Molecular Spectra of Magnesium Octaethylporphyrin: An Algebraic Approach

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ABSTRACT

In this paper, we have applied the Lie algebraic method to calculate Vibrational spectra of Magnesium Octaethylporphyrin (MgOEP) in fundamental mode.

Keywords: Vibrational spectra, MgOEP, Lie algebraic method.

1. INTRODUCTION

In the 20th century, the Lie algebraic method, introduced as a computational tool for the study and interpretation of experimental rotational and vibrational spectra of molecules. In Lie algebraic method, Hamiltonian operator describes the ro-vibrational degrees of freedom of the physical system. Porphyrins are tetra pyrrole cyclic compounds in which various side chains are substituted. Metal ions can be bond with nitrogen atoms of the pyrrole rings to form complexes called Metalloporphyrins. The symmetry point group of MgOEP molecule is D₄h.

Figure: Magnesium Octaethylporphyrin
2. LIE ALGEBRAIC METHOD

Hamiltonian for stretching bonds of Metalloporphyrin:

\[
H = E_0 - 4 \sum_{i=1}^{n} A_{ij} (N_i - v_i) - 4 \sum_{i<j=1}^{n} A_{ij} (v_i - v_j)^2 + \sum_{i<j=1}^{n} \lambda_{ij} M_{ij},
\]

The matrix elements with Majorana operator are as follows:

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

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

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

The vibron number \( N_i \) for stretching bonds calculated by the relation,

\[
N_i = \frac{\omega_e}{\omega_e X_e} - 1, \quad i = 1, 2, \ldots,
\]

where \( \omega_e \) and \( \omega_e X_e \) are the spectroscopic constants.

The parameter, \( A_i \) is obtained by using the eigen energy equation for the single-oscillator fundamental mode,

\[
E (v = 1) = -4A_i (N - 1).
\]

To find an initial guess value for \( \lambda_{ij} \), whose role is to split the initially degenerate local modes is obtained by the relation,

\[
\lambda_{ij} = \frac{|E_1 - E_2|}{2N}
\]

The initial guess for the parameter, \( A_{ij} \) may be taken as zero.

3. RESULTS

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Local coordinates</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1g} )</td>
<td>( \text{C}_6\text{H} )</td>
<td>3021.73</td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>( \text{C}_6\text{H} )</td>
<td>3361.19</td>
</tr>
<tr>
<td>( E_u )</td>
<td>( \text{C}_6\text{H} )</td>
<td>3264.77</td>
</tr>
<tr>
<td>( B_{1g} )</td>
<td>( \text{C}_6\text{C}_6 )</td>
<td>1639.89</td>
</tr>
<tr>
<td>( A_{1g} )</td>
<td>( \text{C}_6\text{C}_6 )</td>
<td>1591.43</td>
</tr>
<tr>
<td>( E_u )</td>
<td>( \text{C}_6\text{C}_6 )</td>
<td>1699.76</td>
</tr>
</tbody>
</table>

\( \text{C}_6\text{H} : N = 44, A = -15.25, A^* = -0.77, \lambda = 0.082, \lambda^* = 0.042 \)

\( \text{C}_6\text{C}_6 : N = 140, A = -2.25, A^* = -0.35, \lambda = 0.088, \lambda^* = 0.059 \)
REFERENCES


2. Wulfman, C. E., Dynamical groups in atomic and molecular physics, in recent advances in group theory and their applications to spectroscopy, Plenum, New York, (1979).

