Absorption of Electromagnetic Waves in Molecular Crystals

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The absorption of electromagnetic waves in molecular crystals at low temperature has been studied using the Green's-function method. The spin dependence of the excitations created by photon absorption has been explicitly considered. In the Hartree-Fock (HF) approximation and in the absence of the radiation field, the poles of the exciton Green's function consist of two frequency modes corresponding to the singlet and triplet exciton fields, respectively, and propagate through the medium independently; beyond the HF approximation, the two modes are no longer independent. The spectral function for the photon field is found to consist of the superposition of symmetric and asymmetric Lorentzian lines. General expressions for the energy shift and spectral width are derived. An example is worked out for the resonance Raman scattering of triplet excitions, where the incident photon becomes a polariton and then decays into two triplet excitons. Physical processes, where a singlet exciton decays into two triplet excitons, as well as the excitation spectrum of triplet excitons, have been studied in detail.

I. INTRODUCTION

THE scattering of electromagnetic waves in molecular crystals has been recently considered[1] by calculating the photon Green's function and, consequently, the polarization operator of the crystal. The spectral function for the photon field has been derived and an extensive investigation of the polariton-exciton and exciton-exciton interactions has been done. However, in this study the effect of the electron spin has been completely neglected and, hence, only excitations with spin-allowed transitions have been considered.

In fact, for most molecular crystals, the valence bands are filled with electrons having opposite spin alignment. Therefore, upon excitation each created electron-hole pair may have its spin component either up or down. The spin degeneracy is removed by the intermolecular interactions with the result that the created excitations are not only the spin-allowed but also the spin-forbidden ones.

An attempt is made here to discuss the excitation spectrum and line shape of absorption bands at low temperature for the physical process, where electromagnetic radiation is absorbed in a molecular crystal. The crystal is assumed to consist of neutral molecules in an undisplaced lattice with the valence bands filled with electrons having antiferromagnetic spin alignment. The motive of the present study is twofold. First, most of the observed exciton absorption spectra manifest asymmetric line shapes[2,3] and, second, the concern about the recently observed spectra in organic solids, which are attributed to the singlet-triplet and triplet-triplet exciton-exciton interactions, respectively.[4–7] It has been pointed out[2,3] that at finite temperatures the asymmetry of the absorption bands is due to the polariton-phonon[3] or the exciton-phonon interactions.[2,3] On the other hand, a recent investigation[8] on the optical excitation spectrum of interacting polariton waves in organic solids at low temperature has revealed that, in general, the spectral function for the process in question is broadened asymmetrically through the polariton-polariton interactions.[8] Hence, for pure crystals and low temperatures, the dynamic behavior of the polariton-exciton and exciton-exciton interactions will govern the shape of the absorption bands.

The problem is formulated in Sec. II, where the total Hamiltonian is diagonalized via the Green's-function method. General expressions for the exciton and photon Green's functions are derived, respectively. The spin degeneracy is removed by the intermolecular interactions with the result of creating two excitation fields, which for convenience (though not very accurate), we shall call the singlet (+) and the triplet (−) exciton fields, respectively. The polarization operator for the photon field is coupled only through the Green's function, which describes the singlet exciton field.

The excitation spectrum is discussed in Sec. III in successive approximations. In the Hartree-Fock (HF) approximation and in the absence of the electromagnetic field, there are two frequency modes corresponding to the singlet and triplet excitons, respectively, which propagate through the crystal independently. The polariton spectrum in the HF approximation is identical to that described in the literature.[9–10]

A general discussion for the excitation spectrum caused by photon absorption is given in Sec. IV. The spectral function for the photon field is found to con-

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[6] R. E. Merrifield, P. Avakian, and R. P. Groff, Chem. Phys. Letters **3**, 155 (1969).
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[9] V. M. Agranovich, Zh. Eksperim. i Teor. Fiz. **37**, 430 (1959) [English transl.: Soviet Phys.—JETP **10**, 307 (1960)].
[10] C. Mavroyannis, J. Math. Phys. **8**, 1515 (1967).

sist of the superposition of symmetric and asymmetric Lorentzian lines provided that certain conditions are satisfied. It is shown that when we go beyond the HF approximation the singlet and the triplet exciton modes are no longer independent. As an example, the resonance Raman scattering spectrum of triplet excitons is considered. This is the polariton-triplet exciton resonance spectrum, where a polariton decays into two triplet excitons; it includes radiative processes as well as those resulting from the correlation between the radiation field and the intermolecular interactions. The corresponding resonance spectrum, when a singlet exciton decays into two triplet excitons, and vice versa, is discussed.

The excitation spectrum of triplet excitons is examined in Sec. V. The Raman resonance spectrum occurs whenever a triplet exciton decays into a triplet exciton and a polariton; a detailed discussion for the process in question is given. Far from resonance, the scattering amplitudes are derived for the physical process where a triplet exciton undergoes a transition to another triplet state, while a polariton is emitted.

II. FORMULATION OF PROBLEM

We consider a simple model of a molecular crystal, consisting of N neutral molecules in the static lattice of volume V, with one molecule per unit cell and with the valence band filled with electrons having opposite spin components. In a tight-binding model of a molecular crystal, an exciton may be viewed as an electron-hole pair tightly bound to one another, and the total exciton Hamiltonian may be taken as[1,9–11]

$$\begin{aligned}\mathcal{H}=E_0&+\sum_{\mathbf{k},\mu,\sigma}\Delta_\mu b_{\mu\sigma}^\dagger(\mathbf{k})b_{\mu\sigma}(\mathbf{k})+\sum_{\mathbf{k},\mu,\mu',\sigma,\sigma'}J_{0\mu,\mu'0}{}^{\sigma,\sigma'}(\mathbf{k})b_{\mu\sigma}^\dagger(\mathbf{k})b_{\mu'\sigma'}(\mathbf{k})\\&+\tfrac{1}{2}\sum_{\mathbf{k},\mu,\mu',\sigma,\sigma'}J_{00,\mu\mu'}{}^{\sigma,\sigma'}(\mathbf{k})[b_{\mu\sigma}(\mathbf{k})b_{\mu'\sigma'}(-\mathbf{k})+b_{\mu\sigma}^\dagger(\mathbf{k})b_{\mu'\sigma'}^\dagger(-\mathbf{k})]\\&+\frac{1}{\sqrt{N}}\sum_{\mathbf{k},\mathbf{q},\sigma,\sigma',\mu,\mu',\mu_1}J_{0\mu,\mu'\mu_1}{}^{\sigma,\sigma'}(\mathbf{k})[b_{\mu\sigma}^\dagger(\mathbf{q})b_{\mu'\sigma'}(\mathbf{k})b_{\mu_1\sigma}(\mathbf{q}-\mathbf{k})\\&+b_{\mu_1\sigma}^\dagger(\mathbf{q}+\mathbf{k})b_{\mu'\sigma'}^\dagger(\mathbf{k})b_{\mu\sigma}(\mathbf{q})]+\sum_{\mathbf{k},\lambda}ck\beta_\lambda^\dagger(\mathbf{k})\beta_\lambda(\mathbf{k})+\tfrac{1}{2}i\omega_p\sum_{\mathbf{k},\lambda,\mu,\sigma}\left(\frac{f_{0\mu}(\mathbf{k},\lambda)\Delta_\mu}{ck}\right)^{1/2}\tilde{b}_{\mu\sigma}(\mathbf{k})\tilde{\beta}_\lambda(\mathbf{k})\\&+\frac{i\omega_p}{N^{1/2}}\sum_{\mathbf{k},\mathbf{q},\lambda,\mu,\mu',\sigma}\left(\frac{f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\lambda)\Delta_{\mu'\mu}}{cq}\right)^{1/2}b_{\mu\sigma}^\dagger(\mathbf{k})b_{\mu'\sigma}(\mathbf{k}-\mathbf{q})\tilde{\beta}_\lambda(\mathbf{q})+\tfrac{1}{4}\omega_p^2\sum_{\mathbf{k},\lambda}(ck)^{-1}\tilde{\beta}_\lambda^\dagger(\mathbf{k})\tilde{\beta}_\lambda(\mathbf{k}),\end{aligned}\tag{1}$$

where

$$\Delta_\mu=\Delta_\mu{}^0+(2/N)\sum_{\mathbf{q},\mu'(\mu'\neq\mu)}J_{\mu\mu',\mu'\mu}{}^{\sigma,\sigma}(\mathbf{q}),$$

$$\tilde{b}_{\mu\sigma}(\mathbf{k})\equiv b_{\mu\sigma}(-\mathbf{k})-b_{\mu\sigma}^\dagger(\mathbf{k}),\quad\tilde{\beta}_\lambda(\mathbf{k})\equiv\beta_\lambda(\mathbf{k})+\beta_\lambda^\dagger(\mathbf{k}),\quad\Delta_{\mu'\mu}\equiv\Delta_{\mu'}-\Delta_\mu,\quad\hbar=1.\tag{2a}$$

The coupling function $J_{0\mu,\mu'0}{}^{\sigma,\sigma'}(\mathbf{k})$ consists of the Coulomb minus the exchange matrix elements between the two molecules located at the lattice sites $\mathbf{n}$ and $\mathbf{m}$ ($\neq\mathbf{n}$) with position vectors $\mathbf{r}_\mathrm{n}$ and $\mathbf{r}_\mathrm{m}$, respectively, i.e.,

$$\begin{aligned}J_{0\mu',\mu0}{}^{\sigma,\sigma'}(\mathbf{k})&=\sum_{(\mathbf{n}-\mathbf{m})}{}'[\langle\mathbf{n}0\sigma,\mathbf{m}\mu'\sigma'|V_{\mathbf{n},\mathbf{m}}|\mathbf{n}\mu\sigma,\mathbf{m}0\sigma'\rangle\\&\quad-\langle\mathbf{n}0\sigma,\mathbf{m}\mu'\sigma'|V_{\mathbf{n},\mathbf{m}}|\mathbf{m}0\sigma',\mathbf{n}\mu\sigma\rangle]\exp[i\mathbf{k}\cdot(\mathbf{r}_\mathrm{n}-\mathbf{r}_\mathrm{m})]\\&\equiv V_{0\mu',\mu0}{}^{\sigma,\sigma'}(\mathbf{k})-V_{0\mu',0\mu}{}^{\sigma,\sigma'}(\mathbf{k}).\end{aligned}\tag{2b}$$

The first five terms in (1) represent the bare exciton spectrum, the sixth term describes the free transverse electromagnetic field, while the exciton-photon interactions are expressed by the seventh and eighth terms; finally, in the last term we have neglected higher-order processes corresponding to photon-phonon scattering, because these terms become important only in the x-ray region of frequencies.[1,11] The compound index μ indicates the exciton band, the corresponding molecular term and the kind of mode, transverse or longitudinal, and σ is the spin component of an electron (↑ or ↓). $\Delta_\mu{}^0$ is the energy of excitation of the μth exciton band, that is independent of the wave vector $\mathbf{k}$, while the coupling functions $f_{0\mu}(\mathbf{k},\lambda)$, $f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\lambda)$, and ω_p denote the oscillator strengths for the allowed transitions in question and the plasma frequency, respectively. Explicit expressions for $\Delta_\mu{}^0$, the oscillator strengths and ω_p are given elsewhere.[10] The exciton operators $b_{\mu\sigma}^\dagger(\mathbf{k})$ and $b_{\mu\sigma}(\mathbf{k})$ create and annihilate an exciton in the $(\mathbf{k},\mu)$ excitation band and satisfy the commutation relation

$$[b_{\mu\sigma}(\mathbf{k}),b_{\mu'\sigma'}^\dagger(\mathbf{k}')]_-=(n_{\mathbf{k}0\sigma}-n_{\mathbf{k}\mu\sigma})\delta_{\mathbf{k}\mathbf{k}'}\delta_{\mu\mu'}\delta_{\sigma\sigma'},$$

where $n_{\mathbf{k}0\sigma}=\alpha_{\mathbf{k}0\sigma}^\dagger\alpha_{\mathbf{k}0\sigma}$ and $n_{\mathbf{k}\mu\sigma}=\alpha_{\mathbf{k}\mu\sigma}^\dagger\alpha_{\mathbf{k}\mu\sigma}$ are the occupation numbers for the holes (valence band) and the electrons in the $(\mathbf{k},\mu)$ and excitation band, respectively. $\beta_\lambda^\dagger(\mathbf{k})$ and $\beta_\lambda(\mathbf{k})$ are the creation and annihilation operators of photons with wave vector $\mathbf{k}$ and polar-

[11] L. N. Ovander, Fiz. Tverd. Tela **3**, 2394 (1961) [English transl.: Soviet Phys.—Solid State **3**, 1737 (1962)].

ization λ $(=1, 2)$, representing the two possible values of polarization perpendicular to the direction of propagation $\mathbf{k}$. Since we are concerned with the low-temperature spectrum of the Hamiltonian (1), it will be sufficient to assume that the exciton operators satisfy Bose statistics. In (1), we have retained only cubic anharmonic terms with respect to the exciton operators, while from the quartic terms we kept only the small correction that appears in the last term of (2a). For notational simplicity, only crystals having one molecule per unit cell are explicitly considered. The generalization to the case of crystals with many molecules per unit cell presents no problems; hence, physical effects like the Davydov splitting, etc., shall not be considered.

To study the excitation spectrum of (1), we introduced the retarded exciton Green's function[12] in a matrix form

$$\begin{aligned} G_\mu(\mathbf{k};t-t')&\equiv\langle\langle A_{\mu\sigma}(\mathbf{k},t);A_{\mu\sigma}{}^\dagger(\mathbf{k},t')\rangle\rangle \\ &=-i\theta(t-t')\langle[A_{\mu\sigma}(\mathbf{k},t),A_{\mu\sigma}{}^\dagger(\mathbf{k},t')]_-\rangle, \end{aligned} \quad (3a)$$

with the operator $A_{\mu\sigma}{}^\dagger(\mathbf{k},t)$ defined as

$$A_{\mu\sigma}{}^\dagger(\mathbf{k},t)=\begin{bmatrix} b_{\mu\uparrow}{}^\dagger(\mathbf{k},t) & b_{\mu\uparrow}(-\mathbf{k},t) \\ b_{\mu\downarrow}{}^\dagger(\mathbf{k},t) & b_{\mu\downarrow}(-\mathbf{k},t)\end{bmatrix}, \quad (3b)$$

where the angular brackets denote the average over the canonical ensemble appropriate to the total Hamiltonian $\mathcal{H}$; the factor $\theta(t)$ is the usual step function, and the operators $b_{\mu\sigma}{}^\dagger(\mathbf{k})$ and $b_{\mu\sigma}(\mathbf{k})$ are in the Heisenberg representation. In what follows, the time arguments of the operators have been suppressed for convenience. The Fourier transform of $G_\mu(\mathbf{k};t-t')$ with respect to the argument t satisfies the equation of motion

$$\begin{aligned} \omega G_\mu(\mathbf{k};\omega)&=\left(\frac{1}{2\pi}\right)\langle[A_{\mu\sigma}(\mathbf{k}),A_{\mu\sigma}{}^\dagger(\mathbf{k})]_-\rangle_{t=t'} \\ &\quad+\langle\langle[A_{\mu\sigma}(\mathbf{k}),\mathcal{H}]_-;A_{\mu\sigma}{}^\dagger(\mathbf{k})\rangle\rangle. \end{aligned} \quad (3c)$$

Using (1) and (3c), the equation of motion for the exciton Green's function $G_\mu(\mathbf{k};\omega)$ is found to be

$$G_\mu{}^{(0)-1}(\mathbf{k};\omega)G_\mu(\mathbf{k};\omega)=I+\langle\langle F_\mu(\mathbf{k});A_{\mu\sigma}{}^\dagger(\mathbf{k})\rangle\rangle. \quad (4)$$

The unperturbed Green's function $G_\mu{}^{(0)}(\mathbf{k};\omega)$ is given by

$$G_\mu{}^{(0)}(\mathbf{k};\omega) =\frac{1}{2\pi}\begin{bmatrix} \omega-R & -\hat{R} & -S & -\hat{S} \\ -\hat{R} & -\omega-R & -\hat{S} & -S \\ -S & -\hat{S} & \omega-R & -\hat{R} \\ -\hat{S} & -S & -\hat{R} & -\omega-R \end{bmatrix}^{-1}, \quad (5a)$$

where

$$\begin{aligned} R&\equiv R_{\mathrm{k}}(\omega)=\Delta_\mu+J_{0\mu,\mu0}{}^{\sigma,\sigma}(\mathbf{k})+L_{\mathrm{k}}(\omega), \\ \hat{R}&\equiv R_{\mathrm{k}}(\omega)=J_{00,\mu\mu}{}^{\sigma,\sigma}(\mathbf{k})-L_{\mathrm{k}}(\omega), \\ S&\equiv S_{\mathrm{k}}(\omega)=V_{0\mu,\mu0}{}^{\uparrow,\downarrow}(\mathbf{k})+L_{\mathrm{k}}(\omega), \\ \hat{S}&\equiv \hat{S}_{\mathrm{k}}(\omega)=V_{00,\mu\mu}{}^{\uparrow,\downarrow}(\mathbf{k})-L_{\mathrm{k}}(\omega), \\ L_{\mathrm{k}}(\omega)&=(\tfrac{1}{2}\omega_p{}^2)\sum_{\mu,\lambda}f_{0\mu}(\mathbf{k},\lambda)\Delta_\mu(\omega^2-c^2k^2-\omega_p{}^2)^{-1}. \end{aligned} \quad (5b)$$

The function $F_\mu(\mathbf{k})$ is

$$F_\mu(\mathbf{k})\equiv B_\mu(\mathbf{k})+C_\mu(\mathbf{k})+U_\mu(\mathbf{k}), \quad (5c)$$

where

$$\begin{aligned} B_\mu(\mathbf{k})&\equiv\frac{i\omega_p}{\sqrt{N}}\sum_{\mathrm{q},\lambda,\mu'}\left(\frac{f_{\mathrm{k}\mu,\mathrm{k-q}\mu'}(\mathbf{q}\lambda)\Delta_{\mu'\mu}}{cq}\right)^{1/2} \times\hat{B}(\mathbf{k}-\mathbf{q}\mu',\mathbf{q}\lambda), \\ C_\mu(\mathbf{k})&\equiv(1/\sqrt{N})\sum_{\mathrm{q},\mu',\mu_1}\Lambda_{\mathrm{k}}(\omega)\hat{C}(\mathbf{q},\mu_1,\mathbf{k}-\mathbf{q}\mu'), \\ U_\mu{}^\dagger(\mathbf{k})&=(1/\sqrt{N})\sum_{\mathrm{q}}\begin{bmatrix} J_{\mu\uparrow}{}^\dagger(\mathbf{k},\mathbf{q}) & J_{\mu\uparrow}(-\mathbf{k},-\mathbf{q}) \\ J_{\mu\downarrow}{}^\dagger(\mathbf{k},\mathbf{q}) & J_{\mu\downarrow}(-\mathbf{k}-\mathbf{q})\end{bmatrix}, \\ \hat{B}^\dagger(\mathbf{k}-\mathbf{q}\mu',\mathbf{q}\lambda)&=[b_{\mu'\uparrow}{}^\dagger(\mathbf{k}-\mathbf{q})\tilde{\beta}_\lambda{}^\dagger(\mathbf{q}) \\ &\quad-b_{\mu\uparrow}(\mathbf{k}-\mathbf{q})\tilde{\beta}_\lambda(\mathbf{q})\;b_{\mu'\downarrow}{}^\dagger(\mathbf{k}-\mathbf{q})\tilde{\beta}_\lambda{}^\dagger(\mathbf{q}) \\ &\quad-b_{\mu'\downarrow}{}^\dagger(\mathbf{k}-\mathbf{q})\tilde{\beta}_\lambda(\mathbf{q})], \\ \hat{C}^\dagger(\mathbf{q}\mu_1,\mathbf{k}-\mathbf{q}\mu') &=\begin{bmatrix} b_{\mu'\uparrow}{}^\dagger(\mathbf{k}-\mathbf{q})b_{\mu_1\uparrow}(-\mathbf{q}) & \\ -b_{\mu'}{}^\dagger(\mathbf{k}-\mathbf{q})b_{\mu_1\uparrow}(-\mathbf{q}) & b_{\mu'\downarrow}{}^\dagger(\mathbf{k}-\mathbf{q})b_{\mu_1\downarrow}(\mathbf{q}) \\ & -b_{\mu'\downarrow}{}^\dagger(\mathbf{k}-\mathbf{q})b_{\mu_1\downarrow}(-\mathbf{q})\end{bmatrix}, \\ J_{\mu\uparrow}(\mathbf{k},\mathbf{q})&=\sum_{\mu',\mu_1,\sigma}\{J_{0\mu',\mu_1\mu}{}^{\uparrow,\sigma}(\mathbf{q})b_{\mu'\uparrow}(\mathbf{k}-\mathbf{q}) \\ &\quad\times[b_{\mu_1\sigma}(\mathbf{q})+b_{\mu_1\sigma}{}^\dagger(-\mathbf{q})]+J_{0\mu',\mu\mu_1}{}^{\sigma,\uparrow} \\ &\quad\times(-\mathbf{k})b_{\mu_1\sigma}{}^\dagger(-\mathbf{q})b_{\mu'\sigma}(\mathbf{k}-\mathbf{q})\}, \\ \Lambda_{\mathrm{k}}(\omega)&=\omega_p{}^2\sum_\lambda[f_{0\mu}(\mathbf{k},\lambda)f_{\mathrm{q}\mu_1,\mathrm{k-q}\mu'}(-\mathbf{k},\lambda) \\ &\quad\times\Delta_\mu\Delta_{\mu'\mu_1}]^{1/2}(\omega^2-c^2k^2-\omega_p{}^2)^{-1}. \end{aligned} \quad (5d)$$

Considering the equation of motion for the Green's function $\langle\langle F_\mu(\mathbf{k});A_{\mu\sigma}{}^\dagger(\mathbf{k})\rangle\rangle$ with respect to the argument t' and substituting the resulting expression into (4), we obtain the Dyson equation

$$[G_\mu{}^{(0)-1}(\mathbf{k};\omega)-\bar{P}_\mu(\mathbf{k};\omega)]G_\mu(\mathbf{k};\omega)=I, \quad (6)$$

where the polarization operator $\bar{P}_\mu(\mathbf{k};\omega)$ is given by

$$\bar{P}_\mu(\mathbf{k};\omega)=P_\mu(\mathbf{k};\omega)[I+G_\mu{}^{(0)}(\mathbf{k};\omega)P_\mu(\mathbf{k};\omega)]^{-1} \quad (7)$$

and

$$P_\mu(\mathbf{k};\omega)=(2\pi)^2\langle\langle F_\mu(\mathbf{k});F_\mu{}^\dagger(\mathbf{k})\rangle\rangle. \quad (8)$$

[12] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

In the range of frequencies ω far from the zeros of the denominator appearing in the expression for the polarization operator (7), we may expand the denominator of (7) in a power series of $P_\mu(\mathbf{k};\omega)$ as

$$\bar{P}_\mu(\mathbf{k};\omega)\approx P_\mu(\mathbf{k};\omega)[1-G_\mu^{(0)}(\mathbf{k};\omega)P_\mu(\mathbf{k};\omega)+\cdots]. \quad (9)$$

In what follows, we shall retain only the first term in the expression (9). Then Dyson's equation (6) becomes

$$[G_\mu^{(0)-1}(\mathbf{k};\omega)-P_\mu(\mathbf{k};\omega)]G_\mu(\mathbf{k};\omega=I. \quad (10)$$

Taking the diagonal and nondiagonal elements of (10), we derive the expressions for the Green's functions

$$\begin{aligned}\langle\langle\tilde{b}_{\mu\uparrow}(\mathbf{k});\tilde{b}_{\mu\uparrow}{}^\dagger(\mathbf{k})\rangle\rangle &=\langle\langle\tilde{b}_{\mu\downarrow}(\mathbf{k});\tilde{b}_{\mu\downarrow}{}^\dagger(\mathbf{k})\rangle\rangle\\ &=\frac{1}{2\pi}\left(\frac{\bar{\Omega}_{\mu+}(\mathbf{k},\omega)}{\omega^2-\Omega_{\mu+}{}^2(\mathbf{k},\omega)}+\frac{\bar{\Omega}_{\mu-}(\mathbf{k},\omega)}{\omega^2-\Omega_{\mu-}{}^2(\mathbf{k},\omega)}\right), \quad (11)\\ \langle\langle\tilde{b}_{\mu\uparrow}(\mathbf{k});\tilde{b}_{\mu\downarrow}{}^\dagger(\mathbf{k})\rangle\rangle &=\langle\langle\tilde{b}_{\mu\downarrow}(\mathbf{k});\tilde{b}_{\mu\uparrow}{}^\dagger(\mathbf{k})\rangle\rangle\\ &=\frac{1}{2\pi}\left(\frac{\bar{\Omega}_{\mu+}(\mathbf{k},\omega)}{\omega^2-\Omega_{\mu+}{}^2(\mathbf{k},\omega)}-\frac{\bar{\Omega}_{\mu-}(\mathbf{k},\omega)}{\omega^2-\Omega_{\mu-}{}^2(\mathbf{k},\omega)}\right),\end{aligned}$$

where the following notation has been used:

$$\Omega_{\mu\pm}{}^2(\mathbf{k},\omega)\equiv\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)\hat{\Omega}_{\mu\pm}(\mathbf{k},\omega)\,, \quad (12)$$

$$\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)=\bar{\omega}_{\mu\pm}(\mathbf{k})+\langle\langle\phi_{\mu\pm}(\mathbf{k});\phi_{\mu\pm}{}^\dagger(\mathbf{k})\rangle\rangle\,, \quad (13)$$

$$\hat{\Omega}_{\mu\pm}(\mathbf{k},\omega)=\hat{\omega}_{\mu\pm}(\mathbf{k})+\langle\langle\theta_{\mu\pm}(\mathbf{k});\theta_{\mu\pm}{}^\dagger(\mathbf{k})\rangle\rangle+2(1\pm1)L_{\mathbf{k}}(\omega)\,, \quad (14)$$

$$\bar{\omega}_{\mu\pm}(\mathbf{k})=\Delta_\mu+J_{0\mu,\mu0}{}^{(\pm)}(\mathbf{k})+J_{00,\mu\mu}{}^{(\pm)}(\mathbf{k})\,, \quad (15)$$

$$\hat{\omega}_{\mu\pm}(\mathbf{k})=\Delta_\mu+J_{0\mu,\mu0}{}^{(\pm)}(\mathbf{k})-J_{00,\mu\mu}{}^{(\pm)}(\mathbf{k})\,,$$

$$J_{0\mu,\mu0}{}^{(\pm)}(\mathbf{k})\equiv J_{0\mu,\mu0}{}^{\sigma,\sigma}(\mathbf{k})\pm V_{0\mu,\mu0}{}^{\uparrow,\downarrow}(\mathbf{k})\,, \quad (16)$$

$$\begin{aligned}\phi_{\mu\pm}(\mathbf{k})=\frac{i\omega_p}{\sqrt{N}}\sum_{\mathbf{q},\lambda,\mu'}\left(\frac{f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\lambda)\Delta_{\mu'\mu}}{cq}\right)^{1/2}\xi_{\mu'\pm}(\mathbf{k}-\mathbf{q})\tilde{\beta}_\lambda(\mathbf{q})\pm\frac{1}{2\sqrt{N}}\sum_{\mathbf{q},\mu',\mu_1}\{J_{0\mu',\mu_1\mu}{}^{(+)}(\mathbf{q})\chi_{\mu_1+}(\mathbf{q})\chi_{\mu'\pm}(\mathbf{k}-\mathbf{q})\\ +J_{0\mu',\mu_1\mu}{}^{(-)}(\mathbf{q})\chi_{\mu_1-}(\mathbf{q})\chi_{\mu'\mp}(\mathbf{k}-\mathbf{q})+\tfrac{1}{2}J_{0\mu',\mu\mu_1}{}^{(\pm)}(-\mathbf{k})[\chi_{\mu_1+}(\mathbf{q})\chi_{\mu'\pm}(\mathbf{k}-\mathbf{q})+\chi_{\mu_1-}(\mathbf{q})\chi_{\mu'\mp}(\mathbf{k}-\mathbf{q})\\ +\xi_{\mu_1+}{}^\dagger(\mathbf{q})\xi_{\mu'\pm}(\mathbf{k}-\mathbf{q})+\xi_{\mu_1-}{}^\dagger(\mathbf{q})\xi_{\mu'\mp}(\mathbf{k}-\mathbf{q})]\}\,, \quad (17)\end{aligned}$$

$$\begin{aligned}\theta_{\mu\pm}(\mathbf{k})=\frac{i\omega_p}{\sqrt{N}}\sum_{\mathbf{q},\lambda,\mu'}\left(\frac{f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\lambda)\Delta_{\mu'\mu}}{cq}\right)^{1/2}\chi_{\mu'\pm}(\mathbf{k}-\mathbf{q})\tilde{\beta}_\lambda(\mathbf{q})\pm\frac{1}{2\sqrt{N}}\sum_{\mathbf{q},\mu',\mu_1}\{J_{0\mu',\mu_1\mu}{}^{(+)}(\mathbf{q})\xi_{\mu'\pm}(\mathbf{k}-\mathbf{q})\chi_{\mu_1+}(\mathbf{q})\\ +J_{0\mu',\mu_1\mu}{}^{(-)}(\mathbf{q})\xi_{\mu'\mp}(\mathbf{k}-\mathbf{q})\chi_{\mu_1-}(\mathbf{q})+\tfrac{1}{2}\Lambda_{\mathbf{k}}(\omega)[\chi_{\mu_1+}(\mathbf{q})\chi_{\mu'\pm}(\mathbf{k}-\mathbf{q})+\chi_{\mu_1-}(\mathbf{q})\chi_{\mu'\mp}(\mathbf{k}-\mathbf{q})\\ +\xi_{\mu_1+}{}^\dagger(\mathbf{q})\xi_{\mu'\pm}(\mathbf{k}-\mathbf{q})+\xi_{\mu_1-}{}^\dagger(\mathbf{q})\xi_{\mu'\mp}(\mathbf{k}-\mathbf{q})]\}\,, \quad (18)\end{aligned}$$

$$\xi_{\mu\pm}(\mathbf{k})\equiv\tilde{b}_{\mu\downarrow}(\mathbf{k})\pm\tilde{b}_{\mu\uparrow}(\mathbf{k});\quad \chi_{\mu\pm}(\mathbf{k})\equiv[b_{\mu\downarrow}(\mathbf{k})+b_{\mu\downarrow}{}^\dagger(-\mathbf{k})]\pm[b_{\mu\uparrow}(\mathbf{k})+b_{\mu\uparrow}{}^\dagger(-\mathbf{k})].$$

From (11) and (12) we derive the expression for the Green's function

$$\begin{aligned}g_{\mu\pm}(\mathbf{k},\omega)&=\langle\langle\xi_{\mu\pm}(\mathbf{k});\ \xi_{\mu\pm}{}^\dagger(\mathbf{k})\rangle\rangle\\ &=\frac{2}{\pi}\times\frac{\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)}{\omega^2-\Omega_{\mu\pm}{}^2(\mathbf{k},\omega)}\end{aligned} \quad (19)$$

which shall be needed later.

The Dyson equation for the photon Green's function

$$D(\mathbf{k};\omega)\equiv\langle\langle\tilde{\beta}_\lambda(\mathbf{k});\tilde{\beta}_\lambda{}^\dagger(\mathbf{k})\rangle\rangle$$

is easily derived by means of the Hamiltonian (1) in the form of

$$D(\mathbf{k};\omega)=D_{00}(\mathbf{k};\omega)[1+\Pi(\mathbf{k};\omega)D_{00}(\mathbf{k};\omega)]\,, \quad (20)$$

where $D_{00}(\mathbf{k},\omega)$ is the unperturbed photon Green's function

$$D_{00}(\mathbf{k};\omega)=(ck/\pi)(\omega^2-c^2k^2-\omega_p{}^2)^{-1}\,,$$

and the scattering function $\Pi(\mathbf{k};\omega)$ for the photon field is given by

$$\Pi(\mathbf{k};\omega)=(\pi^2\omega_p{}^2/ck)\sum_{\mu,\lambda}f_{0\mu}(\mathbf{k},\lambda)\Delta_\mu g_{\mu+}(\mathbf{k};\omega)\,. \quad (21)$$

In deriving (21) we have retained only terms which are linear with respect to the exciton operators. The polarization operator, $\tilde{\Pi}(\mathbf{k};\omega)$, and the scattering function $\Pi(\mathbf{k};\omega)$ are related by

$$\tilde{\Pi}(\mathbf{k};\omega)=\Pi(\mathbf{k};\omega)[1+D_{00}(\mathbf{k};\omega)\Pi(\mathbf{k},\omega)]^{-1}$$

or

$$\Pi(\mathbf{k};\omega)=\tilde{\Pi}(\mathbf{k};\omega)[1+D(\mathbf{k};\omega)\tilde{\Pi}(\mathbf{k},\omega)].$$

III. EXCITATION SPECTRUM

We shall now discuss the excitation spectrum of molecular crystals in successive approximations by using the general expressions for the Green's functions derived in the previous section.

A. HF Approximation

The unperturbed exciton spectrum is described by the Green's function (5a). In the range of wave vectors $\mathbf{k}$, where retardation may be neglected, $L_{\mathbf{k}}(\omega)=0$, the bare unperturbed exciton spectrum is derived from the expressions (11) and (12), which in the HF approximation give

$$\langle\langle\tilde{b}_{\mu\uparrow}(\mathbf{k});\tilde{b}_{\mu\uparrow}{}^{\dagger}(\mathbf{k})\rangle\rangle^{(0)}=\langle\langle\tilde{b}_{\mu\downarrow}(\mathbf{k});\tilde{b}_{\mu\downarrow}{}^{\dagger}(\mathbf{k})\rangle\rangle^{(0)}=\frac{1}{2\pi}\left(\frac{\bar{\omega}_{\mu+}(\mathbf{k})}{\omega^2-\omega_{\mu+}{}^2(\mathbf{k})}+\frac{\bar{\omega}_{\mu-}(\mathbf{k})}{\omega^2-\omega_{\mu-}{}^2(\mathbf{k})}\right),\tag{22a}$$

$$\langle\langle\tilde{b}_{\mu\uparrow}(\mathbf{k})\tilde{b}_{\mu\downarrow}{}^{\dagger}(\mathbf{k})\rangle\rangle^{(0)}=\langle\langle\tilde{b}_{\mu\downarrow}(\mathbf{k});\tilde{b}_{\mu\uparrow}{}^{\dagger}(\mathbf{k})\rangle\rangle^{(0)}=\frac{1}{2\pi}\left(\frac{\bar{\omega}_{\mu+}(\mathbf{k})}{\omega^2-\omega_{\mu+}{}^2(\mathbf{k})}-\frac{\bar{\omega}_{\mu-}(\mathbf{k})}{\omega^2-\omega_{\mu-}{}^2(\mathbf{k})}\right),\tag{22b}$$

where the energies of excitation $\omega_{\mu\pm}(\mathbf{k})$ are defined as

$$\omega_{\mu\pm}{}^2(\mathbf{k})=\bar{\omega}_{\mu\pm}{}^2(\mathbf{k})-\hat{\omega}_{\mu\pm}{}^2(\mathbf{k}).\tag{23}$$

Considering the expressions (15) and (16), we conclude that the energy $\omega_{\mu+}(\mathbf{k})$ arises from Coulomb as well as from exchange interactions, while $\omega_{\mu-}(\mathbf{k})$ only from exchange interactions between the electron-hole pairs; hence, $\omega_{\mu+}(\mathbf{k})$ and $\omega_{\mu-}(\mathbf{k})$ are the energies of excitation for the singlet and triplet excitons, respectively. The expression for $\omega_{\mu+}(\mathbf{k})$ is identical to that found in the literature.[9,10,13] Thus, as should be expected, in the HF approximation, the two energy modes $\omega_{\mu\pm}(\mathbf{k})$ propagate in the crystal independently. In this approximation, the Hamiltonian which gives rise to the excitation spectrum described by (22a) and (22b) may be written as

$$\mathcal{H}^0=E_0+\langle\mathcal{H}^0\rangle+\mathcal{H}_+{}^0+\mathcal{H}_-{}^0,\tag{24}$$

where

$$\langle\mathcal{H}^0\rangle=\tfrac{1}{2}\sum_{\mathbf{k},\mu}\{[\omega_{\mu+}(\mathbf{k})\eta_{\mu+}(\mathbf{k})-\Delta_\mu]+[\omega_{\mu-}(\mathbf{k})\eta_{\mu-}(\mathbf{k})-\Delta_\mu]\},\tag{25}$$

with $\eta_{\mu\pm}(\mathbf{k})=\coth\frac{1}{2}\beta\omega_{\mu\pm}(\mathbf{k})$, is the average energy of the exciton field. Here $\beta=(K_BT)^{-1}$, where K_B is Boltzmann's constant and T the absolute temperature. The expression (25) is derived from (1), (22a), and (22b) in the usual way,[10,13] and consists of the sum of the contributions of the two independent fields; the first term in (25) is in agreement with that derived in the literature.[13] Contributions arising from the mixing of different bands also can be included in the expressions for $\omega_{\mu\pm}(\mathbf{k})$.[13] In (24), $\mathcal{H}_+{}^0$ and $\mathcal{H}_-{}^0$ describe the singlet and triplet bare exciton spectrum, respectively, and they are given by

$$\mathcal{H}_\pm{}^{(0)}=\tfrac{1}{8}\sum_{\mathbf{k},\mu}[\bar{\omega}_{\mu\pm}(\mathbf{k})\chi_{\mu\pm}{}^{\dagger}(\mathbf{k})\chi_{\mu\pm}(\mathbf{k})+\hat{\omega}_{\mu\pm}(\mathbf{k})\xi_{\mu\pm}{}^{\dagger}(\mathbf{k})\xi_{\mu\pm}(\mathbf{k})].\tag{26}$$

We note that the singlet and triplet exciton fields are independent from one another, i.e., the operators $(\xi_{\mu+},\chi_{\mu+})$ and $(\xi_{\mu-},\chi_{\mu-})$ commute, $[\xi_{\mu+}(\mathbf{k}),\xi_{\mu-}(\mathbf{k})]_-=0$, $[\chi_{\mu+}(\mathbf{k}),\chi_{\mu-}(\mathbf{k})]_-=0$.

B. Polariton Spectrum (HF Approximation)

When $L_{\mathbf{k}}(\omega)$ is taken into consideration in the expression (5a) for $G_\mu{}^{(0)}(\mathbf{k};\omega)$, then the corresponding expressions derived from (11) and (12) in the HF approximation are

$$\langle\langle\tilde{b}_{\mu\uparrow}(\mathbf{k});\tilde{b}_{\mu\uparrow}{}^{\dagger}(\mathbf{k})\rangle\rangle_p{}^{(0)}=\langle\langle\tilde{b}_{\mu\downarrow}(\mathbf{k});\tilde{b}_{\mu\downarrow}{}^{\dagger}(\mathbf{k})\rangle\rangle_p{}^{(0)}=\tfrac{1}{4}[g_{\mu+}{}^{(0)}(\mathbf{k};\omega)+g_{\mu-}{}^{(0)}(\mathbf{k};\omega)],\tag{27a}$$

$$\langle\langle\tilde{b}_{\mu\uparrow}(\mathbf{k});\tilde{b}_{\mu\downarrow}{}^{\dagger}(\mathbf{k})\rangle\rangle_p{}^{(0)}=\langle\langle\tilde{b}_{\mu\downarrow}(\mathbf{k});\tilde{b}_{\mu\uparrow}{}^{\dagger}(\mathbf{k})\rangle\rangle_p{}^{(0)}=\tfrac{1}{4}[g_{\mu+}{}^{(0)}(\mathbf{k};\omega)-g_{\mu-}{}^{(0)}(\mathbf{k};\omega)],\tag{27b}$$

where

$$g_{\mu+}{}^0(\mathbf{k};\omega)=\frac{2}{\pi}\frac{(\omega^2-c^2k^2-\omega_p{}^2)\bar{\omega}_{\mu+}(\mathbf{k})}{[\omega^2-\omega_{\mu+}{}^2(\mathbf{k})][\omega^2\eta_0{}^2(\mathbf{k},\omega)-c^2k^2]},\tag{28}$$

$$g_{\mu-}{}^0(\mathbf{k};\omega)=\frac{2}{\pi}\frac{\bar{\omega}_{\mu-}(\mathbf{k})}{[\omega^2-\omega_{\mu-}{}^2(\mathbf{k})]},\tag{29}$$

and the frequency and wave-vector-dependent index of refraction $\eta_0(\mathbf{k},\omega)$ is

$$\eta_0{}^2(\mathbf{k},\omega)=1+\alpha_0(\mathbf{k},\omega),\tag{30a}$$

$$\alpha_0(\mathbf{k},\omega)=2\omega_p{}^2\sum_{\mu,\lambda}\frac{f_{0\mu}(\mathbf{k},\lambda)}{\omega_{\mu+}{}^2(\mathbf{k})-\omega^2},\qquad \tilde{f}_{0\mu}(\mathbf{k},\lambda)\equiv\frac{f_{0\mu}(\mathbf{k},\lambda)\Delta_\mu}{\hat{\omega}_{\mu+}(\mathbf{k})}.\tag{30b}$$

In this case, we have again two modes, the polariton mode and the triplet exciton mode, propagating in the crystal independently. We note that the electromagnetic field is not coupled with the triplet exciton field described by the Green's function $g_{\mu-}{}^0(\mathbf{k};\omega)$. Substitution of (28) into (21) and (20) yields

$$D_0(\mathbf{k};\omega)=(ck/\pi)[\omega^2\eta_0{}^2(\mathbf{k},\omega)-c^2k^2]^{-1}.\tag{31a}$$

The expressions (28), (30), and (31a) are identical with those derived in previous studies.[1,9,10] In this approxi-

[13] C. Mavroyannis, J. Chem. Phys. 42, 1772 (1965).

mation, the crystal Hamiltonian may be written in the polariton representation as

$$\mathcal{H}_p{}^0 = E_0 + \langle\mathcal{H}_p{}^0\rangle + \mathcal{H}_-{}^0 + \sum_{\mathbf{k},\rho} \omega_\rho(\mathbf{k})\zeta_\rho{}^\dagger(\mathbf{k})\zeta_\rho(\mathbf{k}). \quad (31b)$$

The polariton energy $\omega_\rho(\mathbf{k})$ is determined by the ρth root of the equation

$$\omega^2\eta_0{}^2(\mathbf{k},\omega) - c^2k^2 = 0, \quad (31c)$$

and $\zeta_\rho{}^\dagger(\mathbf{k})$, $\zeta_\rho(\mathbf{k})$ are the polariton creation and annihilation operators. $\langle\mathcal{H}_p{}^0\rangle$ is the average energy of the polariton field and its explicit form is given elsewhere.[1,10]

IV. ABSORPTION OF ELECTROMAGNETIC WAVES

The Green's functions $g_{\mu\pm}(\mathbf{k};\omega)$ given by (19) may be written as

$$g_{\mu+}(\mathbf{k};\omega) = \frac{2}{\pi}\frac{(\omega^2 - c^2k^2 - \omega_p{}^2)\bar{\Omega}_{\mu+}(\mathbf{k},\omega)}{[\omega^2 - \mathcal{E}_{\mu+}{}^2(\mathbf{k},\omega)][\omega^2\eta^2(\mathbf{k},\omega) - c^2k^2]}, \quad (32)$$

$$g_{\mu-}(\mathbf{k};\omega) = \frac{2}{\pi}\frac{\bar{\Omega}_{\mu-}(\mathbf{k},\omega)}{[\omega^2 - \Omega_{\mu-}{}^2(\mathbf{k},\omega)]}, \quad (33)$$

where

$$\mathcal{E}_{\mu\pm}{}^2(\mathbf{k},\omega) \equiv \bar{\Omega}_{\mu+}(\mathbf{k},\omega)\tilde{\Omega}_{\mu+}(\mathbf{k},\omega), \quad (34)$$

$$\tilde{\Omega}_{\mu\pm}(\mathbf{k},\omega) = \hat{\omega}_{\mu\pm}(\mathbf{k}) + \langle\langle\theta_{\mu\pm}(\mathbf{k});\theta_{\mu\pm}{}^\dagger(\mathbf{k})\rangle\rangle, \quad (35)$$

and the frequency and wave-vector-dependent index of refraction $\eta(\mathbf{k},\omega)$ is defined by

$$\eta^2(\mathbf{k},\omega) = 1 - \frac{\omega_p{}^2}{\omega^2} + 2\frac{\omega_p{}^2}{\omega^2}\sum_{\mu,\lambda}\frac{f_{0\mu}(\mathbf{k},\lambda)\Delta_\mu\bar{\Omega}_{\mu+}(\mathbf{k},\omega)}{\mathcal{E}_{\mu+}{}^2(\mathbf{k},\omega) - \omega^2}. \quad (36a)$$

Substituting (32) into (21) and making use of (20), we obtain the photon Green's function as

$$D(\mathbf{k};\omega) = (ck/\pi)[\omega^2\eta^2(\mathbf{k},\omega) - c^2k^2]^{-1}. \quad (36b)$$

We remark that when the triplet exciton field is completely ignored in the expressions for $\eta^2(\mathbf{k},\omega)$, then the Green's functions (32) and (36a) are reduced to those derived in I. The scattering function $\Pi(\mathbf{k};\omega)$ is related to the dielectric function $\epsilon(\mathbf{k},\omega)$, for an isotropic medium, by[1]

$$\omega^2[\epsilon(\mathbf{k},\omega) - \eta_\infty{}^2] = -(ck/\pi)\Pi(\mathbf{k};\omega), \quad (37a)$$

where

$$\eta_\infty{}^2 = 1 - \omega_p{}^2/\omega^2.$$

If we make use of (21), (32), and (36a) the expression (37a) becomes

$$\left(\frac{\epsilon(\mathbf{k},\omega) - \eta_\infty{}^2}{\eta^2(\mathbf{k},\omega) - \eta_\infty{}^2}\right) = \frac{D(\mathbf{k};\omega)}{D_{00}(\mathbf{k};\omega)}. \quad (37b)$$

Equation (37b) indicates that the dielectric function is equal to the square of the index of refraction only when the perturbed photon Green's function is replaced by its unperturbed expression. In any other case, it is given by

$$\epsilon(\mathbf{k},\omega) = \eta^2(\mathbf{k},\omega) - \frac{\omega^2[\eta^2(\mathbf{k},\omega) - \eta_\infty{}^2]}{[\omega^2\eta^2(\mathbf{k},\omega) - c^2k^2]}. \quad (37c)$$

We refer to I for details concerning the expression (37c). Having derived the general expressions for the Green's functions given by (32), (33), and (36b), we will discuss now specific physical processes caused by photon absorption.

A. Photon Field

The spectral function for the photon field is

$$J(\mathbf{k},\omega) = -2(e^{\beta\omega} - 1)^{-1}\,\mathrm{Im}D(\mathbf{k};\omega). \quad (38)$$

Substituting the imaginary part of (36b) into (38), we obtain

$$J(\mathbf{k},\omega) = \frac{2ck}{\pi}(e^{\beta\omega} - 1)^{-1} \times \frac{\gamma_{\mu+}(\mathbf{k},\omega) + [\omega^2\,\mathrm{Re}\eta^2(\mathbf{k},\omega) - c^2k^2]\hat{\gamma}_{\mu+}(\mathbf{k},\omega)}{[\omega^2\,\mathrm{Re}\eta^2(\mathbf{k},\omega) - c^2k^2]^2 + [\gamma_{\mu+}(\mathbf{k},\omega)]^2}, \quad (39)$$

where

$$\gamma_{\mu+}(\mathbf{k},\omega) = \alpha(\mathbf{k},\omega)\omega_{\mu+}(\mathbf{k})\,\mathrm{Im}\bar{\Omega}_{\mu+}(\mathbf{k},\omega) + (\omega^2 - c^2k^2 - \omega_p{}^2)\hat{\gamma}_{\mu+}(\mathbf{k},\omega), \quad (40)$$

$$\hat{\gamma}_{\mu+}(\mathbf{k},\omega) = [\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)\,\mathrm{Im}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega) + \mathrm{Re}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)\,\mathrm{Im}\bar{\Omega}_{\mu+}(\mathbf{k},\omega] \times [\epsilon_{\mu+}{}^2(\mathbf{k},\omega) - \omega^2]^{-1}, \quad (41)$$

$$\alpha(\mathbf{k},\omega) = 2\omega_p{}^2\sum_{\mu,\lambda}\frac{f_{0\mu}(\mathbf{k},\lambda)}{\epsilon_{\mu+}{}^2(\mathbf{k},\omega) - \omega^2}, \quad (42)$$

$$\epsilon_{\mu\pm}{}^2(\mathbf{k},\omega) = \mathrm{Re}\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)\,\mathrm{Re}\tilde{\Omega}_{\mu\pm}(\mathbf{k},\omega) - \mathrm{Im}\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)\,\mathrm{Im}\tilde{\Omega}_{\mu\pm}(\mathbf{k},\omega). \quad (43)$$

The expressions for $\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)$, $\mathrm{Im}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)$, and $\mathrm{Re}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)$ $\mathrm{Im}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)$ are determined by the real and imaginary parts of (13) and (35), respectively.

The spectral function (39) consists of two terms. The first term describes an absorption band which is a symmetric Lorentzian line peaked at frequencies $\omega = \omega_\rho(\mathbf{k})$, where the energy of excitation $\omega_\rho(\mathbf{k})$ is determined by the ρth root of the secular equation

$$\omega^2\,\mathrm{Re}\eta^2(\mathbf{k},\omega) - c^2k^2 = 0, \quad (44)$$

provided that in the neighborhood of these frequencies the functions $\gamma_{\mu+}(\mathbf{k},\omega)$ and $\mathrm{Re}\eta^2(\mathbf{k},\omega)$ vary slowly with ω. In this case, the half-width of the absorption band is of the order of $|\gamma_{\mu+}(\mathbf{k},\omega_\rho(\mathbf{k}))|/2ck$ in energy units, provided that the frequency $\omega=\omega_\rho(\mathbf{k})$ satisfies the arguments of the δ functions appearing in the expressions for $\mathrm{Im}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)$ and $\mathrm{Im}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)$, a condition that is required for $\gamma_{\mu+}(\mathbf{k},\omega_\rho(\mathbf{k}))\neq 0$. The second term in (39) represents an asymmetric Lorentzian line for frequencies $\omega\neq\omega_\rho(\mathbf{k})$. Away from the center of the peak $\omega=\omega_\rho(\mathbf{k})$, the effect of the second term in (39) is to broaden the profile of the absorption line and, hence, the spectrum of (39) may be thought of as consisting of the superposition of symmetric and asymmetric Lorentizian lines. The maximum frequencies of the function (39) are determined from the solutions of the equation

$$\frac{\partial}{\partial\omega^2}\left(\frac{\gamma_{\mu+}(\mathbf{k},\omega)+[\omega^2\,\mathrm{Re}\eta^2(\mathbf{k},\omega)-c^2k^2]\hat{\gamma}_{\mu+}(\mathbf{k},\omega)}{[\omega^2\,\mathrm{Re}\eta^2(\mathbf{k},\omega)-c^2k^2]^2+[\gamma_{\mu+}(\mathbf{k},\omega)]^2}\right)=0\,. \quad (45)$$

If we make the assumption that at some frequencies $\omega=\nu_{\mathbf{k}\rho}$, which are solutions of (45), the functions $\gamma_{\mu+}(\mathbf{k},\nu_{\mathbf{k}\rho})\equiv\gamma$ and $\hat{\gamma}_{\mu+}(\mathbf{k},\nu_{\mathbf{k}\rho})\equiv\hat{\gamma}$ may be considered as constants then (45) gives

$$\nu_{\mathbf{k}\rho}{}^2\,\mathrm{Re}\eta^2(\mathbf{k},\nu_{\mathbf{k}\rho})-c^2k^2=(\gamma/\hat{\gamma})[-1\pm\sqrt{(1+\hat{\gamma}^2)}]\,. \quad (46)$$

The solutions of Eq. (46) determine the frequencies $\nu_{\mathbf{k}\rho}$. At $\omega=\nu_{\mathbf{k}\rho}$ and $\hat{\gamma}\neq 0$, the spectral function is

$$J(\mathbf{k},\nu_{\mathbf{k}\rho})=(ck/\pi)(e^{\beta\nu_{\mathbf{k}\rho}}-1)^{-1}\times(\hat{\gamma}^2/\gamma)[-1\pm\sqrt{(1+\hat{\gamma}^2)}]^{-1}, \quad (47)$$

where the height of the absorption band is given by

$$ck(\hat{\gamma}^2/\gamma)[-1\pm\sqrt{(1+\hat{\gamma}^2)}]^{-1}, \quad (48)$$

while the energy half-width $W_{\mathbf{k}}(\nu_{\mathbf{k}\rho})$ is of the order of

$$|W_{\mathbf{k}}(\nu_{\mathbf{k}\rho})|\approx(\gamma/\hat{\gamma}^2)[-1\pm\sqrt{(1+\hat{\gamma}^2)}]/ck\,. \quad (49)$$

We remark that the function $\hat{\gamma}_{\mu+}(\mathbf{k},\omega)$ has been overlooked in I, and only the first term in (40) has been considered. In fact, the function $\hat{\gamma}_{\mu+}(\mathbf{k},\omega)$ causes not only asymmetry in the spectral line of (39) but also makes a contribution to the expression for $\gamma_{\mu+}(\mathbf{k},\omega)$ in (40). To see this, we rewrite $\gamma_{\mu+}(\mathbf{k},\omega)$ as

$$\gamma_{\mu+}(\mathbf{k},\omega)=\alpha(\mathbf{k},\omega)\omega_{\mu+}(\mathbf{k})\,\mathrm{Im}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)+\left(1-\frac{d\omega^2}{d\omega^2}\,\mathrm{Re}\eta^2(\mathbf{k},\omega)\right)[\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)\,\mathrm{Im}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)+\mathrm{Re}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)\,\mathrm{Im}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)]\,. \quad (50)$$

The spectral function (39) can be used to describe the excitation spectrum arising from the physical process of polariton-polariton scattering, where the incident photon or polariton decays into two polaritons. In this case, the operators $\chi_{\mu+}(\mathbf{k})$, $\xi_{\mu+}(\mathbf{k})$, and $\tilde{\beta}_\lambda(\mathbf{k})$ appearing in the expressions for $\bar{\Omega}_{\mu+}(\mathbf{k},\omega)$ and $\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)$, after discarding all terms that correspond to the triplet exciton field, have to be transformed into the polariton representation. Then the resulting expressions for the Green's functions are easily evaluated in the HF approximation by means of the polariton Hamiltonian (31b). The final result, for the excitation spectrum corresponding to the resonance Raman scattering of polaritons, is identical to that derived in our earlier work.[8]

In the limiting case when the functions $\gamma_{\mu+}(\mathbf{k},\omega)$ and $\hat{\gamma}_{\mu+}(\mathbf{k},\omega)$ go to zero, then the spectral function $J(\mathbf{k},\omega)$ as a δ function distribution, i.e.,

$$J(\mathbf{k},\omega)\approx(2ck)(e^{\beta\omega}-1)^{-1}\delta[\omega^2\eta^2(\mathbf{k},\omega)-c^2k^2]\,,$$

$\gamma_{\mu+}(\mathbf{k},\omega)\rightarrow 0$ and $\hat{\gamma}_{\mu+}(\mathbf{k},\omega)\rightarrow 0$. In this case the excitation spectrum is determined by the roots of the equation

$$\omega^2\eta^2(\mathbf{k},\omega)-c^2k^2=0\,,$$

where $\eta^2(\mathbf{k},\omega)$ is given by (36) and is a real quantity.

B. Resonance Raman Scattering of Triplet Excitons

We wish now to study the resonance process, where the incident photon decays into two triplet excitons. In this case the functions $\gamma_{\mu+}{}^t(\mathbf{k},\omega)$ and $\hat{\gamma}_{\mu+}{}^t(\mathbf{k},\omega)$ are given by the expressions (40) and (41), where the functions $\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)$ and $\mathrm{Re}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)$ are determined by the real parts of (13) and (35), respectively, while the expressions for $\mathrm{Im}\bar{\Omega}_{\mu+}{}^t(\mathbf{k},\omega)$ and $\mathrm{Im}\tilde{\Omega}_{\mu+}{}^t(\mathbf{k},\omega)$ are

$$\mathrm{Im}\bar{\Omega}_{\mu+}{}^t(\mathbf{k},\omega)=\mathrm{Im}\langle\langle\phi_{\mu+}{}^t(\mathbf{k});\phi_{\mu+}{}^{t\dagger}(\mathbf{k})\rangle\rangle\,, \quad (51)$$

$$\mathrm{Im}\tilde{\Omega}_{\mu+}{}^t(\mathbf{k},\omega)=\mathrm{Im}\langle\langle\theta_{\mu+}{}^t(\mathbf{k});\theta_{\mu+}{}^{t\dagger}(\mathbf{k})\rangle\rangle\,, \quad (52)$$

$$\phi_{\mu+}{}^t(\mathbf{k})=(1/4\sqrt{N})\sum_{\mathbf{q},\mu',\mu_1}\{J_{0\mu',\mu\mu_1}{}^{(+)}(-\mathbf{k})[\chi_{\mu_1-}{}^\dagger(\mathbf{q})\chi_{\mu'-}(\mathbf{k}-\mathbf{q})+\xi_{\mu_1-}{}^\dagger(\mathbf{q})\xi_{\mu'-}(\mathbf{k}-\mathbf{q})]+2J_{0\mu',\mu_1\mu}{}^{(-)}(\mathbf{q})\chi_{\mu_1-}{}^\dagger(\mathbf{q})\chi_{\mu'-}(\mathbf{k}-\mathbf{q})\}\,, \quad (53a)$$

$$\theta_{\mu+}{}^t(\mathbf{k})=(1/2\sqrt{N})\sum_{\mathbf{q},\mu',\mu_1}\Lambda_{\mathbf{k}}(\omega)[\chi_{\mu_1-}{}^\dagger(\mathbf{q})\chi_{\mu'-}(\mathbf{k}-\mathbf{q})+\xi_{\mu_1-}{}^\dagger(\mathbf{q})\xi_{\mu'-}(\mathbf{k}-\mathbf{q})]+(1/2\sqrt{N})\sum_{\mathbf{q},\mu_1,\mu'}J_{0\mu',\mu_1\mu}{}^{(-)}(\mathbf{q})\xi_{\mu'-}(\mathbf{k}-\mathbf{q})\chi_{\mu_1-}(\mathbf{q})\,. \quad (53b)$$

The Green's functions appearing in (51) and (52) can be easily evaluated in the HF approximation by means of the Hamiltonian $\mathcal{H}_-^0$ given by (26). We find

$$\mathrm{Im}\bar{\Omega}_{\mu+}{}^t(\mathbf{k},\omega)=(1/4N)\sum_{\mathbf{q},\mu',\mu_1}|J_{0\mu',\mu\mu_1}{}^{(+)}(-\mathbf{k})[\bar{\omega}_{\mu_1}{}^{1/2}(\mathbf{q})\bar{\omega}_{\mu'-}{}^{1/2}(\mathbf{k}-\mathbf{q})+\hat{\omega}_{\mu_1-}{}^{1/2}(\mathbf{q})\hat{\omega}_{\mu'-}{}^{1/2}(\mathbf{k}-\mathbf{q})]$$
$$+[J_{0\mu',\mu_1\mu}{}^{(-)}(\mathbf{q})+J_{0\mu_1,\mu'\mu}{}^{(-)}(\mathbf{k}-\mathbf{q})]\hat{\omega}_{\mu_1-}{}^{1/2}(\mathbf{q})\hat{\omega}_{\mu'-}{}^{1/2}(\mathbf{k}-\mathbf{q})|^2$$
$$\times[\omega_{\mu'-}(\mathbf{k}-\mathbf{q})\omega_{\mu_1-}(\mathbf{q})]^{-1}\,\mathrm{Im}G_-{}^t(\mathbf{q}\mu_1,\,\mathbf{k}-\mathbf{q}\mu';\,\omega)\,, \quad (54)$$

$$\mathrm{Im}\tilde{\Omega}_{\mu+}{}^t(\mathbf{k},\omega)=(1/4N)\sum_{\mathbf{q},\lambda,\mu',\mu_1}|\bar{\Lambda}_{\mathbf{k}}(\omega)+J_{0\mu',\mu_1\mu}{}^{(-)}(\mathbf{q})+J_{0\mu_1,\mu'\mu}{}^{(-)}(\mathbf{k}-\mathbf{q})|^2\,\mathrm{Im}G_-{}^t(\mathbf{q}\mu_1,\,\mathbf{k}-\mathbf{q}\mu';\,\omega)\,, \quad (55)$$

where

$$\bar{\Lambda}_{\mathbf{k}}(\omega)=(\sqrt{2}/2)\Lambda_{\mathbf{k}}(\omega)[\bar{\omega}_{\mu_1}{}^{1/2}{}_-(\mathbf{q})\bar{\omega}_{\mu'-}{}^{1/2}(\mathbf{k}-\mathbf{q})+\hat{\omega}_{\mu_1-}{}^{1/2}(\mathbf{q})\hat{\omega}_{\mu'-}{}^{1/2}(\mathbf{k}-\mathbf{q})]/\omega_{\mu_1-}{}^{1/2}(\mathbf{q})\omega_{\mu'-}{}^{1/2}(\mathbf{k}-\mathbf{q})\,,$$

$$G_-{}^t(\mathbf{q}\mu_1,\,\mathbf{k}-\mathbf{q}\mu';\,\omega)=\frac{2}{\pi}\left((\eta_{\mathbf{q}\mu_1-}+\eta_{\mathbf{k}-\mathbf{q}\mu'-})\frac{[\omega_{\mu_1-}(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]}{\omega^2-[\omega_{\mu_1-}(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]^2}\right.$$
$$\left.+(\eta_{\mathbf{k}-\mathbf{q}\mu'-}-\eta_{\mathbf{q}\mu_1-})\frac{[\omega_{\mu_1-}(\mathbf{q})-\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]}{\omega^2-[\omega_{\mu_1-}(\mathbf{q})-\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]^2}\right)\,. \quad (56)$$

The function $G_-{}^t(\mathbf{q}\mu_1,\,\mathbf{k}-\mathbf{q}\mu';\,\omega)$ describes the physical process of Raman scattering of triplet excitons. Its real part is given by the principal value of (56), while its imaginary part is

$$\mathrm{Im}G_-{}^t(\mathbf{q}\mu_1,\,\mathbf{k}-\mathbf{q}\mu';\,\omega)=(\eta_{\mathbf{q}\mu_1-}+\eta_{\mathbf{k}-\mathbf{q}\mu'-})\{\delta[\omega-\omega_{\mu_1-}(\mathbf{q})-\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]-\delta[\omega+\omega_{\mu_1-}(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}+\mathbf{q})]\}$$
$$+(\eta_{\mathbf{k}-\mathbf{q}\mu'-}-\eta_{\mathbf{q}\mu_1-})\{\delta[\omega-\omega_{\mu_1-}(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]-\delta[\omega+\omega_{\mu_1-}(\mathbf{q})-\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]\}\,, \quad (57)$$

with $\eta_{\mathbf{q}\mu_1-}=\coth\frac{1}{2}\beta\omega_{\mu_1-}(\mathbf{q})$. The two terms in (57) represent the Stokes and anti-Stokes components of resonance Raman scattering of triplet excitons. The spectral function for the process in question is described by

$$J^t(\mathbf{k},\omega)=\frac{2ck}{\pi}(e^{\beta\omega}-1)^{-1}\frac{\gamma_{\mu+}{}^t(\mathbf{k},\omega)+[\omega^2\,\mathrm{Re}\eta^2(\mathbf{k},\omega)-c^2k^2]\hat{\gamma}_{\mu+}{}^t(\mathbf{k},\omega)}{[\omega^2\,\mathrm{Re}\eta^2(\mathbf{k},\omega)-c^2k^2]^2+[\gamma_{\mu+}{}^t(\mathbf{k},\omega)]^2}\,. \quad (58)$$

The expressions for $\gamma_{\mu+}{}^t(\mathbf{k},\omega)$ and $\hat{\gamma}_{\mu+}{}^t(\mathbf{k},\omega)$ are greatly simplified in the case when the exchange interactions appearing in (54) and (55) are small in comparison with the Coulomb ones and, hence, can be neglected. Then taking $\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)\sim\mathrm{Re}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)\sim\omega_{\mu+}(\mathbf{k})$ and retaining only the first term in (55), we have

$$|\gamma_{\mu+}{}^t(\mathbf{k},\omega)|\approx(\omega_p{}^2/4N)\sum_{\mathbf{q},\mu_1,\mu',\lambda}[f_{\mathbf{q},\mu_1,\mathbf{k}-\mathbf{q}\mu'}(-\mathbf{k},\,\lambda)\Delta_{\mu'\mu_1}]\,\mathrm{Im}G_-{}^t(\mathbf{q}\mu_1,\,\mathbf{k}-\mathbf{q}\mu';\,\omega)$$
$$+\left[\frac{d\omega^2}{d\omega^2}\,\mathrm{Re}\eta^2(\mathbf{k},\omega)-1\right]\omega_{\mu+}(\mathbf{k})\,\mathrm{Im}\bar{\Omega}_{\mu+}{}^t(\mathbf{k},\omega)\,, \quad (59a)$$

$$\hat{\gamma}_{\mu+}{}^t(\mathbf{k},\omega)\approx\left(\frac{d\omega^2}{d\omega^2}\,\mathrm{Re}\eta^2(\mathbf{k},\omega)-1\right)^{-1}\frac{1}{8N}\sum_{\mathbf{q}}\alpha_{\mathbf{k}\mu+}(\mathbf{q},\omega)\Delta_{\mu'\mu_1}\,\mathrm{Im}G_-{}^t(\mathbf{q}\mu_1,\,\mathbf{k}-\mathbf{q}\mu';\,\omega)$$
$$+\omega_{\mu+}(\mathbf{k})[\epsilon_{\mu+}{}^2(\mathbf{k},\omega)-\omega^2]^{-1}\,\mathrm{Im}\bar{\Omega}_{\mu+}{}^t(\mathbf{k},\omega)\,, \quad (59b)$$

with

$$\alpha_{\mathbf{k}\mu+}(\mathbf{q},\omega)=2\omega_p{}^2\sum_{\mu_1,\mu'}f_{\mathbf{q}\mu_1,\mathbf{k}-\mathbf{q}\mu'}(-\mathbf{k},\,\lambda)/[\omega^2-\epsilon_{\mu+}{}^2(\mathbf{k},\omega)]\,. \quad (59c)$$

The first terms in (59a) and (59b) result from the first term of (55) and represent the radiative transition between the states $(\mathbf{q},\,\mu_1-)$ and $(\mathbf{k}-\mathbf{q},\,\mu'-)$ through the exchange of the photon $(\mathbf{k},\lambda)$. The second term in (59a) arises from the correlation between the electromagnetic field and the intermolecular interactions, while the corresponding term in (59b) has pure intermolecular character. A further approximation can be made in (59) by replacing $\epsilon_{\mu+}(\mathbf{k},\omega)$ by its unperturbed value $\omega_{\mu+}(\mathbf{k})$.

The maximum frequency $\nu_{\mathbf{k}\rho}$, and the spectral width for the spectrum of (58) are expressed by (46) and (49), respectively, with $\gamma\equiv\gamma_{\mu+}{}^t(\mathbf{k},\nu_{\mathbf{k}\rho})$ and $\hat{\gamma}\equiv\hat{\gamma}_{\mu+}{}^t(\mathbf{k},\nu_{\mathbf{k}\rho})$ determined by (59), provided that the frequency $\nu_{\mathbf{k}\rho}$ satisfies the arguments of the δ functions appearing in (57), i.e.,

$$\nu_{\mathbf{k}\rho}=\pm[\omega_{\mu_1-}(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]\,. \quad (60)$$

In writing (60) we have discarded the second term in (57), because it is practically zero even at elevated temperatures. The relation (60) indicates that the polariton $\nu_{\mathbf{k}\rho}$ decays into two triplet excitons with energies $\omega_{\mu_1-}(\mathbf{q})$ and $\omega_{\mu'-}(\mathbf{k}-\mathbf{q})$, respectively; the inverse process also holds, where two triplet excitons with energies $\omega_{\mu_1-}(\mathbf{q})$ and $\omega_{\mu'-}(\mathbf{k}-\mathbf{q})$ recombine to form the polariton $\nu_{\mathbf{k}\rho}$. The two terms in (59a) are proportional to the square and sixth power of the electronic charge, respectively, and hence, the first term dominates. The multiplicative factor, $[(d\omega^2/d\omega^2)\eta^2(\mathbf{k},\omega)-1]$, in the second term, indicates that there is an enhancement in the damping function whenever, for a given frequency,

$$(d\omega^2/d\omega^2)\ \mathrm{Re}\eta^2(\mathbf{k},\omega)>2\,.$$

In view of (60), the enhancement occurs when the frequency $\omega=\nu_{\mathbf{k}p}=\omega_{\mu_1-}(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})$ is close to the frequency $\epsilon_{\mu+}(\mathbf{k},\nu_{\mathbf{k}p})$ or approximately to its unperturbed value $\omega_{\mu+}(\mathbf{k})$. The same conclusion was derived by Knox and Swenberg[14] in their qualitative treatment of the physical process leading to the second term in (59a). The limiting case when the frequency $\omega_{\mu_1-}(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})$ becomes exactly equal to $\omega_{\mu+}(\mathbf{k})$ will be dealt with in Sec. IV C.

C. Bare Exciton Field

In the range of wave vectors $\mathbf{k}$, where retardation effects may be neglected, the spectral function for the bare exciton field is

$$\begin{aligned}J_{\mu\pm}(\mathbf{k},\omega)&=-2(e^{\beta\omega}-1)^{-1}\,\mathrm{Im}g_{\mu\pm}{}^{b}(\mathbf{k},\omega)\\&=\left(\frac{2}{\pi}\right)\mathrm{Re}\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)(e^{\beta\omega}-1)^{-1}\\&\quad\times\frac{\Gamma_{\mu\pm}(\mathbf{k},\omega)+[\omega^2-\epsilon_{\mu\pm}{}^2(\mathbf{k},\omega)]\hat{\Gamma}_{\mu\pm}(\mathbf{k},\omega)}{[\omega^2-\epsilon_{\mu\pm}{}^2(\mathbf{k},\omega)]^2+[\Gamma_{\mu\pm}(\mathbf{k},\omega)]^2}\,,\end{aligned}\tag{61}$$

where

$$\Gamma_{\mu\pm}(\mathbf{k},\omega)=\mathrm{Re}\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)\ \mathrm{Im}\tilde{\Omega}_{\mu\pm}(\mathbf{k},\omega)+\mathrm{Re}\tilde{\Omega}_{\mu\pm}(\mathbf{k},\omega)\ \mathrm{Im}\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)\,,\tag{62}$$

$$\hat{\Gamma}_{\mu\pm}(\mathbf{k},\omega)=\mathrm{Im}\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)/\mathrm{Re}\bar{\Omega}_{\mu\pm}(\mathbf{k},\omega)\,,\tag{63}$$

and $\epsilon_{\mu\pm}(\mathbf{k},\omega)$ is given by (41b). In deriving (61), we have made use of (32), in the limit when retardation effects are discarded, as well as the expression (33). The excitation spectrum of single excitons has been examined in I. If we identify $\bar{\Omega}_{\mu+}(\mathbf{k},\omega)\equiv\mathcal{E}_{\mathbf{k}\mu}{}^{(1)}(\omega)$, $\bar{\Omega}_{\mu+}(\mathbf{k},\omega)\equiv\mathcal{E}_{\mathbf{k}\mu}{}^{(2)}(\omega)$, and $\mathrm{Im}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)\equiv\mathrm{Im}\mathcal{E}_{\mathbf{k}\mu}{}^{(1)}(\omega)$, when contributions from the triplet exciton field are neglected, then the corresponding expressions are described by the equations (59), (60), and (66), (93) of I, respectively, and have been discussed in detail; we refer to I for details. The presence of the terms corresponding to the triplet exciton field will result in enhancing the self-energy of the singlet exciton provided that they are not in resonance. They become important for the physical process when a singlet exciton decays into two triplet excitons. The spectrum, for the process in question, is described by the spectral function (58) in the limit when retardation is neglected, i.e.,

$$\begin{aligned}J_{\mu+}{}^{t}(\mathbf{k},\omega)&=\frac{2}{\pi}\,\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)(e^{\beta\omega}-1)^{-1}\\&\quad\times\frac{\Gamma_{\mu+}{}^{t}(\mathbf{k},\omega)+[\omega^2-\epsilon_{\mu+}{}^2(\mathbf{k},\omega)]\hat{\Gamma}_{\mu+}{}^{t}(\mathbf{k},\omega)}{[\omega^2-\epsilon_{\mu+}{}^2(\mathbf{k},\omega)]^2+[\Gamma_{\mu+}{}^{t}(\mathbf{k},\omega)]^2}\,,\end{aligned}\tag{64}$$

where

$$\begin{aligned}\Gamma_{\mu+}{}^{t}(\mathbf{k},\omega)&\equiv\gamma_{b,\mu+}{}^{t}(\mathbf{k},\omega)\\&=\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)\ \mathrm{Im}\tilde{\Omega}_{\mu+}{}^{t}(\mathbf{k},\omega)\\&\quad+\mathrm{Re}\tilde{\Omega}_{\mu+}(\mathbf{k},\omega)\ \mathrm{Im}\bar{\Omega}_{\mu+}{}^{t}(\mathbf{k},\omega)\,,\end{aligned}\tag{65a}$$

$$\begin{aligned}\hat{\Gamma}_{\mu+}{}^{t}(\mathbf{k},\omega)&\equiv\hat{\gamma}_{b,\mu+}{}^{t}(\mathbf{k},\omega)\\&=\mathrm{Im}\bar{\Omega}_{\mu+}{}^{t}(\mathbf{k},\omega)/\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\omega)\,,\end{aligned}\tag{65b}$$

and the expressions for $\mathrm{Im}\bar{\Omega}_{\mu+}{}^{t}(\mathbf{k},\omega)$ and $\mathrm{Im}\tilde{\Omega}_{\mu+}{}^{t}(\mathbf{k},\omega)$ are determined by (54) and the second and third terms of (55), respectively. The condition for $\Gamma_{\mu+}{}^{t}(\mathbf{k},\nu_{\mathbf{k}\mu+})\equiv\Gamma_{\mu+}\neq0$ and $\hat{\Gamma}_{\mu+}{}^{t}(\mathbf{k},\nu_{\mathbf{k}\mu+})\equiv\hat{\Gamma}_{\mu+}\neq0$ requires that the equation

$$\nu_{\mathbf{k}\mu+}=\pm[\omega_{\mu_1-}(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]\,,\tag{66}$$

must be satisfied, where the maximum frequency $\nu_{\mathbf{k}\mu+}$ is determined by

$$\nu_{\mathbf{k}\mu+}{}^2-\epsilon_{\mu+}{}^2(\mathbf{k},\nu_{\mathbf{k}\mu+})=(\Gamma_{\mu+}|\hat{\Gamma}_{\mu+})[-1\pm\sqrt{(1+\hat{\Gamma}_{\mu+}{}^2)}]\,.\tag{67}$$

The relation (66) implies that the singlet exciton $\nu_{\mu+}(\mathbf{k})$ decays into two triplet excitons $\omega_{\mu_1-}(\mathbf{q})$ and $\omega_{\mu'-}(\mathbf{k}-\mathbf{q})$. The inverse process is also applicable, where two triplet excitons annihilate to form a singlet exciton. If the frequency $\nu_{\mu+}(\mathbf{k})$ satisfies Eq. (66), then the spectral function $J_{\mu+}{}^{t}(\mathbf{k},\omega)$ consists of the superposition of symmetric and asymmetric Lorentizian lines peaked at the maximum frequency $\omega\approx\nu_{\mathbf{k}\mu+}$, and $J_{\mu+}{}^{t}(\mathbf{k},\nu_{\mathbf{k}\mu+})$ is given by

$$\begin{aligned}\pi J_{\mu+}{}^{t}(\mathbf{k},\nu_{\mathbf{k}\mu+})&=\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\nu_{\mathbf{k}\mu+})(e^{\beta\nu_{\mathbf{k}\mu+}}-1)^{-1}\\&\quad\times(\hat{\Gamma}_{\mu+}{}^2/\Gamma_{\mu+})[-1\pm\sqrt{(1+\hat{\Gamma}_{\mu+}{}^2)}]^{-1}\,,\end{aligned}\tag{68a}$$

while the half-width of the absorption band is of the order of

$$W_{\mathbf{k}}{}^{t}(\nu_{\mathbf{k}\mu+})\approx(\Gamma_{\mu+}/\hat{\Gamma}_{\mu+}{}^2)[-1\pm\sqrt{(1+\hat{\Gamma}^2)}]/\mathrm{Re}\bar{\Omega}_{\mu+}(\mathbf{k},\nu_{\mathbf{k}\mu+})\,.\tag{68b}$$

If we compare the second terms of (59) with the corresponding functions $\Gamma_{\mu+}{}^{t}(\mathbf{k},\omega)$ and $\hat{\Gamma}_{\mu+}{}^{t}(\mathbf{k},\omega)$, in the same approximation, we have

$$[\gamma_{\mu+}{}^{t}(\mathbf{k},\omega)\,|\,\Gamma_{\mu+}{}^{t}(\mathbf{k},\omega)]\approx\left(\frac{d\omega^2}{d\omega^2}\eta^2(\mathbf{k},\omega)-1\right),\tag{69}$$

$$[\hat{\gamma}_{\mu+}{}^{t}(\mathbf{k},\omega)\,|\,\hat{\Gamma}_{\mu+}{}^{t}(\mathbf{k},\omega)]\approx\left(\frac{\mathrm{Re}\bar{\Omega}_{\mu+}{}^{t}(\mathbf{k},\omega)}{\epsilon_{\mu+}{}^2(\mathbf{k},\omega)-\omega^2}\right)>1\,.\tag{70}$$

The expression (69) indicates that the ratio $\gamma_{\mu+}{}^{t}(\mathbf{k},\omega)\times|\Gamma_{\mu+}{}^{t}(\mathbf{k},\omega)$ depends entirely on the value of the polarizability for a given frequency, while $\hat{\gamma}_{\mu+}{}^{t}(\mathbf{k},\omega)>\hat{\Gamma}_{\mu+}{}^{t}(\mathbf{k},\omega)$. Therefore, for crystals for which the polarizability for a given frequency takes the value $\alpha(\mathbf{k},\omega)>1$ or $\eta^2(\mathbf{k},\omega)>2$, then $\gamma_{\mu+}{}^{t}(\mathbf{k},\omega)>\Gamma_{\mu+}{}^{t}(\mathbf{k},\omega)$.

V. EXCITATON SPECTRUM OF TRIPLET EXCITONS

We shall now examine the excitation spectrum arising from the Green's function $g_{\mu-}(\mathbf{k},\omega)$. Its spectral function

[14] R. S. Knox and C. E. Swenberg, J. Chem. Phys. 44, 2577 (1966).

is described by (61) while $\Gamma_{\mu-}(\mathbf{k},\omega)$ and $\hat{\Gamma}_{\mu-}(\mathbf{k},\omega)$ are given by (62) and (63), respectively. The expressions for $\bar{\Omega}_{\mu-}(\mathbf{k},\omega)$ and $\tilde{\Omega}_{\mu-}(\mathbf{k},\omega)$ involve the Green's functions $\langle\langle\phi_{\mu-}(\mathbf{k});\phi_{\mu-}^\dagger(\mathbf{k})\rangle\rangle$ and $\langle\langle\theta_{\mu-}(\mathbf{k});\theta_{\mu-}^\dagger(\mathbf{k})\rangle\rangle$, respectively. Inspection of (17) and (18) shows that the Green's functions in question contain not only operators of the triplet exciton field, $\xi_{\mu-}(\mathbf{k}-\mathbf{q})$, $\chi_{\mu-}(\mathbf{k}-\mathbf{q})$, but also photon operators, $\tilde{\beta}_\lambda(\mathbf{q})$, as well as operators of the singlet exciton field $\xi_{\mu+}(\mathbf{k}-\mathbf{q})$, $\chi_{\mu+}(\mathbf{q})$. To calculate the Green's functions $\langle\langle\phi_{\mu-}(\mathbf{k});\phi_{\mu-}^\dagger(\mathbf{k})\rangle\rangle$ and

$$\langle\langle\theta_{\mu-}(\mathbf{k});\theta_{\mu-}^\dagger(\mathbf{k})\rangle\rangle$$

we have first to transform the operators $\tilde{\beta}_\lambda(\mathbf{q})$, $\xi_{\mu+}(\mathbf{q})$, and $\chi_{\mu+}(\mathbf{q})$, respectively, into polariton operators $\zeta_\rho(\mathbf{q})$. The transformation is achieved via the relations

$$\tilde{\beta}_\lambda(\mathbf{k})=\sum_\rho [ck\lambda_{\mathbf{k}}|\omega_\rho(\mathbf{k})]^{1/2}[\zeta_\rho(\mathbf{k})+\zeta_\rho^\dagger(-\mathbf{k})], \tag{71a}$$

$$\xi_{\mu+}(\mathbf{k})=i\sum_\rho [2\bar{\omega}_{\mu+}(\mathbf{k})\bar{\lambda}_{\mathbf{k}}|\omega_\rho(\mathbf{k})]^{1/2}[\zeta_\rho(\mathbf{k})+\zeta_\rho^\dagger(\mathbf{k})], \tag{71b}$$

$$\chi_{\mu+}(\mathbf{k})=i\sum_\rho [2\omega_\rho(\mathbf{k})\bar{\lambda}_{\mathbf{k}}|\bar{\omega}_{\mu+}(\mathbf{k})]^{1/2}[\zeta_\rho(\mathbf{k})-\zeta_\rho^\dagger(\mathbf{k})], \tag{71c}$$

$$\lambda_{\mathbf{k}}=\left(\frac{d\omega^2}{d\omega^2}\eta^2(\mathbf{k},\omega)\right)^{-1}_{\omega=\omega_\rho(\mathbf{k})}, \quad \bar{\lambda}_{\mathbf{k}}=1-\lambda_{\mathbf{k}}. \tag{71d}$$

In deriving (71) use has been made of the relations given in Ref. 10. Substituting (71) into the expressions (17) and (18), we find

$$\begin{aligned}\phi_{\mu-}(\mathbf{k})=\frac{i}{\sqrt{N}}\sum_{\mathbf{q},\mu',\mu_1,\rho}\Bigg[&\omega_p\left(\frac{f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\rho)\Delta_{\mu'\mu}\lambda_{\mathbf{q}}}{\omega_\rho(\mathbf{q})}\right)^{1/2}\\
&-\tfrac{1}{2}J_{0\mu',\mu\mu_1}{}^{(-)}(-\mathbf{k})\left(\frac{2\bar{\omega}_{\mu_1+}(\mathbf{q})\bar{\lambda}_{\mathbf{q}}}{\omega_\rho(\mathbf{q})}\right)^{1/2}\Bigg]\xi_{\mu'-}(\mathbf{k}-\mathbf{q})[\zeta_\rho(\mathbf{q})+\zeta_\rho^\dagger(-\mathbf{q})]\\
&-(i/2\sqrt{N})\sum_{\mathbf{q},\mu',\mu_1,\rho}[J_{0\mu',\mu_1\mu}{}^{(+)}(\mathbf{q})+J_{0\mu',\mu\mu_1}{}^{(-)}(-\mathbf{k})+J_{0\mu_1,\mu'\mu}{}^{(-)}(\mathbf{k}-\mathbf{q})]\\
&\times\left(\frac{2\omega_\rho(\mathbf{q})\bar{\lambda}_{\mathbf{q}}}{\bar{\omega}_{\mu_1+}(\mathbf{q})}\right)^{1/2}\chi_{\mu'-}(\mathbf{k}-\mathbf{q})[\zeta_\rho(\mathbf{q})-\zeta_\rho^\dagger(-\mathbf{q})],\end{aligned} \tag{72}$$

$$\begin{aligned}\theta_{\mu-}(\mathbf{k})=&\frac{i\omega_p}{\sqrt{N}}\sum_{\mathbf{q},\mu',\rho}\left(\frac{f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\rho)\Delta_{\mu'\mu}\lambda_{\mathbf{q}}}{\omega_\rho(\mathbf{q})}\right)^{1/2}\chi_{\mu'-}(\mathbf{k}-\mathbf{q})[\zeta_\rho(\mathbf{q})+\zeta_\rho^\dagger(-\mathbf{q})]\\
&-\frac{i}{2\sqrt{N}}\sum_{\mathbf{q},\mu_1,\mu',\rho}[J_{0\mu',\mu_1\mu}{}^{(+)}(\mathbf{q})+\Lambda_{\mathbf{k}}(\omega)]\left(\frac{2\omega_\rho(\mathbf{q})\bar{\lambda}_{\mathbf{q}}}{\bar{\omega}_{\mu_1+}(\mathbf{q})}\right)^{1/2}\xi_{\mu'-}(\mathbf{k}-\mathbf{q})[\zeta_\rho(\mathbf{q})-\zeta_\rho^\dagger(-\mathbf{q})]\\
&-\frac{i}{2\sqrt{N}}\sum_{\mathbf{q},\mu_1,\mu',\rho}[J_{0\mu_1,\mu'\mu}{}^{(-)}(\mathbf{k}-\mathbf{q})+\Lambda_{\mathbf{k}}(\omega)]\left(\frac{2\bar{\omega}_{\mu_1+}(\mathbf{q})\bar{\lambda}_{\mathbf{q}}}{\omega_\rho(\mathbf{q})}\right)^{1/2}\chi_{\mu'-}(\mathbf{k}-\mathbf{q})[\zeta_\rho(\mathbf{q})+\zeta_\rho^\dagger(-\mathbf{q})].\end{aligned} \tag{73}$$

We calculate now the Green's functions $\langle\langle\phi_{\mu-}(\mathbf{k});\phi_{\mu-}^\dagger(\mathbf{k})\rangle\rangle$ and $\langle\langle\theta_{\mu-}(\mathbf{k});\theta_{\mu-}^\dagger(\mathbf{k})\rangle\rangle$ in the HF approximation by means of the polariton Hamiltonian (31b). The result is

$$\langle\langle\phi_{\mu-}(\mathbf{k});\phi_{\mu-}^\dagger(\mathbf{k})\rangle\rangle^0=(1/4N)\sum_{\mathbf{q},\mu_1,\mu',\rho}|Q(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q},\mu')|^2G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\omega), \tag{74}$$

$$\langle\langle\theta_{\mu-}(\mathbf{k});\theta_{\mu-}^\dagger(\mathbf{k})\rangle\rangle^0=(1/4N)\sum_{\mathbf{q},\mu_1,\mu',\rho}|\hat{Q}(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q}\mu')|^2G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\omega), \tag{75}$$

where the coupling functions $Q(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q},\mu')$ and $\hat{Q}(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q},\mu')$ are

$$\begin{aligned}Q(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q},\mu')=&\,i\omega_p\left(\frac{2f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\rho)\Delta_{\mu'\mu}\lambda_{\mathbf{q}}\bar{\omega}_{\mu'-}(\mathbf{k}-\mathbf{q})}{\omega_{\mu'}(\mathbf{k}-\mathbf{q})\omega_\rho(\mathbf{q})}\right)^{1/2}\\
&-i[J_{0\mu',\mu_1\mu}{}^{(+)}(\mathbf{q})+J_{0\mu_1,\mu'\mu}{}^{(-)}(\mathbf{k}-\mathbf{q})]\left(\frac{\hat{\omega}_{\mu'-}(\mathbf{k}-\mathbf{q})\omega_\rho(\mathbf{q})\bar{\lambda}_{\mathbf{q}}}{\omega_{\mu'-}(\mathbf{k}-\mathbf{q})\bar{\omega}_{\mu_1+}(\mathbf{q})}\right)^{1/2}\\
&-iJ_{0\mu_1,\mu'\mu}{}^{(-)}(-\mathbf{k})\bar{\lambda}_{\mathbf{q}}{}^{1/2}\left[\left(\frac{\bar{\omega}_{\mu_1+}(\mathbf{q})\bar{\omega}_{\mu'-}(\mathbf{k}-\mathbf{q})}{\omega_{\mu'-}(\mathbf{k}-\mathbf{q})\omega_\rho(\mathbf{q})}\right)^{1/2}+\left(\frac{\hat{\omega}_{\mu'}(\mathbf{k}-\mathbf{q})\omega_\rho(\mathbf{q})}{\omega_{\mu'-}(\mathbf{k}-\mathbf{q})\bar{\omega}_{\mu_1+}(\mathbf{q})}\right)^{1/2}\right],\end{aligned} \tag{76}$$

$$\hat{Q}(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q},\mu')=i\omega_p\left(\frac{2f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\rho)\Delta_{\mu'\mu}\lambda_{\mathbf{q}}\hat{\omega}_{\mu'-}(\mathbf{k}-\mathbf{q})}{\omega_{\mu'-}(\mathbf{k}-\mathbf{q})\omega_\rho(\mathbf{q})}\right)^{1/2}-i\{[J_{0\mu',\mu_1\mu}{}^{(+)}(\mathbf{q})+\Lambda_{\mathbf{k}}(\omega)]\omega_\rho(\mathbf{q})\omega_{\mu'-}(\mathbf{k}-\mathbf{q})$$
$$+[J_{0\mu_1,\mu'\mu}{}^{(-)}(\mathbf{k}-\mathbf{q})\bar{\omega}_{\mu_1+}(\mathbf{q})\hat{\omega}_{\mu'}(\mathbf{k}-\mathbf{q})]\}\left(\frac{\lambda_{\mathbf{q}}\bar{\omega}_{\mu'}(\mathbf{k}-\mathbf{q})}{\bar{\omega}_{\mu_1+}(\mathbf{q})\omega_\rho(\mathbf{q})\omega_{\mu'-}{}^3(\mathbf{k}-\mathbf{q})}\right)^{1/2}, \quad (77)$$

and the function $G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\omega)$ is given by

$$G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\omega)$$
$$=\frac{2}{\pi}\left((\eta_{\mathbf{q}\rho}+\eta_{\mathbf{k}-\mathbf{q}\mu'-})\frac{[\omega_\rho(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]}{\omega^2-[\omega_\rho(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]^2}\right.$$
$$\left.+(\eta_{\mathbf{k}-\mathbf{q}\mu'-}-\eta_{\mathbf{q}\rho})\frac{[\omega_\rho(\mathbf{q})-\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]}{\omega^2-[\omega_\rho(\mathbf{q})-\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]^2}\right). \quad (78)$$

The function $G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\omega)$ describes the Raman scattering of the polariton $\omega_\rho(\mathbf{q})$ and the triplet exciton $\omega_{\mu'-}(\mathbf{k}-\mathbf{q})$. Its real part is given by the principal value of (78) while its imaginary part is

$$\mathrm{Im}G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\omega)$$
$$=(\eta_{\mathbf{q}\rho}+\eta_{\mathbf{k}-\mathbf{q}\mu'})\{\delta[\omega-\omega_\rho(\mathbf{q})-\omega_{\mu'}(\mathbf{k}-\mathbf{q})]$$
$$-\delta[\omega+\omega_\rho(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]\}$$
$$+(\eta_{\mathbf{k}-\mathbf{q}\mu'}-\eta_{\mathbf{q}\rho})\{\delta[\omega-\omega_\rho(\mathbf{q})+\omega_{\mu'}(\mathbf{k}-\mathbf{q})]$$
$$-\delta[\omega+\omega_\rho(\mathbf{q})-\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]\}. \quad (79)$$

In the expressions (74)–(78) the dispersion of the scattered polariton $\omega_\rho(\mathbf{q})$ is fully included. Substituting (74) and (75) into (62) and (63), we obtain

$$\Gamma_{\mu-}(\mathbf{k},\omega)=\frac{1}{4N}\sum_{\mathbf{q},\mu',\mu_1,\rho}[\hat{\omega}_{\mu-}(\mathbf{k})|Q(\mathbf{q},\rho',\mu_1;\mathbf{k}-\mathbf{q},\mu')|^2$$
$$+\bar{\omega}_{\mu-}(\mathbf{k})|\hat{Q}(\mathbf{q},\rho',\mu_1;\mathbf{k}-\mathbf{q},\mu')|^2]$$
$$\times\mathrm{Im}G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\omega), \quad (80)$$

$$\hat{\Gamma}_{\mu-}(\mathbf{k},\omega)=[1/4N\omega_{\mu-}(\mathbf{k})]$$
$$\times\sum_{\mathbf{q},\mu',\mu_1,\rho}|Q(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q},\mu')|^2$$
$$\times\mathrm{Im}G(\mathbf{q}\rho',\mathbf{k}-\mathbf{q}\mu';\omega), \quad (81)$$

$$\epsilon_{\mu-}{}^2(\mathbf{k},\omega)=\omega_{\mu-}{}^2(\mathbf{k})+(1/2N)$$
$$\times\sum_{\mathbf{q},\mu',\mu_1,\rho}[\hat{\omega}_{\mu-}(\mathbf{k})|Q(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q}\mu')|^2$$
$$+\bar{\omega}_{\mu-}(\mathbf{k})|\hat{Q}(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q},\mu')|^2]$$
$$\times\mathrm{Re}G(\mathbf{q}\rho',\mathbf{k}-\mathbf{q}\mu';\omega). \quad (82)$$

The spectral function $J_{\mu-}(\mathbf{k},\omega)$, for the process in question, is

$$J_{\mu-}(\mathbf{k},\omega)=\frac{2}{\pi}\bar{\omega}_{\mu-}(\mathbf{k})(e^{\beta\omega}-1)^{-1}$$
$$\times\frac{\Gamma_{\mu-}(\mathbf{k},\omega)+[\omega^2-\epsilon_{\mu-}{}^2(\mathbf{k},\omega)]\hat{\Gamma}_{\mu-}(\mathbf{k},\omega)}{[\omega^2-\epsilon_{\mu-}{}^2(\mathbf{k},\omega)]^2+[\Gamma_{\mu-}(\mathbf{k},\omega)]^2}. \quad (83)$$

The maximum frequencies $\nu_{\mathbf{k}\mu-}$ at which the function $J_{\mu-}(\mathbf{k},\omega)$ is peaked are determined by the expression

$$\nu_{\mathbf{k}\mu-}{}^2-\epsilon_{\mu-}{}^2(\mathbf{k},\nu_{\mathbf{k}\mu-})$$
$$=(\Gamma_{\mu-}/\hat{\Gamma}_{\mu-})[-1\pm\surd(1+\hat{\Gamma}_{\mu-}{}^2)], \quad (84)$$

with $\Gamma_{\mu-}\equiv\Gamma_{\mu-}(\mathbf{k},\nu_{\mathbf{k}\mu-})$, $\hat{\Gamma}_{\mu-}(\mathbf{k},\nu_{\mathbf{k}\mu-})$, and $\epsilon_{\mu-}(\mathbf{k},\nu_{\mathbf{k}\mu-})$ considered as constants. In order to have $\Gamma_{\mu-}(\mathbf{k},\nu_{\mathbf{k}\mu-})\neq0$ and $\hat{\Gamma}_{\mu-}(\mathbf{k},\nu_{\mathbf{k}\mu-})\neq0$, and taking into account that the last term in (79) contributes nothing, the frequency $\nu_{\mathbf{k}\mu-}$ must satisfy the equation

$$\nu_{\mathbf{k}\mu-}=\pm[\omega_\rho(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]. \quad (85)$$

Equation (85) implies that the triplet exciton $\nu_{\mathbf{k}\mu-}$ decays into the triplet exciton $\omega_{\mu'-}(\mathbf{k}-\mathbf{q})$ with the emission or absorption of the polariton $\omega_\rho(\mathbf{q})$. If the relation (85) is satisfied, the spectral half-width for the process in question is of the order of

$$W_{\mathbf{k}}(\nu_{\mathbf{k}\mu-})\approx(\Gamma_{\mu-}/\hat{\Gamma}_{\mu-}{}^2)[-1\pm\surd(1+\hat{\Gamma}_{\mu-}{}^2)]/\omega_{\mu-}(\mathbf{k}). \quad (86)$$

Then the first term in the coupling functions (76) and (77) describe the radiative transition between the states $(\mathbf{k},\mu-)$ and $(\mathbf{k}-\mathbf{q},\mu-)$ via the exchange of the polariton $\omega_\rho(\mathbf{q})$ and is proportional to the square of the electronic charge. The second terms arise from the correlation between the intermolecular interactions and the polariton field; considering the factor $\bar{\lambda}_{\mathbf{q}}$, these processes are proportional to the sixth power of the electronic charge. The third term in (77), $\Lambda_{\mathbf{k}}(\omega)$, represents the small radiative correction to the triplet state $(\mathbf{k},\mu-)$ arising from its indirect interaction with the electromagnetic field with frequency ck. It is easy to show that for $\omega^2-c^2k^2-\omega_p{}^2=0$ the Green's function $g_{\mu-}(\mathbf{k},\omega)$ becomes zero, which indicates that at these frequencies $g_{\mu-}(\mathbf{k},\omega)$ has no poles.

In the range of wave vectors $\mathbf{q}$ where the dispersion of the scattered photon cq can be neglected, the expressions (80) and (81) for $\Gamma_{\mu-}{}^b(\mathbf{k},\omega)$ and $\hat{\Gamma}_{\mu-}{}^b(\mathbf{k},\omega)$ are reduced to

$$\Gamma_{\mu-}{}^{b}(\mathbf{k},\omega)=\frac{\omega_p{}^2}{2N}\sum_{\mathbf{q},\lambda,\mu'} f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\lambda)\frac{\Delta_{\mu'\mu}}{cq\omega_{\mu'-}(\mathbf{k}-\mathbf{q})}[\bar{\omega}_{\mu'-}(\mathbf{k}-\mathbf{q})\hat{\omega}_{\mu-}(\mathbf{k})+\hat{\omega}_{\mu'-}(\mathbf{k}-\mathbf{q})\bar{\omega}_{\mu-}(\mathbf{k})]\,\mathrm{Im}G(cq,\mathbf{k}-\mathbf{q}\mu';\omega)$$
$$+\frac{1}{4N}\sum_{\mathbf{q},\mu',\mu_1}\Bigg\{|J_{0\mu',\mu_1\mu}{}^{(+)}(\mathbf{q})+2J_{0\mu_1,\mu'\mu}{}^{(-)}(-\mathbf{k})+J_{0\mu_1,\mu'\mu}{}^{(-)}(\mathbf{k}-\mathbf{q})|^2\hat{\omega}_{\mu_1+}(\mathbf{q})\hat{\omega}_{\mu'}(\mathbf{k}-\mathbf{q})\hat{\omega}_{\mu-}(\mathbf{k})$$
$$+\frac{\bar{\omega}_{\mu-}(\mathbf{k})}{\hat{\omega}_{\mu'-}(\mathbf{k}-\mathbf{q})\hat{\omega}_{\mu_1+}(\mathbf{q})}|[J_{0\mu',\mu_1\mu}{}^{(+)}(\mathbf{q})+\Lambda_{\mathbf{k}}(\omega)]\bar{\omega}_{\mu'-}(\mathbf{k}-\mathbf{q})\hat{\omega}_{\mu_1+}(\mathbf{q})$$
$$+[J_{0\mu_1,\mu'\mu}{}^{(-)}(\mathbf{k}-\mathbf{q})+\Lambda_{\mathbf{k}}(\omega)]\hat{\omega}_{\mu'}(\mathbf{k}-\mathbf{q})\bar{\omega}_{\mu_1+}(\mathbf{q})|^2\Bigg\}[\omega_{\mu_1+}(\mathbf{q})\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]^{-1}\,\mathrm{Im}G(\mathbf{q}\mu_1,\mathbf{k}-\mathbf{q}\mu';\omega)\,,\quad(87)$$

$$\hat{\Gamma}_{\mu-}{}^{b}(\mathbf{k},\omega)=\frac{\omega_p{}^2}{N\omega_{\mu-}(\mathbf{k})}\sum_{\mathbf{q},\lambda,\mu'} f_{\mathbf{k}\mu,\mathbf{k}-\mathbf{q}\mu'}(\mathbf{q},\lambda)\frac{\Delta_{\mu'\mu}\bar{\omega}_{\mu'}(\mathbf{k}-\mathbf{q})}{cq\omega_{\mu'-}(\mathbf{k}-\mathbf{q})}\mathrm{Im}G(cq,\mathbf{k}-\mathbf{q}\mu';\omega)+\frac{1}{4N\omega_{\mu-}(\mathbf{k})}\sum_{\mathbf{q},\mu',\mu_1}|J_{0\mu',\mu_1\mu}{}^{(+)}(\mathbf{q})$$
$$+2J_{0\mu_1,\mu'\mu}{}^{(-)}(-\mathbf{k})+J_{0\mu_1,\mu'\mu}{}^{(-)}(\mathbf{k}-\mathbf{q})|^2\left(\frac{\hat{\omega}_{\mu_1+}(\mathbf{q})\hat{\omega}_{\mu'-}(\mathbf{k}-\mathbf{q})}{\omega_{\mu_1+}(\mathbf{q})\omega_{\mu'-}(\mathbf{k}-\mathbf{q})}\right)\mathrm{Im}G(\mathbf{q}\mu_1,\mathbf{k}-\mathbf{q}\mu';\omega)\,,\quad(88)$$

where $G(cq,\mathbf{k}-\mathbf{q}\mu';\omega)$ and $G(\mathbf{q}\mu_1,\mathbf{k}-\mathbf{q}\mu';\omega)$ are obtained from (78) by replacing $\omega_\rho(\mathbf{q})$ by cq and $\omega_{\mu_1+}(\mathbf{q})$, respectively. In (87) and (88), the first term represents the radiative interaction between the two triplet excitons $(\mathbf{k},\mu-)$ and $(\mathbf{k}-\mathbf{q},\mu'-)$ through the exchange of the photon $(\mathbf{q},\lambda)$, while the remaining terms, with the exception of $\Lambda_{\mathbf{k}}(\omega)$, correspond to the instantaneous intermolecular interactions leading to the creation of two excitons: the singlet $\omega_{\mu_1+}(\mathbf{q})$ and the triplet $\omega_{\mu'-}(\mathbf{k}-\mathbf{q})$. The necessary conditions for $\mathrm{Im}G(cq,\mathbf{k}-\mathbf{q}\mu';\nu_{\mathbf{k}\mu-})\neq 0$ and $\mathrm{Im}G(\mathbf{q}\mu_1,\mathbf{k}-\mathbf{q}\mu';\nu_{\mathbf{k}\mu-})\neq 0$ are

$$\nu_{\mathbf{k}\mu-}=\pm[cq+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]\,,\quad(89)$$

$$\nu_{\mathbf{k}\mu-}=\pm[\omega_{\mu_1+}(\mathbf{q})+\omega_{\mu'-}(\mathbf{k}-\mathbf{q})]\,,\quad(90)$$

respectively. The maximum frequency $\nu_{\mathbf{k}\mu-}$ is determined by the expression (84) with $\Gamma_{\mu-}$ and $\hat{\Gamma}_{\mu-}$ given by (87) and (88). The relations (89) and (90) indicate that the triplet exciton $\nu_{\mathbf{k}\mu-}$ decays into the state $(\mathbf{k}-\mathbf{q},\mu'-)$ with the simultaneous emission or absorption of the photon $(\mathbf{q},\lambda)$ and the singlet exciton $(\mathbf{q},\mu_1+)$, respectively. The spectral width for the triplet exciton $(\mathbf{k},\mu-)$ is determined by (86) if $\Gamma_{\mu-}(\mathbf{k},\omega)$ and $\hat{\Gamma}_{\mu-}(\mathbf{k},\omega)$ are replaced by $\Gamma_{\mu-}{}^{b}(\mathbf{k},\omega)$ and $\hat{\Gamma}_{\mu-}{}^{b}(\mathbf{k},\omega)$, respectively.

Far from resonance, i.e., in the limit when

$$\mathrm{Im}G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\omega)$$

goes to zero, the spectral function (83) becomes

$$J_{\mu-}(\mathbf{k},\omega)\approx 2\bar{\Omega}_{\mu-}(\mathbf{k},\omega)(e^{\beta\omega}-1)^{-1}\delta(\omega^2-\epsilon_{\mathbf{k}\mu-}{}^2)\,,\quad(91)$$

where the energy of excitation $\epsilon_{\mathbf{k}\mu-}$ is determined by the solutions of the equation

$$\epsilon_{\mathbf{k}\mu-}{}^2=\bar{\Omega}_{\mu-}(\mathbf{k},\epsilon_{\mathbf{k}\mu-})\tilde{\Omega}_{\mu-}(\mathbf{k},\epsilon_{\mathbf{k}\mu-})\quad(92)$$

with

$$\bar{\Omega}_{\mu-}(\mathbf{k},\epsilon_{\mathbf{k}\mu-})=\bar{\omega}_{\mu-}(\mathbf{k})+(1/4N)\times\sum_{\mathbf{q},\mu',\mu_1,\rho}|Q(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q},\mu')|^2\times G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\epsilon_{\mathbf{k}\mu-})\,,\quad(93)$$

$$\tilde{\Omega}_{\mu-}(\mathbf{k},\epsilon_{\mathbf{k}\mu-})=\hat{\omega}_{\mu-}(\mathbf{k})(1/4N)\times\sum_{\mathbf{q},\mu',\mu_1,\rho}|\hat{Q}(\mathbf{q},\rho,\mu_1;\mathbf{k}-\mathbf{q},\mu')|^2\times G(\mathbf{q}\rho,\mathbf{k}-\mathbf{q}\mu';\epsilon_{\mathbf{k}\mu-})\,.\quad(94)$$

The last terms in (93) and (94) represent the scattering amplitudes for the scattering process, where the triplet exciton $\epsilon_{\mathbf{k}\mu-}$ undergoes the transition into the state $\omega_{\mu-}(\mathbf{k}-\mathbf{q})$ while the polariton $\omega_\rho(\mathbf{q})$ is emitted.

VI. CONCLUSION

A systematic approach is presented for the study of the dynamics of interacting polariton-exciton fields caused by photon absorption in molecular and insulating crystals. Emphasis has been given to the line shape of the absorption bands at low temperatures. The dynamical behavior of the absorption bands at elevated temperatures will be mainly determined by the polariton-phonon, exciton-phonon, as well as polariton-exciton-phonon interactions.[2,3] The derived results in the present study need the support of numerical computations for comparison with the observed data.

It is hoped that the present study will stimulate an interest in performing resonance triplet exciton Raman scattering experiments in organic solids at low temperatures and computations as well.