

# NONLINEAR INTERACTION OF PICOSECOND LIGHT PULSES WITH CRYSTAL LATTICE VIBRATIONS

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The enhancement of molecular rotational and translational vibrations in a one-dimensional crystal lattice, due to interaction with a powerful light beam, is shown to be able to account for the electric permittivity increase leading to light trapping. Frequency shifts accompanying it are found to be of the measurable magnitude.

## 1. Introduction

The enhancement of molecular translational vibrations in crystal lattice due to the interaction of the fundamental  $q = 0$  longitudinal optical vibration modes (LO) with the electric field of the light wave leading to the electric permittivity increase has been recently shown by one of the present authors [1, 2].

The problem was approached mathematically by studying the optical behaviour of a one-dimensional lattice composed of atoms or molecules of spherical symmetry. In the present paper, the case where the lattice is built of axially symmetric molecules, is discussed and translational as well as rotational vibrations are taken into account.

Frequency shifts accompanying the enhancement of vibrations, found by one of us for translational vibrations [1], are supposed to be able to account for some of those observed by Sacchi [4]. The results are presented in Section 2. The electric permittivity increase, as a result of the enhancement of lattice vibrations [3], is calculated in Section 3.

## 2. Molecular oscillations in the averaged electric field of a light wave

Following the previous method [3] of solving the problem we consider a linear chain of equidistant axially symmetric molecules exhibiting longitudinal optical vibrations subjected to an external light wave. For simplicity we assume the electric vector of a light beam being parallel to the crystal axis. Polarizabilities of an isolated molecule both along

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its symmetry axis and perpendicularly to it are given by  $\alpha_3$  and  $\alpha_1$ , respectively. Thus, the total potential energy of a molecule of the system consists of two terms

$$H = H_0 + H_E, \quad (1)$$

$H_0$  being the energy describing the interaction with the nearest neighbours, in absence of external electric field,  $H_E$ , in turn, giving the field induced dipole-dipole interaction with two adjacent molecules of the form:

$$\begin{aligned} H_E(x, \theta) = & -\frac{1}{2} \overline{E_0^2} \gamma^{-1} [\alpha_3(1 + \alpha_1 b)^2 - (\alpha_3 - \alpha_1) \sin^2 \theta \\ & \times (1 - 4(\alpha_3 - \alpha_1)(1 + \alpha_1 b)b - \alpha_3 \alpha_1 b^2) - 4(\alpha_3 - \alpha_1)^2 b \sin^4 \theta \\ & \times (1 + 2\alpha_1 b - \alpha_3 b) - 4(\alpha_3 - \alpha_1)^3 b^2 \sin^6 \theta] \end{aligned} \quad (2)$$

with

$$\gamma = (1 - 2\alpha_3 b)(1 + \alpha_1 b) + 3(\alpha_3 - \alpha_1)b \sin^2 \theta, \quad (2a)$$

and

$$b = (a + 2x)^{-3} + (a - 2x)^{-3}, \quad (2b)$$

$a$  — being the lattice constant;  $x$  — is the elongation of molecular translational vibration,  $\theta$  — denotes the angle between the crystal and molecular axes, assuming that according

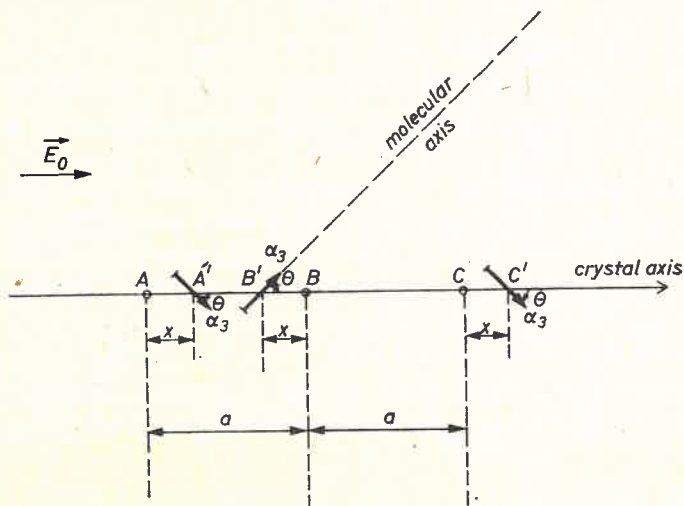


Fig. 1. A one dimensional crystal lattice composed of anisotropic molecules.  $x$  — linear displacements in the translational optical mode;  $\theta$  — angular displacements in rotational antiphase vibrations. Points A, B, C denote equilibrium positions of the molecules. Points A', B', C' denote positions of the translationally displaced molecules

to the  $q \cong 0$ , (LO) vibrating mode adjacent molecules oscillate in opposite directions and with equal amplitudes, rotationally and translationally at the same time, as is shown in Fig. 1. For simplicity we assume them moving in one plane.  $\overline{E_0^2}$  is the mean value of the

light wave intensity. Formula (2) is valid only for molecules that can be considered as point dipoles. The interaction of permanent dipoles, if any, with a light wave as well as with induced dipoles has been neglected because of high frequency of a light beam.

Considering only small translational and rotational vibrations we expand the expression for  $H(x, \theta) = H_0(x, \theta) + H_E(x, \theta)$  retaining only terms of the fourth order in small displacements  $x$  and  $\theta$

$$H(x, \theta) = \frac{1}{2} m \omega_{0t}^2 x^2 (1 + \frac{1}{2} A_t x^2) + \frac{1}{2} I \omega_{0r}^2 \theta^2 (1 + \frac{1}{2} A_r \theta^2) + \frac{1}{2} B x^2 \theta^2 - \frac{1}{2} K_t \bar{E}_0^2 x^2 (1 + \frac{1}{2} A'_t x^2) - \frac{1}{2} K_r \bar{E}_0^2 \theta^2 (1 + \frac{1}{2} A'_r \theta^2) - \frac{1}{2} B' \bar{E}_0^2 x^2 \theta^2, \quad (3)$$

where  $\omega_{0t}$  and  $\omega_{0r}$  are translational and rotational vibration frequencies, respectively, of an undisturbed system;  $m$  being the molecular mass and  $I$  the moment of inertia;  $A_t$ ,  $A_r$  and  $B$  denote the coefficients of anharmonicity due to the structure of molecules and lattice. Constants  $K_t$ ,  $K_r$  and coefficients of anharmonicity  $A'_t$ ,  $A'_r$  and  $B'$  due to the electric field of a light wave have been calculated for two particular directions of the axes of potential energy minima: along crystal axis (case 1) and perpendicular to it (case 2), and are given in Appendix.

Formula (3) leads directly to the following equations of motion for one molecule imbedded in the lattice:

$$\begin{aligned} \ddot{x} + \omega_{0t}^2 x (1 - \eta_t) + \omega_{0t}^2 x^3 (A_t - A'_t \eta_t) + \omega_{0t}^2 x \theta^2 (B_t - B'_t \eta_t) &= 0, \\ \ddot{\theta} + \omega_{0r}^2 \theta (1 - \eta_r) + \omega_{0r}^2 \theta^3 (A_r - A'_r \eta_r) + \omega_{0r}^2 x^2 \theta (B_r - B'_r \eta_r) &= 0, \end{aligned} \quad (4)$$

where

$$B_t = \frac{B}{m \omega_{0t}^2}; \quad B_r = \frac{B}{I \omega_{0r}^2}; \quad B'_t = \frac{B'}{K_t}; \quad B'_r = \frac{B'}{K_r} \quad (4a)$$

$$\eta_t = \frac{K_t \bar{E}_0^2}{m \omega_{0t}^2} \quad \text{and} \quad \eta_r = \frac{K_r \bar{E}_0^2}{I \omega_{0r}^2}. \quad (4b)$$

The sign of  $\eta_r$  depends on the shape of the molecule and on the case considered, whereas  $\eta_t$  is always positive. For  $\alpha_3 > \alpha_1$  (cigar shaped molecule) we obtain  $K_r < 0$ ,  $\eta_r < 0$  for the first case mentioned above and  $K_r > 0$ ,  $\eta_r > 0$  for the second one. Both equations (4) show that the frequencies and amplitudes of molecular vibrations are changed by the electric field of a light wave. The treatment of a crystal lattice as one-dimensional is only a very rough approximation of what happens in real crystals or in liquids. Anyway, the interaction of a molecule with its two neighbours seems to be the only effect with accounts, at least as to the order of magnitude, for starting the light filament formation, in the cases when other mechanisms (e. g. Kerr effect) must be excluded because of the spherical symmetry of molecules. Denoting changed values both of translational and rotational

frequencies by  $\omega_t$ ,  $\omega_r$ , and changed amplitudes by  $x_E$ ,  $\theta_E$ , we find for the ratios  $\left(\frac{x_E}{x_0}\right)$ ,  $\left(\frac{\theta_E}{\theta_0}\right)$ ,  $\left(\frac{\omega_{0t}}{\omega_t}\right)$ ,  $\left(\frac{\omega_{0r}}{\omega_r}\right)$  the following expressions:

$$\begin{aligned} \left(\frac{x_E}{x_0}\right)^2 &\simeq \left(\frac{\omega_{0t}}{\omega_t}\right)^2 = 1 + \eta_t \left[ 1 - \frac{3}{4} x_0^2 (2A_t - A'_t) - \frac{1}{2} \theta_0^2 (2B_t - B'_t) \right] \\ &\quad + \eta_t^2 \left[ 1 - \frac{3}{4} x_0^2 (5A_t - 3A'_t) - \frac{1}{2} \theta_0^2 (5B_t - 3B'_t) \right] \\ \left(\frac{\theta_E}{\theta_0}\right)^2 &\simeq \left(\frac{\omega_{0r}}{\omega_r}\right)^2 = 1 + \eta_r \left[ 1 - \frac{3}{4} \theta_0^2 (2A_r - A'_r) - \frac{1}{2} x_0^2 (2B_r - B'_r) \right] \\ &\quad + \eta_r^2 \left[ 1 - \frac{3}{4} \theta_0^2 (5A_r - 3A'_r) - \frac{1}{2} x_0^2 (5B_r - 3B'_r) \right]. \end{aligned} \quad (5)$$

Hence, owing to the electric field of a light wave, the frequency of translational vibration always decreases and the amplitude increases. On the other hand, the increase of rotational frequency depends on the shape of the molecule and on the equilibrium position of the molecular axes, e. g. if  $\alpha_3 > \alpha_1$  the frequency of rotational vibration increases for the first case and decreases for the second one. Numerical calculations of those frequency shifts were performed for several liquids on the basis of the formulae (5) leading to

$$\omega - \omega_0 = \Delta\omega \simeq -\frac{1}{2} (\eta + \frac{3}{4} \eta^2) \omega_0 \quad (6)$$

given with accuracy to harmonic terms and valid both for translational as well as rotational vibrations. We assume  $\overline{E_0^2} = 10^{10} \text{ esu}^2$ , and intermolecular distance  $a$  being somewhat smaller than the average, according to Ref. [9, 8]. Thus we obtain translational frequency shifts  $\Delta\omega_t$  of the order of several  $\text{cm}^{-1}$ , e. g. for benzene  $\Delta\omega_t \simeq 2-5 \text{ cm}^{-1}$ , for toluene  $3-6 \text{ cm}^{-1}$ , for  $\text{CS}_2$   $2 \text{ cm}^{-1}$  and for  $\text{CCl}_4$  (spherical molecule)  $3 \text{ cm}^{-1}$ , all being smaller than the half-width of spectral line ( $\sim 8 \text{ cm}^{-1}$ , [4]). Rotational frequency shifts  $\Delta\omega_r$ , in turn, appear to be nearly one order of magnitude larger. We have calculated:  $\Delta\omega_r \simeq 10 \text{ cm}^{-1}$  for benzene,  $15 \text{ cm}^{-1}$  for toluene,  $12 \text{ cm}^{-1}$  for  $\text{CS}_2$ . Thus, it is to be seen, that observation of such an effect as the shift of spectral lines could be feasible. Sacchi [4], using picosecond light pulses, observed some new lines in the RS spectrum of the same liquids. Frequency shifts of those lines being of the same order of magnitude as calculated by us may be suggested as due to the mechanism presented in this paper. Anyway, we can not be sure until we prove its dependence on the light wave electric field intensity. The effect of amplitude enhancement as being of transient nature seems to be the only one, leading to self-trapping with picosecond light pulses. Using such short pulses eliminates other processes of longer relaxation time, as e. g. diffusional molecular orientation.

<sup>1</sup> Cf. figures 1 and 2 of Ref. [5].

### 3. Self-trapping as a result of enhancement of lattice vibrations

Taking into account the dipole-dipole interaction of any particular molecule with its two neighbours both dipoles being induced, and considering them as point dipoles one obtains for their changed values of polarizability  $\alpha'_3$  and  $\alpha'_1$  following expressions:

$$\begin{aligned}\alpha'_2 &= \alpha_3 \gamma^{-1} [1 + \alpha_1 b + 2(\alpha_3 - \alpha_1) b \sin^2 \theta], \\ \alpha'_1 &= \alpha_1 \gamma^{-1} [1 + \alpha_3 b - 2(\alpha_3 - \alpha_1) b \sin^2 \theta].\end{aligned}\quad (6)$$

$\gamma$  and  $b$  being expressed by formulae (2a) and (2b), respectively. Expanding expressions (6) over the small displacements  $x$ ,  $\theta$  and using (4), (5) we find the increase of the value of the electric polarizability of molecules for optical frequency under the action of a light wave, given by formula

$$\begin{aligned}\langle \Delta \alpha' \rangle_E &= \langle \alpha' \rangle_E - \langle \alpha' \rangle_0 \\ &= \left\{ \frac{C_t K_t}{m \omega_{0t}^2} \left[ 1 - \frac{3}{4} x_0^2 (2A_t - A'_t) - \frac{1}{2} \theta_0^2 (2B_t - B'_t) \right] \right. \\ &+ \left. \frac{C_r K_r}{I \omega_{0r}^2} \left[ 1 - \frac{3}{4} \theta_0^2 (2A_r - A'_r) - \frac{1}{2} x_0^2 (2B_r - B'_r) \right] \right\} \bar{E}_0^2 \\ &+ \left\{ \frac{C_t K_t^2}{(m \omega_{0t}^2)^2} \left[ 1 - \frac{3}{4} x_0^2 (5A_t - 3A'_t) - \frac{1}{2} \theta_0^2 (5B_t - 3B'_t) \right] \right. \\ &+ \left. \frac{C_r K_r^2}{(I \omega_{0r}^2)^2} \left[ 1 - \frac{3}{4} \theta_0^2 (5A_r - 3A'_r) - \frac{1}{2} x_0^2 (5B_r - 3B'_r) \right] \right\} (\bar{E}_0^2)^2\end{aligned}\quad (7)$$

where the constants  $C_t$ ,  $C_r$  are given in Appendix for both cases mentioned earlier, respectively. Hence, the increase of electric permittivity for optical frequency,  $\Delta \varepsilon$ , is to be calculated from the formula

$$\Delta \varepsilon = 4\pi N \left( \frac{\varepsilon + 2}{3} \right)^2 \langle \Delta \alpha' \rangle_E. \quad (8)$$

The results obtained in previous papers ([5] phenomenologically and [6, 7] theoretically) show that the coefficients in the experimental formula

$$\Delta \varepsilon = \varepsilon_2 E^2 + \varepsilon_4 E^4 \quad (9)$$

must be of the order  $\varepsilon_2 \sim 10^{-13}$  esu<sup>-2</sup>,  $\varepsilon_4 \sim 10^{-24}$  esu<sup>-4</sup> and light-trapping is ensured when  $\varepsilon_2$  is positive and  $\varepsilon_4$  negative. Reasonable values of structural anharmonicity coefficients  $A_t$ ,  $A_r$ ,  $B_t$ ,  $B_r$  (even not taking electric anharmonicity into account as much weaker) fulfil the conditions for  $\varepsilon_2$  and  $\varepsilon_4$ . Thus, it can be seen that the enhancement of molecular vibrations really plays an important part in self-trapping, and probably constitutes a starting process in this phenomenon, even if molecules are of spherical symmetry.

## APPENDIX

The constants in equations (3) are given below.

(a) For the first case (the molecular axis of symmetry vibrates around the crystal axis)

$$K_t = -\frac{1}{E_0^2} \left[ \frac{\partial^2 H_E(x, \theta)}{\partial x^2} \right]_{x, \theta=0} = 192 \left( \frac{\varepsilon+2}{3} \right)^2 \alpha_3^2 a^{-5} \left( 1 - \frac{4\alpha_3}{a^3} \right)^{-3}$$

$$K_r = -\frac{1}{E_0^2} \left[ \frac{\partial^2 H_E(x, \theta)}{\partial \theta^2} \right]_{x, \theta=0} = -(\alpha_3 - \alpha_1) \left( \frac{\varepsilon+2}{3} \right)^2 \left( 1 - \frac{4\alpha_3}{a^3} \right)^{-3} \left( 1 + \frac{2\alpha_1}{a^3} \right)^{-2}$$

$$\times \left[ \left( 1 + \frac{4\alpha_1}{a^3} \right)^2 + \frac{32\alpha_3}{a^6} (\alpha_3 - \alpha_1) \left( 1 + \frac{2\alpha_1}{a^3} \right) + 4 \frac{\alpha_3 \alpha_1}{a^6} \left( 1 + \frac{4\alpha_3}{a^3} \right) \right]$$

$$A'_t = -\frac{1}{6K_t E_0^2} \left[ \frac{\partial^4 H_E(x, \theta)}{\partial x^4} \right]_{x, \theta=0}; \quad B'_t = -\frac{1}{2K_t E_0^2} \left[ \frac{\partial^4 H_E(x, \theta)}{\partial x^2 \partial \theta^2} \right]_{x, \theta=0}$$

$$A'_r = -\frac{1}{6K_r E_0^2} \left[ \frac{\partial^4 H_E(x, \theta)}{\partial \theta^4} \right]_{x, \theta=0}; \quad B'_r = -\frac{1}{2K_r E_0^2} \left[ \frac{\partial^4 H_E(x, \theta)}{\partial x^2 \partial \theta^2} \right]_{x, \theta=0}$$

It can be easily seen that  $K_r > 0$  for disc-shaped molecules ( $\alpha_3 < \alpha_1$ ), which means that under influence of the electric field of the light wave rotational frequency decreases. On the other hand, for cigar-shaped molecules ( $\alpha_3 > \alpha_1$ ),  $K_r < 0$  which means that rotational frequency increases.

(b) For the second case (the molecular axis of symmetry vibrates around the direction perpendicular to the crystal axis)

$$K_t = -\frac{1}{E_0^2} \left[ \frac{\partial^2 H_E \left( x, \frac{\pi}{2} - \theta \right)}{\partial x^2} \right]_{x, \theta=0} = 192 \left( \frac{\varepsilon+2}{3} \right)^2 \alpha_1^2 a^{-5} \left( 1 - \frac{4\alpha_1}{a^3} \right)^{-3}$$

$$K_r = -\frac{1}{E_0^2} \left[ \frac{\partial^2 H_E \left( x, \frac{\pi}{2} - \theta \right)}{\partial \theta^2} \right]_{x, \theta=0} = (\alpha_3 - \alpha_1) \left( \frac{\varepsilon+2}{3} \right)^2 \left( 1 - \frac{4\alpha_1}{a^3} \right)^{-3} \left( 1 + \frac{2\alpha_3}{a^3} \right)^{-2}$$

$$\times \left[ \left( 1 + \frac{4\alpha_3}{a^3} \right)^2 + \frac{32\alpha_1}{a^6} (\alpha_1 - \alpha_3) \left( 1 + \frac{2\alpha_3}{a^3} \right) + \frac{4\alpha_1 \alpha_3}{a^6} \left( 1 + \frac{4\alpha_1}{a^3} \right) \right]$$

$$A'_t = -\frac{1}{6K_t E_0^2} \left[ \frac{\partial^4 H_E \left[ x, \frac{\pi}{2} - \theta \right]}{\partial x^4} \right]_{x, \theta=0}; \quad B'_t = -\frac{1}{2K_t E_0^2} \left[ \frac{\partial^4 H_E \left[ x, \frac{\pi}{2} - \theta \right]}{\partial x^2 \partial \theta^2} \right]_{x, \theta=0}$$

$$A'_r = -\frac{1}{6K_r E_0^2} \left[ \frac{\partial^4 H_E \left( x, \frac{\pi}{2} - \theta \right)}{\partial \theta^4} \right]_{x, \theta=0}; \quad B'_r = -\frac{1}{2K_r E_0^2} \left[ \frac{\partial^4 H_E \left( x, \frac{\pi}{2} - \theta \right)}{\partial x^2 \partial \theta^2} \right]_{x, \theta=0}$$

For disc-shaped molecules ( $\alpha_3 < \alpha_1$ ) we obtain  $K_r < 0$  giving the rotational frequency increase and for cigar-shaped molecules ( $\alpha_3 > \alpha_1$ ) we obtain  $K_r > 0$  giving the rotational frequency decrease.

The coefficients  $C_t$  and  $C_r$  in formulae (7) are of the form

(a) for the first case

$$C_t = 48\alpha_3^2 a^{-5} \left(1 - \frac{4\alpha_3}{a^3}\right)^{-2} \left(\frac{x_0}{a}\right)^2,$$

$$C_r = -2(\alpha_3 - \alpha_1) \left(1 - \frac{4\alpha_3}{a^3}\right)^{-2} \left(1 + \frac{2\alpha_1}{a^3}\right)^{-1} \left(1 + 2\frac{\alpha_3}{a^3}\right) \theta_0^2,$$

(b) for the second case

$$C_t = 48\alpha_1^2 a^{-5} \left(1 - \frac{4\alpha_1}{a^3}\right)^{-2} \left(\frac{x_0}{a}\right)^2,$$

$$C_r = 2(\alpha_3 - \alpha_1) \left(1 - \frac{4\alpha_1}{a^3}\right)^{-2} \left(1 + \frac{2\alpha_3}{a^3}\right)^{-1} \left(1 + 2\frac{\alpha_1}{a^3}\right) \theta_0^2.$$

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