Resonance Raman spectroscopy of red blood cells using lie algebraic technique

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ABSTRACT

Raman spectra of oxygenated and deoxygenated functional erythrocytes are calculated by using Lie algebraic technique. The results are obtained by this method is accuracy with the experimental data. So, the algebraic techniques are appropriate to the Raman spectra of red blood cells.

Keywords: Raman Spectroscopy; Red Blood Cell; Lie Algebraic Technique; Vibrational Assignments

1. INTRODUCTION

To maintain resonance with the rapid development of sophisticated experimental approaches, theoretical physics has been constantly tested to provide a collection of satisfactory models that can account for the experimental observations [1-4]. Characterizing these experimental data is equally important for understanding the dynamics of chemical reactions and structure of these molecules. The model is based on the idea of dynamical symmetry, which is expressed through the language of Lie algebras. Applying algebraic techniques, we obtain an effective Hamiltonian operator that conveniently describes the rotational vibrational degrees of freedom of the physical system.

The algebraic model (Vibron model) was originally developed for diatomic and tri-atomic molecules [5-8]. It is to be pointed out that the $U(4)$ model becomes complicated when the number of atoms in a molecule increases more than four. The Vibron model was applied successfully in describing the overtone frequencies of linear and bent $X_2Y$ molecules. Later, it was extended to linear and quasi-linear tetrameric molecules and could prove itself to be a competitive one to the traditional analysis. The main features and basic applications of these methods have been described by Iachello and Levine [9]. The brief review of the research work done in this field up to 2000 and its perspectives in the first part of 21st century was presented by Iachello and Oss [10]. Lie algebraic approach was found to be successful in our study of vibrational frequencies of HCN, HCCF, HCCD, tetrahedral and Porphyrins molecules [11-20].

In this paper, we have calculated the vibrational energy levels of oxygenated and deoxygenated functional erythrocytes at 785 nm for 15 vibrational bands by using Lie algebraic mode Hamiltonian.

2. REVIEW OF THE THEORY

2.1. An Algebraic Techniques

First, The algebraic theory of polyatomic molecules consists in the separate quantization of rotations and vibrations in terms of vector coordinates $r_1, r_2, r_3, \cdots$ quantized through the algebra

$$ G = U_2(2) \otimes U_2(2) \otimes U_2(2) \otimes \cdots $$

For the stretching vibrations of polyatomic molecules correspond to the quantization of anharmonic Morse oscillators, with classical Hamiltonian

$$ h(p,s) = p_i^2/2\mu + D[1 - \exp(-\beta s)]^2 $$

For each oscillator $i$, states are characterized by representations of

$$ U_i(2) \supset O_i(2) \downarrow \downarrow $$

$$ N_i \quad m_i $$

with $m_i = N_i, N_i - 2, \cdots, 1$ or $0$ ($N_i$—odd or even). The Morse Hamiltonian (1) can be written, in the algebraic approach, simply as

$$ H_i = \epsilon_i + A_i C_i $$

where $C_i$ is the invariant operator of $O_i(2)$, with eigen values.
\[ \varepsilon_i = \varepsilon_{i0} + A \left( m_i^2 - N_i^2 \right) \]

Introducing the vibrational quantum number \( v_i = (N_i - m_i)/2 \), one has
\[ \varepsilon_i = \varepsilon_{i0} - 4A \left( N_i v_i - v_i^2 \right) \tag{4} \]

For non-interacting oscillators the total Hamiltonian is
\[ H = \sum_i H_i \]
with eigenvalues
\[ E = \sum_j \varepsilon_j = E_0 - \sum_i 4A \left( N_i v_i - v_i^2 \right) \tag{5} \]

### 2.2. Hamiltonian for Stretching Vibrations

The interaction potential can be written as
\[ V(s_i, s_j) = k_i \left[ 1 - \exp(-\alpha_i s_i) \right] \left[ 1 - \exp(-\alpha_j s_j) \right] \tag{6} \]
which reduce \( s \) to the usual harmonic force field when the displacements are small
\[ V(s_i, s_j) \approx k_i s_i s_j \]

Interaction of the type Equation (6) can be taken into account in the algebraic approach by introducing two terms [9]. One of these terms is the Casimir operator, \( C_{ij} \), of the combined \( O(2) \otimes O(2) \) algebra. The matrix elements of this operator in the basis Equation (2) are given by
\[ \langle N_j, v_j ; N_j, v_j | C_{ij} | N_i, v_i ; N_i, v_i \rangle = 4 \left[ (v_i + v_j)^2 - (v_i + v_j)(N_i + N_j) \right] \tag{7} \]

The operator \( C_{ij} \) is diagonal and the vibrational quantum numbers \( v_i \) have been used instead of \( m_i \). In practical calculations, it is sometime convenient to subtract from \( C_{ij} \) a contribution that can be absorbed in the Casimir operators of the individual modes \( i \) and \( j \), thus considering an operator \( C'_{ij} \) whose matrix elements are
\[ \langle N_i, v_i ; N_j, v_j | C'_{ij} | N_i, v_i ; N_j, v_j \rangle = 4 \left[ (v_i + v_j)^2 - (v_i + v_j)(N_i + N_j) \right] \tag{8} \]

The second term is the Majorana operator, \( M_{ij} \). This operator has both diagonal and off-diagonal matrix elements
\[ \begin{align*}
\langle N_i, v_i ; N_j, v_j | M_{ij} | N_j, v_j ; N_j, v_j \rangle &= (N_i v_j + N_j v_i - 2v_i v_j) \\
\langle N_i, v_i ; N_j, v_j | M_{ij} | N_i, v_i ; N_j, v_j \rangle &= -[v_j (v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2} \\
\langle N_i, v_i ; N_j, v_j | M_{ij} | N_j, v_i ; N_j, v_j \rangle &= -[v_j (v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2}
\end{align*} \tag{9} \]

The Majorana operators \( M_{ij} \) annihilates one quantum of vibration in bond \( i \) and create one in bond \( j \), or vice versa.

The total Hamiltonian for \( n \) stretching vibrations is
\[ H = E_0 + \sum_{i,j} A_{ij} C_{ij} + \sum_{i,j} A_{ij}^* C_{ij} + \sum_{i,j} A_{ij} M_{ij} \tag{10} \]

If \( \lambda_{ij} = 0 \) the vibrations have local behavior. As the \( \lambda_{ij} \) increase, one goes more and more into normal vibrations. By inspection of the figure, one can see that two types of interactions in the molecule:

1. First-neighbor couplings (Adjacent interactions);
2. Second-neighbor couplings (Opposite interactions).

The symmetry-adapted operators of molecule with symmetry \( D_{ab} \) are those corresponding to these two couplings, that is,
\[ \begin{align*}
S^* &= \sum_{i,j} c'_{ij} M_{ij} \\
S^* &= \sum_{i,j} c''_{ij} M_{ij}
\end{align*} \tag{11} \]

with
\[ c'_{12} = c'_{23} = c'_{34} = c'_{45} = \ldots = 1 \]
\[ c'_{11} = c'_{22} = c'_{33} = c'_{44} = \ldots = 0 \]
\[ c''_{12} = c''_{23} = c''_{34} = c''_{45} = \ldots = 0 \]
\[ c''_{11} = c''_{22} = c''_{33} = c''_{44} = \ldots = 1 \]

The total Majorana operator \( S \) is the sum
\[ S = S^* + S^* \tag{12} \]

Diagonalization of \( S \) produces states that carry representations of \( S \), the group of permutations of objects, while diagonalization of the other operators produces states that transform according to the representations \( A_{1g} \), \( A_{2g} \), \( B_{1g} \), \( B_{2g} \), \( E_{1u} \) of \( D_{ab} \).

### 3. RESULTS AND DISCUSSIONS

The number \( N \) [total number of bosons, label of the irreducible representation of \( U(2) \)] is related to the total number of bound states supported by the potential well. Equivalently it can be put in a one-to-one correspond-
dence [11-19] with the anharmonicities parameters $x_e$ by means of

$$x_e = \frac{1}{N + 2}$$  \hspace{1cm} (13)

We can rewrite the Equation (13) as

$$N_i = \frac{\omega_e}{\omega_x x_e} - 1 \quad (i = 1, 2 \ldots)$$  \hspace{1cm} (14)

Now, for a blood cell molecule, we have the values of $\omega_e$ and $\omega_x x_e$ for the distinct bonds (say CH, CC, CD, CN etc) from the study of K. Nakamoto [21] and that of K. P. Huber and G. Herzberg [22]. Using the values of $\omega_e$ and $\omega_x x_e$ for the bond CH/CC we can have the initial guess for the value of the vibron number $N$.

Depending on the specific molecular structure $N_i$ can vary between ±20% of the original value. The vibron number N between the diatomic molecules C-H and C-C are 44 and 140 respectively. Since the bonds are equivalent, the value of $N$ is kept fixed. This is equivalent to change the single-bond anharmonicity according to the specific molecular environment, in which it can be slightly different.

Again the energy expression for the single-oscillator in fundamental mode is

$$E(v = 1) = -4A(N - 1)$$  \hspace{1cm} (15)

In the present case we have three and six different energies corresponding to symmetric and antisymmetric combinations of the different local mode.

$$A = E/4(1 - N)$$  \hspace{1cm} (16)

The initial guess for $\lambda$ can be obtained by

$$\lambda = |E_1 - E_2|/2N$$  \hspace{1cm} (17)

A numerical fitting procedure is adopted to adjust the parameters $A$ and $\lambda$ starting from the values above and $A'$ whose initial guess can be zero. The complete calculation data in stretching and bending modes are presented in Table 1 and the corresponding algebraic parameters are presented in Table 2.

4. CONCLUSIONS

Using the algebraic model for local to normal transition here we presented a study of Raman spectra of Oxynated and Deoxynated red blood cell molecules. On the basis of the results reported here, we have the conclusion of our study as follows:

In the study of resonance Raman spectra of Oxynated red blood cell molecule for 16 vibrational bands we obtain $\Delta$ (r.m.s) as 7.7892 cm$^{-1}$.

In the study of resonance Raman spectra of Deoxynated red blood cell molecule for 16 vibrational bands we obtain $\Delta$ (r.m.s) as 10.623 cm$^{-1}$.

Using improved set of algebraic parameters, the RMS deviation we reported in this study for Oxynated and

| Assign$^a$ | Sym$^b$ | Local Coo$^b$ | $\nu_{exp}$ | $\nu_{calc}$ | $\delta^c$ | $\sigma^d$ | $\nu_{exp}$ | $\nu_{calc}$ | $\delta^c$ | $\sigma^d$
|--------|--------|-------------|-----------|-----------|--------|-------|-----------|-----------|--------|-------|
| $v_{37}$ | $E_{1u}$ | $\nu(C=O)_{sym}$ | 1583 | 1585.0943 | -2.0943 | 0.1323 | 1582 | 1584.3495 | -2.3495 | 0.1484 |
| $v_{28}$ | $B_{1g}$ | $\nu(C=O)_{asym}$ | 1431 | 1430.7842 | 0.2158 | 0.1509 | 1432 | 1432.9759 | -0.9759 | 0.0682 |
| $v_{39}$ | $B_{1g}$ | $\nu(C=C)$ | 1567 | 1567.2843 | -0.2843 | 0.0181 | 1562 | 1562.0345 | -0.0345 | 0.0130 |
| $v_{10}$ | $B_{1g}$ | $\nu(C=C)$ | 1549 | 1550.9203 | -1.9203 | 0.1241 | 1550 | 1551.0945 | -1.0945 | 0.0707 |
| $v_{28}$ | $E_{1u}$ | $\nu(pyr.breathing)$ | 1526 | 1525.2034 | 0.7966 | 0.0522 | 1526 | 1525.0394 | 0.9606 | 0.0629 |
| $v_{22}$ | $A_{1g}$ | $\nu(pyr.breathing)$ | 790 | 790.0293 | 0.0293 | 0.0037 | 790 | 791.6653 | -1.6653 | 0.2110 |
| $v_{20}$ | $A_{1g}$ | $\nu(pyr.quater ring)$ | 1396 | 1393.8942 | 2.1058 | 0.1507 | 1397 | 1398.3045 | -1.3045 | 0.0933 |
| $v_{12}$ | $B_{1g}$ | $\nu(pyr.half-ring)_{sym}$ | 1383 | 1385.6304 | -2.6304 | 0.1900 | 1385 | 1384.9982 | 0.0018 | 0.0001 |
| $v_{17}$ | $E_{1u}$ | $\nu(pyr.half-ring)_{asym}$ | 1337 | 1338.5792 | -1.5792 | 0.1181 | 1337 | 1339.7645 | -2.7645 | 0.2069 |
| $v_{13} + v_{22}B_{1g}$ or $E_{1u}$ | $\delta(C=C-H)$ | 1227 | 1229.4839 | -2.4839 | 0.2026 | 1225 | 1227.3045 | -2.3045 | 0.1884 |
| $v_{9} + v_{10}A_{1g} + B_{1g}$ | $\delta(C=C-H)$ | 1213 | 1211.8392 | 1.1608 | 0.0957 | 1212 | 1213.2093 | -1.2093 | 0.0996 |

Table 1. Comparison between experimental and calculated resonance Raman bands of oxynated and deoxynated cells (cm$^{-1}$).

Experimental data has taken from references [23]; $^a$Assignments are based mainly on labeling scheme originally devised by Abe et al. [24] for Octaporphysrinato-Ni (II); $^b$Local coordinates based mainly on studies by Hu et al. [25] for myoglobin; $^c$ Expt.-Calc.; $^d$Percentage of error=[|Expt.-Calc.|/Expt.] × 100).

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Table 2. Values of the algebraic parameters used in the calculation of red blood cell molecule.

| Algebraic | C_a-C_m | C_m-C_b | C_m-H | pyr. half ring | pyr. breathing | pyr. quater ring |
|-----------|---------|---------|-------|---------------|---------------|-----------------|
| Oxyinated red blood cell |
| $A$ | -2.2103 | -2.2805 | -9.6825 | -2.6537 | -1.6392 | -1.0283 |
| $A'$ | -1.0172 | 1.0151 | 2.5610 | -1.5721 | 0.2039 | -0.3893 |
| $\lambda$ | 0.0369 | 0.0297 | 0.2581 | 0.2378 | 0.0202 | -0.4039 |
| $\lambda'$ | 0.1073 | 0.1029 | 0.0981 | 0.086 | 0.0034 | 0.0102 |
| $N$ | 140 | 140 | 44 | 140 | 140 | 140 |
| Deoxynated red blood cell |
| $A$ | -2.1230 | -1.9289 | -10.5230 | -2.5093 | -1.8392 | -1.2365 |
| $A'$ | -1.1002 | 0.5234 | 2.4950 | -1.7293 | 0.1098 | -0.6537 |
| $\lambda$ | 0.0594 | 0.0345 | 0.2576 | 0.2459 | 0.0198 | -0.3940 |
| $\lambda'$ | 0.0203 | 0.1302 | 0.0934 | 0.0749 | 0.0102 | 0.02301 |
| $N$ | 140 | 140 | 44 | 140 | 140 | 140 |

All values in cm$^{-1}$ except $N$ which is dimensionless.

Deoxynated red blood cell molecule is lying near about the experimental accuracy. Using only four algebraic parameters, the RMS deviation we reported in this study for red blood cell molecule are good fit. Percentage error corresponding to each of the calculated vibrational energy levels of red blood cell we reported in this study is practically zero.

We hope that this work will stimulate further research in analysis of resonance Raman spectra of isotopes of other red blood cell molecules where the algebraic approach has not been applied so far. The research work concern is in progress, which is one can also discuss the spectroscopic properties and isotopes effects of red blood cell molecules with this algebraic Hamiltonian.

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