

## Influence of the interaction between dipoles, optically induced in a crystal lattice, on the nonlinear refractive index of crystals

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The changes of the vibrational amplitudes of molecules in a crystal lattice, due to interaction between the optically induced dipoles, are shown to account for the nonlinear refractive index of a crystal. The general expressions for the fourth- and sixth-rank tensors,  $\chi_{ijkl}(-\omega, \omega, \omega, -\omega)$  and  $\chi_{ijklmn}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$ , for a crystal lattice, are derived. The results of numerical calculations for diamond and benzene lattices are reported to prove that the contribution to the susceptibility tensors of the effect presented is comparable with the electronic effect of hyperpolarizability.

### I. INTRODUCTION

In previous papers of Piekara<sup>1</sup> and of Piekara and Ratajska,<sup>2</sup> the mechanism of mutual interaction of dipoles induced by a strong optical field in crystal lattice or quasicrystal lattice in liquids was shown to lead to vibrational amplitude and frequency changes and thus to nonlinear refractive index of the medium. The assumption of short-lived ( $\tau \sim 10^{-12}$  s) quasicrystalline structure of liquids<sup>3</sup> in the region of action of short-range forces can be justified by x-ray experimental results.<sup>4,5</sup> Hence, in the case of picosecond excitation in liquids, when the mechanisms with the response time longer than the pulse duration (e.g., orientational effect) are to be almost neglected,<sup>6,7</sup> the effect proposed by Piekara<sup>1,2</sup> should play an important role. In liquids composed of spherically symmetric molecules it remains the sole reason, aside from hyperpolarizability of molecules, for nonlinear refractive index changes.

The same mechanism of vibrational amplitude shifts due to induced-dipole—induced-dipole interaction of an individual molecule with its nearest neighbors should also contribute to nonlinear refractive index of crystals, whereas in the former considerations of this problem only the clearly electronic effect of hyperpolarizability was taken into account.<sup>8-12</sup>

In the present paper the theory presented in Refs. 1 and 2 for a one-dimensional crystal lattice, is extended to the three-dimensional crystal lattice (Secs. II and III). In Sec. IV one derives the expressions for optical susceptibility tensors  $\chi_{ijkl}(-\omega, \omega, \omega, -\omega)$  and  $\chi_{ijklmn}(-\omega, \omega, \omega,$

$-\omega, \omega, -\omega)$ , related to nonlinear coefficients  $n_2$  and  $n_4$  in the expansion of refractive index  $n$  with respect to the optical field  $\vec{E}$ :

$$n = n_0 + n_2 |E|^2 + n_4 |E|^4 \quad (1)$$

by the formulas

$$\begin{aligned} n_2(\omega) &= \frac{2\pi}{n_0} \sum_{ijkl} \chi_{ijkl}(-\omega, \omega, \omega, -\omega) e_{ip} e_{jp} \eta_k \eta_l, \\ n_4(\omega) &= \frac{2\pi}{n_0} \sum_{ijklmn} \chi_{ijklmn}(-\omega, \omega, \omega, -\omega, \omega, -\omega) \\ &\quad \times e_{ip} e_{jp} \eta_k \eta_l \eta_m \eta_n, \end{aligned} \quad (2)$$

where the index  $p$  denotes a chosen direction in which the refractive index is measured;  $e_{ip}$  is a cosines direction between axes  $\vec{i}$  and  $\vec{p}$  and  $\eta_i = E_i / |\vec{E}|$ . The results of numerical calculations performed for diamond and benzene lattices are reported and compared with the results due to electronic effect (Sec. V).

### II. MOLECULAR FIELD IN CRYSTAL

We are considering a crystal lattice composed of identical, rigid, nondipolar molecules or atoms performing translational and rotational vibrations around their equilibrium positions. Small displacements of the ( $ln$ )th molecule, where  $l$  is the number of elementary cells and  $n$  is the number of molecules in a cell, are denoted by  $\vec{u}(ln)$  and  $\vec{\theta}(ln)$  for translational and rotational vibrations, respectively. We use an assumption, often used in molecular crystals,<sup>13,14</sup> that the rotational vibrations take

place around the molecular symmetry axes. Hence, the vector

$$\vec{\theta}(ln) = [\theta_w(ln), \theta_u(ln), \theta_v(ln)]$$

is defined in a coordinate system of molecular symmetry axes ( $w, u, v$ ), whereas the vector

$$\vec{u}(ln) = [u_x(ln), u_y(ln), u_z(ln)]$$

$$\alpha_{ij}(ln) = W_{i\eta}(ln) R_{\eta\kappa}(\theta_w(ln)) R_{\kappa\lambda}(\theta_u(ln)) R_{\lambda\mu}(\theta_v(ln)) \alpha_{\mu\nu} R_{\nu\rho}^{-1}(\theta_v(ln)) R_{\rho\sigma}^{-1}(\theta_u(ln)) R_{\sigma\tau}^{-1}(\theta_w(ln)) W_{\tau j}^{-1}(ln), \quad (3)$$

where

$$i, j = x, y, z; \eta, \kappa, \lambda, \mu, \nu, \rho, \sigma, \tau = w, u, v.$$

$[W(ln)]$  is a transformation matrix from the ( $ln$ )th molecular axes to crystallographic axes,  $[R(\theta_w)], [R(\theta_u)], [R(\theta_v)]$  are matrices of rotation around  $\vec{w}, \vec{u},$  and  $\vec{v}$  molecular symmetry axes, respectively, and  $[\alpha_{\mu\nu}]$  denotes a polarizability tensor of an isolated molecule, determined on molecular axes. If the crystal is subjected to an external electric field  $\vec{E} = \vec{E}(\omega) \cos \omega t$  of a light wave, the total electric field acting on each ( $ln$ )th molecule is not only a macroscopic local field,  $F_i = f_i(\omega) E_i$ , but also a field of dipoles induced in adjacent molecules:

$$E_i^{ef}(ln) = f_i(\omega) E_i + \sum_{j'l'n'} A_{ij}(ln, l'n') E_j^{ef}(l'n'), \quad (4a)$$

where  $f_i(\omega)$  is a local-field factor, which in this paper is assumed to be a Lorentz factor  $f_i(\omega) = [\epsilon_i(\omega) + 2]/3$  and

$$A_{ij}(ln, l'n') = \sum_k \frac{\alpha_{kj}(l'n')}{r^3(ln, l'n')} \times \left[ \frac{r_k(ln, l'n') r_i(ln, l'n')}{r^2(ln, l'n')} - \delta_{ik} \right] \quad (4b)$$

is a  $3Ns$  rank tensor ( $N$  is the number of elementary cells,  $s$  is the number of molecules in a cell) of

is defined in a system of crystallographic axes,  $x, y, z$ .

The polarizability tensor of an isolated molecule, determined on crystallographic axes, denoted by  $[\alpha_{ij}(ln)]$  and dependent on small rotational displacements, is given by<sup>14</sup>:

dipole-dipole interactions.

$$\vec{r}(ln, l'n') = \vec{r}_0(ln, l'n') + \vec{u}(ln) - \vec{u}(l'n')$$

is a vector between molecules ( $ln$ ) and ( $l'n'$ ), whereas  $\vec{r}_0(ln, l'n')$  is a vector between their equilibrium sites. The summation in (4a) is taken only over the nearest neighbors ( $l'n'$ ) of a given molecule ( $ln$ ). The molecular field acting on a molecule embedded in a crystal lattice is obtained as a general solution of the Eq. (4a):

$$E_i^{ef}(ln) = \sum_j T_{ij}(ln) F_j, \quad (5)$$

where  $T_{ij}(ln) = \sum_{l'n'} T_{ij}(ln, l'n')$ , and  $T_{ij}(ln, l'n')$  is the  $[iln, jl'n']$ th element of matrix  $(I - A)^{-1}$ , the inverse of  $(I - A)$ .

### III. VIBRATIONAL FREQUENCY AND AMPLITUDE SHIFTS

According to (5) the Hamiltonian of interaction of a crystal with an optical field,

$$H_I = -\frac{1}{2} \sum_{lnij} \alpha_{ij}(ln) E_i^{ef}(ln) E_j^{ef}(ln), \quad (6)$$

has the form

$$H_I = -\frac{1}{2} \sum_{lnijpk} \alpha_{ij}(ln) T_{ik}(ln) T_{jp}(ln) F_k F_p. \quad (7)$$

If we denote a small displacement of a molecule by  $w_r(ln)$ , where

$$w_r(ln) = \begin{cases} \sqrt{m} u_r(ln) & \text{for translational vibrations } r = x, y, z \\ \sqrt{I_r} \theta_r(ln) & \text{for rotational vibrations } r = w, u, v \end{cases} \quad (8)$$

( $m$  is the molecular mass,  $I_r$  is the molecular moment of inertia with respect to the  $r$ th axis), then the equation of motion for the ( $ln$ )th molecule with accuracy to the third-order terms in small displacements  $w_r(ln)$  has the form:

$$\begin{aligned}
\ddot{w}_r(ln) + \sum_{l'n'r'} \left[ H_{0rr'}^{(2)}(ln, l'n') - \sum_{pk} \mathcal{H}_{pk,rr'}^{I(2)}(ln, l'n') F_p F_k \right] w_{r'}(l'n') \\
= \sum_{pk} \mathcal{H}_{pk,r}^{I(1)}(ln) F_p F_k - \frac{1}{2} \sum_{l'n'l''n''r''} \left[ H_{0,rr'r''}^{(3)}(ln, l'n', l''n'') \right. \\
\left. - \sum_{pk} \mathcal{H}_{pk,rr'r''}^{I(3)}(ln, l'n', l''n'') F_p F_k \right] w_{r'}(l'n') w_{r''}(l''n'') \\
- \frac{1}{6} \sum_{l'n'l''n''l''''n''''r''r''''} \left[ H_{0,rr'r''r''''}^{(4)}(ln, l'n', l''n'', l''''n''') \right. \\
\left. - \sum_{pk} \mathcal{H}_{pk,rr'r''r''''}^{I(4)}(ln, l'n', l''n'', l''''n''') F_p F_k \right] w_{r'}(l'n') w_{r''}(l''n'') w_{r''''}(l''''n''') , \quad (9a)
\end{aligned}$$

where

$$H_{0r_1' \dots r_j'}^{(j)}(ln, \dots, l_j n_j) = \left[ \frac{\partial^j H_0}{\partial w_{r_1}(ln) \dots \partial w_{r_j}(l_j n_j)} \right]_0 ,$$

are the succeeding derivatives of the Hamiltonian  $H_0$  of an undisturbed system, whereas the corresponding derivatives of the interaction Hamiltonian  $H_I = - \sum_{pk} \mathcal{H}_{pk}^I F_p F_k$ ,

$$\mathcal{H}_{pk}^I = \frac{1}{2} \sum_{lnij} \alpha_{ij}(ln) T_{ik}(ln) T_{jp}(ln) , \quad (9b)$$

are given in Appendix A.

Taking advantage of translational symmetry of a crystal, we introduce normal coordinates  $Q_{\vec{q}\alpha}^E$ , defined by the relation<sup>15</sup>:

$$w_r(ln) = \frac{1}{\sqrt{N}} \sum_{\vec{q}\alpha} Q_{\vec{q}\alpha}^E e_r^E(n | \vec{q}\alpha) e^{i\vec{q} \cdot \vec{r}(ln)} , \quad (10a)$$

where  $\vec{q}$  is the reciprocal lattice vector,  $\alpha$  is the number of vibrational modes corresponding to  $\vec{q}$ , and the vectors  $\vec{e}^E(n | \vec{q}\alpha)$  fulfill orthonormality relations:

$$\begin{aligned}
\sum_{in} e_i^{*E}(n | \vec{q}\alpha) e_i^E(n | \vec{q}'\alpha') &= \delta(\vec{q} - \vec{q}') \delta_{\alpha\alpha'} , \\
\sum_{\vec{q}\alpha} e_i^{*E}(n | \vec{q}\alpha) e_j^E(n' | \vec{q}\alpha) &= \delta_{ij} \delta_{nn'} . \quad (10b)
\end{aligned}$$

Substituting (10a) into (9a) we obtain:

$$\begin{aligned}
\ddot{Q}_{\vec{q}\alpha}^E + (w_{\vec{q}\alpha}^E)^2 Q_{\vec{q}\alpha}^E &= \sum_{pk} \mathcal{H}_{pk}^{I(1)}(\alpha) F_p F_k \\
- \frac{1}{2} \sum_{\vec{q}'\vec{q}''\alpha'\alpha''} \left[ H_0^{(3)} \left[ \begin{array}{ccc} \vec{q} & \vec{q}' & \vec{q}'' \\ \alpha & \alpha' & \alpha'' \end{array} \right] - \sum_{pk} \mathcal{H}_{pk}^{I(3)} \left[ \begin{array}{ccc} \vec{q} & \vec{q}' & \vec{q}'' \\ \alpha & \alpha' & \alpha'' \end{array} \right] F_p F_k \right] & Q_{\vec{q}'\alpha'}^E Q_{\vec{q}''\alpha''}^E \\
- \frac{1}{6} \sum_{\vec{q}'\vec{q}''\vec{q}'''\alpha'\alpha''\alpha'''} \left[ H_0^{(4)} \left[ \begin{array}{cccc} \vec{q} & \vec{q}' & \vec{q}'' & \vec{q}''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{array} \right] \right. \\
\left. - \sum_{pk} \mathcal{H}_{pk}^{I(4)} \left[ \begin{array}{cccc} \vec{q} & \vec{q}' & \vec{q}'' & \vec{q}''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{array} \right] F_p F_k \right] & Q_{\vec{q}'\alpha'}^E Q_{\vec{q}''\alpha''}^E Q_{\vec{q}'''\alpha'''}^E \quad (11)
\end{aligned}$$

where

$$\begin{aligned} \mathcal{H}_{pk}^{I(1)}(\alpha) &= \sqrt{N} \sum_{nr} \mathcal{H}_{pk,r}^{I(1)}(n) e_r^E(n | \vec{q}\alpha) \delta(\vec{q}), \\ H_0^{(3)} \left[ \begin{array}{ccc} \vec{q} & \vec{q}' & \vec{q}'' \\ \alpha & \alpha' & \alpha'' \end{array} \right] &= \frac{1}{\sqrt{N}} \sum_{ln'l'n''r'r''} H_{0rr'r''}^{(3)}(ln,l'n',l''n'') \\ &\quad \times e_r^E(n | \vec{q}\alpha) e_{r'}^E(n' | \vec{q}'\alpha') e_{r''}^E(n'' | \vec{q}''\alpha'') e^{i[\vec{q} \cdot \vec{r}(l) + \vec{q}' \cdot \vec{r}(l') + \vec{q}'' \cdot \vec{r}(l'')]}, \\ H_0^{(4)} \left[ \begin{array}{cccc} \vec{q} & \vec{q}' & \vec{q}'' & \vec{q}''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{array} \right] &= \frac{1}{N} \sum_{ln'l'n''l'''n''''r'r''r'''} H_{0rr'r''r'''}^{(4)}(ln,l'n',l''n'',l'''n''') e_r^E(n | \vec{q}\alpha) e_{r'}^E(n' | \vec{q}'\alpha') \\ &\quad \times e_{r''}^E(n'' | \vec{q}''\alpha'') e_{r'''}^E(n''' | \vec{q}'''\alpha''') \\ &\quad \times e^{i[\vec{q} \cdot \vec{r}(l) + \vec{q}' \cdot \vec{r}(l') + \vec{q}'' \cdot \vec{r}(l'') + \vec{q}''' \cdot \vec{r}(l''')]}, \end{aligned}$$

and analogically for

$$\mathcal{H}_{pk}^{I(3)} \left[ \begin{array}{ccc} \vec{q} & \vec{q}' & \vec{q}'' \\ \alpha & \alpha' & \alpha'' \end{array} \right]$$

and

$$\mathcal{H}_{pk}^{I(4)} \left[ \begin{array}{cccc} \vec{q} & \vec{q}' & \vec{q}'' & \vec{q}''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{array} \right].$$

If we consider only one monochromatic wave incident on a crystal,  $\vec{E} = \vec{E}(\omega) \cos \omega t$ , our interaction Hamiltonian is time independent because

$$E_p(t) E_k(t) = \frac{1}{2} E_p(\omega) E_k(\omega) (1 + \cos 2\omega t), \quad (12)$$

and the term oscillating with frequency  $2\omega$  can be neglected because it is very quick in comparison with vibrational frequencies of a crystal lattice,  $\omega_{\vec{q}\alpha} \sim 10^{13} \text{ s}^{-1} \ll \omega \sim 10^{15} \text{ s}^{-1}$ .  $\omega_{\vec{q}\alpha}^E$  in Eq. (11) denotes the frequency of normal vibration  $\alpha$  of a crystal lattice in the presence of a light-wave electric field and is to be found as an eigenvalue of a secular equation:

$$(\omega_{\vec{q}\alpha}^E)^2 e_r^E(n | \vec{q}\alpha) = \sum_{r'n'} \left[ H_{0rr'}^{(2)}(n, n', \vec{q}) - \sum_{pk} \mathcal{H}_{pk,rr'}^{I(2)}(n, n', \vec{q}) F_p F_k \right] e_{r'}^E(n' | \vec{q}\alpha), \quad (13)$$

where

$$\begin{aligned} H_{0rr'}^{(2)}(n, n', \vec{q}) &= \sum_l H_{0rr'}^{(2)}(0n, ln') e^{i\vec{q} \cdot \vec{r}(l)}, \\ \mathcal{H}_{pk,rr'}^{I(2)}(n, n', \vec{q}) &= \sum_l \mathcal{H}_{pk,rr'}^{I(2)}(0n, ln') e^{i\vec{q} \cdot \vec{r}(l)}. \end{aligned}$$

This equation can be solved by the perturbation method because

$$|\mathcal{H}_{pk,rr'}^{I(2)}(n, n', \vec{q}) F_p F_k| \sim \frac{d^2}{dr_i dr_j} \left[ \frac{(\alpha)}{1 - (\alpha)/r^3} \right] E^2 \simeq 10^2 E^2 \text{ esu},$$

[( $\alpha$ ) is molecular polarization] whereas

$$|H_{0rr'}^{(2)}(n, n', \vec{q})| \sim m \omega_\alpha^2 \sim 10^{14} \text{ esu} \quad (m \sim 10^{-23} \text{ g}, \omega_\alpha \sim 10^{13} \text{ s}^{-1}),$$

which means

$$|\mathcal{H}_{pk,rr}^{I(2)}(n, n', \vec{q}) F_p F_k| \ll |H_{0rr}^{(2)}(n, n', \vec{q})|$$

even for  $E^2 \sim 10^{10}$  esu. Thus the vibrational frequency, changed by the optical field, is obtained from (13) in the form:

$$(\omega_{\vec{q}\alpha}^E)^2 = \omega_{\vec{q}\alpha}^2 (1 + \eta_{\vec{q}\alpha}^{(2)} + \eta_{\vec{q}\alpha}^{(4)} + \dots), \tag{14}$$

where  $\omega_{\vec{q}\alpha}$  denotes the vibrational frequency of a mode  $\alpha$ , with the eigenvector  $\vec{e}(n | \vec{q}\alpha)$  in the absence of an external field, being an eigenvalue of (13) after putting  $\vec{E} = 0$ , and

$$\eta_{\vec{q}\alpha}^{(2)} = \frac{1}{\omega_{\vec{q}\alpha}^2} \sum_{pk} K_{pk}^{(2)}(\vec{q}\alpha) F_p F_k; \quad \eta_{\vec{q}\alpha}^{(4)} = \frac{1}{\omega_{\vec{q}\alpha}^2} \sum_{pkmn} K_{pkmn}^{(4)}(\vec{q}\alpha) F_p F_k F_m F_n,$$

with

$$K_{pk}^{(2)}(\vec{q}\alpha) = - \sum_{n, n', r, r'} e_r^*(n | \vec{q}\alpha) \mathcal{H}_{pk,rr}^{I(2)}(n, n', \vec{q}) e_{r'}(n' | \vec{q}\alpha),$$

$$K_{pkmn}^{(4)}(\vec{q}\alpha) = \sum_{\alpha' \neq \alpha} \sum_{n, n', n'', n'''} \sum_{r, r', r'', r'''} \frac{1}{\omega_{\vec{q}\alpha}^2 - \omega_{\vec{q}\alpha'}^2} [e_r^*(n | \vec{q}\alpha) \mathcal{H}_{pk,rr}^{I(2)}(n, n', \vec{q}) e_{r'}(n' | \vec{q}\alpha') \times [e_{r''}^*(n'' | \vec{q}\alpha') \mathcal{H}_{pk,r''r'''}^{I(2)}(n'', n''', \vec{q}) e_{r'''}(n''' | \vec{q}\alpha)]]$$

Equation (11), in turn, has the following solution:

$$Q_{\vec{q}\alpha}^E(t) = Q_{\vec{q}\alpha}^E(0) \cos(\tilde{\omega}_{\vec{q}\alpha} t + \gamma_{\vec{q}\alpha}) + d_{\vec{q}\alpha} - \frac{1}{2\omega_{\vec{q}\alpha}^2} \sum_{\vec{q}' \vec{q}'' \alpha' \alpha''} H_0^{(3)} \begin{bmatrix} \vec{q} & \vec{q}' & \vec{q}'' \\ \alpha & \alpha' & \alpha'' \end{bmatrix} d_{\vec{q}'\alpha'} d_{\vec{q}''\alpha''}$$

$$- \frac{1}{4} \sum_{\substack{\vec{q}' \vec{q}'' \alpha' \alpha'' \\ \omega_{\vec{q}'\alpha'} + \omega_{\vec{q}''\alpha''} \neq \omega_{\vec{q}\alpha} \\ \gamma_{\vec{q}'\alpha'} + \gamma_{\vec{q}''\alpha''} \neq \gamma_{\vec{q}\alpha}}} \Gamma^{(3)} \begin{bmatrix} \vec{q} & \vec{q}' & \vec{q}'' \\ \alpha & \alpha' & \alpha'' \end{bmatrix} \times \left[ Q_{\vec{q}'\alpha'}^E(0) Q_{\vec{q}''\alpha''}^E(0) \frac{\cos[(\omega_{\vec{q}'\alpha'} + \omega_{\vec{q}''\alpha''})t + \gamma_{\vec{q}'\alpha'} + \gamma_{\vec{q}''\alpha''}]}{\omega_{\vec{q}\alpha}^2 - (\omega_{\vec{q}'\alpha'} + \omega_{\vec{q}''\alpha''})^2} + 2Q_{\vec{q}'\alpha' \neq \vec{q}\alpha}^E(0) d_{\vec{q}''\alpha''} \frac{\cos(\omega_{\vec{q}'\alpha'} t + \gamma_{\vec{q}'\alpha'})}{\omega_{\vec{q}\alpha}^2 - \omega_{\vec{q}'\alpha'}^2} \right]$$

$$- \frac{1}{24} \sum_{\substack{\vec{q}' \vec{q}'' \vec{q}''' \alpha' \alpha'' \alpha''' \\ \omega_{\vec{q}'\alpha'} + \omega_{\vec{q}''\alpha''} + \omega_{\vec{q}'''\alpha'''} \neq \omega_{\vec{q}\alpha} \\ \gamma_{\vec{q}'\alpha'} + \gamma_{\vec{q}''\alpha''} + \gamma_{\vec{q}'''\alpha'''} \neq \gamma_{\vec{q}\alpha}}} \left[ H_0^{(4)} \begin{bmatrix} \vec{q} & \vec{q}' & \vec{q}'' & \vec{q}''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{bmatrix} - \sum_{pk} \mathcal{H}_{pk}^{I(4)} \begin{bmatrix} \vec{q} & \vec{q}' & \vec{q}'' & \vec{q}''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{bmatrix} F_p F_k \right] \times Q_{\vec{q}'\alpha'}^E(0) Q_{\vec{q}''\alpha''}^E(0) Q_{\vec{q}'''\alpha'''}^E(0)$$

$$\times \frac{\cos[(\omega_{\vec{q}'\alpha'} + \omega_{\vec{q}''\alpha''} + \omega_{\vec{q}'''\alpha'''})t + \gamma_{\vec{q}'\alpha'} + \gamma_{\vec{q}''\alpha''} + \gamma_{\vec{q}'''\alpha'''}]}{\omega_{\vec{q}\alpha}^2 - (\omega_{\vec{q}'\alpha'} + \omega_{\vec{q}''\alpha''} + \omega_{\vec{q}'''\alpha'''})^2}, \tag{15}$$

where we have introduced the denotations  $\omega_{-\vec{q}\alpha} = -\omega_{\vec{q}\alpha}$ , and the sum is over  $-\infty \leq \vec{q}\alpha \leq \infty$ .

$$\Gamma^{(3)} \begin{bmatrix} \bar{q} & \bar{q}' & \bar{q}'' \\ \alpha & \alpha' & \alpha'' \end{bmatrix} = H_0^{(3)} \begin{bmatrix} \bar{q} & \bar{q}' & \bar{q}'' \\ \alpha & \alpha' & \alpha'' \end{bmatrix} - \sum_{pk} \mathcal{H}_{pk}^{I(3)} \begin{bmatrix} \bar{q} & \bar{q}' & \bar{q}'' \\ \alpha & \alpha' & \alpha'' \end{bmatrix} F_p F_k + \sum_{\alpha'''} H_0^{(4)} \begin{bmatrix} \bar{q} & \bar{q}' & \bar{q}'' & \bar{q}''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{bmatrix} d_{\bar{q}'''\alpha'''} ,$$

whereas

$$d_{\bar{q}\alpha} = \frac{1}{\omega_{\bar{q}\alpha}^2} \sum_{pk} \mathcal{H}_{pk}^{I(1)}(\bar{q}\alpha) F_p F_k$$

determines the change of the equilibrium position for a vibration  $\alpha$ . In the case of rotational vibrations it corresponds to the change of the equilibrium angle between the molecular and crystal axes.  $\tilde{\omega}_{\bar{q}\alpha}$  is the vibrational frequency of a mode  $\alpha$  in the presence of an electric field:

$$\tilde{\omega}_{\bar{q}\alpha} = \frac{\omega_{\bar{q}\alpha} (1 + \eta_{\bar{q}\alpha}^{(2)} + \eta_{\bar{q}\alpha}^{(4)})^{1/2}}{1 - \epsilon_{\bar{q}\alpha}^E} , \quad (16)$$

with

$$\epsilon_{\bar{q}\alpha}^E = \frac{1}{8(\omega_{\bar{q}\alpha}^E)^2} \left\{ \sum_{\bar{q}'\bar{q}''\alpha'\alpha''} \Gamma^{(3)} \begin{bmatrix} \bar{q} & \bar{q}' & \bar{q}'' \\ \alpha & \alpha' & \alpha'' \end{bmatrix} \times \left[ \frac{Q_{\bar{q}'\alpha'}^E(0) Q_{\bar{q}''\alpha''}^E(0)}{Q_{\bar{q}\alpha}^E(0)} \delta(\omega_{\bar{q}'\alpha'} + \omega_{\bar{q}''\alpha''} - \omega_{\bar{q}\alpha}) + 4d_{\bar{q}'\alpha'} d_{\bar{q}''\alpha''} \right] \right. \\ \left. + \frac{1}{6} \sum_{\bar{q}'\bar{q}''\alpha'\alpha''\alpha'''} \left[ H_0^{(4)} \begin{bmatrix} \bar{q} & \bar{q}' & \bar{q}'' & \bar{q}''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{bmatrix} - \sum_{pk} \mathcal{H}_{pk}^{I(4)} \begin{bmatrix} \bar{q} & \bar{q}' & \bar{q}'' & \bar{q}''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{bmatrix} F_p F_k \right] \times \frac{Q_{\bar{q}'\alpha'}^E(0) Q_{\bar{q}''\alpha''}^E(0) Q_{\bar{q}'''\alpha'''}^E(0)}{Q_{\bar{q}\alpha}^E(0)} \delta(\omega_{\bar{q}'\alpha'} + \omega_{\bar{q}''\alpha''} + \omega_{\bar{q}'''\alpha'''} - \omega_{\bar{q}\alpha}) \right\} .$$

The vibrational amplitude of a mode  $\alpha, Q_{\bar{q}\alpha}^E(0)$ , is found from the initial conditions:

$$\begin{aligned} Q_{\bar{q}\alpha}^E(t=0) &= Q_{\bar{q}\alpha}^{E=0}(t=0) , \\ \dot{Q}_{\bar{q}\alpha}^E(t=0) &= \dot{Q}_{\bar{q}\alpha}^{E=0}(t=0) . \end{aligned} \quad (17)$$

We are interested only in a mean amplitude and a mean-square amplitude, as will be shown in the next section. Hence, we have obtained the following expressions: (i) for the mean amplitude:

$$\begin{aligned} \langle \langle Q_{\bar{q}\alpha}^E(0) \rangle \rangle_{\gamma} &= d_{\bar{q}\alpha} - \frac{1}{2\omega_{\bar{q}\alpha}^2} \sum_{\bar{q}'\bar{q}''\alpha'\alpha''} H_0^{(3)} \begin{bmatrix} \bar{q} & \bar{q}' & \bar{q}'' \\ \alpha & \alpha' & \alpha'' \end{bmatrix} d_{\bar{q}'\alpha'} d_{\bar{q}''\alpha''} \\ &\quad - \frac{1}{4\omega_{\bar{q}\alpha}^2} \sum_{\bar{q}'\alpha'} \Gamma^{(3)} \begin{bmatrix} \bar{q} & \bar{q}' & -\bar{q}' \\ \alpha & \alpha' & \alpha' \end{bmatrix} \langle | Q_{\bar{q}'\alpha'}^{E=0}(0) |^2 \rangle , \end{aligned} \quad (18)$$

and (ii) for the mean-square amplitude:

$$\begin{aligned} \langle \langle | Q_{\bar{q}\alpha}^E(0) |^2 \rangle \rangle_{\gamma} &= \langle | Q_{\bar{q}\alpha}^{E=0}(0) |^2 \rangle [1 - \frac{1}{2} \eta_{\bar{q}\alpha}^{(2)} (1 - \zeta_{\bar{q}\alpha}^{(1)}) \\ &\quad + \frac{1}{2} (\eta_{\bar{q}\alpha}^{(2)})^2 (1 - \zeta_{\bar{q}\alpha}^{(2)}) - \frac{1}{2} \eta_{\bar{q}\alpha}^{(4)} (1 - \zeta_{\bar{q}\alpha}^{(3)})] + 2d_{\bar{q}\alpha}^2 (1 - \zeta_{\bar{q}\alpha}^{(4)}) , \end{aligned} \quad (19)$$

where the anharmonic terms  $\zeta_{\vec{q}\alpha}^{(1)}, \zeta_{\vec{q}\alpha}^{(2)}, \zeta_{\vec{q}\alpha}^{(3)}, \zeta_{\vec{q}\alpha}^{(4)}$  are given in Appendix B.

$\langle |Q_{\vec{q}\alpha}^{E=0}|^2 \rangle$  denotes a mean-square vibrational amplitude in the absence of an external electric field, while averaging is performed according to the formula:

$$\langle \dots \rangle = \frac{\text{Tr}(\dots e^{-H_0/kT})}{\text{Tr} e^{-H_0/kT}} \quad (20)$$

with a Hamiltonian

$$H_0 = \sum_{\vec{q}\alpha} (|\dot{Q}_{\vec{q}\alpha}^{E=0}|^2 + \omega_{\vec{q}\alpha}^2 |Q_{\vec{q}\alpha}^{E=0}|^2)$$

taken in a harmonic approximation. Such an approximation is sufficient to get (18) and (19) with accuracy to the terms linear in anharmonic coefficients. The sign  $\langle \langle \dots \rangle \rangle$  denotes that the result has been averaged over all possible phases of a vibration at a moment  $t=0$ , when the field  $\vec{E}$  appears.

#### IV. SUSCEPTIBILITY TENSORS

We assume the polarizability of a crystal to be a sum of effective polarizabilities of the molecules composing it:

$$\mathcal{P}_{ij} = \sum_{ln} \alpha_{ij}^{ef}(ln), \quad (21)$$

the effective polarizability being a polarizability of a molecule embedded in a crystal lattice. Then, according to the definition [Eq. (5)] of an effective electrical field acting on such a molecule, the dipole moment  $\vec{\mu}(ln)$  induced in a ( $ln$ )th molecule can be determined in two ways,

$$\begin{aligned} \mu_i(ln) &= \sum_j \alpha_{ij}^{ef}(ln) F_j \\ &= \sum_j \alpha_{ij}(ln) E_j^{ef}(ln), \end{aligned} \quad (22)$$

which leads to the following definition of a crystal polarizability, dependent on molecular displacements:

$$\mathcal{P}_{ij} = \sum_{ln,k} \alpha_{ik}(ln) T_{kj}(ln). \quad (23)$$

Such a model of crystal polarizability is a good approximation in molecular crystals, where intermolecular forces are much weaker than intramolecular forces. It justifies treating molecules as being rigid and neglecting their internal vibrations.

The similar model has been used by Schettino and Califano<sup>16</sup> in molecular crystals. They introduce the molecular electric field acting on an individual molecule due to dipoles and quadrupoles induced in adjacent molecules by an external electric field. It allows them to find the dependence of effective polarizability on rotational and translational displacements of molecules and to determine Raman-active modes.

The polarizability [Eq. (23)] can be expanded in power series of small vibrational amplitudes<sup>15</sup>:

$$\begin{aligned} \mathcal{P}_{ij} &= \mathcal{P}_{ij}^{(0)} + \sum_{\alpha} \mathcal{P}_{ij}^{(1)}(\alpha) Q_{\alpha}^E \\ &+ \frac{1}{2} \sum_{\vec{q}\alpha\alpha'} \mathcal{P}_{ij}^{(2)} \begin{bmatrix} \vec{q} & -\vec{q} \\ \alpha & \alpha' \end{bmatrix} Q_{\vec{q}\alpha}^E Q_{-\vec{q}\alpha'}^E + \dots, \end{aligned} \quad (24)$$

where

$$\begin{aligned} \mathcal{P}_{ij}^{(1)}(\alpha) &= \sqrt{N} \sum_{lnn'} \sum_{kr} [\alpha_{ik,r}^{(1)}(0n, ln') T_{kj}^{(0)}(n) + \alpha_{ik}^{(0)}(n) T_{kj,r}^{(1)}(0n, ln')] e_r(n' | \vec{q}\alpha) \delta(\vec{q}), \\ \mathcal{P}_{ij}^{(2)} \begin{bmatrix} \vec{q} & -\vec{q} \\ \alpha & \alpha' \end{bmatrix} &= \sum_{ln'l'n''} \sum_{krr'} [\alpha_{ik,rr'}^{(2)}(0n, ln', l'n'') T_{kj}^{(0)}(n) + \alpha_{ik}^{(0)}(n) T_{kj,rr'}^{(2)}(0n, ln', l'n'') \\ &+ \alpha_{ik,r}^{(1)}(0n, ln') T_{kj,r'}^{(1)}(0n, l'n'') + \alpha_{ik,r'}^{(1)}(0n, l'n'') T_{kj,r}^{(1)}(0n, ln')] \\ &\times e_r(n | \vec{q}\alpha) e_{r'}^*(n' | \vec{q}\alpha') e^{i\vec{q} \cdot \vec{r}(l-l')}, \end{aligned}$$

and the displacement derivatives  $T_{kj,r}^{(1)}(0n, ln')$ ,  $T_{kj,rr'}^{(2)}(0n, ln', l'n'')$  are given in Appendix A.

Substituting (24) into the definition of the polarization vector  $\vec{P}(t)$ , which is a mean dipole moment  $\vec{M}(t)$  of a crystal per unit volume ( $V$  is the volume of a crystal),

$$P_i(t) = \frac{1}{V} \langle M_i(t) \rangle = \frac{1}{V} \sum_j \langle \mathcal{P}_{ij} \rangle f_j(\omega) E_j(\omega) \cos \omega t, \quad (25)$$

and taking its Fourier transform yields:

$$P_i(\omega) = \frac{1}{V} \sum_j \left[ \mathcal{P}_{ij}^{(0)} + \sum_\alpha \mathcal{P}_{ij}^{(1)}(\alpha) \langle \langle Q_\alpha^E \rangle \rangle_\gamma + \frac{1}{4} \sum_{\vec{q}\alpha} \mathcal{P}_{ij}^{(2)} \begin{pmatrix} \vec{q} & -\vec{q} \\ \alpha & \alpha \end{pmatrix} \langle \langle |Q_{\vec{q}\alpha}^E|^2 \rangle \rangle_\gamma + \dots \right] f_j(\omega) E_j(\omega), \quad (26)$$

where  $\langle \langle Q_\alpha^E \rangle \rangle_\gamma$  and  $\langle \langle |Q_{\vec{q}\alpha}^E|^2 \rangle \rangle_\gamma$  are given by (18) and (19).

Comparing (26) with the phenomenological formula for  $P_i(\omega)$ ,<sup>17</sup>

$$P_i(\omega) = \chi_{ij}(\omega) E_j(\omega) + 3\chi_{ijkl}(-\omega, \omega, \omega, -\omega) E_j(\omega) E_k(\omega) E_l(-\omega) \\ + 10\chi_{ijklmn}(-\omega, \omega, \omega, -\omega, \omega, -\omega) E_j(\omega) E_k(\omega) E_l(-\omega) E_m(\omega) E_n(-\omega), \quad (27)$$

we obtain the optical susceptibility tensors of fourth and sixth rank, connected with nonlinear refractive index coefficients  $n_2$  and  $n_4$  by (2),

$$\chi_{ijkl}(-\omega, \omega, \omega, -\omega) = \frac{1}{6V} f_i(\omega) f_j(\omega) f_k(\omega) f_l(\omega) \\ \times \left[ \sum_\alpha [\mathcal{P}_{ij}^{(1)}(\alpha) B_{kl}^{(1)}(\alpha) + \mathcal{P}_{ik}^{(1)}(\alpha) B_{jl}^{(1)}(\alpha)] \right. \\ \left. - \frac{1}{2} \sum_{\vec{q}\alpha} \left[ \mathcal{P}_{ij}^{(2)}(\vec{q}\alpha) \frac{K_{kl}^{(2)}(\vec{q}\alpha)}{\omega_{\vec{q}\alpha}^2} [1 - \zeta_{kl}^{(1)}(\vec{q}\alpha)] + \mathcal{P}_{ik}^{(2)}(\vec{q}\alpha) \frac{K_{jl}^{(2)}(\vec{q}\alpha)}{\omega_{\vec{q}\alpha}} [1 - \zeta_{jl}^{(1)}(\vec{q}\alpha)] \right] \right. \\ \left. \times \langle \langle |Q_{\vec{q}\alpha}^{E=0}|^2 \rangle \rangle \right] \quad (28)$$

and

$$\chi_{ijklmn}(-\omega, \omega, \omega, -\omega, \omega, -\omega) \\ = \frac{1}{120V} f_i(\omega) f_j(\omega) f_k(\omega) f_l(\omega) f_m(\omega) f_n(\omega) \\ \times \left[ \sum_\alpha \left[ \mathcal{P}_{ij}^{(1)}(\alpha) [B_{klmn}^{(2)}(\alpha) + B_{knml}^{(2)}(\alpha) + B_{mnkl}^{(2)}(\alpha) + B_{mlkn}^{(2)}(\alpha)] \right. \right. \\ \left. \left. + \mathcal{P}_{ik}^{(1)}(\alpha) [B_{jlmn}^{(2)}(\alpha) + B_{jnml}^{(2)}(\alpha) + B_{mnjl}^{(2)}(\alpha) + B_{mljn}^{(2)}(\alpha)] \right. \right. \\ \left. \left. + \mathcal{P}_{im}^{(1)}(\alpha) [B_{kljn}^{(2)}(\alpha) + B_{knjl}^{(2)}(\alpha) + B_{jnkl}^{(2)}(\alpha) + B_{jilkn}^{(2)}(\alpha)] \right] \right. \\ \left. + \frac{1}{8} \sum_{\vec{q}\alpha} \{ \mathcal{P}_{ij}^{(2)}(\vec{q}\alpha) [B_{klmn}^{(3)}(\vec{q}\alpha) + B_{knml}^{(3)}(\vec{q}\alpha) + B_{mnkl}^{(3)}(\vec{q}\alpha) + B_{mlkn}^{(3)}(\vec{q}\alpha)] \right. \\ \left. + \mathcal{P}_{ik}^{(2)}(\vec{q}\alpha) [B_{jlmn}^{(3)}(\vec{q}\alpha) + B_{jnml}^{(3)}(\vec{q}\alpha) + B_{mnjl}^{(3)}(\vec{q}\alpha) + B_{mljn}^{(3)}(\vec{q}\alpha)] \right. \\ \left. + \mathcal{P}_{im}^{(2)}(\vec{q}\alpha) [B_{kljn}^{(3)}(\vec{q}\alpha) + B_{knjl}^{(3)}(\vec{q}\alpha) + B_{jnkl}^{(3)}(\vec{q}\alpha) + B_{jilkn}^{(3)}(\vec{q}\alpha)] \} \right], \quad (29)$$



where

$$\begin{aligned}
 B_{kl}^{(1)}(\alpha) &= B_{lk}^{(1)}(\alpha) \\
 &= \frac{\mathcal{H}_{kl}^{I(1)}(\alpha)}{\omega_\alpha^2} + \frac{1}{4\omega_\alpha^2} \sum_{\alpha' \neq \alpha, \vec{q}} \left[ \mathcal{H}_{kl}^{I(3)} \begin{pmatrix} 0 & \vec{q} & -\vec{q} \\ \alpha & \alpha' & \alpha' \end{pmatrix} - \frac{3}{2} H_0^{(3)} \begin{pmatrix} 0 & \vec{q} & -\vec{q} \\ \alpha & \alpha' & \alpha' \end{pmatrix} K_{kl}^{(2)}(\vec{q}\alpha') \right] \langle |Q_{\vec{q}\alpha'}|^2 \rangle, \\
 B_{klmn}^{(2)}(\vec{q}\alpha) &= B_{klmn}^{(2)}(\vec{q}\alpha) = B_{lkmn}^{(2)}(\vec{q}\alpha) = B_{lknm}^{(2)}(\vec{q}\alpha) \\
 &= -\frac{\delta(\vec{q})}{2\omega_{\vec{q}\alpha}^2} \left[ \sum_{\alpha'\alpha''} H_0^{(3)} \begin{pmatrix} 0 & 0 & 0 \\ \alpha & \alpha' & \alpha'' \end{pmatrix} \frac{\mathcal{H}_{kl}^{I(1)}(\alpha') \mathcal{H}_{mn}^{I(1)}(\alpha'')}{\omega_\alpha^2 \omega_{\alpha'}^2} \right. \\
 &\quad \left. - \frac{3}{4} \omega_{\vec{q}\alpha}^2 \sum_{\vec{q}, \alpha' \neq \alpha} \mathcal{H}_{kl}^{I(3)} \begin{pmatrix} 0 & \vec{q} & -\vec{q} \\ \alpha & \alpha' & \alpha' \end{pmatrix} K_{mn}^{(2)}(\vec{q}\alpha') \langle |Q_{\vec{q}\alpha'}|^2 \rangle \right],
 \end{aligned}$$

$$\begin{aligned}
 B_{klmn}^{(3)}(\vec{q}\alpha) &= B_{klmn}^{(3)}(\vec{q}\alpha) = B_{lkmn}^{(3)}(\vec{q}\alpha) = B_{lknm}^{(3)}(\vec{q}\alpha) \\
 &= \frac{K_{kl}^{(2)}(\vec{q}\alpha) K_{mn}^{(2)}(\vec{q}\alpha)}{\omega_{\vec{q}\alpha}^4} \langle |Q_{\vec{q}\alpha}|^2 \rangle [1 - \xi_{klmn}^{(2)}(\vec{q}\alpha)] + K_{klmn}^{(4)}(\vec{q}\alpha) \langle |Q_{\vec{q}\alpha}|^2 \rangle [1 - \xi_{klmn}^{(3)}(\vec{q}\alpha)] \\
 &\quad + 2 \frac{\mathcal{H}_{kl}^{I(1)}(\alpha) \mathcal{H}_{mn}^{I(1)}(\alpha)}{\omega_\alpha^4} [1 - \xi_{klmn}^{(4)}(\alpha)] \delta(\vec{q}),
 \end{aligned}$$

and  $\xi_{kl}^{(1)}(\vec{q}\alpha)$ ,  $\xi_{klmn}^{(2)}(\vec{q}\alpha)$ ,  $\xi_{klmn}^{(3)}(\vec{q}\alpha)$ ,  $\xi_{klmn}^{(4)}(\vec{q}\alpha)$  are given in Appendix B.

The assumption of neglecting the term oscillating with frequency  $2\omega$  in interaction Hamiltonian (Sec. III)  $H_I$  corresponds with neglecting the terms of the order  $\omega_\alpha/\omega \sim 10^{-2}$  in Eqs. (28) and (29).

On the other hand, while treating the molecules or atoms in a lattice as rigid, we do not take into account temporary dipole moments arising as a function of their small displacements. This simplification does not influence Eqs. (28) and (29) because the terms connected with the dipole moment would also be of the order  $\omega_\alpha/\omega$ .

The results obtained in this paper for the tensor  $\chi_{ijkl}(-\omega, \omega, \omega, -\omega)$  may be compared with the general expression for the phonon part of the susceptibility tensor  $\chi_{ijkl}(-(2\omega_1 - \omega_2), \omega_1, \omega_1, -\omega_2)$ , responsible for four wave mixing in crystals,<sup>18,19</sup> after putting  $\omega_1 = \omega_2$ . The outline of the approach to this problem is similar. Substituting the solution of the anharmonic equation of motion for normal vibrations in crystal to the expansion of crystal polarizability, with respect to the amplitudes of those vibrations, Flytzanis and Bloembergen<sup>19</sup> find the form of the tensor  $\chi_{ijkl}(-(2\omega_1 - \omega_2), \omega_1, \omega_1, -\omega_2)$ . They do not take into account the change of the vibrational amplitudes, which is a function of an external electric field. Hence, they obtain only the term corresponding to the first

term,  $\sim \mathcal{P}_{ij}^{(1)}(\alpha)$  in Eq. (28). The problem of dispersion of the mechanism discussed in this paper has already been treated and will be published elsewhere.

## V. NUMERICAL RESULTS AND DISCUSSION

Using the Eqs. (28) and (29) we have calculated the susceptibility tensors due to the optical-field induced vibrational amplitude shifts of  $\vec{q}=0$  optical modes in diamond and benzene lattices. Acoustic  $\vec{q}=0$  modes do not incur any shifts. The structural forces acting between the molecules (or atoms) in the lattice are assumed to be of a Lennard-Jones type.

### A. Diamond

In diamond, the optical field cancels the triple degeneration of the only optical  $\vec{q}=0$  mode of a frequency  $\omega_0 = 1332 \text{ cm}^{-1}$ . Table I shows the frequency shifts [see (14)] obtained for three different directions of an optical-field vector  $\vec{E}$  towards crystallographic axes. It can be seen that the optical field necessary to cause the frequency shifts of  $1 \text{ cm}^{-1}$  has to be as strong as  $E^2 \sim 10^9 \text{ esu}$ . Simi-

TABLE I.  $\Delta\omega^2 = \omega^{E^2} - \omega_0^2 = \omega_0^2 \eta^{(2)}$ ;  $\Delta\nu = \nu_0[\frac{1}{2}\eta^{(2)} + \frac{1}{8}(\eta^{(2)})^2]$ ;  $\eta^{(4)} = 0$  for diamond. The signs  $\parallel$  and  $\perp$  denote the vibrations parallel or perpendicular to field  $\vec{E}$  direction.

Direction of $\vec{E}$	$\frac{\Delta\omega_{\parallel\vec{E}}^2}{E^2}$ ( $10^{16} \text{ s}^{-2}$ )	$\frac{\eta_{\parallel\vec{E}}}{E^2}$ ( $10^{-10}$ )	$\frac{\Delta\nu_{\parallel\vec{E}}}{E^2}$ ( $10^{-10} \text{ cm}^{-1}$ )	$\frac{\Delta\omega_{\perp\vec{E}}^2}{E^2}$ ( $10^{16} \text{ s}^{-2}$ )	$\frac{\eta_{\perp\vec{E}}}{E^2}$ ( $10^{-10}$ )	$\frac{\Delta\nu_{\perp\vec{E}}}{E^2}$ ( $10^{-10} \text{ cm}^{-1}$ )	$\frac{\Delta\omega_{\perp\vec{E}}^2}{E^2}$ ( $10^{16} \text{ s}^{-2}$ )	$\frac{\eta_{\perp\vec{E}}}{E^2}$ ( $10^{-10}$ )	$\frac{\Delta\nu_{\perp\vec{E}}}{E^2}$ ( $10^{-10} \text{ cm}^{-1}$ )
$\vec{E} = E[1,0,0]$	2.15	0.004	2.3	-6.25	-0.01	-6.5	-6.25	-0.01	-6.5
$\vec{E} = \frac{E}{\sqrt{2}}[1,1,0]$	-5.3	-0.008	-5.7	0.55	0.001	0.6	-6.25	-0.01	-6.5
$\vec{E} = \frac{E}{\sqrt{3}}[1,1,1]$	-8.5	-0.014	-9.3	-0.93	-0.0015	-1	-0.93	-0.001	-1

lar results were presented by Ganesan, Maradudin, and Oitmaa<sup>20</sup> for a dc electric field interacting with a diamond crystal. There are differences in the signs of the shifts due to the other model of polarizability assumed by the authors<sup>20</sup> which is a sum of the electronic polarizabilities of bonds between the pairs of atoms.

Table II shows the fourth- and sixth-rank susceptibility tensors, respectively, calculated from Eqs. (28) and (29). In the last column of Table II are the results: (i) theoretically calculated as due to electronic hyperpolarizability of diamond crystal,<sup>11</sup> (ii) obtained in the experiment of four wave mixing<sup>21</sup> and interpreted by the authors as a non-resonant part of the susceptibility tensor arising from the redistribution of electronic density. However, on the basis of the theory presented in this paper, we suggest that the experiment (Ref. 21) should show the contribution to susceptibility ten-

sors from both mechanisms clearly electronic and connected with the changes of lattice vibrational amplitudes. The very good agreement of the order of magnitude of the numerical results of Table II with experimental results<sup>21</sup> confirms this suggestion.

Table III contains the nonlinear refractive index coefficients  $n_2$  and  $n_4$ , obtained from the Eq. (2) for three optical-field directions. They fulfill the conditions required for the self-trapping of light beams to occur,<sup>22</sup> which has been observed recently in diamond crystal.<sup>23</sup>

## B. Crystalline benzene

In this case we have to consider 21,  $\vec{q} = 0$ , optical vibrational modes, which means 12 rotational and 12 translational modes.<sup>24</sup> The frequency shifts,

TABLE II. Nonvanishing, different components of fourth- and sixth-rank susceptibility tensors in diamond.

	The results obtained in this paper for		
	$\lambda = 6328$	Ref. 11	Ref. 21
$\chi_{xxxx}(-\omega, \omega, \omega, -\omega)$	$2.58 \times 10^{-14}$ esu	$4.3 \times 10^{-14}$ esu	$4.6 \times 10^{-14}$ esu
$\chi_{xxyy}(-\omega, \omega, \omega, -\omega)$	$1.42 \times 10^{-14}$ esu		$1.84 \times 10^{-14}$ esu
$\chi_{xyyx}(-\omega, \omega, \omega, -\omega)$	$3.31 \times 10^{-14}$ esu		$1.72 \times 10^{-14}$ esu
$\chi_{xxxxxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	$-6.11 \times 10^{-26}$ esu		
$\chi_{yyxxxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	$-2.99 \times 10^{-26}$ esu		
$\chi_{yxxxy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	$-7.00 \times 10^{-26}$ esu		
$\chi_{xxyyxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	$0.13 \times 10^{-26}$ esu		
$\chi_{xxxxyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	$1.91 \times 10^{-26}$ esu		
$\chi_{xyxyxy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	$-1.73 \times 10^{-26}$ esu		
$\chi_{xzzzyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	$2.21 \times 10^{-26}$ esu		
$\chi_{xzzzyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	$-0.51 \times 10^{-26}$ esu		

TABLE III. Coefficients  $n_2$  and  $n_4$  in the direction of a field  $\vec{E}$  for diamond.

Direction of $\vec{E}$	$n_2$	$n_4$
$\vec{E}=E [1,0,0]$	$2.0 \times 10^{-13}$ esu	$-1.55 \times 10^{-24}$ esu
$\vec{E}=\frac{E}{\sqrt{2}} [1,-1,0]$	$4.32 \times 10^{-13}$ esu	$-0.82 \times 10^{-24}$ esu
$\vec{E}=\frac{E}{\sqrt{3}} [1,1,1]$	$5.1 \times 10^{-13}$ esu	$-0.86 \times 10^{-24}$ esu

shown in Table IV for an electric field directed along each of crystallographic axes, appear to be also of the order of  $1 \text{ cm}^{-1}$  for  $E^2 \sim 10^9$  esu. The susceptibility tensors are due to two mechanisms [see Eq. (15)]: (i) the change of the equilibrium position for rotational vibrations, which can be treated as quasioientational effect, (ii) the change of the vibrational amplitudes. The results of calculations for both effects are shown in Tables V and VI. In the last column of Table V there are the susceptibility tensors due to hyperpolarizability of benzene molecules, calculated by the author from the formula:

$$\chi_{ijkl}(-\omega, \omega, \omega, -\omega) = \frac{N}{V} f_i(\omega) f_j(\omega) f_k(\omega) f_l(\omega) \times \sum_{nprs} \gamma_{iprs}(n) T_{pj}^{(0)}(n) \times T_{rk}^{(0)}(n) T_{sl}^{(0)}(n), \quad (30)$$

where  $\gamma_{iprs}(n)$  is the hyperpolarizability tensor of a benzene molecule,<sup>25</sup> shown on crystallographic

axes, and the tensors  $T_{pj}^{(0)}(n)$  are defined by (5) for molecular displacements equal to zero. Comparison of the results contained in Tables V and VI proves that both effects discussed above are of the same order of magnitude. The nonlinear refractive index coefficients  $n_2$  and  $n_4$  [calculated from Eqs. (2) and due to the effect of elastic lattice vibrations] are presented in Table VII.

The general conclusion of this paper is that a nonlinear refractive index change in crystal is due to two comparable effects: distortion of electronic clouds and the shift of vibrational amplitudes of molecules (or atoms) in crystal lattice. Accompanying vibrational frequency shifts are too small to be observed in dc electric fields, but they should be observed in the area of a focused light beam, where  $E^2 \sim 10^9 - 10^{10}$  esu.

### C. Liquid benzene

According to the theory of the quasicrystalline structure of liquids in the region of action of short-range forces,<sup>3</sup> we make an assumption that a liquid is composed of very small, randomly situated, short-lived crystals. If we ascribe to each of them the susceptibility tensor  $\chi_{ijkl}$  calculated for the crystal lattice of a given substance, then the susceptibility tensor of a liquid can be obtained by isotropic averaging of  $\chi_{ijkl}$  over all possible directions of crystallographic axes with respect to the frame of reference connected with the optical field. Let  $\vec{E}=E \vec{i}_1$  be an electric field vector expressed in a new frame of reference (1,2,3), then

$$\epsilon_{\mu\nu} = \sum_{ij} \epsilon_{ij} \langle e_{i\mu} e_{j\nu} \rangle, \quad (31)$$

TABLE IV. The vibrational shifts  $\Delta\nu/E^2 = \frac{1}{2} \nu_0(\eta^{(2)}/E^2)$  in benzene. The denotations of the vibrational modes are explained in Ref. 24. (a) Translational vibrations along  $\vec{x}, \vec{y}, \vec{z}$  axes; (b) rotational vibrations around  $\vec{u}, \vec{v}$  axes. The vibrations around  $\vec{w}$  axis are not shifted in the model applied in this paper.

(a)	Vibrations								
	$A_u(x)$	$A_u(y)$	$A_u(z)$	$B_{1u}(y)$	$B_{1u}(z)$	$B_{2u}(x)$	$B_{2u}(z)$	$B_{3u}(x)$	$B_{3u}(y)$
Direction of $\vec{E}$					$10^{-10} \text{ cm}^{-1}$				
$\vec{E}=E[1,0,0]$	-1.02	0.09	-0.20	0.16	1.84	0.05	1.96	-1.47	-1.07
$\vec{E}=E[0,1,0]$	-3.60	1.30	0.70	-0.92	-2.30	0.40	-2.30	0	0.25
$\vec{E}=E[0,0,1]$	1.78	-0.72	0.12	0.14	-0.60	-0.08	-2.16	1.08	-0.05
(b)									
Direction of $\vec{E}$	$A_g(u)$	$A_g(v)$	$B_{1g}(u)$	$B_{1g}(v)$	$B_{2g}(u)$	$B_{2g}(v)$	$B_{3g}(u)$	$B_{3g}(v)$	
					$10^{-10} \text{ cm}^{-1}$				
$\vec{E}=E[1,0,0]$	-0.98	-0.64	-0.05	-0.52	-0.41	-1.75	-0.23	0.56	
$\vec{E}=E[0,1,0]$	1.41	0	0.26	0	1.19	0	0.72	0	
$\vec{E}=E[0,0,1]$	-1.49	-0.28	-0.48	0.35	-0.41	-0.70	-0.26	0.35	

TABLE V. The fourth-rank susceptibility tensors for crystalline benzene;  $\chi_{ijkl}^0$  denotes a quasioientational mechanism of the change in the equilibrium position for rotational vibrations;  $\chi_{ijkl}^A$  denotes the effect of vibrational amplitude change.

$10^{-13}$ esu	$\chi_{ijkl}^0$	$\chi_{ijkl}^A$	Total $\chi_{ijkl}$	Effect of hyperpolarizability
$\chi_{xxxx}(-\omega, \omega, \omega, -\omega)$	3.910	-2.697	1.213	0.434
$\chi_{xxyy}(-\omega, \omega, \omega, -\omega)$	-0.404	-4.925	-5.329	0.830
$\chi_{xyyx}(-\omega, \omega, \omega, -\omega)$	-0.807		-0.807	0.830
$\chi_{yyxx}(-\omega, \omega, \omega, -\omega)$	-0.135	3.340	3.205	0.970
$\chi_{yxyx}(-\omega, \omega, \omega, -\omega)$	-0.270		-0.270	0.970
$\chi_{yyyy}(-\omega, \omega, \omega, -\omega)$		0.0318	0.0318	0.662
$\chi_{zzzz}(-\omega, \omega, \omega, -\omega)$	0.842	0.835	1.677	0.429
$\chi_{zzxz}(-\omega, \omega, \omega, -\omega)$	-1.338	-0.104	-1.442	0.030
$\chi_{zzzx}(-\omega, \omega, \omega, -\omega)$	0.036		0.036	0.030
$\chi_{zzxx}(-\omega, \omega, \omega, -\omega)$	-2.431	-1.255	-3.686	0.033
$\chi_{zzxz}(-\omega, \omega, \omega, -\omega)$	0.036		0.036	0.033
$\chi_{yyzz}(-\omega, \omega, \omega, -\omega)$	0.253	-1.288	-1.035	0.960
$\chi_{yyzy}(-\omega, \omega, \omega, -\omega)$	0.507		0.507	0.960
$\chi_{zzyy}(-\omega, \omega, \omega, -\omega)$	0.253	3.040	3.293	1.012
$\chi_{zyyz}(-\omega, \omega, \omega, -\omega)$	0.507		0.507	1.012

$$\chi_{\mu\nu\rho\sigma} = \sum_{ijkl} \chi_{ijkl} \langle e_{i\mu} e_{j\nu} e_{k\rho} e_{l\sigma} \rangle, \quad (32)$$

$$\chi_{\mu\nu\rho\sigma\tau\theta} = \sum_{ijklmn} \chi_{ijklmn} \langle e_{i\mu} e_{j\nu} e_{k\rho} e_{l\sigma} e_{m\tau} e_{n\theta} \rangle, \quad (33)$$

where  $i, j, k, l$  are crystallographic axes,  $\mu, \nu, \rho, \sigma, \theta = 1, 2, 3$ , are laboratory frames of reference, and  $e_{i\mu}$  is the cosines direction between  $\vec{i}$  and  $\vec{\mu}$  axes. Numerical results obtained from Eqs. (31)–(33) are shown in Table VIII. The picture of liquid presented here is a very rough approximation. However, it allows one to appreciate the order of magnitude of nonlinear refractive index changes due to the effects discussed in this paper. It ap-

pears to be of the same order of magnitude as hyperpolarizability of molecules and 1 order of magnitude smaller than the orientational Kerr effect. However, in the case of spherically symmetrical molecules it can play an important role. As the results of Table VIII show, the mechanism discussed ensures the self-trapping effect.<sup>22</sup>

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#### APPENDIX A.

The succeeding displacement derivatives of interaction Hamiltonian (9b) are of the form:

$$\mathcal{H}_{pk,r,r',\dots,r_j}^{I(i)}(ln, l'n', \dots, l^n n^j) = \frac{1}{2} \sum_{LNij} \left[ \frac{\partial^j [\alpha_{ij}(LN) T_{ik}(LN) T_{jp}(LN)]}{\partial w_r(ln) \partial w_{r'}(l'n') \cdots \partial w_{r_j}(l^n n^j)} \right]_0 \quad (A1)$$

where, according to (5),

$$T_{ij}^{(0)}(LN) = T_{ij}^{(0)}(N) = \sum_{N'} (I - A^{(0)})_{ij}^{-1}(N, N'), \quad (A2)$$

$$\begin{aligned} T_{ij,r}^{(1)}(LN, ln) &= T_{ij,r}^{(1)}(ON, l - Ln) \\ &= \sum_{L'N'N''pk} (I - A^{(0)})_{ik}^{-1}(NN') A_{kp,r}^{(1)}(L'N', ON'', l - Ln) T_{pj}^{(0)}(N''), \end{aligned} \quad (A3)$$

TABLE VI. The only different components of sixth-rank susceptibility tensors in crystalline benzene.

$10^{-24}$ esu	$\chi_{ijkmn}^0$	$\chi_{ijklmn}^A$	Total $\chi_{ijklmn}$
$\chi_{xxxxxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.35	0.026	-0.324
$\chi_{yyxxxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.011	-0.003	0.007
$\chi_{yxyxxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.071		0.071
$\chi_{zzxxxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.070	0.011	0.081
$\chi_{zxzzxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.0109		-0.0109
$\chi_{yyyyyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$		0.227	0.227
$\chi_{xxyyyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.008	0.040	0.032
$\chi_{xyyyyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.023		-0.023
$\chi_{zzyyyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.029	0.0003	-0.029
$\chi_{zyzyzy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.088		-0.088
$\chi_{zzzzzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.0497	0.027	0.077
$\chi_{xxzzzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.025	0.018	-0.007
$\chi_{zzzzzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.004		-0.004
$\chi_{yyzzzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.006	0.006	0.012
$\chi_{yzyzzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.017		0.017
$\chi_{xxxxyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.012	0.088	0.100
$\chi_{xxxxyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$		0.133	0.133
$\chi_{xxyyxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.023	0.044	0.067
$\chi_{xxxxzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.114	-0.036	0.078
$\chi_{xxxxzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$		-0.055	-0.055
$\chi_{zzzzzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.017	-0.018	-0.001
$\chi_{yyyyzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.015	-0.0002	-0.015
$\chi_{yyyzyz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$		-0.001	-0.001
$\chi_{yyzyzy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.029	-0.0001	-0.029
$\chi_{yyzyxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.004	0.028	0.024
$\chi_{yyzyxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$		0.042	0.042
$\chi_{yyxyxy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.007	0.014	0.007
$\chi_{zzzzxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.018	0.026	0.008
$\chi_{zzzzxx}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$		0.035	0.035
$\chi_{zzzzzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.016	0.013	-0.003
$\chi_{zzzyzy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.075	0	-0.075
$\chi_{zzzyzy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$		0	0
$\chi_{zzzyzy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.089	0	-0.089
$\chi_{xxzzyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.005	0	0.005
$\chi_{xxzzyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.014	0	0.014
$\chi_{xxyzyz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.003	0	0.003
$\chi_{zzxxyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.016	0	0.016
$\chi_{zzxxyy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.020	0	0.020
$\chi_{zzxyxy}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.011	0	0.011
$\chi_{yyxxzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0	0.005	0.005
$\chi_{yyxxzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	-0.001	0.005	0.004
$\chi_{yyzzzz}(-\omega, \omega, \omega, -\omega, \omega, -\omega)$	0.007	0.005	0.012

$$\begin{aligned}
T_{ij,rr'}^{(2)}(LN,ln,l'n') &= T_{ij,rr'}^{(2)}(ON,l-Ln,l'-Ln') \\
&= \sum_{\substack{\text{permutations } L'N'N''pk \\ r,r'}} \left[ \frac{1}{2}(I-A^{(0)})_{ik}^{-1}(NN')A_{kp,rr'}^{(2)}(L'N',ON'',l-Ln,l'-Ln') \right. \\
&\quad + \sum_{L''N'''N^{IV}} (I-A^{(0)})_{ik}(NN')A_{kl,r}^{(1)}(L'N',ON''',l-Ln) (I-A^{(0)})_{lm}(N''',N^{IV}) \\
&\quad \left. \times A_{lp,r'}^{(1)}(L''N^{IV},ON'',l'-Ln') \right] T_{pj}^{(0)}(N''), \tag{A4}
\end{aligned}$$

TABLE VII. Coefficients  $n_2$  and  $n_4$  in the direction of the electric field  $\vec{E}$  for benzene.

Direction of $\vec{E}$	$n_2$ ( $10^{-12}$ esu)	$n_4$ ( $10^{-14}$ esu)
$\vec{E}=E$ [1,0,0]	1.64	-1.33
$\vec{E}=E$ [0,1,0]	0.04	0.88
$\vec{E}=E$ [0,0,1]	2.22	0.33

$$\begin{aligned}
& T_{ij,rr',r''}^{(3)}(LN,ln,l'n',l''n'') \\
&= T_{ij,rr',r''}^{(3)}(ON,l-Ln,l'-Ln',l''-Ln'') \\
&= \sum_{\substack{\text{permutations} \\ r,r',r''}} \sum_{L'N'N''pk} \left[ \frac{1}{6} (I-A^{(0)})_{ik}^{-1} (NN') A_{kp,rr',r''}^{(3)}(L'N',ON'',l-Ln,l'-Ln',l''-Ln'') \right. \\
&\quad + \frac{1}{2} \sum_{L''N'''N^{IV}lm} [(I-A^{(0)})_{ik}^{-1} (NN') A_{kl,rr'}^{(2)}(L'N',ON''',l-Ln,l'-Ln') \\
&\quad \quad \times (I-A^{(0)})_{lm}^{-1} (N''',N^{IV}) A_{mp,r''}^{(1)}(L''N^{IV},ON'',l''-Ln'') \\
&\quad \quad + (I-A^{(0)})_{ik}^{-1} (NN') A_{kl,r''}^{(1)}(L'N',ON''',l''-Ln'') \\
&\quad \quad \times (I-A^{(0)})_{lm} (N''',N^{IV}) A_{mp,rr'}^{(2)}(L''N^{IV},ON'',l-Ln,l'-Ln')] \\
&\quad + \sum_{L''L'''N''''N^{IV}N^V N^{VI}lmns} (I-A^{(0)})_{ik}^{-1} (N,N') A_{kl,r}^{(1)}(L'N',ON''',l-Ln) \\
&\quad \quad \times (I-A^{(0)})_{lm}^{-1} (N''',N^{IV}) A_{mn,r'}^{(1)}(L''N^{IV},ON^V,l''-Ln') \\
&\quad \quad \times (I-A^{(0)})_{ns}^{-1} (N^V,N^{VI}) A_{sp,r''}^{(1)}(L'''N^{VI},ON'',l''-Ln'') \left. \right] T_{pj}^{(0)}(N''),
\end{aligned}
\tag{A5}$$

TABLE VIII. Numerical results from Eqs. (31)–(33).

Mechanism	$n_2(10^{-12}$ esu)	Ref.	$n_4(10^{-24}$ esu)
Orientational effect	7.58	26	
	1.4	27	
Hyperpolarizability	0.34	26	
	0.33	27	
Discussed effect	0.45		-2.4
Experimental results	1.95	28	
	2.25	29	

$$\begin{aligned}
 & T_{ij,rr',r'',r'''}^{(4)}(LN,ln,l'n',l''n'',l'''n''') \\
 &= T_{ij,rr',r'',r'''}^{(4)}(ON,l-Ln,l'-Ln',l''-Ln'',l'''-Ln''') \\
 &= \sum_{\substack{\text{permutations} \\ r,r',r'',r'''}} \sum_{L'N'N''pk} \left[ \frac{1}{24}(I-A^{(0)})_{ik}^{-1}(NN') A_{kp,rr',r'',r'''}^{(4)}(L'N',ON'',l-Ln,l'-Ln',l''-Ln'',L'''-Ln''') \right. \\
 &\quad + \frac{1}{6} \sum_{L''N''N^{IV}Im} [(I-A^{(0)})_{ik}^{-1}(NN')A_{ki,rr',r'',r'''}^{(3)}(L'N',ON''',l-Ln,l'-Ln',l''-Ln'') \\
 &\quad \times (I-A^{(0)})_{lm}^{-1}(N''',N^{IV})A_{mp,r'''}^{(1)}(L''N^{IV},ON'',L'''-ln''') \\
 &\quad + (I-A^{(0)})_{ik}^{-1}(N,N')A_{ki,r'''}^{(1)}(L'N',ON''',L'''-ln''') \\
 &\quad \times (I-A^{(0)})_{lm}^{-1}(N''N^{IV})A_{mp,rr',r''}^{(3)}(L''N^{IV},ON'',l-Ln,l'-Ln',l''-Ln'') \\
 &\quad + \frac{3}{2}(I-A^{(0)})_{ik}^{-1}(NN')A_{ki,rr'}^{(2)}(L'N',ON''',l-Ln,l'-Ln') \\
 &\quad \left. \times (I-A^{(0)})_{lm}^{-1}(N''',N^{IV})A_{mp,r'''}^{(2)}(L''N^{IV},ON'',l''-Ln'',l'''-Ln''') \right] \\
 &+ \frac{1}{2} \sum_{L''L''''N''N^{IV}N^V N^{VI}Imns} [(I-A^{(0)})_{ik}^{-1}(NN')A_{ki,rr'}^{(2)}(L'N',ON''',l-Ln,l'-Ln') \\
 &\quad \times (I-A^{(0)})_{lm}^{-1}(N''',N^{IV})A_{mn,r''}^{(1)}(L''N^{IV},ON^V,l''-Ln'') \\
 &\quad \times (I-A^{(0)})_{ns}^{-1}(N^V,N^{VI})A_{sp,r'''}^{(1)}(L'''N^{VI},ON'',l'''-Ln''') \\
 &\quad + (I-A^{(0)})_{ik}^{-1}(NN')A_{ki,r''}^{(1)}(L'N',ON''',l''-Ln'') \\
 &\quad \times (I-A^{(0)})_{lm}^{-1}(N''',N^{IV})A_{mn,rr'}^{(2)}(L''N^{IV},ON^V,l-Ln,l'-Ln') \\
 &\quad \times (I-A^{(0)})_{ns}^{-1}(N^V N^{VI})A_{sp,r'''}^{(1)}(L'''N^{VI},ON'',l'''-Ln''') \\
 &\quad + (I-A^{(0)})_{ik}^{-1}(NN')A_{ki,r''}^{(1)}(L'N',ON''',l''-Ln'') \\
 &\quad \times (I-A^{(0)})_{lm}^{-1}(N''',N^{IV})A_{mn,r'''}^{(1)}(L''N^{IV},ON^V,l'''-Ln''') \\
 &\quad \left. \times (I-A^{(0)})_{ns}^{-1}(N^V,N^{VI})A_{sp,rr'}^{(2)}(L'''N^{VI},ON'',l-Ln,l'-Ln') \right] \\
 &+ \sum_{L''L''''L^{IV}N''N^{IV}N^V N^{VI}N^{VII}N^{VIII}Imnstw} (I-A^{(0)})_{ik}^{-1}(NN')A_{ki,r}^{(1)}(L'N',ON''',l-Ln) \\
 &\quad \times (I-A^{(0)})_{lm}^{-1}(N''',N^{IV})A_{mn,r'}^{(1)}(L''N^{IV},ON^V,l'-Ln') \\
 &\quad \times (I-A^{(0)})_{ns}^{-1}(N^V,N^{VI})A_{st,r''}^{(1)}(L'''N^{VI},ON^{VII},l''-Ln'') \\
 &\quad \times (I-A^{(0)})_{tw}^{-1}(N^{VII},N^{VIII}) \\
 &\quad \left. \times A_{wp,r'''}^{(1)}(L^{IV}N^{VIII},ON'',l'''-Ln''') \right] T_{Pj}^{(0)}(N'') \quad (A6)
 \end{aligned}$$

and the matrix  $A_{ij}(LN,L'N')$  is given by (4b).

## APPENDIX B

$$\begin{aligned} \zeta_{kl}^{(1)}(\vec{q}\alpha) = & \frac{1}{8} \sum_{\vec{q}'\alpha'} \left[ \frac{H_0^{(4)} \begin{bmatrix} \vec{q} & -\vec{q} & \vec{q}' & -\vec{q}' \\ \alpha & \alpha & \alpha' & \alpha' \end{bmatrix}}{\omega_{\vec{q}\alpha}^2} + \frac{\mathcal{H}_{kl}^{(4)} \begin{bmatrix} \vec{q} & -\vec{q} & \vec{q}' & -\vec{q}' \\ \alpha & \alpha & \alpha' & \alpha' \end{bmatrix}}{K_{kl}^{(2)}(\vec{q}\alpha)} \right] \frac{\langle |Q_{\vec{q}\alpha}|^2 |Q_{\vec{q}'\alpha'}|^2 \rangle}{\langle |Q_{\vec{q}\alpha}|^2 \rangle} \\ & + \frac{1}{16} \sum_{\vec{q}'\alpha' \neq \vec{q}\alpha} \frac{H_0^{(4)} \begin{bmatrix} \vec{q} & -\vec{q} & \vec{q}' & -\vec{q}' \\ \alpha & \alpha & \alpha' & \alpha' \end{bmatrix} K_{kl}^{(2)}(\vec{q}'\alpha')}{\omega_{\vec{q}\alpha}^2 K_{kl}^{(2)}(\vec{q}\alpha)} \langle |Q_{\vec{q}'\alpha'}|^2 \rangle, \end{aligned} \quad (\text{B1})$$

$$\begin{aligned} \zeta_{klmn}^{(2)}(\vec{q}\alpha) = & \left[ \frac{9}{32} \frac{H_0^{(4)} \begin{bmatrix} \vec{q} & -\vec{q} & \vec{q} & -\vec{q} \\ \alpha & \alpha & \alpha & \alpha \end{bmatrix}}{\omega_{\vec{q}\alpha}^2} + \frac{1}{4} \frac{\mathcal{H}_{kl}^{(4)} \begin{bmatrix} \vec{q} & -\vec{q} & \vec{q} & -\vec{q} \\ \alpha & \alpha & \alpha & \alpha \end{bmatrix}}{K_{kl}^{(2)}(\vec{q}\alpha)} \right] \frac{\langle |Q_{\vec{q}\alpha}|^4 \rangle}{\langle |Q_{\vec{q}\alpha}|^2 \rangle} \\ & + \frac{1}{4} \sum_{\vec{q}'\alpha' \neq \vec{q}\alpha} \left[ \frac{H_0^{(4)} \begin{bmatrix} \vec{q} & -\vec{q} & \vec{q}' & -\vec{q}' \\ \alpha & \alpha & \alpha' & \alpha' \end{bmatrix}}{\omega_{\vec{q}\alpha}^2} \left[ 1 + \frac{K_{kl}^{(2)}(\vec{q}'\alpha')}{4K_{kl}^{(2)}(\vec{q}\alpha)} \left[ 4 - \frac{\omega_{\vec{q}\alpha}^2}{\omega_{\vec{q}'\alpha'}(\omega_{\vec{q}'\alpha'} + \omega_{\vec{q}\alpha})} \right] \right. \right. \\ & \left. \left. + \frac{K_{kl}^{(2)}(\vec{q}'\alpha') K_{mn}^{(2)}(\vec{q}'\alpha')}{4K_{kl}^{(2)}(\vec{q}\alpha) K_{mn}^{(2)}(\vec{q}\alpha)} \left[ 1 - \frac{4\omega_{\vec{q}\alpha}}{3\omega_{\vec{q}'\alpha'}} \right] \right] \right. \\ & \left. + 5 \mathcal{H}_{kl}^{(4)} \frac{\begin{bmatrix} \vec{q} & -\vec{q} & \vec{q}' & -\vec{q}' \\ \alpha' & \alpha & \alpha' & \alpha' \end{bmatrix}}{4K_{kl}^{(2)}(\vec{q}\alpha)} \right] \langle |Q_{\vec{q}'\alpha'}|^2 \rangle. \end{aligned} \quad (\text{B2})$$

$$\begin{aligned} \zeta_{klmn}^{(3)}(\vec{q}\alpha) = & \frac{9}{32} \frac{H_0^{(4)} \begin{bmatrix} \vec{q} & -\vec{q} & \vec{q} & -\vec{q} \\ \alpha & \alpha & \alpha & \alpha \end{bmatrix}}{\omega_{\vec{q}\alpha}^2} \frac{\langle |Q_{\vec{q}\alpha}|^4 \rangle}{\langle |Q_{\vec{q}\alpha}|^2 \rangle} \\ & + \sum_{\vec{q}'\alpha' \neq \vec{q}\alpha} \frac{H_0^{(4)} \begin{bmatrix} \vec{q} & -\vec{q} & \vec{q}' & -\vec{q}' \\ \alpha & \alpha & \alpha' & \alpha' \end{bmatrix}}{\omega_{\vec{q}\alpha}^2} \left[ \frac{1}{4} - \frac{K_{klmn}^{(4)}(\vec{q}'\alpha')}{K_{klmn}^{(4)}(\vec{q}\alpha)} \left[ 1 - \frac{4}{3} \frac{\omega_{\vec{q}\alpha}}{\omega_{\vec{q}'\alpha'}} \right] \right] \langle |Q_{\vec{q}'\alpha'}|^2 \rangle, \end{aligned} \quad (\text{B3})$$

$$\begin{aligned} \zeta_{klmn}^{(4)}(\vec{q}\alpha) = & \frac{3}{8} \frac{H_0^{(4)} \begin{bmatrix} \vec{q} & -\vec{q} & \vec{q} & -\vec{q} \\ \alpha & \alpha & \alpha & \alpha \end{bmatrix}}{\omega_{\vec{q}\alpha}^2} \langle |Q_{\vec{q}\alpha}|^2 \rangle + \frac{15}{2} \sum_{\vec{q}'\alpha' \neq \vec{q}\alpha} \frac{\mathcal{H}_{kl}^{(1)}(\vec{q}'\alpha') \mathcal{H}_{mn}^{(1)}(\vec{q}'\alpha')}{\mathcal{H}_{kl}^{(1)}(\vec{q}\alpha) \mathcal{H}_{mn}^{(1)}(\vec{q}\alpha)} \frac{\omega_{\vec{q}\alpha}^4}{\omega_{\vec{q}'\alpha'}^4} \left[ 1 - \frac{1}{15} \frac{\omega_{\vec{q}\alpha}}{\omega_{\vec{q}'\alpha'}} \right] \\ & + \frac{1}{8} \sum_{\vec{q}'\alpha' \neq \vec{q}''\alpha'' \neq \vec{q}\alpha} \mathcal{H}_0^{(4)} \begin{bmatrix} \vec{q} & \vec{q}' & \vec{q}'' & -\vec{q} \\ \alpha & \alpha' & \alpha'' & \alpha \end{bmatrix} \langle |Q_{\vec{q}\alpha}|^2 \rangle \frac{\mathcal{H}_{kl}^{(1)}(\vec{q}'\alpha') \mathcal{H}_{mn}^{(1)}(\vec{q}''\alpha'')}{\mathcal{H}_{kl}^{(1)}(\vec{q}\alpha) \mathcal{H}_{mn}^{(1)}(\vec{q}\alpha)} \\ & \times \frac{\omega_{\vec{q}\alpha}^4}{\omega_{\vec{q}'\alpha'}^2 \omega_{\vec{q}''\alpha''}^2} \left[ 1 + \frac{\omega_{\vec{q}\alpha} (3\omega_{\vec{q}'\alpha'} + 2\omega_{\vec{q}''\alpha''})}{2\omega_{\vec{q}'\alpha'} (\omega_{\vec{q}'\alpha'} + \omega_{\vec{q}''\alpha''})} \right]. \end{aligned} \quad (\text{B4})$$



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