Vibrational spectra of nickel metalloporphyrins: An algebraic approach

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Abstract. One of the most interesting areas of current research in molecular physics is the study of the vibrationally excited states of medium and large molecules. In view of the considerable amount of experimental activity in this area, one needs theoretical models within which to interpret experimental data. Using Lie algebraic method, the vibrational energy levels of nickel metalloporphyrins like Ni(OEP), Ni porphyrin and Ni(TPP) are calculated for 16 vibrational modes. The algebraic Hamiltonian

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

where A_i, A_{ij} and λ_{ij} are the algebraic parameters which vary from molecule to molecule and C_i, C_{ij} and M_{ij} are algebraic operators. The vibrational energy levels are calculated using algebraic model Hamiltonian and the results are compared with the experimental values. The results obtained by this model are very accurate.

1. Introduction

Porphyrins and their derivatives have received considerable attention in recent years because of their great biological importance. Many experimental techniques have been applied to elucidate the physical and chemical properties of porphyrin [1]. At the same time many theoretical approaches including quantum chemical calculations have been attempted by several workers [2]. 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 commutations $[x, p_x] = \hbar$ 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 1970s, when it was introduced in a systematic fashion by Arima and Iachello in the study of spectra of atomic nuclei (interacting boson model) [3]. Wulfman played a great role in the algebraic approach to the molecules [4]. He was the pioneer to publish the first paper on the algebraic approach to molecules (the approach to the Morse oscillator) in 1979 [5]. Later, in 1981 Iachello used Lie algebraic methods in the 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 [6]. Soon after, the algebraic method was extended to rotation–vibration spectra of polyatomic molecules [7]. 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 the case of linear triatomic and tetratomic molecules [8]. The $U(4)$ model takes 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 is 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 [9]. 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 [10]. The algebraic approach of vibrational stretching mode in polyatomic molecule was also proposed by Moret, Michelot, Bailly and Leroy [8] using unitary group $U(n)$ with $(n-1)$ vibrational degrees of freedom. This method is quite complex and less flexible than $SU(2)$ approach. Iachello and Oss are the pioneers to introduce the $SU(2)$ model [11] in the algebraic approach. Later, in 1994, Lemus and Frank applied the $SU(2)$ model in the study of molecules like methane [11]. A brief review of the work done in the aforementioned algebraic approach up to 2002 is stated in the study of Iachello and Oss [12].

Recently, using Lie algebraic method we have reported better results [13a] for the vibrational energy levels of HCN, HCCF, $SnBr_4$, CCl_4 than those reported earlier and also we have reported the stretching vibrational spectra of Ni(OEP), nickel porphyrin by $U(2)$ model [13b]. The $U(2)$ model was particularly successful in explaining stretching vibrations of polyatomic molecules such as octahedral, benzene and pyrrole-like molecules [14]. As such, the approach is particularly appropriate for many challenges of modern spectroscopy. This approach is important for the representation of higher accuracy spectroscopic data especially for larger molecules. The algebraic approach starts with a Hamiltonian and hence such a fit provides more than just a compact parametrization 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 nickel metalloporphyrins like Ni(OEP), Ni porphyrin, Ni(TPP) are calculated for the first time using Lie algebraic model Hamiltonian. In §2, we discuss briefly the theory of the algebraic model applied to metalloporphyrin molecules. In §3, we present the results and discussions of the vibrational energy levels of Ni(OEP), Ni porphyrin, Ni(TPP) molecules along with Lie algebraic parameters, followed by the conclusion in §4.

2. Theory: An algebraic method

In constructing this model, we use the isomorphism of the Lie algebra of $U(2)$ with that of the one-dimensional Morse oscillator [15]. The eigenstates of the one-dimensional Schrödinger equation, $h\psi = \varepsilon\psi$, with a Morse potential [9]

$$h(p, x) = p^2/2\mu + D[1 - \exp(-\alpha x)]^2 \tag{1}$$

can be put into one-to-one correspondence with the representations of $U(2) \supset O(2)$, characterized by the quantum numbers $|N, m\rangle$, with the provison that one takes only the positive branch of m, i.e. $m = N, N - 2, \ldots, 1$ or 0 for $N =$ odd or even ($N =$ integer). The Morse Hamiltonian (1) corresponds in the $U(2)$ basis to a simple Hamiltonian, $h_i = \varepsilon_0 + AC$, where C is the invariant operator of $O(2)$, with eigenvalues $(m^2 - N^2)$.

The eigenvalues of h are

$$\varepsilon = \varepsilon_0 + A(m^2 - N^2), \quad m = N, N - 2, \ldots, 1 \text{ or } 0, \quad (N = \text{ integer}). \tag{2}$$

Introducing the vibrational quantum number $\nu = (N - m)/2$, eq. (2) can be rewritten as

$$\varepsilon = \varepsilon_0 - 4A(N\nu - \nu^2), \\ \nu = 0, 1, \ldots, N/2 \text{ or } N - 1/2 \ (N = \text{ even or odd}). \tag{3}$$
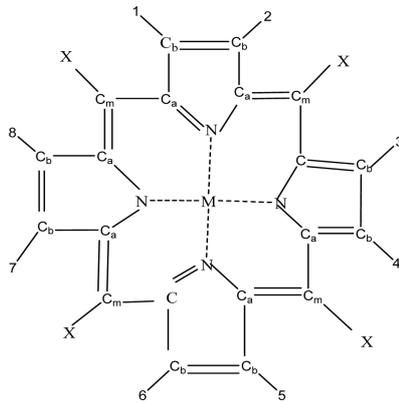
Figure 1. Structure of metalloporphyrin (M – metal). Different porphyrins are obtained by specific substitution at X or 1 to 8 positions.

The values of ε_0, A, and N are given in terms of μ, D, and α by $\varepsilon_0 = -D$, $-4AN = \hbar\alpha(2D/\mu)^{1/2}$, $4A = -\hbar^2\alpha^2/2\mu$. One can immediately verify that these are the eigenvalues of the Morse oscillator.

Consider now a molecule with n bonds. In the algebraic model [6], each bond i is replaced by an algebra (here $U_i(2)$), with Hamiltonian $h_i = \varepsilon_{0i} + A_i C_i$, where C_i is the invariant operator of $O_i(2)$ with eigenvalues $-4(N_i\nu_i - \nu_i^2)$. The bonds interact with a bond–bond interaction. Two types of interactions are usually considered [6], which we denote by C_{ij} and M_{ij}, and call Casimir and Majorana interactions, respectively.

The algebraic model Hamiltonian we consider is thus

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i<j}^{n} A_{ij} C_{ij} + \sum_{i<j}^{n} \lambda_{ij} M_{ij}. \tag{4}$$

In eq. (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.

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)] \tag{5}$$

while the operator M_{ij} has both diagonal and non-diagonal matrix elements

$$\langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i, N_j, v_j \rangle = (N_i v_j + N_j v_i - 2v_i v_j)$$
$$\langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle$$
$$= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2}$$
$$\langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle$$
$$= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2}. \tag{6}$$

Equation (6) is a generalization to n bonds of the two-bond model of ref. [9]. The operators C_{ij} and M_{ij} have been called Casimir and Majorana, because of their group-theoretic properties.

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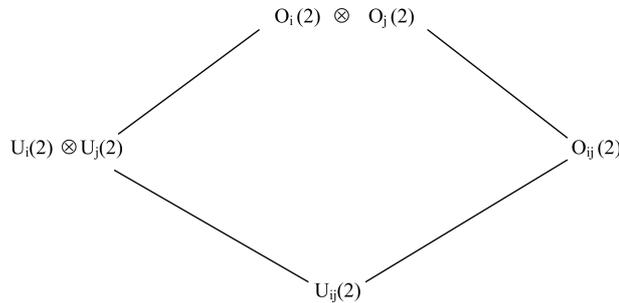

Figure 2. Couple scheme of Lie groups.

Table 1. Comparison between experimental and calculated fundamental energy levels of nickel octaethyl porphyrin (in cm^{-1}).

(a)

Symmetry	ν_i	Description	Exp.[a]	Calc.	Δ(Exp.$-$Calc.)
A_{1g}	ν_1	$\nu(C_m-H)$	3041	3041.9544	-0.9544
B_{2g}	ν_{27}	$\nu(C_m-H)$	3040	3040.9548	-0.9548
E_u	ν_{36}	$\nu(C_m-H)$	3040	3040.9546	$+0.9546$

Stretching parameters: All oscillators are equivalent, $N_1 = N_2 = N_3 = N_4 = N = 44$, $A = -17.6802$ cm^{-1}, $A' = -0.24$ cm^{-1}, $\lambda = 0.01136$ cm^{-1}.

(b)

E_u	ν_{45}	$\nu(C_b-C)_{asym}$	996	994.4080	$+1.60$
B_{2g}	ν_{31}	$\nu(C_b-C)_{sym}$	1015	1010.5280	$+4.47$
A_{2g}	ν_{23}	$\nu(C_b-C)_{sym}$	1058	1065.5548	-7.50
B_{1g}	ν_{14}	$\nu(C_b-C)_{sym}$	1131	1104.4480	$+26.56$
A_{1g}	ν_5	$\nu(C_b-C)_{sym}$	1138	1143.3471	-5.34
E_u	ν_{43}	$\nu(C_b-C)_{sym}$	1153	1159.4680	-6.46

Stretching parameters: All oscillators are equivalent, $N_1 = N_2 = N_3 = N_4 = N_5 = N_6 = N_7 = N_8 = N = 140$, $A = -1.7812$ cm^{-1}, $A' = -1.0152$ cm^{-1}, $\lambda = 0.1965$ cm^{-1}

(c)

A_{1g}	ν_2	$\nu(C_b-C_b)$	1602	1590.132	$+11.87$
B_{1g}	ν_{11}	$\nu(C_b-C_b)$	1577	1567.662	$+9.34$
E_u	ν_{38}	$\nu(C_b-C_b)$	1604	1612.605	-8.60

Stretching parameters: All oscillators are equivalent, $N_1 = N_2 = N_3 = N_4 = N = 140$, $A = -2.8105$ cm^{-1}, $A' = -1.256$ cm^{-1}, $\lambda = 0.08025$ cm^{-1}

[a]Ref. [17]. All parameters are in cm^{-1} except N which is dimensionless.
Δ(r.m.s.) $= 19.60$ cm^{-1}.

Their physical meaning can be seen in figure 2 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.

3. Results and discussions

Using the algebraic model Hamiltonian to study the vibrational spectra, the stretching vibrations of molecules Ni(OEP), nickel porphyrin and Ni(TPP) are shown in tables. Here from figure 1 the considered vibrational bands are equivalent so that the individual and interaction term algebraic parameters are $A_1 = A_2 = A_3 =$

Table 2. Comparison between experimental and calculated fundamental energy levels of nickel porphyrin (in cm^{-1}).

(a)

Symmetry	ν_i	Description	Exp.[a]	Calc.	Δ(Exp.−Calc.)
A_{1g}	ν_1	$\nu(C_m–H)$	3042	3042.03	−0.03
B_{2g}	ν_{27}	$\nu(C_m–H)$	3041	3041.04	−0.04
E_u	ν_{36}	$\nu(C_m–H)$	3041	3043.00	+1.00

Stretching parameters: All oscillators are equivalent, $N_1 = N_2 = N_3 = N_4 = N = 44$, $A = -17.65$ cm^{-1}, $A' = -1.3108$ cm^{-1}, $\lambda = 0.0113$ cm^{-1}

(b)

A_{1g}	ν_3	$\nu(C_a–C_m)_{sym}$	1463	1460.90	+2.10
B_{1g}	ν_{10}	$\nu(C_b–C_m)_{asym}$	1654	1644.28	+9.72
A_{2g}	ν_{19}	$\nu(C_a–C_m)_{asym}$	1615	1615.56	−0.56
B_{2g}	ν_{28}	$\nu(C_a–C_m)_{asym}$	1492	1486.10	+5.90
E_u	ν_{37}	$\nu(C_a–C_m)_{asym}$	1624	1629.92	−5.92
E_u	ν_{39}	$\nu(C_a–C_m)_{sym}$	1462	1473.50	−11.50

Stretching parameters: All oscillators are equivalent, $N_1 = N_2 = N_3 = N_4 = N_5 = N_6 = N_7 = N_8 = N = 140$, $A = -2.6200$ cm^{-1}, $A' = -1.046$ cm^{-1}, $\lambda = 0.045$ cm^{-1}

(c)

A_{1g}	ν_2	$\nu(C_b–C_b)$	1579	1529.01	+49.99
B_{1g}	ν_{11}	$\nu(C_b–C_b)$	1509	1509.06	−0.05
E_u	ν_{38}	$\nu(C_b–C_b)$	1547	1548.97	−1.97

Stretching parameters: All oscillators are equivalent, $N_1 = N_2 = N_3 = N_4 = N = 140$, $A = -2.691$ cm^{-1}, $A' = -3.216$ cm^{-1}, $\lambda = 0.0713$ cm^{-1}

[a]Ref. [17]. All parameters are in cm^{-1} except N which is dimensionless. Δ(r.m.s.) = 48.64 cm^{-1}.

$A_4 = A, A_{12} = A_{23} = A_{34} = A_{41} = A, \lambda_{12} = \lambda_{23} = \lambda_{34} = \lambda_{41} = \lambda$ and the vibron number $N_1 = N_2 = N_3 = N_4 = N$.

The vibron number N is related to the total number of bound states supported by the potential well. Equivalently, it can be put in a one-to-one correspondence with the anharmonicity parameters x_e by means of

$$x_e = 1/(N + 1). \tag{7}$$

The values of vibron number can be determined [16] by the relation

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \quad \omega_e \to \text{Spectroscopic constant}, \tag{8}$$

where ω_e and $\omega_e x_e$ are the harmonic frequencies and anharmonic constants of diatomic molecules C–H, C–C, and from eq. (8), we can have the value of N. It may

Table 3. Comparison between experimental and calculated fundamental energy levels of nickel tetraphenyl porphyrin (in cm^{-1}).

(a)

Symmetry	ν_i	Description	Exp.[a]	Calc.	Δ(Exp.−Calc.)
A_{1g}	ν_1	$\nu(C_m\text{–}C)$	1235	1234.42	+0.58
B_{2g}	ν_{27}	$\nu(C_m\text{–}C)$	1269	1270.68	−1.68
E_u	ν_{36}	$\nu(C_m\text{–}C)$	–	1306.94	–

Stretching parameters: All oscillators are equivalent, $N_1 = N_2 = N_3 = N_4 = N = 140$, $A = -2.213$ cm^{-1}, $A' = -0.9985$ cm^{-1}, $\lambda = 0.1295$ cm^{-1}.

(b)

Symmetry	ν_i	Description	Exp.[a]	Calc.	Δ(Exp.−Calc.)
A_{1g}	ν_3	$\nu(C_a\text{–}C_m)_{sym}$	1470	1469.15	+0.85
B_{1g}	ν_{10}	$\nu(C_a\text{–}C_m)_{asym}$	1594	1595.29	−1.29
A_{2g}	ν_{19}	$\nu(C_a\text{–}C_m)_{asym}$	1550	1550.88	−0.88
B_{2g}	ν_{28}	$\nu(C_a\text{–}C_m)_{asym}$	[1481]	1483.02	−2.02
E_u	ν_{37}	$\nu(C_a\text{–}C_m)_{asym}$	–	1639.70	–
E_u	ν_{39}	$\nu(C_a\text{–}C_m)_{sym}$	–	1496.90	–

Stretching parameters: All oscillators are equivalent, $N_1 = N_2 = N_3 = N_4 = N_5 = N_6 = N_7 = N_8 = N = 140$, $A = -2.635$ cm^{-1}, $A' = -1.0236$ cm^{-1}, $\lambda = 0.0495$ cm^{-1}

(c)

Symmetry	ν_i	Description	Exp.[a]	Calc.	Δ(Exp.−Calc.)
A_{1g}	ν_2	$\nu(C_b\text{–}C_b)$	1572	1571.93	+0.07
B_{1g}	ν_{11}	$\nu(C_b\text{–}C_b)$	1504	1504.65	−0.65
E_u	ν_{38}	$\nu(C_b\text{–}C_b)$	–	1639.22	–

Stretching parameters: All oscillators are equivalent, $N_1 = N_2 = N_3 = N_4 = N = 140$, $A = -2.7205$ cm^{-1}, $A' = -1.986$ cm^{-1}, $\lambda = 0.2403$ cm^{-1}

[a]Ref. [17], [ ] calculated values, all parameters are in cm^{-1} except N which is dimensionless.
Δ(r.m.s.) $= 5.02$ cm^{-1}.

be noted here that during the calculation of the vibrational energy levels of nickel metalloporphyrins, the value of N is kept fixed and not used as free parameter.

In the fitting, we fit 48 observed data of nickel metalloporphyrins, which come from literature [17], using the least-squares procedure. With regard to the calculation of vibrational spectra of Ni(OEP), nickel porphyrin, and Ni(TPP), one can also use the Dunham expansion method. However, one has to take too many coefficients into account in order to obtain the same r.m.s.

Partial calculated vibrational results and the fitting parameters A, A', λ, N which are used in this study for the vibrational energy levels of Ni(OEP), nickel porphyrin and Ni(TPP) for each of the 16 stretching vibrational bands are given in tables 1–3, together with the experimental data.

4. Conclusion

In this study, we reported that the vibrational energy levels of nickel octaethyl porphyrin, nickel porphyrin and nickel tetraphenyl porphyrin molecules are in good agreement with experimental data. (i) In the study of vibrational spectra of nickel octaethyl porphyrin for 16 vibrational bands, we obtain Δ(r.m.s.) as 19.60 cm^{-1}. (ii) In the study of vibrational spectra of nickel porphyrin for 16 vibrational bands, we obtain Δ(r.m.s.) as 46.70 cm^{-1}. (iii) In the study of vibrational spectra of nickel tetraphenyl porphyrin for 16 vibrational bands, we obtain Δ(r.m.s.) as 4.42 cm^{-1}.

Hence, it may be concluded that in the calculation of vibrational energy levels, the $U(2)$-based Lie algebraic model Hamiltonian of Iachello, Oss, Lemus and Frank gives better fit to nickel metalloporphyrins.

Acknowledgement

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