

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 tetratomic 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 and Oss [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, \dots quantized through the algebra

$$G \equiv U_1(2) \otimes U_2(2) \otimes U_3(2) \otimes \dots$$

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

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

For each oscillator i , states are characterized by representations of

$$\left| \begin{array}{cc} U_i(2) \supset O_i(2) \\ \downarrow \quad \downarrow \\ N_i \quad m_i \end{array} \right\rangle \quad (2)$$

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

$$H_i = \varepsilon_{0i} + A_i C_i \quad (3)$$

where C_i is the invariant operator of $O_i(2)$, with eigen values

$$\varepsilon_i = \varepsilon_{0i} + A_i (m_i^2 - N_i^2)$$

Introducing the vibrational quantum number $v_i = (N_i - m_i)/2$, [9] one has

$$\varepsilon_i = \varepsilon_{0i} - 4A_i (N_i v_i - v_i^2) \tag{4}$$

For non-interacting oscillators the total Hamiltonian is

$$H = \sum_i H_i,$$

with eigenvalues

$$E = \sum_i \varepsilon_i = E_0 - \sum_i 4A_i (N_i v_i - v_i^2) \tag{5}$$

2.2. Hamiltonian for Stretching Vibrations

The interaction potential can be written as

$$V(s_i, s_j) = k'_{ij} [1 - \exp(-\alpha_i s_i)] [1 - \exp(-\alpha_j s_j)] \tag{6}$$

which reduce s to the usual harmonic force field when the displacements are small

$$V(s_i, s_j) \approx k_{ij} s_i s_j$$

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 $O_i(2) \otimes O_j(2)$ algebra. The matrix elements of this operator in the basis Equation (2) are given by

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4 \left[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j) \right] \tag{7}$$

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

$$\begin{aligned} & \langle N_i, v_i; N_j, v_j | C'_{ij} | N_i, v_i; N_j, v_j \rangle \\ &= 4 \left[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j) \right] \\ &+ \left[(N_i + N_j)/N_i \right] 4(N_i v_i - v_i^2) \\ &+ \left[(N_i + N_j)/N_j \right] 4(N_j v_j - v_j^2) \end{aligned} \tag{8}$$

The second term is the Majorana operator, M_{ij} . This operator has both diagonal and off-diagonal matrix elements

$$\begin{aligned} & \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &= (N_i v_j + N_j v_i - 2v_i v_j) \\ & \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &= -[v_j (v_j + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2} \\ & \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &= -[v_i (v_i + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2} \end{aligned} \tag{9}$$

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

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i < j} A_{ij} C_{ij} + \sum_{i < j} \lambda_{ij} M_{ij} \tag{10}$$

If $\lambda_{ij} = 0$ the vibrations have local behavior. As the λ_{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_{4h} are those corresponding to these two couplings, that is,

$$\begin{aligned} S' &= \sum_{i < j}^n c'_{ij} M_{ij} \\ S'' &= \sum_{i < j}^n c''_{ij} M_{ij} \end{aligned} \tag{11}$$

with

$$\begin{aligned} c'_{12} &= c'_{23} = c'_{34} = c'_{45} = \dots = 1 \\ c'_{13} &= c'_{24} = c'_{35} = c'_{46} = \dots = 0 \\ c''_{12} &= c''_{23} = c''_{34} = c''_{45} = \dots = 0 \\ c''_{13} &= c''_{24} = c''_{35} = c''_{46} = \dots = 1 \end{aligned}$$

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_{4h} .

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

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

We can rewrite the Equation (13) as

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1 \quad (i = 1, 2, \dots) \quad (14)$$

Now, for a blood cell molecule, we have the values of ω_e and $\omega_e x_e$ 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 ω_e and $\omega_e x_e$ 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 $\pm 20\%$ 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

$$E(v=1) = -4A(N-1) \quad (15)$$

In the present case we have three and six different en-

ergies corresponding to symmetric and antisymmetric combinations of the different local mode.

$$A = E/4(1-N) \quad (16)$$

The initial guess for λ can be obtained by

$$\lambda = |E_1 - E_2|/2N \quad (17)$$

A numerical fitting procedure is adopted to adjust the parameters A and λ 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 Δ (*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 Δ (*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

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

Assig ^a	Sym ^b	Local Coor ^b	Oxynated				Deoxynated			
			ν_{exp}	ν_{calc}	Δ^c	δ^d	ν_{exp}	ν_{calc}	Δ^c	δ^d
ν_{37}	E_{1u}	$\nu(C_a-C_m)_{\text{asym}}$	1583	1585.0943	-2.0943	0.1323	1582	1584.3495	-2.3495	0.1484
ν_{28}	B_{1g}	$\nu(C_a-C_m)_{\text{sym}}$	1431	1430.7842	0.2158	0.1509	1432	1432.9759	-0.9759	0.0682
ν_{19}	B_{1g}	$\nu(C_b-C_b)$	1567	1567.2843	-0.2843	0.0181	1562	1562.2034	-0.2034	0.0130
ν_{11}	B_{1g}	$\nu(C_b-C_b)$	1549	1550.9203	-1.9203	0.1241	1550	1551.0945	-1.0945	0.0707
ν_{38}	E_{1u}	$\nu(\text{pyr.breathing})$	1526	1525.2034	0.7966	0.0522	1526	1525.0394	0.9606	0.0629
ν_6	A_{1g}	$\nu(\text{pyr.breathing})$	790	790.0293	0.0293	0.0037	790	791.6653	-1.6653	0.2110
ν_{20}	A_{2g}	$\nu(\text{pyr.quater ring})$	1396	1393.8942	2.1058	0.1507	1397	1398.3045	-1.3045	0.0933
ν_{12}	B_{1g}	$\nu(\text{pyr.half-ring})_{\text{sym}}$	1383	1385.6304	-2.6304	0.1900	1385	1384.9982	0.0018	0.0001
ν_{41}	E_{1u}	$\nu(\text{pyr.half-ring})_{\text{sym}}$	1337	1338.5792	-1.5792	0.1181	1337	1339.7645	-2.7645	0.2069
$\nu_{13}/\nu_{42} B_{1g}$ or E_{1u}		$\delta(C_m-H)$	1227	1229.4839	-2.4839	0.2026	1225	1227.3045	-2.3045	0.1884
$\nu_5 + \nu_{18} A_{1g} + B_{1g}$		$\delta(C_m-H)$	1213	1211.8392	1.1608	0.0957	1212	1213.2093	-1.2093	0.0996
					7.7892				10.623	

Experimental data has taken from references [23]; ^aAssignments are based mainly on labeling scheme originally devised by Abe *et al.* [24] for Octaporphyrinato-Ni (II); ^bLocal coordinates based mainly on studies by Hu *et al.* [25] for myoglobin; ^c(Expt.-Calc.); ^dPercentage of error={[(Expt.-Calc.)/Expt.] × 100}.

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

Algebraic Parameters	Oxynated red blood cell					
	C_a-C_m	C_b-C_b	C_m-H	pyr. half ring	pyr. breathing	pyr. quater ring
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
λ	0.0369	0.0297	0.2581	0.2378	0.0202	-0.4039
λ'	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
λ	0.0594	0.0345	0.2576	0.2459	0.0198	-0.3940
λ'	0.0203	0.1302	0.0934	0.0749	0.0102	0.02301
N	140	140	44	140	140	140

^eAll 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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