PHOTO-ACOUSTIC SPECTROSCOPY WITH INFRARED FEL

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Abstract

We are proposing a new photo acoustic spectroscopy (PAS) method with an infrared free electron laser (FEL). The FEL-PAS, using the infrared FEL as the light source, can be applied in various samples with high sensitivity, because the FEL has continuous tunability in the infrared wavelength range. We measured the photo-acoustic spectrum of a polyethylene terephtarate (PET) film using the FEL-PAS method and confirmed a high level of agreement as compared to the absorption spectrum by a Fourier transform infrared (FTIR) spectroscope. In addition, we constructed an imaging system of the FEL-PAS. The imaging system can make a map of the PAS signal with a high spatial resolution that is a diffraction limit of the IR-FEL.

INTRODUCTION

Free-electron laser (FEL) is a useful laser having two advantages: continuously coverage of a wide wavelength range from infrared (IR) to ultra violet (UV); very short pulse duration. The FEL in the IR wavelength region is expected to be applied in various researches because there are few lasers that can cover a wide range of wavelengths continuously. The 5 ~ 15-μm wavelength range, known as the molecular fingerprint region, is especially useful because it corresponds to the unique absorption features of various molecular structures. Thus, the IR-FEL of the wavelength range has been applied to research using excitation of specific molecular vibration [1].

We applied the IR-FEL to the photo acoustic process, known as photo acoustic spectroscopy (PAS). In ordinary PAS, a modulating laser beam at a wavelength that overlaps with a spectral feature of the target molecule excites the target molecule by absorption of the incident radiation. The excited molecule is deactivated via collisions during which the absorbed radiation energy is converted into periodic local heating at the modulation frequency. We then monitor the resulting acoustic waves with a microphone. In this study we used the IR-FEL as the modulating laser radiation. The IR-FEL irradiation excites the target molecule more efficiently than an ordinary laser pulse by matching the photon energy of the IR-FEL to the excitation energy. In addition the sensitive PAS method can be developed to make a PAS image by micro-spectroscopy. Thus, we measured the PA spectrum of a polymer sample for the preliminary experiment of the new PAS method and constructed the PAS imaging system in this paper.

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PHOTO ACOUSTIC SPECTROSCOPY WITH FREE ELECTRON LASER

The PAS is a sensitive method of measuring the absorbance of various samples [2]. In the PA process, the conversion of heat input from the incident laser radiation into acoustic waves is described in the following equation 1.

$$\nabla^2 p - \frac{1}{c^2}\frac{\delta^2 p}{\delta^2 t} = -\frac{(\gamma-1)}{c^2}\frac{\delta H}{\delta t} \tag{1}$$

where p is the pressure, H is the generated heat, and γ is the ratio of specific heat.

The heat will be modulate, if the laser radiation is modulated ($\delta p/\delta t$ is not 0). The magnitude of the photo acoustic signal is described in the following equation 2.

$$S = CPN\,\Delta t \sigma S_m \tag{2}$$

where C is a cell specific constant, P is the incident laser power, N is the number density of absorbing molecules, σ is absorption cross section of the transition that is being interrogated, Δt is the cycle period of the modulated radiation and S_m is the sensitivity of the microphone.

The signal magnitude (S) is proportional to the absorption cross section (σ) of the transition. Carbon dioxide (CO_2) lasers have long been used in the laboratory because of the ability to produce discrete wavelengths that are effectively absorbed by a variety of molecules. CO_2 lasers have approximately 120 discrete wavelengths between 9 μm and 11 μm with high output power. They have nearly coincident with one of the target spectral line, because the CO_2 lasers are not a continuous tunable laser. On the other hand, the IR-FEL is a continuous tunable laser and can be matched perfectly with the absorption line of the target molecule. Thus, the PAS with the IR-FEL is a more highly-sensitive method than ordinary PAS methods.

In this study we used MIR-FEL at the FEL user facility of Osaka University in Japan as the infrared FEL. The MIR-FEL is one of the four FEL machines (MIR-, NIR-, UVV-, FIR-FEL) at the facility and that covers the wavelength range of 5 ~ 18 μm [3, 4]. The wavelength range corresponds to the fingerprint region. Table 1 shows the specifications of the MIR-FEL.

Another advantage of the MIR-FEL is short pulse duration with high power. The MIR-FEL has a double micropulse structure of ~3-ps duration and a macropulse of ~20-μs duration. The short duration pulse is sensitive to the surface of the sample.

Table 1: Specifications of the MIR-FEL.

Wavelength	5 ~ 20 μm
Peak power	~3 MW
Average power	~20 mW
Pulse duration	~3 ps (micropulse) ~20 μs (macropulse)
Pulse repetition rate	22.3 MHz (micropulse) 10 Hz (macropulse)

Although many kinds of PAS methods using other spectroscopic lights such as the Fourier Transform Infrared (FTIR), the synchrotron infrared radiation are proposed in the past, the FEL-PAS proposed in this paper has other advantages.

(1) The FEL-PAS has a sensitivity of the sample surface comparing with the synchrotron radiation (SR) in the infrared wavelength region, because the pulse duration of the FEL is much shorter than one of the SR.

(2) In the FEL-PAS method the PAS spectrum can be measured in a short time, although in the FTIR-PAS the enough time is needed for storing the data. Thus, the FEL-PAS enables real-time diagnosis of the sample.

FEL-PAS SPECTRA OF POLYMER FILM

We measured a FEL-PAS spectrum of the polyethylene terephtarate (PET) film to show the feasibility of the FEL-PAS. The spectrum was detected by a developed PA cell with a microphone. The output signal from the microphone was recorded by a digital oscilloscope under the FEL irradiation. The PA cell has a transparent window (ZnSe) for introducing the IR-FEL to the sample. The irradiation power of the IR-FEL is ~5mW. The PA signals were detected from 9.2 to 12.2 μm by 0.1-μm steps. Figure 1 shows the normalized PA signals of the PET with the IR-FEL and the normalized absorption spectrum measured by the FTIR (Nicolet 750). The film thickness was about 100 μm. The FEL-PA signals almost correspond to the curve of the FTIR spectrum.

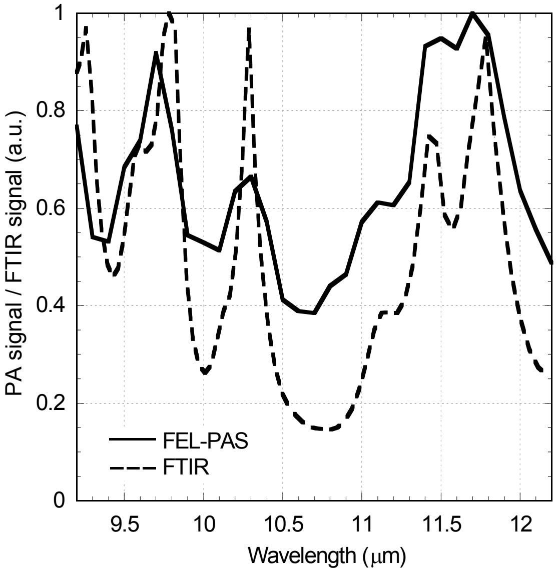

Figure 1: Spectra of PAS signal and FTIR signal from the PET film. The solid line and the dashed line are the PAS spectrum and the FTIR spectrum, respectively. Both are normalized with the maximum value.

FEL-PAS IMAGING SYSTEM

We constructed a new FEL-PAS imaging system with the IR-FEL. The new FEL-PAS imaging system is designed for making a PAS image with the infrared FEL. The FEL-PAS imaging system takes a full infrared PA spectrum at each point on the sample. A spatial resolution is limited to the diffraction limit of the IR-FEL, approximately equal to the wavelength. The spatial resolution of the system is one of the important parameters for making PA image. Samples are precisely scanned by a XY-stage for producing magnitude maps of the PA signal corresponding to the absorption coefficient of the wavelength.

The FEL-PAS imaging system consists of an optical microscope, a PA cell and a focusing mirror of the IR-FEL shown in Figure 2. The sample cell has a microphone to detect the PA signal and placed on the XY-stage. The focusing mirror, an off-axis parabolic mirror, is placed upon the PA cell. After observation of the measuring area using the optical microscope, we can irradiate the sample using the parabolic mirror. The sample can be moved with the raster scanning. Simultaneously, the PAS signal from the irradiated points can be detected by the microphone. The signal value can be reformed to the PAS image of the sample. Elimination of the mirror aberrations leads to better confinement of the beam and the spot size is almost equal to the diffraction limit of the IR-FEL.

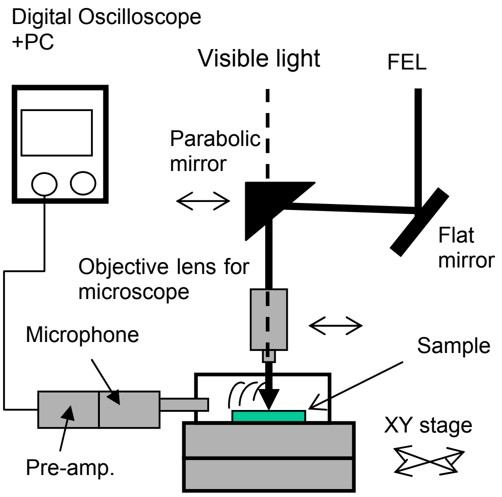

Figure 2: Schematic of optical path inside the FEL-PAS system. A parabolic mirror is removed and the objective lens is installed, when observed with microscope.

SUMMARY

We have proposed a new PA spectroscopy with the IR-FEL (FEL-PAS) in this paper. The FEL-PAS offers unique capabilities that allow analysis of very broad range of sample types with high sensitivity. In the case of a PET film, the signals from the FEL-PAS are good agreement with absorption spectra from the FTIR between 9.2 μm and 12.2 μm. In addition, the FEL-PAS imaging system is also described. The FEL-PAS imaging system is useful for microscopic analysis of a sample surface. The spatial resolution is more or less limited by the wavelength of the IR-FEL. Although the PET sample is stable in time, the FEL-PAS will be especially useful in time resolved analysis of the sample because of its high power during short pulse duration. Thus, the FEL-PAS is expected to play an important role in the field of bio-medical research and semiconductor research.

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