Vibrational spectroscopy of C_m–C/C_b–C_b stretching vibrations of copper tetramesityl porphyrin: An algebraic approach

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Abstract. Using Lie algebraic techniques and simpler expressions of the matrix elements of Majorana and Casimir operators given by us, we obtain an effective Hamiltonian operator which conveniently describes stretching vibrations of biomolecules. For a copper tetramesityl porphyrin molecule, the higher excited vibrational levels are calculated by applying the $U(2)$ algebraic approach.

Keywords. Lie algebraic techniques; vibrational spectra; copper tetramesityl porphyrin.

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A comprehensive treatment to understand the spectroscopic features of microsize molecules is by far one of the most challenging aspects of current studies in chemical physics problems [1]. On the one side, experimental techniques are producing a rapidly increasing amount of data and clear evidence for intriguing mechanisms characterizing several aspects of molecular dynamics in porphyrins [2]. On the other side, theoretical approaches are heavily pushed towards their intrinsic limits; in an attempt to provide reliable answers to hitherto unresolved questions concerning very complex situations of porphyrins [3]. The appearance of new experimental techniques to produce higher vibrational excitations in biopolyatomic molecule requires reliable theoretical methods for their interpretation [3]. An algebraic approach has been proposed for the study of molecular spectra. The first step towards an algebraic approach was given by Iachello, Levine, and their co-workers with the introduction of the vibron model, where the rotation–vibration spectra of diatomic molecules are described in terms of a $U(4)$ algebra [4]. Even though this model has the advantage of treating the rotations and vibrations simultaneously, it is rather difficult to apply when the number of atoms in the molecule becomes more than

four [5]. The $U(2)$ model was particularly successful in explaining stretching vibrations of polyatomic molecules [6]. In this paper, we use the $U(2)$ algebraic model to study the higher excited stretching vibrations of copper tetramesityl porphyrin [Cu(TMP)] and its cation radical molecule [Cu(TMP)$^+$].

In constructing this model, we use the isomorphism of the Lie algebra of $U(2)$ with that of the one-dimensional Morse oscillator [4]. The eigenstates of the one-dimensional Schrödinger equation, $h\psi = \varepsilon\psi$, with a Morse potential

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

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 provision 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 negative branch describes the mirror image of the potential.) In the $U(2)$ basis the Morse Hamiltonian (1) corresponds to a simple Hamiltonian, $h = \varepsilon_0 + AC$, where C is the invariant operator of $O(2)$, with eigenvalues $(m^2 - N^2)$ and A is an arbitrary constant related to the Morse parameter. The eigenvalues of h are

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

Introducing the vibrational quantum number $\nu = (N - m)/2$, eq. (1a) can be rewritten as

$$\begin{aligned} &\varepsilon = \varepsilon_0 - 4A(N\nu - \nu^2), \\ &\nu = 0, 1, \ldots, N/2 \text{ or } N - 1/2 \quad (N = \text{ even or odd}). \end{aligned} \tag{1b}$$

One can immediately verify that these are the eigenvalues of the one-dimensional Morse oscillator.

Consider now a molecule with n bonds. In the algebraic model [4], 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 [4], which we denote by C_{ij} and M_{ij}, are called Casimir and Majorana interactions, respectively.

The algebraic model Hamiltonian we consider is thus

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i<j}^{n} A_{ij} C_{ij} + \sum_{i<j}^{n} \lambda_{ij} M_{ij}. \tag{2}$$

In eq. (2), 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.

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)] \tag{3}$$

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

$$\langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle$$
$$= (N_i v_j + N_j v_i - 2 v_i v_j),$$
$$\langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle$$
$$= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2},$$
$$\langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle$$
$$= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2}. \tag{4}$$

The eigenvalues of eq. (2) can be calculated easily and provide a description of n-coupled one-dimensional Morse oscillators.

The algebraic model (eq. (2)) is particularly well-suited to describe stretching vibrations of polyatomic molecules. We consider here the case of C_m–C and C_b–C_b stretching vibrations of metalloporphyrins, Cu(TMP) and Cu(TMP)$^+$. Thus, we must have an account of the symmetry of the metalloporphyrin molecule, $N_i = N, A_i = A$ (any i) and $A_{ij} = A'$ (any i and j). Non-diagonal couplings are two types: nearest-neighbour couplings and opposite bond couplings. An account of the symmetry of metalloporphyrins, the strengths of couplings of the same type must be equal,

$$\lambda_{12} = \lambda_{23} = \lambda_{34} = \lambda_{45} = \cdots = \lambda \quad \text{(nearest-neighbour couplings)},$$
$$\lambda_{13} = \lambda_{24} = \lambda_{35} = \lambda_{46} = \cdots = \lambda' \quad \text{(opposite couplings)}. \tag{5}$$

Equation (2) and the conditions (5) provide a description of C_m–C and C_b–C_b stretching modes of metalloporphyrins in terms of four algebraic parameters $(A, A', \lambda, \lambda')$. An important feature of the algebraic model discussed here is that it not only provides a description of stretching modes, but also gives a simple solution to a crucial problem in the description of polyatomic molecules, namely the construction of states that transforms accordingly to the irreducible representations of the appropriate point group. For the fundamental stretches of metalloporphyrins, with D_{4h} symmetry, these are the symmetry species A_{1g}, B_{1g}, A_{2g}, B_{2g} and E_{1u}. The construction of these 'symmetry adapted states' is an extremely difficult task, as discussed, for example, in ref. [4]. With D_{4h} symmetry here, the operators (on the basis of the considerations mentioned above) are

$$S = \sum_{i<j}^{n} M_{ij}, \quad S' = \sum_{i<j}^{n} c'_{ij} M_{ij}, \quad S'' = \sum_{i<j}^{n} c''_{ij} M_{ij},$$
$$c'_{12} = c'_{23} = c'_{34} = c'_{45} = \cdots = 1, \quad c'_{13} = c'_{24} = c'_{35} = c'_{46} = \cdots = 0,$$
$$c''_{12} = c''_{23} = c''_{34} = c''_{45} = \cdots = 0, \quad c''_{13} = c''_{24} = c''_{35} = c''_{46} = \cdots = 1. \tag{6}$$

Diagonalization of S' produces states that carry representations transform according to the representations $A_{1g}, B_{1g}, A_{2g}, B_{2g}$ and E_{1u} of D_{4h}. The S' operator is thus the 'symmetry adapter' operator. This result, which, at first sight, appears to be surprising, can be easily verified by computing the characters of the representations carried by the eigenstates of S' in the usual way. Here, in this case the value of n is 4 ($j = 4$, $i = 3$).

We have used $U(2)$ algebraic model to study the stretching vibrational spectra of the copper metalloporphyrin molecules. The fitting algebraic parameters are A, A',
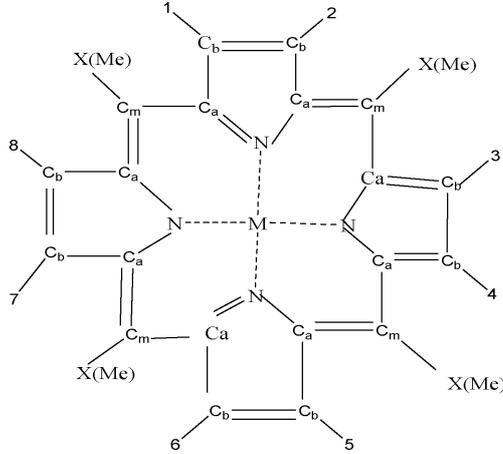
Figure 1. Structure of copper tetramesityl porphyrin [M – metal (Cu), Me – mesityl]. Different porphyrins are obtained by specific substitution at the X or 1 to 8 positions.

λ, λ' and N (vibron number). The values of vibron number (N) can be determined by the relation

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1, \quad i = 1, 2, \ldots, \tag{7}$$

where ω_e and $\omega_e x_e$ are the spectroscopic constants of diatomic molecules [5]. This numerical value must be seen as initial guess; depending on the specific molecular structure, one can expect changes in such an estimate, which, however, should not be larger than $\pm 20\%$ of the original value (eq. (7)). The vibron number N between the diatomic molecule C–C is 140. From figure 1, it is noticed that some of the bonds are equivalent. It may be noted that during the calculation of the vibrational frequencies of copper tetramesityl porphyrin [Cu(TMP)] and its radical [Cu(TMP)$^+$], the value of N is kept fixed and not used as a free parameter.

The second step is to obtain a starting guess for the parameter A. As such, the expression for the single-oscillator fundamental mode is

$$E(\nu = 1) = -4A(N - 1). \tag{8}$$

In the present case we have three different energies, corresponding to symmetric and antisymmetric combinations of different local modes. A possible strategy is to use the centre of gravity of these modes.

$$\bar{A} = \frac{\bar{E}}{4(1 - N)}. \tag{9}$$

The third step is to obtain an initial guess for λ. Its role is to split the initially degenerate local modes, placed here at the common value E used in eq. (8). Such an estimate is obtained by considering the simple matrix structure, and we can find

$$\lambda = \frac{|E_{E_u} - E_{A_{1g}}|}{2N} \tag{10}$$

$$\lambda' = \frac{|E_{B_{2g}} - E_{A_{1g}}|}{4N}. \tag{11}$$

Finally, a numerical fitting procedure is to be carried out to adjust (in a least-square sense, for example) the parameters A and λ starting from values eqs (9) and (10), and A (whose initial guess can be zero).

With the four algebraic parameters, in table 1 we reported the results of fits to C_m–C and C_b–C_b stretching modes of metalloporphyrins, Cu(TMP), Cu(TMP)$^+$, using the Hamiltonian

Table 1.

(a) Experimental and calculated frequencies of C_m–C stretching vibrations of Cu(TMP) and Cu(TMP)$^+$

	Cu(TMP)			Cu(TMP)$^+$		
	Energy (cm^{-1})			Energy (cm^{-1})		
n Species	Obs.[a]	Cal.	Obs.−Cal.	Obs.[a]	Cal.	Obs.−Cal.
$A_{1g}(\nu_1)$	1235 sh, m	1236.88	−1.88	1239 br, w	1239.38	−0.38
$B_{2g}(\nu_{27})$	–	1246.39	–	–	1247.70	
$E_{1u}(\nu_{36})$	1256 br, vw	1256.72	−0.72	–	1256.03	
E_{1u}		2464.18			2458.06	
B_{1g}		2470.74			2463.34	
A_{2g}		2484.84			2474.69	
E_{1u}		2488.61			2515.69	
E_{1u}		2495.17			2526.20	
E_{1u}		2524.26			2544.50	
E_{1u}		2554.31			2483.01	
A_{1g}		3681.89			3672.73	
E_{1u}		3692.22			3681.05	
E_{1u}		3695.99			3684.09	
E_{1u}		3702.55			3689.37	
B_{1g}		3723.94			3706.58	
E_{1u}		3733.55			3714.31	
E_{1u}		3754.21			3730.95	
A_{1g}		3755.76			3732.19	
E_{1u}		3764.54			3937.80	
E_{1u}		3832.11			3739.26	
B_{1g}		3958.29			3816.79	
E_{1u}		3961.34			3829.30	
	Δ (r.m.s) = 1.42 cm^{-1}			Δ (r.m.s) = 0.38 cm^{-1}		

Table 1. *Continued.*

(b) Experimental and calculated frequencies of C_b–C_b stretching vibrations of Cu(TMP) and Cu(TMP)$^+$

n Species	Obs[a]	Cal.	Obs.−Cal.	Obs.[a]	Cal.	Obs.−Cal.
$A_{1g}(\nu_2)$	1567 sh, m	1567.55	−0.55	–	1481.73	–
$B_{2g}(\nu_{11})$	1495 br, vw	1495.29	−0.29	–	1548.31	–
$E_{1u}(\nu_{38})$	–	1639.77	–	–	1614.89	–
E_{1u}		2976.77			2954.38	
B_{1g}		3022.66			2997.11	
A_{2g}		3121.30			3087.54	
E_{1u}		3013.70			3002.54	
E_{1u}		3147.68			3011.32	
E_{1u}		3193.57			3030.74	
E_{1u}		3059.17			3154.13	
A_{1g}		4444.41			4419.27	
E_{1u}		4516.70			4485.85	
E_{1u}		4543.08			4510.16	
E_{1u}		4588.97			4552.44	
B_{1g}		4738.57			4690.27	
E_{1u}		4805.78			4752.19	
E_{1u}		4950.31			4885.36	
A_{1g}		4961.15			4895.35	
E_{1u}		4697.14			4640.81	
E_{1u}		5022.58			4951.94	
B_{1g}		4581.78			4539.67	
E_{1u}		5127.49			4592.43	

Δ (r.m.s.)
= 0.44 cm^{-1}

[a]Ref. [7].

$$H = AC + A'C' + \lambda S + \lambda' S' + \lambda'' S'',$$

$$C = \sum_i C_i, \quad C = \sum_{i<j} C_{ij}. \tag{12}$$

In view of the fact that there are very few available data, table 1 should be considered more as a prediction of unknown states rather than a fit. Using eqs (9)–(11), A, λ and λ' are calculated [4–6] using the available data points. The values of the parameters A, A', λ, λ' and vibron number N are shown in table 2. We have taken $\lambda'' = 0$ (In this case, the next-nearest-neighbour couplings are omitted.) The three C_m–C stretching fundamental frequencies A_{1g}, B_{2g} and E_{1u} are denoted as $\nu_1, \nu_{27}, \nu_{36}$ and other three C_b–C_b fundamental frequencies B_{1g}, A_{1g} and E_{1u} are denoted as $\nu_2, \nu_{11}, \nu_{38}$ in Wilson numbering. As one can see from table 1, the agreement with experiment is good and thus we think that the parameter set of table 2 can

Table 2. Values of the algebraic parameters used in the calculation of Cu(TMP) and Cu(TMP)ᵃ.

| Parameter | C_m–C vibrational mode | | C_b–C_b Vibrational mode | |
	Cu(TMP)	Cu(TMP)$^+$	Cu(TMP)	Cu(TMP)$^+$
A	-2.2173	-2.2218	-2.6825	-2.6537
A'	-1.0182	-1.015	0.9561	-1.5721
λ	0.0369	0.0297	0.2581	0.2378
λ'	0.1073	0.1029	0.0981	0.086
N	140	140	140	140

ᵃAll values are in cm^{-1} except N which is dimensionless.

be used reliably to compute energies of highly excited overtones. Table 1 shows the complete set of overtone frequencies up to second overtone.

In view of this result, we think that simple and yet reliable calculations of stretches of molecules of any geometry can now be done in terms of a few parameters representing the interbond interactions. The model presented here describes the splitting of local C_m–C; C_b–C_b stretching modes due to residual interbond interactions. The splitting pattern ($E_u, A_{1g}, A_{2g}, B_{1g}, B_{2g}$) determines the nature of the interbond interaction.

The calculated fundamental vibrational energy levels of metalloporphyrin molecules are: for C_m–C vibrational modes of Cu(TMP): $\nu_1 = 1236.88$ cm^{-1}, $\nu_{27} = 1246.39$ cm^{-1}, $\nu_{36} = 1256.72$ cm^{-1}; Cu(TMP)$^+$: $\nu_1 = 1239.38$ cm^{-1}, $\nu_{27} = 1247.70$ cm^{-1}, $\nu_{36} = 1256.03$ cm^{-1} (figure 2); and for C_b–C_b vibrational modes of Cu(TMP): $\nu_2 = 1567.55$ cm^{-1}, $\nu_{11} = 1495.29$ cm^{-1}, $\nu_{38} = 1639.77$ cm^{-1}; Cu(TMP)$^+$: $\nu_2 = 1481.73$ cm^{-1}, $\nu_{11} = 1548.31$ cm^{-1}, $\nu_{38} = 1614.89$ cm^{-1} (figure 3). From the view of group theory, the molecule of Cu(TMP) takes a square planar structure with the D_{4h} symmetry point group. For the fundamental stretches of metalloporphyrins, Cu(TMP) and Cu(TMP)$^+$, with D_{4h} symmetry, the symmetry species are $A_{1g}, B_{1g}, A_{2g}, B_{2g}$ and E_{1u}. The four identical C_m–C oscillators describing the fundamental stretching modes are given by A_{1g} (ν_1), B_{2g} (ν_{27}), E_u (ν_{36}) irreps and the other four identical C_b–C_b oscillators describing the fundamental stretching modes are given by A_{1g} (ν_2), B_{2g} (ν_{11}), E_u (ν_{38}) irreps. Here A_{1g} represents the symmetry irreps while B_{2g} represents antisymmetric irreps with respect to C_2 perpendicular to the principal axis and E_u represents two-dimensional antisymmetric irreps with respect to the centre of inversion.

Using the $U(2)$ algebraic model Hamiltonian, the stretching frequencies of C_m–C and C_b–C_b up to second overtone ($\nu = 2$) of two molecules are given in table 1. However, due to lack of sufficient database, we could not compare the calculated vibrational frequencies with that of the observed data of copper metalloporphyrins at higher overtones. This study will be useful to the experimentalist to analyse the predicted vibrational frequencies with the observed data. The model presented here describes the splitting of local (C_m–C) and (C_b–C_b) stretching modes due to residual interbond interactions. The splitting pattern determines the nature of interaction (parameter λ, λ'). Once we get the parameter, we predict the splitting

Eu — 1256.72

B2g — 1246.39

A1g — 1236.88

Eu — 1256.03

B2g — 1247.70

A1g — 1239.38
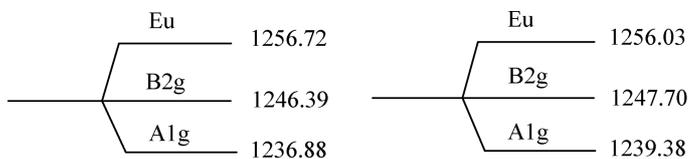
Figure 2. Splitting of the local C_m–C modes in copper tetramesityl porphyrin [Cu(TMP)] and its cation radical [Cu(TMP)$^+$]. The total splitting is 19.84 cm^{-1} and 16.65 cm^{-1} in Cu(TMP) and Cu(TMP)$^+$ respectively.

Eu — 1639.77

A1g — 1567.55

B2g — 1495.29

Eu — 1614.89

B2g — 1548.31

A1g — 1481.73
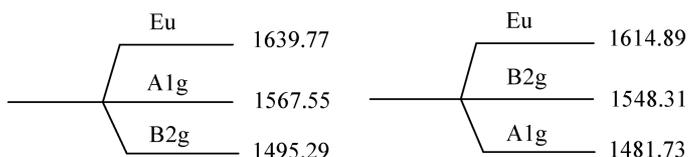
Figure 3. Splitting of the local C_b–C_b modes in copper tetramesityl porphyrin [Cu(TMP)] and its cation radical [Cu(TMP)$^+$]. The total splitting is 144.48 cm^{-1} and 133.16 cm^{-1} in Cu(TMP) and Cu(TMP)$^+$ respectively.

pattern of overtones. Since the experimental locations of these states have crucial importance for understanding the accuracy of our calculation and consequently the local vs. normal behaviour of stretching modes of metalloporphyrins, it would be interesting to scan the region around the predicted energies to see whether or not those two states are there.

The local vs. normal behaviour of stretching modes of polyatomic molecule can be characterized in the same way as in triatomic molecules [5] by introducing the quantity $\xi = (2/\pi) \arctan[8(\lambda + \lambda')/(A + A')]$. We find $\xi = 0.00023$ for the C_m–C bond, $\xi = 0.002$ for the C_b–C_b bond of Cu(TMP), $\xi = 0.00019$ for the C_m–C bond and $\xi = 0.0034$ for the C_b–C_b bond of Cu(TMP)$^+$, thus confirming the highly local behaviour of the stretching modes of these metalloporphyrins.

The present calculations demonstrate that $U(2)$ model can be applied successfully to the higher excited states of metalloporphyrin molecules. It is believed that once we get sufficient observed frequencies of higher overtones, the comparison of overtones and combinational bands of higher overtones (calculated with the help of computer programming and using the model Hamiltonian) can be made with that of the experimental frequencies. In addition, the $U(2)$ algebraic model can be applied to the stretching vibrations of other biopolyatomic molecules and nanoparticles.

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