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Vasyl Stefanyk Precarpathian National University

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Aleksandr Avramenko

Do Quantum Effects Influence the Energy of Polariton States?

United States Department of Health and Human Services, Food and Drug Administration Detroit Medical Products Laboratory, Detroit, MI, U.S. aleksandr.avramenko@fda.hhs.gov

If an ensemble of molecules is placed inside a nano-scaled Fabry-Pérot cavity capable of trapping a photon resonant with a transition level of the molecule, the photonic and molecular (excitonic) states will exchange energy. If the exchange of energy between the two states is faster than the decay rate of either state, a pair of hybridized light-matter states known as polaritons may form. Polaritons involving a single photon and one type of molecular excitation can be modeled using a two-level Hamiltonian, with the eigenvalues of the matrix serving as the energies of the polariton states. At resonance, the separation between the two polariton states is referred to as the Rabi splitting, and is proportional to the square root of the concentration ($\sqrt{C}$) of the molecules involved in the coupling. In this manuscript data from previously reported cavity polariton measurements is analyzed, and it is found that while the $\sqrt{C}$ relationship holds for the overall energy difference between the polariton states, it is observed that this relationship does not hold for individual polariton energy levels. The basic particle in a box model and harmonic oscillator models of quantum mechanics are invoked in an attempt to qualitatively account for this discrepancy.

Keywords: polaritons, Rabi splitting, cavity, energy level, porphyrin, molecular vibration.

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Introduction

The study of strong light-matter coupling continues to play an important role in the physical chemistry community. This is due to the fact that the excitonic state and the photon participating in strong light-matter coupling form two new polariton states which must be described in terms of both, the photonic and excitonic parts, as seen in Eqs. 1 & 2 [1, 2]. In Eqs. 1 & 2 the term $|e\rangle_e|0\rangle_c$ serves to denote the excited state with zero photons coupled with a ground state with one photon ($|g\rangle_e|1\rangle_c$). The formation of these polariton energy levels is thought to have an effect on the potential energy surface of the coupling molecules [3, 4]. Indeed, recent studies have both, computationally, and experimentally shown that molecules under strong light-matter coupling will possess different chemical reactivity to their uncoupled counterparts, as well as possess unique intermolecular decay pathways [3, 5, 6]. Moreover, studies involving multilayer cavities have shown promise that polaritons could be used to facilitate long-range energy transfer beyond the Förster limit [7-9].

$$|\mathrm{UP}\rangle = \frac{1}{\sqrt{2}}[|e\rangle_e|0\rangle_c + |g\rangle_e|1\rangle_c] \tag{1}$$

$$|\mathrm{LP}\rangle = \frac{1}{\sqrt{2}}[|e\rangle_e|0\rangle_c - |g\rangle_e|1\rangle_c] \tag{2}$$

The energies of the two polaritons can be calculated if the polariton system is described in terms of a two-level interaction Hamiltonian, as seen in Eq. 3. The eigenvalues of the Hamiltonian, shown in Eqs. 4 & 5, describe the upper and lower polariton energy levels [8, 10]. Note that the energies of each state is dependent on the photon incidence angle, $E_{ph(\theta)} = E_0\left(1 - \frac{sin^2\theta}{n}\right)^{-1/2}$, where $E_0 = \frac{hc}{2nL_{cav}}$ is the minimum photon energy and nL_{cav} is the length of the Fabry-Perot cavity adjusted for the refractive index [8]. The eigenvectors of the Hamiltonian represent the Hopfield coefficients, which describe the photonic and excitonic contributions to each polariton energy level [11]. The photonic Hopfield coefficients can be estimated using equations 6 & 7 [12, 13]. In the case of Eqs. 6 & 7, c_{ph} is the variable used to denote the photonic fraction of the two polariton states, either the lower polariton (LP) or the upper polariton (UP). The terms σ_{ex} and σ_{ph} represent the linewidth of the exciton and photon respectively. Finally, it should be noted that E_{ex} denotes the energy of the molecular exciton to which the photon is coupling.

Meanwhile, solving for the imaginary part of Eq. 3 would yield the full width half maximum (FWHM) of the two states.

$$\begin{bmatrix} E_{ex} + i\sigma_{ex} & V \\ V & E_{ph} + i\sigma_{ph} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \epsilon \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \tag{3}$$

$$E_{UP(\theta)} = \frac{E_{ph(\theta)}+i\sigma_{ph}+E_{ex}+i\sigma_{ex}}{2} + \frac{1}{2}\sqrt{\left[(E_{ex}+i\sigma_{ex}) - (E_{ph(\theta)} - i\sigma_{ph})\right]^2 + 4V^2} \tag{4}$$

$$E_{LP(\theta)} = \frac{E_{ph(\theta)}+i\sigma_{ph}+E_{ex}+i\sigma_{ex}}{2} - \frac{1}{2}\sqrt{\left[(E_{ex}+i\sigma_{ex}) - (E_{ph(\theta)} - i\sigma_{ph})\right]^2 + 4V^2} \tag{5}$$

$$c_{ph(lp)} = \frac{V^2}{V^2+(E_{LP(\theta)}-E_{ph(\theta)})^2} \tag{6}$$

$$c_{ph(up)} = \frac{V^2}{V^2+(E_{UP(\theta)}-E_{ph(\theta)})^2} \tag{7}$$

Some basic conclusions about polariton energy levels can be made based on Eqs. 3-7. One is that there will exist some resonance angle at which the lower polariton (LP) and the upper polariton (UP) will have an equal photonic characteristic. Moreover, the separation between the UP and the excitonic energy level, as well as the LP and the excitonic energy levels at this resonance angle will be equal, but opposite. That is, the UP will be equally above the originating exciton as the LP is below it. At the resonance angle the UP and the LP are separated by a factor known as the Rabi splitting, which is defined by Eq. 8. Conveniently, the Rabi splitting ($\hbar\Omega$) can also be the value used to estimate the coupling strength V in Eqs. 3-7. Note that the factors that influence the Rabi splitting are the dipole moment (d), the coupling frequency $\hbar\omega$, the volume of the electromagnetic mode, and the vacuum permittivity $\epsilon_0 \nu$. Because the volume of the electromagnetic mode of a cavity is typically very large, the Rabi splitting is often simplified to: $\hbar\Omega \propto \sqrt{N/v} = \sqrt{C}$, where the Rabi splitting is proportional to the square root of the concentration of the molecules in the sample used to form the polariton state [14].

$$\hbar\Omega = 2d\left(\frac{\hbar\omega}{2\epsilon_0 v}\right)^{1/2}\left(n_{photon}+1\right)^{1/2} \tag{8}$$

In this work data from two independent research groups involving the strong light-matter coupling of Copper (II) tetraphenyl porphyrin (CuTPP), Zinc (II) tetraphenyl porphyrin (ZnTPP), and 1-phenyl-2-trimethylsilylacetylene (PTA) molecule are analyzed [15, 16]. As expected, the $\hbar\Omega \propto \sqrt{C}$ relationship holds when it is applied to the overall Rabi splitting. However, the individual UP and LP energy levels appear to shift in an unexpected manner. Mainly, for the porphyrin molecules it is found that at higher Rabi splitting the LP is shifted less than expected, while at lower Rabi splitting it is shifted more than expected, as seen in Fig. 1. For vibrationally coupled polaritons formed from PTA, the lower polariton is shifted less than expected at all coupling strengths. This manuscript will proceed to analyze the shifts in the reported data, as well as provide possible reasoning for their occurrence.

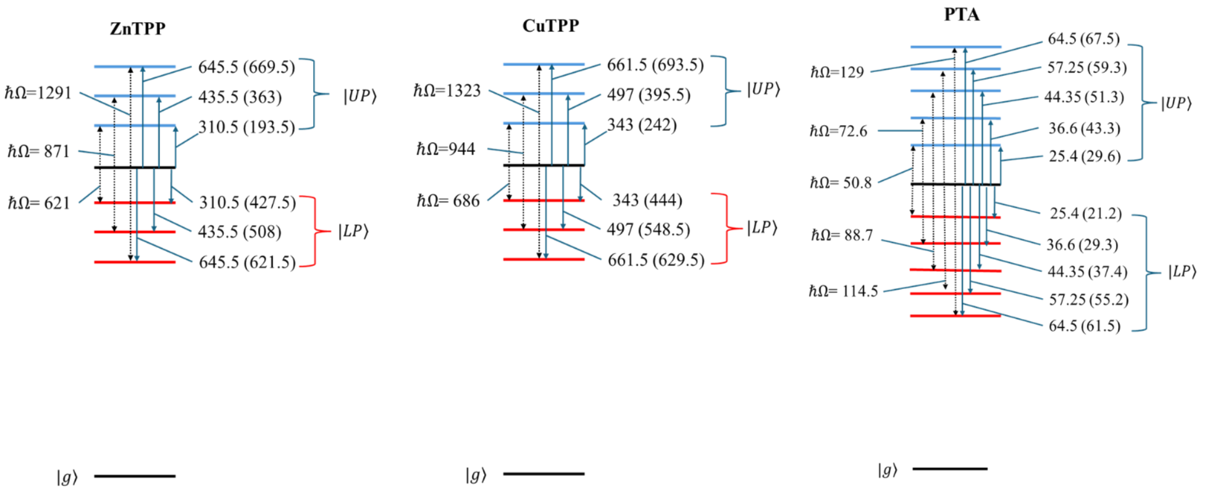

Fig. 1. The reported polariton energy levels formed from ZnTPP (left), CuTPP (center), and PTA (right). The Rabi splitting ($\hbar\Omega$) is reported in wavenumbers (cm^{-1}). The expected energy shift of the UP and LP from the molecular excitation is expected to be $\hbar\Omega/2$. The numbers in the parenthesis represent the observed values at which the LP and UP are shifted.

I. Results and Discussion

This work relies on analyzing data reported by the Rury and the Ebbesen research teams [15, 16]. The latter designed a Fabry-Perot microcavity from gold mirrors resonant about the 860 cm^{-1} Si-C stretch of the PTA molecule. The Si-C vibration was then coupled to the cavity photon. The full width half maximum of the cavity mode was reported to be 28 cm^{-1}, with the FWHM of the Si-C stretch reported to be 39 cm^{-1}. In order to achieve strong-light matter coupling the Rabi splitting must be larger than the FWHM of either state [16]. The authors reported that at the lowest concentration the Rabi splitting was approximately 50 cm^{-1}, satisfying the strong coupling requirements [1, 16]. Rury *et al*. formed Fabry-Perot cavities centered about the Soret band of CuTPP and ZnTPP, located at approximately 24067 cm^{-1} and 23640 cm^{-1} respectively. The equation $FSR = \frac{c}{2nL}$ can be used to estimate the required cavity length [17]. The cavities were constructed using a combination of a distributed Bragg reflector (DBR) and an aluminum mirror. The authors reported a cavity mode having a FWHM of 393.6 cm^{-1}, with the FWHM of the CuTPP excitation being 456.9 cm^{-1} and that of the ZnTPP being 323.6 cm^{-1}. The smallest reported Rabi slitting value was 621 cm^{-1}, signifying all of the samples were in the strong coupling regime [15].

As seen in Fig. 2, the relationship between the Rabi splitting and the concentration appear to be proportional to the square of concentration. Using MATLAB software to fit the data in Fig. 2. to a function in which Rabi Splitting $(\mathrm{cm}^{-1}) \propto \sqrt{C}$, the R^2 values are obtained at each concentration. For the ZnTPP cavity the R^2 values is found to be 0.9989, for the CuTPP cavity the R^2 value is calculated to be 0.9960, and for the PTA cavity the R^2 values was calculated to be 0.9867. The intercept of 0 was added to the model. As expected, the Rabi splitting relationship holds across not only different molecules, but also across polaritons involving physically different coupling mechanisms. The coupling in the porphyrin polaritons involves the interaction of a near UV cavity photon with an electronic excitation. On the contrary, the coupling of the PTA cavity involves the coupling of an IR photon to a vibrational excitation.

As stated in the introduction, the energy of the UP and the LP is expected to be equidistant from the molecular excitation which is responsible for their formation. Therefore, a simple method to calculate the distance of the UP would be to take one half of the Rabi splitting and add it to the energy of the exciton. Similarly, the energy of the LP could be calculated by taking one half of the Rabi splitting energy and subtracting it from the excitation energy. However, as seen in Fig. 1, the observed energies do not appear to coincide with this simple theory. Using MATLAB software to plot the energy difference versus concentration in Fig. 3 two unique patters in the porphyrin spectra appear. First, the UP appears not to be proportional to $\sqrt{C}$, rather it appears to have a linear relationship in which: $(E_{up} - E_{ex}) \propto C$. Second, the lower polariton relationship appears to be more complex, in which $(E_{ex} - E_{lp}) \propto \sqrt{C} + X$. For the lower polariton, X appears to be a sort of a dampening factor which reduces the rate at which the state would move to a lower energy level at higher concentrations and must be added to the collective coupling model to ensure a proper fit when modeling the LP of the porphyrin based cavities. For the vibrationally coupled PTA cavity both, the UP and the LP appear to fit the $\sqrt{C} + X$ model. However, the LP being consistently shifted by less than predicted by the $\hbar\Omega/2$ model. For the regression curves calculated in Fig. 3, the $(E_{up} - E_{ex}) \propto C$ model resulted in a calculated R^2 for the UP of the ZnTPP of 0.9758 and for the CuTPP it was found to be 0.9757. The R^2 for the LP of ZnTPP was calculated at 0.9843 and for the CuTPP it was found to be 0.9999. Finally, the regression lines for the PTA cavity from Fig. 3 resulted in an R^2 of 0.9859 for the LP and 0.9994 for the UP.

In order to account for the discrepancy in the expected energy levels of the LP and UP in porphyrin molecules the particle in a box model is invoked. In the case of

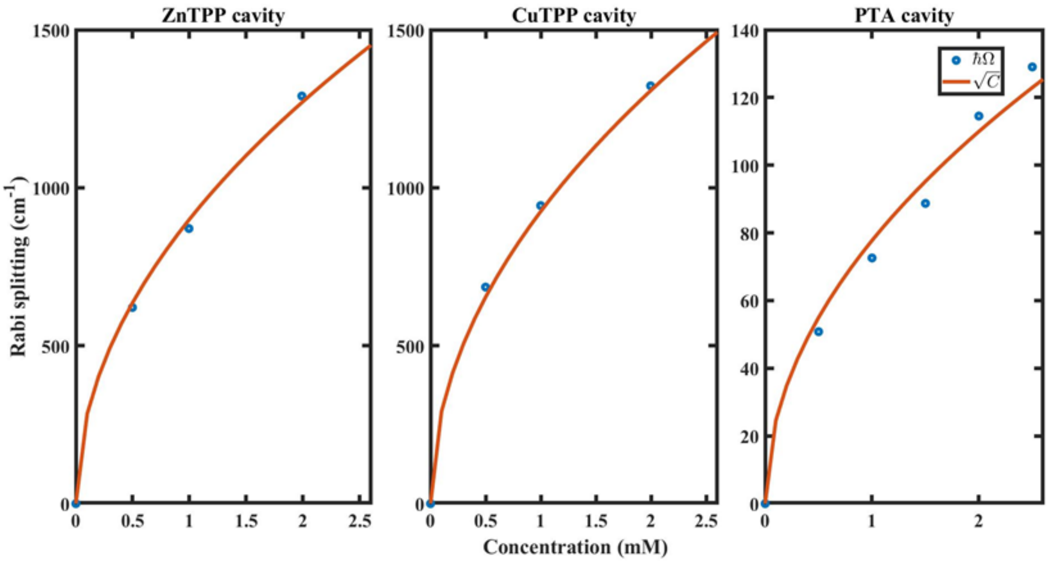

Fig. 2. The relationship between the Rabi slitting ($\hbar\Omega$) and the concentration compared to the collective coupling model $\sqrt{C}$.

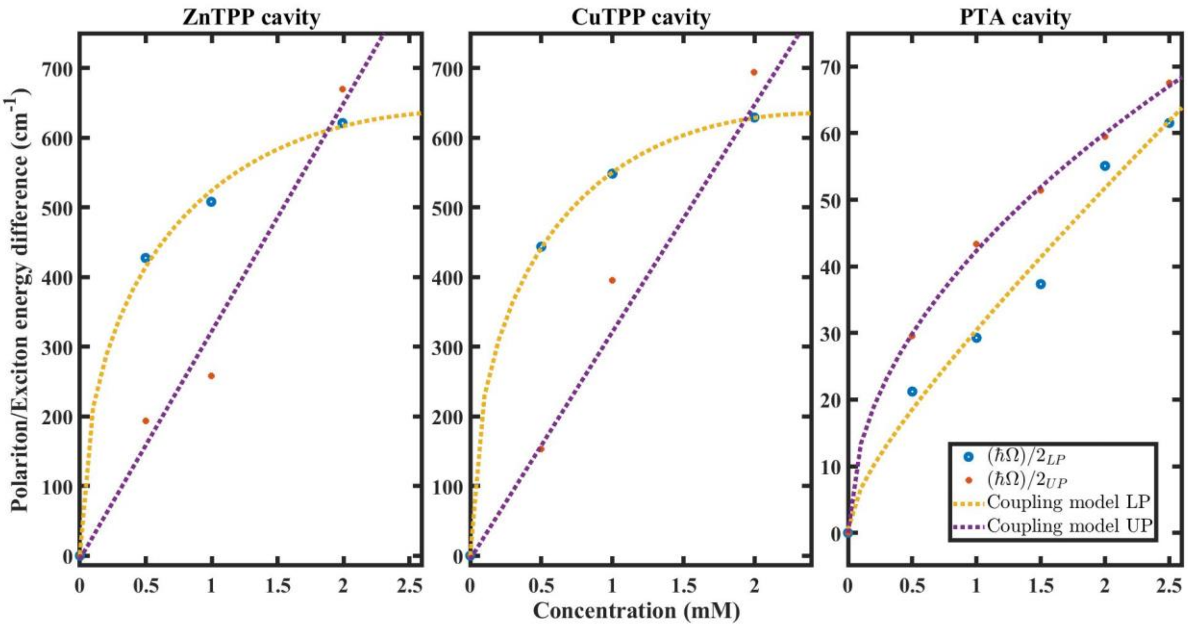

Fig. 3. The relationship between concentration and the energy difference between the polariton and the excitation. The energy difference of the UP was calculated as: $E_{up} - E_{ex}$, while the energy difference for the LP was calculated as: $E_{ex} - E_{lp}$. The Coupling model for the LP in the porphyrin cavities was modeled as $(E_{ex} - E_{lp}) \propto \sqrt{C} + X$, while the LP was modeled as $(E_{up} - E_{ex}) \propto C$. For the PTA cavities both polaritons were modeled as being proportional to $\sqrt{C} + X$.

porphyrins, the lower polariton is located at an energy level of hundreds of wavenumbers below the molecular excitation responsible for its formation. As the number of molecules in the cavity increases, the LP is pushed further and further away from the molecular excitation to a lower energy level. However, it must be maintained that a polariton not only inherits light-like properties from the cavity photon, but retains a part of its molecular nature. Energy eigenstates of a molecule are most easily modeled through the particle in a box model: $E = \hbar\omega = \frac{n^2h^2}{8mL^2}$ [18, 19]. The energy is proportional to n^2, meaning that at higher energies the separation between states is larger. Therefore, as the lower polariton is pushed closer to the S_1 energy state of the porphyrin, it may experience greater Coulombic repulsion from the lower lying states, causing a slowdown in the rate at which it decreases at higher concentrations. In effect, at high Rabi splitting, the Coulombic repulsion from the lower lying states acts as a sort of damper on the LP. On the contrary, the UP appears to not experience a similar dampening effect, likely due to the higher lying states being either not populated, or too far away in energy. It should be noted that reports of complete energy inversion have been made, in which the LP is lowered below that of a nearby triplet state [20]. Note that this model does not forbid any such case, its only conclusion is that the relationship between the LP and the concentration is more complex than $\sqrt{C}$. Moreover, because triplet states by definition involve the change of electron spin, it is not entirely clear how polariton energy levels would be treated. One possibility is to simply treat the LP as an eigenstate which becomes populated with electrons with a set spin while adding a separate photonic decay channel [15, 21]. However, as per Eq. 2, it must be noted that the LP should at all times be though of as a hybrid of both, the photonic and the excitonic matrix elements. Indeed, it is not entirely clear if the spin of the triplet system being the same as the spin of the photon would allow for more efficient decay into the triplet state.

For the vibrationally coupled polariton sample, the harmonic oscillator model is invoked. The energy of a Harmonic oscillator can be modeled as: $E = \hbar\omega\left(n + \frac{1}{2}\right) = \hbar\sqrt{\frac{k}{\mu}}(n + \frac{1}{2})$, where k is the so-called spring constant and mu is the reduced mass [19, 22]. Despite vibrational polaritons being studied for several decades, it remains unclear how to incorporate the concept of "mass" unto a photonic system. However, some reasonable postulations can be made. First, when the reduced mass increases, the vibrational frequency will decrease [19]. Therefore, the LP being at the lowest frequency should have the greatest reduced mass. Looking at Eqs. 3-7, which govern the modeling of polaritons it is clear that the UP and LP should possess an equal amount of photonic and molecular character at resonance. However, it is also clear that their reduced masses must be different. Another possibility is that the spring constant, or the bond strength, is different for the two vibrationally formed polaritons. In such a scenario the strength of the LP weakens as compared to the starting vibration, while the strength of the UP is enhanced. In either case it is clear that the two-level Hamiltonian which is used to model the behavior of cavity polaritons appears to be inadequate to accurately model the behavior of vibrationally strong-coupled states.

Finally, we note that the two-level Hamiltonian model has been shown to produce erroneous results before when modeling cavity polaritons. Most notably, if it is used to predict the FWHM of polaritons [23]. It has been experimentally shown by Whittaker *et al*. that polariton motional narrowing plays a significant role in determining the FWHM of a cavity polariton, which is also not accounted for in Eqs. 3-7 [23-25]. In order to properly model the FWHM of the polaritonic states Whittaker *et al*. suggests that the LP be modeled using the relationship: $\Gamma_{lp} = \frac{|c_{ex}|^4}{|c_{ph}|^2}$. In the Whittaker model gamma is the polariton linewidth while c_{ex} and c_{ph} are the Hopfield coefficients representing the photonic and excitonic parts of the LP [23]. The motional narrowing effect is manifest most notably in quantum well based polaritons, however, it has also been reported in cavities involving strong-light matter coupling with multilayer porphyrin molecules [26]. The fact that the current model of polaritons is unable to accurately model both, polariton motional narrowing, as well as the individual energies of the polariton states suggests that a more robust algorithm for polariton modeling must be considered by scientists. Moreover, studies by Scholes *et al.* have proposed that the UP occupies a thermodynamically lower energy state as compared the LP, going as far as suggesting a shift away from utilizing spectroscopic techniques to characterize polaritons is needed to understand their physical properties [27]. This analysis may support the Scholes hypothesis in that the purely spectroscopic analysis of polaritons, in which they are modeled using a Hamiltonian model to predict their spectroscopic behavior, appears to be insufficient.

Conclusion

Polaritons offer a unique perspective to modify the physical properties of matter utilizing light. In particular, they have been thought after for their abilities to modify chemical reactions, optical properties, energy transfer, and serve as a novel laser media [28]. This manuscript analyzed the data from two research groups which studied the behavior of CuTPP, ZnTPP, and PTA molecules in the strong coupling regimes. It was found that the collective coupling model in which the Rabi splitting is modeled as being proportional to the square root of the concentration of the molecules involved in polariton formation holds. However, when examining the individual polariton energies $E_{up} - E_{ex}$ and $E_{ex} - E_{lp}$ it was found that this relationship requires modification. For example; in the case of porphyrins the relationship changes to: $(E_{up} - E_{ex}) \propto C$ and $(E_{ex} - E_{lp}) \propto \sqrt{C} + X$.
It is proposed that Coulombic repulsion from the lower lying state plays a role in influencing the relationship between the LP and $\sqrt{C}$ in the porphyrin based polaritons. For the vibrationally strong coupled molecule, the Harmonic oscillator model is invoked. It is proposed that either the changes in reduced mass, or the spring constant of the molecule due to strong light-matter coupling result in unexpected changes in the polariton energy levels. These results suggest that quantum effects should be accounted for when estimating the energies of polariton energy levels, and further work on constructing a comprehensive equation that supersedes the two level Hamiltonian model is required in order to accurately model a cavity polariton's behavior.

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Aleksandr Avramenko – Ph.D. Chemist, United States Department of Health and Human Services, Food and Drug Administration, Detroit Medical Products Laboratory.

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Олександр Авраменко

Чи впливають квантові ефекти на енергію поляритонних станів?

Міністерство охорони здоров’я та соціальних служб США, Детройтська лабораторія медичної продукції Управління з контролю за продуктами й ліками, Детройт, MI 48207, США; aleksandr.avramenko@fda.hhs.gov

Якщо ансамбль молекул помістити всередину нанорозмірної порожнини Фабрі-Перо, здатної захопити фотон, резонансний з перехідним рівнем молекули, фотонний і молекулярний (екситонні) стани обміняються енергією. Якщо обмін енергією між двома станами відбувається швидше, ніж швидкість розпаду будь-якого стану, може утворитися пара

гібридизованих станів світло-матерія, відомих як поляритони. Поляритони, що включають один фотон і один тип молекулярного збудження, можна моделювати за допомогою дворівневого гамільтоніана, при цьому власні значення матриці виступають як енергії станів поляритонів. Під час резонансу поділ між двома поляритонними станами називається розщепленням Рабі та пропорційний квадратному кореню з концентрації молекул, які беруть участь у зв’язку. У цьому рукописі аналізуються дані, отримані з раніше повідомлених вимірювань поляритону в порожнині, і виявлено, що в той час як зв’язок між квадратним коренем із концентрації та розщепленням Рабі виконується для загальної різниці енергій між станами поляритону, спостерігається, що цей зв’язок не для окремих рівнів енергії поляритону. У спробі якісно пояснити цю розбіжність використовуються базова частинка в коробковій моделі та моделі гармонічних осциляторів квантової механіки.

Ключові слова: поляритони, розщеплення Рабі, порожнина, енергетичний рівень, порфірин, молекулярна вібрація.