Multipolar contributions to coherent optical second-harmonic generation at an interface between two isotropic media: A quantum-electrodynamical calculation

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Using a molecular-quantum-electrodynamics method, we calculate the optical second-harmonic generation at the interface of two isotropic media caused by the multipolar contribution from the bulk. The most significant part of the radiation in both reflection and transmission is coherent, and the magnitude is generally comparable to that due to a monolayer of noncentrosymmetric molecules. This supports the previous treatments that started directly from Maxwell equations and a macroscopic-polarization-field formalism.

I. INTRODUCTION

In recent years, optical second-harmonic generation (SHG) at the interface of two media has been increasingly used as a probe to various properties of the interface layer. They include, not exhaustively, structural symmetries, the orientational order of adsorbed species, interface states, and molecular dynamics such as adsorption, desorption, and even transport along surfaces.[1-3] Optical SHG is most effective when the two bulk media have either a center(s) of inversion or an isotropic order over a volume linearly small compared with the involved optical wavelengths. In these cases, no coherent optical SHG is generated from the bulk when the electric dipole approximation is made in both the electric current density and the interaction Hamiltonian.[1-4] At the same time, because the inversion symmetry and the isotropic order are necessarily lifted in the interface layer, a coherent and electric dipole-allowed second-harmonic radiation can be generated from such a layer.[1-3]

In practice, it is known that the nonlinear polarization or electric current due to higher-order multipolar Hamiltonian, and the multipolar electric current terms within a layer of a coherence length ($\sim$ the optical wavelength λ) in the bulk can yield a coherent SHG in both reflection and transmission directions.[1-3,5-12] In fact, in the direction of transmission, the coherence length can be much longer.[13] Such a bulk contribution has been shown to be generally comparable to the interfacial electric dipole-allowed SHG. Consequently, in order to extract information about the interface layer from SHG, one needs sufficient knowledge of the bulk multipolar contribution. This has prompted rather extensive treatments of the bulk multipolar terms by numerous authors, more completely by Guyot-Sionnest and Shen.[2,5-12]

Since most calculations of SHG start, rather than from quantum electrodynamics, directly from Maxwell equations involving the macroscopic polarization fields or the macroscopic electric current density, the question has been raised by some authors, based upon molecular electrodynamics consideration, as to whether the bulk electric quadrupole and magnetic dipole contributions to the SHG at the interface of two isotropic fluids would indeed be *coherent* and *comparable* to the overall SHG radiation.[14,15] This issue, which has been debated recently,[14-17] is in part due to the lack of a calculation based upon quantum electrodynamics, which *explicitly* yields the same results as obtained in the previous calculations using the macroscopic polarization fields and Maxwell equations. A calculation of this type will help to justify the previous macroscopic treatments of isotropic fluids.

In this paper, we present the result of such a calculation. Specifically, we carry out a molecular-quantum-electrodynamical calculation of the multipolar second-harmonic generation in two adjoining isotropic media. By appropriately performing a rotational average and an integration over a half-space, we show that in the presence of the interface, the optical second-harmonic generation due to the electric quadrupole response of an isotropic bulk fluid is *mostly coherent* and generally comparable to the nominal surface or interfacial SHG. This result thus agrees with the previous macroscopic calculations.[5-10]

II. THE MULTIPOLAR SECOND-HARMONIC GENERATION FROM ISOTROPIC FLUIDS

For simplicity, the physical system under investigation is an interface adjoining an isotropic molecular fluid a and another isotropic medium b, with b having vanishing electric quadrupole and magnetic dipole moments so that only the multipolar response of the molecular fluid a has to be considered. An example is an interface of the air and a molecular liquid. We assume that the linear dielectric constants for the two media are the same, $\epsilon_{\omega,a} = \epsilon_{\omega,b} = \epsilon_\omega$, so that the macroscopic local-field factor can be neglected.[2] Let a coherent plane-wave optical field $\mathbf{E}(\mathbf{r},\omega,t) = \mathbf{E}(\omega)\exp(i\mathbf{k}_\omega \cdot \mathbf{r} - i\omega t)$ incident from the medium b. The beam cross section A is assumed much larger than $\lambda^2 = (2\pi c/\omega)^2$, so that $\mathbf{E}(\omega)$ is considered infinitely extended. The z axis is along the normal of the interface, pointing into the molecular fluid a. We choose $\mathbf{k}_\omega$ in the x-z plane. The interfacial layer is defined as the molecular fluid layer in which the isotropic order is no longer preserved. We assume that such a layer is thin compared to λ. Beyond such a layer, we assume that the isotropic

order is restored in any macroscopic volume element linearly small compared with λ.

Based upon the molecular-quantum-electrodynamics calculation, it has been established that there is no coherent second-harmonic generation from both isotropic media in the electric dipole approximation.[3,4] We thus consider only the second-harmonic generation due to multipolar contributions, specifically from the electric quadrupole response of the molecular fluid a.

According to Adler,[12] both the spatial Fourier transform of the electric current density $\mathbf{J}(\mathbf{k},t)$ and the interaction Hamiltonian H_{int} for a molecular fluid and radiation fields can be partitioned into an electric dipole, an electric quadrupole, and a magnetic dipole term,

$$\mathbf{J}(\mathbf{k},t)=\sum_j [\ \partial\mathbf{p}_j/\partial t+i\mathbf{k}\cdot\partial\mathbf{Q}_j/\partial t$$

$$-ic\mathbf{k}\times\mathbf{m}_j]\exp(i\mathbf{k}\cdot\mathbf{r}_j)\ , \tag{1}$$

$$H_{int}=-\sum_{j,\alpha}\{\ \mathbf{p}_j\cdot\mathbf{E}(\omega_\alpha)-i\mathbf{k}_{\omega_\alpha}\cdot\mathbf{Q}_j\cdot\mathbf{E}(\omega_\alpha)$$

$$+(c/\omega_\alpha)[\mathbf{k}_{\omega_\alpha}\times\mathbf{E}(\omega_\alpha)]\cdot\mathbf{m}_j\}$$

$$\times\exp(i\mathbf{k}_{\omega_\alpha}\cdot\mathbf{r}_j-i\omega_\alpha t)\ . \tag{2}$$

The summation (j) is over the fluid molecules in the radiation field $\mathbf{E}(\omega_\alpha)$. The summation ($\alpha$) is over all radiation fields $\mathbf{E}(\omega_\alpha)$, including the fundamental incident field and the second-harmonic field. $\mathbf{p}_j$, $\mathbf{Q}_j$, and $\mathbf{m}_j$ are the electric dipole, electric quadrupole, and magnetic dipole operators for the jth molecule, respectively. $\mathbf{r}_j$ labels its center of mass. The optical second harmonics generated from the electric quadrupole and magnetic dipole responses comes from four combinations of interaction terms [Eq. (2)] and the electric current terms [Eq. (1)].[12] Instead of calculating all the terms up to the electric quadrupole and magnetic dipole approximation, we focus on one of the electric quadrupole terms: the electric dipole radiation (corresponding to $\partial\mathbf{p}/\partial t$) at second harmonics due to the second-order perturbation involving one electric dipole interaction and one electric quadrupole interaction term in Eq. (2). The other combinations can be treated accordingly.

In the quantum-electrodynamics formalism, instead of considering the radiation fields and the molecular system separately, and thus calculating the radiation fields from the expectation value of the electric current density or the macroscopic nonlinear polarization, quantized radiation fields at both the fundamental frequency ω and the second harmonics 2ω are treated as parts of one quantum-mechanical system which includes all the molecules in the radiation fields.[4] Under the perturbation of H_{int}, the system undergoes the transition characterized by "annihilating two fundamental photons" and "creating one second-harmonic photon" while leaving the molecular part of the system unchanged. Thus, for the second-harmonic generation through an electric quadrupole process, we may consider annihilating two fundamental photons by actions of an electric dipole interaction and an electric quadrupole interaction term, and creating a second-harmonic photon through an electric

dipole term. The differential rate of the second-harmonic generation is then calculated by use of the *Fermi golden rule*,[4]

$$d\Gamma(2\omega)=\frac{2\pi}{\hbar}|M_{fi}(2\omega)|^2 d\rho(2\omega)\ . \tag{3}$$

Here, the radiation density of state $d\rho(2\omega)$ into a differential solid angle $d\Omega$ is

$$d\rho(2\omega)=\frac{\epsilon_{2\omega}^{3/2}(2\omega/c)^2 V}{(2\pi)^3\hbar c}d\Omega\ . \tag{4}$$

V is the irradiated volume of the molecular fluid. The matrix element $M_{fi}(2\omega)$ is calculated through a third-order perturbation,[4]

$$M_{fi}(2\omega)=\sum_j M_{fi,j}(2\omega)$$

$$=\frac{4\pi\hbar\omega}{V\epsilon_\omega}\left[\frac{8\pi\hbar\omega}{V\epsilon_{2\omega}}\right]^{1/2}\sqrt{(n_{2\omega}+1)n_\omega(n_\omega-1)}$$

$$\times k_{2\omega,q}e_{2\omega,r}e_{\omega,s}e_{\omega,t}$$

$$\times\sum_j\beta_{qrst}^{(j)}\exp[i(2\mathbf{k}_\omega-\mathbf{k}_{2\omega})\cdot\mathbf{r}_j]\ , \tag{5}$$

$$\beta_{qrst}^{(j)}=\sum_{u,v}\left[\frac{Q_{j,qr}^{gu}p_{j,s}^{uv}p_{j,t}^{vg}}{(E_{ug}-2\hbar\omega)(E_{vg}-\hbar\omega)}\right.$$

$$+\frac{p_{j,s}^{gu}Q_{j,qr}^{uv}p_{j,t}^{vg}}{(E_{ug}+\hbar\omega)(E_{vg}-\hbar\omega)}$$

$$\left.+\frac{p_{j,s}^{gu}p_{j,t}^{uv}Q_{j,qr}^{vg}}{(E_{ug}+\hbar\omega)(E_{vg}+2\hbar\omega)}\right]\ . \tag{6}$$

n_ω is the initial photon number at the fundamental frequency ω and the incident wave vector $\mathbf{k}_\omega$. $n_{2\omega}$ is the initial photon number at the second-harmonic frequency 2ω with the wave vector $\mathbf{k}_{2\omega}$, and is taken to be zero. The three terms in Eq. (6) correspond to three different time orders with which the two fundamental photon are "annihilated" and the second-harmonic photon is "created." The radiated second-harmonic power is hence

$$S(2\omega)=2\hbar\omega\int_{(\Omega=4\pi)}d\Gamma(2\omega)\ . \tag{7}$$

III. ROTATIONAL AVERAGE OF $M_{fi}(2\omega)$ FOR ISOTROPIC FLUIDS

Since the spacing between neighboring molecules in the molecular fluid is much smaller than the wavelength λ, we may perform a full rotational average of $|M_{fi}(2\omega)|^2$ in a volume element ΔV, which contains a large number of molecules and yet small compared with λ^3. *Effectively*, such an average can be taken to be independent of $\mathbf{r}_j$. According to Craig and Thirunamachandran,[4]

$$|M_{fi}(2\omega)|^2=\langle|M_{fi}(2\omega)|^2\rangle$$

$$=\left\langle\left|\sum_j M_{fi,j}(2\omega)\right|^2\right\rangle$$

$$=\sum_j\langle|M_{fi,j}|^2\rangle+\sum_{j\neq j'}\langle M_{fi,j}\rangle\langle M_{fi,j'}^*\rangle\ . \tag{8}$$

The first term gives the usual incoherent radiation term, which is proportional to the total number N of the irradiated molecules.[4,14] We concentrate on the second term, which usually yields the coherent second-harmonic radiation into a well-defined direction. We show that in the presence of the interface, even though the magnitude of the second term from an isotropic bulk fluid is reduced from N^2 after the rotational average and an integration over r_j, it still yields a coherent radiation comparable to a nominal surface second-harmonic generation.

We first proceed with the full rotation average in Eq. (8). The quantity of interest is[4,14]

$$\langle \beta_{qrst} \rangle \equiv \langle \beta_{qrst}^{(j)} \rangle = I_{qrst,\alpha\beta\chi\delta}^{(4)} \beta_{\alpha\beta\chi\delta} \ . \tag{9}$$

Here $\beta_{\alpha\beta\chi\delta}$'s are defined in the molecular frame. After a full rotational average (see Appendix A),

$$\langle \beta_{qrst} \rangle k_{2\omega,q} e_{2\omega,r} e_{\omega,s} e_{\omega,t}$$
$$= \tfrac{1}{15}(-\beta_{\alpha\alpha\chi\chi} + 3\beta_{\alpha\beta\alpha\beta})(\mathbf{k}_{2\omega}\cdot\mathbf{e}_\omega)(\mathbf{e}_{2\omega}\cdot\mathbf{e}_\omega) \ . \tag{10}$$

Here, the summation convention over repeated subindices is assumed. We have used the fact that $Q_{j,\alpha\beta}$ is symmetric with respect to the exchange of α and β, and $(\mathbf{k}_{2\omega}\cdot\mathbf{e}_{2\omega})=0$. We arrive at

$$\sum_{j\neq j'} \langle M_{fi,j} \rangle \langle M_{fi,j'}^* \rangle = \frac{16\pi^3 g^{(2)} I_\omega^2 \hbar\omega}{\epsilon_{2\omega}\epsilon_\omega V} |\langle\beta_{qrst}\rangle k_{2\omega,q} e_{2\omega,r} e_{\omega,s} e_{\omega,t}|^2 \left| \sum_j \exp[i(2\mathbf{k}_\omega - \mathbf{k}_{2\omega})\cdot\mathbf{r}_j] \right|^2 \ . \tag{11}$$

$g^{(2)} \equiv \langle n_\omega(n_\omega - 1)\rangle / \langle(n_\omega)^2\rangle$ is the second-order correlation function.[4] I_ω is the intensity of the fundamental radiation field.

IV. INTEGRATION OVER A HALF-SPACE WITH $+\infty > z > 0$

If there is no interface, so that we consider a medium uniformly extended in all directions, the summation in Eq. (11) can be written into the products of three integrals from $-\infty$ to $+\infty$. This yields $\delta(2\mathbf{k}_\omega - \mathbf{k}_{2\omega})$. Together with Eq. (10), the total coherent radiation vanishes since $\mathbf{k}_\omega \cdot \mathbf{e}_\omega = 0$. This has been observed by Andrews and Blake.[13] When there is an interface, the integration along the x and y axes still yields $\delta(2k_{\omega,x} - k_{2\omega,x})\delta(2k_{\omega,y} - k_{2\omega,y})$. The integration along the z axis, however, has to be treated with care as z_j now only varies from 0 to $+\infty$. We use the following identity (see Appendix B):

$$\int_0^{+\infty} dz \exp[i(2k_{\omega,z} - k_{2\omega,z})z]$$
$$= \pi\delta(2k_{\omega,z} - k_{2\omega,z}) + \frac{i}{2k_{\omega,z} - k_{2\omega,z}} \ . \tag{12}$$

The second term has been omitted in previous molecular electrodynamical calculations.[14,15] The first term in Eq. (12) again leads to a vanishingly small coherent second-harmonic signal as pointed out by Andrews and Blake.[14,15] We emphasize at this point that it is the second term which gives rise to a coherent, nonzero contribution from the bulk molecular fluid to the nominal interface SHG. We note that $\mathbf{k}_{2\omega}$ is independently restricted by Maxwell equations, or specifically, $(\mathbf{k}_{2\omega}\cdot\mathbf{k}_{2\omega}) = \epsilon_{2\omega}(2\omega/c)^2$. When two components of $\mathbf{k}_{2\omega}$ are determined, the third component is also determined up to a plus (transmission direction) or a minus sign (reflection direction). We arrive at

$$\int_{(\Omega=4\pi)} d\Omega \left| \sum_j \exp[i(2\mathbf{k}_\omega - \mathbf{k}_{2\omega})\cdot\mathbf{r}_j] \right|^2$$
$$= \left[\frac{N}{V}\right]^2 \frac{\pi^2 A}{\cos^2(\theta_i)\epsilon_{2\omega}(\omega/c)^2|2k_{\omega,z} - k_{2\omega,z}|^2} \ . \tag{13}$$

The total second-harmonic radiation power is

$$S(2\omega) = \frac{32\pi^3\omega^2\sec^2(\theta_i)}{c^3\epsilon_{2\omega}^{1/2}\epsilon_\omega} |N_{s,\text{eff}}\alpha_{\text{eff}}^{(2)}|^2 I_\omega^2 A \ . \tag{14}$$

This result is the same as those obtained from the macroscopic polarization fields or the macroscopic electric current density.[2,5–10] Here, for comparison with the second-harmonic generation from a noncentrosymmetric monolayer of molecules, we have defined the effective surface density,

$$N_{s,\text{eff}} = \frac{N}{V} \frac{1}{2k_{\omega,z} - k_{2\omega,z}} \ , \tag{15}$$

and the *effective* second-order molecular polarizability

$$\alpha_{\text{eff}}^{(2)} \equiv \tfrac{1}{15}(-\beta_{\alpha\alpha\chi\chi} + 3\beta_{\alpha\beta\alpha\beta})(\mathbf{k}_{2\omega}\cdot\mathbf{e}_\omega)(\mathbf{e}_{2\omega}\cdot\mathbf{e}_\omega) \ . \tag{16}$$

For the second-harmonic radiation in the transmission direction (i.e., into the molecular fluid),

$$2k_{\omega,z} - k_{2\omega,z} = (2\omega/c)\{\epsilon_\omega^{1/2}\cos(\theta_i)$$
$$- [\epsilon_{2\omega} - \epsilon_\omega\sin^2(\theta_i)]^{1/2}\} \ ,$$

and in the reflection direction,

$$2k_{\omega,z} - k_{2\omega,z} = (2\omega/c)\{\epsilon_\omega^{1/2}\cos(\theta_i)$$
$$+ [\epsilon_{2\omega} - \epsilon_\omega\sin^2(\theta_i)]^{1/2}\} \ .$$

We note that the radiated powers in two directions are comparable as $\mathbf{k}_{2\omega}\cdot\mathbf{e}_\omega = (\mathbf{k}_{2\omega} - 2\mathbf{k}_\omega)\cdot\mathbf{e}_\omega = -(2k_{\omega,z} - k_{2\omega,z})e_{\omega,z}$, and the effective surface susceptibility $\chi_{\text{eff}}^{(2)} \equiv N_{s,\text{eff}}\alpha_{\text{eff}}^{(2)}$ is reduced to

$$\chi_{\text{eff}}^{(2)} = -\frac{1}{15}(-\beta_{\alpha\alpha\chi\chi} + 3\beta_{\alpha\beta\alpha\beta})\frac{N}{V}(\mathbf{e}_{2\omega}\cdot\mathbf{e}_{\omega})e_{\omega,z} \ . \tag{17}$$

V. DISCUSSION

We make the following observations. Since $\beta \sim d_m \alpha^{(2)}$, with d_m being the linear dimension of the molecule, $\chi_{\text{eff}}^{(2)} \equiv N_{s,\text{eff}}\alpha_{\text{eff}}^{(2)} \sim N_s \alpha^{(2)}$. Consequently, the coherent electric quadrupole contribution given by Eq. (14) is *generally comparable* to a nominal surface SHG from monolayer noncentrosymmetric molecules with a nonlinear polarizability $\alpha^{(2)}$.[1-3]

Furthermore, it is clear that the coherent radiation is still much larger than the incoherent contribution. Within the detection solid angle $\Delta\Omega = 1/[(k_{2\omega})^2 A]$, the ratio of the incoherent power to the coherent power is that of the total number of the irradiated molecules, $(N/V)AL$ (with L being the length of the irradiated part of the molecular fluid) and the square of the number of the irradiated molecules in the *coherent volume*, $[(N/V)A/(2k_{\omega,z}-k_{2\omega,z})]^2$. For $L \sim 1$ cm, $N/V \sim 10^{22}/\text{cm}^3$, $A \sim 1$ cm^2, $1/(2k_{\omega,z}-k_{2\omega,z}) \sim 10^{-5}$ cm, the ratio is estimated to be $\sim 10^{-12}$.

Another electric quadrupole term arises from the processes in which two fundamental photons are annihilated by actions of electric dipole interaction, and one second-harmonic photon is created through an electric quadrupole interaction.[4,12] One part of this additional term can be easily incorporated by adding another term in both $\beta_{\alpha\alpha\beta\beta}$ and $\beta_{\alpha\beta\beta\alpha}$ in Eq. (10).[10,12] For the other part, stemming from the abrupt change of the electric quadrupole density $(N/V)\beta$ at the interface, one may refer to the treatment by Guyot-Sionnest and Shen (GS) in Ref. 10. Our present β term corresponds to the χ^P term in GS's definition. One can proceed similarly with the calculation of the magnetic dipole contribution. Once again, when the integration along the z axis is properly carried out as in Appendix B, one obtains a coherent second-harmonic radiation which is again comparable in magnitude to a nominal surface SHG. Since the rotational average is performed over a third-rank tensor involving $\mathbf{k}_\omega \times \mathbf{e}_\omega$, the total second-harmonic intensity from a magnetic dipole term is proportional to $(\mathbf{k}_\omega \cdot \mathbf{e}_{2\omega})^2$.

Finally, in the present calculation, we have assumed that the two isotropic media have the same dielectric constants. This can be easily extended to general cases when $\epsilon_{\omega,a} \neq \epsilon_{\omega,b}$ by introducing the macroscopic local-field factors as discussed in Ref. 2 by Shen.

VI. CONCLUSION

We reiterate that the bulk contribution due to the electric quadrupole and magnetic dipole responses of isotropic bulk fluids to optical second-harmonic generation from an interface is *coherent* and *generally comparable* to a nominal surface or interface SHG. This conclusion can be obtained equally by the calculation starting with the macroscopic polarization fields or the macroscopic electric current density, and by the calculation based upon molecular quantum electrodynamics.

APPENDIX A: FULLY ROTATIONAL AVERAGE OF TENSORS

According to Craig and Thirunamachandran,[4] the fully rotational average of the direction cosines connecting two fourth-rank tensors, β_{qrst} in the laboratory frame and $\beta_{\alpha\beta\chi\delta}$ in the molecular frame, is given by

$$I_{qrst,\alpha\beta\chi\delta}^{(4)} = \frac{1}{30}\begin{bmatrix}\delta_{qr}\delta_{st}\\\delta_{qs}\delta_{rt}\\\delta_{qt}\delta_{rs}\end{bmatrix}^T\begin{bmatrix}4 & -1 & -1\\-1 & 4 & -1\\-1 & -1 & 4\end{bmatrix}\begin{bmatrix}\delta_{\alpha\beta}\delta_{\chi\delta}\\\delta_{\alpha\chi}\delta_{\beta\delta}\\\delta_{\alpha\delta}\delta_{\beta\chi}\end{bmatrix} \ . \tag{A1}$$

Thus, combined with $k_{2\omega,q}e_{2\omega,r}e_{\omega,s}e_{\omega,t}$, one finds

$$\langle\beta_{qrst}\rangle k_{2\omega,q}e_{2\omega,r}e_{\omega,s}e_{\omega,t}$$
$$= \frac{1}{30}[(4\beta_{\alpha\alpha\beta\beta} - \beta_{\alpha\beta\alpha\beta} - \beta_{\alpha\beta\beta\alpha})(\mathbf{k}_{2\omega}\cdot\mathbf{e}_{2\omega})(\mathbf{e}_\omega\cdot\mathbf{e}_\omega)$$
$$+ (-2\beta_{\alpha\alpha\beta\beta} + 3\beta_{\alpha\beta\alpha\beta} + 3\beta_{\alpha\beta\beta\alpha})$$
$$\times(\mathbf{k}_{2\omega}\cdot\mathbf{e}_\omega)(\mathbf{e}_{2\omega}\cdot\mathbf{e}_\omega)] \ . \tag{A2}$$

From the transversality relation, $\mathbf{k}_{2\omega}\cdot\mathbf{e}_{2\omega} = 0$, the first term in (A2) vanishes. The second term can be further simplified from the fact that $\beta_{\alpha\beta\chi\delta}$ as defined by Eq. (6) is symmetric with respect to the exchange of α and β. We then arrive at Eq. (10).

APPENDIX B

The integration on the right-hand side of Eq. (12) plays the most important part in the present paper. The previous calculation by Andrews and Blake did not treat this integral completely.[14,15] The integral is partitioned into a real part and an imaginary part:

$$\int_0^{+\infty}dz\,\exp[i(2k_{\omega,z}-k_{2\omega,z})z] = X + iY \ . \tag{B1}$$

The real part gives the usual Krönecker δ function $\delta(2k_{\omega,z}-k_{2\omega,z})$ since

$$X = \frac{1}{2}\text{Re}\left[\int_{-\infty}^{+\infty}dz\,\exp[i(2k_{\omega,z}-k_{2\omega,z})z]\right]$$
$$= \pi\delta(2k_{\omega,z}-k_{2\omega,z}) \ . \tag{B2}$$

The imaginary part should be obtained as a limit defined as

$$Y = \frac{1}{i}\left[\int_0^{+\infty}dz\,\exp[i(2k_{\omega,z}-k_{2\omega,z}-\gamma)z]\right]_{\gamma\to0+}$$
$$= \frac{1}{2k_{\omega,z}-k_{2\omega,z}} \ . \tag{B3}$$

By combining (B2) and (B3), we obtain Eq. (12).

It is easy to see that such an imaginary part vanishes when we integrate from $-\infty$ to $+\infty$,

$$Y = \frac{1}{i}\left[\int_{-\infty}^{+\infty}dz\,\exp[i(2k_{\omega,z}-k_{2\omega,z})z-\gamma|z|]\right]_{\gamma\to0+}$$
$$= 0 \ . \tag{B4}$$

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