://nvlpubs.nist.gov/nistpubs/Legacy/NSRDS/nbsnrsds39.pdf>

КОЛИВАЛЬНИЙ ГАМІЛЬТОНІАН КАРБОНІЛСУЛЬФІДУ ТА ЦІАНІДУ ВОДНЮ

К. Лаванья^{а,с}, А. Ганапати Рао^б, Дж. Віджаясекхар^с

^аВідділ математики, жіночий коледж Св. Франциска, Бегумпет, Гайдарабад, Індія

^бВідділ фундаментальних і гуманітарних наук, Технологічний інститут GMR, Раджам, Індія

^сДепартамент математики, GITAM, Хайдарабад, Індія

В роботі досліджено частоти коливань карбонілсульфіду (12C16O32S) і ціаніду водню (HCN) до рівня п'ятої гармоніки. Пропонується всебічне розуміння режимів коливань за допомогою формалізму оператора Гамільтона та концентрації на інваріантних операторах і алгебраїчних параметрах за допомогою одновимірного алгебраїчного методу Лі. Ці результати мають важливе значення для хімії атмосфери, спектроскопії та квантової хімії, сприяючи глибшому розумінню молекулярної динаміки. Дослідження закладає основу для майбутніх досліджень порівнянних сполук і застосувань.

Ключові слова: оператор Гамільтона; алгебраїчний метод Лі; карбонілсульфід; ціаністий водень; осцилятор Морзе