Generation of intense monocycle THz pulse and THz nonlinear spectroscopy of amino-acid micro crystals

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Abstract: -

We succeeded the generation of intense monocycle terahertz (THz) pulse with maximum electric field above 200 kV/cm using tilted pulse front excitation beam by $LiNbO_3$. We optimize this generation process via $\chi^{(2)}$ cascaded processes causing optical pulse compression. We experimentally demonstrated THz transmission spectroscopy of amino-acid micro-crystals using intense monocycle THz pulse and observed spectral changes of intermolecular vibration modes above the critical incident electric field amplitude. These large amplitude THz motions are explained with coherent transition process between quantum energy levels in an anharmonic potential.

1. Introduction:-

Recent developments of intense terahertz (THz) pulse generation technique give us the opportunities to discuss the unique regime of nonlinear oscillators in condensed matters [1]. In particular, it has been reported that intense THz field (several kV/cm) to semiconductors strongly modulates and controls the optical properties. Large amplitude motions of ions or molecules driven by optical pulse would also show peculiar wave packet motions and attract many researchers in the view point of conformational transition [2]. There are several demonstrations of large amplitude coherent phonon bringing in softening, additionally; vibrational modes of the biological macromolecules such as proteins are governed by hydrogen bonded network. These large amplitude motions play a key role in structural transformation of macromolecules, which decisively influences the chemical reaction and biological function. However, significant nonlinearity of vibrations is less apparent compared to the electron system. Large potential barriers and smaller spatial distribution of wave function requires above hundreds kV/cm for nonlinearity appearance.

Recently intense THz wave generation technique has been demonstrated using $LiNbO_3$ crystal [3]. $LiNbO_3$ is also a good candidate for the THz emitter crystal for optical rectification process because of high $\chi^{(2)}$ value, but strong

dispersion permits non-collinear phase matching condition in $LiNbO_3$. The pulse front tilting of the ultrashort pulse allows the phase matching condition in the direction of THz wave propagation even for broadband pulse excitation. The output power of THz wave is large enough to observe the THz nonlinear responses. In this paper, we experimentally perform more optimized generation and succeeded THz pulse generation with maximum electric field amplitude above 200 kV/cm. Using this light source we performed the nonlinear transmission spectroscopy of amino-acid microcrystalline powder pellet, which is well suited for the investigation of large amplitude vibrational modes.

2. Optimized THz pulse generation via $\chi^{(2)}$ cascaded process

Figure 1 shows the schematic of experimental setup for nonlinear transmission spectroscopy. This is based on conventional THz time-domain spectroscopy. We used optical pulse from amplified Ti:sapphire laser system (Clark-MXR Inc. Ltd CPA 1000, 1KHz, 580mW, 780nm, 150fs). Laser beam is split into two beams for THz wave generation and sampling. Grating and lens control the lateral dispersion of excitation pulse. We used a Mg doped (1.5%) $LiNbO_3$ as THz emitter.

Left graphs in figure 2 shows the temporal profile of emitted THz electric field from $LiNbO_3$ crystal. This profile is calibrated from electro-optic (EO) signal, Si plate attenuators, and phase mismatching in GaP detector. In this setup, emitter image is transferred on the surface of the EO crystal with half size and calibrated maximum electric field is 202kV/cm [4]. We also measured the profile of THz pulse at different input powers as shown in right graph, the super-linear behavior of output THz pulse is apparent when output electric field is about 10kV/cm. This is beyond optical rectification process, because output electric field should be proportional to input power. We interpret such kind of behavior using the following assumptions. When intense THz electric field generated by optical rectification lies in EO crystal, optical pulse frequency itself gets modulated by emitted THz electric field. On one particular occasion pulse compression of excitation can raises the conversion

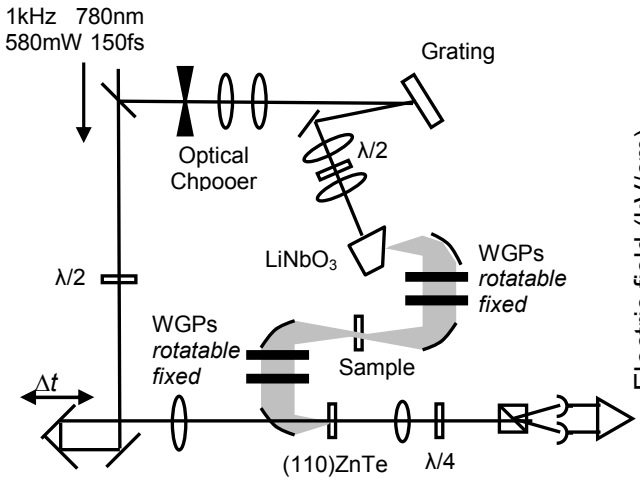

Fig. 1: Experimental setup of THz nonlinear transmission spectroscopy

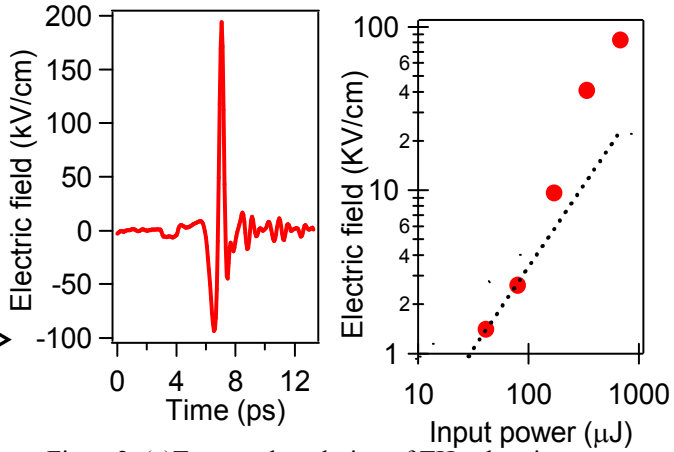

Figure2. (a)Temporal evolution of THz electric field from $LiNbO_3$ using tilted pulsefront ultrashort pulse. (b) Input power dependence of peak electric field of THz radiation

efficiency and coincidently cascade $\chi^{(2)}$ process can gives rise to the electric field with the frequency. So for the enhancement of this effect, subpicsecond-duration optical pulse, which seems rather unfavorable, is desirable. We have experimentally demonstrated broadband THz electric filed generation using 600fs-duration fiber laser beyond the excitation pulse limitation. [5]

3. THz Nonlinear spectroscopy:-

We experimentally demonstrated terahertz (THz) nonlinear transmission spectroscopy of the amino acids micro-crystals using this intense monocycle THz pulse light source. We measured L-arginine powder in polyethylene matrix pellet as the sample. A 30mg of arginine powder is mixed with polyethene powder in the ratio of 1:5 and pressed into a 1mm thick pellet. This pellet is uniform because orientation of microcrystal is random. Figure 3 shows transmission spectra of arginine pellet at 10 K, 100 K and 300 K using high-repetition THz spectroscopy system. One can see two asymmetric peaks around 1.0 and 1.6 THz. In particular the absorption band at 1 THz is sharp and asymmetric. Since these absorption bands are absent in the arginine solution, we assign them as intermolecular vibration modes in microcrystal. These absorption bands shift monotonously towards low frequency side with increasing temperature. Korter *et el.* investigated temperature dependence of THz frequency spectra of biotin systematically [6]. They made approximation of the simplest Morse potential for intermolecular vibration mode as shown in the inset of Fig. 3 and thermal distribution of the vibrational modes. We also applied similar model and succeed in reproducing the spectrum shape and its temperature dependence of the THz absorption spectrum of arginine. We measured the electric field amplitude dependence of arginine microcrystals. For systematic measurements of electric field amplitude dependence we use two wiregrid polarizer pairs as variable attenuators, as shown in Fig. 1. If we change input power of optical pump pulse for changing emitted THz electric field amplitude, profile of THz wave is strongly distorted due to cascaded $\chi^{(2)}$ process distorts [5]. We have checked carefully that the profile of THz electric field maintained up to 1/32 amplitude attenuation by changing the azimuthal-angle of one polarizer. We put the sample at the focus position and set WGP pairs before and after this point. Thus THz electric field is attenuated enough not to saturate the sensitivity with a 1mm-thick ZnTe EO detector and we can measure the profile of electric field in time domain by varying the time

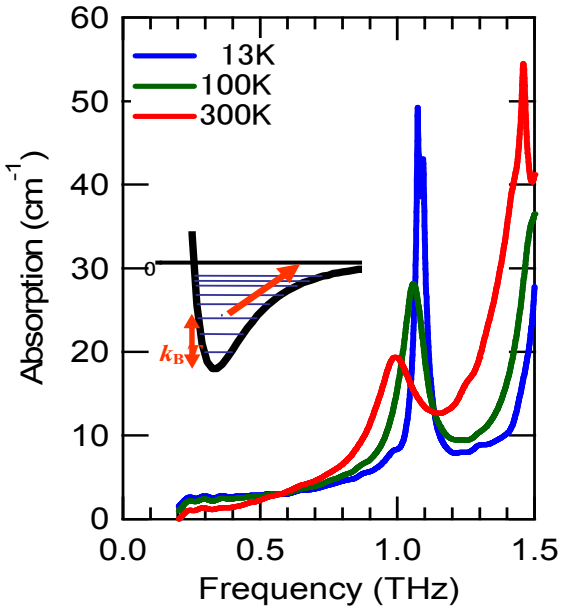

Fig. 3: (a) Linear absorption spectra of L-arginine pellet at 13 K, 100 K, and 300 K,

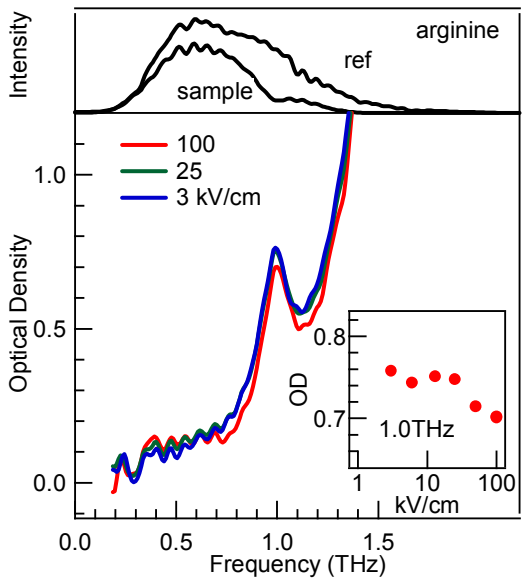

Fig. 4: (a) Power spectrum of the transmitted THz wave and the reference THz wave. (b) Optical density at different electric field amplitude at 300K

delay between the probe beam and the THz beam, with good signal-noise ratio even at different amplitudes of electric field.

In Fig. 4 upper panel shows the power spectra of the averaged incident THz electric field that passed without the sample and with the sample and below shows the optical density spectra using single cycle THz pulse at different amplitudes of the incident THz electric fields of 3, 25 and 100 kV/cm. With increasing incident electric field amplitude, absorption at higher frequency region is gradually reduced and alternatively, optical density below 0.7 THz is increases. Inset shows the electric field dependence of optical density at 1.0 THz. Saturation of absorption is apparent above 20 kV/cm in the electric field amplitude. We expect large amplitude intermolecular vibration mode in arganine microcrystal driven by intense THz pulse which brings in nonlinearity.

One may consider it as the heating of specific inter-molecular vibration modes by intense THz pulse the rearrangement of population of vibration mode in anharmonic potential which causes nonlinear response. However coherently driven vibration is far beyond thermally driven vibrations because the spectra in Fig. 4 are different from those in Fig. 3. This result shows that THz pulse can control THz motion of molecules coherently.

These results using intense THz pulse source shows THz multi-dimension spectroscopy is possible, which reveals complex mode coupling in macromolecules system and also show the potential of driving collective and functional molecular motion.

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