Vibrational Frequencies of Dichlorine Monoxide: A Mathematical Model

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ABSTRACT

We have determined stretching vibrational frequencies of a triatomic molecule, i.e. Dichlorine monoxide (Cl₂O) up to 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 (Cl₂O).

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 noticeable 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 operator¹-⁶.

Lie algebraic method for Cl₂O

Dichlorine monoxide (Cl₂O) contains two chlorine (Cl) atoms and one oxygen atom with two Cl-O bonds. Symmetry point group is Cᵥ with symmetry species A¹ (Cl-O symmetric stretching), B₂ (Cl-O asymmetric stretching) and A₁ (Cl-O-Cl bending). This framework explains the stretching bonds in Cl₂O molecule using two Lie algebras i.e.

Below mentioned two chains, explains the molecular dynamical group.

\[
\begin{align*}
\text{Chain(I):} & \quad U₁(2) \otimes U₂(2) \Rightarrow O₁(2) \otimes O₂(2) \Rightarrow O₃(2) \\
& \quad N₁ \quad N₂ \quad n \quad m \quad n+m \\
\text{Chain(II):} & \quad U₁(2) \otimes U₂(2) \Rightarrow U₃(2) \Rightarrow O₃(2) \\
& \quad N₁ \quad N₂ \quad v₁ \quad v₂
\end{align*}
\]

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 \( \nu_i, \nu_j \). 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 \( U_2(2) \) and combined with the algebra associates with the \( U_2(2) \otimes U_2(2) \) coupled stretching vibrations. Hamiltonian operator\(^9,10\) (stretching vibrations) of this molecule:

\[
H = E_0 + A_1 C_1 + A_2 C_2 + A_{12} C_{12} + l_{12} M_{12}
\]

In equation (1), \( A_1, A_2, A_{12} \) are \( \lambda_{12} \) the algebraic parameters, which are calculated from experimental spectra. The local stretching vibrations are denoted by \( (\nu_j) \) and \( (\nu_i) \), whereas \( (\nu_{ij}) \) representing bending vibrations for \( \text{Cl}_2\text{O} \). 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 \(-4( N_i \nu_i - v_i^2) \) \( (i = 1, 2) \) and \( C_{ij} \) \( (i = 1, 2) \) operator for coupled bonds is diagonal with matrix elements.

\[
\left[ N_i \nu_i, N_j \nu_j \right] C_{ij} \left[ N_i \nu_i, N_j \nu_j \right] = -4 \left( \nu_i + \nu_j \right) \left[ (N_i + N_j) - (\nu_i + \nu_j) \right]
\]

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.

\[
\left[ N_i \nu_i, N_j \nu_j \right] M_{ij} \left[ N_i \nu_i, N_j \nu_j \right] = \left[ (N_i + N_j) - (\nu_i + \nu_j) \right]
\]

The Hamiltonian matrix for the local modes is given by

\[
H = \begin{bmatrix}
-4\lambda(N-1) - 4\lambda_{ij}(2N-1) + \lambda_{ij}N & \lambda_{ij}N \\
\lambda_{ij}N & -3\lambda(N-1) - 4\lambda_{ij}(2N-1) + \lambda_{ij}N
\end{bmatrix}
\]

RESULTS AND DISCUSSION

The parameters for stretching bonds of the water molecule in equations (1), (2) and (3) as \( N = N_i, A = A_1, A_2 = A_{12}, \lambda = \lambda_{ij} \) \( (i = 1, 2) \) \( . \) The vibron number \( N_i \) \( (i = 1, 2) \) calculated from the relation\(^9\):

\[
N_i = \frac{\omega_i}{\omega_x x_i} - 1
\]

Here \( \omega_i \) and \( \omega_x x_i \) 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

\[
E(\nu = 1) = 4A(1 - N)
\]

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

\[
\bar{A} = \frac{\bar{E}}{(4N - 4)}
\]

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 \( \lambda_{12} \) estimate by the relation\(^10\),

\[
\lambda_{ij} \approx \frac{|E_i - E_j|}{3N}
\]

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

<table>
<thead>
<tr>
<th>vib. quantum no.</th>
<th>observed(^11)</th>
<th>calculated</th>
</tr>
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<tr>
<td>(1 0 0)</td>
<td>639</td>
<td>638.274</td>
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<tr>
<td>(0 0 1)</td>
<td>686</td>
<td>686.932</td>
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<tr>
<td>(2 0 0)</td>
<td>-</td>
<td>1245.407</td>
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<tr>
<td>(0 0 2)</td>
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<td>1357.652</td>
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<tr>
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<td>1911.094</td>
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<tr>
<td>(0 0 3)</td>
<td>-</td>
<td>2043.086</td>
</tr>
<tr>
<td>(4 0 0)</td>
<td>-</td>
<td>2537.335</td>
</tr>
<tr>
<td>(0 0 4)</td>
<td>-</td>
<td>2687.320</td>
</tr>
</tbody>
</table>

\( N = 154, A_i = -1.9091, A_{ij} = 0.9328, \lambda_{ij} = 0.1863 \)

CONCLUSION

Stretching vibrational frequencies of \( \text{Cl}_2\text{O} \) up to third overtone are calculated and compared with experimental data in fundamental mode. Vibrational frequencies (stretching) of \( \text{Cl}_2\text{O} \) are
in close agreement with experimental values in fundamental mode.

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Conflicts of Interest

The authors declare no conflict of interest.

REFERENCES