

VIBRATIONAL FREQUENCIES OF FUNCTIONAL ERYTHROCYTES USING SYMMETRY-ADAPTED LIE ALGEBRAIC APPROACH

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Abstract

This study contributes to our understanding of vibrational frequencies in functional erythrocytes by applying the U(2) Lie algebraic model. The central objective of this research revolves around a comprehensive exploration of Raman spectra, particularly concerning the higher overtone vibrational frequencies. These investigations are conducted within the unique physiological contexts of oxygenated and deoxygenated erythrocytes. The Hamiltonian operator, which is related to the Lie algebraic model, is at the core of this framework. This operator plays a vital role in understanding the complex vibrational modes within these specialized cells, particularly those related to C-H and C-C stretching. This study improves our understanding of the vibrational dynamics within erythrocytes by applying the U(2) Lie algebraic model and sheds light on how their vibrational modes may vary under different oxygenation states.

Keywords: Metalloporphyrins; Functional erythrocytes; Lie algebraic model; Hamiltonian operator

Introduction

The Lie algebraic model, proposed by Iachello (Iachello and Levine, 1995; Oss, 1996), is a powerful mathematical tool used to analyze molecular vibrations, focusing on symmetry analysis and interpreting findings from experiments in molecular physics. This model provides a systematic framework for understanding the vibrational behavior of molecules by determining their molecular point group, which determines the

specific symmetry operations that preserve the molecule's integrity. These operations include transformations such as rotations, reflections, and inversions. Each molecular point group relates to a mathematical group with an associated Lie algebra. Using the Lie algebraic model, researchers can create symmetry-adapted basis functions that correspond to the irreducible representations of the molecular point group. These basic functions are

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essential in the understanding of vibrational modes. By studying the Lie algebraic properties, researchers can deduce selection rules governing vibrational-rotational couplings, further enriching our understanding of molecular dynamics. The Hamiltonian operator, integral to the Lie algebraic model, plays a pivotal role in providing insights into the vibrational spectra of molecules, as demonstrated by (Malleswara Rao and Vijayasekhar, 2021; 2022; Vijayasekhar *et al.*, 2022, 2023). In molecular spectroscopy, infrared and Raman spectroscopy are widely utilized methods for obtaining vibrational spectra, particularly in the study of metalloporphyrins, as highlighted by Wood *et al.* (2007). It correctly emphasizes the importance of understanding metalloporphyrin vibrational frequencies in various scientific fields, including biology and materials science. It also highlights their significance in catalytic processes, particularly in environmental and pharmaceutical applications. The assertion that this knowledge transcends disciplines and drives progress in biology, materials science, and catalysis is also well-founded. Metalloporphyrins are coordination complexes composed of a central metal ion and a porphyrin ligand. These compounds exhibit intriguing vibrational spectra due to the presence of both metal-ligand and ligand-ligand vibrations. Notably, the central metal ion in metalloporphyrins can vary and include transition metals like iron, cobalt, nickel, copper, or zinc. In biological relevance, red blood cells, known as erythrocytes, are specialized entities within the bloodstream responsible for transporting oxygen to tissues and removing carbon dioxide. Heme, a metalloporphyrin, stands out as a primary component within erythrocytes. It contains a metal ion, typically iron, coordinated by nitrogen atoms from the porphyrin ligand at the center of the porphyrin ring. Building upon this foundation, Karumuri *et al.* conducted pioneering work in 2008, utilizing the Lie algebraic model to investigate the fundamental stretching vibrations of medium-sized molecules, including nickel octaethyl porphyrins. Their research extended to various metalloporphyrins, such as nickel tetraphenyl porphyrin, copper octaethyl porphyrin, magnesium octaethyl porphyrin, and copper tetramesityl porphyrin, as well as the resonance Raman spectra of oxygenated and deoxygenated functional erythrocytes belonging to the D_{4h} molecular point group (Karumuri *et al.*, 2008; 2009; 2010; 2011; 2012; 2013; 2015; 2016). While these previous studies predominantly focused on fundamental mode vibrations, it is essential to note that this paper presents a groundbreaking exploration of the first and second overtone vibrational spectra in

both oxygenated and deoxygenated functional erythrocytes. This research promises to expand our knowledge of these critical biological entities and their vibrational dynamics, potentially leading to significant advancements in the field.

Symmetry adapted Lie algebraic framework for metalloporphyrins

Here, we use metalloporphyrins as an example to show how symmetry-adapted operators and the Hamiltonian operator are made for polyatomic molecules. To commence this construction, it is imperative first to generate a visual representation of the molecular geometry (see Figure 1). This graphical depiction is a vital reference point for our subsequent endeavors.

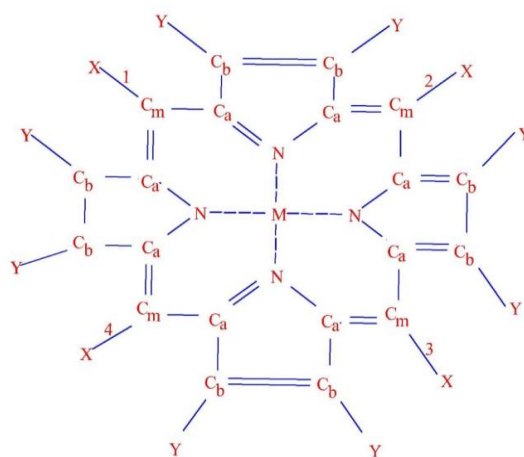


Figure 1. Chemical composition and density of high entropy alloys

Once the structural framework is established, determine the number of degrees of freedom that warrant description. Upon close examination of the figure, it becomes evident that there are two distinctive types of interactions within metalloporphyrins:

1. First-Neighbor Couplings (Adjacent Interactions): These interactions pertain to the immediate neighbors within the molecular structure, wherein atoms or groups of atoms are close.

2. Second-Neighbor Couplings (Opposite Interactions): In contrast, these interactions involve elements within the molecular structure situated at a greater distance, exhibiting an opposite or more distant relationship.

This analytical breakdown lets us figure out how strong these interactions are and then include them in the design of symmetry-adapted and Hamiltonian operators. A methodical approach like

this helps us learn more about how molecules behave and sets the stage for precise and insightful quantum mechanical analyses of polyatomic molecules like metalloporphyrins. The Hamiltonian operator represents the total energy of a physical system. In the context of symmetry-adapted Lie algebraic models, we are dealing with a specialized approach to solving quantum mechanical systems, particularly those with symmetries. In this context, the Hamiltonian operator will be expressed as a generator of the relevant Lie algebra. These generators correspond to operators representing symmetry transformations. Using the Lie algebraic approach, one can gain insight into the system's behavior and solve for its energy states more systematically and efficiently, especially in cases with high degrees of symmetry. The advantage of symmetry-adapted Lie algebraic methods is that they can significantly simplify quantum mechanical calculations, allowing for a more intuitive understanding of the system's behavior and leading to analytical or semi-analytical solutions that might be challenging to obtain using other methods. The symmetry-adapted Lie algebraic model and the Hamiltonian operator are potent ways to solve quantum mechanical systems with symmetries. This gives us a better understanding of their behavior and makes figuring out their energy states easier. This framework is rooted in the principles of group theory and algebraic methods, allowing researchers to analyse and understand molecules' vibrational properties with a strong emphasis on their symmetry.

The Hamiltonian operator associated with the symmetry-adapted operators of metalloporphyrins possessing D_{4h} symmetry, corresponds to the coupling of two adjacent and opposite n vibrations as represented by (Karumuri *et al.*, 2011; 2015; 2016).

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i<j} A_{ij} C_{ij} + \sum_{i<j} (m_{ij}^1 + m_{ij}^2) \lambda_{ij} M_{ij}, \quad (1)$$

with adjacent and opposite interaction coefficients are given by

$$m_{ij}^1 = \{1, (i, j) = (1, 2), (2, 3), (3, 4), (4, 5), \dots, 0, \text{ otherwise}\}$$

$$m_{ij}^2 = \{1, (i, j) = (1, 3), (2, 4), (3, 5), (4, 6), \dots, 0, \text{ otherwise}\}$$

Here, C_i, C_{ij}, M_{ij} are operators, and $A_i, A_{ij}, \lambda_{ij}$ are algebraic parameters, which are determined from the expressions.

$$\langle C_i \rangle = -4(N_i v_i - v_i^2) \quad (2)$$

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4(v_i + v_j)(v_i + v_j - N_i - N_j) \quad (3)$$

$$\begin{aligned} \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle &= v_i N_j + v_j N_i - 2v_i v_j \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2} \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2} \dots \quad (4) \\ \langle C_i \rangle &= -4(N - 1), \langle C_{ij} \rangle = -4(2N - 1), \langle M_{ij} \rangle = \{-N \ (i \neq j) \ N \ (i = j)\} \quad (5) \end{aligned}$$

$$E = -4A_i(N - 1), \lambda_{ij} = \frac{|E_a - E_b|}{2N}, \lambda'_{ij} = \frac{|E_a - E_b|}{4N} \quad (6)$$

Where v_i and v_j are the vibrational quantum numbers of bonds i and j , respectively, and N indicates the vibron number. E_a and E_b are the energies of two local modes.

Results

In our study, we used the Lie algebraic model's powerful features, as described by Karumuri *et al.* (2011; 2013; 2015; 2016), to look at the vibrational properties of both oxygenated and deoxygenated erythrocytes. To achieve this, we particularly tailored the algebraic parameters to suit the system's unique properties under study, as depicted in Table 1. Table 1 serves as a valuable reference, showcasing the precise configurations of these algebraic parameters that were judiciously selected to represent the erythrocyte system accurately. This accurate parameterization is pivotal for ensuring the model's fidelity in capturing the intricacies of vibrational behavior within these specialized blood cells. Having employed this rigorously calibrated Lie algebraic model, we have generated a wealth of insightful results, which we have precisely compiled in Table 2. This table provides a comprehensive overview of the Raman spectra obtained for oxygenated and deoxygenated erythrocytes. The data details the vibrational frequencies corresponding to the first, second and third overtones. These findings enhance our understanding of the vibrational dynamics within erythrocytes and offer a valuable reference for future research in this domain. The precise frequencies of these overtones have significance because they contain the key to understanding the complex physiological and metabolic processes that occur within these vital blood cells. As such, Table 2 represents a significant contribution to the field, shedding light on the vibrational intricacies of oxygenated and deoxygenated erythrocytes.

Table 1. Values of the parameters (in cm⁻¹, N is dimensionless)

Parameters	oxygenated			deoxygenated		
	C _a -C _m	C _b -C _b	C _m -H	C _a -C _m	C _b -C _b	C _m -H
A_i	-1.907	-2.061	-8.982	-2.201	-0.906	-0.449
A_{ij}	-0.112	1.340	1.524	-0.341	0.371	2.393
λ_{ij}	0.032	0.093	0.302	0.065	0.097	0.484
λ'_{ij}	0.110	0.152	0.063	0.114	0.359	0.061
N	140	140	44	140	140	44

Table 2. Vibrational frequencies of erythrocytes (cm⁻¹)

Vibrational mode	Local coordinates	Symmetry species	Lie algebraic model			
			Overtone			
			I	II	III	IV
ν_{10}	(C _a -C _m) <i>a-str</i>	B _{1g}	28785	54329	76297	929063
ν_{37}	(C _a -C _m) <i>a-str</i>	E _{1u}	2865	4249	8195	1109
ν_{28}	(C _a -C _m) <i>str</i>	B _{2g}	2495	3690	7261	9349
ν_{19}	(C _b -C _b)	B _{1g}	2690	4032	8265	12941
ν_{11}	(C _b -C _b)	B _{1g}	2720	4296	8067	11759
ν_{21}	(C _m -H)	B _{1g}	2234	3368	6222	8730
ν_{42}	(C _m -H)	E _{1u}	2190	3192	6154	8672
ν_{13}	(C _m -H)	B _{1g}	2178	3047	5943	7950
$\nu_5 + \nu_{18}$	(C _m -H)	B _{1g}	2174	3039	6296	8862

Conclusions

Focusing on the higher overtone frequencies in the Raman spectra of oxygenated and deoxygenated erythrocytes has given us important information about their vibrational properties. This investigation represents a significant stride towards comprehending the intricate molecular dynamics within these vital blood cells. Our study homes in on several vital vibrational modes that play pivotal roles in the overall behavior of erythrocytes. These modes include the asymmetric stretching mode of Ca-Cm, which signifies the motion of carbon atoms in the molecule; the stretching mode of Cb-Cb, highlighting the interactions between carbon atoms; and the in-plane bending mode of Cm-H, illustrating the bending motion of carbon-hydrogen bonds. Analysing these modes provides a nuanced understanding of the vibrational dynamics within erythrocytes, shedding light on the molecular interactions and structural changes that occur in response to oxygenation state changes. Furthermore, our findings have broader implications beyond the scope of erythrocytes. By delving into the first, second and third overtone frequencies of these essential biomolecules, we have unveiled the potential for further exploration into the higher overtone frequencies of various biomolecules. In essence, our research contributes to our understanding of erythrocytes and paves the way for future investigations in vibrational spectroscopy. As we explore higher overtone frequencies in

biomolecules, we may uncover new insights that could have far-reaching implications in biophysics and biochemistry, ultimately deepening our understanding of biological processes and their relevance in health and disease.

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