Vibrational spectra of distorted structure macro & nano molecules: An algebraic approach

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ABSTRACT

Using the Lie algebraic method the vibrational frequencies of 97 resonances Raman lines (A_{1g} + B_{1g} + A_{2g} + B_{2g}) and 38 infrared bands (E_u) of octaethylporphyrinato-Ni (II) and its mesodeuterated and ^{15}N-substituted derivates and Fullerenes C_{60} and C_{70} of 7 vibrational bands are calculated using U(2) algebraic Hamiltonian with four fitting algebraic parameters. The results obtained by the algebraic technique have been compared with experimental data; and they show great accuracy.

Keywords: Lie Algebra; Vibrational Spectra; Ni (OEP); Ni (OEP)-d_4 & Ni (OEP)-N_4; Fullerenes

1. INTRODUCTION

Nanoscience is an interdisciplinary field that seeks to bring about nature nanotechnology. Focusing on the nanoscale intersection of fields such as Physics, Biology, Engineering, Chemistry, Computer Sciences and more, Nanoscience is rapidly expanding [1]. A comprehensive treatment and understanding of spectroscopic features of nano-size molecules is by far one of the most challenging aspects of current studies in molecular spectroscopy. On 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 nano-bio molecules [2]. On the other side, theoretical approaches are heavily pushed towards their intrinsic limits; in the attempt to provide reliable answers to hitherto unresolved questions concerning very complex situations of nano-bio molecules. The appearance of new experimental techniques to produce higher vibrational excitations in nano-bio polyatomic molecule requires reliable theoretical methods for their interpretation. Two approaches have mostly been used so far in an analysis of experimental data: 1) the familiar Dunham like expansion of energy levels in terms of rotations-vibrations quantum numbers and 2) the solution of Schrodinger equation with potentials obtained either by appropriately modifying *ab-initio* calculations or by more phenomenological methods. In this article, we begin a systematic analysis of vibrational spectra of bio-nano molecules in terms of novel approach; 3) Vibron model [3-6].

Recently Lie algebraic model introduction [7-18] could proved itself to be a successful model in the study of vibrational spectra of small, medium size and polyatomic molecules [19,20]. The algebraic model is fully based on the dynamical symmetry and through the language of Lie algebra. For the triatomic, tetratomic, Tetrahedral and poly-atomic Bio-molecules (*i.e.* metalloporphyrins, Ni (OEP), Ni (TTP), Ni Porphyrin) we studied earlier [21-25] using algebraic model. Using the algebraic model in this study we have calculated the vibrational frequencies of octaethylporphyrinato-Ni(II) and its meso-deurated and N substituted derivatives for 97 vibrational bands each using $U(2)$ algebraic model Hamiltonian. In our study we used four fitting parameters which provide better comparisons between the experimental and theoretical calculations throughout the study.

In this paper, we have considered only the In-Plane Vibrations of Nickel Octaethylporphyrin and its meso substituent and ^{15}N derivatives for 97 vibrational bands and fullerenes C_{60} and C_{70} for 7 vibrational bands (both stretching and bending) are calculated by using $U(2)$ algebraic mode Hamiltonian.

2. ALGEBRAIC FRAMEWORK

A complete description of the theoretical foundations needed to formulate the algebraic model for a vibrating molecule. We apply the one-dimensional algebraic model, consisting of a formal replacement of the interatomic, bond coordinates with unitary algebras. To say it in different words, the second-quantization picture suited to describe anharmonic vibrational modes, is specialized through an extended use of Lie group theory and dynamical symmetries. By means of this formalism, one can attain algebraic expressions for eigenvalues and eigenvectors of even complex Hamiltonian operators, including intermode coupling terms as well expectation values of any operator of interest (such as electric dipole and quadrupole interactions). Algebraic model are not *ab-initio* methods, as the Hamiltonian operator depends on a certain number of a priori undetermined parameters. As a consequence, algebraic techniques can be more convincingly compared with semi-empirical approaches making use of expansions over power and products of vibrational quantum numbers, such as a Dunham-like series. However, two noticeable advantages of algebraic expansions over conventional ones are that 1) algebraic modes lead to a (local) Hamiltonian formulation of the physical problem at issue (thus permitting a direct calculation of eigenvectors in this same local basis) and 2) algebraic expansions are intrinsically anharmonic at their zero-order approximation. This fact allows one to reduce drastically the number of arbitrary parameters in comparison to harmonic series, especially when facing medium- or large-size molecules. It should be however also noticed that, as a possible drawback of purely local Hamiltonian formulations (either algebraic or not) compared with traditional perturbative approaches, the actual eigenvectors of the physical system. Yet, for very local situations, the aforementioned disadvantage is not a serious one. A further point of import here is found in the ease of accounting for proper symmetry adaptation of vibrational wave functions. This can be of great help in the systematic study of highly excited overtones of not-so-small molecules, such as the present one. Last but not least, the local mode picture of a molecule is enhanced from the very beginning within the algebraic framework. This is an aspect perfectly lined up with the current tendencies of privileging local over normal mode pictures in the description of most topical situations.

We address here the explicit problem of the construction of the vibrational Hamiltonian operator for the polyatomic molecule. According to the general algebraic description for one-dimensional degrees of freedom, a dynamically-symmetric Hamiltonian operator for n interacting (not necessarily equivalent) oscillators cab written as

$$H = E_0 + A_i C_i + A_{ij} C_{ij} + \lambda_{ij} M_{ij}. \quad (1)$$

In this expresssion, one finds three different classes of effective contributions. The first one, $\sum_{i=1}^{n} A_i C_i$ is devoted to the description of *n* independent, anharmonic sequences of vibrational levels (associated wih *n* independent, local oscillator) in terms of the operators C_i. The second one, $\sum_{i=1}^{n} A_{ij} C_{ij}$ leads to cross-anharmonicities between pairs of distinct local oscillators in terms of the operators C_{ij}. The third one, $\sum_{i=1}^{n} \lambda_{ij} M_{ij}$, describes anharmonic, non-diagonal interactions involving pairs of local oscillators in terms of the operators M_{ij}. The C_i, C_{ij} operators are invariant (Casimir) operators of certain Lie algebras, whilst the M_{ij} are invariant (Majorana) operators associated with coupling schemes involving algebras naturally arising from a systematic study of the algebraic formulation of the one-dimensional model for *n* interacting oscillators. We work in the local (uuncoupled oscillaators) vibrational basis written as

$$|v\rangle \equiv |v_1 v_2 v_3 .... v_n\rangle.$$

In which the aforementioned operators have the following matrix elements

$$\langle v|C_i|v\rangle = -4v_i\left(N_i - v_i\right)$$

$$\langle v|C_{ij}|v\rangle = -4\left(v_i + v_i\right)\left(N_i + N_j - v_i - v_j\right)$$

$$\langle v'|M_{ij}|v\rangle = \left(v_i N_i + v_j N_j - 2v_i v_j\right)\delta_{v_i' v_i}\delta_{v_j' v_j}$$

$$\langle v'|M_{ij}|v\rangle = -\left[\left(v_i + 1\right)\left(N_i - v_i\right)v_j\left(N_j - v_j + 1\right)\right]^{1/2} \quad (2)$$
$$\times \delta_{v_i'-1 v_i}\delta_{v_j'+1 v_j}$$

$$\langle v'|M_{ij}|v\rangle = -\left[\left(v_j + 1\right)\left(N_j - v_j\right)v_i\left(N_i - v_i + 1\right)\right]^{1/2}$$
$$\times \delta_{v_i'+1 v_i}\delta_{v_j'-1 v_j}.$$

We note, in particular, that the expressions above depend on the numbers N_i (Vibron numbers). Such numbers have to be seen as predetermined parameters of well-defined physical meaning, as they relate to the intrinsic anharmonicity of a single, uncoupled oscillator through the simple relation. We report in Table the values of the Vibron numbers used in the present study.

The general Hamiltonian operator 1) can be adapted to describe he internal, vibrational degrees of freedom of any polyatomic molecule in two distinct steps. First, we associate three mutually perpendicular one-dimensional anharmonic oscillators to each atom. This procedure eventually leads to a redundant picture of the whole molecule, as it will include spurious (*i.e.* translational/rotational) degrees of freedom. It is however possible to remove easily such spurious modes through a technique de-

scribed elsewhere [19-21]. One is thus left with a Hamiltonian operator dealing only with true vibrations. Such modes are given in terms of coupled oscillators in the local basis; 2) The coupling is induced by the Majorana operators. A sensible use of these operators is such that the correct symmetries of vibrational wave functions are properly taken into account. As a second step, the algebraic parameters A_i, A_{ij}, λ_{ij} of **Eq.1** need to be calibrated to reproduce the observed spectrum.

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, $\cdots$. quantized through the algebra

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

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

$$H(p_s, s) = p_s^2 / 2\mu + D\left[1 - \exp(-\beta s)\right]^2 \qquad (3)$$

For each oscillator i, states are characterized by representations of

$$\left| \begin{array}{ccc} U_i(2) & \supset & O_i(2) \\ \downarrow & & \downarrow \\ N_i & & m_i \end{array} \right\rangle \qquad (4)$$

with $m_i = N_i$, $N_i - 2$, $\cdots$, 1 or 0 (N_i—odd or even). The Morse Hamiltonian (3) can be written, in the algebraic approach, simply as

$$H_i = \varepsilon_{0i} + A_i C_i, \qquad (5)$$

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

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

Introducing the vibrational quantum number $v_i = (N_i - m_i)/2$, [20] one has

$$\varepsilon_i = \varepsilon_{0i} - 4A_i \left(N_i v_i - v_i^2 \right) \qquad (6)$$

For non-interacting oscillators the total Hamiltonian is

$$H = \sum_i H_i$$

with eigen-values

$$E = \sum_i \varepsilon_i = E_0 - \sum_i 4A_i \left(N_i v_i - v_i^2 \right) \qquad (7)$$

2.1. Hamiltonian for Stretching Vibrations

The interaction potential can be written as

$$V(s_i, s_j) = k'_{ij}\left[1 - \exp(-\alpha_i s_i)\right]\left[1 - \exp(-\alpha_j s_j)\right], \quad (8)$$

which reduces 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 **Eq.8** can be taken into account in the algebraic approach by introducing two terms. 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 **Eq.2** are given by

$$
\begin{aligned}
&\left\langle N_i, v_i; N_j, v_j \left| C_{ij} \right| N_i, v_i; N_j, v_j \right\rangle ? \\
&= 4\left[\left(v_i + v_j \right)^2 - \left(v_i + v_j \right)\left(N_i + N_j \right) \right].
\end{aligned}
\qquad (9)
$$

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 substract 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

$$
\begin{aligned}
&\left\langle N_i, v_i; N_j, v_j \left| C_{ij} \right| N_i, v_i; N_j, v_j \right\rangle \\
&= 4\left[\left(v_i + v_j \right)^2 - \left(v_i + v_j \right)\left(N_i + N_j \right) \right] \\
&+ \left[\left(N_i + N_j \right) / N_i \right] 4\left(N_i v_i - v_i^2 \right) \\
&+ \left[\left(N_i + N_j \right) / N_i \right] 4\left(N_j v_j - v_j^2 \right).
\end{aligned}
\qquad (10)
$$

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

$$
\begin{aligned}
&\left\langle N_i, v_i; N_j, v_j \left| M_{ij} \right| N_i, v_i; N_j, v_j \right\rangle \\
&= \left(N_i v_j + N_j v_i - 2v_i v_j \right) \\
&\left\langle N_i, v_i + 1; N_j, v_j - 1 \left| M_{ij} \right| N_i, v_i; N_j, v_j \right\rangle \\
&= -\left[v_j \left(v_i + 1 \right)\left(N_i - v_i \right)\left(N_j - v_j + 1 \right) \right]^{1/2} \\
&\left\langle N_i, v_i - 1; N_j, v_j + 1 \left| M_{ij} \right| N_i, v_i; N_j, v_j \right\rangle \\
&= -\left[v_i \left(v_j + 1 \right)\left(N_j - v_j \right)\left(N_j - v_i + 1 \right) \right]^{1/2}.
\end{aligned}
\qquad (11)
$$

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

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 de-

generacies of figure and 2) in addition it generates states with the appropriate transformation properties under the point group. In order to achieve this result the λ_{ij} must be chosen in an appropriate way that reflects the geometric symmetry of the molecule. The total Majorana operator

$$S = \sum_{i<j}^{n} M_{ij} \qquad (12)$$

is divided into subsets reflecting the symmetry of the molecule

$$S = S' + S' + \cdots \qquad (13)$$

The operators $S = S' + S' + \cdots$ are the symmetryadapted operators. The construction of the symmetryadapted operators of any molecule will become clear in the following sections where the cases of Metalloporphyrins (D$_{4h}$) will be discussed.

2.3. Hamiltonian for Bending Vibrations

We emphasize once more that the quantization scheme of bending vibrations in $U(2)$ is rather different from $U(4)$ and implies a complete separation between rotations and vibrations. If this separation applies, one can quantize each bending oscillator i by means of an algebra $U_i(2)$ as in **Eq.4**. The Poschl-Teller Hamiltonian

$$H(p_s, s) = |2\mu - D| \cosh^2(\alpha s) \qquad (14)$$

where we have absorbed the $\lambda(\lambda - 1)$ part into D, can be written, in the algebraic approach, as

$$H_i = \varepsilon_{0i} + A_i C_i, \qquad (15)$$

This Hamiltonian is identical to that of stretching vibration (**Eq.5**). The only difference is that the coefficients A_i in front of C_i are related to the parameters of the potential, D and α, in a way that is different for Morse and Poschl-Teller potentials. The energy eigen-values of uncoupled Poschl-Teller oscillators are, however, still given by

$$E = \sum_i \varepsilon_i = E_0 - \sum_i 4A_i \left(N_i v_i - v_i^2\right). \qquad (16)$$

One can then proceed to couple the oscillators as done previously and repeat the same treatment.

2.4. 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 do the construction, draw a figure corresponding to the geometric structure of the molecule (**Figure 1**). Number of degree of freedom we wish to describe.
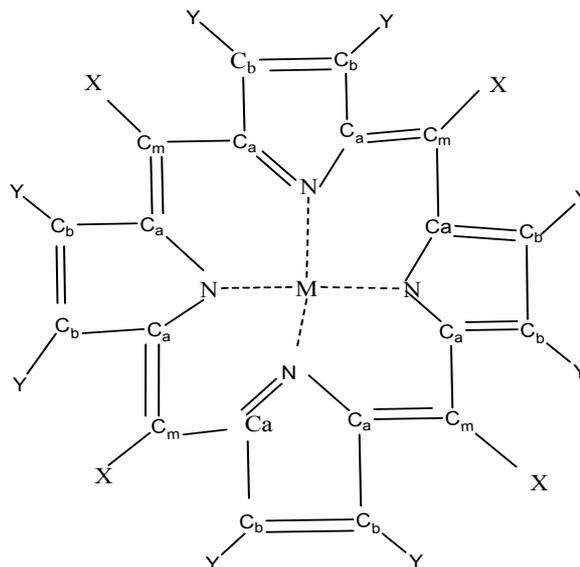
Figure 1. Structure of Metalloporphyrins.

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)

The symmetry-adapted operators of Metalloporphyrins with symmetry D$_{4h}$ are those corresponding to these two couplings, that is,

$$S' = \sum_{i<j}^{n} c'_{ij} M_{ij}, \quad S'' = \sum_{i<j}^{n} c''_{ij} M_{ij}, \qquad (17)$$

with

$$c'_{12} = c'_{23} = c'_{34} = c'_{45} = \cdots = 1$$
$$c'_{13} = c'_{24} = c'_{35} = c'_{46} = \cdots = 0$$
$$c''_{12} = c''_{23} = c''_{34} = c''_{45} = \cdots = 0$$
$$c''_{13} = c''_{24} = c''_{35} = c''_{46} = \cdots = 1$$

The total Majorana operator S is the sum

$$S = S^1 + S^{11} \qquad (18)$$

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$_{2g}$ and E$_{1u}$ of D$_{4h}$.

2.5. Local to Normal Transition: The Locality Parameter (ξ)

The local-to-normal transition is governed by the dimensionless locality parameter (ξ). The local-to-normal transition can be studied [19,20] for polyatomic molecules, for which the Hamiltonian is

$$H = H^{\text{local}} + \lambda_{12} M_{12} = A_i C_i + A_{ij} C_{ij} + \lambda_{ij} M_{ij} \qquad (19)$$

For these molecules, the locality parameters are

$$\xi_i = (2/\Pi)\tan^{-1}\left[8\lambda_{ij}/\left(A_i + A_{ij}\right)\right], i, j = 1, 2, 3. \quad (20)$$

Corresponding to the two bonds. *A* global locality parameter for XYZ molecules can be defined as the geometric mean [20]

$$\xi = \left(|\xi_1\xi_2|\right)^{1/2}. \quad (21)$$

Locality parameters of this metalloporphyrins is given in the results and discussions With this definition, due to Child and Halonen [21], local-mode molecules are near to the $\xi = 0$ limit, normal mode molecules have $\xi \to 1$.

3. RESULTS AND DISCUSSIONS

The number N [total number of bosons, label of the ire-ducible representation of $U(4)$] 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

$$x_e = \frac{1}{N+2}. \quad (22)$$

We can rewrite the **Eq.22** as

$$N_i = \frac{\omega_e}{\omega_e x_e} - 1 \left(i = 1, 2\cdots\right). \quad (23)$$

Now, for a blood cell molecule, we can 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 [22] and that of K.P. Huber and G. Herzberg [23]. Using the values of ω*e* and ω*exe* 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 ±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

$$E(v = 1) = -4A(N - 1) \quad (24)$$

In the present case we have three and six different energies corresponding to symmetric and antisymmetric combinations of the different local mode.

$$A = E/4(1 - N) \quad (25)$$

where E = Average energy, The initial guess for λ can be obtained by

$$\lambda = |E_1 - E_2|/2N \quad (26)$$

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 of different Bio & Nano molecules are presented in **Tables 1-5** and the corresponding algebraic parameters are presented in **Tables 6** and **7**.

4. CONCLUSIONS

We have presented here a vibrational analysis of the stretching/bending modes of Bio molecules (*i.e.* Nickel Porphyrins) and Nano molecules (Fullerenes C_{60}, C_{70}) in terms of one-dimensional Vibron model *i.e.* U(2) algebraic model.

From the view of group theory, the molecule of Ni(OEP), Ni(OEP)-d_4 & Ni(OEP)-$^{15}N_4$ takes a square planar structure with the D_{4h} symmetry point group. Molecular vibrations of metalloporphyrins are classified into the in-plane and out of plane modes. For Octaethyl dimmers of D_{4h} structure assuming the peripheral ethyl group is point mass the in-plane vibrations of Octaethyl dimmers are factorized into 35 gerade and 18 ungerade. Out of planes are factorized into 8 gerade and 18 ungerade modes. The A_{2u} and E_u modes are IR active where the A_{1g}, B_{1g}, A_{2g}, B_{2g} & E_g modes are Raman active in an ordinary sense. The Nano-molecules C_{60} and C_{70} are I_h and D_{5h} point group symmetry respectively.

In this study the resonance Raman spectra of Ni(OEP), Ni(OEP)-d_4 and Ni(OEP)$^{15}N_4$ for 97 vibrational bands, we obtain the RMS deviation *i.e.* Δ(r.m.s) = 40.92 cm^{-1}, 33.03 cm^{-1}, 4.04 cm^{-1} and the locality parameters are ξ_1 = 0.0765, ξ_2 = 0.0468, ξ_3 = 0.0685 respectively.

In this study the vibrational frequencies of Nano molecules C_{60} and C_{70} for 7 vibrational bands, we obtain the RMS deviation *i.e.* Δ(r.m.s) = 6.439 cm^{-1}, 3.2029 cm^{-1}, and the locality parameters are ξ_1 = 0.0384, ξ_2 = 0.0493, ξ_3 = 0.0590 respectively.

Using improved set of algebraic parameters, the RMS deviation we reported in this study for Bio and Nano molecule is lying near about the experimental accuracy. Using only four algebraic parameters, the RMS deviation we reported in this study for Bio-Nano molecule are better fit.

The above two points confirm that in four parameters fit, the set of algebraic parameters we reported in this study of local to normal transition provide the best fit to the spectra of Bio-Nano molecules.

We hope that this work will be stimulate further research in analysis of vibrational spectra of other Nano molecules like fullerenes and protein molecules where the algebraic approach has not been applied so far.

Table 1. Comparison between the experimental and Calculated frequencies of the resonance Raman active fundamental modes of Ni(OEP) (cm^{-1}).

Symmetry	Mode	Description	Exp[a]	Cal	Δ(Exp-Calc)
A$_{1g}$	ν1	ν(Cm - H)	-	3041.94	-
	ν2	ν(Cb - Cb)	1602	1602.04	−0.04
	ν3	ν(Ca-Cm)sym	1519	1525.06	−6.06
	ν4	ν(Pyrhalf-ring)sym	1383	1383.45	−0.45
	ν5	ν(Cb - C)sym	1025	1010.52	14.48
	ν6	ν(Pyr breathing)	806	803.76	2.24
	ν7	δ(Pyr def)sym	674	685.99	−11.99
	ν8	ν(Ni - N)	344	344.36	−0.36
	ν9	δ(Cb - C)sym	226	225.66	0.34
B$_{1g}$	ν10	ν'(Ca - Cm)sym	1655	1639.26	15.74
	ν11	ν(Cb - Cb)	1576	1577.96	−1.96
	ν12	ν(Pyr half-ring)sym	-	1293.43	-
	ν13	δ(Cm - H)	1220	1219.69	0.31
	ν14	ν(Cb - C)sym	-	1065.55	-
	ν15	ν(Pyr breathing)	-	750.51	-
	ν16	δ(Pyr def)sym	751	752.43	−1.43
	ν17	δ(Cb - C)sym	-	304.08	-
	ν18	ν(Ni-N)	-	423.15	-
A$_{2g}$	ν19	ν'(Ca - Cm)sym	1603	1589.26	13.74
	ν20	ν(Pyr quarter-ring)	1397	1396.89	0.11
	ν21	δ(Cm - H)	1308	1327.40	−19.40
	ν22	ν'(Pyr half-ring)sym	1121	1121.87	−0.87
	ν23	ν'(Cb - C)sym	-	1104.44	-
	ν24	δ'(Pyr def)sym	739	732.81	6.19
	ν25	δ(Pyr rot)	-	523.70	-
	ν26	δ'(Cb - C)sym	-	382.51	-
B$_{2g}$	ν27	ν(Cm - H)	-	3040.95	-
	ν28	ν'(Ca - Cm)sym	-	1507.32	-
	ν29	ν(Pyr quarter-ring)	1409	1408.53	0.47
	ν30	ν'(Pyr half-ring)sym	1159	1142.34	16.66
	ν31	ν'(Cb - C)sym	-	1159.46	-
	ν32	δ'(Pyr def)sym	785	773.06	11.94
	ν33	δ(Pyr rot)	-	528.26	-
	ν34	δ'(Cb - C)sym	-	437.96	-
	ν35	δ(Pyr transl)	-	178.96	-
Eu	ν36	ν(Cm - H)	-	3040.95	-
	ν37	ν'(Ca - Cm)sym	1604	1642.79	−38.79
	ν38	ν(Cb - Cb)	1557	1604.28	−47.28
	ν39	ν(Ca - Cm)sym	1487	1474.88	12.12
	ν40	ν(Pyr quarter-ring)	1443	1442.36	0.64
	ν41	ν'(Pyr half-ring)sym	1389	1392.45	−3.45
	ν42	δ(Cm-H)	1268	1266.81	1.19
	ν43	ν'(Cb-C)sym	1148	1143.34	4.66
	ν44	ν'(Pyr half-ring)sym	1113	1113.39	−0.39
	ν45	ν'(Cb-C)sym	993	994.40	−1.60
	ν46	δ'(Pyr)sym	924	925.56	−1.56
	ν47	ν(Pyr breathing)	726	727.94	−1.94
	ν48	δ(Pyr)sym	605	604.92	0.08
	ν49	δ(Pyr rot)	550	552.48	−2.48
	ν50	ν(Ni - N)	-	501.94	-
	ν51	δ'(Cb - C)sym	-	460.94	-
	ν52	δ(Cb - C)sym	287	288.26	−1.26
	ν53	δ(Pyr transl)	-	183.77	-

[a]Experimental data has taken from Reference [24]. Δ (r.m.s) = 40.92 cm^{-1}

Table 2. Comparison between the experimental and Calculated frequencies of the resonance Raman active fundamental modes of Ni(OEP)-d_4 (cm^{-1}).

Symmetry	Mode	Description	Exp[a]	Cal	Δ(Exp-Calc)
A$_{1g}$	ν1	ν(Cm - D)	-	2265.10	-
	ν2	ν(Cb - Cb)	1602	1612.99	−10.99
	ν3	ν(Ca - Cm)sym	1512	1513.86	−1.86
	ν4	ν(Pyr half-ring)sym	1382	1384.58	−2.58
	ν5	ν(Cb - C)sym	1026	1026.81	−0.81
	ν6	ν(Pyr breathing)	802	802.86	−0.86
	ν7	δ(Pyr def)sym	667	668.34	−1.34
	ν8	ν(Ni - N)	342	340.76	1.24
	ν9	δ(Cb - C)sym	226	227.40	−1.40
B$_{1g}$	ν10	ν'(Ca - Cm)sym	1645	1650.13	−5.13
	ν11	ν(Cb - Cb)	1576	1578.24	−2.24
	ν12	ν(Pyr half-ring)sym	-	1272.24	-
	ν13	δ(Cm - D)	950	951.44	−1.44
	ν14	ν(Cb - C)sym	1187	1188.94	−1.94
	ν15	ν(Pyr breathing)	-	762.93	-
	ν16	δ(Pyr def)sym	684	683.18	0.82
	ν17	δ(Cb - C)sym	-	296.58	-
	ν18	ν(Ni - N)	-	171.41	-
A$_{2g}$	ν19	ν'(Ca - Cm)sym	1582	1565.75	16.25
	ν20	ν(Pyr quater-ring)	1397	1397.12	−0.12
	ν21	δ(Cm - D)	890	891.24	−1.24
	ν22	ν'(Pyr half-ring)sym	1202	1203.64	−0.64
	ν23	ν'(Cb - C)sym	1029	1028.43	0.57
	ν24	δ'(Pyr def)sym	733	736.96	−3.96
	ν25	δ(Pyr rot)	-	524.78	-
	ν26	δ'(Cb - C)sym	-	277.35	-
B$_{2g}$	ν27	ν(Cm - D)	-	2268.85	-
	ν28	ν'(Ca - Cm)sym	-	1712.19	-
	ν29	ν(Pyr quater-ring)	1408	1408.90	−0.90
	ν30	ν'(Pyr half-ring)sym	1159	1159.91	−0.91
	ν31	ν'(Cb - C)sym	-	1165.43	-
	ν32	δ'(Pyr def)sym	785	805.59	−20.59
	ν33	δ(Pyr rot)	-	493.73	-
	ν34	δ'(Cb - C)sym	-	252.37	-
	ν35	δ(Pyr transl)	-	182.17	-
Eu	ν36	ν(Cm - D)	-	3040.95	-
	ν37	ν'(Ca - Cm)sym	1595	1592.94	2.06
	ν38	ν(Cb - Cb)	1542	1543.50	−1.50
	ν39	ν(Ca - Cm)sym	1480	1480.76	−0.76
	ν40	ν(Pyr quater-ring)	1440	1445.84	−5.84
	ν41	ν(Pyr half-ring)sym	1383	1384.58	−1.58
	ν42	δ(Cm - D)	1175	1175.14	−1.14
	ν43	ν'(Cb - C)sym	1114	1112.05	1.95
	ν44	ν'(Pyr half-ring)sym	1018	1002.44	15.56
	ν45	ν'(Cb - C)sym	943	944.41	−1.41
	ν46	δ'(Pyr)sym	843	840.20	2.80
	ν47	ν(Pyr breathing)	722	723.01	−0.01
	ν48	δ(Pyr)sym	597	598.28	−1.28
	ν49	δ(Pyr rot)	537	536.54	−1.95
	ν50	ν(Ni - N)	-	256.08	-
	ν51	δ'(Cb - C)sym	-	302.32	-
	ν52	δ(Cb - C)sym	-	295.01	-
	ν53	δ(Pyr transl)	-	188.27	-

[a]Experimental data has taken from Reference [24]. Δ (r.m.s) = 33.03 cm^{-1}

Table 3. Comparison between the experimental and Calculated frequencies of the resonance Raman active fundamental modes of Ni(OEP)-$^{15}N_4$ (cm^{-1}).

Symmetry	Mode	Description	Exp[a]	Cal	Δ(Exp-Calc)
A_{1g}	ν1	ν(Cm - N)	-	2089.8	-
	ν2	ν(Cb - Cb)	1602	1603.02	−1.02
	ν3	ν(Ca - Cm)sym	1519	1525.06	−6.06
	ν4	ν(Pyr half-ring)sym	1377	1371.10	5.90
	ν5	ν(Cb - C)sym	1022	1021.12	0.88
	ν6	ν(Pyr breathing)	801	803.76	2.76
	ν7	δ(Pyr def)sym	673	685.99	−12.99
	ν8	ν(Ni - N)	344	344.26	−0.26
	ν9	δ(Cb - C)sym	226	226.28	−0.28
B_{1g}	ν10	ν'(Ca - Cm)sym	1655	1639.26	15.74
	ν11	ν(Cb - Cb)	1576	1575.39	0.61
	ν12	ν(Pyr half-ring)sym	-	1337.81	-
	ν13	δ(Cm - N)	1220	1220.05	−0.05
	ν14	ν(Cb - C)sym	-	1273.68	-
	ν15	ν(Pyr breathing)	-	750.51	-
	ν16	δ(Pyr def)sym	749	752.43	−3.43
	ν17	δ(Cb - C)sym	-	330.59	-
	ν18	ν(Ni - N)	-	369.38	-
A_{2g}	ν19	ν'(Ca - Cm)sym	1603	1589.26	13.74
	ν20	ν(Pyr quater-ring)	1396	1396.89	−0.89
	ν21	δ(Cm - N)	1305	1309.28	−4.28
	ν22	ν'(Pyr half-ring)sym	1108	1113.39	−5.39
	ν23	ν'(Cb-C)sym	-	1065.55	
	ν24	δ'(Pyr def)sym	732	732.81	−0.81
	ν25	δ(Pyr rot)	-	523.70	-
	ν26	δ'(Cb - C)sym	-	304.08	-
B_{2g}	ν27	ν(Cm - N)	-	2105.12	-
	ν28	ν'(Ca - Cm)sym	-	1474.88	-
	ν29	ν(Pyr quater-ring)	1408	1408.53	−0.53
	ν30	ν'(Pyr half-ring)sym	1150	1142.34	7.66
	ν31	ν'(Cb - C)sym	-	1010. 52	-
	ν32	δ'(Pyr def)sym	785	773.06	11.94
	ν33	δ(Pyr rot)	-	528.26	-
	ν34	δ'(Cb - C)sym	-	460.94	-
	ν35	δ(Pyr transl)	-	178.96	-
Eu	ν36	ν(Cm - N)	-	2120.38	-
	ν37	ν'(Ca - Cm)sym	1603	1603.02	−0.02
	ν38	ν(Cb - Cb)	1555	1562.23	−7.23
	ν39	ν(Ca - Cm)sym	1484	1483.30	0.70
	ν40	ν(Pyr quater-ring)	1442	1442.36	0.36
	ν41	ν(Pyr half-ring)sym	1386	1383.45	2.55
	ν42	δ(Cm - N)	1266	1265.11	0.89
	ν43	ν'(Cb - C)sym	1140	1147.40	−7.40
	ν44	ν'(Pyr half-ring)sym	1108	1113.39	−5.39
	ν45	ν'(Cb - C)sym	986	994.40	−8.40
	ν46	δ'(Pyr)sym	921	918.06	2.94
	ν47	ν(Pyr breathing)	719	727.94	−8.94
	ν48	δ(Pyr)sym	602	601.10	0.90
	ν49	δ(Pyr rot)	550	552.48	−2.48
	ν50	ν(Ni - N)	-	394.50	-
	ν51	δ'(Cb - C)sym	-	374.90	-
	ν52	δ(Cb - C)sym	-	288.26	-
	ν53	δ(Pyr transl)	-	183.77	-

[a]Experimental data has taken from Reference [24]. Δ (r.m.s) = 4.04 cm^{-1}.

Table 4. Comparisons between the experimental and calculated frequencies of the Raman active fundamental modes of C_{60} (cm^{-1}).

Vibrational mode	Exp[b]	Cal	Δ(Exp-Calc)
$\nu1$	273	275.9303	−2.9303
$\nu2$	497	498.3048	−1.3048
$\nu3$	528	530.2039	−2.2039
$\nu4$	577	577.3049	−0.3049
$\nu5$	1183	1182.2093	0.7907
$\nu6$	1429	1431.9848	−2.9848
$\nu7$	1469	1470.5968	−1.5968

Δ (r.m.s) = 6.439 cm^{-1}.

Table 5. Comparisons between the experimental and Calculated frequencies of the Raman active fundamental modes of C_{70} (cm^{-1}).

Vibrational mode	Exp[b]	Cal	Δ(Exp-Calc)
$\nu1$	260	259.3543	0.6457
$\nu2$	571	573.0294	−2.0294
$\nu3$	1062	1064.3029	−2.3029
$\nu4$	1185	1186.0928	−1.0928
$\nu5$	1232	1233.2930	−1.2930
$\nu6$	1513	1513.2087	−2.9848
$\nu7$	1568	1565.3392	2.6608

[b]Experimental data has taken from Reference[25], Δ (r.m.s) = 3.2029 cm^{-1}.

Table 6. Fitting algebraic parameters of octaethylporphyrinato Ni(II) and its meso-deuterated and N-substituted derivatives.

	Cm-H	Cb-Cb	Cb-C	Ca-Cm	Ni-N	Pyr.half	Pyr.quater	Pyr.breath	Pyr.rot	Pyr.def
					Ni(OEP) molecule					
A	−1.8972	−1.7829	−1.8293	−1.5403	−2.2832	−1.0293	−2.3940	−1.2930	−1.2394	−1.2930
A'	−0.3094	−0.3049	−0.3833	−0.3209	−0.4954	−0.4859	−0.4930	−0.4938	−0.2918	−0.3820
λ	0.0394	0.0238	0.0495	0.0594	0.0293	0.0433	0.0867	0.0594	0.0637	0.0322
λ'	0.1029	0.0384	0.3902	0.0293	0.0390	0.0902	0.0293	0.0783	0.0394	0.9200
					Ni(OEP)-d_4 molecule					
A	−1.9567	−1.7394	−1.7574	−1.4839	−2.4758	−1.9438	−1.5783	−1.4839	−1.3489	−1.4938
A'	−0.4039	−0.5493	−0.4938	−0.2345	−0.5489	−0.2390	−0.4465	−0.3493	−0.2930	−0.4930
λ	0.0840	0.0349	0.0657	0.0405	0.0349	0.0128	0.0928	0.0647	0.0493	0.0574
λ'	0.2349	0.0504	0.0394	0.0192	0.0128	0.0495	0.0112	0.0349	0.0325	0.0932
					Ni(OEP)-$15N_4$ molecule					
A	−1.7849	−1.7839	−1.8495	−1.3849	−2.3948	−1.0490	−2.4930	−1.3049	−1.3829	−1.2389
A'	−0.4302	−0.3940	−0.3647	−0.2784	−0.4304	−0.3920	−0.4289	−0.3940	−0.3920	−0.4673
λ	0.0333	0.0394	0.0432	0.0394	0.0239	0.0320	0.0788	0.0403	0.0433	0.0333
λ'	0.0938	0.0574	0.2987	0.0293	0.0293	0.0843	0.0392	0.0563	0.0233	0.0945

Table 7. Fitting algebraic parameters of fullerenes C_{60} and $C_{70.}$

	Vibron number	Algebraic parameters			
	N	A	A'	λ	λ'
C60	140	−1.4309	0.0384	0.0739	−0.4932
C70	140	0.9837	0.0456	0.0348	0.5903

All values in cm^{-1} except N, which is dimensionless.

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