Semiconductor Physics, Quantum Electronics & Optoelectronics. 2001. V. 4, N 4. P. 331-336.

PACS: 42.70.M; N

Microwave-induced optical non-linearity of amino acid crystals

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Abstract. Changes (ΔR) of amino acid crystals infrared (IR) reflectance (R) induced by simultaneous irradiation of IR and microwaves (MW) or extremely high frequency (EHF) radiation have been observed. It was shown that under the microwave action, components of dielectric permeability tensor, ε_{ij}, which is responsible for the alteration of the R, are changed. Square dependence of $\Delta R/R$ on power of EHF radiation has been observed. An attempt for explanation of the observed effect as non-linear phenomenon with participation of two EHF photons (Ω_m) and one IR photon (ω_i) was made. The estimation shows that the third order non-linear polarizability coefficient, $\chi^{(3)}(\Omega_m, -\Omega_m, \omega_i)$, reaches the gigantic value – 10 cm/erg for α-Gly single crystal.

Keywords: gigantic non-linearity, amino acid crystal, infra-red reflectance, microwaves, extremely high frequency radiation, polarization indicatrix.

Paper received 30.11.00; revised manuscript received 26.11.01; accepted for publication 12.12.01.

1. Introduction

Non-linear optical effects, e.g. generation of the second harmonics, mixing the frequencies or auto focusing are observed in the crystals under the action of the high power of laser radiation. However, it is well known that in the living matter, the process of photosynthesis or transformation of solar energy in other types of energy occurs at very low power and high efficiency. So, we can expect that molecular crystals as the amino acids single crystals could show non-linear properties at the lower level of the applied power. The attempt to find non-linear optical effects in the amino acids was made. The amino acids are the building blocks of the proteins, the main parts of living matter. We applied to amino acid crystals the microwaves (MW) of millimeter range or extremely high frequency radiation (EHF) in the 37.5–78.5 GHz range and registered the infrared (IR) spectra during application of the MW radiation. The EHF range of electromagnetic radiation is specific and very important for living organisms. This caused by the fact that MW radiation background at the Earth surface is very small, practically negligible. Modern detectors do not register it, however, the influence of this radiation on the biological process should be taken into account [1]. E.g., the MW irradiation of the biologically active points of human body leads to the positive therapeutic effects in the treating of some diseases [2]. Some new data shows that low-intensity MW radiation causes the increase of single and double breaks in rat brain [3], the effect on protein kinase C and gene expression in a human mast cell line [4], enhancement of folding of globular proteins [5], etc.

The properties of alive and non-alive matter in this range are studied not well and ambiguous experimental data are not so numerous. It is due to the technical and methodical difficulties, which arise during the measurement of physical properties in the millimeter range. That is why we took the following way: using the method of vibration spectroscopy (IR range), we registered the response of single crystals of amino acids to the MW field action. In the experiment we registered the IR reflectance spectra of amino acids under the simultaneous action on the crystal of IR irradiation and MW irradiation of certain frequency [6]. The result of action we estimated by comparison of IR reflectance spectra at different MW frequencies and without application of MW field.

2. Materials and methods

Amino acid crystals, glycine (α-Gly), alanine (β-Ala), as well as triglycinesulphate crystals were used for investigation. The crystals were grown from aqueous solutions of chemically pure grade reagent additionally purified by triple recrystallization. IR reflectance spectra have been recorded with grating spectrometer Jasco DS-402 (Japan) in the 2000-600 cm^{-1} region with 0.5 cm^{-1} resolution and wave number definition 0.5 cm^{-1}. The experimental setup is presented in Fig.1. The generators G4-141 and G4-142 (USSR) were applied as the MW sources. The MW radiation was tuned in the 37.5–53.5 GHz region with stability ± 5 MGz and output power of 80 mW/cm^2. The amino acid crystals, which have the form of plates of 5×10 mm^2 and of 2–3 mm thickness was placed in the reflection attachment. The MW radiation was applied to the surface of the amino acid crystals by the metal or flexible teflon wave-guide. The IR radiation was incident at 5–7° to the opposite side of the amino acid crystal, and the reflected IR radiation was directed to the input slit of the spectrometer.

3. Results and discussion

The IR reflectance spectra of the crystals under MW irradiation have been shown in Figs 2–4. Under simultaneous action of the MW field as applied radiation and of the IR radiation as the test one, the IR reflectance of some amino acid bands is drastically changed. Absolute values of the observed changes of the *R* are small, however they are 3–5 times greater than the errors of the experiment indicated in Figs 2–4. The most sensitive to MW field are the bands: at 1560 cm^{-1} assigned to symmetric stretching vibration of COO$^-$ group and at 1505 cm^{-1} assigned to symmetric deformation vibration of NH^{3+} group. We have observed that ΔR is dependent on mutual orientation of optical axes of crystal, direction of vectors E for both IR and EHF fields. Quantitative estimation of the effect of MW action on the amino acid vibration spectra could be done with ratio $\Delta R/R$ (ΔR are changes of IR reflectance under the MW action to the crystal, *R* is an IR reflectance of the crystal without application of MW field) at the certain IR wavelength.

It is difficult to explain the obtained results on the basis of traditional points of view. This is due to the fact that the energy of the EHF quanta is equal to 10^{-4} eV that is 2 orders less than kT. That is why one should suppose that thermal effect could miss the MW effect of the EHF field action. However, the effects of MW influence on the

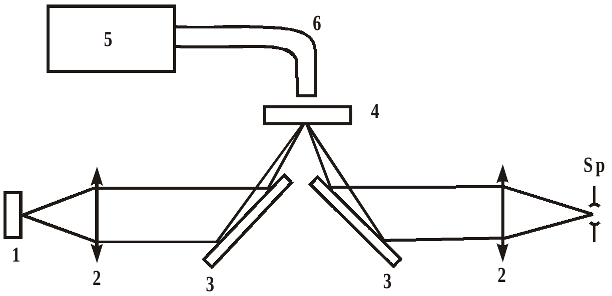

Fig.1. The experimental setup: 1 – IR radiation source (globar), 2 – optic lenses, 3 – mirrors, 4 – the sample of amino acid crystal, 5 – MW generator, 6 – flexible waveguide, Sp – input spectrometer slit.

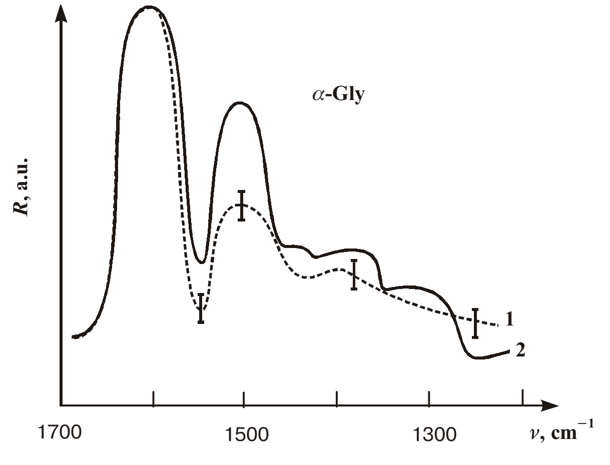

Fig.2. Reflectance spectra of single crystal of α-Gly under the MW field action at *f* = 46.9 GHz (1) and without MW field (2).

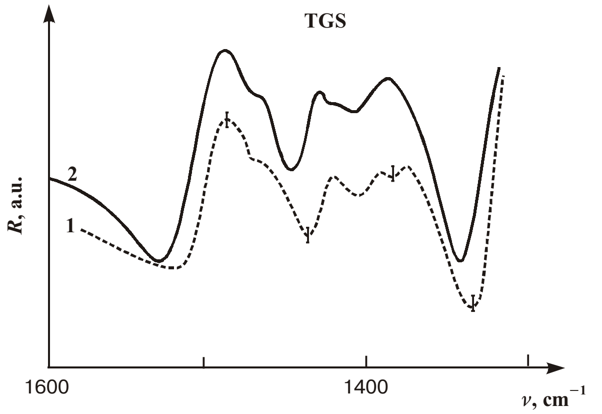

Fig.3. Reflectance spectra of TGS single crystal under the MW field action at *f* = 51 GHz (1) and without MW field (2).

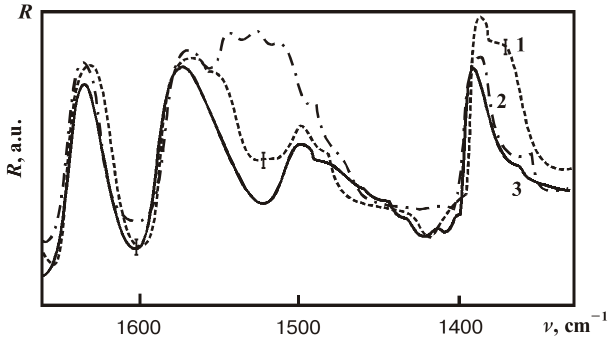

Fig.4. The changes in reflection spectra of β-Ala single crystal under the MW field action at *f* = 46.57 GHz (1) and *f* = 46.59 GHz (2); (3) – spectra without MW action.

amino acid crystals was registered in the experiment very clearly (Figs 2–4) and was always repeated. It should be noted that despite small EHF power density (10 mW/cm^2), the number of EHF quanta is great enough. So, with 10 mW/cm^2 incident power density, 10^{20} quanta falls every 1 s onto the surface of 1 cm^2. By the way all this EHF radiation is the coherent one.

The dependence of $\Delta R/R$ on power density (P) of EHF radiation is presented in Fig.5. For β-Ala vibration band at 1520 cm^{-1}, frequency (f) of applied EHF irradiation is $f = 46.50$ GHz, and for α-Gly at 1552 cm^{-1}, frequency of applied EHF irradiation is $f = 46.91$ GHz. Here the curves of $\sim P^2$ and $\sim P^4$ dependences of the effect are presented for comparison.

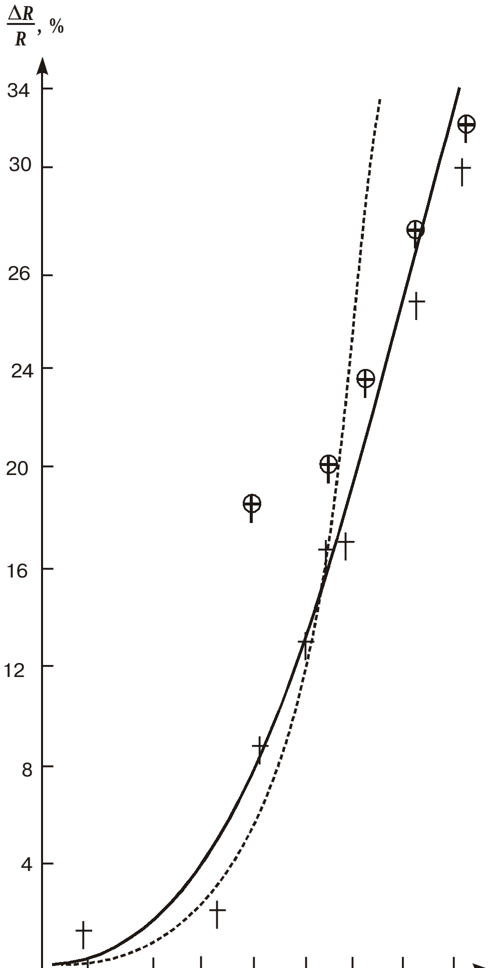

Fig.5. The dependence of $\Delta R/R$ on power P of MW field: Crosses-experiment for vibration mode at ν = 1520 cm^{-1} β-Ala crystal under the application of MW radiation at f = 46.59 GHz. Circles – the same for α-Gly, ν = 1552 cm^{-1}, f = 46.69 GHz. Solid line – theoretical curve y = const P^2, dash line – theoretical curve; y = const P^4. The size of crosses equals to the errors of $\Delta R/R$ and P measurements.

4. Polarization indicatrices of IR reflectance

Reflection coefficient R is determined by reflection index n ($n = \sqrt{\varepsilon}$) and any changes in R (say ΔR) can be attributed to some changes ($\Delta\varepsilon_{ij}$) in components of dielectric permeability tensor ε_{ij} as compared with their initial value ε_{ij}^0. Some additional experiment was done to prove that the value of ΔR observed in the experiment during the MW action on the crystal is connected with $\Delta\varepsilon_{ij}$. We have measured the polarization indicatrices of reflected light of the α-Gly and TGS crystals. Both these crystals have the glycine ion as a structural unit. The crystals of α-Gly and TGS belongs to the $C^2{}_{2h}$, while β-Ala – to $D^{15}{}_{2h}$ space group. The total element symmetry for all these crystals is C_2. Theoretical analysis of the intensity of reflected light for crystals of $C_{2h}{}^2$ group symmetry (α-Gly and TGS) was made for the case of normal light incidence on the XOZ surface of the crystal, which was cut perpendicular to the second order axis (Y-surface). Coordinate system was chosen in such a manner that the second order axis coincided with OY direction, and crystallographic axis OX_1 coincided with OX direction (the so-called «set up 1» [7]), and in this case OX⊥OY⊥OZ. The crystal was placed in such manner that OX axis was set to be parallel to the input slit of the spectrometer (Fig.6). In this case the wave vector of the incident wave K_0, the wave vector of the reflectance wave K_1 and the wave vector of the transmittance wave K_2 were considered to be

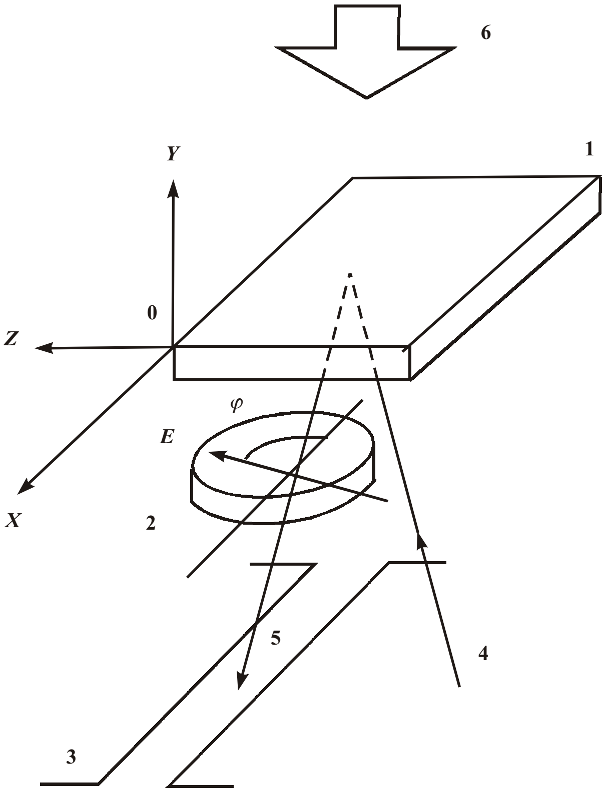

Fig.6. Geometry of the experiment in polarization indicatrix measurements: 1 – sample, 2 – polarizator, 3 – input spectrometer split, 4 – incident IR radiation, 5 – reflected IR radiation, 6 – MW radiation.

parallel. In this geometry of the experiment, the expression for the intensity of the reflected light $I_R(\varphi)$ for crystals of monoclinic singony was obtained in [7]. The φ angle determines the reflected light polarization in the XOZ plane relating to OX axes. As far as OX axis of the crystal was parallel to the input slit of the spectrometer, the φ angle equals to the angle between vector E of reflected IR radiation set by polarizer and the input slit of the spectrometer (Fig. 6). In this case, the incident IR radiation was naturally polarized. Dependence of the intensity of reflected light on angle – $I_R(\varphi)$, which we named polarization indicatrix, can be written in the form:

$$I_R(\varphi) = I_0 R_p F(\varphi) \tag{1}$$

Where, I_0 is an intensity of incident light, R_p is an amplitude coefficient, $F(\varphi)$ is a function for description of polarization structure of reflected light:

$$F(\varphi) = D_1 + D_2 \sin\varphi + D_3 \sin 2\varphi \tag{2}$$

Coefficients D_1, D_2, D_3 are determined by the following formulae:

$$\begin{gathered} D_1 = [1 + (\varepsilon_{xx} - \varepsilon_{zz})\, U]^2 + 4\,[\varepsilon_{xz}\, U]^2, \\ D_2 = -4Re\,[(\varepsilon_{xx} - \varepsilon_{zz})\, U], \\ D_3 = 4Re\,[\varepsilon_{xz}\, U]. \end{gathered} \tag{3}$$

The expression for U function is not presented here due to the fact that it has a rather complex form (see [8]). However, we should note that U is determined only by the components of the dielectric permeability tensor ε_{xx}, ε_{zz} and ε_{xz} [8].

This function, which in polar coordinates is described by equation (2), has the dumb-bell like form. The angle between its big axis and OX axis is determined by the formula:

$$\varphi = -\mathrm{arctg}(2D_3 / D_1) \tag{4}$$

The polarization indicatrices for deformation vibration of NH_3^+ group of the glycine ion in α-Gly and TGS crystals that are characterized by different intermolecular interaction are presented in Fig. 7. Both crystals have the same space group of C_{2h}^2 symmetry, that is why the formula (1) for $I_R(\varphi)$ function is valid for both crystals. As it is seen from Fig.7, both indicatrices have a dumb-bell like form and were rotated on φ angle relating to OX axis because for this space symmetry group $\varepsilon_{xz} \neq 0$.

The changes of the indicatrix form under the action of EHF radiation are presented in Fig. 7. It is seen that for α-Gly and TGS these changes are different. This result says that EHF radiation influence the components of dielectric permeability tensor ε_{ij} unlikely. Indeed, according to (2), the indicatrix form is determined by the D_1, D_2 and D_3 coefficients, which are the functions of the components of ε_{ij}. We know that the orientation of the glycine ion and the character of intermolecular interaction in these crystals are different, so we can suppose that there are differences in ε_{ij} and consequently in the indicatrix form under EHF action. It is that we have got in the experiment.

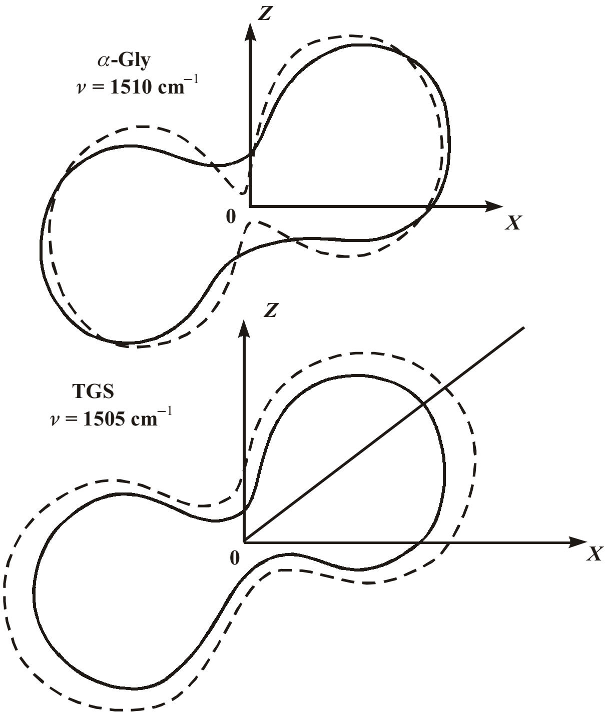

Fig.7. Polarization indicatrices of deformation vibration of NH_3^+ for α-Gly (ν = 1510 cm^{-1}) and for TGS (ν = 1505 cm^{-1}) under the action of MW radiation at f = 46.69 GHz.

The results of measuring intensity of IR reflectance from α-Gly and TGS after EHF radiation switching on and switching off at polarization angle φ_{min} set in the reflectance minimum by polarizer are presented in Fig. 8.

Spectrometer was set in the certain spectral position, which is equal to maximum signal of IR reflectance (1505 cm^{-1} for TGS and 1510 cm^{-1} for α-Gly) and during 3 minutes the signal of reflectance was recorded. A height of stroke in Fig. 8 means changes of the background signal for this period of time. Then we moved recorded tape and again for 3 minutes the signal of reflectance was recorded in the form of the next strokes. So, the packet from 10 strokes shows the changes of reflectance signal, which was registered by detector for 30 minutes. So, this packet of 10 strokes was recorded for certain spectral IR bands after MW field switching off (top curve in Fig. 8) and switching on it (bottom curve in Fig. 8). It was seen that irradiation of the crystal by MW field did not cause visible "memory" effect and average value of R and $R + \Delta R$ was not dependent on time. As it is seen in Fig. 8, the values of ΔR are considerably larger than the value of noise and error of the experiment.

We could suppose that the observed changes R could be caused by thermal effect connected with heating of the crystal under its irradiation by the EHF field. However, the measurement of the temperature of the crystal under the experimental conditions with the thermocouple showed that at the application of the EHF field, the temperature of the crystal increased by not more than 1° C. Tempera-

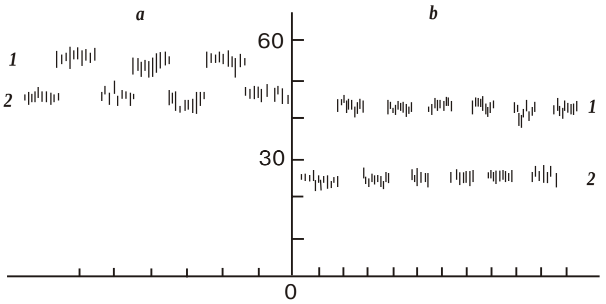

Fig.8. Changes of reflectance properties of the crystals under MW field switching on and switching off. Polarizer is set in the position $\varphi = \varphi_{\min}$; *a* – TGS (ν = 1505 cm^{-1}, f = 46.69 GHz); *b* – α-glycine (ν = 1510 cm^{-1}, f = 46.69 GHz). Power density – 5 mW/cm^2; *1* – switch off MW field, *2* – switch on MW field.

ture studies of vibration spectra of amino acid crystals, made in [9], did not detected changes in vibrational spectra when heating the crystal by 1° C in the 20–40° C temperature range.

Moreover, we carried out the model experiment to clear up the role of the temperature effect under influence of EHF field and IR field on the amino acid crystals. We used thermo-visor Agema-405 (Sweden) with the accuracy of temperature registration 0.1° C. The measurement registered that the temperature of the crystal under IR globar irradiation for 30 minutes and without EHF field action was equal to 34° C. Under simultaneous application of IR globar radiation and EHF field of 60 mW/cm^2 at the frequencies, which give the maximum changes of ΔR of the crystal for 30 minutes, the temperature increase was not more than 0.5–0.7° C.

5. Nonlinear permeability under double resonance conditions

The results presented in Fig. 5 gave us the basis to suppose that the observed changes of R have square dependence on EHF field power, at least that is valid in some range of powers. Within the framework of this supposition, we could consider the changes of dielectric permeability tensor under simultaneous action of EHF field (frequency Ω) and IR radiation (frequency ω) as some non-linear process with participation of two quanta of frequency Ω and one quanta of frequency ω [9].

$$\varepsilon_{ij}(\omega) = \varepsilon_{ij}^{0} + \Delta\varepsilon_{ij}(\omega) \qquad (5)$$

$$\Delta\varepsilon_{ij}(\omega) = 4\pi\chi_{ijkl}(\Omega, -\Omega, \omega)E_k(\Omega)E_l^{*}(\Omega) \qquad (6)$$

Here ε_{ij}^{0} is an initial (equilibrium) value of the dielectric permeability tensor in the absence of external action, χ_{ijkl}- nonlinear permeability tensor. Using Eqs (1)–(3) and ignoring the tensor character of the coefficients, in the resonance case we can write:

$$\frac{\Delta I_R}{I_R} \approx \frac{\Delta\varepsilon}{\varepsilon^0} \approx \frac{\chi_{res}^{(3)}\left|E(\Omega)\right|^2}{\varepsilon^0} \qquad (7)$$

where, ΔI_R is the change of the reflected light intensity under the action of the EHF field, $\chi_{res}^{(3)}$ is a characteristic value of nonlinear permeability tensor in the double resonance (EHF and IR) conditions. Using (10), we can estimate the constant $\chi_{res}^{(3)}$ of this nonlinear process, as ΔI_R and I are experimental determined value, the $E(\Omega)$ is determined by power density of applied EHF radiation and ε^0 is known from literature. The estimation for α-Gly showed that $\chi_{res}^{(3)} \approx \chi^{(3)}(\Omega_m, -\Omega_m, \omega_i) \sim 10$ cm/erg. This value is abnormally great as compared with similar values observed under non-resonance field condition [10]. This value is more than 1 order greater than the greatest value $\chi^{(3)} = 3 \cdot 10^{-1}$ cm/erg that is well known for nematic liquid crystals [11]. Such a great value of nonlinear constant in liquid crystals is connected with orientation rearrangements of the molecules in the structure of the crystal at transition into metaphase. We could suppose that in the double resonance condition the glycine molecules transition, for example of deformation type, can occur.

Although the molecules of glycine are placed in the crystal lattice, their fragments could have some freedom degrees. For example, terminal groups COO^- and NH_3^+ can have several equilibrium positions relating to the main molecular backbone, which gives a reason for conformation transformations. Indeed, in α-Gly, one observed 9 different conformation states that correspond to different positions of NH_3^+ group [12]. Transition energies between some of these states lie in the MW region. It should be noted that the frequency of EHF field is 3 orders less than the characteristic frequencies of intramolecular vibrations. In this case we can consider the displacement or movement of atoms under intramolecular vibrations as movement of atoms under applying some certain external force with certain frequency. Besides, EHF field is coherent and in a correlated manner influences the macro region of the crystal. This means that conformation transformation of the molecules under the application of the external field could take place simultaneously and could be synchronized as in the "effect of domino". This needs essentially less energy than during transformation of single (isolated) molecules.

Thus, in the double resonance experimental conditions (on EHF and IR field) we have found drastic non-linearity, which leads to essential changes in the dielectric permeability tensor of amino acid crystals.

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