

-Plasmon model for carbon nano structures: Application to porphyrin

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π -Plasmon model for carbon nano structures: Application to porphyrin

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Abstract. In traditional concept, the optical properties of semiconductors and semimetals near their fundamental optical band gaps are attributed to single excitations (such electron-hole pairs, excitons...). In our earlier article, we proposed the collective mechanism of π -plasmons for optical properties of low dimensional carbon nano structures. A simple way to calculate the peak positions of UV-vis absorption spectra was pointed out and gave a good agreement with experimental data. In this work we analyze different schemas to calculate the UV-vis absorption peaks. A new parameter k which characterizes the dependence of schema on geometry and number of carbon sites is defined. As an example, the case of porphyrin was investigated.

1. Introduction

In recent years, optical properties of low dimensional systems, nano structures semiconductors and semimetals have attracted great intention due to their enormous, vast, and important application in modern nano technologies.

In traditional concept, the optical properties of semiconductors and semimetals near their fundamental optical band gaps are attributed to single excitations (such electron-hole pairs in one-particle picture, or excitons in two-particle picture ...). At high concentration, an electron-hole plasma in many particle-particle picture will formed, and the corresponding collective excitation is called plasmon.

Similarly, in carbon nano structures, such as graphene, graphene nano ribbons, carbon nanobots, Fullerton, C_{60} molecules, etc, the optical properties determined by the interbank πe transitions (in the free π optoelectronic scheme), or from the ground sate to excited states (in the π exciton scheme), or by π -plasmas mechanism.

Porphyrins have been intensively investigated due to their wide range of applications such as for photon capture photons[1], photo dynamic therapy of tumors[2, 3], and selective catalysts[4]. Moreover, porphyrin-based materials also play substantial roles in biological systems as oxygen transporters[5], photoreceptor in green plants[6]. It is apparent that most applications of porphyritic 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.

The absorption peak of the Soret band of porphyritic is at 400nm with a strong intensity. The intensities of optical peaks decline when increasing wavelength. The maximum positions



in the absorption spectra remain almost unchanged in different solvents with different kinds of porphyrin. In the previous work[7] we proposed 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.

In this work, we introduce a new concept: topological-dependent parameter k of porphyrin, then investigate various models: between a porphyrin and a monolayer graphene plate which have the same density, or the same area, or the same atoms number.

2. π -Plasmon model for optical properties of flat carbon nano structures

To take in consideration, the chosen monolayer graphene, porphyrin, and flat bio-macro molecules 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, porphyrin, and flat bio-macro molecules can be treated as bulk systems. Plasmons in the bulk oscillate at plasma frequency ω_p , determined by

$$\omega_P = \sqrt{\frac{ne^2}{m^*\epsilon_0}}, \quad (1)$$

where n is the 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 formula

$$n_i = \frac{N_C^i}{S^i d}, \quad (2)$$

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

The distance between nearest-neighbor carbon atoms in graphene is $l = 1.24\text{\AA}$. The area of a hexagonal unit cell in graphene is $A = 3\sqrt{3}l^2/2$. Thus, the area of porphyrin corresponds to 11.5 hexagonal unit cells in graphene. Experimental data for π -plasmon are approximately $\omega_{\pi P} = 4.7\text{ eV}$.

3. π -Plasmon model for the Soret band of porphyrin

The structure of porphyrin can be seen in [7], and represented here in Fig.3 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].

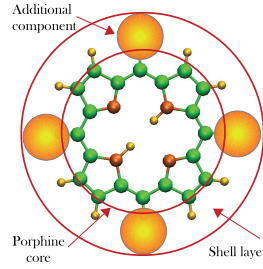


Figure 1. (Color online) Atomic structure of porphyrin, with 20 carbon atoms [(green) spheres], 14 hydrogen atoms [small (yellow) spheres], and 4 nitrogen atoms [(brown) spheres], and the reference compound [large (orange) spheres].

The typical absorption spectra of a porphyrin molecule is also described in our previous work which showed that the strongest absorption localized at around $414nm$ ($3eV$), corresponds to the Soret band. The four weak absorption peaks are due to Q bands.

The behaviors of the optical spectra are similar to those of other kinds of porphyrin family. However, the peak positions are shifted due to the additional components. This phenomenon can be explained by the conjugated systems creating a shell covering the porphyrin core. The core-shell interactions in porphyrins behave similarly to what we observe in the optical spectrum of core-shell nanoparticle systems. On the other side, plasmon is also found in low-dimensional materials. Based on these facts, they have made a suggestion of the possible exist of plasmon in porphyrins. They proposed an assumption for the nature of the largest peak, the Soret band or B band.

The ratio of the plasma frequency of porphyrin to that of graphene is given by[7]

$$\frac{\omega_P^{por}}{\omega_P^g} = k_{por} \sqrt{\frac{N_C^{por}}{N_C^g} \frac{S^g}{S^{por}}}, \quad (3)$$

where k_{por} 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, N_C^{por} and N_C^g are the number of carbon atoms in the area S^{por} and S^g of porphyrin and graphene, respectively. For porphyrin $N_C^{por} = 20$, the area of porphyrin S^{por} corresponds to 11.5 hexagonal unit cells in graphene, so $N_C^g = 48$. Experimental data for π -plasmon are approximately $\omega_{\pi P} = 4.7$ eV. The our calculated $\omega_P^{por} \simeq 3.03$ eV, which is very closed to the position of the absorption peak of the Soret band $\omega_{Soret} \simeq 3$ eV. The value of topological-dependent parameter of porphyrin $k_{por} \simeq 0.64$. The position of the Soret band gives $\omega_{Soret} \simeq 3$ eV.

Generalize above result, we introduce a topological-dependent parameter k_i of the nano-carbon or bio-macro-molecule structures i , which is defined by the equation

$$\frac{\omega_P^i}{\omega_P^g} = k_i \sqrt{\frac{N_C^i}{N_C^g} \frac{S^g}{S^i}}, \quad (4)$$

where ω_P^i is the plasma frequency, and N_C^i is the number of carbon atoms in its area S^i of the nano-carbon or bio-macro-molecule structures i .

4. Topological-dependent parameter k of porphyrin:

4.1. The dependence of k on carbon atoms density:

With x, y the number of hexagonal unit cells of each edge, N is the number of carbon atoms, S is the considered area, A is the area of a hexagonal unit cell, means S is the number of hexagonal unit cells in the considered area.

$$n = \frac{N}{S}. \tag{5}$$

As stated before, the thickness of porphyrins molecules and monolayer graphene are supposed to be the same, so we examine the variation of k along with number of carbon atoms over the corresponding area ($n = N/S$), which can be considered as the carbon atom density. The investigation is made for three different monolayer graphene plate type: the parallelogram, the rhombus, and the equilateral triangle.

In the case of parallelogram:

$$N_{\text{paral}} = 2(xy + x + y); S_{\text{paral}} = xy, n_{\text{paral}} = 2 + 2\frac{(x + y)}{xy}. \tag{6}$$

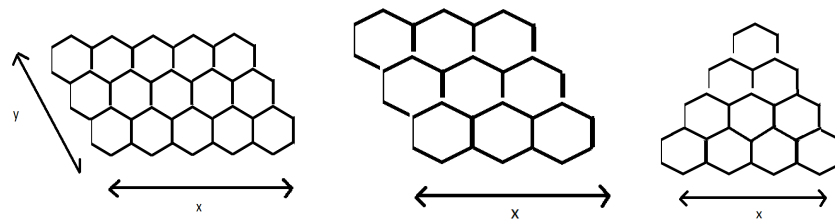


Figure 2. **Left:** Parallelogram molecule. **Center:** Rhombus molecule. **Right:** Equilateral triangle molecule.

Application of similar methods for the rhombus:

$$N = 2x(x + 2), S = x^2, n = 2 + \frac{4}{x} \tag{7}$$

In case of equilateral triangle:

$$N = x^2 + 4x + 1, S = \frac{x + 1}{2}x, n = 2\frac{x^2 + 4x + 1}{x^2 + x}. \tag{8}$$

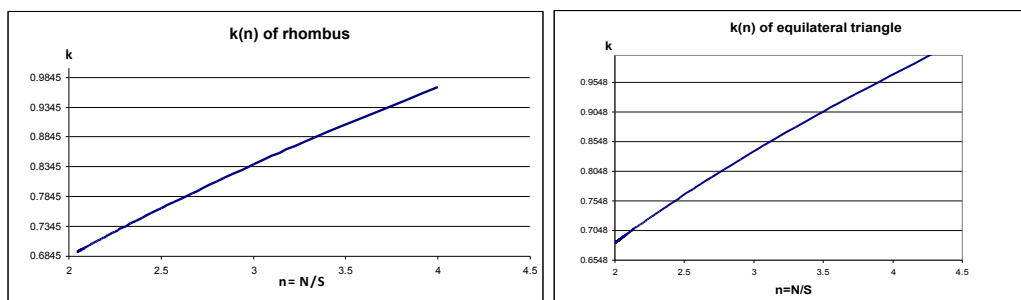


Figure 3. **Left:** The dependence of k on density of rhombus model. **Right:** The dependence of k on density of "equilateral" triangle model.

As shown in Fig.3, when the size of models increases, the value of $n = N/S$ decreases. As the size reaches to infinite (or the number of carbon atoms reach to infinite), $n \rightarrow 2$ in all three models. Then, $k=0.6845$ when $size \rightarrow \infty, N \rightarrow \infty, n \rightarrow 2$. k increases linearly but differently in each case.

4.2. The dependence of k on the considered area

We consider the case where porphyrin and graphene have the same number of carbon atoms $N_c = 20$, which is the number of carbon atoms of porphine core. Four different models of monolayer graphene are investigated in Fig.4 Fig.5.

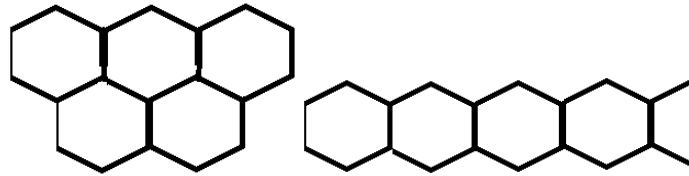


Figure 4. Left: With the arrangement of carbon atoms as shown, the respective area of graphene is $S=5A$, which lead to the result of $k = 0.968$.

Right: The area of graphene now is $S=4A+0.5A=4.5A$, so k is 1.02.

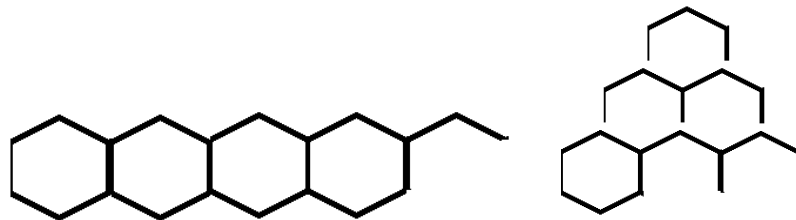


Figure 5. Left: $S=4A+1/6A=25/6A$. $k= 1.06$. **Right:** $S=17/3A$, $k = 0.91$.

4.3. The dependence of k on the number of carbon atoms

In case that considered area of porphyrin and monolayer graphene is the same ($S=11.5A$), four different models are investigated in Fig.6 and Fig.7.

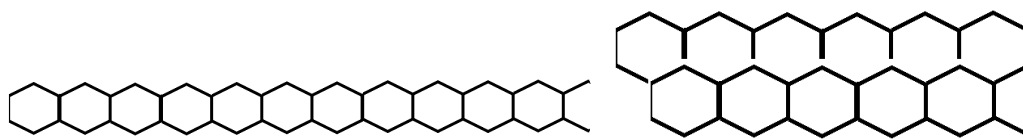


Figure 6. Left: The number of carbon atoms in this case is $N_g=50$, substitute the result in formula (3), we get $k=1.009$.

Right: $N_g=42$, so $k=0.925$.

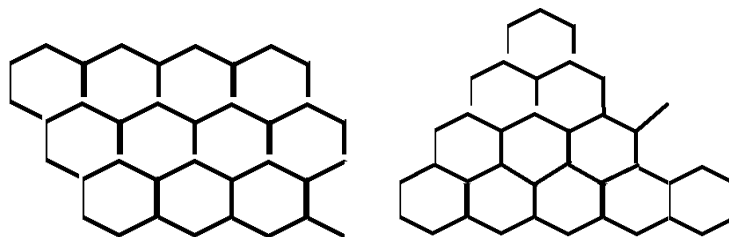


Figure 7. Left: The number of carbon atoms of graphene is 36, k corresponding is 0.856.

Right: $N_g=38$, $k=0.88$.

5. Conclusion

As the continuous results of our previous works on theoretical model for calculating the absorption spectrum of porphyrin and carbon nano structures, the topological dependence of k has opened various possibilities on biological macromolecules research. It has been shown obviously that $k \simeq 1$, which helps to verify our proposed theoretical model on the π -plasmon nature of main optical properties of porphyrin and carbon nano structures. Above investigations showed that there exist each constant k for each corresponding molecule type. It has important meaning that k can be used to categorize biological macromolecules. The theoretical k in this work will be compared with experimental one in our next investigations.

Acknowledgement

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