Prediction of an extremely large nonlinear refractive index for crystals at terahertz frequencies

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We develop a simple analytical model for calculating the vibrational contribution to the nonlinear refractive index n_2 (Kerr coefficient) of a crystal in terms of known crystalline parameters such as the linear refractive index, the coefficient of thermal expansion, the atomic density, and the reduced mass and the natural oscillation frequency of the vibrational modes of the crystal lattice. We show that the value of this contribution in the terahertz spectral region can exceed the value of the nonlinear refractive index n_2 in the visible and near-IR spectral ranges (which is largely electronic in origin) by several orders of magnitude. For example, for crystal quartz the value of the Kerr coefficient in the low-frequency limit is $n_2 = 2.2 \times 10^{-9}$ esu or, equivalently, 4.4×10^{-16} m²/W, which is very much larger than its value of 3×10^{-20} m²/W in the visible range. Furthermore, we present an analysis of the dispersion of n_2 in the terahertz spectral range and show that even larger values of n_2 occur at frequencies close to the vibrational resonances.

I. INTRODUCTION

Intensive research in the field of terahertz (THz) radiation has celebrated the beginning of its third decade. Since their first demonstrations, THz techniques continue to find new applications from medical diagnostics and therapy to the detection of hidden substances, including explosives and drugs [1–3]. In recent years, pulsed sources of THz radiation with sufficient intensity for the observation of nonlinear optical effects have appeared in a number of laboratories [4–9]. Investigation of the nonlinear optical effects in the THz spectral range has now become feasible [10,11]. The dependence of the refractive index of an optical medium on light intensity is a fundamental phenomenon in nonlinear optics. This phenomenon leads to well-known self-action effects of light, including self-phase modulation, self-focusing of light, or self-broadening of its spectrum [12]. The nonlinear response of a medium that leads to these self-action effects in a transparent medium (i.e., for nonresonant interactions of light with matter) relies on its nonlinear refractive index n_2 as a material characteristic. This quantity is responsible for the strength of self-action effects; it is thus important to find ways to measure and theoretically calculate the n_2 coefficient in various material systems.

In this paper, we propose a method for calculating the coefficient n_2 of crystals in the THz spectral range. It is shown that the vibrational contribution to the nonlinear response in the far-infrared (IR) spectral range can be several orders of magnitude larger than the electronic nonlinearity, which is the dominant contribution for ultrashort pulses in the visible and near-IR spectral ranges [12,13]. The paper is organized as follows. In Sec. II, we introduce the basic expression for the coefficient n_2 of a crystal whose structural unit is considered to be a classical anharmonic oscillator with quadratic and cubic nonlinearities. In Sec. III, we calculate expressions for the linear refractive index and the coefficient of thermal expansion of the crystal in the framework of the same model. The comparison of these results allows us to

write the expression for the vibrational contribution to the coefficient n_2 in terms of known characteristics of the crystal. To determine the contribution of the dynamic Stark shift of the ion vibrational frequency to the nonlinear response, we use a quantum mechanical approach. In Sec. IV, we evaluate the derived formula for n_2 for crystalline quartz. We show that the values of that coefficient in the THz spectral range are several orders of magnitude greater than the corresponding values in the visible and near-IR ranges. In Sec. V, we discuss the dispersion properties of the coefficient n_2 of quartz in the THz range. In conclusion, we summarize the main results of the paper in Sec. VI.

II. THE VIBRATIONAL CONTRIBUTION TO THE NONLINEAR REFRACTIVE INDEX OF CRYSTALS

There are many different mechanisms contributing to the nonlinear optical response in optical media [12,13]. Some of these mechanisms are based on the nonlinear response of each atom or molecule to the radiation field, while others are based on the change in the concentration of these particles, for example, due to the thermal expansion of the substance in the presence of high-intensity radiation. We refer to the former situation as "low-inertia" sources of nonlinearity, and to the latter as "high-inertia" sources. For the case of ultrashort optical pulses, including intense picosecond THz pulses [4–9], the dominant source of nonlinearity tends to be the low-inertia, single-particle sources [13]. For the pulses in the visible and near IR spectral ranges, the dominant low-inertia mechanism of nonlinearity is electronic [12–14]. For the pulses in the far-IR range, one expects the dominant mechanism of nonlinearity to be associated with anharmonic vibrations of the lattice.

Let us analyze the vibrational nonlinearity of a crystalline material by considering the dynamics of ions in the lattice resulting from the force induced by the electromagnetic field. In this analysis, we make use of a classical model of the anharmonic oscillator:

$$\ddot{x} + 2\gamma\dot{x} + \omega_0^2 x + ax^2 + bx^3 = \alpha E. \tag{1}$$

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Here x is the deviation of an ion from its equilibrium position, γ is the damping coefficient, E is the applied electric field, a and b are the nonlinear coefficients, and

$$\alpha = \frac{q}{m}, \tag{2}$$

where q is the ionic change, and m is the reduced mass of the vibrational mode. We solve Eq. (1) using perturbation theory that involves introducing an expansion parameter $0 \leqslant \lambda \leqslant 1$, characterizing the strength of the perturbation, to the right-hand side of Eq. (1):

$$\ddot{x} + 2\gamma\dot{x} + \omega_0^2 x + ax^2 + bx^3 = \lambda\alpha E. \tag{3}$$

We are looking for the solution to Eq. (3) in the form of a power-series expansion with respect to λ:

$$x = \lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)} + \ldots. \tag{4}$$

We substitute x in the form of Eq. (4) into the Eq. (3), while retaining the terms up to λ^3. Equation (3) then splits into three equations for the terms proportional to λ, λ^2, and λ^3:

$$\ddot{x}^{(1)} + 2\gamma\dot{x}^{(1)} + \omega_0^2 x^{(1)} = \alpha E, \tag{5a}$$

$$\ddot{x}^{(2)} + 2\gamma\dot{x}^{(2)} + \omega_0^2 x^{(2)} + a[x^{(1)}]^2 = 0, \tag{5b}$$

and

$$\ddot{x}^{(3)} + 2\gamma\dot{x}^{(3)} + \omega_0^2 x^{(3)} + 2ax^{(1)}x^{(2)} + b[x^{(1)}]^3 = 0. \tag{5c}$$

We assume that the electric field interacting with the ions is monochromatic with the frequency ω:

$$E(\omega) = E_\omega e^{-i\omega t} + \text{c.c.} \tag{6}$$

Within this study, we treat the nonlinear optical effects that occur without change in the frequency spectrum. We thus consider the oscillations of the crystalline ions at the fundamental frequency only:

$$x = x_\omega e^{-i\omega t} + \text{c.c.} \tag{7}$$

We are looking for the solution to Eq. (3) describing the amplitude of the vibrations in the crystalline lattice at the fundamental frequency. Substituting Eq. (7) into Eq. (5a), we obtain the solution for $x^{(1)}$ in the form

$$x_\omega^{(1)} = \frac{\alpha E}{\omega_0^2 - \omega^2 - 2\gamma i\omega}. \tag{8}$$

We next use Eqs. (6) and (8) to evaluate Eq. (5b). The resulting solution breaks down into two equations:

$$x_{2\omega}^{(2)} = -\frac{a\alpha^2\left(E_\omega^2 e^{-i2\omega t} + \text{c.c.}\right)}{\left(\omega_0^2 - \omega^2 - 2i\omega\gamma\right)^2\left(\omega_0^2 - 4\omega^2 - 4i\omega\gamma\right)} \tag{9a}$$

and

$$x_0^{(2)} = -\frac{a\alpha^2\, 2|E_\omega|^2}{\left(\omega_0^2 - \omega^2 - 2i\omega\gamma\right)^2\omega_0^2} \tag{9b}$$

for the components of x oscillating at the frequencies 2ω and 0, respectively. While these components are not of direct interest in the current study, they contribute in a nonlinear fashion to the oscillations of the deviation x at the fundamental frequency,

corresponding to self-action effects. We then use Eqs. (8) and (9) in Eq. (5c) to find these nonlinear contributions:

$$x_\omega^{(3)} = \left[\frac{2a^2\alpha^3}{\left(\omega_0^2 - \omega^2 - 2\gamma i\omega\right)^4}\frac{3\omega_0^2 - 8\omega^2 - 8\gamma i\omega}{\omega_0^2\left(\omega_0^2 - 4\omega^2 - 4\gamma i\omega\right)}\right.$$
$$\left. + \frac{3b\alpha^3}{\left(\omega_0^2 - \omega^2 - 2\gamma i\omega\right)^4}\right]|E_\omega|^2 E. \tag{10}$$

Next, we combine Eqs. (8) and (10) for the terms oscillating at the frequency ω in Eq. (4), while setting $\lambda = 1$, to obtain the final expression for x:

$$x_\omega = \frac{\alpha E_\omega}{\omega_0^2 - \omega^2 - 2\gamma i\omega} + \frac{1}{\left(\omega_0^2 - \omega^2 - 2\gamma i\omega\right)^4}$$
$$\times \left[2a^2\alpha^3\frac{3\omega_0^2 - 8\omega^2 - 8\gamma i\omega}{\omega_0^2\left(\omega_0^2 - 4\omega^2 - 4\gamma i\omega\right)} + 3b\alpha^3\right]|E_\omega|^2 E_\omega. \tag{11}$$

We next turn to evaluating the nonlinear susceptibility associated with the Kerr effect. We first introduce the total polarization in the medium, including both electronic P_{el} and vibrational P_{v} contributions.

$$P = P_{\text{el}} + P_{\text{v}} = Nqx = P_\omega e^{-i\omega t} + \text{c.c.} \tag{12}$$

The amplitude of the polarization component, oscillating at frequency ω and including both linear and nonlinear contributions, can be represented as

$$P_\omega = \chi^{(1)}E_\omega + 3\chi^{(3)}|E_\omega|^2 E_\omega. \tag{13}$$

Introducing the effective susceptibility

$$\chi_{\text{eff}} = \chi^{(1)} + 3\chi^{(3)}|E_\omega|^2$$
$$= \chi_{\text{el}}^{(1)} + \chi_{\text{v}}^{(1)} + 3\chi_{\text{el}}^{(3)}|E_\omega|^2 + 3\chi_{\text{v}}^{(3)}|E_\omega|^2, \tag{14}$$

where $\chi_{\text{el}}^{(i)}$ and $\chi_{\text{v}}^{(i)}$ are its electronic and vibrational contributions, we can rewrite the polarization (13) as

$$P_\omega = \chi_{\text{eff}}E_\omega. \tag{15}$$

The complex overall refractive index of the medium, including its linear and nonlinear, electronic and vibrational contributions, can now be expressed in terms of χ_{eff} as

$$\tilde{n}^2 = 1 + 4\pi\chi_{\text{eff}}. \tag{16}$$

Using the definition [12]

$$\tilde{n} = \tilde{n}_0 + \tilde{n}_2\langle E^2\rangle, \tag{17}$$

where $\langle E^2\rangle$ is the time average of the field, (6), which is explicitly given by

$$\langle E^2\rangle = 2|E_\omega|^2, \tag{18}$$

we find that

$$\tilde{n} = \tilde{n}_0 + 2\tilde{n}_2|E_\omega|^2. \tag{19}$$

In Eqs. (16)–(19) and below, we emphasize the complex nature of the refractive indices by adding a tilde above the letters that denote them. We drop the tilde sign when we switch to the real parts of these quantities later. Here and below, we use the notation $\bar{n}_2$ for the Kerr coefficient to emphasize that it is

considered in electrostatic units (esu). Later, when we convert its value to SI units, we drop the bar sign.

Combining Eqs. (14)–(19), we obtain

$$\tilde{n}_0^2 + 4\tilde{n}_0\tilde{n}_2|E_\omega|^2 = 1 + 4\pi\chi^{(1)} + 12\pi\chi^{(3)}|E_\omega|^2, \quad (20)$$

and the expressions for the linear and nonlinear refractive indices now take the forms

$$\tilde{n}_0 = \sqrt{1 + 4\pi\chi^{(1)}} \quad (21)$$

and

$$\tilde{n}_2 = \tilde{n}_{2,\mathrm{el}} + \tilde{n}_{2,\mathrm{v}} = \frac{3\pi\chi^{(3)}}{\tilde{n}_0}. \quad (22)$$

Here $\tilde{n}_{2,\mathrm{el}}$ and $\tilde{n}_{2,\mathrm{v}}$ are the electronic and vibrational contributions to the nonlinear refractive index. Using Eqs. (11)–(13), we can express the linear and nonlinear susceptibilities in terms of the parameters of the resonance as

$$\chi^{(1)} = qN\frac{\alpha}{\omega_0^2 - \omega^2 - 2\gamma i\omega} \quad (23)$$

and

$$\chi^{(3)} = \frac{qN}{3}\frac{\alpha^3}{\left(\omega_0^2 - \omega^2 - 2\gamma i\omega\right)^4}$$
$$\times\left[2a^2\frac{3\omega_0^2 - 8\omega^2 - 8\gamma i\omega}{\omega_0^2\left(\omega_0^2 - 4\omega^2 - 4\gamma i\omega\right)} + 3b\right]. \quad (24)$$

Finally, substituting Eq. (24) into Eq. (22), we obtain the equation for the nonlinear refractive index,

$$\tilde{n}_2 = \frac{\pi qN}{\tilde{n}_0}\frac{\alpha^3}{\left(\omega_0^2 - \omega^2 - 2\gamma i\omega\right)^4}$$
$$\times\left[2a^2\frac{3\omega_0^2 - 8\omega^2 - 8\gamma i\omega}{\omega_0^2\left(\omega_0^2 - 4\omega^2 - 4\gamma i\omega\right)} + 3b\right]. \quad (25)$$

Separating $\tilde{n}_0$ and $\tilde{n}_2$ into their real and imaginary parts, one can find the linear and nonlinear refractive indices and absorption coefficients from Eqs. (21)–(25):

$$n_0 = \mathrm{Re}\,(\tilde{n}_0) = \mathrm{Re}\,(\sqrt{1 + 4\pi\chi^{(1)}}), \quad (26)$$

$$\alpha_0 = \frac{2\omega}{c}\mathrm{Im}\,(\tilde{n}_0) = \frac{2\omega}{c}\mathrm{Im}\,(\sqrt{1 + 4\pi\chi^{(1)}}), \quad (27)$$

$$\bar{n}_2 = \mathrm{Re}\,(\tilde{n}_2) = 3\pi\,\mathrm{Re}\left(\frac{\chi^{(3)}}{\sqrt{1 + 4\pi\chi^{(1)}}}\right), \quad (28)$$

and

$$\alpha_2 = \frac{2\omega}{c}\,\mathrm{Im}\,(\tilde{n}_2) = 6\pi\frac{\omega}{c}\,\mathrm{Im}\left(\frac{\chi^{(3)}}{\sqrt{1 + 4\pi\chi^{(1)}}}\right). \quad (29)$$

Here n_0 and α_0 are the linear refractive index and absorption coefficient, and $\bar{n}_2$ and α_2 are the nonlinear refractive index and two-photon absorption coefficient, respectively.

The general result for $\tilde{n}_2$ is given by Eq. (25). It is useful to find the approximate form of this expression in three special cases of interest.

(1) In the low-frequency limit $\omega \ll \omega_0$, Eq. (25) takes the form

$$\bar{n}_2^{\omega\ll\omega_0} \equiv \mathrm{Re}\left[\tilde{n}_2^{\omega\ll\omega_0}\right] \approx \frac{\pi qN}{n_0}\frac{\alpha^3}{\omega_0^8}\left(\frac{6a^2}{\omega_0^2} + 3b\right). \quad (30)$$

(2) At two-photon resonance, $\omega \simeq \omega_0/2$, and

$$\tilde{n}_2^{\omega\simeq\omega_0/2} \approx \sqrt{\frac{3\omega_0^2 - 4\gamma i\omega_0}{3\omega_0^2 - 4\gamma i\omega_0 + 16\pi qN\alpha}}$$
$$\times\frac{256\pi qN\alpha^3}{\left(3\omega_0^2 - 4\gamma i\omega_0\right)^4}$$
$$\times\left[2a^2\frac{-\omega_0 + 4i\gamma}{2i\gamma\omega_0^2} + 3b\right]. \quad (31)$$

(3) For the near-resonance case ($\omega \simeq \omega_0$), we obtain

$$\tilde{n}_2^{\omega\simeq\omega_0} \approx \sqrt{\frac{i\gamma\omega_0}{i\gamma\omega_0 - 2\pi qN\alpha}}\frac{\pi qN\alpha^3}{16\omega_0^4\gamma^4}$$
$$\times\left[2a^2\frac{5\omega_0^2 + 8\gamma i\omega_0}{\omega_0^2\left(3\omega_0^2 + 4\gamma i\omega_0\right)} + 3b\right]. \quad (32)$$

(4) And, finally, at the frequencies much higher than the vibrational resonance frequencies, the approximation $\omega \gg \omega_0$ holds, and Eq. (25) becomes

$$\bar{n}_2^{\omega\gg\omega_0} \equiv \mathrm{Re}\left[\tilde{n}_2^{\omega\gg\omega_0}\right] \approx \frac{\pi qN}{n_0}\frac{\alpha^3}{\omega^8}\left(\frac{4a^2}{\omega_0^2} + 3b\right). \quad (33)$$

We performed the derivation of Eq. (25) under the assumption that there is a single vibrational resonance. This approximation is suitable for a situation in which a single resonance dominates over the others. Equation (25) can, however, be rewritten to treat the case of multiple resonances contributing to the value of $\tilde{n}_2$:

$$\tilde{n}_2 = \frac{\pi qN\alpha^3}{\tilde{n}_0}\sum_i\frac{1}{\left(\omega_{0,i}^2 - \omega^2 - 2\gamma_i i\omega\right)^4}$$
$$\times\left[2a_i^2\frac{3\omega_{0,i}^2 - 8\omega^2 - 8\gamma_i i\omega}{\omega_{0,i}^2\left(\omega_{0,i}^2 - 4\omega^2 - 4\gamma_i i\omega\right)} + 3b_i\right], \quad (34)$$

where the summation over i is to be performed over all of the vibrational modes of the material.

III. RELATIONSHIP BETWEEN THE NONLINEAR REFRACTIVE INDEX AND OTHER MEASURABLE PARAMETERS OF THE CRYSTAL

Equation (25) allows one to estimate the value of the vibrational contribution to $\bar{n}_2$ including both nonlinear terms of Eq. (3). However, it is not always straightforward to make use of this equation, because the values of the parameters appearing in this equation are not well known. We therefore use the model of Eq. (1) to calculate the values of other properties of the crystal that are known or easily measurable. In this manner we determine the values of many of the parameters that appear in expression (25) for $\bar{n}_2$. As the first step, we find the relationship between the vibrational contribution to the nonlinear refractive index and the thermal expansion

coefficient of the crystal. For our present purposes we assume that there is one dominant vibrational resonance and that the electronic contribution to both the linear and the nonlinear refractive indices is swamped by the vibrational contribution. We show below, in the discussion following Eq. (56), that this assumption is satisfied to reasonably good accuracy.

In order to proceed, we first integrate the force term $F(x)$ of Eq. (1) to obtain the potential energy function $U = -\int F(x)dx$ in the form

$$U(x) = \frac{m\omega_0^2}{2}x^2 + \frac{ma}{3}x^3 + \frac{mb}{4}x^4. \tag{35}$$

The probability of the displacement of an atom from its equilibrium position is given by the function

$$f(x) = Ae^{-\frac{U(x)}{k_B T}}. \tag{36}$$

The average deviation of the ion from its equilibrium position in thermal equilibrium is given in [14] by

$$\bar{x} = \frac{\int x f(x)\,dx}{\int f(x)\,dx} = -\frac{ak_B T}{m\omega_0^4}. \tag{37}$$

Here k_B is the Boltzmann constant and T is the temperature of the crystal in kelvins. The deviation from the equilibrium position determines the overall linear extension of a solid, which can be expressed as

$$L_T = L_0(1 + \alpha_T T). \tag{38}$$

Here L_T and L_0 are the solid's linear dimensions at temperature T and 0 K, respectively, and

$$\alpha_T = \frac{\bar{x}}{a_1 T} \tag{39}$$

is the linear expansion coefficient; here a_1 is the lattice constant. We can relate the thermal expansion coefficient to the crystalline parameters by substituting Eq. (37) into Eq. (39):

$$\alpha_T = -\frac{ak_B}{m\omega_0^4 a_1}. \tag{40}$$

Through use of this equation we are able to relate the nonlinear coefficient a to the measurable thermal expansion coefficient α_T.

We now apply this result to the case of the nonlinear refractive index in the low-frequency regime. We express Eq. (30) as

$$\bar{n}_{2,v}^{\omega \ll \omega_0} \approx \frac{\pi q N}{n_0}\left(\frac{6a^2\alpha^3}{\omega_0^{10}} + \frac{3b\alpha^3}{\omega_0^8}\right). \tag{41}$$

We can express this result as the sum of two terms,

$$\bar{n}_{2,v}^{\omega \ll \omega_0} = \bar{n}_{2,v}^{(1)} + \bar{n}_{2,v}^{(2)}, \tag{42}$$

where

$$\bar{n}_{2,v}^{(1)} = \frac{\pi q N}{n_0}\frac{6a^2\alpha^3}{\omega_0^{10}} \tag{43a}$$

and

$$\bar{n}_{2,v}^{(2)} = \frac{\pi q N}{n_0}\frac{3b\alpha^3}{\omega_0^8}. \tag{43b}$$

Here and below, we use the subscript "v" to emphasize the fact that the optical response in the frequency range $\omega \ll \omega_0$ is primarily vibrational.

We next estimate the two contributions (43) to $\bar{n}_{2,v}^{\mathrm{THz}}$ in terms of the readily measurable properties of the material. We see that both contributions depend on the third power of the parameter α of Eq. (2). Even though α is just equal to q/m, it is not obvious what value to use for either of these parameters. The quantity m can be identified as the reduced mass of the vibrational mode, which, in principle, can be calculated. However, the quantity q represents the strength of the electrical coupling of the vibrational mode to the electric field vector of the radiation field. The value of q will thus depend on the degree to which the chemical bonding is ionic or vibrational. We therefore choose a different means to determine the value of the parameter α. First, we note that Eq. (23) in the low-frequency limit becomes

$$\chi_v^{(1),\,\omega \ll \omega_0} \approx \frac{qN\alpha}{\omega_0^2}. \tag{44}$$

We next relate the susceptibility of this equation to the refractive index using the standard result $n^2 = 1 + 4\pi\chi$ and thereby find that the parameter α is related to the linear refractive index through

$$\alpha = \frac{\omega_0^2}{4\pi q N}\left[(n_{0,v}^{\omega \ll \omega_0})^2 - 1\right]. \tag{45}$$

In addition, we use Eq. (40) to express the nonlinear coefficient a in terms of the thermal expansion parameter as

$$a = -\frac{a_1 m \omega_0^4}{k_B}\alpha_T. \tag{46}$$

Using Eqs. (45) and (46) in Eq. (43a), we finally obtain

$$n_{2,v}^{(1)} = \frac{3a_1^2 m^2 \omega_0^4 \alpha_T^2}{32n_0\pi^2 q^2 N^2 k_B^2}\left[(n_{0,v}^{\omega \ll \omega_0})^2 - 1\right]^3. \tag{47}$$

Some remarks with regard to the relationship between the vibrational nature of the linear refractive index and the thermal expansion coefficient are available in the literature [13,15].

The second contribution to the vibrational nonlinear refractive index, (43b), appears as a result of a change in the frequency of oscillations to $\omega_0 \pm bx^2$ in the intense radiation field (the dynamic Stark effect). In the most general case (when we include in consideration all possible resonances), the expression for the third-order susceptibility takes the form given by Eq. (3.7.14) in [12]. If we limit our consideration to the case of a nonresonant isotropic medium at low THz frequencies ($\omega \ll \omega_0$), this equation reduces to

$$\chi_{\mathrm{ST}}^{(3)} = \frac{2N}{3\hbar^3}\sum_{lmn}' \frac{\mu_{gn}\mu_{nm}\mu_{ml}\mu_{lg}}{(\omega_{ng} - \omega)(\omega_{mg} - 2\omega)(\omega_{lg} - \omega)}$$
$$- \frac{2N}{3\hbar^3}\sum_{ln} \frac{\mu_{gn}\mu_{ng}\mu_{gl}\mu_{lg}}{(\omega_{ng} - \omega)(\omega_{lg} - \omega)(\omega_{lg} - \omega)}. \tag{48}$$

Here the prime on the first summation indicates that the terms corresponding to $m = g$ are to be omitted from the summation over m; these terms are displayed explicitly in the second summation. See, for instance, the discussion on page 205 of Ref. [12]. If only one excited state makes a significant

contribution (two-level atom model), and $\omega \ll \omega_0$, Eq. (48) further reduces to

$$\chi_{v,ST}^{(3)\,\omega \ll \omega_0} = -\frac{2N|\mu|^4}{3\hbar^3\omega_0^3}. \tag{49}$$

The corresponding expression for the Stark contribution to the vibrational nonlinear refractive index can be found from Eqs. (22) and (49):

$$\bar{n}_{2,v,ST}^{\omega \ll \omega_0} \equiv \bar{n}_{2,v}^{(2)} = \frac{3\pi}{n_0}\chi_{v,ST}^{(3),\,\omega \ll \omega_0} = -\frac{2\pi N|\mu|^4}{n_0\hbar^3\omega_0^3}. \tag{50}$$

Ideally, we would like to express the transition dipole moment μ entering Eq. (50) in terms of a measurable material parameter, e.g., the vibrational contribution to the linear refractive index. For this, we can use the expression for the linear susceptibility [12]:

$$\chi^{(1)} = \frac{N}{3\hbar}\sum_n |\mu_{na}|^2 \left[\frac{1}{(\omega_{na}-\omega)-i\gamma_{na}} \right. $$
$$\left. + \frac{1}{(\omega_{na}+\omega)+i\gamma_{na}} \right]. \tag{51}$$

For a two-level transition at $\omega \ll \omega_0$, Eq. (51) reduces to

$$\chi_v^{(1),\,\omega \ll \omega_0} = \frac{2N}{3\hbar}\frac{|\mu|^2}{\omega_0}. \tag{52}$$

Then the corresponding linear refractive index can be expressed as

$$\left(n_{0,v}^{\omega \ll \omega_0}\right)^2 - 1 = 4\pi\chi_v^{(1),\,\omega \ll \omega_0} = \frac{8\pi N|\mu|^2}{3\hbar\omega_0}. \tag{53}$$

Equation (50) can now be rewritten making use of Eq. (53) as

$$\bar{n}_{2,v}^{(2)} = -\left[\left(n_{0,v}^{\omega \ll \omega_0}\right)^2-1\right]^2 \frac{9}{32}\frac{1}{\pi N}\frac{1}{n_0\hbar\omega_0}. \tag{54}$$

The formula for the total vibrational contribution to the nonlinear refractive index, Eq. (42), can now be obtained by adding the two contributions of Eqs. (54) and (47). We obtain

$$\bar{n}_{2,v}^{\omega \ll \omega_0} = \bar{n}_{2,v}^{(1)} + \bar{n}_{2,v}^{(2)} = \frac{3a_1^2m^2\omega_0^4\alpha_T^2}{32n_0\pi^2q^2N^2k_B^2}\left[\left(n_{0,v}^{\omega \ll \omega_0}\right)^2-1\right]^3$$
$$- \frac{9}{32}\frac{1}{\pi N}\frac{1}{n_0\hbar\omega_0}\left[\left(n_{0,v}^{(\omega \ll \omega_0)}\right)^2-1\right]^2. \tag{55}$$

IV. NUMERICAL EXAMPLES

In this section, we use Eq. (55) to evaluate the nonlinear refractive index of crystalline quartz. The values of the thermal expansion coefficient in this case are $\alpha_T = 7.6 \times 10^{-6}$ (ºC)$^{-1}$ parallel to the optic axis and $\alpha_T = 14 \times 10^{-6}$ (ºC)$^{-1}$ perpendicular to the optic axis (see, e.g., Ref. [16]). For simplicity, we assume that there is a dominant vibrational mode, the Si-O stretch mode, and we thus neglect the influence of lower-frequency phonon resonances [17]. The justification of this assumption is that the absorption spectrum of crystal quartz [18] shows a dominant feature at the frequency of the Si-O stretch mode and a very much weaker feature at lower frequencies. The frequency of the fundamental vibrational mode is 1242 cm^{-1}, or 37.2 THz [19].

The lattice constant of crystalline quartz is 4.91 Å along the c axis and 5.40 Å along the a and b axes. We can define a mean lattice constant with the value 5.24 Å or 5.24×10^{-8} cm. The reduced mass m of the stretch mode is calculated as follows. The mass of the silicon atom is $m_{Si} = 28.1$ amu, and that of the oxygen atom is $m_O = 16$ amu. The reduced mass is thus $m_{Si}m_O/(m_{Si}+m_O) = 10.2$ amu or 1.69×10^{-23} g.

The number density N of the vibrational units is calculated as follows. The specific gravity of crystal quartz is 2.65, and the formula weight of SiO_2 is $28 + 16 \times 2 = 60$. Each silicon atom is thus associated with the total mass of $60 \times 1.67 \times 10^{-24}$ g $= 1.00 \times 10^{-22}$ g. The number of silicon atoms in 1 cm^3 of quartz is thus $2.65/(1.00 \times 10^{-22}) = 2.65 \times 10^{22}$.

Our expression [Eq. (55)] for the nonlinear refractive index depends both on the overall refractive index n_0 and on its vibrational contribution $n_{0,v}$. We determine them individually as follows. The low-frequency ($\omega \ll \omega_0$) value of the refractive index of quartz is known to have the value $n_0 = 2.1$ [20]. This refractive index value has both a vibrational and an electronic contribution. To good approximation, we take the electronic contribution to correspond to the value 1.4, the same value as in the visible for frequencies much lower than the electronic resonance frequencies. To determine the vibrational contribution to the low-frequency refractive index, we note that Eq. (21) can be expressed as

$$n_0^{\omega \ll \omega_0} = \sqrt{1+4\pi\chi^{(1),\,\omega \ll \omega_0}}$$
$$= \sqrt{1+4\pi\chi_{el}^{(1),\,\omega \ll \omega_0}+4\pi\chi_v^{(1),\,\omega \ll \omega_0}}. \tag{56}$$

We know that the low-frequency limit of n_0 is 2.1, and we thus see that $\chi_{tot}^{(1)}$ is equal to $[(2.1)^2-1]/4\pi = 0.27$. We also know that the nonresonant electronic contribution leads to a refractive index of 1.4. We thus conclude that $\chi_{el}^{(1)}$ is equal to $[(1.4)^2-1]/4\pi = 0.077$. By taking the ratio of these values, we see that, at the level of the susceptibility, the vibrational response is 3.5 times stronger than the electronic response. Also, because $\chi_{tot}^{(1)} = \chi_{el}^{(1)} + \chi_v^{(1)}$, we see that $\chi_v^{(1)} = 0.19$. We also deduce that the value that the refractive index would have due to the vibrational response alone is $n_{0,v}^{(\omega \ll \omega_0)} = \sqrt{1+4\pi(0.19)} = 1.8$. This is the value that should be used, for example, for $n_{0,v}^{(\omega \ll \omega_0)}$ in Eq. (55).

Another parameter that enters the expressions for the nonlinear refractive index is the ionic charge q associated with a particular vibrational mode. As we noted above, the value of q depends on the nature of the chemical bonding. For simplicity, for the present calculation we take $q = +e$.

Using the parameter values given above, we evaluate the two contributions to the nonlinear refractive index given by Eq. (55), and we find $\bar{n}_{2,v}^{(1)} \approx 2.24 \times 10^{-9}$ esu and $\bar{n}_{2,v}^{(2)} \approx -3.27 \times 10^{-11}$ esu. The overall value of the nonlinear refractive index of crystalline quartz is thus $\bar{n}_{2,v}^{(\omega \ll \omega_0)} \approx 2.21 \times 10^{-9}$ esu.

Many workers prefer to quote values of n_2 in SI units of m^2/W rather than $\bar{n}_2$ in esu. We now briefly indicate how to express the results of our calculation in SI units. We note that the change in refractive index produce by the nonlinear optical interaction must be the same for calculations performed in
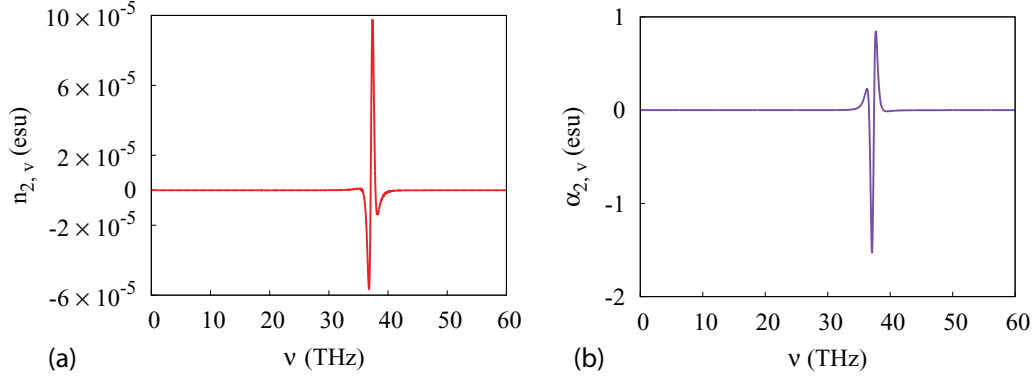
FIG. 1. (Color online) Dispersion of (a) n_2 (solid red lines) and (b) α_2 in the terahertz frequency range for crystalline quartz (solid blue lines).

Gaussian and in SI units. We thus note that

$$\Delta n = \bar{n}_2(\text{esu})\langle E(\text{esu})^2\rangle = n_2(\text{m}^2/\text{W})\,I(\text{W/m}^2). \quad (57)$$

We next note that $\langle E(\text{esu})^2\rangle = 2E_0(\text{esu})^2$, where E_0 is the field amplitude using the convention of Eq. (6). We also note that $I(\text{W/m}^2) = 2n_0\epsilon_0 c E_0(\text{V/m})^2$. And we recall that $E_0(\text{V/m}) = 3 \times 10^4\,E_0(\text{esu})$. By introducing these results into Eq. (57) we find that

$$n_2(\text{m}^2/\text{W}) = 4.2 \times 10^{-7}\,\frac{\bar{n}_2(\text{esu})}{n_0}. \quad (58)$$

For $\bar{n}_2 \equiv \bar{n}_{2,\text{v}}^{\omega \ll \omega_0} = 2.21 \times 10^{-9}$ esu and $n_0 = 2.1$, we obtain $n_2 \equiv n_{2,\text{v}}^{\omega \ll \omega_0} = 4.42 \times 10^{-16}$ m^2/W. By means of comparison, we note that the value of n_2 at optical frequencies is 3×10^{-20} m^2/W. Preliminary laboratory results [21] support the conclusion that the value of n_2 in the THz frequency range can be 1000 times larger than its value in the visible range.

V. DISPERSION OF THE NONLINEAR REFRACTIVE INDEX IN THE TERAHERTZ SPECTRAL RANGE

In Fig. 1, we plot the dispersion relation of the nonlinear refractive index and absorption coefficient for crystalline quartz in the frequency range from 0 to 60 THz. Figure 1(a) represents the frequency dependence of the real part of Eq. (25), which is the nonlinear refractive index, while Fig. 1(b) shows the nonlinear absorption coefficient, obtained from

Eqs. (25) and (29). We chose for illustration purposes the value for the resonant peak width $\gamma = 5 \times 10^{12}$ rad/s. The value of the nonlinear parameter b that enters Eq. (25) was estimated using Eq. (43b). A very strong vibrational resonance with largely enhanced values of n_2 and α_2 is evident from the graphs: the resonant value of n_2 is 4 orders of magnitude higher than its low-frequency value $n_2 \approx 2.2 \times 10^{-9}$ esu. Note that with the sign conventions of our paper a positive (negative) value of α_2 implies absorption that increases (decreases) with intensity. One example of such a decrease is nonlinear absorption bleaching observed as a consequence of the change in the carrier density in a GaAs semiconductor [22].

In Fig. 2, we plot the same data in the frequency range between 0 and 25 THz. They resolve the two-photon resonance that appears due to the presence of the term $(\omega_0^2 - 4\omega^2)$ in the denominator of Eq. (25). The resonant value of n_2 exhibits more than one order of magnitude enhancement compared to its low-frequency value. It is evident from the inset in Fig. 2(a) that one can neglect the dispersion of a wide-spectrum pulse, as long as the entire pulse width lies in the range between 0 and 6 THz. In this case, one can treat the dynamics of the electric field of a THz wave in an optical medium using the formalism described in Ref. [23]. For waves with a spectrum in the range between 0 and 12 THz, the nonlinear refractive index doubles in value; one can no longer neglect the dispersion of n_2 when analyzing the interaction of a broad-spectrum radiation with an optical medium. In the frequency range beyond 12 THz
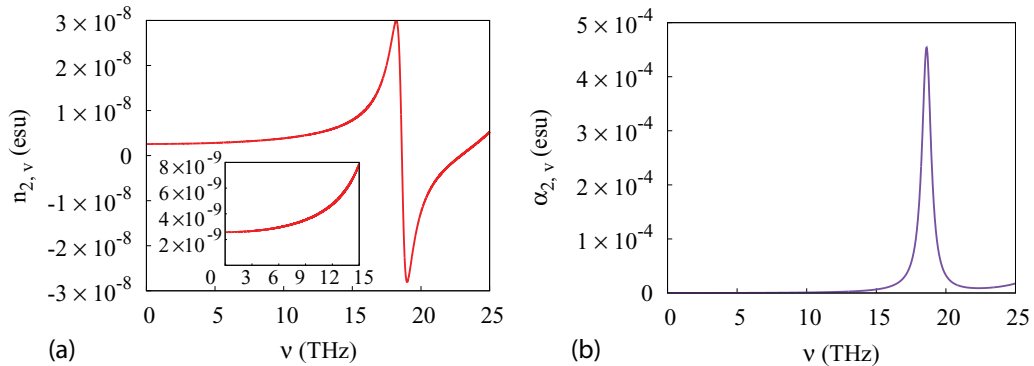

FIG. 2. (Color online) Dispersion of (a) n_2 (solid red lines) and (b) α_2 in the terahertz frequency range for crystalline quartz (solid blue lines). The resonant feature appearing in these graphs is due to the two-photon resonance.

the dispersion is significant; the optical nonlinearity exhibits inertia. Some methods of calculating the dispersion of n_2 are described in Ref. [24].

VI. CONCLUSIONS

We have developed a simple analytical model that allows one to deduced the dispersion characteristics of the nonlinear refractive index n_2 and two-photon absorption coefficient α_2. Additionally, we have established the relationship between the vibrational contribution to n_2 and some measurable parameters of a crystal, such as the linear refractive coefficient and thermal expansion coefficient. Using our model, we have performed an estimate of the value of n_2 for crystalline quartz in the THz spectral range and found that in the low-frequency limit it is four orders of magnitude larger than its value of n_2 in the visible range. Our model also predicts a large variation of n_2 with frequency, as well as the variation in α_2 from positive to negative values in the vicinity of the vibrational resonance. The model we propose here is not limited to dielectric materials. Despite their more complex nature, our model could be extended to treat the vibrational nonlinearity in semiconductors. Multiple phonon modes, as well as the local vibrational modes of impurities, are expected to contribute to the value of the vibrational Kerr coefficient in a similar fashion.

In the calculations reported here, we have assumed that the THz radiation is quasimonochomatic. Many THz experiments are conducted with very short pulses, which may contain only a few optical cycles (or even just one) [11]. The nature of the nonlinear phenomena under these conditions can differ drastically from the case treated here. This represents an interesting subject for future exploration.

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