
Polariton Effects in Molecular Crystals Studied by Classical and Quantum-Electrodynamic Approaches

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In memory of Professor Jerzy Prochorow

A quantum-electrodynamic approach is studied as an alternative to the classical description of polaritons in molecular crystals, with the focus on future interpretation of oligothiophene spectra. As expected, the results of the two approaches coincide, but the quantum description is better suited for future generalizations, notably for detailed studies of vibronic coupling. The quantum approach is used here to probe the importance of inherent polaritonic effects. They are found to be minor, being superseded by vibronic interactions; the latter are responsible for most peculiarities observed in oligothiophene spectra.

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1. Introduction

As the van der Waals forces operative in a molecular crystal are relatively weak, the constituent molecules retain their individuality to a large extent. In effect, the electronic absorption spectra of such crystals are usually dominated by excitations of intramolecular origin (Frenkel excitons). The influence of the crystalline environment is mainly due to the resonance interaction of an excited molecule with its unexcited surroundings, resulting in exciton delocalization and, for crystals with several molecules per unit cell, in the splitting of molecular absorption bands into several components with different polarizations (referred to as the factor group splitting or the Davydov splitting).

The long-range character of the resonance interactions between the transition dipole moments results in the non-analyticity of the exciton energies at the centre of the Brillouin zone [1], giving rise to the dependence of exciton energy on crystal

orientation. This effect, depending on the square of the transition dipole moment, is negligible for weak transitions, but is crucial for the transitions endowed with large oscillator strength.

Another effect governed by the magnitude of the transition dipole moment is the coupling of the crystal exciton states to the photon field of incident radiation. For sufficiently strong transitions coherent superpositions of exciton and photon states (called polaritons) are formed [2, 3]. These new quasi-particles are characterized by a forbidden gap in the energy spectrum, manifested as a “stopping band” of metallic reflection.

Comprehensive theoretical studies on the Frenkel excitons in molecular crystals started in late 1940s [4] and resulted in firm interpretation of the absorption and reflection spectra of some model crystals such as naphthalene or anthracene. The polariton effects were also studied, both within the scope of classical electrodynamics [2] and of full-fledged quantum theory [3]. In this latter framework, the polariton effects are attributed to retardation, resulting from inter-exciton exchange of virtual perpendicular photons.

As most of the experimental work was focused on the low-energy transitions of low or medium intensity, for which the exciton–photon coupling is of lesser importance, the polariton effects were for a long time out of the main stream of molecular crystal research. This situation has changed recently because of the current interest in the physics of oligothiophene crystals, where the lowest electronic transition is very intense. Polaritons were invoked to explain some features of the absorption and electroabsorption spectra of α -sexithiophene [5, 6]. A detailed investigation based on classical electrodynamics falsified the newly introduced interpretational paradigm for electroabsorption spectroscopy [7, 8], rooted in an erroneous understanding of polariton properties.

Nonetheless, the misunderstanding did not pertain to absorption spectroscopy. Yet, the observed vibronic absorption spectra still turned out to exhibit some peculiar features that might potentially be attributable to polaritons, the most dramatic being a massive intensity transfer to higher energies (with respect to the spectrum of the isolated molecule). A recent study [9] shows that the effect is of vibronic provenance: owing to the strong resonance interactions characteristic of intense transitions, oligothiophenes represent the case of strong intermolecular (weak vibronic) coupling. The blue shift of the dominant absorption band merely reconstitutes the result that is standard in the situation approaching the adiabatic Born–Oppenheimer limit, and seems to be puzzling only as long as the interpretation is couched in terms of the strong-vibronic-coupling basis set, evidently inapplicable in this context but traditionally used in molecular crystal spectroscopy.

These circumstances create a demand for an approach where vibronic coupling could be adequately described at least in the Born–Oppenheimer limit, or preferably at a still more sophisticated level of theory, capable of handling also

the intermediate cases. Unfortunately, this is not possible within the commonly used classical formalism (inherently based on the approximation of strong vibronic coupling) where the excitons are represented as a set of classical oscillating dipoles which interact with each other.

A consistently quantum-electrodynamic approach [3] provides the needed theoretical framework. The present paper is a topical study targeted at the performance of this approach and at the actual importance of polariton effects. We investigate the influence of polariton effects on the absorption spectra of a model crystal, its structure resembling the low-temperature phase of α -sexithiophene. The oscillator strength of the molecular transition is varied to study the weak, intermediate, and strong-coupling range.

2. Model crystal

In order to mimic the low-temperature phase of α -sexithiophene [10], the model crystal is assumed to be monoclinic and to contain in the unit cell four molecules arranged in two pairs with long axes almost parallel to each other and nearly perpendicular to the unique monoclinic axis b . Only one electronic transition is taken into account, corresponding to the lowest-energy $1B_u$ excitation polarized along the long axis of the α -sexithiophene molecule and located at 2.50 eV. In the crystal, this state is split into four components. Two of them (a_g and b_g) are dipole forbidden. The other two are dipole allowed, but due to the special arrangement of the molecules in the unit cell the lower one (a_u , b polarized) is very weak. For the same reason, the upper Davydov component (b_u), polarized in the ac plane, carries almost all the oscillator strength of the molecular transition. Because of their perpendicular polarizations, the upper and the lower Davydov component can be probed selectively by light polarized along the b or c crystal axes.

As the present paper is meant as a parametric study, the transition dipole moment assumes the alternative values of 0.4 eÅ, 1.0 eÅ, 1.6 eÅ and 2.2 eÅ; the last one is appropriate for the α -sexithiophene molecule. In Sect. 3 the electronic transition is followed by a vibronic progression in one intramolecular mode of frequency 0.18 eV and the Franck–Condon distortion parameter 1.2. In Sect. 4 only a purely electronic transition is considered.

3. Exciton–photon coupling

3.1. Classical description

In the classical polariton theory a Frenkel state localized at molecule s is represented by an oscillating point dipole [2, 7, 8]. Its equation of motion in the external field complemented by the combined electric field of all the other dipoles is solved in conjunction with the Maxwell equations describing the driving fields. The external field comprises the electric field of the incident light wave and potentially also the modulating static electric field if electroabsorption phenomena are stu-

died [7]. In the present paper, where only absorption spectroscopy is addressed, this additional field is set equal to zero (in contrast to Ref. [7]).

The solution to the aforementioned set of equations expresses the refractive index of the crystal in terms of the frequencies (ω_u) and oscillator strengths (f_u) of the electronic transitions in the molecule. For monoclinic crystals a compact formula is obtained for certain directions of wave vector \mathbf{k} , i.e. for \mathbf{k} parallel or perpendicular to the unique monoclinic axis. In the case of four molecules per unit cell, with all transitions polarized along the long molecular axis, the result is [8]:

$$n_{\pm}^2(\omega, \mathbf{k}) = 1 + \frac{\sum_u \frac{\omega_0^2 f_u}{\omega_u^2 - \omega^2} (\hat{\mathbf{e}} \cdot \mathbf{d}_{\pm})}{4 + 4 \sum_u \frac{\omega_0^2 f_u}{\omega_u^2 - \omega^2} T_{\pm}(\mathbf{k})}, \quad (1)$$

where the plus sign stands for the upper and the minus sign for the lower Davydov component, ω_0 is the plasma frequency, $\hat{\mathbf{e}}$ is the light polarization versor, \mathbf{d}_{\pm} is a symmetry-adapted linear combination of the versors of transition dipole moments of the four molecules contained in the unit cell, and $T_{\pm}(\mathbf{k})$ is the corresponding symmetry-adapted linear combination of the lattice sums (the Fourier transforms of the crystal dipolar tensor per unit dipole moment). The index u runs over all electronic transitions of the molecule (there is only one in our present model).

The generalization of the above result to include vibronic effects is straightforward. Every vibronic replica of the electronic transition is considered as a separate state and is represented by an oscillating dipole. The amplitude of n -th vibronic satellite is modified by the vibrational overlap integral S_0^n and enters Eq. (1) as a separate term in the sum-over-states expression, with its own frequency ($\omega_u + n\omega_{\text{osc}}$) and oscillator strength $f_u(S_0^n)^2$. This approach corresponds to the limit of strong vibronic coupling; as Eq. (1) couples the states with different number of phonons, it is tantamount to the *modified* strong-coupling (MSC) approximation of Ref. [9].

When damping is taken into account by adding the term $-i\omega\gamma$ in the denominator of the sum-over-states expressions in Eq. (1), the refractive index becomes complex. Its imaginary part defines the extinction coefficient

$$\alpha(\omega, \mathbf{k}) = \frac{2\omega\Im[n(\omega, \mathbf{k})]}{c} \quad (2)$$

thereby yielding the absorption spectrum.

3.2. Quantum theory

The quantum-electrodynamic approach has a great interpretational advantage over classical theory. It splits the process of finding the refractive index into two stages. At first the excitonic Hamiltonian is diagonalized, yielding the exciton energies and oscillator strengths; these are subsequently applied in the calculation of the refractive index using the formula [3, 11]:

$$n_{\pm}^2(\omega, \mathbf{k}) = 1 - \frac{1}{2} \sum_s \frac{\omega_0^2 f_s(\mathbf{k})}{\omega^2 - \Omega_s^2(\mathbf{k})} \left(1 - (\hat{\mathbf{d}}_s \cdot \hat{\mathbf{k}})^2\right)$$

$$\pm \frac{1}{2} \left[\left(\sum_s \frac{\omega_0^2 f_s(\mathbf{k})}{\omega^2 - \Omega_s^2(\mathbf{k})} \left[(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{d}}_s)^2 - (\hat{\mathbf{e}}_2 \cdot \hat{\mathbf{d}}_s)^2 \right] \right)^2 + 4 \left(\sum_s \frac{\omega_0^2 f_s(\mathbf{k})}{\omega^2 - \Omega_s^2(\mathbf{k})} (\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{d}}_s)(\hat{\mathbf{e}}_2 \cdot \hat{\mathbf{d}}_s) \right)^2 \right]^{1/2}, \quad (3)$$

where ω_0 is the plasma frequency, $f_s(\mathbf{k})$, $\Omega_s(\mathbf{k})$ and $\hat{\mathbf{d}}_s$ are the oscillator strength, frequency and the versor of the transition dipole moment corresponding to the s -th exciton band of the crystal, $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are versors perpendicular to \mathbf{k} . In complete analogy with the classical approach, damping is introduced by adding the term $-i\omega\gamma$ in the denominator of the above expressions; then the imaginary part of the refractive index defines the extinction coefficient and yields the absorption spectrum.

This two-step procedure of finding the refractive index offers two distinct advantages which are absent from the classical description. In the first place, the calculation of exciton properties (determined by Coulombic interactions in the crystal), done in the initial step, is automatically separated from the calculation of the interaction with incident radiation which is accounted for in the second step. Thereby, the pure polariton effects may be identified by comparison of the polaritonic and excitonic spectra (the latter corresponding to the limit of infinitesimal exciton–photon interaction). In classical theory this feature is missing, since the intrinsic interactions within the crystal are treated on equal footing with the interaction with radiation; technically, there is no access to the oscillator strengths of crystal excitons, even though their energies can be found as the poles of n^2 .

The second advantage of quantum theory is the possibility of using different approximations for the excitonic Hamiltonian. Specifically, this allows one to test alternative approaches to vibronic coupling, in contrast to the classical theory, inherently based on the modified strong-vibronic-coupling approximation. Furthermore, this flexibility may be potentially used to extend the treatment by including the excitations of intermolecular origin (charge-transfer states).

3.3. Numerical calculations and their results for a model crystal

The input data for the calculations of the absorption spectra, both on the classical and quantum level of theory, are adopted from the literature pertaining to the low-temperature phase of α -sexithiophene. Apart from the crystal structure and molecular properties specified in Sect. 2, the input includes the dipole tensors calculated by Munn et al. [12] and the geometry of the experiment. The latter is identical with the one used by Weiser and collaborators [6]: the wave vector of incident light is normal to the bc plane of the crystal and the light is polarized along the c crystal axis. This allows one to probe only the upper Davydov component; the weak lower component (where polariton effects are negligible) is obviously of

no interest in the present context. The damping parameter γ , responsible for the signal half-width, is set to 0.1 eV.

The “purely excitonic” absorption spectrum, corresponding to the limit of infinitesimal exciton–photon interaction, is in fact a hypothetical construct, since in reality there is no way to switch this interaction off. Yet, this fictitious construct is instrumental in identifying indirectly the polaritonic effects. It is obtained by plotting the oscillator strengths of the exciton eigenstates against their energies; both are obtained by diagonalizing the Hamiltonian matrix in the first step of the procedure described in the preceding section. In this section, the Hamiltonian is truncated to eliminate the terms that do not conserve the total number of excitons (Heitler–London approximation, HLA).

In the following, we report the absorption spectra calculated in three alternative ways: at the classical level of theory [from Eqs. (1), (2)]; at quantum level of theory [from Eqs. (3), (2)], based on the exciton eigenstates found in the Heitler–London approximation; and the “excitonic” spectra generated as described above, also in the Heitler–London approximation. In this last case, the shape of the absorption bands was assumed to be Lorentzian in order to facilitate comparison with polaritonic spectra. For the sake of consistency with the classical model, for quantum calculations the modified strong-vibronic-coupling approximation was used.

The spectra were calculated for several values of the molecular transition dipole (as listed in Sect. 2); they are displayed in Fig. 1.

The most conspicuous feature of the polariton spectra calculated both on the classical and quantum level is the intensity accumulation in the high-energy region. As expected, for small transition dipole moment (i.e. when the coupling of excitons with the photon field is weak) the polaritonic spectrum of the crystal resembles to a large extent the spectrum of the isolated molecule, exhibiting the familiar Franck–Condon progression. With growing transition dipole moment, both the spacing between the vibronic bands and their intensity pattern gradually changes to yield a single blue-shifted band, reminiscent of the experimental spectra of oligothiophene crystals.

If the results of classical polariton theory (solid line) were the sole source of information, one would be tempted to attribute this peculiar effect to the influence of exciton–photon coupling, as it was done in some recent papers. This hypothesis can be tested by comparing the hypothetical “purely excitonic” spectra (broken line) with the polaritonic spectra obtained at the quantum level of theory (dotted line). It is readily seen that virtually all the intensity transfer to high energy regions is already present in the excitonic spectra; hence, it cannot result from exciton–photon coupling. In fact, it is a consequence of vibronic interactions, merely approaching the standard Born–Oppenheimer result [9]; this was only to be expected for large transition dipoles where the exciton-resonance interaction dominates over vibronic coupling. The true polaritonic effects (revealed by com-

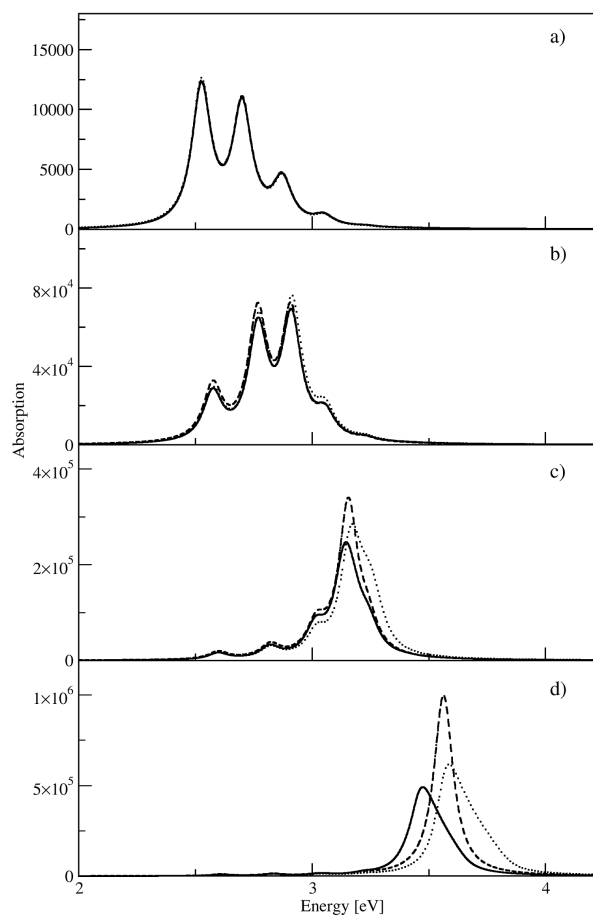


Fig. 1. Calculated absorption spectra of a model crystal with different transition dipole moments of constituent molecules. (a) $d = 0.4 \text{ e\AA}$, (b) $d = 1.0 \text{ e\AA}$, (c) $d = 1.6 \text{ e\AA}$, (d) $d = 2.2 \text{ e\AA}$. Solid line — classical theory of polaritons, dashed line — exciton theory with HLA, dotted line — quantum theory of polaritons.

paring the broken curve with the dotted curve) turn out to be rather small even for the strongest transitions considered here; they just give rise to some broadening of the absorption signal and to a minor blue shift.

4. Mixing with two-exciton states

The results exhibit one slightly disturbing feature: there is a difference between the polaritonic spectra resulting from the classical and quantum level of theory. Small discrepancies already show up for the transition dipole moment of 1.0 e\AA . For $d = 2.2 \text{ e\AA}$ the position of the main maximum in the absorption spectrum differs by about 0.1 eV ; moreover, the spectrum obtained from the quantum approach is considerably more intense.

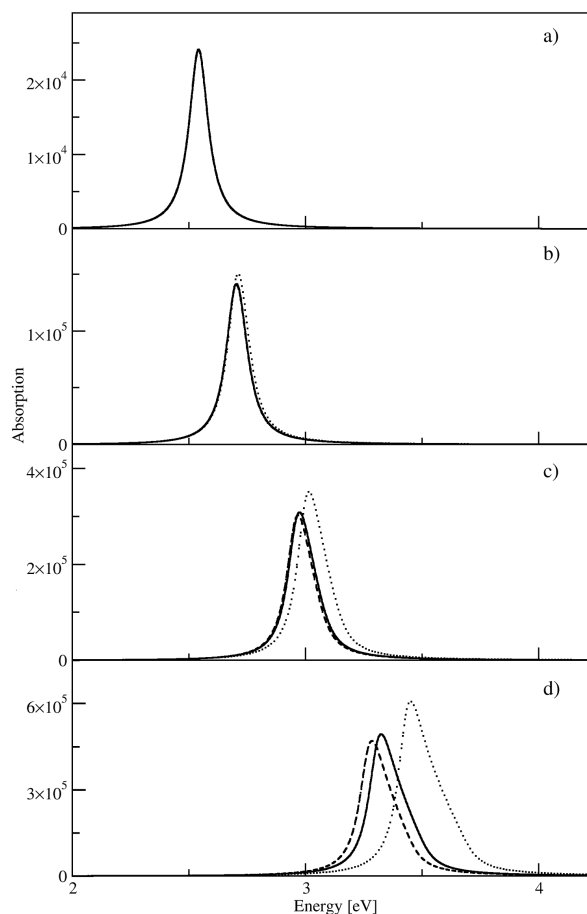


Fig. 2. Calculated absorption spectra of a model crystal with different transition dipole moments of constituent two-level molecules. (a) $d = 0.4 \text{ e\AA}$, (b) $d = 1.0 \text{ e\AA}$, (c) $d = 1.6 \text{ e\AA}$, (d) $d = 2.2 \text{ e\AA}$. Solid line — classical theory of polaritons, dotted line — quantum theory of polaritons based on HLA, dashed line — HLA-corrected quantum theory of polaritons.

The possible source of these discrepancies is the Heitler–London approximation applied in the evaluation of exciton energies and oscillator strengths. This simplification, commonly used in the theory of molecular crystals, consists in neglecting the terms of the Hamiltonian that fail to conserve the total number of excitations. Thereby, the mixing between the states involving different number of excited molecules is disregarded; for low excitation densities, the approach seems reasonable, but even then its accuracy is limited by the “off-resonance” corrections. These are of the order of V/E_0 , where V is the Davydov splitting and E_0 is the exciton energy; hence, while negligible for weak transitions, for strong transitions they may be substantial. In contrast, the classical-electrodynamical theory of

polaritons accounts for the coupling of all multi-exciton states (which is also an approximation, violating the constraints of exciton quantum statistics); accordingly, there is a good reason for some discrepancies.

Going beyond the Heitler–London approximation in a quantum approach is a formidable task. Therefore in order to verify the above conjecture we apply the perturbational results of Agranovich and Basko [13]. To simplify the problem even further we disregard the vibronic phenomena in the model crystal and consider only the purely electronic transitions. Owing to these simplifications, the closed formulas available for the second-order correction to the excitation energy and for the first-order correction to the oscillator strength in a crystal consisting of two-level molecules may be readily applied. The calculated corrections for the case of the molecular transition dipole moment of 2.2 eÅ reduce the exciton energy by 0.16 eV and its oscillator strength by about 30%. The resultant polariton absorption spectra are shown in Fig. 2, along with the polariton spectra based on exciton energies and oscillator strengths from the Heitler–London approximation and with the spectra obtained from the classical-electrodynamic approach.

Evidently, for weak transitions (where the discrepancies are small anyway) inclusion of the first non-vanishing corrections to the Heitler–London exciton energies and oscillator strengths leads to a perfect agreement of the absorption spectra calculated within the classical and quantum polariton theories. For stronger transitions, the HLA-corrected spectra are still in much better agreement with the results of classical theory than the uncorrected ones, although the corrections are apparently slightly overestimated. This is not surprising; it is reasonable to expect that inclusion of the next order of perturbation theory would compensate this error. By and large, the detected discrepancies may be convincingly attributed to the inherent inaccuracies of the Heitler–London approximation and, as expected, the classical and the quantum approach may be safely considered equivalent.

5. Conclusions

Our results suggest that the quantum-electrodynamic approach is a feasible alternative to classical polariton theory. It allows one to separate the procedure of finding the exciton eigenstates from the calculation of the refraction index and ultimately of the absorption spectrum. By eliminating the necessity to use the strong-vibronic-coupling approximation, inherent to the classical model, it opens a way to test other approaches, potentially more appropriate for molecular crystals with very intense transitions. It also bridges the gap between the dielectric and Hamiltonian formulation of exciton theory [14], enabling one to solve the problem by standard methods of matrix diagonalization. Although this is most easily done in the Heitler–London approximation which introduces some inherent errors, these errors are of quantitative rather than qualitative nature, in contrast to the strong-vibronic-coupling approximation where even the qualitative picture is substantially distorted [9]. Moreover, the errors may be partially corrected by perturbation theory. Altogether, the quantum-electrodynamic approach is a promising

option for future studies of weak and intermediate vibronic interactions in molecular crystals, and for generalizations aimed to incorporate charge–transfer (CT) excitons.

For the time being, the quantum-electrodynamic approach has allowed us to probe the importance of inherent polaritonic effects due to the retarded exciton interactions mediated by perpendicular photons. The results demonstrate that these effects are of secondary importance, merely giving rise to some broadening of the absorption signal and to a minor blue shift. This corroborates the recent conjecture [9] that most of the peculiarities which in current literature have often been attributed to polariton formation are in fact due to vibronic coupling mediated mostly by intramolecular vibrations, thereby motivating an in-depth study of vibronic interactions in crystal excited states which is currently underway in our laboratory.

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