

Overtone Frequencies of NO₂ using Lie algebraic model

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ABSTRACT

In this paper, we used the one dimensional unitary Lie algebraic model to compute the vibrational frequencies of nitrogen dioxide (NO₂) molecule in the gas phase up to the sixth overtone. In this model, the Hamiltonian operator describes the stretching and bending vibrations with algebraic parameters. The calculated fundamental vibrational frequencies are compared with experimental values and results consistent with the reference values.

Keywords: Vibrational frequencies, Lie algebraic model, Nitrogen dioxide.

INTRODUCTION

The subject of the vibrational spectra of molecules is an interesting and innovative work in molecular spectroscopy. Studying the vibrational spectra of small-sized molecules at the fundamental and higher overtones aids in a better understanding of their molecular structure and allows to compare *In vivo* experimental results. The advent of novel experimental techniques to compute vibrational frequencies (higher overtones) of molecules requires a robust theoretical method for their elucidation of molecular structure. This paper examines vibrational spectra of nitrogen dioxide in higher overtones using a theoretical approach-Lie algebraic model. In this model, Hamiltonian operator describes the vibrational energies of the molecule. In 1991, Iachello and co-researchers applied U(2) Lie algebraic approach for the analysis of ro-vibrational spectra of small size molecules¹ and then this method was improved in subsequent works to study molecular spectra of polyatomic molecules²⁻¹⁰.

Lie algebraic model

Nitrogen dioxide is a bent molecule with C_{2v} point group symmetry with symmetry species- A₁ (Symmetric Stretch), B₂ (Antisymmetric Stretch) and A₁ (Bend).

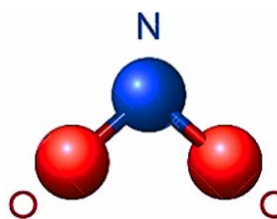


Fig. 1. Structure of nitrogen dioxide

The general Hamiltonian for n vibrational modes (N-O and N-O) is

$$H = E_0 + \sum_{i=1}^n d_i C_i + \sum_{i < j}^n d_{ij} C_{ij} + \sum_{i < j}^n e_{ij} M_{ij} \dots (1)$$

In the equation (1), C_i and C_{ij} are invariant operators of uncoupled and coupled bonds respectively and known as

$$\langle C_i \rangle = -4(N_i^{N-O} v_i - v_i^2) \dots (2)$$

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

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

$$\begin{aligned} \langle N_i^{N-O}, v_i; N_j^{N-O}, v_j | M_{ij} | N_i^{N-O}, v_i; N_j^{N-O}, v_j \rangle &= (N_i^{N-O} v_j + N_j^{N-O} v_i - 2v_i v_j) \\ \langle N_i^{N-O}, v_i + 1; N_j^{N-O}, v_j - 1 | M_{ij} | N_i^{N-O}, v_i; N_j^{N-O}, v_j \rangle &= -[v_i(v_i + 1)(N_i^{N-O} - v_i)(N_j^{N-O} - v_j + 1)]^{1/2} \\ \langle N_i^{N-O}, v_i - 1; N_j^{N-O}, v_j + 1 | M_{ij} | N_i^{N-O}, v_i; N_j^{N-O}, v_j \rangle &= -[v_i(v_j + 1)(N_j^{N-O} - v_j)(N_i^{N-O} - v_i + 1)]^{1/2} \dots (4) \end{aligned}$$

Hamiltonian for two stretching vibrations of nitrogen dioxide can be written as

$$H = E_0 + d_1 C_1 + d_2 C_2 + d_{12} C_{12} + e_{12} M_{12} \dots (5)$$

In equation (5), d_1 , d_2 , d_{12} and e_{12} are algebraic parameters (cm^{-1}), determined from available spectroscopic data. From the structure of nitrogen dioxide, two bonds (N-O) are equivalent; hence we consider as $d_1 = d_2 = d$, $N_1^{N-O} = N_2^{N-O} = N^{N-O}$ in equations (2), (3) and (4). Vibrational frequencies of the molecule can be determined from the Hamiltonian matrix.

For the first two local oscillators, the Hamiltonian matrix is

$$H = \begin{bmatrix} -4d(N^{N-O} - 1) - 4d_{12}(2N^{N-O} - 1) + e_{12}N^{N-O} & -e_{12}N^{N-O} \\ -e_{12}N^{N-O} & -4d(N^{N-O} - 1) - 4d_{12}(2N^{N-O} - 1) + e_{12}N^{N-O} \end{bmatrix}$$

RESULTS AND DISCUSSION

The energy equation (6) is used to determine the starting value of parameter d ,

$$E(v=1) = -4d(N^{N-O} - 1) \dots (6)$$

and the value for e_{12} calculated from the relation,

$$e_{12} = \frac{E_1 - E_2}{2N^{N-O}} \dots (7)$$

Where, E_1 , E_2 are symmetric and antisymmetric vibrational frequencies of the molecule, respectively. The Lie algebraic method was used to calculate nitrogen dioxide vibrational frequencies, which are presented in Table (2) and Table (3).

The Vibron number N_i (dimensionless) for stretching bonds of nitrogen dioxide using

$$N_i^{N-O} = \frac{\dot{u}_e}{\dot{u}_e x_e} - 1, i = 1, 2.$$

Where, $u_e (=1906.52)$, $x_e (=14.504)$ are harmonic vibrational frequency and vibrational anharmonicity (spectroscopic) constants, respectively for the bond N-O¹².

Table 1: Fitted algebraic parameters

N^{N-O} (stretch)	130
N^{N-O} (bend)	72
d (stretch)	-2.7221
d (bend)	-2.5213
d_{12} (stretch)	0.1447
d_{12} (bend)	-0.0033
e_{12} (stretch)	1.1538
e_{12} (bend)	3.3641

Table 2: The fundamental vibrational frequencies (in cm^{-1}) of NO_2

Vibrational Mode	Experimental [#]	Lie algebraic method
A_1 (Symmetric Stretch)	1318	1318.0976
B_2 (Antisymmetric Stretch)	1618	1618.0856
A_1 (Bend)	750	751.656

#<https://cccbdb.nist.gov/exp2x.asp?casno=10102440&charge=01974sve/kov>

Table 3: Vibrational frequencies (in cm^{-1}) of NO_2 in higher overtones (Lie algebraic method)

Overtone	Vibrational mode		
	A_1 (Symmetric Stretch)	B_2 (Antisymmetric Stretch)	A_1 (Bend)
I	2566.2043	3212.8301	1456.0532
II	3912.0712	4787.0381	2186.84
III	5297.0095	6446.8082	2954.4269
IV	6575.9632	7975.3307	3687.482
V	7893.751	9679.4237	4476.7362
VI	9184.0196	10877.3129	5175.6613

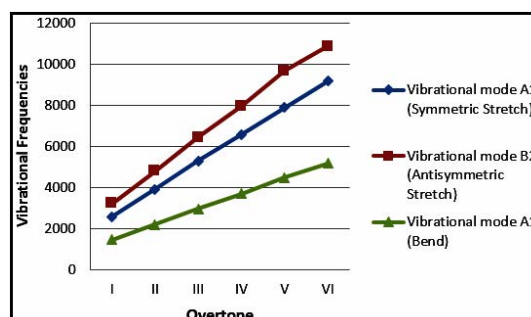


Fig. 2. Graphical representation of higher overtone vibrational frequencies

CONCLUSION

In the Table (2), the estimated vibrational

frequencies in fundamental mode were compared with the experimental data available and in Table (3), vibrational frequencies upto the fifth harmonic by Lie algebraic approach are reported. The calculated results can be helpful for experimentalists and theorists to extend the vibrational spectra of NO₂ in higher overtones.

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Conflict of interest

The author declare that we have no conflict of interest.

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