

Theoretical model for optical properties of porphyrin

Anh D. Phan,^{1,2,*} Do T. Nga,^{2,†} The-Long Phan,^{3,‡} Le T. M. Thanh,⁴ Chu T. Anh,² Sophie Bernad,⁵ and N. A. Viet²

¹*Department of Physics, University of Illinois, 1110 West Green Street, Urbana, Illinois 61801, USA*

²*Institute of Physics, Vietnam Academy of Science and Technology, 10 Dao Tan, Ba Dinh, Hanoi 10000, Vietnam*

³*Department of Physics, Chungbuk National University, Cheongju 361-763, Korea*

⁴*Faculty of Basic Science, Posts and Telecommunications Institute of Technology, 122 Hoang Quoc Viet, Hanoi 10000, Vietnam*

⁵*Laboratoire de Chimie Physique, CNRS UMR 8000, Université Paris-Sud, 91405 Orsay Cedex, France*

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We propose a simple model to interpret the optical absorption spectra of porphyrin in different solvents. Our model successfully explains the decrease in the intensity of optical absorption at maxima of increased wavelengths. We also prove the dependence of the intensity and peak positions in the absorption spectra on the environment. The nature of the Soret band is supposed to derive from π plasmon. Our theoretical calculations are consistent with previous experimental studies.

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I. INTRODUCTION

Porphyrins have been intensively investigated due to their wide range of applications such as for photon capture photons [1], photodynamic therapy of tumors [2,3], and selective catalysts [4]. Moreover, porphyrin-based materials also play substantial roles in biological systems. Hemes, the porphyrin-iron compounds found in hemoglobin protein, are oxygen transporters [5]. Magnesium-porphyrin complexes, so-called chlorophyll, are found to be photoreceptors in green plants [6]. It is apparent that most applications of porphyrins are based on their optical properties. Understanding the nature of the visible light absorption of porphyrins, therefore, is of great importance to the advancement of technology.

While using simulations can quantitatively determine physical values in optical spectra, describing the optical phenomena of porphyrin by theory provides various physical meanings. The four-orbital model introduced by Gouterman successfully explains the presence of peaks in the absorption spectra of porphyrin and metal-free porphyrins [7]. However, it is unclear why the absorption peak of the Soret band of porphyrin is at 400 nm with such a strong intensity. This model also cannot answer why the intensities of optical peaks decline with increasing wavelength. Another failure of the Gouterman model and other theoretical models is that they cannot explain why the maximum positions in the absorption spectra remain almost unchanged when measured in different solvents with different kinds of porphyrins. A new approach must be provided to overcome these weaknesses found in the available models.

In this paper, our simple model based on the Mie theory for an oblate spheroid allows us to understand the absorption spectra of porphyrin. The properties of the Soret band and Q bands can be explained by the plasmon mechanism. We have developed a theoretical model for the optical spectrum based on plasmonic excitation [8]. We explicitly point out the π -plasmonic feature of the Soret band. π -plasmon is the

collective oscillations of π -electrons, which have recently been found to exist in low-dimensional systems such as graphene [9], graphite, and carbon nanotubes [10]. Because π -plasmon is caused by the excitation of a semilocalized electron, the properties of π -plasmon are quite different from the usual plasmons found in metallic materials. More insights into the nature of plasmon in the porphyrin molecule would open various new applications for such porphyrin-based materials.

II. THEORETICAL CALCULATIONS OF THE OPTICAL ABSORPTION SPECTRUM OF PORPHYRIN

We can describe the porphyrin molecule as an oblate spheroid, with a , b , and c the characteristic dimensions (as depicted in Fig. 1; $a = b = R > c$). We have the lengths of two semimajor axes $a = b = R$, with $R = 0.44$ nm for free-base porphyrin (porphine) and $R = 1.4$ nm for 5,10,15,20-tetrakis(4-pyridyl)porphyrin (H_2 TPyP). The thickness of porphyrin ($c = 0.22$ nm) corresponds to the semiminor axis ($a = b > c$).

The optical absorption cross section of porphyrin can be calculated by [11–13]

$$\sigma_{\text{abs}} = \frac{2\pi V \varepsilon_m^{3/2}}{3\lambda} \sum_{k=a,b,c} \frac{1}{P_k^2} \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + \frac{1-P_k}{P_k} \varepsilon_m]^2 + \varepsilon_2^2(\omega)}, \quad (1)$$

where $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is the dielectric function of porphyrin, $\varepsilon_2(\omega)$ is the imaginary part of $\varepsilon(\omega)$, ε_m is the dielectric constant of the medium, $V = 4\pi abc/3$ is the volume of the oblate spheroid, and λ is the wavelength of the incident light. The geometrical factor determined for the ellipsoid shape is given by

$$P_a = \frac{(1 - e^2)^{1/2}}{2e^3} \left[\frac{\pi}{2} - \arctan\left(\frac{(1 - e^2)^{1/2}}{e}\right) \right] - \frac{1 - e^2}{2e^2}, \quad (2)$$

where $e = \sqrt{1 - \eta^2}$ and $\eta = c/a$. Since $a = b$, $P_a = P_b$ and $P_c = 1 - 2P_a$.

*anhphan2@illinois.edu

†dtnga1711@gmail.com

‡ptlong2512@yahoo.com

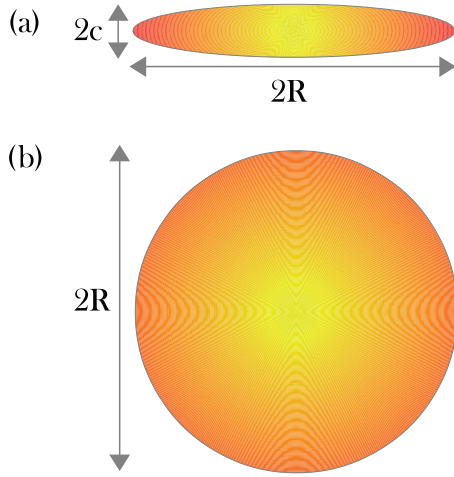


FIG. 1. (Color online) Illustration of the oblate spheroid modeled for porphyrins; different views.

The dielectric function of porphyrin is expressed by the Lorentz model,

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_{j=1}^N \frac{f_j \omega_{pj}^2}{\omega_{pj}^2 - i\omega\Gamma_j - \omega^2}, \quad (3)$$

where $\varepsilon_\infty = 10$ is the permittivity at infinite frequency, and ω_{pj} , f_j , and Γ_j are the resonant frequency, the oscillator strength, and the damping parameter at the j th mode, respectively. The values of parameters listed in Table I come from Ref. [8].

The calculated optical absorption spectrum of H₂TPyP porphyrin in various solutions such as water and CHCl₃, calculated by the Mie theory for shape-anisotropic colloidal particles above, is presented in Fig. 2. The strongest absorption, around 414 nm (3 eV), corresponds to the Soret band. The four weak absorption peaks are due to Q bands. These peak maxima are in excellent agreement with experimental data in previous studies [8]. Chen and coauthors [8] introduced ω_{pj} for the B band as a collective plasmonic resonance. However, they have not shown the physical nature of plasmon in the B band. Due to the similarity of the UV/vis absorption spectra of porphyrins, the parameters in Table I can be applied to a wide range of organic compounds. The only points differentiating the optical spectra are the intensities.

Equation (1) also suggests that the optical peak positions and their magnitudes in Fig. 2 are closely related to the porphyrin's dielectric function. Therefore, investigating the imaginary and real parts of the dielectric function of porphyrin

TABLE I. Values of parameters for the dielectric function of H₂TPyP [8].

Parameter	$f_j \omega_{pj}^2$ (eV ²)	ω_{pj} (eV)	Γ_j (eV)
B band	5.108	2.95	0.37
$Q_y(10)$	0.1521	2.40	0.10
$Q_y(00)$	0.1369	2.23	0.12
$Q_x(10)$	0.25	2.12	0.16
$Q_x(00)$	0.1369	1.94	0.11

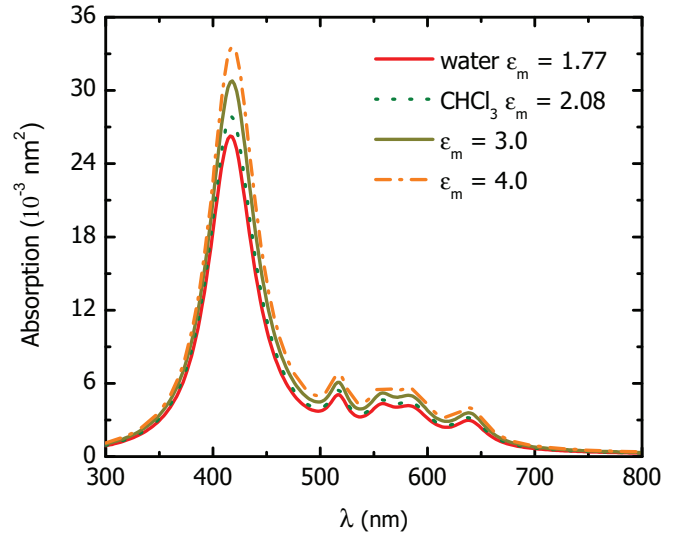


FIG. 2. (Color online) Absorption spectrum of H₂TPyP dispersed in water with $\varepsilon_{\text{water}} = 1.77$, CHCl₃ with $\varepsilon_{\text{CHCl}_3} = 2.07$, and other kinds of solvents as a function of the wavelength of incident light calculated by the Mie theory.

give us some predictions of the positions of optical absorption maxima. We replotted Fig. 5 from Ref. [8] over a broad range and describe the dielectric function as a function of the wavelength in Fig. 3. As shown in Fig. 3, $\varepsilon_1(\omega)$ is nearly unchanged and much larger than $\varepsilon_2(\omega)$ for $\omega < 2.5$ eV. Thus $\varepsilon_2^2(\omega)$, found in the denominator of Eq. (1), can be ignored. Resonances and the curve trend of σ_{abs} for this frequency range are strongly dependent on $\omega\varepsilon_2(\omega)$. An increase in $\varepsilon_2^2(\omega)$ with respect to the frequency is equivalent to a decrease in the absorption, while the incident light wavelength increases. Maximum sites in the absorption spectrum are also identical to those on the curve of the imaginary part of the porphyrin dielectric function. The Soret band forms due to the highest peak in $\omega\varepsilon_2(\omega)$ and the substantial reduction of $\varepsilon_1(\omega)$ at about 2.95 eV.

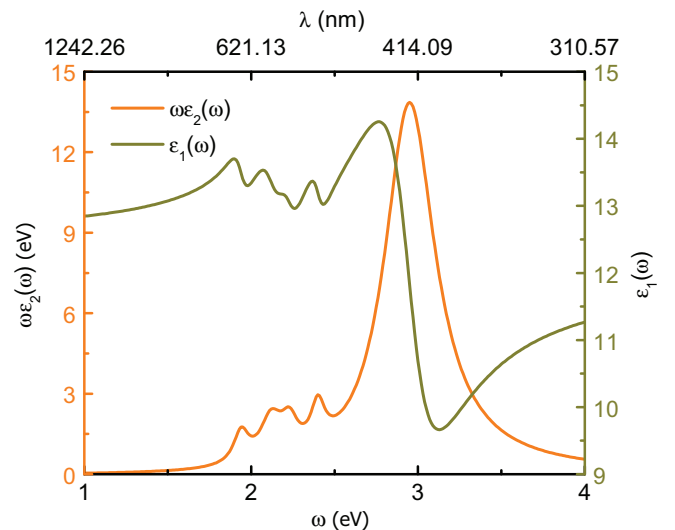


FIG. 3. (Color online) Imaginary and real parts of $\varepsilon(\omega)$ as a function of ω .

Apparently, the optical spectra are varied when measured in different solvents. For most configurations of porphyrins $c \ll a$ so $e \rightarrow 1$, $P_a = P_b \rightarrow 0$, and $P_c \rightarrow 1$. For $k = a$ or b , the denominator becomes $P_a^2[\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)]$, while for $k = c$ the denominator is expressed by ε_m^2 . In all cases, ε_m plays no role in changing the positions of optical peaks. This finding is in good agreement with experimental results in Refs. [14] and [15]. As a result, for our porphyrin, $\omega\varepsilon_2(\omega)$ is a decisive factor for the maximum positions in Fig. 2 and ε_m is responsible for the magnitude of σ_{abs} . An increase in the dielectric constant of the medium leads to an increase in the absorption curves. A rise at ambient temperature leads to a decrease in the dielectric constant ε_m and the absorption.

The absorption spectrum is also strongly dependent on the shape of porphyrin. For $c \ll a$, as discussed above, $\sigma_{abs} \sim 2V/P_a^2$. A decrease in the ratio c/a induces an increase in the intensity of optical absorption. However, the absorption peaks are not shifted due to the variation of c/a in this limit. For relatively large values of c/a , P_k becomes larger and $(1 - P_k)\varepsilon_m/P_k$ can be comparable to $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. An increment in c/a causes a slight blue-shift in optical peaks and a substantial reduction in the intensity of absorption.

The above calculations are valid for dilute solutions but may be modified for dense solutions of porphyrin. When porphyrins are far apart, the interactions between them can be neglected. Many-body effects become greater as the distance between two arbitrary porphyrins decreases. In order to determine the impact of the collective interactions on the absorption spectrum, we consider a simple system including two porphyrins located in the $x - y$ plane. Each porphyrin is described as a dipole. The polarization of two dipoles, \mathbf{p}_1 and \mathbf{p}_2 , can be expressed by [16]

$$\mathbf{p}_1 = \alpha_{01}(\mathbf{E}_0 + \mathbf{G}_{12}\mathbf{p}_2), \quad (4)$$

$$\mathbf{p}_2 = \alpha_{01}(\mathbf{E}_0 + \mathbf{G}_{21}\mathbf{p}_1), \quad (5)$$

where \mathbf{E}_0 is the incident electric field on each dipole, \mathbf{G}_{12} and \mathbf{G}_{21} are the Green functions describing the mutual interaction of the system, and α_{01} and α_{02} are the polarizabilities of dipoles 1 and 2 as they are isolated, respectively.

Suppose that \mathbf{E}_0 is placed along the line joining the centers of these two dipoles; the Green function is given by

$$G_{12} = G_{21} = \frac{e^{ikr}}{2\pi} \left(-\frac{ik}{r^2} + \frac{1}{r^3} \right), \quad (6)$$

where $k = \omega\sqrt{\varepsilon_m}/c$ and r is the center-to-center distance between two porphyrins.

For the case of an oblate spheroid,

$$\alpha_{01} = \alpha_{02} = V \frac{\varepsilon(\omega) - \varepsilon_m}{P_a [\varepsilon(\omega) - \varepsilon_m] + \varepsilon_m}. \quad (7)$$

After straightforward calculations, we can obtain the polarizability of a porphyrin including the interaction from another porphyrin,

$$\alpha_1 = \alpha_2 = \frac{\alpha_{01}}{1 - \alpha_{01}G_{21}}. \quad (8)$$

For a large distance $r \gg R$, $G_{21}(r) \approx 0$, $\alpha_1 = \alpha_{01}$. Therefore, the absorption spectrum does not change. For $\lambda \gg r > 2R$, k/d^2 is small compared to $1/d^3$, and the Green function

can be recast as $e^{ikr}/2\pi r^3$. Consequently, $V/r^3 \ll 1$ and we still see that $\alpha_1 = \alpha_{01}$ for $r \geq 4$ nm. The absorption spectrum has a minor variation when $4 \text{ nm} \geq r \geq 3 \text{ nm}$. These findings suggest that the many-body effect can be ignored when the concentration of the porphyrin solution is lower than 3×10^{22} molecules/ml or 49.8 mol/liter. However, 49.8 mol/liter is a really high concentration for biological samples. Therefore, when researchers measure the absorption of a porphyrin solution, it means that they obtain the optical spectrum of a porphyrin molecule, and other molecules have no influence on this spectrum.

III. PLASMA FREQUENCY FOR THE SORET BAND

The features of the absorption spectra of porphyrin discussed in the previous section are caused by the core component of porphyrins, namely, porphine, illustrated in Fig. 4. The behaviors of the optical spectra are similar to those of other kinds of porphyrin [17]. The peak positions, however, are shifted due to additional components. This phenomenon can be explained by the conjugated systems creating a shell covering the porphine core [7]. The core-shell interactions in porphyrins behave similarly to what we observe in the optical spectrum of core-shell nanoparticle systems [18]. This finding together with the fact that plasmon is found in low-dimensional materials suggests the possibility that plasmon exists in porphyrins.

In this section, we propose an assumption for the nature of the largest peak, the so-called Soret band or B band. The presence of the Soret band can be understood by a plasmon mechanism. This idea was mentioned previously [8], however, the authors did not point out what kind of plasmon is implied in the Soret band.

Monolayer graphene and a porphyrin molecule are supposed to have the same thickness, $d = 3.4 \text{ \AA}$, equal to the diameter of a carbon atom. This assumption suggests that both graphene sheets and porphyrin molecules can be treated as bulk

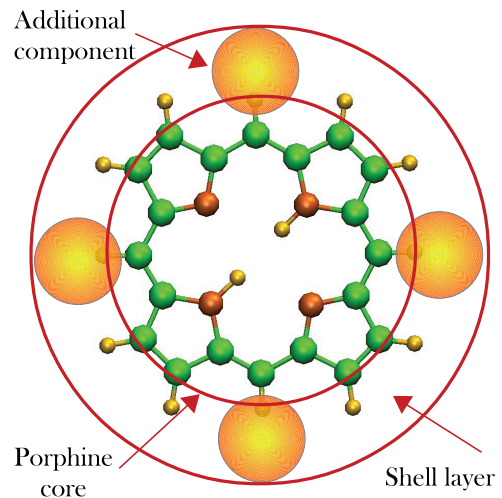


FIG. 4. (Color online) Atomic structure of porphine, with 20 carbon atoms [(green) spheres], 14 hydrogen atoms [small (yellow) spheres], and 4 nitrogen atoms [(brown) spheres], and the reference compound [large (orange) spheres].

systems. Plasmons in the bulk oscillating at ω_p are determined by the free electron density and effective mass. The plasma frequency is calculated by the expression

$$\omega_p = \sqrt{\frac{ne^2}{m^*\epsilon_0}}, \quad (9)$$

where n is the number density of electrons, m^* is the electron effective mass, e is the electron charge, and ϵ_0 is the permittivity of the vacuum.

The electron density n is calculated by

$$n = \frac{N_c}{S.d}, \quad (10)$$

where N_c and S are the number of carbon atoms and the considered area, respectively.

From Eqs. (9) and (10), the ratio of the plasma frequency of porphyrin to that of graphene is given by

$$\frac{\omega_p^{\text{por}}}{\omega_p^g} = k \sqrt{\frac{N_c^{\text{por}} S^g}{N_c^g S^{\text{por}}}}, \quad (11)$$

where k is a topological-dependent parameter of porphyrin, ω_p^{por} is the plasma frequency of porphyrin, ω_p^g is the plasma frequency of graphene, and N_c^{por} and N_c^g are the number of carbon atoms in porphyrin and graphene, respectively. As illustrated in Fig. 4, $N_c^{\text{por}} = 20$.

Let l be the distance between nearest-neighbor carbon atoms in graphene, where $l = 1.42 \text{ \AA}$. The area of a hexagonal unit cell in graphene is given by $A = 3\sqrt{3}l^2/2$. This result suggests that the area of porphyrin corresponds to 11.5 hexagonal unit cells in graphene, so $N_c^g = 48$. Experimental data [19] for π -plasmon are approximately 4.7 eV and the value gives rise to $\omega_p^{\text{por}} = 3.03 \text{ eV}$. This result is close to the

position of the Soret band, $\omega_p \approx 3 \text{ eV}$. The difference between ω_p^{por} and ω_p is induced by the deviation of geometry. Therefore, it is necessary to introduce the geometrical parameter k for the porphyrin geometry and correction purposes, to obtain $\omega_p^{\text{por}} \approx 3 \text{ eV}$. This approach has been used [20] to describe the main resonance in the optical spectra of C_{60} .

The similarities between graphene and porphyrin suggest that the absorption spectrum of porphyrin can be changed by applying external fields. It is well known that electric and magnetic fields can be used to tune the optical properties of graphene [21]. As a result, these external fields may have a certain role in changing the absorption spectrum of porphyrin.

IV. CONCLUSIONS

In summary, we have proposed a theoretical model for calculating the absorption spectrum of porphyrin. If the interaction between porphyrins and solvent can be ignored, the absorption spectrum in dilute solutions does not show variation in peak positions but the absorption intensities are changed. These calculations confirm previous experimental studies. π -plasmon was assumed to exist in biological macromolecules due to the similarity of graphene and porphyrin and ideas in recent studies. Our model also shows the π -plasmonic nature of the Soret band by a simple approach that has been successfully used to understand the major resonance in C_{60} .

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- [1] S. Fukuzumi, *The Porphyrin Handbook* (Academic Press, San Diego, CA, 2000).
- [2] A. M. Battle, *J. Photochem. Photobiol. B* **20**, 5 (1993).
- [3] K. Sugisaki, T. Usui, N. Nishiyama, W.-D. Jang, Y. Yanagi, S. Yamagami, S. Amano, and K. Kataoka, *Invest. Ophthalmol. Vis. Sci.* **49**, 894 (2008).
- [4] S. Gharaati, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, B. Barati, and F. Sadegh, *J. Organomet. Chem.* **741-742**, 78 (2013).
- [5] Y.-H. Chen, S.-F. Yet, and M. A. Perrella, *Exp. Biol. Med.* **228**, 447 (2003).
- [6] C. B. Storm, A. H. Corwin, R. R. Arellano, M. Martz, and R. Weintraub, *J. Am. Chem. Soc.* **88**, 2525 (1966).
- [7] V. N. Nemykin and R. G. Hadt, *J. Phys. Chem. A* **114**, 12062 (2010).
- [8] Y. C. Chen, M. W. Lee, L. L. Li, and K. J. Lin, *J. Macromol. Sci., Phys.* **47**, 955 (2008).
- [9] V. Despoja, D. Novko, K. Dekanić, M. Šunjić, and L. Marušić, *Phys. Rev. B* **87**, 075447 (2013).
- [10] C. Kramberger *et al.*, *Phys. Rev. Lett.* **100**, 196803 (2008).
- [11] O. L. Muskens, N. Del Fatti, F. Valle, J. R. Huntzinger, P. Billaud, and M. Broyer, *Appl. Phys. Lett.* **88**, 063109 (2006).
- [12] V. Amendola and M. Meneghetti, *J. Phys. Chem. C* **113**, 4277 (2009).
- [13] O. Muskens, D. Christofilos, N. D. Fatti, and F. Vallee, *J. Opt. A: Pure Appl. Opt.* **8**, S264 (2006).
- [14] M. Y. Choi, J. A. Pollard, M. A. Webb, and J. L. McHale, *J. Am. Chem. Soc.* **125**, 810 (2003).
- [15] R. Dong, Y. Bo, G. Tong, Y. Zhou, X. Zhu, and Y. Lu, *Nanoscale* **6**, 4544 (2014).
- [16] S. Toroghi and P. G. Kik, *Appl. Phys. Lett.* **100**, 183105 (2012).
- [17] H. V. Knorr and V. M. Albers, *J. Chem. Phys.* **9**, 197 (1941).
- [18] A. D. Phan, T. X. Hoang, T. H. L. Nghiem, and L. M. Woods, *Appl. Phys. Lett.* **103**, 163702 (2013).
- [19] T. Eberlein, U. Bangert, R. R. Nair, R. Jones, M. Gass, A. L. Bleloch, K. S. Novoselov, A. Geim, and P. R. Briddon, *Phys. Rev. B* **77**, 233406 (2008).
- [20] A. V. Verkhovtsev, A. V. Korol, A. V. Solovoyov, P. Bolognesi, A. Ruocco, and L. Avaldi, *J. Phys. B: At. Mol. Opt. Phys.* **45**, 141002 (2012).
- [21] George W. Hanson, *IEEE Trans. Antennas Propag.* **56**, 747 (2008).