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Second harmonic generation by charge-transfer excitons interacting with phonons

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Effects of exciton-phonon interaction on the nonlinear optical response of charge-transfer excitons (CTE) are studied in the framework of an exactly solvable model. It is found that the second order excitonic optical polarizability β is modified due to the CTE-phonon interaction. For a nonresonant frequency range, where β is relatively small, the change is not significant. On the contrary, in the vicinity of resonances (when the light frequency $\omega \approx \omega_0$ or $\omega \approx \omega_0/2$, ω_0 is the CTE transition frequency), the CTE-phonon interaction may remarkably diminish the value of β. This should be taken into account when considering CTE systems in nonlinear optics.

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There is considerable research interest in molecular systems where molecular optical excitations are accompanied by an electronic charge transfer (see, e.g., Ref. 1). Studies of systems with charge-transfer excitons (CTEs) are stimulated by recent progress in the fabrication of organic multilayer structures (OMS); see, e.g., Refs. 2–4. Considerable attention has been devoted to nonlinear optical phenomena in CTE systems. It has been shown, for instance, that effects of mutual interaction between CTEs may show up in the generation of higher spatial harmonics of the initial grating of the CTE density.[5] A novel photovoltaic effect in strongly pumped CTE systems has been proposed.[6] Particular optical nonlinearities have been predicted for moderately pumped CTE systems.[7] A characteristic feature of systems with charge-transfer electronic excitations is that the transition is accompanied by a change of the *static* dipole moment. This is in contrast to usual Frenkel excitons which possess only a *transition* dipole moment, with vanishing static dipole moments in both ground and excited states. The occurrence of a nonzero static dipole moment with the excitations of CTEs destroys the inversion symmetry and allows for a nonzero second order optical response and, in particular, for second harmonic (SH) generation.[8,9] The SH generation process may occur also in a composite medium consisting of centrosymmetric molecules and containing in addition a small amount of charge transfer complexes.[10]

In the present paper we study effects of the exciton-phonon interaction on the second-order optical properties of charge-transfer molecular transitions. The charge transfer causes a perturbation of the crystal lattice which results in an enhanced exciton-phonon interaction, a broadening of excitonic optical absorption lines, and a decrease of the exciton hopping rate.[1] For strong coupling, the complicate CTE-phonon system may be modeled[11] as localized electronic excitations interacting with phonons and light (see, e.g., Ref. 12). This model, also known as the independent boson model,[13] allows an exact treatment and is widely used in studies of optical absorption, hot luminescence, and resonant Raman effect of localized electron centers (see, e.g., Ref. 14), etc. Here we use this model to study the second order polarizability β of a localized charge-transfer center interacting with phonons. We shall show that the CTE-phonon interaction may change considerably the value of β.

The model Hamiltonian is taken in the form $H = H_0 + V(t)$. Here the Hamiltonian of the unperturbed exciton-phonon system reads

$$H = \omega_0 a^\dagger a + a^\dagger a \sum_\nu (g_\nu^* b_\nu^\dagger + g_\nu b_\nu) + \sum_\nu \Omega_\nu b_\nu^\dagger b_\nu, \quad (1)$$

where $a^\dagger$ (a) and $b_\nu^\dagger$ (b_ν) are the exciton and phonon creation (annihilation) operators, the lower index ν enumerates phonon modes. The perturbation Hamiltonian $V(t) = -\hat{\mathbf{p}}\mathbf{E}(\mathbf{t})$, where

$$\hat{\mathbf{p}} = \boldsymbol{\mu}(a^\dagger + a) + \boldsymbol{\mu}^0 a^\dagger a \quad (2)$$

is the operator of the exciton dipole moment and $\mathbf{E}(t) = \boldsymbol{\mathcal{E}} \exp(-i\omega t) + \text{c.c.}$ is an external electromagnetic field of frequency ω. In Eq. (2), the first term has nonzero matrix elements only between the ground and excited states, therefore $\boldsymbol{\mu}$ is the transition dipole moment of the molecule. On the contrary, the second term in Eq. (2) has a nonzero (diagonal) matrix element only in the excited state, hence $\boldsymbol{\mu}^0$ is the change of the static dipole moment associated with the real charge transfer in course of the electronic excitation. As has been noted above, this change of the static dipole moment is just a feature of CTEs.

The applicability of the model (1) to exciton systems is based on two common physical assumptions. The first one is a restriction to only linear phonon terms in the exciton-phonon interaction and also the neglect of phonon-phonon interactions. This neglect of anharmonic terms is a widely accepted approximation when considering excitonic systems (see, e.g., Ref. 12), which seems reasonable as far as one is not interested in subtle details (like the finite width of the zero-phonon transition line). The second physical assumption of the model (1) is the conservation of the number of charge-transfer excitons. This idealization disregards nonradiative exciton decay processes. The usual justification of this assumption is based on the considerable difference between exciton and phonon energy scales: exciton creation energies are typically tens times higher than phonon energies. Therefore, nonradiative exciton decay processes are associated with a big number of emitted phonons and are relatively weak. Below we shall restrict ourselves to the case of a single molecular transition and do not take into account any collective effects (such as the appearance of a static electric field, local field corrections, etc.) in a highly pumped dense molecular system.

The induced molecular polarization $\mathbf{p}(t)$ is determined by standard response theory expressions. The first and the second order of the polarization in the perturbation $V(t)$ read

$$p_i^{(1)}(t)=i\int dt_1\,\theta(t-t_1)\langle[\hat{p}_i(t),\hat{p}_j(t_1)]\rangle E_j(t_1) \tag{3}$$

and

$$\begin{aligned}p_i^{(2)}(t)=-\int dt_1 dt_2\,\theta(t-t_2)\,\theta(t_2-t_1)&\\ \times\langle[[\hat{p}_i(t),\hat{p}_k(t_2)],\hat{p}_j(t_1)]\rangle E_j(t_1)E_k(t_2),&\end{aligned} \tag{4}$$

respectively; latin lower indices $i,j,k=1,2,3$ correspond to Cartesian vector components. Heisenberg operators in Eqs. (3) and (4) are determined with respect to the unperturbed Hamiltonian (1); averaging $\langle\cdots\rangle$ is performed over the electronic ground state (no exciton) and the thermal phonon distribution.

For a monochromatic external field, the linear response polarization of Eq. (3) may be expressed in the form

$$\begin{aligned}p_i^{(1)}(\omega)\equiv\alpha_{ij}\mathcal{E}_j=i\mu_i\mu_j\mathcal{E}_j\int dt_1\,\theta(t-t_1)&\\ \times\langle[a(t)a^{\dagger}(t_1)-a(t_1)a^{\dagger}(t)]\rangle\exp[i\omega(t-t_1)],&\end{aligned} \tag{5}$$

and thus the linear polarizability $\alpha(\omega)$ is given by

$$\alpha_{ij}=-\mu_i\mu_j\{G(\omega)+[G(-\omega)]^*\}. \tag{6}$$

Here the retarded Green's function has been introduced:

$$G(t)=-i\,\theta(t)\langle a(t)a^{\dagger}(0)\rangle=\int\frac{d\omega}{2\pi}G(\omega)\exp(-i\omega t)\,. \tag{7}$$

The linear polarizability $\alpha(\omega)$ (6) is determined only by the transition dipole moment $\boldsymbol{\mu}$ and does not depend on the static dipole moment $\boldsymbol{\mu}^0$ associated with the charge transfer.

Returning to the second-order polarization of interest, we find the following expression for the double commutator in the integrand of Eq. (4):

$$\begin{aligned}&\langle[[\hat{p}_i(t),\hat{p}_k(t_2)],\hat{p}_j(t_1)]\rangle\\ &\quad=\mu_i\mu_j\mu_k^0\langle a(t)a^{\dagger}(t_2)a(t_2)a^{\dagger}(t_1)+a(t_1)a^{\dagger}(t_2)\\ &\qquad\times a(t_2)a^{\dagger}(t)\rangle-\mu_i^0\mu_j\mu_k\langle a(t_2)a^{\dagger}(t)a(t)a^{\dagger}(t_1)\\ &\qquad+a(t_1)a^{\dagger}(t)a(t)a^{\dagger}(t_2)\rangle.\end{aligned} \tag{8}$$

An important feature of the model (1) is the conservation of the number of excitons, i.e., $[H,a^{\dagger}a]=0$. Therefore, the Heisenberg operator $a^{\dagger}(t)a(t)$ does not depend on time, so that the operators $a^{\dagger}a$ in the middle of the four-operator products in Eq. (8) may be replaced by unity. This leads to a much simpler expression for the second-order polarization of Eq. (4)

$$\begin{aligned}p_i^{(2)}(2\omega)&\equiv\beta_{ijk}(2\omega)\mathcal{E}_j\mathcal{E}_k\\ &=-i\mathcal{E}_j\mathcal{E}_k\int dt_1 dt_2\,\theta(t-t_2)\,\theta(t_2-t_1)\\ &\quad\times\exp[i\omega(2t-t_1-t_2)]\{\mu_i\mu_j\mu_k^0[G(t-t_1)\\ &\quad-G^*(t-t_1)]-\mu_i^0\mu_j\mu_k[G(t_2-t_1)\\ &\quad-G^*(t_2-t_1)]\}.\end{aligned} \tag{9}$$

Performing the time integrations we obtain for the second order polarizability $\beta(2\omega)$

$$\begin{aligned}\beta_{ijk}(2\omega)=\frac{\mu_i\mu_j\mu_k^0+\mu_i\mu_j^0\mu_k}{2\omega}&\{G(\omega)-[G(-\omega)]^*\\ &-G(2\omega)+[G(-2\omega)]^*\}\\ &+\frac{\mu_i^0\mu_j\mu_k}{2\omega}\{G(\omega)-[G(-\omega)]^*\}.\end{aligned} \tag{10}$$

A remarkable fact is that both the first- and the second-order polarizabilities, Eqs. (6) and (10), are expressed via the Green's function $G(\omega)$ given by Eq. (7). The imaginary part of $G(\omega)$ is directly connected with the shape $\kappa(\omega)$ of the linear absorption line $\kappa(\omega)=-(1/\pi)\mathrm{Im}\,G(\omega)$, and the real part may be obtained, in principle, via the Kramers-Kronig relations. Below we shall exploit the fact that for the model Eq. (1) there exists an explicit exact expression for the function $G(t)$.

In the absence of the exciton-phonon interaction, we have

$$G(t)=-i\,\theta(t)\exp(-i\omega_0 t);\quad G(\omega)=\frac{1}{\omega-\omega_0+i\delta},\quad \delta\to+0. \tag{11}$$

In this limiting case we arrive at the usual expressions for $\alpha(\omega)$ and $\beta(2\omega)$;[8,9] both $\alpha(\omega)$ and $\beta(2\omega)$ possess a resonance at $\omega=\omega_0$; in addition, $\beta(2\omega)$ possesses also a resonance at $\omega=\omega_0/2$ (for definiteness, we assume $\omega>0$).

In the presence of the exciton-phonon interaction, both $\alpha(\omega)$ and $\beta(2\omega)$ change considerably. However, in the vicinity of the above resonances we may still express $\beta(2\omega)$ directly in terms $\alpha(\omega)$. So, in the resonance range $\omega\approx\omega_0$, one may keep only the term $G(\omega)$ in Eqs. (6) and (10), which results in

$$\beta_{ijk}(2\omega)\approx-\frac{1}{2\omega_0}[\alpha_{ij}(\omega)\mu_k^0+\alpha_{jk}(\omega)\mu_i^0+\alpha_{ik}(\omega)\mu_j^0];\quad \omega\approx\omega_0\,. \tag{12}$$

Similarly, for the resonance range $2\omega\approx\omega_0$ we find

$$\beta_{ijk}(2\omega)\approx\frac{1}{\omega_0}[\alpha_{ij}(2\omega)\mu_k^0+\alpha_{ik}(2\omega)\mu_j^0];\quad \omega\approx\omega_0/2. \tag{13}$$

The above relationships are rather general, they are obtained under the only assumption that the exciton-phonon interaction conserves the number of excitons. Now we use the known exact expression for $G(t)$ in order to get more detailed information about $\beta(2\omega)$. The Green's function $G(t)$ for the model of Eq.(1) is given by (see, e.g., Refs. 12,13)

$$G(t)=-i\theta(t)\exp[-i\omega_0 t+F(t)], \tag{14}$$

where

$$F(t)=-it\sum_\nu\frac{|g_\nu|^2}{\Omega_\nu}-\sum_\nu\frac{|g_\nu|^2}{\Omega_\nu^2}(2n_\nu+1)+\sum_\nu\frac{|g_\nu|^2}{\Omega_\nu^2}[n_\nu\exp(i\Omega_\nu t)+(n_\nu+1)\exp(-i\Omega_\nu t)], \tag{15}$$

$n_\nu=1/[\exp(-\Omega_\nu/T)-1]$ is the phonon occupation number at temperature T. Although exact, Eq. (15) is rather complicate which does not allow us to obtain a closed explicit expression for $G(\omega)$. That is why we consider the following limiting situations.

(1) The frequency detuning $|\omega-\omega_0|$ (and $|2\omega-\omega_0|$) is large compared to the absorption band width in the presence of the exciton-phonon coupling. The leading contribution to $G(\omega)$ stems from a small time integration range $t\sim 1/|\omega-\omega_0|$. As $F(t)\to 0$ at $t\to 0$, we return in this limit to the case with no exciton-phonon interaction, where $\beta(2\omega)$ is determined by Eqs. (10) and (11). Therefore, the exciton-phonon interaction *does not influence* the second-order response of the charge-transfer system to a *nonresonant* external field.

(2) Consider now the opposite limiting case, when the frequency ω (or 2ω) is in resonance with a zero-phonon transition. The leading contribution to $G(\omega)$ stems from long integration times so that the third (oscillating) term in Eq. (15) may be neglected. One obtains

$$G(\omega)=G_0(\omega+\Delta)\exp(-S), \tag{16}$$

where $\Delta=\Sigma_\nu|g_\nu|^2/\Omega_\nu$ describes the shift of the transition frequency; $\omega_0\to\omega_0-\Delta$, and $\exp(-S)$ is the Debye-Waller factor $S=\Sigma_\nu(2n_\nu+1)|g_\nu|^2/\Omega_\nu^2$. With the replacement $\omega\to 2\omega$, Eq. (16) would describe also the resonance $2\omega\approx\omega_0-\Delta$. As follows from Eq. (16), the exciton-phonon interaction may strongly influence the resonant second-order polarizability. For small values of the Debye-Waller factor $\exp(-S)$, the resonant second harmonic generation may be considerably suppressed.

(3) In the intermediate case of not too large detuning, one may obtain an estimate for $G(\omega)$ keeping the second order terms of the expansion of Eq. (15) in t (the first order terms cancel identically):

$$G(\omega)=-i\int_0^\infty dt\,\exp[i(\omega-\omega_0)t-\gamma^2t^2]=-i\frac{\sqrt{\pi}}{2\gamma}\exp\left[-\frac{(\omega-\omega_0)^2}{4\gamma^2}\right]\left[1-\Phi\left(-i\frac{\omega-\omega_0}{2\gamma}\right)\right], \tag{17}$$

where

$$\gamma^2=\sum_\nu|g_\nu|^2(n_\nu+1/2) \tag{18}$$

and $\Phi(z)=(2/\sqrt{\pi})\int_0^z\exp(-x^2)dx$ is the Gaussian error function. If the detuning $|\omega-\omega_0|$ is small as compared to the absorption band width γ, we have

$$G(\omega)\approx-i\frac{\sqrt{\pi}}{2\gamma}. \tag{19}$$

On the contrary, if the detuning $|\omega-\omega_0|$ is large as compared to the absorption band width γ, we return back to the nonresonant situation described in item 1. With the replacement $\omega\to 2\omega$, Eqs. (17),(19) describe also the resonance range $2\omega\approx\omega_0$.

The above expressions for $G(\omega)$ $[G(2\omega)]$ completely determine the second order polarizability $\beta(2\omega)$ near the two resonances

$$\beta_{ijk}(2\omega)\approx\frac{G(\omega)}{2\omega_0}[\mu_i\mu_j\mu_k^0+\mu_i^0\mu_j\mu_k+\mu_i\mu_j^0\mu_k];\quad \omega\approx\omega_0, \tag{20}$$

$$\beta_{ijk}(2\omega)\approx-\frac{G(2\omega)}{\omega_0}[\mu_i\mu_j\mu_k^0+\mu_i\mu_j^0\mu_k];\quad \omega\approx\omega_0/2. \tag{21}$$

In conclusion, we have considered the second-order polarizability $\beta(2\omega)$ for the charge-transfer molecular transition in the presence of the exciton-phonon interaction. Under the assumption that the exciton-phonon interaction conserves the number of excitons, a closed expression for $\beta(2\omega)$ has been obtained in terms of the single-exciton Green's function $G(t)$. With the use of the exact representation of $G(t)$ for model (1), we have described the influence of the exciton-phonon interaction on the second-order polarizability of the charge-transfer molecular transition. In the off-resonance frequency range, where the second-order polarizability is rather small, this influence is weak and $\beta(2\omega)$ coincides with the usual result in the absence of the exciton-phonon interaction. However, in the near resonance range ($\omega\approx\omega_0$ or $\omega\approx\omega_0/2$), the second-order polarizability of the charge-transfer molecular transition may be strongly diminished by the exciton-phonon interaction as compared to the noninteracting system. This fact may be important for studies of the second harmonic generation in systems with charge-transfer transitions.

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