ANALYSIS OF RESONANCE RAMAN SPECTRA OF NICKEL OCTAETHYL PORPHYRIN USING LIE ALGEBRA

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ABSTRACT

One of the most interesting areas of current research in Molecular Physics is the study of the vibrational excited states of medium and large molecules. In view of the considerable amount of the experimental activity in this area, one needs theoretical models within which to interpret experimental data. We propose an algebraic model of n coupled one-dimensional anharmonic oscillators and apply it to the study of the stretching modes of metalloporphyrin molecules. Using Lie algebraic method the fundamental vibrational energy levels of metalloporphyrin molecules like Ni (OEP) are calculated for 24 stretching vibrational modes. Using the algebraic Hamiltonian is

\[ H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i,j}^{n} A_{ij} C_{ij} + \sum_{i,j}^{n} \lambda_{ij} M_{ij} \]

Where \( A_i, A_{ij} \) and \( \lambda_{ij} \) are the algebraic parameters which varies from molecule to molecule and \( C_i, C_{ij} \) and \( M_{ij} \) are algebraic operators. The vibrational energy levels are calculated using model Hamiltonian and result compared with the experimental values. The results obtained by this model are in good accuracy with the observed data.

Key Words: Lie algebra, Raman Spectra, Ni (OEP), Resonance.

INTRODUCTION

Porphyrin and its derivatives have received considerable attention during recent years because of their great biological importance\(^1,2\). They play major roles in the electron transfer reactions in many enzymes and photosynthesis in the green plants\(^3\). They form importance chromphores in haeme protein, chlorophylls, cytochrome oxidase etc. Furthermore, renewed interest on these
systems has aroused because of their technological possibilities in various types of devices such as solid catalysts, photoconductors, organic semiconductors and also because they are used for photothermotherapy in photodynamic therapy and diagnosis of malignant tumors. Several experimental techniques such as electronic luminescence spectroscopy, X-ray, ESR, NMR, Mossbauer spectroscopy, magnetic susceptibility measurements, absorption, infrared and Raman spectroscopy have been applied to elucidate the physical and chemical properties of Porphyrin. At the same time many theoretical approaches including quantum chemical calculations have been attempted by several workers. Although extensive studies by all these techniques on these systems have clarified several aspects, many others remain in question. One of these is the analysis of vibrational spectra of porphyrins correctly and hence to determine symmetries, particularly when they attain distorted structure. In this work we study the vibrational spectra of metalloporphyrin molecules using Lie algebraic method.

Lie algebraic methods have been useful in the study of problems in physics ever since Marius Sophus Lie introduced Lie algebras at the end of the 19th century, especially after the development of quantum mechanics in the first part of the 20th century. This is because quantum mechanics makes use of commutators $[x, p_x] = \hbar$ which are the defining ingredients of Lie algebras. The use of Lie algebras as a tool to systematically investigate physical systems (the so-called spectrum generating Lie algebras) did not however develop fully until the 1970’s, when it was introduced in a systematic fashion by A. Arima and F. Iachello in the study of spectra of atomic nuclei (interacting boson model). Wulfman played a great role in the algebraic approach to the molecules. He is the pioneer to publish the first paper on the algebraic approach to molecules (the approach to the Morse oscillator) in 1979. Later, in 1981 F. Iachello used Lie algebraic methods in systematic study of spectra of molecules (vibron model). This introduction was based on the second quantization of Schrödinger equation with a three dimensional Morse potential and described rotation-vibration spectra of diatomic molecules. Soon after the algebraic method was extended to rotation-vibration spectra of polyatomic molecules. Among algebraic methods, the U(4) and U(2) algebraic models have mostly been used so far in the analysis of experimental data. Later on the U(4) algebra was used for each bond in case of linear triatomic and four atomic molecules. The U(4) model takes the rotation and vibration into account simultaneously but becomes quite complicated when the number of atoms in a molecule is larger than four, while the U(2) model particularly well suited for dealing with the vibrations of polyatomic molecules. In 1984, Van Roosmalen et al. proposed an algebraic model to describe stretching vibrational modes of ABA molecules. This model is based on the isomorphism between one dimensional Morse potential and SU(2) algebra and correspond to the algebraic version of coupled Morse oscillator method developed by Halonen and Child. The algebraic approach of vibrational stretching mode in polyatomic molecule was also proposed by Moret, Michelot, Bailly and Leroy using unitary group U(n) with $(n-1)$ vibrational degrees of freedom. This method is quite complex and less flexible than SU(2) approach. In 1994, Lemus and Frank proposed an algebraic SU(2) model.
based on group theoretical ideas in molecules like methane\textsuperscript{17}. Recently, using Lie algebraic method we have reported better results\textsuperscript{18} for the vibrational energy levels of HCN, HCCF and HCCD than those reported earlier. The U(2) model was particularly successful in explaining stretching vibrations of polyatomic molecules such as octahedral, benzene and pyrrole like molecules\textsuperscript{19,20,21}. As such the approach particularly appropriate for many challenges of modern spectroscopy. This approach is important for the representation of higher accuracy spectroscopic data and especially so far larger molecules. The algebraic approach starts with a Hamiltonian and hence such a fit provides more than just a compact parameterization of the data. Rather, it determines some of the parameters in the Hamiltonian and so provides explicit predictions (including information on the potential).

In this paper, the fundamental vibrational energy levels of metalloporphyrin molecules like Ni (OEP) are calculated for the first time by using Lie algebraic model Hamiltonian. In Sec.2, we will discuss briefly the theory of the algebraic model applied to metalloporphyrin molecules. In Sec.4, we shall present the calculation for getting the vibrational energy levels along with Lie algebraic parameters. The discussions of this Ni (OEP) molecule are given in Sec.3, followed by the conclusion in Sec.5.

**Theory : The Algebraic Model**

In constructing this model, we use the isomorphism of the Lie algebra of U(2) with that of the one-dimensional Morse oscillator\textsuperscript{22}. The eigen states of the one-dimensional Schrodinger equation, \( h\psi = E\psi \), with a Morse potential\textsuperscript{15}.

\[
h(p,x) = p^2/2\mu + D \left[ 1 - \exp(-\alpha x) \right]^2
\]

The eigen values of \( h \) are

\[
E = E_0 + A (m^2 - N^2)
\]

\(
m = N, N-2, \ldots, 1 \text{ or } 0 (N=\text{integer}).
\)

The values of \( E_0, A, \text{ and } N \) are given in terms of \( \mu, D, \text{ and } \alpha \) by

\[
E_0 = -D, \quad -4AN = \frac{\hbar}{2\mu} (2D/\mu)^{1/2}, \quad 4A = -\frac{\hbar^2\alpha^2}{2\mu}.
\]

One can immediately verify that these are the eigen values of the Morse oscillator.

Consider now a molecule with \( n \) bonds. In the algebraic model\textsuperscript{10}, each bond \( i \) is replaced by an algebra (here \( U_i(2) \)), with Hamiltonian \( h_i = C_0 + A_i C_i \), where \( C_i \) is the invariant operator of \( O_i(2) \) with eigenvalues -4(\( N_i^2 - v^2 \)). The bonds interact with a bond-bond interaction. Two types of interaction are usually considered\textsuperscript{10}, which we denote by \( C_{ij} \) and \( M_{ij} \), and call Casimir and Majorana interactions, respectively.
The algebraic model Hamiltonian we consider is thus

\[ H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i<j} A_{ij} C_{ij} + \sum_{i<j} \lambda_{ij} M_{ij} \]  

(4)

In the equation (4), \( C_i \) is an invariant operator with eigenvalues \( 4(v_i^2 - N_i v_i) \) and the operator \( C_{ij} \) is diagonal with matrix elements.

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

(5)

while the operator \( M_{ij} \) has both diagonal and non-diagonal matrix element

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

(6)

Equation (6) is a generalization to \( n \) bonds of the two-bond model. The operators \( C_{ij} \) and \( M_{ij} \) have been called Casimir and Majorana, because of their group-theoretic properties.

For a Porphyrin molecule, we choose the parameters \( N_i, N_j, A_i, A_j \) (for \( i, j = 1 \) to \( n \)), \( A_{ij} = A_{12} \) (any \( i \) and \( j \)) and \( \lambda_{ij} \) for stretching mode. The values of vibron number can be determined by the relation

\[ N_i = \frac{\omega_i}{\omega_{i}X_e} - 1, \quad (i = 1, 2) \]  

(8)

where \( \omega_{i} \) and \( \omega_{i}X_e \) are the spectroscopic constants of diatomic molecules.

They are the invariant operators of the combined algebras \( O_{ij}(2) \) and \( U_{ij}(2) \) in the group lattice

\[ U_{ij}(2) \otimes U_{ij}(2) \supset \left\{ \begin{array}{c} O_{ij}(2) \otimes O_{ij}(2) U_{ij}(2) \end{array} \right\} \supset O_{ij}(2) \]

Their physical meaning can be seen from the matrix elements (5) and (6). The operators \( C_{ij} \) describe anharmonic terms of the type \( v_i v_j \), while the operators \( M_{ij} \) describe interbond couplings which, in configuration space, are of the type \( r_i r_j \), where \( r_i \) and \( r_j \) are the displacement vectors of bonds \( i \) and \( j \) from their equilibrium values.
RESULTS AND DISCUSSION

As an example, we report in tables the results of fundamental vibrational energies \( A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_u \) (stretching) for metalloporphyrin molecule like Ni (OEP)\(^{24}\). Using the estimated values the vibron number and other algebraic parameters \( (A_1, A_{12}, \lambda_{12} \) for stretching) are shown in the tables which vary from molecule to molecule. In our work, we report \( \Delta \text{(r.m.s.)} = 274.4852 \text{ cm}^{-1} \) for 24 stretching vibrational bands.

Comparison between calculated and observed fundamental energy levels of Nickel Octaethyl Porphyrin (in cm\(^{-1}\))

Table 1

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>( \nu )</th>
<th>Description</th>
<th>Exp.(^{a})</th>
<th>Calc</th>
<th>( \Delta \text{(Exp-Cal)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1g} )</td>
<td>( \nu_1 )</td>
<td>( v (C_m-H) )</td>
<td>3041</td>
<td>3041.9544</td>
<td>-0.9544</td>
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<tr>
<td>( B_{2g} )</td>
<td>( \nu_{27} )</td>
<td>( v (C_m-H) )</td>
<td>3040</td>
<td>3040.9548</td>
<td>-0.9548</td>
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<tr>
<td>( E_u )</td>
<td>( \nu_{36} )</td>
<td>( v (C_m-H) )</td>
<td>3040</td>
<td>3040.9546</td>
<td>+0.0454</td>
</tr>
</tbody>
</table>

Stretching Parameters: All Oscillator are identical \( N_1=N_2=N_3=N_4=N=44 \),

\( A_1 = -17.6802 \text{ cm}^{-1}, A_{12} = -0.24 \text{ cm}^{-1}, \lambda_{12} = 0.01136 \text{ cm}^{-1} \)

Table 2

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>( \nu )</th>
<th>Description</th>
<th>Exp.(^{a})</th>
<th>Calc</th>
<th>( \Delta \text{(Exp-Cal)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_u )</td>
<td>( \nu_{45} )</td>
<td>( v (C_{\beta}-C)_{\text{asym}} )</td>
<td>996</td>
<td>994.4080</td>
<td>+1.60</td>
</tr>
<tr>
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<td>( \nu_{31} )</td>
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<td>1015</td>
<td>1010.5280</td>
<td>+4.47</td>
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<td>( \nu_{23} )</td>
<td>( v (C_{\beta}-C)_{\text{sym}} )</td>
<td>1058</td>
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<td>( B_{1g} )</td>
<td>( \nu_{14} )</td>
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<td>( A_{1g} )</td>
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<td>( v (C_{\beta}-C)_{\text{sym}} )</td>
<td>1138</td>
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<tr>
<td>( E_u )</td>
<td>( \nu_{36} )</td>
<td>( v (C_{\beta}-C)_{\text{sym}} )</td>
<td>1153</td>
<td>1159.4680</td>
<td>-6.46</td>
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</table>

Stretching Parameters: All Oscillator are identical \( N_1=N_2=N_3=N_4=N_5=N_6=N_7=N_8=N = 140 \),

\( A_1 = -17.8112 \text{ cm}^{-1}, A_{12} = -1.0152 \text{ cm}^{-1}, \lambda_{12} = 0.1965 \text{ cm}^{-1} \)

Table 3

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>( \nu )</th>
<th>Description</th>
<th>Exp.(^{a})</th>
<th>Calc</th>
<th>( \Delta \text{(Exp-Cal)} )</th>
</tr>
</thead>
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<td>( A_{1g} )</td>
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<tr>
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<td>( \nu_{38} )</td>
<td>( v (C_{\beta}-C_{\beta}) )</td>
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<td>1612.605</td>
<td>-8.60</td>
</tr>
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</table>

Stretching Parameters: All Oscillator are identical \( N_1=N_2=N_3=N_4=N =140 \),

\( A_1 = -2.8105 \text{ cm}^{-1}, A_{12} = -1.256 \text{ cm}^{-1}, \lambda_{12} = 0.08025 \text{ cm}^{-1} \)
Table 4

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>ν</th>
<th>Description</th>
<th>Exp.</th>
<th>Calc</th>
<th>Δ(Exp-Calc)</th>
</tr>
</thead>
<tbody>
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<td>A1g</td>
<td>ν3</td>
<td>(Cα-Cm)_{sym}</td>
<td>1520</td>
<td>1525.06</td>
<td>-5.06</td>
</tr>
<tr>
<td>B1g</td>
<td>ν10</td>
<td>(Cα-Cm)_{asyms}</td>
<td>1655</td>
<td>1549.264</td>
<td>105.736</td>
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<tr>
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<td>ν19</td>
<td>(Cα-Cm)_{asym}</td>
<td>1603</td>
<td>1549.264</td>
<td>53.736</td>
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<tr>
<td>B2g</td>
<td>ν28</td>
<td>(Cα-Cm)_{sym}</td>
<td>1483</td>
<td>1474.884</td>
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<tr>
<td>Eu</td>
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<td>1542.797</td>
<td>94.203</td>
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<td>Eu</td>
<td>ν39</td>
<td>(Cα-Cm)_{sym}</td>
<td>1501</td>
<td>1507.322</td>
<td>-6.322</td>
</tr>
</tbody>
</table>

Stretching Parameters: \(N_1=N_2=N_3=N_4=N_5=N_6=N_7=N_8=N=140\), \(A_1=-2.635\) cm\(^{-1}\), \(A_{12}=-2.456\) cm\(^{-1}\), \(\lambda_{12}=0.0896\) cm\(^{-1}\).

\(^{a}\) Observed frequencies values\(^{24}\).

All parameters are in cm\(^{-1}\) except \(N\) which is dimensionless quantity.

\(\Delta\) (r.m.s) = 274.4852 cm\(^{-1}\).

CONCLUSION

In this paper, we present a first, systematic analysis of the most spectral features of the Ni (OEP) molecule in the framework making use of the one dimensional vibron model. The full vibrational spectrum has been computed, even though we discuss here only (Cm-H), (Cβ-C), (Cβ-Cβ) and (Cα-Cm) of 24 stretching vibrational bands, we reported \(\Delta\) (r.m.s) = 274.4852 cm\(^{-1}\). The local versus normal behavior of stretching modes of polyatomic molecule can be characterized by the quantity \(\xi = 2/\pi \arctan [8(\lambda_{12})/(A_1+A_{12})]\). We find \(\xi = 0.0007\) for Ni (OEP), thus confirming the highly local behavior of the stretching modes of Ni (OEP). Hence using this model, the fundamental vibrational energy levels of some metalloporphyrin molecules can be found out accurately. Once we calculate the vibrational fundamental modes of a molecule accurately, the overtone and combination bands as well can be calculated with the help of such a model Hamiltonian.

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REFERENCES


The Earth is Yours, Save it