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Infrared and Raman Spectroscopic Characterization of Porphyrin and its Derivatives

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Abstract

Density functional theory (DFT) was employed to investigate protonation, deuteration, and substitution effects on the vibrational spectra of porphyrin molecules. The results of the calculations were compared with experimental data. The calculations show that meso-substitutions produced a substantial shift in frequencies when the meso-carbons within the parent porphine are involved in the vibrational motion of molecules, while protonation of the N atoms leads to a significant blue shift when the H atoms covalent bonded to the N atoms that are substantially involved in the vibrational motion. Deuteration of N atoms at the porphyrin core is found to result not only in a red shift in the frequencies of the corresponding peaks below 1600 cm\(^{-1}\), but also to generate new Raman bands of frequencies in the range of 2565–2595 cm\(^{-1}\), resulting from N-D bond stretching. Also, the deuteration of O atoms within the sulfonato groups (\(-SO_3^-\)) results in a new peak at near 2642 cm\(^{-1}\) due to O-D bond stretching. Calculated IR spectra of the compounds studied here showed similar differences. Finally, we discuss solvent effects on the IR spectrum of TSPP.

Keywords: porphyrins, protonation, Raman, IR, DFT calculation

1. Introduction

Molecular vibrations may be induced through two well-known optical excitation processes. One is the absorption of photons and the other is the inelastic scattering of photons. Excitation of molecular vibration by absorption of photons is achieved by irradiation of a species using radiation containing photons of a frequency equivalent to the frequency difference \(\Delta \nu\) between the initial (i) and the final (f) vibrational states of the species; i.e., \(\Delta \nu = \nu_f - \nu_i\). Unlike IR spectroscopy, the scattering mechanism for exciting molecular vibrations generally exploits monochromatic radiation. In this latter case, a number of incident photons is scattered...
inelastically such that the frequency of the scattered photons ($\nu_s$) differs from that of the incident photons ($\nu_0$). And with conversation of the energy, this energy difference is the energy change associated with a transition from the initial (i) vibrational state to the final (f) vibrational state of the scattering species; i.e., $\nu_0 - \nu_s = \nu_i - \nu_f$. Inelastic scattering of the photons was first discovered by the Indian scientist C. V. Raman in 1928 and is referred to as the Raman effect.

In this chapter, we discuss IR and Raman spectra of protonated, deuterated, and meso-substituted parent porphyrin using density functional theory (DFT) to calculate the IR and Raman spectra, and, where possible, make comparison to experimental spectra. We also discuss spectra of aggregates involving several of the porphyrin species, using vibrational band assignments to ascertain which motions of the vibrating molecule couple more effectively, with excitonic motion, and as a result, we derive molecular alignment information from the enhancement that certain vibronic bands in the Raman spectrum experience for the various porphyrins.

2. Overview of Raman spectroscopy

In this section, we focus on Raman scattering. It is convenient to define the Raman scattering cross-section for the $n \rightarrow m$ vibrational transition as $\sigma_{n \rightarrow m}$ and to relate it to the scattering intensity as follows:

$$I_{n \rightarrow m} = \sigma_{n \rightarrow m} I_0$$

(1)

In this equation, $I_0$ is the intensity of the incident radiation and $I_{n \rightarrow m}$ the intensity of the light scattered by molecules integrated over all scattering angles and polarization directions for randomly oriented molecules. The Raman cross-section is associated with the Raman polarizability by utilizing the fact that the intensity for electric dipole radiation scales as the fourth power of the frequency:

$$\sigma_{n \rightarrow m} \propto (\nu_0 + \nu_k)^4 \sum_{\rho, \sigma} |\alpha_{\rho\sigma}|^2$$

(2)

In this equation, the indices $\rho$ and $\sigma$ indicate the molecule-fixed directional coordinates. Moreover, for this equation, the scattering tensor $\alpha_{\rho\sigma}$ can be formulated in terms of Kramers-Heisenberg-Dirac dispersion theory, as indicated in Eq. (3) below [1]:

$$[\alpha_{\rho\sigma}]_{nm} = \frac{1}{\hbar} \sum_{s, r} \left\{ \frac{(\nu G M_p | S_r | \nu G M_p | S_r)}{\nu S_r - \nu_k - \nu_0 + i \nu S} + \frac{(\nu G M_p | G_m | \nu G M_p | S_r)}{\nu S_r - \nu_k + \nu_0 + i \nu S} \right\}$$

(3)

where $M_p$ and $M_r$ represent the electronic transition dipole moment in a molecule-fixed coordinate system [Albrecht [2] and Warshel and Dauber [3]]. The symbols $\nu_0$ and $\nu_k$ represent the frequencies of the excitation radiation and the normal mode $Q_k$, respectively, $S$ and $r$...
represent the respective electronic and vibrational states of the molecule, and $\Gamma_s$ is a damping constant, which is associated with the lifetime of the vibroelectronic state $S_r$. The sum in Eq. (3) indicates that for the Raman transition of all vibronic states must be used, which indicates that the scattering tensor, and thus, the Raman intensity, is controlled by the transition probabilities involving all vibronic states, even though the initial and final states refer to the vibrational ground and excited states of the electronic ground state. Thus, the sum of integrals in Eq. (3) describes the transitions: $|nG\rangle \rightarrow |S_r\rangle$ and $|S_r\rangle \rightarrow |n\rangle$. When the excitation frequency $\nu_0$ is in resonance or preresonance with the frequency of an electronic transition, the scattering is referred to as resonance Raman (RR) scattering. In this case, Eq. (3) may be simplified to:

$$\left[\alpha_{\rho\sigma}\right]_{nm} = \frac{1}{\hbar} \sum_{S,r} \left\langle nG|M_\rho|Sr\rangle(rS|M_\sigma|Gm)\right\rangle \delta_{\nu_S-\nu_r-\nu_0+i\Gamma_S}$$

(4)

where the summation is now restricted to the vibrational states $r$ of the resonantly excited electronic state (Albrecht [2]; Warshel and Dauber [3]). The wave functions of the integrals in Eq. (4) depend on the electronic and nuclear coordinates and may be separated by taking into account the Born-Oppenheimer approximation:

$$\langle nG|M_\rho|Sr\rangle = \langle G|M_\rho|S\rangle\langle n|r\rangle = M_{GS,\rho}\langle n|r\rangle$$

(5)

Here, the $\langle n|r\rangle$ integral represents the Franck-Condon factor, which is the integral over the product of two vibrational wave functions. With this approximation, Eq. (4) becomes:

$$\left[\alpha_{\rho\sigma}\right]_{nm} = \frac{1}{\hbar} \sum_{r} \left\langle M_{GS,\rho}\frac{M_{GS,\sigma}(n|r)(r|m)}{\nu_S-\nu_r-\nu_0+i\Gamma_S}\right\rangle$$

(6)

where $M_{GS,\rho}$ is the electronic transition-dipole moment associated with the electronic transition from the ground state $G$ to the electronically excited state $S$. Thus, $M_{GS,\rho}$ can be expanded in a Taylor series with respect to the normal coordinates $Q_k$:

$$M_{GS,\rho}(Q_k) = M_{GS,\rho}^0(Q_k) + \sum_k Q_k \left( \frac{\partial M_{GS,\rho}}{\partial Q_k} \right)^0_0 + \cdots$$

(7)

And, within the harmonic approximation, we neglect higher order terms and combine Eqs. (6) and (7) to obtain the scattering tensor as the sum of two terms, the so-called Albrecht A and B terms:

$$\left[\alpha_{\rho\sigma}\right]_{nm} \approx A_{\rho\sigma} + B_{\rho\sigma} + \cdots$$

(8)

$$A_{\rho\sigma} = \frac{1}{\hbar} \sum_{r} \left\langle M_{GS,\rho}^0 M_{GS,\sigma}^0(n|r)(r|m)\right\rangle \delta_{\nu_S-\nu_r-\nu_0+i\Gamma_S}$$

(9)
In the above equations, $M_{GS,\rho}^0$ and $M_{GS,\sigma}^0$ are the components of transition dipole moment of the vertical electronic transition $G \rightarrow S$.

The $A$ and $B$ terms represent different scattering mechanisms, but the dominators are minimized in both terms when the frequency of the excitation $v_0$ is in preresonance or resonance with the frequency of an electronic transition. In such a case, both the $A$ and the $B$ terms are enhanced, leading to amplified scattering of radiation.

It is to be noted that if the resonant electronic transition exhibits a large oscillator strength, i.e., a large transition dipole moment $M_{GS}$, then the $A$ term may be increased substantially more than the $B$ term, and therefore become the more important scattering term. In this case, the enhancement of a normal mode depends on the products of Franck-Condon factors, i.e., the term $(n|r)(r|m)$. It is to be noted that whether or not a normal mode is resonance enhanced via the Franck-Condon mechanism depends on the geometry of the resonant excited state.

The intensity of a vibrational band attributable to a normal mode $Q_k$ of frequency $v_k$ can be estimated in the double harmonic approximation. For the nonresonant situation (for a normal mode $Q_k$ of frequency $v_k$ and excitation frequency $v_0$), the Raman intensity $I_{Qk}$ can be computed according to the following equations [1, 4]:

\[
I_{Qk} = \frac{f(v_0-v_k)^4}{v_0[1-\exp(-\frac{hv}{kT})]} S_{Qk}
\]  

(11)

\[
S_{Qk} \equiv \left\{ 45 \left( \frac{\partial \alpha}{\partial Q_k} \right)^2 + 7 \left( \frac{\partial \gamma}{\partial Q_k} \right)^2 \right\}
\]  

(12)

\[
\left( \frac{\partial \alpha}{\partial Q_k} \right)^2 = \frac{1}{3} \left\{ \left( \frac{\partial \alpha_x}{\partial Q_k} \right)^2 + \left( \frac{\partial \alpha_y}{\partial Q_k} \right)^2 + \left( \frac{\partial \alpha_z}{\partial Q_k} \right)^2 \right\}
\]

(13)

\[
\left( \frac{\partial \gamma}{\partial Q_k} \right)^2 = \frac{1}{2} \left\{ \left( \frac{\partial \alpha_x}{\partial Q_k} - \frac{\partial \alpha_y}{\partial Q_k} \right)^2 + \left( \frac{\partial \alpha_y}{\partial Q_k} - \frac{\partial \alpha_z}{\partial Q_k} \right)^2 + \left( \frac{\partial \alpha_z}{\partial Q_k} - \frac{\partial \alpha_x}{\partial Q_k} \right)^2 \right\}
\]

(14)

In the above equations, $S_{Q_k}$ is the Raman activity for a normal mode $Q_k$, $\left( \frac{\partial \alpha}{\partial Q} \right)$ and $\left( \frac{\partial \gamma}{\partial Q} \right)$ are, respectively, the derivatives of the polarizability tensor and the corresponding anisotropy with respect to the normal mode $Q$, and $f$ is a physical constant that includes the intensity of the incident radiation. We have calculated Raman intensities of the Raman active modes using Eq. (11), which is implemented in Gauss Sum software [5]. The software provides $S_{Q_k}$ (the Raman activity, Eq. 12) and the frequency $v_{Qk}$ from the output files of the quantum chemical calculation program (specifically, Gaussian 09).
We explore in this chapter the effect of protonation, deuteration, and meso-substitutions on the vibronic spectra of porphyrin and some of its derivatives. Specific molecules considered are the following: parent porphyrin (FBP), diprotonated FBP (H$_4$FBP), deuterated H$_4$FBP (D$_4$FBP); meso-tetraphenylporphyrin (TPP), diprotonated TPP (H$_4$TPP or dicationic TPP) deuterated H$_4$TPP (D$_4$TPP); meso-tetraakis (p-sulfonatophenyl) porphyrin (TSPP), diprotonated TSPP (H$_4$TSPP or dianionic TSPP), deuterated H$_4$TSPP (D$_4$TSPP), dicationic TSPP (H$_8$TSPP), as well as deuterated H$_8$TSPP (D$_8$TSPP). We also deal with how molecular aggregation of some of the aforementioned species affects Raman spectra. Density functional theory has been employed to calculate the vibronic structural properties for both IR and Raman spectra.

Our motivation for focusing on the porphyrin monomers and aggregates is that porphyrin monomers and their aggregates play fundamental roles in natural systems and increasingly in artificial photonic devices. As regards aggregates, the primary mechanism through which molecular aggregate structures are formed in both natural and artificial systems is self-assembly through intrinsic intermolecular interactions, without the formation of covalent linkages. Self-assembled molecular aggregates often assume a structure that can be classified as being of J- or H-type, defined by the relative orientations of induced transition dipoles of the constituent molecules, either “head-to-tail” or “head-to-head,” respectively [6]. Structural pictures such as those provided by J- and H-aggregates have provided a framework for theoretical analysis of structure and dynamics of aggregated systems.

Moreover, aggregated porphyrin species are model composite structures for gaining insight into the roles that optically induced transient structural changes and photon dynamics play in photosynthesis [7, 8]. And through the study of spectral properties and photodynamic behaviors of aggregated porphyrin structures, an important outcome sought is the translation of the electron transfer specificities and speeds often found for biological reactions to the realm of molecular photonic devices (i.e., biomimetics) or photonic materials; indeed, enormous interest in the applications area has been evidenced [9, 10]. Thus, experimental and quantum chemical calculations of structures and optical dynamics of porphyrin monomers and aggregates have both scientific and technological importance.

We deduce that the observed Raman bands of the TPP, TSPP, H$_8$TSPP, and aggregated H$_8$TSPP may most properly be characterized by the vibrations of the pyrrole and pyrrolidine rings, the sulfonatophenyl groups, and their combinations rather than as vibrations of isolated chemical bonds.

As regards IR spectra, we have found that calculated IR spectra of H$_8$TSPP can be assigned by comparison with the calculated IR spectra of other porphyrin derivatives and the experimentally measured IR spectra that are obtained from the literature. We further point out that the experimental and theoretical data used in this chapter are taken from prior experimental measurements performed in our laboratories [11–13].

The Raman and IR spectra of porphyrin derivatives in water, used as solvent in the calculations, were calculated at the B3LYP/6-311G (d, p) level of density functional theory.
3. The Raman spectra of porphyrin and derivatives

Figure 1 provides the measured Raman spectra of the TPP (Figure 1B) and H₄TSPP (Figure 1G) from our previous works [11–13]. Many Raman bands with strong and medium intensity, as well as numerous weak bands are found throughout the spectrum. The Raman spectrum of the H₄TSPP when compared to that of the TPP are quite similar, however, the positions of several bands are substantially shifted in frequency. As examples, in the observed Raman spectrum of the TPP, the strongest band at 1564 cm⁻¹ and the bands at 334, 1234, 1327, 1438, 1577, and 1595 cm⁻¹ (with relatively weak intensity) are respectively red shifted to 1537 cm⁻¹ (the most intense peak), 312, 1229, 1339, 1427, 1562, and 1494 cm⁻¹ in the H₄TSPP spectrum. Also, the bands at 201, 334, 962, and 1002 cm⁻¹ are respectively blue shifted to 236, 314, 983, and 1014 cm⁻¹ in the H₄TSPP spectrum. Additionally, the bands at 1476 and 701 cm⁻¹ in the H₄TSPP spectrum are considerably enhanced compared to their corresponding ones in the TPP.

Figure 1. The predicted Raman spectra of porphyrin derivatives: (A) free-base porphyrin (FBP) and deuterated FBP (D₂FBP); (B) the experimentally measured Raman spectrum of the TPP; (C) meso-tetraphenylporphyrin (TPP) and (D) TPP; (E) anionic meso-tetraakis(p-sulfonatophenyl)porphyrin (TSPP) and deuterated TSPP (D₂TSPP); (F) diprotonated FBP (H₂FBP) and deuterated H₄FBP (D₂FBP); (G) diprotonated-TPP (H₂TPP) and deuterated H₄TPP (D₂TPP); (H) diprotonated TSPP (H₂TSPP) and deuterated-H₄TSPP (D₂TSPP); and (I) dicationic TSPP (H₈TSPP) and deuterated H₈TSPP (D₈TSPP). The plotted spectra in the gray color belong to the deuterated molecules. The calculations were carried out in water at B3LYP/6-311G(d, p) level of DFT, and the line arrows show the frequency shift in the deuterated molecule [11].

Also, calculated Raman spectra of the FBP/D₂FBP, H₂FBP/D₂FBP, TPP/D₂TPP, H₄TPP/D₄TPP, TSPP/D₂TSPP, H₄TSPP/D₂TSPP, and H₄TSPP/D₈TSPP in water used as a solvent are given in Figure 1, with the observed Raman spectra of the TPP and H₄TSPP for comparison. (It is important to note that the D₂TSPP symbolize the dicationic TSPP where four of eight deuterium atoms (D) covalently bounded to the nitrogen atoms at the core and the other four covalent bonded to one of three oxygen atoms within each of four meso-sulfonatophenyl substituted groups.)
TPP  TSPP  H2TPP  Assignments

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<td>C-C bond stretching within phenyl rings and rocking of their H, no any contribution comes from macrocycle and sulfonato groups (SO_3^-).(SO_3^-).</td>
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<td>C-C bond stretching within phenyl rings and rocking of their H, accompanied by relatively weak asymmetric stretching of C-C=C=C bonds, ν(C-C=C=C) that leads to bending deformation of the C-N=C bonds, θ(C-C=C=C).</td>
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<td>ν(C-C=C=C) rocking of C-N=C and H on N atoms, ρ(CH-N=C-H) (ρ(CH-N=C-H).</td>
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<td>ν(C-C=C=C) and rocking of the H on C atoms within macrocycle (not on the phenyl groups), ρ(CH), and relatively weak ρ(C-C=N-C).</td>
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<td>C-C=C=C bond stretching, ν(C-C=C=C), symmetric stretching of C-C=C=C bonds, ν(C-C=C=C) that leads to bending deformation of the C-N=C bonds, θ(C-C=C=C).</td>
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<td>ν(C-C=C-C) (primarily)ν(CH-C-C) (ρ(CH))/ν(CH-C-C) (relatively weak).</td>
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<td>ν(O-S-O) within sulfonato groups.</td>
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<td>ν(S-O)/ν(CH-C) within sulfonato groups.</td>
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<td>ν(CH) within the phenyl groups.</td>
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The calculations were obtained in water used as solvent at B3LYP/6-311G(d,p) level. Where $\Delta\nu_{\text{sc}}$ symbolizes the scaled vibrational frequencies, $\Delta\nu_{\text{sc}} = 0.96 (\Delta\nu_{\text{calc}}) + 40$, and $\text{SR}$ and $\text{IR}$ represents, respectively, the predicted Raman scattering activity and intensity; and $\Delta\nu_{\text{exp}}$ and $I_{\text{exp}}$ symbolize the measured Raman frequency and Intensity, respectively [11–13].
The assignment of the observed vibrational bands in the Raman spectra of the TPP and H₄TSPP were made based on the density functional prediction at the B3LYP/6-311G (d, p) level and on the atomic displacements visualized by using the GaussView program. The calculated vibrational frequencies coincided with those observed in their Raman spectra. We used the calculated frequencies and, to some degree, the predicted intensity distribution to attribute observed vibrational frequencies and intensities to specific intramolecular motions of the H₄TSPP and TPP. These latter assessments were facilitated by analysis of the calculated nuclear displacements, combined with animation of their vibrations, to identify specific motions as the dominant movements within the molecule. This is not a truly rigorous approach but should provide adequate insight. The assignments of the vibrational mode are provided in Tables 1 and 3, whereas Figure 2 presents the nuclear displacement for several selected vibrational modes.
<table>
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<tr>
<td>In plane rotational motion of the pyrroline rings, including relatively weak out-of-plane twisting deformation of the phenyl rings, but no contributions come from the pyrroline rings</td>
<td>414</td>
<td>521</td>
<td>584</td>
<td>59</td>
<td>439</td>
<td>484</td>
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<td>Rocking of phenyl rings (ν(phenyl) and wagging of macrocycle w(macrocycle))</td>
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<td>521</td>
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<td>Out-of-plane bending of phenyl groups only.</td>
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<td>Twisting of phenyl τ(phenyl) and w(macrocycle)</td>
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<td>521</td>
<td>584</td>
<td>59</td>
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<tr>
<td>w(NH only)</td>
<td>414</td>
<td>521</td>
<td>584</td>
<td>59</td>
<td>439</td>
<td>484</td>
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<tr>
<td>Due to bending deformation of the SO$_3^-$ groups like closing and opening umbrella shape.</td>
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<td>521</td>
<td>584</td>
<td>59</td>
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<td>In plane bending deformation of phenyl rings, including w(NH and C$_β$H only) and out of plane deformation of the macrocycle.</td>
<td>414</td>
<td>521</td>
<td>584</td>
<td>59</td>
<td>439</td>
<td>484</td>
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<tr>
<td>w(CH on phenyl) and relatively weak out of plane deformation of the phenyl rings.</td>
<td>414</td>
<td>521</td>
<td>584</td>
<td>59</td>
<td>439</td>
<td>484</td>
</tr>
<tr>
<td>w(CH on phenyl) and out of plane deformation of the phenyl rings and macrocycle.</td>
<td>414</td>
<td>521</td>
<td>584</td>
<td>59</td>
<td>439</td>
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<tr>
<td>Primarily due to ν(S-C)/θ(phenyl) and relatively weak w(CH an NH) and out of plane bending (or twisting) deformation of macrocycle,</td>
<td>414</td>
<td>521</td>
<td>584</td>
<td>59</td>
<td>439</td>
<td>484</td>
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<tr>
<td>Primarily due to w(C$_β$H an NH) and out of plane bending (or twisting) deformation of macrocycle, relatively weak out of plane deformation of the phenyl.</td>
<td>414</td>
<td>521</td>
<td>584</td>
<td>59</td>
<td>439</td>
<td>484</td>
</tr>
<tr>
<td>w(CH in phenyl and macrocycle) and out of plane bending (or twisting) deformation of phenyl rings the macrocycle.</td>
<td>414</td>
<td>521</td>
<td>584</td>
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### Assignments

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<th>( \Delta \nu_{v}^- )</th>
<th>( \Delta \nu_{v}^+ )</th>
<th>( \Delta \nu_{as} )</th>
<th>( \Delta \nu_{as}^- )</th>
<th>( \Delta \nu_{as}^+ )</th>
<th>( \Delta \nu_{IR}^- )</th>
<th>( \Delta \nu_{IR}^+ )</th>
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<td>B2</td>
<td>776 749 21 746 748</td>
<td>B2 767 1</td>
<td>A1 769 32</td>
<td>Mainly due to ( \nu(S-O(H)) ), including ( \nu(C=H) ) and out of plane bending (or twisting) deformation of macrocycle, relatively weak out of plane deformation of the phenyl.</td>
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<td>B1 823 7</td>
<td>B1 825 2</td>
<td>800</td>
<td>B1 826 3</td>
<td>W(( C=H )s and NH) and out of plane bending deformation of macrocycle</td>
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<td>A1 829 20</td>
<td>A1 848 23</td>
<td>854</td>
<td>A1 852 15</td>
<td>W(( C=H )s and NH) and out of plane bending deformation of macrocycle</td>
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<tr>
<td>B1</td>
<td>894 869 10 875 871</td>
<td>B1 896 1</td>
<td>0(( N-C_{C}C ) and ( N-C_{C}C ) in the same phase)</td>
<td>0(( C=C-C_{N} ))</td>
<td>0(( C=C-C_{C} ))</td>
<td>0(( phenyl ))/(( C=H ))</td>
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<tr>
<td>B1</td>
<td>985 960 91 964 962</td>
<td>B1 968 5</td>
<td>B1 974 1</td>
<td>966</td>
<td>B1 998 2</td>
<td>W(CH on phenyl)</td>
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<tr>
<td>B2</td>
<td>980 63 62</td>
<td>B2 980 100 984</td>
<td>ve(( O-S-O ))</td>
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<td>B1</td>
<td>1001 977 34</td>
<td>B2 1002 5</td>
<td>B2 1004 2</td>
<td>1012</td>
<td>B2 1014 9</td>
<td>0(( N-C_{C}C ) and ( N-C_{C}C ) in the same phase)</td>
<td>0(( C=C-C_{N} ))</td>
<td>0(( C=C-C_{C} ))</td>
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<td>A1 1020 0</td>
<td>A1 1036 2</td>
<td>1039</td>
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<td>Expansion of the pyrrole/pyrrole groups along ( N(H)…N(H) ) direction due to ( \nu(C=\beta C) ), leading to macrocycle getting rectangular shape instead of square shape.</td>
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<tr>
<td>B1</td>
<td>1014 991 11</td>
<td>0(( C=C-C ) in phenyl)</td>
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<td>B2</td>
<td>1016 993 33 999 1002</td>
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<td>( \rho(( C=H ))/(( C=C-C ) in phenyl))/(( C=C-C_{C} ))</td>
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<tr>
<td>B1</td>
<td>1049 1026 9 1031 1032</td>
<td>B1 1033</td>
<td>( \rho(CH ) in phenyl)/(( C=C-C_{C} ))</td>
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<td>1087 1065 9 1069 1072</td>
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<td>( \rho(( C=H ))</td>
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<td>A1</td>
<td>1094 1072 10</td>
<td>0(( C=\beta H ) and CH on phenyl).</td>
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<tr>
<td>B1</td>
<td>1109 21</td>
<td>B1 1108 11</td>
<td>B1 1107 3</td>
<td>( \nu(C=C)/(( C=C-C ) in phenyl))/(( CH ) on phenyl only)</td>
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<tr>
<td>A1</td>
<td>1116 14</td>
<td>A1 1125 6</td>
<td>1125</td>
<td>A1 1133 1</td>
<td>( \rho(CH ) on phenyl only)</td>
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<td>B2</td>
<td>1146 64</td>
<td>B1 1151 30</td>
<td>var(( O-S-O )</td>
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<td>A1/B1</td>
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<td>A1/B1 1160 35</td>
<td>1188a A1/B1 1151 100</td>
<td>var(( O-S-O ))/(( CH ) on phenyl)</td>
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<tr>
<td>B2</td>
<td>1180 1159 38</td>
<td>B2 1180 8</td>
<td>var(( C-N-C ))/(( C-N-C ))/(( C=H ))</td>
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<td>1189 1168 4 1174 1176</td>
<td>B2 1188 0</td>
<td>B2 1193 9</td>
<td>B2 1200 3</td>
<td>( \rho(CH ) on phenyl only)</td>
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<tr>
<td>B1</td>
<td>1204 1183 25 1187 1187</td>
<td>B1 1204 4</td>
<td>( \rho(NH ) and relatively weak ( \theta )(whole molecule)</td>
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<tr>
<td>B1</td>
<td>1224 2013 13</td>
<td>1211 1211 A1 1224 2</td>
<td>B1 1220 14</td>
<td>1218 B1 1221 2</td>
<td>( \nu(C-N-C)/(\nu(C=C-C_{C})/(\nu(NH ) and CH)</td>
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</table>
Where $\Delta \nu_{sc}$ represents the scaled vibrational frequencies ((a) $\Delta \nu_{sc} = 0.96(\Delta \nu_{calc}) + 40$ as used for the Raman spectra for all compounds studied here) and $I_{IR}$ symbolizes the predicted IR intensity. In the assignments, the symbols $\nu$, $\delta$, $\rho$, and $\omega$ represent the bonding stretching, bending deformation, rocking, and wagging, respectively. It is worthy to note that two different scaling factor used for the TPP: (a) $\Delta \nu_{sc} = 0.96(\Delta \nu_{calc}) + 40$ and (b) $\Delta \nu_{sc} = 0.976(\Delta \nu_{calc})$. The latter one, (b), gives best fitting to measured IR spectrum (from ref. [15, 16]) of the TPP only; not for others. However, the scaling factor of $\Delta \nu_{sc} = 0.96(\Delta \nu_{calc}) + 40$ gives the best fitting to measured IR spectrum of $H_4$TSPP (from ref. [16]). The results of calculations were obtained in water used as solvent at the B3LYP/6-311G (d,p) level of the theory.

### Table 3. Assigned IR features of the meso-substituted porphyrin derivatives: TPP (C$_2$v point group), TSPP (C$_2v$), H$_4$TSPP (C$_{2v}$), and H$_8$TSPP (C$_{2v}$).
Our assignments may be summarized as follows:

1. The observed Raman peak at 1593 cm\(^{-1}\): The calculations, as shown in Figure 1, produce a peak at around 1600 cm\(^{-1}\) in the Raman spectra of all of the molecules studied here. The motions of atoms within the molecules suggest that this calculated band is as a result of principally C-C bond stretching, \(\nu(C-C)\), within phenyl rings and rocking of their H, \(\rho(CH)\). No contribution appears to derive from the macrocycle and sulfonato groups (-SO\(_3\)) motions. Calculations for the parent porphyrin (FBP) and diprotonated FBP (H\(_4\)FBP) also predicted a band at about 1600 cm\(^{-1}\), resulting from asymmetric stretching of the \(C_m-C_m\) (\(\nu_a(C_m-C_m)\)) and bending deformation of the C-N(H)-C and C-N-C bonds, and rocking of H atoms covalent bonded to meso-carbon atoms (\(C_m\)), \(\rho(C_mH)\); see Figure 2. Consequently, we can conclude that the vibrational motion of the substituted phenyl is responsible for the observed Raman band at 1593 cm\(^{-1}\) in the observed spectrum of diprotonated TSPP (H\(_4\)TSPP). It is to be noted that, in our prior publication [13], the observed and predicted Raman spectra of the TPP showed the similar Raman pattern; these results are also presented in Table 1 and Figure 1.

2. The experimental peak at 1563 cm\(^{-1}\): Even though the measured Raman spectrum of the H\(_4\)TSPP displays a relatively weak bands at 1563 cm\(^{-1}\), the calculation indicates only a very weak peak at 1568 cm\(^{-1}\), attributed to C-C bond stretching within the phenyl rings and rocking of their attached H atoms, as well as a relatively weak asymmetric stretching of \(C_m-C_m\) bonds. However, there is no contribution from the sulfonato group. Upon examination of this peak for vibrational motions for the TPP, TSPP, H\(_4\)TPP, and H\(_4\)TSPP, we find extremely weak peaks at 1588, 1574, 1585, and 1578 cm\(^{-1}\), respectively. As seen in Figure 1 and Table 1, the calculated spectrum of the TSPP produces the most intense band at 1564 cm\(^{-1}\), but its vibrational motions indicated that this mode is shifted to 1524 cm\(^{-1}\) in the H\(_4\)TSPP spectrum. Therefore, we believe that the DFT calculations might underestimate the intensity of this peak.

3. The observed strong Raman bands at 1553 cm\(^{-1}\) (with a shoulder at 1540 cm\(^{-1}\)) and at 1537 cm\(^{-1}\) (with a shoulder at 1528 cm\(^{-1}\)) are, respectively, in the spectra of TPP and H\(_4\)TSPP: Their calculated spectra display the strongest Raman band at 1564 and 1524 cm\(^{-1}\) for TPP and H\(_4\)TSPP, respectively. Both of experimental and calculated Raman spectra show that the strongest band in the observed spectrum of the TPP is significantly red shifted in the H\(_4\)TSPP spectrum. The large red shift in the peak position for the observed and calculated bands are, respectively, 16 cm\(^{-1}\) and ca. 40 cm\(^{-1}\), and is not due to the substitution effect, which is mainly caused by the out-of-plane distortion of the macrocycle resulting from protonation of the N atoms at porphyrin core. Correspondingly, the Raman band associated with the same vibrational motions within FBP, TPP, and TSPP display a similar red shift when compared to diprotonated species (i.e., H\(_4\)FBP, H\(_4\)TPP, and H\(_4\)TSPP). Additionally, the observed shoulders at 1540 cm\(^{-1}\) (TPP) and at 1528 cm\(^{-1}\) (H\(_4\)TSPP) correspond to the calculated peaks at 1555 cm\(^{-1}\) and 1529 cm\(^{-1}\), respectively, which results from the \(\nu(C_m-C_m)\) and \(\theta(C-N(H)-C)\) motions, respectively.

4. Calculated Raman spectra of TPP, H\(_4\)TPP, TSPP, H\(_4\)TSPP, and H\(_8\)TSPP reveal a relatively strong peak around 1238 cm\(^{-1}\), arising from predominantly \(\nu(C=C_m)\), as well as contribu-
tions from $\nu(C-N(H)-C)$, $\rho(CH)$ and a comparatively weak $\nu(C_\beta-C_\beta)$. This vibrational mode is attributed to the measured Raman bands at 1229 cm$^{-1}$ in H$_4$TSPP spectrum and 1234 cm$^{-1}$ in the TPP. However, in calculated spectra of the unsubstituted free-base porphyrin (FBP and H$_4$FBP), this peak is respectively red shifted to 1194 and 1217 cm$^{-1}$, owing to the rocking of the H atom (covalent bonded to meso-carbon atom (C$_m$)), $\rho(C_mH)$, including vibrational bond stretching within the macrocycle (see Figure 2). There is a question here we need to answer that while the peak (at 1238 cm$^{-1}$) is not significantly shifted in the predicted Raman spectra of the diprotonated and/or meso-substituted porphyrin molecules, relative to each other, but it is substantially shifted in the FBP and H$_4$FBP spectra.

This may be explained by the electrostatic repulsive interactions or steric effect between the H atoms covalent bonded to the C$_m$ and C$_p$ atoms in the FBP and H$_4$FBP structures. The effect decreases with increasing in the distance between the H atoms on the C$_p$ and C$_m$ atoms because of the out-of-plane distortion from planarity in the H$_4$FBP molecule (diprotonated porphyrin). In the case of meso-phenyl or meso-sulfonatophenyl substituted porphyrin molecules, the steric effect between the H atoms on the C$_p$ and C$_m$ (in the meso-phenyl substituent) give rise to the rotation of these meso-substituted groups about C$_m$-C$_p$ bond, in their ground state structure, up to the tilt angle of about 71° and 48° for their unprotonated and protonated structures, respectively. Due to reduced electrostatic repulsion or steric effect by the C$_m$-C$_p$ bond rotation, the calculations do not reveal a substantial frequency shift in this peak position ($\sim$1238 cm$^{-1}$) in the meso-substituted porphyrin molecules.

(5) In region of 1050–950 cm$^{-1}$, there are two Raman peaks that are affected by diprotonated and deuterated parent porphyrin molecule. For instance, the observed two peaks at 1002 and 962 cm$^{-1}$ in the TPP spectrum (exc. at 488 nm) are respectively blue shifted to 1016 and 1002 cm$^{-1}$ in the H$_4$TSPP (exc. at 514 nm). Calculation indicates that the peaks at 1020 and 983 cm$^{-1}$ in the TPP spectrum occurs at 1020 and 986 cm$^{-1}$ in the TSPP. These same bands are blue shifted to 1036 and 1005 cm$^{-1}$ in the calculated spectrum of the protonated-TSPP (H$_4$TSPP). Our results clearly show that these shifts in the observed peak positions are due to protonation of the porphyrin core that leads to saddle-type distortions of the porphyrin core (i.e., leads to an increase in the degree of freedom of the rocking of the N-H bonds as a consequence of the reduced repulsive interaction or steric effect between these hydrogen atoms). Moreover, GaussView visualization software shows that the peak at 1036 cm$^{-1}$ (in H$_4$TSPP) is caused by expansion of the pyrrole groups along N(H)...N(H) direction, but in opposite phase (Figure 2), as a consequence of $\nu(C_\alpha-C_\beta)$, which causes the macrocycle to assume a rectangular shape rather than square shape. The band at 1005 cm$^{-1}$ (H$_4$TSPP) is caused by expansion of the pyrroles along N(H)...N(H) direction likewise macrocycle breathing (or breathing of pyrroles in the same phase) as assigned by Rich and McHale [14].

(6) Another two fundamental Raman bands in the range of low frequency are found at 248 and 338 cm$^{-1}$ in the H$_4$TSPP spectrum, and at 235 and 365 cm$^{-1}$ in the TPP are respectively attributed to out-of-plane twisting from the macrocycle and breathing of whole molecule, which are in agreement with their experimental values of 242 and 338 cm$^{-1}$ for the H$_4$TSPP; 235 and 334 cm$^{-1}$ for the TPP. These blue and red shifted bands in the measured and predicted Raman spectrum of the H$_4$TSPP (dianionic or diprotonated-TSPP) result from the protonation of the
nitr**o**gen atoms at the core, not owing to the meso-sulfonato substituted groups. Additional assignments are provided in Table 1.

### 3.1. Isotope effect on the Raman spectrum

The polarized resonance Raman scattering (RRS) spectra, exc. at 488 nm, of the aggregated H$_4$TSPP (diprotonated TSPP) and deuterated TSPP (D$_4$TSPP) by Rich and McHale [14] displayed a frequency shifts in the positions of some of the well-known Raman peaks, in addition to changes in the relative intensities of the Raman bands upon deuteration. The authors have reported that the observed Raman bands at 983 and 1013 cm$^{-1}$ in the aggregated H$_4$TSPP (or diprotonated-TSPP) spectrum are respectively shifted to 957 and 1004 cm$^{-1}$ in the aggregated D$_4$TSPP spectrum. Additionally, they suggested that these two modes are pyrrole breathing modes and thus these red shifts may be attributed to the substitution of deuterium ions with the labile protons in the porphyrin core [14].

By comparing the spectral positions of these two peaks in the calculated Raman spectra of diprotonated and deuterated porphyrin core with their corresponding nonprotonated ones (see Table 2), we see that while the protonated and meso-substituted parent porphyrin cause a blue shift in frequency of the two Raman peaks, the deuteration causes a red shift. For example, in the calculated spectrum of the TSPP, while these bands at 1020 and 985 cm$^{-1}$ are blue shifted respectively to 1036 and 1005 cm$^{-1}$ in the H$_4$TSPP (diprotonated TSPP), they are red shifted to 1012 and 977 cm$^{-1}$ in the D$_4$TSPP (deuterated TSPP) spectrum, respectively. When all four nitrogen atoms at the porphyrin core are deuterated, these Raman bands are shifted from 1036 and 1005 cm$^{-1}$ (in the H$_4$TSPP) to 1026 and 983 cm$^{-1}$ in the D$_4$TSPP (deuterated H$_4$TSPP), respectively.

For the other moderately intense Raman peaks in the predicted spectrum, the shift in their spectral positions, due to the deuterated nitrogen atoms at the core, is not more than 5 cm$^{-1}$, which is in agreement with the experimental observation [14]. However, there are several weaker bands in the calculated spectra that displayed a significant shift in frequency (Figure 1). The other meso-substituted and free-base porphyrin derivatives displayed analogous results, which are in agreement with the experimental findings as argued above. Moreover, the results of calculations suggest that the meso-substituted groups do not significantly alter the spectral position of these two Raman bands.

Consequently, the blue shift of the two Raman bands associated with diprotonated nitrogen atoms at the core is not unexpected when considering the steric effect (or electrostatic repulsive effect) between the hydrogen atoms bounded to nitrogen atoms at the core. This effect may be reduced by departing from the planarity of the porphyrin core (or macrocycle) as argued earlier. The red shift also is to be expected because of the isotopic effect since the vibrational frequency is inversely related to the square root of atomic mass that contributes to the vibrational mode. The deuterated nitrogen atoms at the core and one of three oxygen atoms in each of four sulfonato groups (-SO$_3$D) revealed new Raman peaks in the 2630–2720 cm$^{-1}$ region, which could be an experimental evidence for the presence of the deuterated TSPP (D$_4$TSPP) or deuterated H$_4$TSPP (D$_8$TSPP) in samples.
4. IR spectra of porphyrin and derivatives

We also calculated (at the same level of the DFT) the IR spectra of FBP, TPP, TSPP, H₄FBP, H₄TPP, H₄TSPP, and H₈TSPP, as well as their deuterated structures (D₂FBP, D₂TPP, D₂TSPP, D₄FBP, D₄TPP, D₄TSPP, and D₈TSPP). It is worthy to note that the D₈ represent that the four of eight deuterium atoms covalent bounded to nitrogen at the core and another four bounded to four sulfonato groups (-SO₃D). Calculated spectra exhibit dispersed about the full spectral range many IR features with medium and relatively weak intense, in addition to intense IR bands (see Figure 3). The results of the calculations together with their animated motions indicate that the predicted IR vibrational modes are predominantly linked with: (1) symmetric and asymmetric skeletal deformations of the macrocycle and phenyl rings; (2) wagging and rocking of the hydrogen atoms bonded to carbon and nitrogen atoms, CH and NH; and (3) out-of-plane distortion of the phenyl rings and the parent porphyrin or macrocycle. The selected IR bands in the calculated spectra of these compounds studied here are assigned using GaussView animation software. The assigned IR features are given in Table 3.

To test the reliability of the calculated IR spectra of the molecules investigated, we compared the IR bands in the calculated spectra of TPP and H₄TSPP (diprotonated TSPP) with experimentally measured IR spectra of TPP [15] and H₄TSPP [16]; as seen in Table 3, the spectra correlate quite well. This analysis indicates that the calculated IR spectra of these compounds (FBP/H₄FBP, TPP/H₄TPP, and TSPP/H₄TSPP) are reasonable. We assigned the predicted IR features for the H₄TSPP in connection with the predicted IR spectra of the FBP/H₄FBP, TPP/...
H$_4$TPP, and TSPP/H$_4$TSPP/H$_8$TSPP (in water used as solvent) by taking into account their vibrational motions. Our key conclusions concerning the calculated IR spectra are as following:

1. The predicted IR features at 1603, 1566, 1405, 1193, 1125, 974, and 439 cm$^{-1}$ in the H$_4$TSPP spectrum are attributable to structural distortion of the meso-phenyl substitution, e.g., rocking and/or wagging of hydrogen atoms and bond stretching, no contribution is derived from motions of the sulfonato groups, -SO$_3$.

2. The following IR bands arise from the vibrational motion of the -SO$_3$ groups: the most intense IR band at 980 cm$^{-1}$ in the calculated spectrum of the H$_4$TSPP, which originates from the symmetric stretching of O-S-O bonds, $\nu_s$(O-S-O); one medium intensity at 1151 cm$^{-1}$, caused by asymmetric stretching of O-S-O, $\nu_a$(O-S-O); and a moderately intense band at 624 cm$^{-1}$ is as a result of bending distortion of the -SO$_3$ groups, as would describe the closing and opening of an umbrella.

3. A relatively strong IR peak at 1160 cm$^{-1}$ in the spectrum of the H$_4$TSPP is caused by $\nu_s$(O-S-O) and rocking of CH in phenyl rings, $\rho$(CH on phenyl).

4. The vibrational motion of the meso-sulfonatophenyl rings, $\nu$(S-C), $\theta$(C-C(S)-C) and $\rho$(CH on phenyl only), produced an IR band with very weak intensity at 1108 cm$^{-1}$.

5. While the $\nu$(S-C), $\theta$(bending distortion of phenyl), relatively weak wagging of the CH and NH, and twisting of the macrocycle induced an IR peaks at 748 cm$^{-1}$; twisting of the entire molecule, including bending distortion of the O-S-O bonds and wagging of the CH and NH bonds produced an IR band with very weak intensity at 566 cm$^{-1}$.

6. The two IR bands with frequencies of ca. 510 and 559 cm$^{-1}$ are indicated as associated with hydrogen atom motions (NH), and are very weak in intensity.

7. A very weak peak at 1089 cm$^{-1}$ is due to the $\rho$(C$_\beta$H), which appears essentially at the same spectral position in the calculated IR spectra for the other molecular structures studied here.

8. The calculated IR features, with very weak intensity, at 1386, 1299, 1240, 1036, 848, 825, and 751 cm$^{-1}$ arise from the bond stretching ($\nu$), rocking ($\rho$), wagging ($w$), and bending deformation ($\theta$) of the C and H atoms within macrocycle. These calculated features are found to be spectrally shifted from those in protonated porphyrins, which is in agreement with experimental observation as provided in Table 3 from references [15] and [16].

9. The peaks at 1004 (weak), 1460 (strong), and 1545 (weak) cm$^{-1}$ are results of symmetric/asymmetric bond stretching, bending deformation, and/or wagging/rocking vibrational motion of the atoms within the porphyrin macrocycle.

10. While in-plane rotational motion of the pyrroline rings, including relatively weak out-of-plane twisting deformation of the phenyl rings, produced weak peak at 439 cm$^{-1}$; and rocking of phenyl rings and wagging of macrocycle induced a weak IR peak at 427 cm$^{-1}$ in the H$_4$TSPP spectrum. Another weak one is found at 484 cm$^{-1}$ that originated from the twisting of phenyl and wagging of macrocycle. Complete descriptions for each IR features are provided in Table 3.
4.1. Isotopic (or deuteration) effect on the IR spectrum

Calculated IR spectra of the molecules clearly indicate that deuterated porphyrin exhibits relatively intense IR peaks in the range of 2565–2600 cm\(^{-1}\). Such bands are associated with N-D bond stretching. And bands around 2640 cm\(^{-1}\) are attributable to O-D bond stretching. The largest frequency shifts are calculated for bands at 540 and 490 cm\(^{-1}\) \((\text{H}_4\text{TSPP}, \text{where all N atoms at porphyrin core are protonated})\) that are shifted to 396 and 366 cm\(^{-1}\) in the \(\text{D}_4\text{HTSPP}\) (deuterated-\(\text{H}_4\text{TSPP}\)); in the low-frequency region (below 700 cm\(^{-1}\)) bands are attributable to wagging of the N-D bond, \(w(\text{ND})\).

In the region of high or mid frequency, where deuterium atom is included in vibrational mode frequency, a red shift in frequency by up to 10 cm\(^{-1}\) is shown in the \(\text{D}_2\text{TSPP}\). Deuteration also has an influence on the intensity of the IR bands; see Figure 3. Shift in the region of high frequency of \(\text{D}_2\text{FBP}, \text{D}_4\text{FBP},\) and \(\text{D}_4\text{TPP}\) spectra are more significant than those in the spectra of \(\text{D}_2\text{TSPP}\) and \(\text{D}_4\text{TSPP}\). These results imply that above the low-frequency region, the frequency shifts as a result of the deuteration decrease with increasing size of the substituent group.

5. Solvent effect on the IR spectrum

We investigated the solvent effect on the IR spectrum of the \(\text{H}_4\text{TSPP}\) by using toluene, dimethyl sulfoxide (DMSO) and water as a solvent. Calculations indicate that below 1100 cm\(^{-1}\) there is no significant frequency, shift in peak positions \(\text{H}_4\text{TSPP}\), but above 1100 cm\(^{-1}\) shifts do occur. Specifically, the IR peak centered at around 1200 cm\(^{-1}\) is shifted to 1188 cm\(^{-1}\) (toluene), 1166 cm\(^{-1}\) (DMSO), and 1160 cm\(^{-1}\) (water). Also, the IR peaks centered about 1453 and 1477 cm\(^{-1}\) in the gas phase spectrum are shifted to 1468 and 1490 cm\(^{-1}\) (toluene), 1480 and 1497 cm\(^{-1}\) (DMSO), and 1481 and 1499 cm\(^{-1}\) (water), respectively. This observation suggests that the IR features, especially in high energy region, of the parent porphyrin and its derivatives, at least for \(\text{H}_4\text{TPSP}\), are responsive to its surroundings.

6. Resonance Raman spectra of aggregated diprotonated-TSPP

In the section, we will discuss the results vibroelectronic properties of the aggregated-\(\text{H}_4\text{TSPP}\) (known as acidic-, dianionic-, or diprotonated-TSPP). Several structural and spectroscopic studies have shown that TSPP aggregates in acidic aqueous solution. Figure 4 shows the absorption spectra of free-base TSPP (pH = 12), \(\text{H}_4\text{TSPP}\) (pH = 4.5), and aggregated \(\text{H}_4\text{TSPP}\) (pH = 1.6), with concentration of \(5 \times 10^{-5}\) M in aqueous solution.

While the spectrum of the TSPP [17] exhibited a Soret band at 410 nm and several weak Q bands in the region of 500–640 nm, the monomeric \(\text{H}_4\text{TSPP}\) spectrum exhibited the Soret band at 432 nm, and Q-bands at 594 and 642 nm. Figure 4 shows the Soret band of the \(\text{H}_4\text{TSPP}\) is split into H- and J-band components in the \(\text{H}_4\text{TSPP}\) aggregate as a sharp and intense absorption
band at 489 nm (J-aggregate) and a broad and weak absorption band at 422 nm (H-aggregate) are formed. The Q-bands at 594 and 642 nm (in the monomeric \( H_{4}TSPP \)) is also shifted to ca. 670 and 706 nm in the aggregated \( H_{4}TSPP \) spectrum, respectively. The UV-vis spectra results suggest that aggregation evolves through the formation of diprotonated \( H_{4}TSPP \), and only occurs at a pH below 5. These observations have also reported by other researchers [18, 19].

**Figure 4.** UV-vis spectra of the free-base TSPP (the maximum of the absorption band at 410 nm), monomeric \( H_{4}TSPP \) (the maximum at 432 nm) and aggregated \( H_{4}TSPP \) (the maximum at 489 nm) [20]. The concentration of compounds in each case is \( 5 \times 10^{-5} \) M in the aqueous solution. The pH = 12 for the free-base TSPP; pH = 4.5 for the monomeric \( H_{4}TSPP \); pH = 1.6 for the aggregated \( H_{4}TSPP \); and \([KCl] = 0.1 \) M. Spectra above ca. 500 nm have been offset by +0.2 absorbance units and amplified by the indicated factor to aid presentation. The structure on the band at around 500 nm for the free-base TSPP is an artifact attributable to the absorption spectrometer.

Moreover, DFT calculations (at B3LYP/6-311G(d, p) level) show that while the band at 317 cm\(^{-1}\) is due to breathing of the whole molecule, the enhanced band at 241 cm\(^{-1}\) results from the out-of-plane wagging of the macrocycle. Hence, computationally these two Raman bands of porphyrins originate from out-of-plane modes—in conjunction with bending of the \( C_{n}\)OPh
bond (ph representing phenyl) and deformation of the core of the porphinato macrocycle caused by pyrrole ring tilt and swivel [20–22]. Moreover, in the case of lanthanide sandwich dimer porphyrins, low-frequency Raman bands have been hypothesized to reflect the degree of intramolecular π–π interaction and to be connected with the intradimer vibration that modulates the separation between the two porphyrin moieties, or owing to symmetrical linear combinations of out-of-plane distortions of the neighboring porphinato macrocycles [23].

Given the enhancement of scattering associated with bands having motions that can strongly couple with excitonic motion, which helps define the aggregate’s structure, we report in Table 1 assignments made through such a scheme and by comparison to the literature. It is to be noted that a theoretical construct known as “aggregation-enhanced Raman scattering (AERS),” has been advanced by one of us (DLA) to explain which bands would experience significant enhancement upon aggregation of the scattering species. And, indeed, the two bands discussed above that show enormous enhancement upon aggregation of H₄TSPP have motions that couple to exciton movement through the aggregate and would be expected to experience significantly enhanced Raman intensities [12].

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