# Resonance Raman study on distorted symmetry of porphyrin in nickel octaethyl porphyrin

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**Abstract.** The resonance Raman (RR) spectra of nickel octaethyl porphyrin, Ni(OEP), in $CH_2Cl_2$ (solvent) at different excitations such as 514.5, 488.0, 441.6 and 406.7 nm are recorded and analysed. The results of the theory of distortion-induced RR intensity is applied to the observed spectra to determine the excited electronic state symmetry of porphyrin in Ni(OEP). It is concluded that the porphyrin molecule ($D_{4h}$ structure) attains a non-polar distorted structure of $D_2$ symmetry rather than $S_4$ symmetry in $CH_2Cl_2$ solution.

## 1. Introduction

Porphyrin and its derivatives have received considerable attention during recent years because of their great biological importance [1–42]. They play major roles in the electron transfer reactions in many enzymes and photosynthesis in the green plants [32]. They form important chromphores in haeme protein, chlorophylls, cytochrome oxidase etc.

Nickel ocatethyl porphyrin, Ni(OEP), plays a central role in studies of the molecular properties of porphyrins and porphyrin containing enzymes [9]. Thus, the resonance Raman (RR) study of Ni(OEP) is very important. Furthermore, renewed interest on these systems has aroused because of their technological possibilities in various types of devices such as solid catalysts, photoconductors, organic semiconductors and also because they are used for photochemotherapy in photodynamic therapy and diagnosis of malignant tumours [19–23].

Several experimental techniques [4,6,9,13,17] such as electronic luminescence spectroscopy including fine structure quasiline spectra, X-ray, ESR, NMR

Mössbauer spectroscopy, magnetic susceptibility measurements, absorption, infrared and Raman spectroscopy have been applied to elucidate the physical and chemical properties of porphyrin. At the same time many theoretical approaches including quantum chemical calculations have been attempted by several workers [8,10,11]. Although extensive studies by all these techniques on these systems have clarified several aspects, many others remain in question. One of these is the non-planar structure of porphyrin in solution.

Considering a planar $D_{4h}$ symmetry of porphyrin, the RR spectra of metalloporphyrins have been studied by many scientists [1–12,26–28]. However, one aspect of porphyrin structure that is of current interest is its propensity for forming non-planar structure [12]. These non-planar ruffled, domed or flexed conformations influence many chemical and photochemical properties of porphyrins in biological reactions; the non-planar conformations have been proposed to play a major role in reactions catalysed by vitamin $B_{12}$ [35] in the formation of co-factor of $F_{430}$ in methyl reductase of tetrapyrrole pigments of photosynthetic reaction centers [11].

Recently, using the principles of group theory and the perturbation methods, a quantitative theory of distortion-induced resonance Raman intensity due to different modes of molecular units is formulated by Bhattacharjee [43–46]. The central idea of the work is that the electric field associated with the exciting frequency serves as the source of perturbation that distorts the molecule (e.g. when the electric field is in the $x$-direction, the molecule attains a polar type of distortion in the $x$-direction) and hence, modifies its dynamics [44]. In such a case, one has to use a set of 'propensity rules'. The rules predict that for active modes: (i) when the distortion is along the $x$-direction the $\alpha_{xx}$ modes of molecule will be more intense than the modes having $\alpha_{xy}$ or $\alpha_{xz}$, (ii) in $y$-distortion, intensities of $\alpha_{yy} > (\alpha_{yx}$ or $\alpha_{yz}) > (\alpha_{xx}$ or $\alpha_{zz})$, (iii) in the $z$-distortion, $\alpha_{zz} > (\alpha_{zx}$ or $\alpha_{zy}) > (\alpha_{xx}$ or $\alpha_{yy})$. For forbidden modes it is revealed that the forbidden transitions become active due to structural distortion of the unit and they need to be ascribed as distortion-induced transitions. Such transitions of different symmetry species are characterized by different order of distortion-induced activity (DIA), i.e., DIA-I/DIA-II.../DIA-h representing first/second.../higher order effect of distortion [43–51].

In this work the RR spectra of nickel octaethyl porphyrin, Ni(OEP), in $CH_2Cl_2$ (solvent) at different excitations such as 514.5, 488.0, 441.6 and 406.7 nm have been analysed and using the results of the theory of distortion-induced RR intensities of molecular units, the excited electronic state structure of the porphyrin molecule in Ni(OEP) has been determined.

## 2. Experiment

The nickel octaethyl porphyrin, Ni(OEP), is purchased from Porphyrin Products (presently known as Hydrus Chemical Inc., Tokyo). Methylene chloride ($CH_2Cl_2$) is obtained from Aldrich Chemicals.

The absorption spectrum (figure 1) of Ni(OEP) in $CH_2Cl_2$ is recorded with a Hitachi 1245 spectrophotometer.

For a highly symmetric porphyrin with $D_{4h}$ symmetry, the highest and next highest occupied and the lowest unoccupied orbitals belong to the $a_{2u}$, $a_{1u}$ and $e_g$ species respectively [8]. Accordingly, both the nearby $\pi\pi^*$ states, that is $a_{2u}e_g$ and
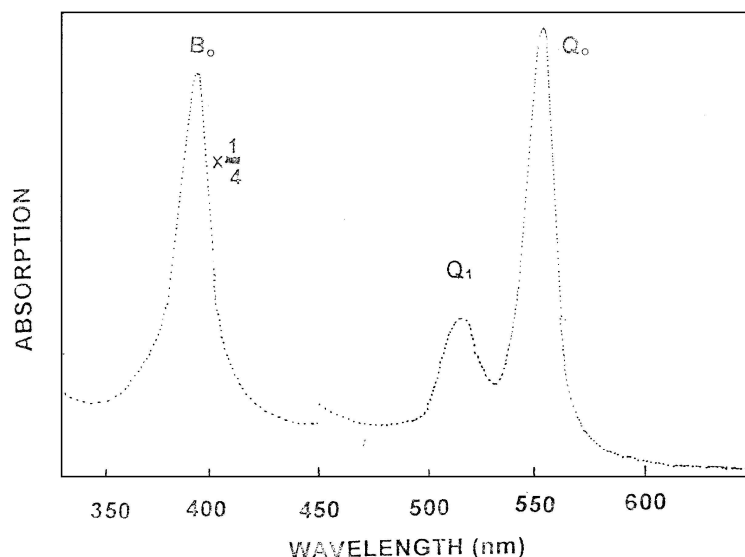
**Figure 1.** Visible absorption spectrum of Ni(OEP) in $CH_2Cl_2$.

$a_{1u}e_g$, have $e_u$ symmetry. Due to strong configuration interaction between the two states, the transition dipole in one of the resultant transitions becomes additive and the other becomes subtractive. Since the magnitude of the transition dipole of the original two $\pi\pi^*$ transitions are similar, the subtractive component, after the configuration interaction has very small transition dipole and thus, results in weak absorption of light, while the additive counterpart leads to strong absorption. The weak and strong absorption bands are designated as $Q_0$ and $B_0$ (Soret Band) respectively (shown in figure 1); $Q_1$ is due to vibronic transition of $Q_0$. The transition dipoles of the $Q_0$ and $B_0$ bands are in the porphyrin plane ($\mu_x$ and $\mu_y$ are degenerate).

The resonance Raman (RR) spectra of Ni(OEP) in $CH_2Cl_2$ are recorded by: (i) JEOL-400D double monochromator equipped with a RCA-31034a photomultiplier and (ii) DMA-11 system (PAR 1215) and a reticon detector (PAR 1420) attached to a double monochromator (Spex 1404).

RR spectra are obtained with: (a) 514.4 nm and 488.0 nm radiation from an $Ar^+$ ion laser (NEC GLG 3200) (figures 2a and 2b), (b) 441.6 nm radiation from He-CD Laser Kinmon Electrics, Model 80 mge) (figure 2c) and (c) 406.7 nm radiation from $Kr^+$ ion laser (spectra Physics 164) (figure 2d). 10 mW laser output power is used to record the RR spectra. The errors of peak frequencies are less than 1 $cm^{-1}$ for well-defined bands. The Ni(OEP) bands at different excitation wavelengths are shown in table 1.

## 3. Results and discussion

Molecular vibrations of metalloporphyrins are classified into the in-plane and out-of-plane modes [1–12]. For Ni(OEP) of $D_{4h}$ stucture, assuming that the peripheral
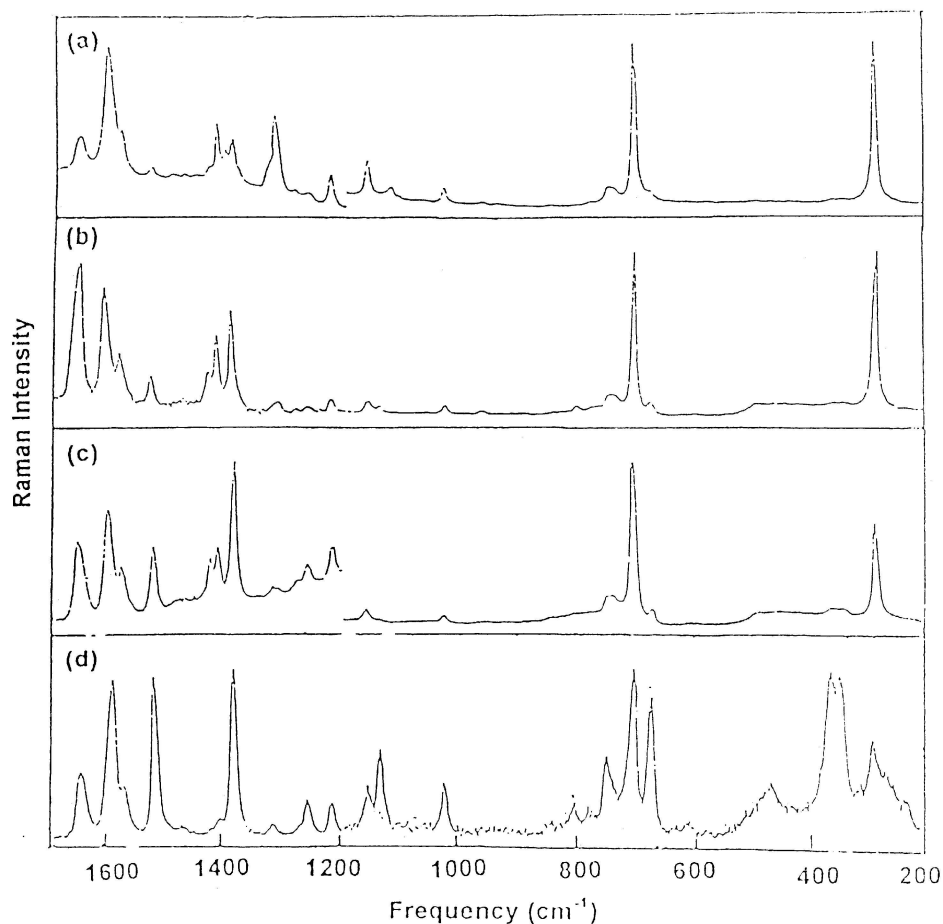
**Figure 2.** Resonance Raman spectra of Ni(OEP) in CH$_2$Cl$_2$ at (**a**) 514.5 nm, (**b**) 488.0 nm, (**c**) 441.6 nm and (**d**) 406.7 nm excitation wavelengths.

ethyl group is a point mass, the in-plane vibrations of Ni(OEP) are factorized into 35 gerade (9A$_{1g}$ + 9B$_{1g}$ +8A$_{2g}$ + 9B$_{2g}$ including 1A$_{1g}$ + 1B$_{1g}$C$_m$–H stretching modes). The out-of-plane modes are factorized into 8 gerade (8E$_g$) and 18 ungerade modes (3A$_{1u}$ + 6A$_{2u}$ + 4B$_{2u}$ +5B$_{1u}$). The A$_{2u}$ and E$_u$ modes are IR active whereas the A$_{1g}$, B$_{1g}$, B$_{2g}$, and E$_g$ modes are Raman active in an ordinary sense. However, if the structure of the planar porphyrin is distorted, additional modes may appear in the spectra.

In the present work, the different frequencies of Ni(OEP) (cm$^{-1}$) observed are (see figures 2a, b, c, d and table 1): $\nu_{10}$ (B$_{1g}$ stretch mode), $\nu_2$ (B$_{1g}$ skeletal mode), $\nu_{11}$ (B$_{1g}$ skeletal mode), $\nu_3$ (A$_{1g}$ skeletal mode), $\nu_{29}$ (B$_{1g}$ skeletal mode), $\nu_{21}$ (A$_{2g}$ skeletal mode), $\nu_{13}$ (B$_{1g}$ skeletal mode), and $\nu_{30}$ (B$_{2g}$ skeletal mode) at 1654, 1601, 1573, 1517, 1408, 1308, 1219 and 1157 cm$^{-1}$ (average value) in all the four excitations, viz. at 514.5, 488.0, 441.6 and 406.7 nm.

**Table 1.** Observed frequencies of Ni(OEP) $(cm^{-1})$ in $CH_2Cl_2$.

| $\lambda_{ex}$ = 514.5 nm | $\lambda_{ex}$ = 488.0 nm | $\lambda_{ex}$ = 441.6 nm | $\lambda_{ex}$ = 406.7 nm | Average | Assignment |
|---|---|---|---|---|---|
| 1654 w,br | 1655 s,br | 1656 m,br | 1650 m,br | 1654 | $\nu_{10}$ ($B_{1g}$ stretch mode) |
| 1604 s,br | 1601 m,br | 1600 m,br | 1597 s,br | 1601 | $\nu_2$ ($B_{1g}$ skeletal mode) |
| 1575 so | 1573 w,br | 1572 w,br | 1573 so | 1573 | $\nu_{11}$ ($B_{1g}$ stretch mode) |
| 1516 vw | 1518 w,br | 1519 m,br | 1516 s,sh | 1517 | $\nu_3$ ($A_{1g}$ skeletal mode) |
| 1485 vvw | | | | 1485 | $\nu_{39}$ ($E_u$ skeletal mode) |
| 1468 vvw | | | 1468 vvw | 1468 | – |
| 1445 | | | | | Solvent |
| 1423 so | 1422 so | 1423vw | | 1423 | – |
| 1409 w,sh | 1407 w,sh | 1409 w | 1408 | 1408 | $\nu_{29}$ ($B_{1g}$ skeletal mode) |
| 1397 w | | | | 1397 | $\nu_{20}$ ($A_{2g}$ skeletal mode) |
| 1382 vw,sh | 1382 m,sh | 1382 s,sh | 1381 s,sh | 1382 | $\nu_4$ ($A_{1g}$ skeletal mode) |
| 1372 so | | | | 1372 | – |
| – | – | 1317 vw | 1316 w,br | 1317 | – |
| – | – | 1312 vvw | – | 1312 | $CH_2$ wag ($B_1$ Ethyl substituent mode) |
| 1308 m,sh | 1308 w,br | 1308 vw | – | 1308 | $\nu_{21}$ ($A_{2g}$ skeletal mode) |
| 1278 vvw | 1276 vvw | 1277 vw | – | 1277 | $CH_2$ twist ($B_1$ Ethyl substituent mode) |
| 1257 vvw | 1256 vvw | 1261 w,bn | 1260 w,br | 1259 | $CH_2$ twist ($A_{1u}$ Ethyl substituent mode) |
| 1220 w,sh | 1219 w,br | 1219 w,br | 1218 w,br | 1219 | $\nu_{13}$ ($B_{1g}$ skeletal mode) |
| 1158 w,sh | 1154 w,br | 1159 w,br | 1158 w,br | 1157 | $\nu_{30}$ ($B_{2g}$ skeletal mode) |
| – | 1136 vw | – | 1137 m,sh | 1137 | $\nu_{14}$ ($B_{1g}$ skeletal mode) |
| 1120 w | 1121 vw | – | – | 1121 | $\nu_{22}$ ($A_{2g}$ skeletal mode) |
| 1108 so | – | – | – | 1108 | – |
| 1025 vw | – | 1024 vw | 1024 m,br | 1024 | $\nu_5$ ($A_{1g}$ skeletal mode) |
| – | 959 vvw | – | – | 959 | – |
| – | – | – | 844 vvw | 844 | – |
| – | – | – | 806 w,br | 806 | $\nu_6$ ($A_{1g}$ skeletal mode) |
| 780 vvw | – | – | – | 780 | – |
| – | – | – | 760 w,br | 761 | – |
| 749 | – | 749 | – | 749 | Solvent |
| 739 | 739 | 739 | – | – | Solvent |
| 670 | 670 | 670 | 670 | – | Solvent |
| – | – | 489 vw | – | 489 | – |
| – | – | – | 465 w,vbr | 465 | – |
| – | – | – | 427 vvw | 427 | – |
| 360 | 360 | 360 | 360 | – | Solvent |
| 343 | 343 | 343 | 343 | – | Solvent |
| – | – | – | 308 vvw | 308 | – |
| 266 | 266 | 266 | 266 | – | Solvent |
| – | – | – | 259 so | 259 | $\nu_9$ ($A_{1g}$ skeletal mode) |
| – | – | – | 227 vvw | 227 | – |

s, m, w – Strong, medium, weak intensity respectively.

v – very, so – shoulder, br – broad, sh – sharp

$\nu_{39}$ ($E_u$ skeletal mode) is observed at 1485 cm$^{-1}$ only in 514.5 nm excitation with very very weak intensity. $\nu_{20}$ ($A_{2g}$ skeletal mode) is observed at 1397 cm$^{-1}$ in all the excitations except in 406.7 nm. $\nu_{14}$ ($B_{1g}$ skletal mode) is observed at 1137 cm$^{-1}$ in 488.0 and 406.7 nm excitations. $\nu_{22}$ ($A_{2g}$ skeletal mode) is observed at 1124 cm$^{-1}$ in all excitations except in 488.0 nm. At 806 cm$^{-1}$ with weak intensity $\nu_6$ ($A_{1g}$ skeletal mode) is observed only in 406.7 nm excitation. At 259 cm$^{-1}$ as a shoulder $\nu_9$ ($A_{1g}$ skeletal mode) is observed in 406.7 nm excitation.

As mentioned above, the one aspect of porphyrin structure that is of current interest is its propensity for forming non-planar structure. Alden *et al* [11] reports that Ni(OEP) crystallizes in three dramatically different structures. Two of the Ni(OEP) structures are of planar triclinic forms (designated as A and B), and the third is a ruffled tetragonal form. The ruffling effectively reduces the molecular symmetry from $D_{4h}$ to $D_{2d}$. Czernuszewicz *et al* [10] suggest that in tetragonal crystals, porphyrin ruffling lowers the symmetry to $S_4$. Stoll *et al* [41] have suggested the different structures of Ni(OEP) as $S_4$, $C_{2h}$, $C_s$, $C_2$, $D_4$ and $D_2$. In the following we determine the structure of Ni(OEP) in $CH_2Cl_2$ solution using the results of the DIA theory.
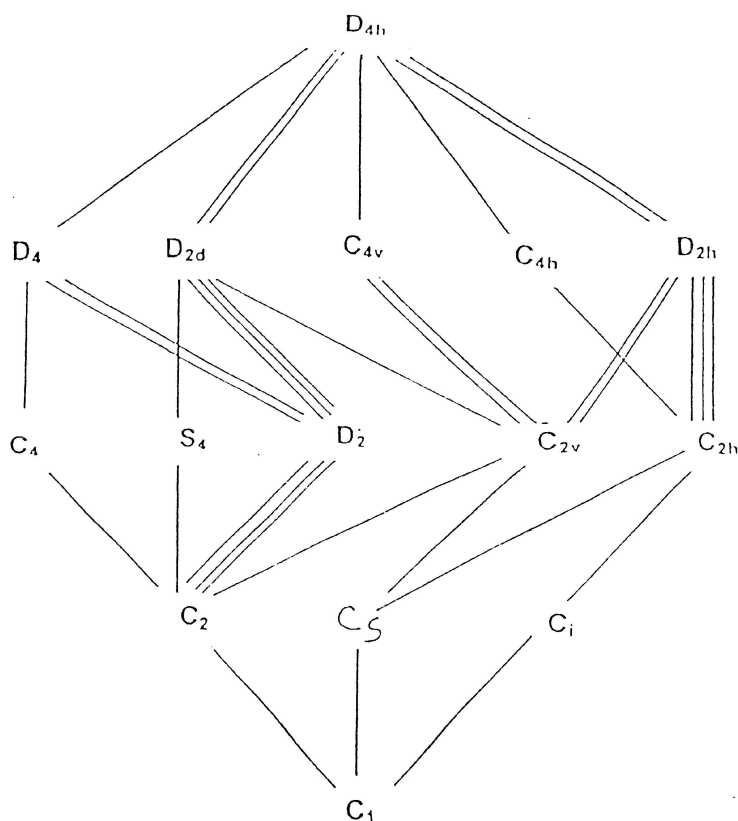


**Figure 3.** Different subgroups of $D_{4h}$ symmetry.

A $D_{4h}$ point group has $A_{1g}$ ($\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$), $A_{2g}$, $B_{1g}$ ($\alpha_{xx} - \alpha_{yy}$). $B_{2g}$ ($\alpha_{xy}$), $E_g$ ($\alpha_{yz}, \alpha_{zx}$), $A_{1u}$, $A_{2u}$ ($T_z$), $B_{1u}$, $B_{2u}$ and $E_u$ ($T_x, T_y$) symmetry species. Out of these $A_{2g}$, $A_{1u}$, $A_{2u}$, $B_{2u}$ and $E_u$ are Raman forbidden [52–56].

Different subgroups of $D_{4h}$ are shown in figure 3. A $D_{4h}$ symmetric molecule may attain any one of these, viz., $D_4$, $D_{2d}$, $C_{4h}$, $C_{4h}$, $D_{2h}$, $C_4$, $S_4$, $D_2$, $C_{2v}$, $C_{2h}$, $C_2$, $C_s$, $C_i$ and $C_1$ distorted symmetries [52–56]. The theory of DIA [47–51] reveals that the first-order distortion-induced activity in polar distortion [DIA–I($\mu$)] is the only transition that could in general be expected to appear in the Raman spectra with observable intensity. In exceptional cases, if DIA–II($\mu$) and DIA-I (Q) (Q: quadruple) transitions are observed, it would be indicative of strong electric field and high field gradient respectively. Based on these results in table 2, symmetry classification of forbidden modes of molecular unit belonging to $D_{4h}$ point group symmetry attaining different order of distortion-induced activity at different lower (distorted) symmetries are calculated. These are based on the following results [47–51]:

(a) In polar ($\mu$) type of distortion, i.e. $C_n$, $C_{nv}$ and $C_s$ symmetries, in first-order distortion-induced activity (DIA-I($\mu$) and in second-order distortion-induced activity (DIA-II($\mu$), forbidden modes belonging to $M \otimes IR \otimes IR$ attain DIA-II ($\mu$).

(b) In non-polar (quadrupolar) type of distortion, i.e. $C_i$, $C_{nh}$, $D_n$, $D_{nh}$, $T_d$, $O_h$ symmetries, forbidden modes belonging to $M \otimes$ Raman attain DIA-I(Q) and those belonging to $M \otimes$ Raman $\otimes$ Raman attain DIA-II(Q).

From table 2, we find that $E_u$ modes become active in first-order polar distortion (DIA-I ($\mu$)) in $C_1$, $C_s$, $C_4$, $C_{2v}$ and $C_{4v}$ symmetries. And in such symmetries $A_{2g}$ modes become active in DIA-II($\mu$), DIA-I(Q) or in higher order of DIA. So, it is expected that the forbidden $E_u$ modes after becoming active should have more intensity compared to $A_{2g}$ modes. However, in the RR spectra (figure 1) we observe that the $A_{2g}$ modes are present at 1397, 1308, 1120 cm$^{-1}$ in $\lambda_{ex} = 514.5$ nm; at 1308 cm$^{-1}$ in $\lambda_{ex} = 488.0$ and 441.6 nm; and at 1121 cm$^{-1}$ in $\lambda_{ex} = 514.5$ nm. The $E_u$ mode is not present in other excitations. So, it can be inferred that the porphyrin molecule attains a distorted structure. However, the distortion is not of polar type.

In non-polar type distortions such as $C_i$, $C_{2h}$ and $D_{2h}$ (having centre of symmetry), the $E_u$ modes remain forbidden in Raman. So, the molecule does not attain such distorted structures.

Similarly, in $D_4$ and $D_{2d}$, $A_{2g}$ modes are to remain forbidden. However, we have observed such modes in the RR spectra. So, the molecule does not attain such distorted symmetry.

Hence, the possibilities of the molecule attaining distorted symmetries are only $D_2$ or $S_4$. In $D_2$ symmetry, the $A_{2g}$ modes attain DIA-I(Q), and $A_{1u}$, $A_{2u}$, $B_{1u}$, $B_{2u}$ and $E_u$ modes become active in higher order DIA. The DIA-I(Q) modes are supposed to have higher intensity compared to DIA-h modes. In $S_4$ distorted symmetry, all the forbidden modes, viz. $A_{1u}$, $A_{2u}$, $B_{1u}$, $B_{2u}$ and $E_u$ become active in DIA-h. Hence, if at all they appear in the spectra they are to appear with very low intensity and the possibility is that their intensity may be uniform. However, in the RR spectra we find $E_u$ modes appear with very very weak intensity. Hence, it may

**Table 2.** Symmetry classification of forbidden modes of molecular units belonging to $D_{4h}$ point group attaining different orders of distortion-induced activity (DIA).

| Point group symmetry | Forbidden species in Raman | Distorted symmetry | Type and order of DIA | Distortion-induced Raman active species |
|---|---|---|---|---|
| $D_{4h}$ | $A_{2g}$ | $C_1, C_2$ | $\mu^{I}$ $\mu^{II}$ | $A_{1u}$ $A_{2u}$ $B_{1u}$ $B_{2u}$ $E_u$ $A_{2g}$ |
| | $A_{1u}$ | $C_2$ | $\mu^{I}$ $Q^{I}$ h | $A_{2u}$ $B_{1u}$ $B_{2u}$ $E_u$ $A_{2g}$ $A_{1u}$ |
| | $A_{2u}$ | $C_2$ | $\mu^{I}$ $\mu^{II}$ | $A_{1u}$ $A_{2u}$ $B_{1u}$ $B_{2u}$ $E_u$ $A_{2g}$ |
| | | $C_4$ | $\mu^{I}$ h | $A_{2u}$ $B_{1u}$ $B_{2u}$ $E_u$ $A_{2g}$ $A_{1u}$ |
| | | $C_{2v}$ | $\mu^{I}$ $Q^{I}$ h | $A_{2u}$ $B_{1u}$ $B_{2u}$ $E_u$ $A_{2g}$ $A_{1u}$ |
| | | $C_{4v}$ | $\mu^{I}$ | $A_{2u}$ $B_{1u}$ $B_{2u}$ $E_u$ |
| | | $C_1$ | $Q^{I}$ | $A_{2g}$ |
| | | $C_{2h}$ | $Q^{I}$ | $A_{2g}$ |
| | | $C_{4h}$ | h | $A_{2g}$ |
| | | $D_2$ | $Q^{I}$ h | $A_{2g}$ $A_{1u}$ $A_{2u}$ $B_{1u}$ $B_{2u}$ $E_u$ |
| | | $D_4$ | h | $A_{1u}$ $B_{1u}$ $B_{2u}$ $E_u$ |
| | | $D_{2d}$ | h | $A_{1u}$ $A_{2u}$ $B_{2u}$ $E_u$ |
| | | $D_{2h}$ | $Q^{I}$ | $A_{2g}$ |
| | | $S_4$ | h | $A_{2g}$ $A_{1u}$ $A_{2u}$ $B_{1u}$ $B_{2u}$ $E_u$ |

$\mu^{I}$ and $\mu^{II}$ are DIA-I($\mu$) and DIA-II($\mu$) respectively; $Q^{I}$ is DIA-I(Q); h is DIA-h.

be concluded that the porphyrin molecule ($D_{4h}$ structure) attains a non-planar distorted structure of $D_2$ rather than $S_4$ symmetry in $CH_2Cl_2$ solution. Thus, the above study appears to be a good choice for determining the complex structures of metalloporphyrins.

**Acknowledgement**

**References**

[1] L D Spaulding, C C Chang, N T Yu and R H Felton, *J. Am. Chem. Soc.* **97**, 2517 (1975)
[2] T Kitagawa, M Abe and H Ogoshi, *J. Chem. Phys.* **69**, 4516 (1978)

[3] M Abe, T Kitagawa and Y Kyogoku, *J. Chem. Phys.* **69**, 4526 (1978)
[4] O Dolphin (ed.), *The porphyrins* (Academic, New York, 1978) vols 3,4
[5] T Kitagawa, H Ogoshi, E Watanabe and Z Yashida, *J. Phys. Chem.* **79**, 2629 (1979)
[6] D Kim, L A Miller, G Rakhit and T G Spiro, *J. Phys. Chem.* **90**, 3320 (1986)
[7] Y Ozaki, K Iriyama, H Ogoshi, T Ochiai and T Kitagawa, *J. Phys. Chem.* **90**, 6102 (1986)
[8] T Kitagawa and Y Ozaki, *Structure and bonding* (Springer-Verlag, Berlin, 1987) vol. 64, p. 71
[9] T D Brenhan, W R Scheidt and J A Shelnut, *J. Am. Chem. Soc.* **110**, 3919 (1988)
[10] R S Czernuszewicz, K A Macar, Li Xiao-Yuan, J R Kincaid and T G Spiro, *J. Am. Chem. Soc.* **111**, 3860 (1989)
R S Czernuszewicz, Xiao-yuan Li and T G Spiro, *J. Am. Chem. Soc.* **III**, 7024 (1989)
[11] R G Alden, B A Crawford, R Doolan, M R Ondrias and J A Shelnut, *J. Am. Chem. Soc.* **111**, 2070 (1989)
[12] M E Blackwood Jr, T S Rush, A Medlock, H A Daileg and T G Spiro, *J. Am. Chem. Soc.* **119**, 12170 (1997)
[13] K M Smith (ed.), *Porphyrins and metallo porphyrins* (Elesevier, Amsterdam, 1975)
[14] D L Rousseau, J M Friedman and P E William, *Topic in current physics* **11**, 203 (1979)
[15] A Warsheel, *Ann. Rev. Biophys. Bioeng.* **6**, 273 (1977)
[16] J A Shelnutt, D C Oishea, N T Yu, L D Cheung and R H Felton, *J. Chem. Phys.* **64**, 1156 (1976)
[17] J M Burke, J R Kincaid and T G Spiro, *J. Chem. Phys.* **100**, 6077 (1978)
[18] J A Hofmann and D F Bocian, *J. Phys. Chem.* **88**, 1472 (1984)
[19] H Yamamoto, T Okunaka, K Furukawa, T Hiyashi, C Konaka and H Kato, *Curr. Sci.* **77**, 894 (1999)
[20] W M Sharman, C M Allen and J E Vanlies, *Drug Discovery Today* **14**, 507 (1999)
[21] L Milgrom and S Mack Robert, *Chem. Britain* 45 (1998) (May issue)
[22] R Bonnett, *Chem. Soc. Rev.* **24**, 19 (1995)
[23] D Dolphin, *J. Can. Chem.* **72**, 1005 (1994)
[24] R Koerner, M M Olmstead, A Ozarowski, S L Phillips, P M V Calar, K Winkler and A L Bach, *J. Am. Chem. Soc.* **120**, 1274 (1998); *J. Phys. Chem.* **96**, 4804 (1992)
[25] P Collman, S T Hanford, Franzon Stefan, T A Eberpaches, R K Shoemaker and W H Woodruff, *J. Am. Chem. Soc.* **120**, 1456 (1998)
[26] P M Jardan, *Curr. Opin. Struct. Biol.* **4**, 902 (1994)
[27] S Hu, A Mukherjee, C Piffat, R S Mak, X Y Li and T C Spiro, *Bio Spectroscopy* **1**, 395 (1995)
[28] S Sato, M Someda Asano and T Kitagawa, *Chem. Phys. Lett.* **189**, 443 (1992)
[29] S Hu, K M Smith and T G Spiro, *J. Am. Chem. Soc.* **118**, 12638 (1994)
[30] J H Perng and D F Bocian, *J. Phys. Chem.* **96**, 4804 (1992)
[31] T G Spiro and X Y Li, in *Biological applications of Raman spectroscopy* edited by T G Spiro (Wiley, New York, 1998) vol. 3
[32] J Seth, V Palaniappen, T E Jhonson, S Prathapan, J S Lindsey and D F Bocain, *J. Am. Chem. Soc.* **116**, 10578 (1994)
[33] R S Wolfe, *Trends Biochem. Sci.* **10**, 396 (1985)
[34] D L Cullen and E F Meyer, *J. Am. Chem. Soc.* **96**, 2095 (1974)
[35] M K Geno and J Halpern, *J. Am. Chem. Soc.* **109**, 1238 (1987)
[36] S Sunder and H Bernstein *J. Raman Spectrosc.* **5**, 351 (1976)
[37] L L Gladkov, A T Gradyushko, A M Shulga, K N Solovyov and A S Starukhin, *J. Mol. Struct.* **47**, 463 (1978)

[38] P Stein, J M Burke and T G Spiro, *J. Am. Chem. Soc.* **97**, 2304 (1975)
[39] D L Willems and D F Bocain, *J. Am. Chem. Soc.* **106**, 880 (1984)
[40] J A Shelnutt, D C O'shea, N T Yu, L D Cheung and R H Felton, *J. Chem. Phys.* **64**, 1154 (1976)
[41] L K Stoll, M Z Zgierski and P M Kozlowski, *J. Phys. Chem.* **A106**, 170 (2002)
[42] Y Mizutani and T Kitagawa, *Bull. Chem. Soc. Jpn.* **75**, 623 (2002)
[43] R Bhattacharjee, *Proceedings of the Twelfth International Conf. on Raman Spect.* (Colombia, South Carolina, 1990) p. 84
[44] R Bhattacharjee, *J. Assam Univ.* **3(1)**, 130 (1998)
[45] R Bhattacharjee, *J. Chem. Phys.* **88**, 4018 (1988)
[46] R Bhattacharjee, *J. Raman Spectrosc.* **21**, 301 (1990)
[47] Y S Jain and R Bhattacharjee, *J. Phys.* **C18**, 5299 (1985)
[48] Y S Jain and R Bhattacharjee, *Mol. Phys.* **57**, 379 (1986)
[49] R Bhattacharjee and Y S Jain, *Spectrochim. Acta, Part A* **44**, 227 (1988)
[50] R Bhattacharjee and Y S Jain, *Spectrochim. Acta, Part A* **44**, 943 (1988)
[51] R Bhattacharjee, *J. Raman Spectrosc.* **19**, 301 (1988)
[52] D A Long, *Raman spectroscopy* (McGraw Hill, New York, 1977)
[53] G Placzek, *Leipziger Vertage* 71 (1931)
[54] M Tinkham, *Group theory and quantum mechanics* (Tata McGraw Hill, New Delhi, 1974)
[55] M C Tobin, *Laser Raman spectroscopy* (Wiley Intersciences, New York, 1971)
[56] E B Wilson Jr, J C Decius and P C Cross, *Molecular vibrations*: *The theory of infrared and Raman vibrational spectra* (McGraw Hill, New York, 1955)