Journal of Molecular Spectroscopy 259 (2010) 86–92

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Feature Article

Calculation of vibrational spectra by an algebraic approach: Applications to Copper Tetramesityl Porphyrin and its Cation radicals

Srinivasa Rao Karumuri

Department of Physics, Post-Graduate Centre, P.B. Siddhartha College of Arts & Sciences, Vijayawada 520010, India

ARTICLE INFO

Article history:
Received 5 August 2009
In revised form 9 November 2009
Available online 16 November 2009

Keywords:
Lie algebra
Raman spectra
Copper Tetramesityl Porphyrin
Cu (TMP)$^+$

ABSTRACT

Using the Lie algebraic model, Hamiltonian vibrational frequencies of Copper Tetramesityl Porphyrin and its Cation radicals are calculated for 64 vibrational bands.

1. Introduction

Porphyrins are naturally occurring heterocyclic compounds with many important biological representatives including chlorophyll, prosthetic groups, and various metalloenzymes/proteins such as hemoglobin, myoglobin and vitamin B_{12} [1]. Additionally, there are a multitude of symmetric prophyrinoid molecules that have been prepared for purposes ranging from basic research to real life applications. All of these molecules exhibit the Porphyrin macro cyclic substructure comprising four pyrrolic subunits linked by four methylene bridges [2]. Several experimental techniques, such as electronic luminescence spectroscopy, including fine structure quasline spectra, X-ray, NMR, Mossbauer spectroscopy, magnetic susceptibility measurements, absorption, Infrared and Raman spectroscopy have been applied in order to elucidate the physical and chemical properties of Porphyrin. At the same time, many theoretical approaches including quantum mechanical calculations have been attempted by several scientists [3]. Although extensive studies using all of these techniques have clarified several aspects of the system, many others remain in question. One of these, is the correct analysis of the vibrational spectra of Porphyrins and the subsequent determination of symmetries, particularly when they attain distorted structure. In this work, we study the Resonance Raman spectra of such distorted structure molecules (specifically Copper Tetramesityl Porphyrin and its Cation radicals) using a Lie algebraic approach.

Lie algebraic solutions were introduced by Marius Sophus Lie (1842–1899) at the end of the 19th century after the development of quantum mechanics in the first part of the 20th century. The reason for this is that quantum mechanics makes use of commutations $[x, p_x] = \hbar$ which are the defining ingredients of Lie algebra. The essence of the algebraic method can be traced to the Heisenberg formulation of quantum mechanics [4]. The use of Lie algebras as a tool to systematically investigate physical systems(the so called spectrum generating algebras) did not develop fully until the 1970s when it was introduced in a systematic fashion by F. Iachello and A. Arima in a study of spectra of atomic nuclei (interacting boson model) [5]. In 1981 F. Iachello introduced Lie algebraic methods in a systematic study of spectra of molecules (the vibron model) [6]. This introduction of the model was based on the second quantization of the Schrodinger equation with a three dimensional Morse potential and described rotation–vibration spectra of diatomic molecules [7]. Soon after, the algebraic method was extended to include rotation–vibration spectra of polyatomic molecules [8]. In the intervening years, much work was done. Most notable advances were the extension to two coupled one-dimensional oscillators and generalization to many coupled one-dimensional oscillators, which led to a simple treatment of vibrational modes in polyatomic molecules, and extension to two dimensional oscillators, which allowed a simpler description emerge of bending modes in linear molecules [9]. The situation up to 1995 has been reviewed in [10]. After 1995, the brief review work of F. Iachello and S. Oss reflects the scenario in the field up to 2002, along with the perspectives of the algebraic method in the first decade of the 21st century [11]. Recently, using the Lie algebraic method, we have reported better results [12] for the vibrational energy levels of HCN, HCCF and HCCD than those reported earlier and we have also reported some vibrational bands of tetrahedral molecules such as CCl_4, $SnBr_4$ and Nickel Metalloporphyrins [13].

E-mail address: drsrkarumuri@rediffmail.com

0022-2852/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2009.11.005

In this paper, the vibrational frequencies of Copper Tetramesityl Porphyrin and its Cation radicals for 64 vibrational bands are calculated using the Hamiltonian algebraic model. The locality parameter (ξ) and the formation of Cation radicals are also completed for 64 vibrational bands of Cu (TMP) & Cu (TMP)$^+$.

2. Review of the theory

The algebraic theory of polyatomic molecules consists of the separate quantization of rotations and vibrations in terms of vector coordinates r_1, r_2, r_3,..... quantized using the algebra

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

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

$$H(p_s, s) = p_s^2/2\mu + D[1 - \exp(-\beta s)]^2. \tag{1}$$

For each oscillator i, states are characterized by representations of

$$\left| \begin{matrix} U_i(2) & \supset & O_i(2) \\ \downarrow & & \downarrow \\ N_i & & M_i \end{matrix} \right\rangle, \tag{2}$$

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

$$H_i = \varepsilon_{0i} + A_i C_i, \tag{3}$$

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

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

Introducing the vibrational quantum number $v_i = (N_i - m_i)/2$, [10] 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

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

2.1. 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 reduces to the usual harmonic force field when the displacements are small, i.e.

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

Interaction of the type found in Eq. (6) can be taken into account in the algebraic approach by introducing two terms [10]. 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 of Eq. (2) are given by

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

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

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

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

$$\begin{aligned} &\langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle = (N_i v_j + N_j v_i - 2 v_i v_j) \\ &\langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &\quad = -\sqrt{v_j(v_i + 1)(N_i - v)i)(N_j - v)j + 1)} \\ &\langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle \\ &\quad = -\sqrt{v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)}. \end{aligned} \tag{9}$$

The Majorana operators M_{ij} either annihilâte one quantum of the vibration in bond i and create one in bond j, or vice versa.

The total Hamiltonian for n stretching vibrations is

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

If $\lambda_{ij} = 0$ the vibrations have local behavior. As λ_{ij}s increases, one goes further and further into the normal vibrations.

2.2. Symmetry-adapted operators

In polyatomic molecules, the geometric point group symmetry of the molecule plays an important role. States must transform according to representations of the point symmetry group. In the absence of the Majorana operators M_{ij}, states are degenerate. The introduction of the Majorana operators has two effects: (1) it splits the degeneracies of figure, and (2) in addition, it generates states with the appropriate transformation properties for the point group. In order to achieve this result, the λ_{ij} must be chosen in an appropriate way to reflect the geometric symmetry of the molecule. The total Majorana operator

$$S = \sum_{i<j}^{n} M_{ij}. \tag{11}$$

is divided into subsets reflecting the symmetry of the molecule

$$S = S' + S'' + \ldots\ldots. \tag{12}$$

The operators S', S'', ... are the symmetry-adapted operators. The construction of the symmetry-adapted operators of any molecule will become clear in the following sections where the case of Metalloporphyrins (D_{4h}) will be discussed.

2.3. The Metalloporphyrins molecule

The construction of the symmetry-adapted operators and of the Hamiltonian operator of polyatomic molecules will be illustrated using the example of Metalloporphyrins. In order to carry out the construction, we can draw a figure corresponding to the geometric structure of the molecule (Fig. 1). Thus, we number the degree of freedom we wish to describe.

By inspection of the figure, one can see that two types of interactions in Metalloporphyrins:

1. First-neighbor couplings (adjacent interactions)
2. Second-neighbor couplings (opposite interactions)