(BL6B)

Far-Infrared Pump-Probe Measurement of an Organic Semiconductor β'-(BEDT-TTF)$_2$ICl$_2$ using Synchrotron Radiation Source

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Time-resolved spectroscopy (TRS) provides decisive information about fast-decay phenomena in solid state as well as in liquid or gaseous state. The investigations for the phenomena observable in infrared-visible regions have been achieved in stages by the development of nano-, pico-, and femto-second pulsed lasers. For far-infrared (FIR) region, however, it is still difficult to carry out TRS because (1) suitable crystals that can generate short FIR pulses with non-linear optical process are not available and (2) the response of ordinary FIR detectors is too slow to trace the changes faster than nanosecond order. Synchrotron radiation (SR) affords picosecond optical pulses ranging from FIR to x-ray, pulses which enable a picosecond FIR-TRS over unlimited measurable ranges when we can induce detectable changes in a sample by irradiation of the picosecond laser pulses synchronized with the SR.

We have constructed a FIR-TRS system at UVSOR BL6B beamline, the schematic diagram of which is shown in Fig. 1. We employed a Bruker IFS 113v for FIR spectrometer. The pumping laser pulses and the probing SR pulses are focused and overlapped on a sample. The relative timing of the laser pulses to the SR pulses, which is variable through a phase shifter, was measured by a single-photon counting technique. The time resolution in the current system is about 1 ns, predominantly determined by the duration of the SR.

We chose in this study an organic semiconductor β'-(BEDT-TTF)$_2$ICl$_2$ as a candidate for the pump-probe experiment. Figure 2 shows the $\boldsymbol{E}||\boldsymbol{b}$ polarized conductivity of β'-(BEDT-TTF)$_2$ICl$_2$ obtained by a Kramers-Krönig transformation of the reflectance that was measured on a mosaic consisting of three single crystals aligned so as to make a large (001) face: the absolute reflectivity was obtained by normalizing the sample spectrum with the spectrum measured again after evaporating gold on the sample surface. The line width of each absorption band becomes narrower and consequently sharper at low temperature, and we choose the spectrum at 6.7 K for the band assignment (see the inset of Fig. 2). In the β'-type crystal, BEDT-TTF molecules are stacked along the b-axis, forming strongly dimerized chains. In such cases intermolecular electron density oscillations appear only as a result of totally symmetric (A_g) vibrations of the dimer forming molecule through electron-molecular-vibration (EMV) coupling[1].

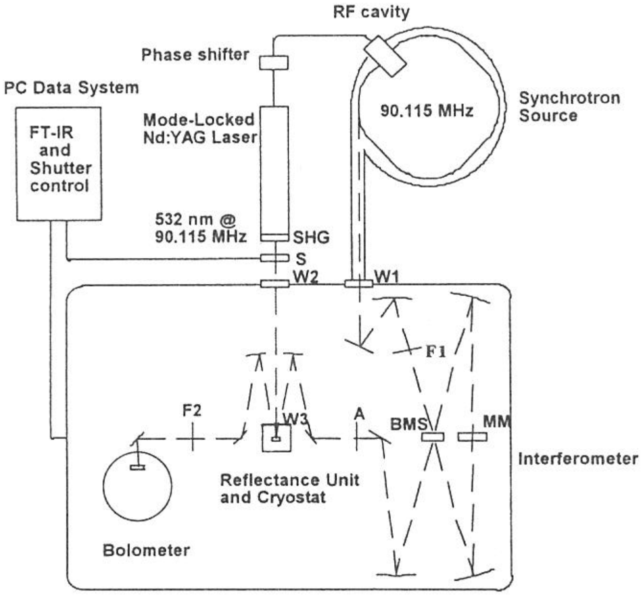

Fig. 1. Diagram of FIR-TRS system at UVSOR BL6B. All of optics are placed under the vacuum (~5 Torr) to exclude the influence of vapor water and carbon dioxide. W1: wedged silicon window; W2: quartz window; W3: white polyethylene-quartz hybrid window; F1, F2: black polyethylene filter; BMS: beam splitter; MM: moving mirror; A: aperture; S: solenoid shutter. Some mirrors are not drawn for simplicity.

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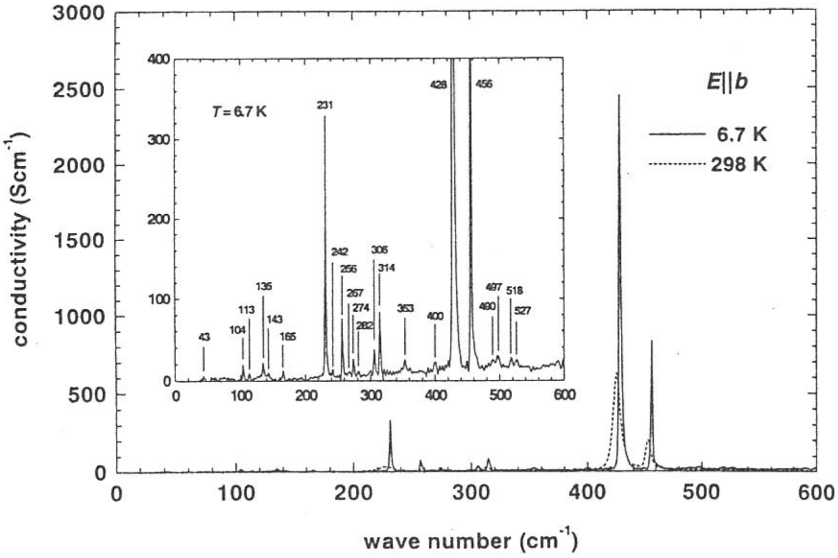

Fig. 2. Far-infrared conductivity of β'(BEDT-TTF)$_2$ICl$_2$ measured at 298K and 6.7 K with the ***E***||***b*** polarization.

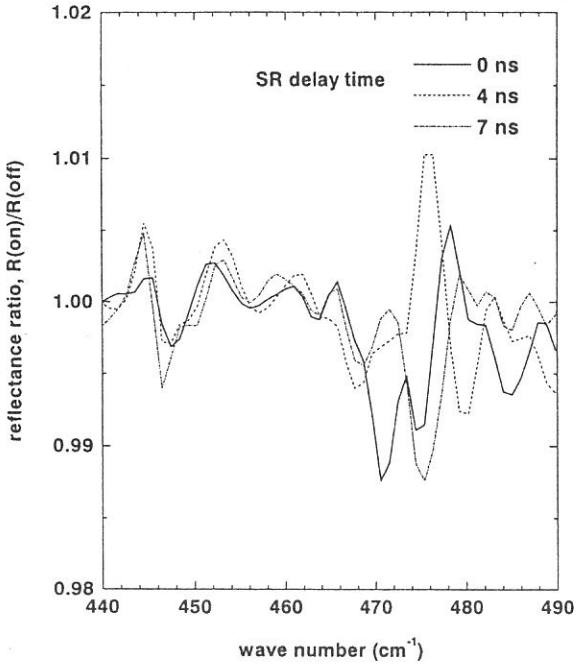

Fig. 3. Time-resolved difference spectra of β'(BEDT-TTF)$_2$ICl$_2$ measured at 8.3 K, with the probing SR delay time of 0 ns (solid), 4ns (dash), and 7ns (dash-dot).

More than twenty absorption bands are observed below 600 cm^{-1}, three of which are assigned to the normal modes of the counter anion ICl$_2^-$, at 231 cm^{-1} (angle distortion), 256 cm^{-1} (totally symmetric stretching), and 428 cm^{-1} (totally anti-symmetric stretching), respectively. We here concentrate on the A_g modes of BEDT-TTF^{+1}, some of which can strongly couple with the HOMO of BEDT-TTF$^+$ where an unpaired electron is located [2]. The band at 456 cm^{-1}, one of the A_g modes of BEDT-TTF molecule [2], demonstrates a very strong absorption intensity compared to the other bands, implying that this band is enhanced due to the EMV coupling. This band is expected to show some photo-induced features accordingly.

In Fig. 3 is shown the time-resolved difference spectra at 8.3 K at the probing SR delay time of 0, 4, and 7 ns, with the pumping laser power of 10 mW. The most prominent change was observed around 230 cm^{-1}, originating from the counter anion, but it did not depend on the delay time. However, we observed the delay-time dependent change around 475 cm^{-1}. Although the signal-to-noise ratio is not high, we believe that this time-dependent change is due to the far-infrared dynamic phenomenon relating to the A_g mode in this organic semiconductor.

We acknowledge D.B. Tanner for providing A.U. with the opportunity to carry out this experiment at IMS.

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