



Vibrational Spectra of Ozone (O_3) Using Lie Algebraic Method

J. VIJAYASEKHAR

Department of Mathematics, School of Technology, GITAM, Hyderabad, India.
Corresponding author E-mail: vijayjalparthi@gmail.com

<http://dx.doi.org/10.13005/ojc/3404065>

(Received: April 01, 2018; Accepted: June 03, 2018)

ABSTRACT

We have calculated the vibrational frequencies of Ozone (O_3) upto second overtone using Hamiltonian operator which is based on the Lie algebra. The determined symmetric and antisymmetric fundamental vibrational frequencies by Lie algebraic method are compared with experimental data. It has been observed that results from the method reveal near to the exact, consistent with the experimental data.

Keywords: Vibrational spectra, Lie algebraic method, Ozone.

INTRODUCTION

In 1981, Lachello presented Lie algebraic framework to molecular spectra of small molecules^{1,2}. This framework based on Schrodinger equation with a Morse potential function and described ro-vibration spectra of diatomic molecules^{3,4}. Later this method was extended to calculate medium and large molecules⁵⁻¹⁶. Apart from this framework, there are two other well-known methods established to calculate vibrational spectra of molecules. The first one is Dunham expansion¹⁷. In this expansion the energy levels are expanded in ro-vibrational quantum numbers. In the second approach interatomic potential can be expanded in terms of interatomic variables and potential coefficients by solving Schrodinger equation. The coefficients are fitted with an available experimental data. The major drawback

in both the methods is large experimental data is required to fit parameters, which is not possible everytime. In order to this major difficulty we consider the third approach Lie algebraic method.

Lie algebraic method for the triatomic molecule Ozone

Ozone (O_3) contains three oxygen (O) atoms. The Ozone consists of two O-O bonds. The symmetry point group is C_{2v} .

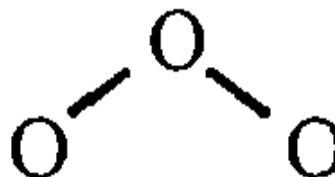


Fig. 1. Structure of Ozone



The Hamiltonian¹⁸ in the case of stretching vibrations for Ozone (O₃) is H as follows.

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

In Hamiltonian, C_i and C_{ij} are invariant operators of uncoupled and coupled bonds respectively and given by.

$$\langle C_i \rangle = -4(N_i v_i - v_i^2) \quad (2)$$

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4 \left[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j) \right] \quad (3)$$

and the Majorana operator, M_{ij} is used to describe local mode interactions in pairs. This contains diagonal and non-diagonal matrix elements,

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

$$\langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = - \left[v_j (v_i + 1)(N_i - v_i)(N_j - v_j + 1) \right]^{1/2} \quad (4)$$

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

Here i vary from 1 to 2 for two stretching bonds (O-O and O-O). Eq. (1) can be written as

$$H = E_0 + A_1 C_1 + A_2 C_2 + A_{12} C_{12} + \lambda_{12} M_{12} \quad (5)$$

Where A_1, A_2, A_{12} and λ_{12} are parameters, which are determined by spectroscopic data. The parameters λ_{ij} illustrate the interactions between stretching bonds (λ_{12}). The local stretching vibrations are denoted by v_1 and v_3 , while v_2 denotes bending vibrations for Ozone (O₃). Since, two bonds (O-O) are equivalent, place $A_1 = A_2 = A, N_1 = N_2 = N$ in equations (2), (3) and (4). All parameters are in cm⁻¹, except N , which is dimension less. Eigen values of the Hamiltonian matrix will be considered as vibrational frequencies of Ozone.

Hamiltonian matrix for the first two 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

First calculate the Vibron number for stretching bonds of Ozone using

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

In this equation, $\omega_e, \omega_e x_e$ are harmonic vibrational frequency and vibrational anharmonicity (spectroscopic) constants respectively. For the stretching mode, the values of ω_e and $\omega_e x_e$ for the O-O bond are 1580.161 and 11.95127 respectively¹⁹.

The initial value for the parameter A is obtained by using the energy equation^{20, 21},

$$E(v=1) = -4A(N-1) \quad (6)$$

Hence, \bar{A} can be evaluated as,

$$\bar{A} = \frac{\bar{E}}{4(1-N)} \quad (7)$$

Where \bar{E} is the average of two different energies, related to symmetric (E_1) and antisymmetric (E_2) combinations of local modes.

To find an initial value for λ_{12} , whose role is to split the initially degenerate local modes is calculated by the relation¹¹,

$$\lambda_{12} = \frac{|E_1 - E_2|}{2N} \quad (8)$$

A mathematical fitting procedure is used to adjust the parameter A_{12} and calculated as 0.028. Calculated vibrational frequencies of Ozone by the Lie algebraic method are reported in the Table (1).

Table 1: The experimental and calculated vibrational frequencies (in cm⁻¹) of Ozone

(v_1, v_2, v_3)	Symmetry species	Experimental [http://vpl.astro.washington.edu/spectra/o3.htm]	Calculated
(1 0 0)	A ₁ (Symmetric)	1103	1103.792
(0 0 1)	B ₁ (Antisymmetric)	1042	1043.008
(2 0 0)	-	-	2206.002
(0 0 2)	-	-	2061.0671
(1 0 1)	-	-	2109.2761
(3 0 0)	-	-	3289.0042
(0 0 3)	-	-	3046.9751
(2 0 1)	-	-	3187.0953
(1 0 2)	-	-	3085.9872

$$N = 131, \bar{A} = -2.062, A_{12} = 0.028, \lambda_{12} = 0.232$$

CONCLUSION

In the Table (1), vibrational frequencies of Ozone (O₃) upto second overtone by Lie algebraic method are reported and also symmetric and antisymmetric fundamental vibrational frequencies

compared with available experimental data. For the fundamental vibrational frequencies we observed that the root mean square deviation is 0.3542. The obtained results are useful for the experimentalists and theorists to develop the vibrational frequencies of Ozone in higher overtones.

REFERENCES

1. Iachello, F., Interacting Bose-Fermi systems in nuclei, (Plenum, New York, **1981**).
2. Iachello, F., Interacting Bosons in nuclear physics, (Plenum, New York, **1979**).
3. Iachello, F., *Chem. Phys. Lett.*, **1981**, *78*, 581-585.
4. Iachello, F.; Levine, R. D., *J. Chem. Phys.*, **1982**, *77*, 3046-3055.
5. Karumuri, S. R.; Sravani, K. G.; Sekhar, J. V.; Reddy, L. S. S. *Acta Phys. Pol.*, A. **2012**, *122*(1), 1111-1114.
6. Rao, K. S.; Srinivas, G.; Sekhar, J. V.; Rao, V. U. M.; Srinivas, Y.; Babu, K. S.; Kumar, V. S. S.; Hanumaiah, A. *Chin. Phys.*, B. **2013**, *22*(9), 090304 (1-8).
7. Rao, K. S.; Sekhar, J. V.; Sreeram, V.; Rao, V. U. M.; Rao, M. V. B. *J. Mol. Spectrosc.*, **2011**, *269*, 119-123.
8. Sekhar, J. V.; Rao, K. S.; Prasad, B. V. S. N. *Orient. J. Chem.*, **2016**, *32*(3), 1717-1719.
9. Van Roosmalen, O. S.; Dieperink, A.E.L.; Iachello, F. *Chem. Phys. Lett.*, **1982**, *85*, 32-36.
10. Van Roosmalen, O. S.; Iachello, F.; Levine, R.D.; Dieperink, A.E.L. *J. Chem. Phys.*, **1983**, *79*, 2515-2536.
11. Van Roosmalen, O. S.; Benjamin, I.; Levine, R.D. *J. Chem. Phys.*, **1984**, *81*, 5986-5997.
12. Iachello, F.; Oss, S. *Phys. Rev. Lett.*, **1991**, *66*, 2976-2979.
13. Iachello, F.; Oss, S. *J. Chem. Phys.*, **1996**, *104*, 6956-6963.
14. Frank, A.; Van Isacker, P. Algebraic methods in molecular and nuclear structure physics, (Wiley, New York, **1994**).
15. Iachello, F.; Levine, R. D. Algebraic theory of molecules, (Oxford University Press, Oxford, **1995**).
16. Iachello, F.; Oss, S. *Eur. Phys. J. D.*, **2002**, *19*, 307-314.
17. Dunham, J. L., *Phys. Rev.*, **1932**, *41*, 721-731.
18. Karumuri, S.R.; Rao, V. U. M.; Sekhar, J. V.; Babu, M. S. S.; Patrudu, T. B.; Krishna, N. V.; Babu, K. S.; Kumar, V. S. S.; Srinivas, G. *Ukr. J. Phys.*, **2013**, *58*(9), 836-840.
19. Karl K. Irikura, *J. Phys. Chem. Ref. Data.*, **2007**, *36*(2), 389-397.
20. Oss, S., *Adv. Chem. Phys.*, **1996**, *93*, 455-649.
21. Iachello, F.; Oss, S. *J. Mol. Spectrosc.*, **1992**, *153*, 225-239.