Two-Dimensional Terahertz Time-Domain Spectroscopy of Classical Oscillators

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***Abstract*— A theoretical framework for the description of two-dimensional nonlinear terahertz time-domain spectroscopy has been developed based on weakly nonlinear classical oscillators. Obtained 2D spectra show rich information of the system such as order and origin of nonlinearity, inhomogeneity, and nonlinear mode coupling as well as the dynamics.**

I. Introduction And Background

RECENT progresses in generation of intense terahertz (THz) pulses have enabled us to observe nonlinear THz response of various materials, and opened a new field of nonlinear TH spectroscopy. In this presentation, I summarize expected features of signals of second-order ($\chi^{(2)}$) and third-order ($\chi^{(3)}$) nonlinear two-dimensional THz time-domain spectroscopy (2D THz-TDS) using a simple phenomenological and classical model[1], which is applicable to systems of phonons, vibrations, and molecular orientational motions.

Time sequences of experiments assumed are shown in Fig. 1. It is assumed that the sample is excited collinearly by two or three pump pulses and the waveform of the nonlinear THz field emitted is observed. Time separations between pump THz pulses and probe are t_1 and t_2 for $\chi^{(2)}$ processes and t_1, t_2, and t_3 for $\chi^{(3)}$ processes. The theoretical model is based on a classical harmonic oscillator, to which a weak nonlinearity is introduced. Two types of nonlinearity, anharmonicity (AH) and nonlinear coupling (NC), are assumed. NC describes nonlinear dependence of polarization on the coordinate. In either case, three types of systems are considered, which are homogeneous single-mode systems (homo.), inhomogeneously broadened single-mode systems (inhomo.), and nonlinearly coupled two-mode systems (MC).

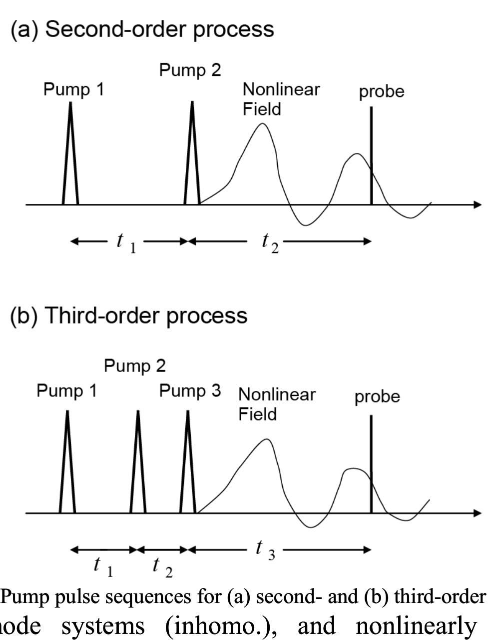


Fig. 1. Pump pulse sequences for (a) second- and (b) third-order processes.

II. Results

Analytical expressions have been obtained for the general situations described above using the classical model. Numerical calculations have been performed for delta-function incident THz pulses. For $\chi^{(2)}$ processes, time domain THz field $E(t_1, t_2)$ and the 2D Fourier transform $S(\omega_1, \omega_2)$ are calculated. For $\chi^{(3)}$ processes, time domain field $E(t_1, 0, t_3)$ and $E(0, t_2, t_3)$ and their 2D spectra $S(\omega_1, t_2=0, \omega_3)$ and $S(t_1=0, \omega_2, \omega_3)$ are calculated. Parameters in the calculations are damping rate, inhomogeneous broadening, and frequency ratio of the coupled modes.

Figure 2 shows a part of the catalog of the 2D spectra obtained. It is seen that the 2D spectra exhibit a wide variety of behaviors and rich information of the systems can be obtained from them. Two types of nonlinearity origin, AH and NC, result in completely different 2D spectra in each case.

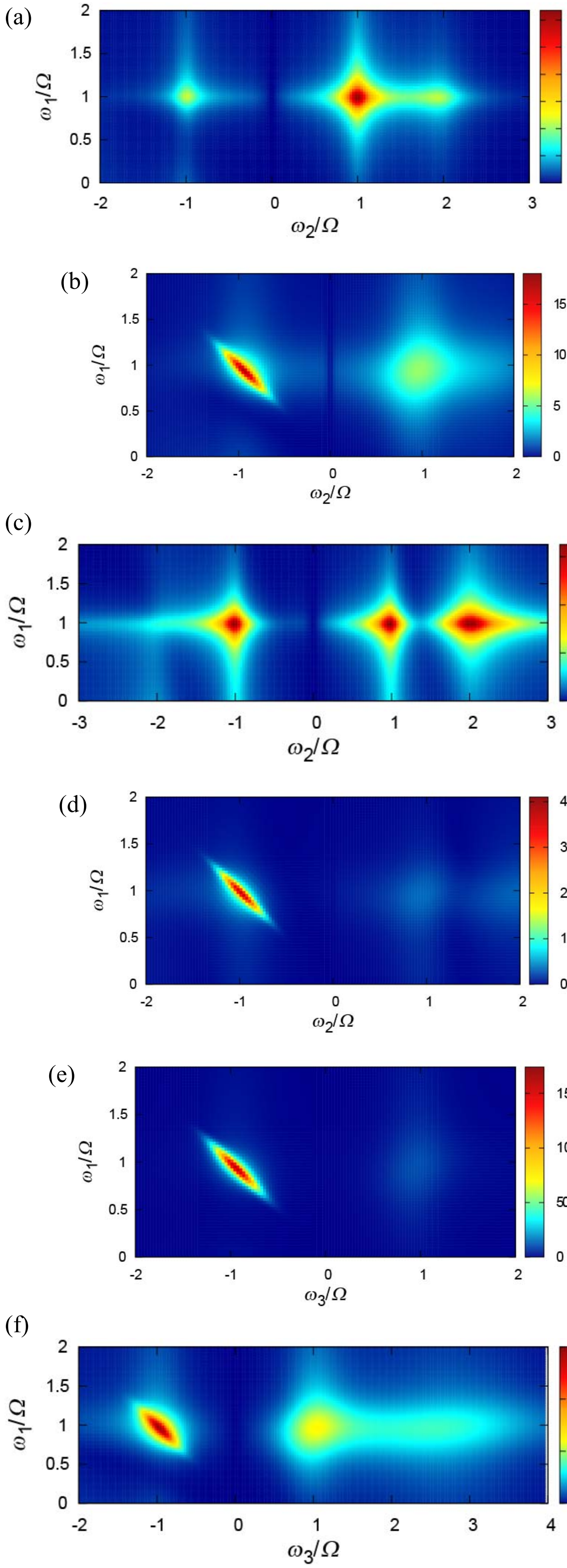
In inhomogeneous systems, rephasing effects are observed as a diagonal line in the second quadrant ($\omega_1+\omega_3=0$) in the 2D spectra for $\chi^{(2)}$ processes and $S(\omega_1, t_2=0, \omega_3)$ for $\chi^{(3)}$ processes (Fig. 2(b), (d), (e), and (f)). A weaker but clearly discernible diagonal line ($\omega_2+2\omega_3=0$) in the $S(t_1=0, \omega_2, \omega_3)$ spectrum for $\chi^{(3)}$ signal is due to rephasing in two-photon coherence (Fig. 2(g)). In either case, homogeneous and inhomogeneous broadenings can be separately obtained from the 2D spectrum, which is not possible in linear spectroscopies.

Relationship of the present 2D THz-TDS with conventional 2D spectroscopies is mentioned briefly. Spectra for $\chi^{(2)}$ processes correspond to the 2D $\chi^{(5)}$ Raman spectra, and $\chi^{(3)}$ $S(\omega_1, t_2=0, \omega_3)$ spectra to conventional 2D infrared spectra, while $\chi^{(3)}$ $S(t_1=0, \omega_2, \omega_3)$ spectra have not been discussed in conventional 2D spectroscopies because resonance peaks can be observed only when the pump pulses can impulsively excite two- or three-photon coherence.

In summary, a classical theoretical framework for 2D THz-TDS has been developed and analytical expressions of the signals have been obtained. A catalog of 2D spectra has been made by calculations based on the single and simple classical model. They clarify the features of 2D spectra depending on the origin and order of nonlinearity, inhomogeneity, and nonlinear mode coupling. The results show that rich information of the system can be obtained from 2D THz-TDS.

References

[1] T. Hattori, "Classical theory of two-dimensional time-domain terahertz spectroscopy," J. Chem. Phys. **133**, 204503 (2010).



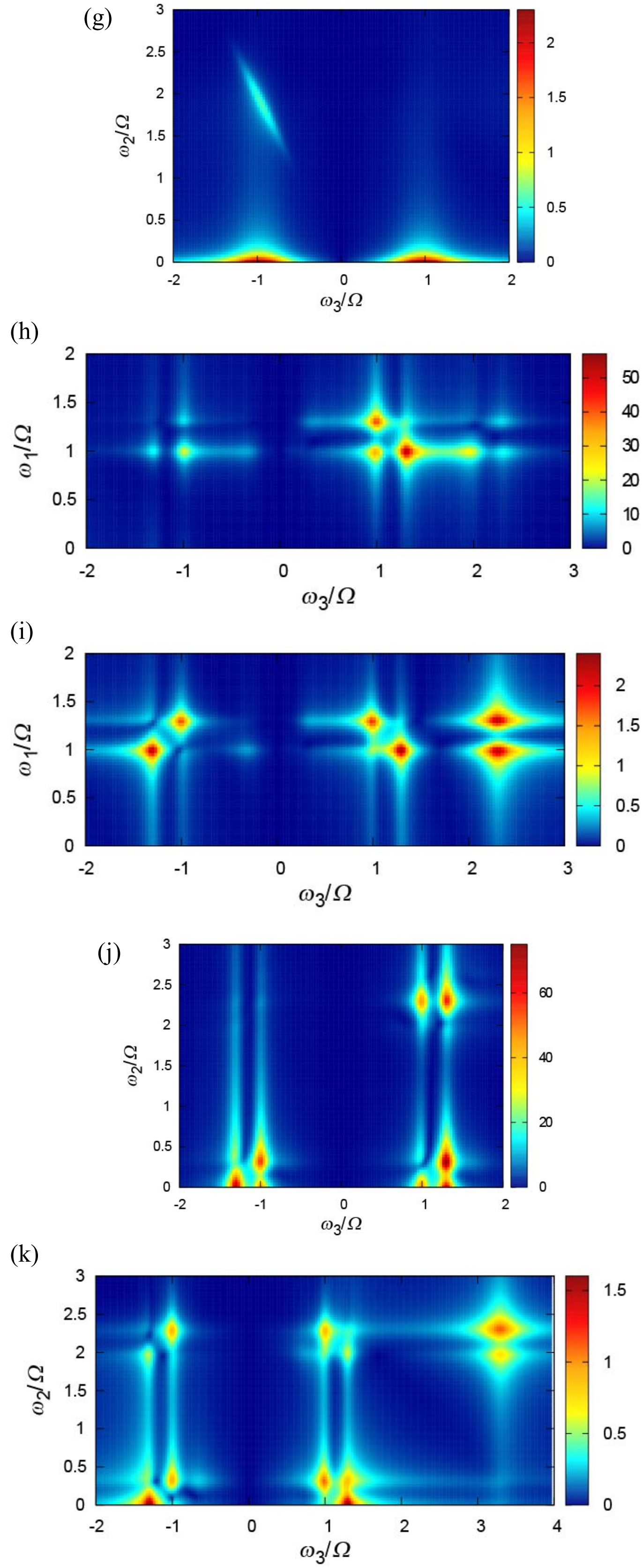


Fig.2. An incomplete catalog of 2D-THz-TDS spectra (amplitude). (a) $\chi^{(2)}$, AH, homo. (b) $\chi^{(2)}$, AH, inhomo. (c) $\chi^{(2)}$, NC, homo. (d) $\chi^{(2)}$, NC, inhomo. (e) $\chi^{(3)}$, AH, $S(\omega_1, t_2=0, \omega_3)$, inhomo. (f) $\chi^{(3)}$, NC, $S(\omega_1, t_2=0, \omega_3)$, inhomo. (g) $\chi^{(3)}$, NC, $S(t_1=0, \omega_2, \omega_3)$, inhomo. (h) $\chi^{(2)}$, AH, MC. (i) $\chi^{(2)}$, NC, MC. (j) $\chi^{(3)}$, AH, $S(t_1=0, \omega_2, \omega_3)$, MC. (k) $\chi^{(3)}$, NC, $S(t_1=0, \omega_2, \omega_3)$, MC.