Aleksandr G. Avramenko [a, b], *Mindy Spiehs* [b]

PHOTOPHYSICAL PROPERTIES OF PORPHYRINS AND THEIR APPLICATIONS TO POLARITON CHEMISTRY (A REVIEW)

[a] **Detroit Medical Products Laboratory, Food and Drug Administration, United States Department of Health and Human Services, Detroit, MI, United States**
[b] **United States Meat Animal Research Center, Agricultural Research Service, United States Department of Agriculture, Clay Center NE, United States**

Porphyrins are a fundamental class of molecules involved in a multitude of biological and chemical functions ranging from photosynthesis in plants to biomarkers in medicine to optoelectronic devises. Despite the porphyrin molecule being such an important class of molecules known for centuries, its photophysics are surprisingly complex and models describing the spectroscopic behavior of porphyrins did not emerge until the 1950s. This review aims to distil the basics of porphyrin photophysics, describing how the Soret band and the Q band of the molecule are formed. In particular, a discussion of the four orbital theory and Hertzberg-Teller coupling will be conducted, both of which are necessary to understand the spectral properties of the porphyrin molecule. The review further aims to complement previous work discussing the chemical applications of hybrid light-matter states by discussing how the spectroscopic behavior of porphyrins is particularly useful in polariton chemistry.

Keywords: porphyrin, polariton, spectroscopy, perturbation theory, vibronic coupling.

Introduction

Porphyrins are a class of organic molecules which serve as the building blocks of numerous vital biological molecules. In particular, they serve as the building block of the heme coordination complex responsible for carrying out oxygen distribution through the bloodstream, as well as the building block of chlorophyll, which serves as one of the chief molecules in photosynthesis [1]. What makes porphyrins a unique molecule to spectroscopists is the strong, vibrant color these molecules produce, which stems from strong absorbance in two areas of the spectrum [1]. One of these strongly absorptive bands is referred to as the «Soret» band, located in the 3 eV region. This Soret band (sometimes referred to as the B band) possesses a very large extinction coefficient of ≈400,000 M^{-1} cm^{-1} [2,3]. The other area of prominent absorption is a weaker band located approximately 0.8 eV below the absorption of the Soret band, referred to as the Q band. These spectral characteristics are demonstrated

in Fig. 1. The B band stems from the absorbance between the ground and the second excited state ($S_0 \rightarrow S_2$), while the Q band absorbance stems from absorbance from the ground state into the first excited state ($S_0 \rightarrow S_2$) [4,5]. While this configuration seems benign at first, the observance of the lower lying Q band appears to violate the LePorte selection rule, which states that absorbance between states that possess the same center of inversion are forbidden [6].

Gouterman [4,5] explained the appearance of the porphyrin spectra by using the «Four Orbital» theory. This explanation described the porphyrin molecules as possessing a pair of degenerate highest occupied molecular orbital (HOMO) a_{2u}/a_{1u} orbitals and a pair of degenerate lowest unoccupied molecular orbital (LUMO) e_{gx}/e_{gy} orbitals. Because both of these excited state configurations are degenerate, there is an equal chance of the molecule being in either configuration, either the (HOMO a_{2u}/a_{1u})/(LUMO e_{gx}/g_{gy}) states. The two degenerate states are mixed via
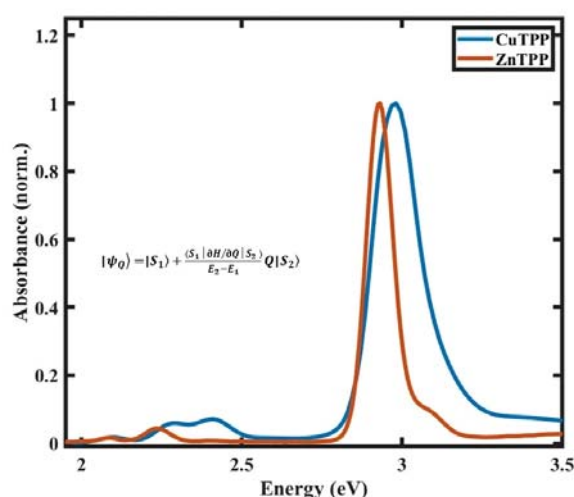
Fig. 1. Spectra of copper (II) tetraphenyl porphyrin (blue) and zinc (II) tetraphenyl porphyrin (red) while dissolved in toluene. Both spectra were created from a 0.1 mM starting solution dissolved in toluene using a 1 mm UV cell. Note the characteristic Soret band near 3 eV stemming from absorption into the second excited state, followed by smaller Q absorbance bands approximately 0.8 eV below originating from absorption into the first excited state. The copper variant is also displaying a blue shifted «hypso» characteristic. The two observed energy levels in the spectra are vibronically coupled as shown in the equation embedded in the figure
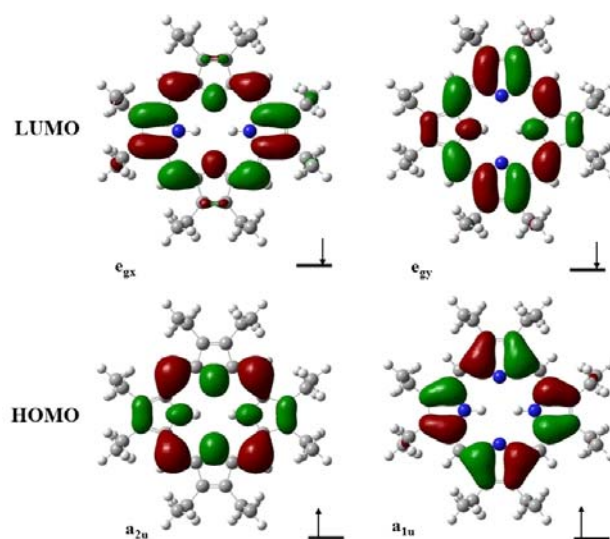

Fig. 2. Gouterman's «Four Orbital» model describing the spectra of an octoethyl porphyrin (OeTPP) molecule. There is an equal probability of the porphyrin being in the $a_{1u}e_{gy}$ or the $a_{2u}e_{gx}$ excited state configuration. The configuration interaction between the two degenerate states creates one state in which the dipole moments of the excited state configurations reinforce, and another in which the dipole moments cancel. The molecular orbitals (MOs) were calculated using Gaussian 16 software [7,8]

configuration interaction [5]. The final, mixed states are a symmetric and an antisymmetric superposition of the original excited state configurations. The B state is the symmetric superposition in which the wavefunction of the two degenerate states reinforce,

$$B = \left[\frac{1}{\sqrt{2}} \left(a_{2u}e_g + a_{1u}e_g \right) \right].$$ Meanwhile, the Q state is the antisymmetric superposition;

$$Q = \left[\frac{1}{\sqrt{2}} \left(a_{2u}e_g - a_{1u}e_g \right) \right],$$ in which the two wavefunctions of the degenerate states cancel each other out, as displayed in Fig. 2. In summary, quantum interference between the two wave functions that form the Q state should make this state effectively dark. However, it is still observed, possessing a sizable extinction coefficient of around $10,000-20,000$ $M^{-1} \cdot cm^{-1}$. Moreover, the absorbance can be tuned by substituting the metal complex at the center of the porphyrin complex, as well as by manipulating the substituent groups on and around the porphin ring structure [4,5]. This tunability makes the molecule of particular interest to spectroscopists, and must be accounted for by any model trying to explain the porphyrin spectra.

Spectroscopic behavior of porphyrin molecules

The observance of the Q band in porphyrin spectra is thought to be due to Herzberg-Teller (HT) coupling between the higher lying B and lower lying Q states [9,10]. This coupling effectively allows a lower lying, less energetic state to «borrow» energy from the higher lying B state. Hertzberg-Teller coupling can be thought of in terms of perturbation theory, $\psi_n = \psi_n^0 + \lambda\psi_n^1$, in which Q absorbance stems from a perturbation along the potential energy of the B state. Rewriting HT coupling in terms of the more familiar first order perturbation theory:

$$\left| Q \right\rangle = \left| S_1 \right\rangle + \frac{\left\langle S_2 | V | S_1 \right\rangle_0}{E_{S2} - E_{S1}} \left| S_2 \right\rangle \qquad (1)$$

In Eq. (1), S_1 is the first excited state in equilibrium geometry; S_2 is the second excited state responsible for the B peak; and $V = \left(\frac{\partial H}{\partial q} \right)_q$ is the Hertzberg-Teller coupling between the initial and final states along a vibrational coordinate q.

If during a transition there is a non-symmetric

Aleksandr G. Avramenko, Mindy Spiehs

vibration that shifts the S_2 energy level away from equilibrium, then H (the electronic Hamiltonian) would change with respect to vibrational coordinate q. Thus, the symmetry of the porphyrin molecule becomes distorted, relaxing the LaPorte rule and allowing the Q band to be observed.

The probability of making a transition between two states is dependent on the transition dipole moment $\mu_{ab} = \langle \psi_b | \mu | \psi_a \rangle$ where μ_{ab} is the probability of making a transition from the ψ_a to the ψ_b state. Rewriting Eq. (1) in terms of a probability of making a transition from the ground (S_0) to the ψ_Q state, we get:

$$\langle \psi_Q | \mu | S_0 \rangle \langle 0 | n \rangle = \langle S_1 | \mu | S_0 \rangle \langle 0 | n \rangle + \frac{S_1 | \partial H / \partial Q | S_2}{E_2 - E_1} \langle S_2 | \mu | S_0 \rangle \langle 0 | Q | n \rangle . \quad (2)$$

In Eq. (2), the $\langle \psi_Q | \mu | S_0 \rangle$ term is the probability of making an electronic transition between the ground and the vibrationally coupled ψ_Q state, with the probability of making vibrational transitions, $\langle 0 | n \rangle$, included. The $\langle S_1 | \mu | S_0 \rangle \langle 0 | n \rangle$ term represents the probability of making a transition between the ground and first excited state of the porphyrin molecule (responsible for the appearance of the Q absorption band), while also considering the probability of the transitions into the vibrational levels. The potential energy surface of the first excited state of the molecule is assumed to have no displacement with the ground state. Keeping with the principles of orthogonality and normality in Hilbert space, in Eq. (2), $\langle 0 | n \rangle = 1$ is normalized when the eigenvector n=0. On the contrary, $\langle 0 | n \rangle = 0$ when n does not equal 0. In a physical sense, when two states are orthogonal to each other and $\langle 0 | n \rangle = 0$, the two states are mutually exclusive.

In Eq. (2), the term $\langle S_2 | \mu | S_0 \rangle \langle 0 | Q | n \rangle$ represents the probability of making a transition from the ground to the second excited state of the porphyrin molecule (responsible for the absorbance of the B spectral band). However, now the probability of making transitions into different vibrational levels is impacted by Q operating on n. It is assumed that the potential energy surfaces of the involved states are described by the harmonic oscillator model. Using this assumption, the nuclear coordinate Q serves as the position operator which can be rewritten as $Q = (a + a^+)/\sqrt{2}$ where $a | n \rangle = \sqrt{n} | n - 1 \rangle$ and $a^+ | n \rangle = \sqrt{n + 1} | n + 1 \rangle$ [6]. Operating Q on n in Eq. (2) would result in:

$$\langle 0 | Q | n \rangle = \langle 0 | \sqrt{n} | n - 1 \rangle + \langle 0 | \sqrt{n + 1} | n + 1 \rangle \quad (3)$$

Using the orthogonality principle; $\langle 0 | \sqrt{n} | n - 1 \rangle$ would equal 1 when n was 1 and $\langle 0 | \sqrt{n + 1} | n + 1 \rangle$ would equal 1 when n was −1. Since energy levels that are below a ground state do not have a physical meaning, only a transition into the first vibrational state should be considered as valid. Note that in Eq. (2) if either the perturbation term or the transition dipole $\langle S_2 | \mu | S_0 \rangle$ go to 0 the probability of a transition into the ψ_Q state would simply be represented as $\langle S_1 | \mu | S_0 \rangle$. Therefore, in order for the «forbidden» state to be observed, it must satisfy one major condition, that is, it must combine with a state that has a large transition dipole moment. Moreover, this treatment shows that two major vibrational levels are involved in the transition of porphyrins, the ground vibrational energy level (n=0) and an excited vibrational energy level (n=1). Note that because the Hertzberg-Teller model involves vibrational levels to couple the two states, the phenomenon is sometimes referred to simply as vibronic coupling.

Upon close inspection, the previously described vibronic structure reveals that the Frank-Condon approximation for electronic transitions is not followed in porphyrins. While the total intensity of an electronic transition is dependent on the complex conjugate of the electronic dipole transition, , the Frank-Condon approximation states that this intensity is then distributed among allowed vibration sublevels. The intensity of vibrational sublevels will depend on the overlap between the vibrational wavefunctions of the ground and excited states [6]. If a potential energy surface of the excited and ground state are similar, the Frank-Condon approximation predicts the 0−0 vibrational transition to be the strongest, with the 0−1 to be weaker, and any subsequent transition to be weaker still. On the other hand, if the potential energy surfaces of the excited and ground states are different, then the Frank-Condon approximation predicts that 0−0 transitions will be weak, and the intensity will peak at some higher transitions where the wave functions better overlap, at either the 0−1, or 0−2 transition, followed by an intensity decrease [6]. Note that the Frank-Condon approximation upon which most chemists rely on to describe the spectroscopic behavior of molecules does not include

the possibility of Hertzberg-Teller coupling between states, which is why the approximation cannot fully describe the behavior of porphyrin molecules. It is perhaps best to think of the Hertzberg-Teller vibrational borrowing phenomena as an extension of the Condon approximation. In both cases, the transition dipole is treated independent of nuclear coordinates, with the Teller approximation adding a perturbative step.

Finally, the impact of the bonding metal and the substituents on the porphin ring on the spectra of porphyrins must be explained. With prophyrins containing both, electron withdrawing groups, such as phenyl, and electron donating groups such as alkyls, their behavior will generally follow the four orbital model, with the relative strength of the B and Q band impacted. This phenomenon can be explained by Fermi's Golden Rule, in which the transition rate between two states is not only dependent on the coupling strength between two states, but also on the density of the final states [6]. The particle in a box model can also be used to explain the effect of substituents on the Soret absorbance, $E = \dfrac{n^2 h^2}{8mL^2}$. A large molecule would increase L, the lowering the observed energy. The impact of the metal on the spectra is more nuanced. Unique spectra may appear due to the presence of the metal orbitals which are near the same energy as the MOs of the porphin ring. Such is the case in Copper (II) tetraphenyl porphyrin, in which the $3d_{x2-y2}$ orbital is nearly degenerate with the LUMO e_g orbitals of the porphyrin ring, leading to a set of «sing doublet», «trip doublet», and «trip quartet» states, where the «sing» and «trip» refers to the electron configuration on the porphyrin

ring, and the «doublet» and «quartet» to the spin multiplicity of the whole system, as shown in Fig. 3 [11,12]. Moreover, the interaction between the d orbitals of the metal and the porphyrin ligand can lead to spectroscopic shifts in the porphyrin spectra. In the case of the aforementioned copper example, the Soret band is blue shifted as compared to the spectra of H_2TPP giving it a «hypso» porphyrin assignment. A «hyper» porphyrin stems from the presence of an empty p orbital, in particular group 14 metalloids such as germanium, which can interact with the porphin ring. This interaction results in a red shift of the Soret spectral band, therefore, these class of porphyrins are referred to as 'hyper' porphyrins [1,13−16]. A «normal» porphyrin is one that experiences neither a redshift nor a blueshift, this can be due to a presence of a metal with a filled d and p orbital, such as zinc [13,14].

Overview of polariton states

Polariton states are a state of hybridization between light and matter [17]. More specifically, they involve the interaction between the photons of an optical cavity, and the molecular excitations of matter. While an astute observer will note that matter and light interact frequently with each other, it is often in the weak coupling regime. In the weak coupling regime the physical nature of the photon and the matter can be considered as separate entity and neither system undergoes a physical change. Weak coupling regimes can often be solved using perturbation theory [6,17,18]. On the contrary, in the strong coupling regime, the photonic and excitonic states undergo a fundamental physical change, they hybridize and each state must be described while also referencing to the other. Some of the first experimental polariton states were formed using quantum wells, as seen in Fig. 4.
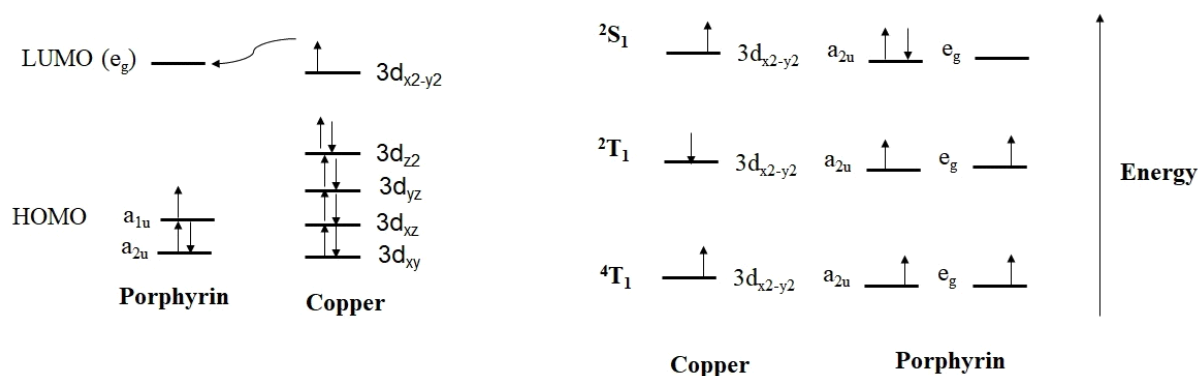

Fig. 3. Copper has a d9 electron configuration. The unpaired electron in the d orbital moves into the LUMO orbital of the porphyrin centered around the nitrogen atoms of the porhyrin ring. The interaction of the unpaired electron from the copper d orbital with the electrons of the porphyrin ring can result in several different configurations. The trip quartet state is the lowest in energy since the exchange interaction between the electrons is higher

Aleksandr G. Avramenko, Mindy Spiehs

To understand how to study the photophysics of these polariton structures, it is first necessary to understand how quantum well structures work. In essence, a quantum well is a material in which charge carriers, or electrons, are confined to a thin layer. A quantum well is formed when two semi-conducting materials with wide band gaps are separated by a material by a material having a smaller band gap, resulting in an energy «well». If such a structure is placed inside an optical cavity, which is capable of trapping light near the energy of the band gap, and if the exchange of energy between the photons and the excitons is faster, than the decay rate of the photonic and the excitonic states, polariton formation may occur [19]. Of particular interest, if the two level interaction Hamiltonian for the photonic and exciton states for this example is examined closely one will notice that the equation will carry two solutions for the eigenvalues and the eigenvectors, as seen in Eq. (4) [20,21]:

$$\begin{bmatrix} E_{ph} - i\sigma_{ph} & \hbar\Omega/2 \\ \hbar\Omega/2 & E_{ex} - i\sigma_{ex} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \in \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \tag{4}$$

In Eq. (4), the cross diagonal terms represent the coupling strength between the photonic and excitonic states, while sigma represents the decay of each state. The two eigenvalue solutions that will be obtained represent the upper polariton state (UP) and the lower polariton state (LP). The two eigenvectors represent the Hopfield coefficients, which determine the photonic and excitonic character of each state. Due to their hybrid light-matter nature, the UP and LP must be described in terms of both, the photonic and excitonic parts: $|UP\rangle = \frac{1}{\sqrt{2}}\left[|e\rangle_e|0\rangle_c + |g\rangle_e|1\rangle_c\right]$ and

$|LP\rangle = \frac{1}{\sqrt{2}}\left[|e\rangle_e|0\rangle_c - |g\rangle_e|1\rangle_c\right]$ [17,22]. Note that the number of polariton states formed is the same as the number of starting interacting states, that is one excitonic state interacting with one photonic state will form two polariton states. Therefore, it is often easiest to describe polaritons in terms of molecular orbital theory, in which two atomic orbitals can interact to form two molecular orbitals at different energy levels. The separation between the UP and LP is referred to as the Rabi splitting which is defined as [17]:

$$\hbar\Omega = 2d\left(\frac{\hbar\omega}{2\varepsilon_0 v}\right)^{1/2}\left(n_{photon} + 1\right)^{1/2} \tag{5}$$

Note that factors such as the dipole moment (d), the permittivity of vacuum ε_0, the electromagnetic volume n, and resonance energy hw are all critical components. However, the number of photons can be reduced to 0, suggesting that polaritons are always well separated even in the absence of light.

While scientists were able to describe the photophysics of polariton states using semiconductor based polaritons, their usability was limited due to several factors. The main issue was the small exciton binding energy and oscillator strengths which produced polaritons with Rabi splittings of a few dozen meV, with room temperature being ~26 meV [23,24]. This resulted in the need to use cryogenic temperatures to create and maintain the polariton states.

A major advancement in polariton-based chemistry was pioneered by Lidzey et al. [25] in which the research team was able to use porphyrins, an organo-metallic molecule, to create room temperature polariton states. Moreover, the linewidths
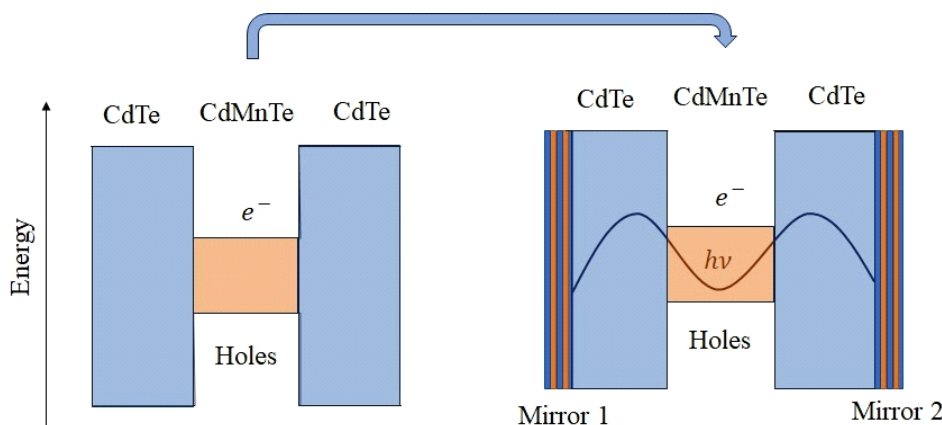

Fig. 4. Summary of the formation of a quantum well polariton. If the quantum well structure is placed such that it is forced to interact with the photons of an optical cavity polariton formation may occur

of many organic materials, including porphyrins, have an inhomogeneous character as the individual molecules are highly influenced by the surrounding environment. However, the large oscillator strength of the porphyrin molecule negates this drawback, allowing it to reach the strong coupling regime. This advancement was possible due to the large dipole moment possessed by porphyrin molecules, which per Eq. (5), results in a substantial Rabi splitting, easily on the order of hundreds of millielectron volts [25,26]. Contemporary polariton models now resemble the construction seen in Fig. 5 [27].

Upon close examination of the linewidths in Fig. 5, it is clear that the UP has a larger full width half maximum (FWHM) than the LP, suggesting the lifetime of the UP is shorter. The issue of homogenous and inhomogeneous broadening must now be discussed. The homogenous broadening can be explained by solving the Lorentz oscillator model to find the imaginary part of the refractive index:

$$\left(n+ik\right)^2 = 1 + \frac{\omega_p^2}{\omega_0^2 - i\omega\gamma - \omega^2}$$ [28]. The FWHM of a

homogeneously broadened line will possess a Lorentzian lineshape, γ. Homogeneous, or Gaussian broadening, on the other hand is a result of molecules absorbing at slightly different energy levels due to the surrounding bath impacting the energy gap between the involved states. Being a hybrid light-matter state, a polariton's lineshape was predicted to be an average of the cavity photon's and the exciton's lineshapes, $\left(\gamma_c + \sigma_{ex}\right)/2$ [29]. However, a phenomenon of «motional narrowing» was observed along the LP in

quantum well polaritons where the FWHM became substantially narrower than predicted theory [29,30]. The motional narrowing phenomenon occurs as electrons move in their disorder potential, resulting in shifts in energy depending on the nature of the potential. The size of the disorder potential is determined by the characteristic De Broglie wavelength of the molecule, that is, molecules only interact or «see» within this wavelength. For a fully localized molecule embedded the disorder potential can be estimated by its spectrum. This spectrum will have some Gaussian characteristic because one must average all of the localized molecules which are located in unique environments that will absorb slightly different wavelength of light. However, during strong-light matter coupling the molecules form polaritons and become delocalized over a large area. Therefore, the disorder is now averaged over the size of the cavity used to form the polariton structure, typically at least hundreds of nanometers. Therefore, the photonic nature of the polariton must be accounted for when describing the FWHM of the LP [30,31]:

$$\Gamma_{lp} = \Gamma_{ex} \frac{\left|c_{ex}\right|^2}{\left|c_{ph}\right|^2} \tag{6}$$

In Eq. (6), the terms c_{ex} and c_{ph} represent the Hopfield coefficients, which can be calculated by solving the eigenvectors in Eq. (4). Note that this treatment only applies to the LP. The lifetime of UP in quantum well polaritons was described as being shorter using Fermi's Golden Rule. The density of dark states which lie intermediate to the LP and UP in a polariton states remains large, the UP will
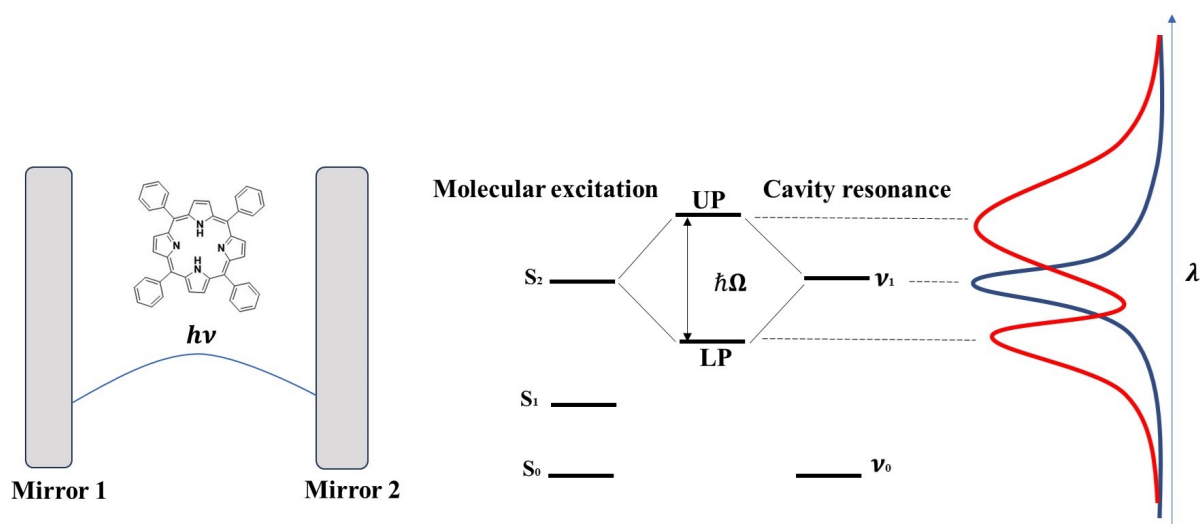

Fig. 5. Basics of polariton construction [27]. The porphyrin molecule is placed inside an optical cavity in which light of energy near the Soret energy band is able to resonate. If the lifetime of the photons is sufficient, as governed by the mirror reflectivity, the cavity photon and the molecular excitation is able to form cavity polaritons

Aleksandr G. Avramenko, Mindy Spiehs

therefore, favorably decay into the lower lying dark states, greatly reducing the state's lifetime [32,33]. In porphyrin-based polaritons, the presence of vibrational energy levels on the polariton levels creates another decay pathway for the UP. It has been proposed that if the Rabi splitting is such that the ground vibration energy level of the UP overlaps with an excited vibrational energy level of the LP, the UP will quickly decay into the lower lying state [32], as seen in Fig. 6. Interestingly, the motional narrowing phenomenon was only attributed to quantum well style polariton structures. In general, chemists working with polaritons formed from porphyrin molecules do not observe this phenomenon. However, recently observations involving multimode porphyrin cavities involving alternating layers of Copper and free space porphyrin molecules showed evidence of motional narrowing along the LP [34]. This observation may suggest that a periodic medium is necessary for motional narrowing to occur.

Conclusions

The aim of this review is to serve as an introduction to the basics of porphyrin photophysics and describe how this class of molecules is particularly useful in the study of cavity polaritons.

First, the unique electronic configuration of the porphyrin molecule results in a particularly bright absorption band, known as the Soret band. The large dipole moment of this transition results in it being able to couple readily to cavity photons, forming well-resolved polariton structures. Moreover, the FWHM of this absorption band is well defined, allowing for easy construction of mirrors that can trap a cavity photon required to interact with the molecular exciton. Also, note that in Eq. (2) as the energies in the perturbation term are made closer, the probability of a molecular electronic transition increases, all other things being held constant. Therefore, as the energy of the E_2 «Soret» state gets closer to the E_1 «Q» state the probability of the S_2 to S_1 transition increases. This is an analogous result to the conclusions made by the Englman «gap law» which states that the internal conversion rate is inversely proportional to the gap between two states [35].

Second, the vibronic coupling between the second exited state, which forms the Soret band, and the first excited state results in another visible absorption band, the Q band. This allows the porphyrin molecule to serve as a good model to study photophysical and photochemical phenomena such as internal conversion under strong light matter-coupling conditions.

Third, porphyrin molecules are easily tunable by changing the central metal or the substituents around the main ring. The molecules can also be linked together to form oligomeric molecules to observe charge transfer, making the porphyrin an attractive candidate to study such phenomena.

In the end, porphyrins are a fundamental class of molecules critical to biological and chemical functions of life. Moreover, their unique spectroscopic behavior makes them an ideal model for optoelectronic
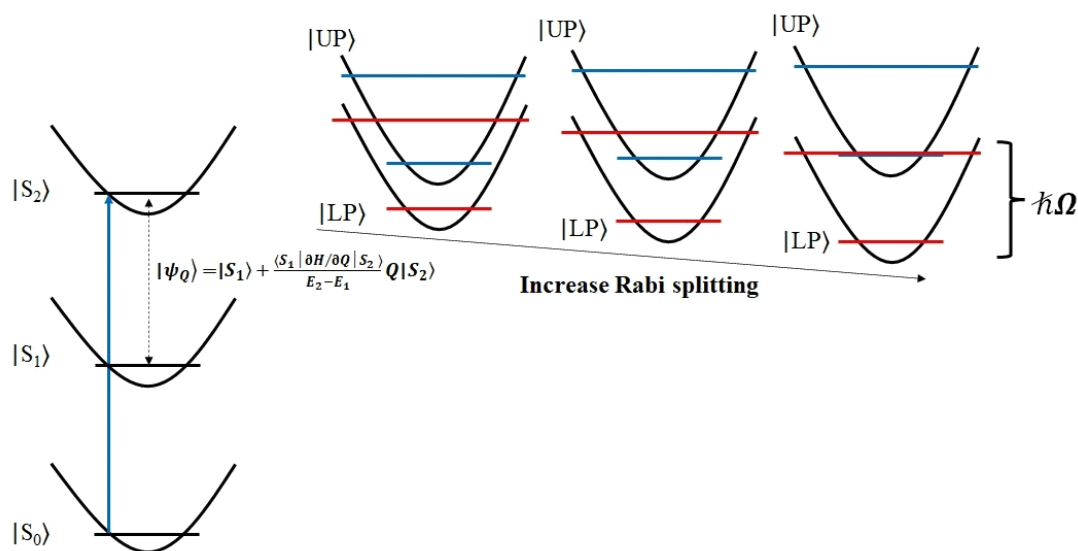

Fig. 6. Energy diagram of a polariton resulting formed by coupling to the second excited state of a porphyrin molecule. As the Rabi splitting increases the vibrational energy levels of the UP and LP can overlap, causing the lifetime of the UP to decrease as a new decay pathway into the LP opens. The vibronic coupling between the second and first excited state is also displayed for reference

and light-harvesting applications. Porphyrins, therefore, serve as a model molecule for scientists to study the behavior of a complex organic molecule under strong light-matter coupling conditions.

Disclaimers

Mention of a trade name, proprietary product, techniques, or specific agreement does not constitute a guarantee or warranty by the United States Department of Agriculture or the United States Department of Health and Human Services. The mention of a specific product or scientific technique also does not imply approval of the USDA or the DHHS. This article reflects the views of the authors and should not be construed to represent the views or policies of the USDA, the DHHS or the FDA. The USDA and the DHHS are equal opportunity providers and employers. The authors declare that they have no known competing financial interests that could have appeared to influence the work reported in this paper.

REFERENCES

1. *Wamser C.C., Ghosh A.* The hyperporphyrin concept: a contemporary perspective // JACS Au. − 2022. − Vol.2. − No. 7. − P.1543-1560.

2. *Gill M., Steglich W.* Progress in the chemistry of organic natural products. − Springer, 2012.

3. *Highly* non-planar dendritic porphyrin for pH sensing: observation of porphyrin monocation / Thyagarajan S., Leiding T., Cheprakov A.V., Vinogradov S.A. // Inorg. Chem. − 2010. − Vol.49. − No. 21. − P.9909-9920.

4. *Gouterman M.* Study of the effects of substitution on the absorption spectra of porphin // J. Chem. Phys. − 1959. − Vol.30. − P.1139-1161.

5. *Gouterman M.* Spectra of porphyrins. J. Mol. Spectrosc. − 1961. − Vol.6. − P.138-163.

6. *Kelley A.M.* Condensed-phase molecular spectroscopy and photophysics. − John Wiley & Sons, 2012.

7. *Gaussian 16* / Frisch M.J, Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Petersson G.A., Nakatsuji H., Li X., Caricato M., Marenich A.V., Bloino J., Janesko B.G., Gomperts R., Mennucci B., Hratchian H.P. − Wallingford CT.: Gaussian, Inc., 2016.

8. *Avramenko A.G., Spiehs M.* Porphyrin mediated photodegradation of tylosin in aqueous media by near-UV light // J. Photochem. Photobiol. A. − 2023. − Vol.441. − Art. No. 114698.

9. *Albrecht A.C.* «Forbidden» character in allowed electronic transitions // J. Chem. Phys. − 1960. − Vol.33. − P.156-169.

10. *Orlandi G., Siebrand W.* Theory of vibronic intensity borrowing. Comparison of Herzberg Teller and Born Oppenheimer coupling. J. Chem. Phys. − 1973. − Vol.58. − No. 10. − P.4513-4523.

11. *Light-induced* electron spin polarization in the ground state of water-soluble copper porphyrins / Rozenshtein V., Berg A., Levanon H., Krueger U., Stehlik D., Kandrashkin Y., Van Der Est A. // Isr. J. Chem. − 2003. − Vol.43. − No. 3-4. − P.373-381.

12. *Porphyrins.* XIX. Tripdoublet and quartet luminescence in Cu and VO complexes / Gouterman M., Mathies R.A., Smith B.E., Caughey W.S. // J. Chem. Phys. − 1970. − Vol.52. − P.3795-3802.

13. *Magnetic* circular dichroism studies. 51. Magnetic circular dichroism studies of non-iron «hyper» porphyrin complexes as models for reduced + carbon monoxide cytochrome P-450 / Dawson J.H., Trudell J.R., Barth G., Linder R.E., Bunnenberg E., Djerassi C., et al. // J. Am. Chem. Soc. − 1977. − Vol.99. − No. 2. − P.641-642.

14. *Boucher L.J., Katz J.J.* The infrared spectra of metalloporphyrins (4000−160 cm^{-1}) // J. Am. Chem. Soc. − 1967. − Vol.89. − No. 6. − P.1340-1345

15. *Yan X., Holten D.* Effects of temperature and solvent on excited-state deactivation of copper(II) octaethyl- and tetraphenylporphyrin: relaxation via a ring-to-metal charge-transfer excited state // J. Phys. Chem. − 1988. − Vol.92. − No. 21. − P.5982-5986.

16. *Asano M., Kaizu Y., Kobayashi H.* The lowest excited states of copper porphyrins // J. Chem. Phys. − 1988. − Vol.89. − P.6567-6576.

17. *Ebbesen T.W.* Hybrid light-matter states in a molecular and material science perspective // Acc. Chem. Res. − 2016. − Vol.49. − No. 11. − P.2403-2412.

18. *Strong* light−matter coupling as a new tool for molecular and material engineering: quantum approach / Kolaric B., Maes B., Clays K., Durt T., Caudano Y. // Adv. Quantum Technol. − 2018. − Vol.1. − Art. No. 1800001.

19. *Spectroscopy* of polaritons in CdTe-based microcavities / Andre R., Heger D., Dang L.S., D'Aubignk Y.M. // J. Cryst. Growth. − 1998. − Vol.184-185. − P.758-762.

20. *Skolnick M.S., Fisher T.A., Whittaker D.M.* Strong coupling phenomena in quantum microcavity structures // Semicond. Sci. Technol. − 1998. − Vol.13. − No. 7. − P.645-670.

21. *Room* temperature Frenkel-Wannier-Mott hybridization of degenerate excitons in a strongly coupled microcavity / Slootsky M., Liu X., Menon V.M., Forrest S.R. // Phys. Rev. Lett. − 2014. − Vol.112. − No. 7. −

Aleksandr G. Avramenko, Mindy Spiehs

Art. No. 076401.

22. Kowalewski M., Bennett K., Mukamel S. Non-adiabatic dynamics of molecules in optical cavities // J. Chem. Phys. − 2016. Vol.144. − Art. No. 054309.

23. *Room* temperature exciton−polariton condensation in silicon metasurfaces emerging from bound states in the continuum / Berghuis A.M., Castellanos G.W., Murai S., Pura J.L., Abujetas D.R., van Heijst E., et al. // Nano Lett. − 2023. − Vol.23. − No. 12. − P.5603-5609.

24. *Room-temperature* electrical control of polarization and emission angle in a cavity-integrated 2D pulsed LED / Gonzalez Marin J.F., Unuchek D., Sun Z., Cheon C.Y., Tagarelli F., Watanabe K., et al. // Nat. Commun. − 2022. − Vol.13. − No. 1. − Art. No. 4884.

25. *Strong* exciton−photon coupling in an organic semiconductor microcavity / Lidzey D.G., Bradley D.D.C., Skolnick M.S., Virgili T., Walker S., Whittaker D.M. // Nature. − 1998. − Vol.395. − No. 6697. − P.53-55.

26. *Avramenko A.G., Rury A.S.* Quantum control of ultrafast internal conversion using nanoconfined virtual photons // J. Phys. Chem. Lett. − 2020. − Vol.11. − No. 3. − P.1013-1021.

27. *Avramenko A.G.* Chemical applications of hybridized light-matter states (a review) // Voprosy Khimii i Khimicheskoi Tekhnologii. − 2023. − No. 4. − P.3-16.

28. *Peatross J., Ware M.* Physics of light and optics. − Optica Publishing Group, 2010.

29. *Motional* narrowing in semiconductor microcavities / Whittaker D.M., Kinsler P., Fisher T.A., Skolnick M.S., Armitage A., Afshar A.M., et al. // Phys. Rev. Lett. − 1996. − Vol.77. − No. 23. − P.4792-4795.

30. *Skolnick M.S., Fisher T.A., Whittaker D.M.* Strong coupling phenomena in quantum microcavity structures // Semicond. Sci. Technol. − 1998. − Vol.13. − No. 7. − P.645-669.

31. *Hopfield J.J.* Theory of the contribution of excitons to the complex dielectric constant of crystals // Phys. Rev. − 1958. − Vol.112. − No. 5. − P.1555-1567.

32. *Avramenko A.G., Rury A.S.* Local molecular probes of ultrafast relaxation channels in strongly coupled metalloporphyrin-cavity systems // J. Chem. Phys. − 2021. − Vol.155. − No. 6. − Art. No. 064702.

33. *Ultrafast* polariton relaxation dynamics in an organic semiconductor microcavity / Virgili T., Coles D., Adawi A.M., Clark C., Michetti P., Rajendran S.K., et al. // Phys. Rev. B. − 2011. − Vol.83. − Art. No. 245309.

34. *Avramenko A.G., Rury A.S.* Dynamics of cavity multipolaritons formed from quasi-degenerate porphyrin excitons // Laser Sci. − 2022. − Art. No. LW6F.3.

35. Englman R., Jortner J. The energy gap law for radiationless transitions in large molecules // Mol. Phys. − 1970. − Vol.18. − No. 2. − P.145-164.

ФОТОФІЗИЧНІ ВЛАСТИВОСТІ ПОРФІРИНІВ ТА ЇХ ЗАСТОСУВАННЯ В ПОЛЯРИТОННІЙ ХІМІЇ (ОГЛЯД)

А.Г. Авраменко, М. Спіес

Порфірини є фундаментальним класом молекул, які беруть участь у багатьох біологічних і хімічних функціях, починаючи від фотосинтезу у рослин і біомаркерів у медицині до оптоелектронних пристроїв. Незважаючи на те, що молекула порфірину є важливим класом молекул, відомим протягом століть, її фотофізика є напрочуд складною, і моделі, що описують спектроскопічну поведінку порфіринів, з'явилися лише у 1950-х роках. Цей огляд має на меті викласти основи фотофізики порфіринів, описуючи, як утворюються смуга Соре та смуга Q молекули. Зокрема, проведено обговорення теорії чотирьох орбіталей і зв'язку Герцберга-Теллера, які є необхідними для розуміння спектральних властивостей молекули порфірину. Огляд також має на меті доповнити попередні роботи, які обговорюють хімічні застосування гібридних світло-матеріальних станів, розглядаючи, як спектроскопічна поведінка порфіринів є особливо корисною у поляритонній хімії.

Ключові слова: порфірин, поляритон, спектроскопія, теорія збурень, вібраційне зчеплення.

PHOTOPHYSICAL PROPERTIES OF PORPHYRINS AND THEIR APPLICATIONS TO POLARITON CHEMISTRY (A REVIEW)

*Aleksandr G. Avramenko [a, b, *], Mindy Spiehs [b]*

[a] **Detroit Medical Products Laboratory, Food and Drug Administration, United States Department of Health and Human Services, Detroit, MI, United States**

[b] **United States Meat Animal Research Center, Agricultural Research Service, United States Department of Agriculture, Clay Center NE, United States**

[*] **e-mail: aleksandr.avramenko@fda.hhs.gov**

Porphyrins are a fundamental class of molecules involved in a multitude of biological and chemical functions ranging from photosynthesis in plants to biomarkers in medicine to optoelectronic devises. Despite the porphyrin molecule being such an important class of molecules known for centuries, its photophysics are surprisingly complex and models describing the spectroscopic behavior of porphyrins did not emerge until the 1950s. This review aims to distil the basics of porphyrin photophysics, describing how the Soret band and the Q band of the molecule are formed. In particular, a discussion of the four orbital theory and Hertzberg-Teller coupling will be conducted, both of which are necessary to understand the spectral properties of the porphyrin molecule. The review further aims to complement previous work discussing the chemical applications of hybrid light-matter states by discussing how the spectroscopic behavior of porphyrins is particularly useful in polariton chemistry.

Keywords: porphyrin; polariton; spectroscopy; perturbation theory; vibronic coupling.

REFERENCES

1. Wamser CC, Ghosh A. The hyperporphyrin concept: a contemporary perspective. *JACS Au.* 2022; 2(7): 1543-1560. doi: 10.1021/jacsau.2c00255.

2. Gill M, Steglich W. *Progress in the chemistry of organic natural products.* Springer; 2012. doi: 10.1007/978-3-7091-6971-1.

3. Thyagarajan S, Leiding T, Arskold SP, Cheprakov AV, Vinogradov SA. Highly non-planar dendritic porphyrin for pH sensing: observation of porphyrin monocation. *Inorg Chem.* 2010; 49(21): 9909-9920. doi: 10.1021/ic100968p.

4. Gouterman M. Study of the effects of substitution on the absorption spectra of porphin. *J Chem Phys.* 1959; 30: 1139-1161. doi: 10.1063/1.1730148.

5. Gouterman M. Spectra of porphyrins. *J Mol. Spectrosc.* 1961; 6: 138-163. doi: 10.1016/0022-2852(61)90236-3.

6. Kelley AM. *Condensed-phase molecular spectroscopy and photophysics.* John Wiley & Sons; 2012. doi: 10.1002/9781118493052.

7. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. *Gaussian 16.* Wallingford CT: Gaussian, Inc.; 2016.

8. *Avramenko A.G., Spiehs M.* Porphyrin mediated photodegradation of tylosin in aqueous media by near-UV light // J. Photochem. Photobiol. A. − 2023. − Vol.441. − Art. No. 114698.

9. Albrecht AC. «Forbidden» character in allowed electronic transitions. *J Chem Phys.* 1960; 33: 156-169. doi: 10.1063/1.1731071.

10. Orlandi G, Siebrand W. Theory of vibronic intensity borrowing. Comparison of Herzberg-Teller and Born-Oppenheimer coupling. *J Chem Phys.* 1973; 58: 4513-4523. doi: 10.1063/1.1679014.

11. Rozenshtein V, Berg A, Levanon H, Krueger U, Stehlik D, Kandrashkin Y, et al. Light-induced electron spin polarization in the ground state of water-soluble copper porphyrins. *Isr J Chem.* 2003; 43: 373-381. doi: 10.1560/FF1Q-02XD-Q4VC-DHX0.

12. Gouterman M, Mathies RA, Smith BE, Caughey WS. Porphyrins. XIX. Tripdoublet and quartet luminescence in Cu and VO complexes. *J Chem Phys.* 1970; 52: 3795-3802. doi: 10.1063/1.1673560.

13. Dawson JH, Trudell JR, Barth G, Linder RE, Bunnenberg E, Djerassi C, et al. Magnetic circular dichroism studies. 51. Magnetic circular dichroism studies of non-iron «hyper» porphyrin complexes as models for reduced + carbon monoxide cytochrome P-450. *J Am Chem Soc.* 1977; 99(2): 641-642. doi: 10.1021/ja00444a070.

14. Boucher LJ, Katz JJ. The infrared spectra of metalloporphyrins (4000−160 cm⁻¹). *J Am Chem Soc.* 1967; 89(6): 1340-1345. doi: 10.1021/ja00982a011.

15. Yan X, Holten D. Effects of temperature and solvent on excited-state deactivation of copper(II) octaethyl- and tetraphenylporphyrin: relaxation via a ring-to-metal charge-transfer excited state. *J Phys Chem.* 1988; 92(21): 5982-5986. doi: 10.1021/j100332a029.

16. Asano M, Kaizu Y, Kobayashi H. The lowest excited states of copper porphyrins. *J Chem Phys.* 1988; 89: 6567-6576. doi: 10.1063/1.455379.

17. Ebbesen TW. Hybrid light-matter states in a molecular and material science perspective. *Acc Chem Res.* 2016; 49(11): 2403-2412. doi: 10.1021/acs.accounts.6b00295.

18. Kolaric B, Maes B, Clays K, Durt T, Caudano Y. Strong light−matter coupling as a new tool for molecular and material engineering: quantum approach. *Adv Quantum Technol.* 2018; 1: 1800001. doi: 10.1002/qute.201800001.

19. Andre R, Heger D, Dang LS, D'Aubignk YM. Spectroscopy of polaritons in CdTe-based microcavities. *J Cryst Growth.* 1998; 184-185: 758-762. doi: 10.1016/S0022-0248(98)80158-9.

20. Skolnick MS, Fisher TA, Whittaker DM. Strong coupling phenomena in quantum microcavity structures. *Semicond Sci Technol.* 1998; 13(7): 645-670. doi: 10.1088/0268-1242/13/7/003.

21. Slootsky M, Liu X, Menon VM, Forrest SR. Room temperature Frenkel-Wannier-Mott hybridization of degenerate excitons in a strongly coupled microcavity. *Phys Rev Lett.* 2014; 112(7): 076401. doi: 10.1103/PhysRevLett.112.076401.

22. Kowalewski M, Bennett K, Mukamel S. Non-adiabatic dynamics of molecules in optical cavities. *J Chem Phys.* 2016; 144: 054309. doi: 10.1063/1.4941053.

23. Berghuis AM, Castellanos GW, Murai S, Pura JL, Abujetas DR, van Heijst E, et al. Room temperature exciton−polariton condensation in silicon metasurfaces emerging from bound states in the continuum. *Nano Lett.* 2023; 23(12): 5603-5609. doi: 10.1021/acs.nanolett.3c01102.

24. Gonzalez Marin JF, Unuchek D, Sun Z, Cheon CY, Tagarelli F, Watanabe K, et al. Room-temperature electrical control of polarization and emission angle in a cavity-integrated 2D pulsed LED. *Nat Commun.* 2022; 13(1): 4884. doi: 10.1038/s41467-022-32292-2.

25. Lidzey DG, Bradley DDC, Skolnick MS, Virgili T, Walker S, Whittaker DM. Strong exciton−photon coupling in an organic semiconductor microcavity. *Nature.* 1998; 395(6697): 53-55. doi: 10.1038/25692.

26. Avramenko AG, Rury AS. Quantum control of ultrafast internal conversion using nanoconfined virtual photons. *J Phys Chem Lett.* 2020; 11(3): 1013-1021. doi: 10.1021/acs.jpclett.9b03447.

27. Avramenko AG Chemical applications of hybridized light-matter states (a review). *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2023; (4): 3-16. doi: 10.32434/0321-4095-2023-149-4-3-16.

28. Peatross J, Ware M. *Physics of light and optics.* Optica Publishing Group; 2010.

29. Whittaker DM, Kinsler P, Fisher TA, Skolnick MS, Armitage A, Afshar AM, et al. Motional narrowing in semiconductor microcavities. *Phys Rev Lett.* 1996; 77(23): 4792-4795. doi: 10.1103/PhysRevLett.77.4792.

Aleksandr G. Avramenko, Mindy Spiehs

30. Skolnick MS, Fisher TA, Whittaker DM. Strong coupling phenomena in quantum microcavity structures. *Semicond Sci Technol*. 1998; 13(7): 645-669. doi: 10.1088/0268-1242/13/7/003.

31. Hopfield JJ. Theory of the contribution of excitons to the complex dielectric constant of crystals. *Phys Rev*. 1958; 112(5): 1555-1567. doi: 10.1103/PhysRev.112.1555.

32. Avramenko AG, Rury AS. Local molecular probes of ultrafast relaxation channels in strongly coupled metalloporphyrin-cavity systems. *J Chem Phys*. 2021; 155(6): 064702. doi: 10.1063/5.0055296.

33. Virgili T, Coles D, Adawi AM, Clark C, Michetti P, Rajendran SK, et al. Ultrafast polariton relaxation dynamics in an organic semiconductor microcavity. *Phys Rev B*. 2011; 83: 245309. doi: 10.1103/PhysRevB.83.245309.

34. Avramenko AG, Rury AS. Dynamics of cavity multipolaritons formed from quasi-degenerate porphyrin excitons. *Laser Sci*. 2022; LW6F.3. doi: 10.1364/LS.2022.LW6F.3.

35. Englman R, Jortner J. The energy gap law for radiationless transitions in large molecules. *Mol Phys*. 1970; 18(2): 145-164. doi: 10.1080/00268977000100171.