

DEVELOPMENT OF MID-INFRARED PHOTOACOUSTIC SPECTROSCOPY SYSTEM FOR SOLID SAMPLES AT KYOTO UNIVERSITY FREE ELECTRON LASER FACILITY

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Abstract

A Photoacoustic Spectroscopy (PAS) system for solid samples using a Mid-Infrared Free Electron Laser (MIR-FEL) with a high-resolution grating monochromator is under development at Kyoto University Free Electron Laser Facility. Our target is to achieve 0.2% resolution in 10 μm . We designed a PAS cell whose internal volume was small for reducing the loss of the acoustic energy and by using cups for the sample holder to exchange the samples easily. We also conducted experiments to check the sensitivity of the developed PAS system using powdered $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 as samples. The monochromator had the wavelength resolution of 0.015 μm (0.15% at 10- μm wavelength) in the experiments. As the result, we obtained quite high S/N ratio PAS signals with the FEL beam whose expected spectral width was 0.15% and whose power was reduced to one-eightieth by the monochromator.

INTRODUCTION

When material (whether solid, liquid or gas) is illuminated by light, acoustic wave is generated. This is called Photoacoustic effect. Especially with solid, this phenomenon is explained by RG Theory [1]. According to this theory, light is absorbed by the sample and its energy is converted to a thermal energy. The thermal energy causes the temperature distribution at the circumambient gas of the sample, and a pressure variation is arisen. Thus, the acoustic pressure wave is produced. Since the intensity of the acoustic pressure wave depends on the light absorption of the sample, we can directly obtain the absorption spectrum of the sample by measuring the intensity of pressure wave as the function of the illumination wavelength. This method is called Photoacoustic Spectroscopy (PAS).

When we use a pulsed infrared (IR) laser, PAS enables us IR absorption spectrum measurements of solid samples without pre-processing of samples such as the KBr pellet preparation and fine polish to very small thickness. As a feature of the PAS, its sensitivity and resolution depend on the intensity and spectral width of the IR light, respectively. Since a mid-infrared Free Electron Laser (MIR-FEL) is an intense, quasi-monochromatic and tunable laser in MIR region, the method of PAS with MIR-FEL (FEL-PAS) was proposed [2, 3]. In these previous works on the FEL-PAS, the spectral resolution was limited be

cause the used FEL beam had the spectral width of 1%. Therefore, they could not resolve sharp peaks in previous experiments. The spectral resolution can be significantly improved by inserting a monochromator on the optical path of the PAS system.

In order to realize this idea and targeting 0.02 μm resolution in 10 μm wavelength region, a high-resolution PAS system for solid samples using an MIR-FEL with a monochromator is under development at Kyoto University Free Electron Laser Facility (KU-FEL). We designed a new PAS cell and conducted demonstration experiments using this system to evaluate the system performance. In this paper, the outline of PAS system and demonstration experiments are briefly reported.

HIGH-RESOLUTION PAS SYSTEM

Figure 1 shows the outline of a high-resolution PAS system for solid samples. As the light source, we use KU-FEL [4]. A grating monochromator (DK240, CVI) whose grating was 75 groove/mm was put into the optical path. The monochromator had the wavelength resolution of 0.015 μm when the entrance and exit slit were adjusted to 0.3 mm. The FEL beam after passing through the monochromator was injected to a parabolic mirror and converted to the quasi-parallel beam. Then the FEL beam was split into two by a beam splitter. The transmitted light was monitored by a pyroelectric detector and the reflected light was focused on the sample within the PAS cell by the focusing mirror.

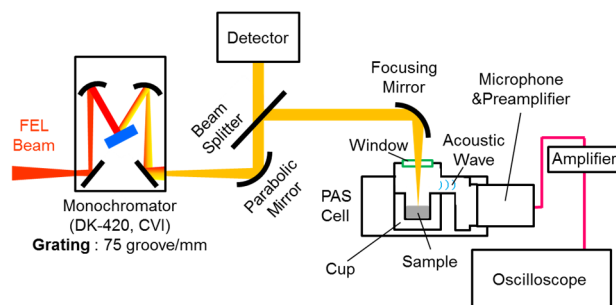


Figure 1: The outline of a high-resolution PAS system for solid samples using KU-FEL and monochromator.

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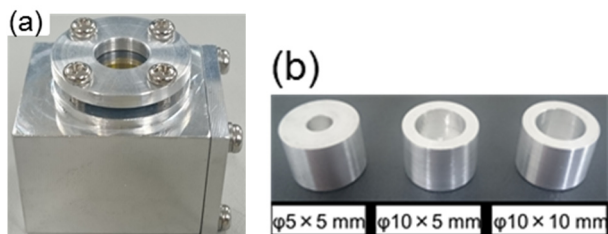


Figure 2: (a) The PAS cell made of aluminium and containing a ZnSe window. (b) Three cup-type sample holders which was detachable from the cell structure. Left one: $\phi 5 \times 5$ mm, Middle one: $\phi 10 \times 5$ mm, Right one: $\phi 10 \times 10$ mm.

The PAS cell was made of aluminium and it had an uncoated ZnSe window to transmit the FEL light. The internal volume of this cell was designed as small as possible (about 0.98 cm^3) to reduce the loss of the acoustic energy. The solid samples in the new PAS cell can be easily exchanged by using cup type sample holders which was detachable from the cell structure (Fig. 2 (b)). The acoustic wave was detected by the microphone (MI-1233, Ono Sokki), and converted into a voltage signal and amplified by a preamplifier (MI-3110, Ono Sokki), and sensor amplifier (SR-2200, Ono Sokki).

We conducted two demonstration experiments using standard samples to check the sensitivity of the developed PAS system. We measured the signal in wider wavelength region from 8.0 to 11.0 μm with 0.5 μm step in the first experiment, and in narrower region from 8.0 to 9.5 μm with 0.1 μm step in the second experiment, respectively.

DEMONSTRATION EXPERIMENTS

The experimental setup is shown in Fig. 3. The typical parameters of the FEL beam used in this experiment are shown in Table 1. The macro-pulse energy was reduced to one-eightieth after the monochromator, and the expected spectral width was 0.015 μm (0.15% at 10 μm). Powdered $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 were used as standard samples, because $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has the strong IR absorption peak at the range from 8.0 to 11.0 μm , whereas CaCO_3 does not have such peak [5].

The transmittance spectra of those samples measured by FT-IR are shown in Fig. 4. In addition, powdered carbon samples (called Carbon Black) was used in order to normalize the signal. The gain of sensor amplifier was set to +30 dB. The sampling rate and the number of data points of the oscilloscope used for recording the voltage waveform from the microphone were set to 500 kHz and 10^5 , respectively. At one measurement condition, we recorded the voltage signal waveform 100 times for each sample and took an average.

Macro-pulse duration	$\sim 2 \mu\text{s}$
Macro-pulse repetition rate	2 Hz
Macro-pulse energy (before the monochromator)	$\sim 24 \text{ mJ}$
Macro-pulse energy (after the monochromator)	$\sim 0.3 \text{ mJ}$
Expected spectral width	$\sim 0.015 \mu\text{m}$ at 10 μm

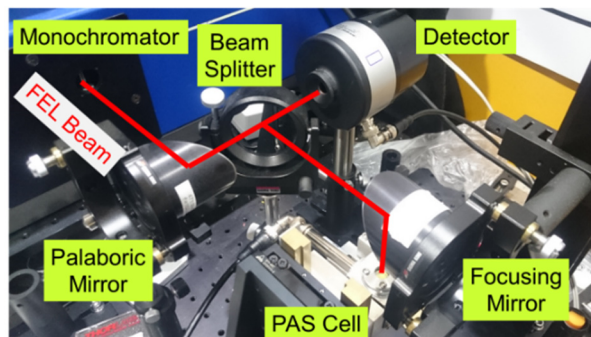


Figure 3: Key components of the experimental setup.

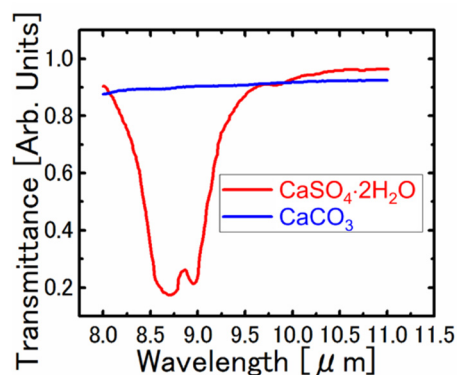


Figure 4: The IR transmittance spectra of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 [5].

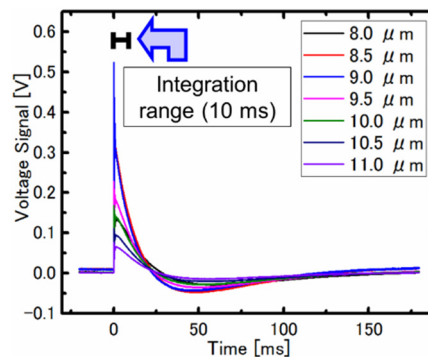


Figure 5: The voltage signal waveforms for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ from 8.0 to 11.0 μm with the interval of 0.5 μm .

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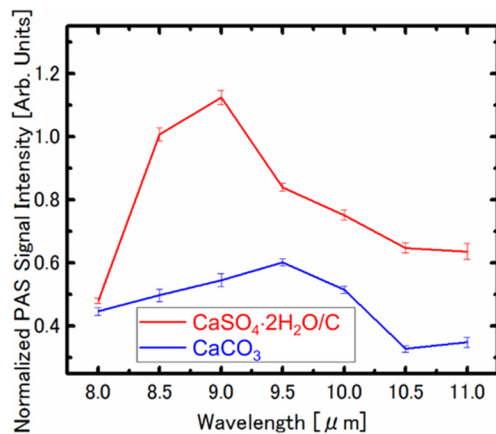


Figure 6: The wavelength dependence of the integrated voltage signal waveforms for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 . They are normalized by FEL intensity and Carbon Black. The specific peaks at 8.5 and 9.0 μm were observed in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The error bars represent the standard deviation of 100 samples.

Figure 5 shows the waveforms of the averaged voltage signal for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at different excitation wavelength. According to this graph, it was confirmed that a high S/N ratio voltage signal could be measured. The integrals of the voltage signal waveform in the time range from 0.06 to 10.06 ms (for 10 ms) were calculated and normalized by the FEL intensity measured by the reference detector for each sample. The normalized integrated values of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 were also normalized by that of Carbon Black. Figure 6 shows the wavelength dependence of the PAS signal from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 . As is shown in the figure, the specific peaks at 8.5 and 9.0 μm were observed in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This result is consistent with the reported IR transmittance spectrum (Fig. 4) [5]. Therefore, we successfully measured the PAS signals (the voltage signals) by using the developed system.

In Fig. 7, the frequency power spectra of the voltage signal waveforms for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is shown at the frequency range from 0 to 20000 Hz, because the frequency response range of the microphone is from 20 to 20000 Hz. In this graph, a strong peak is observed at around 4000 Hz, and small peak was observed at around 13000 Hz. These peaks are considered as the primary and tertiary order resonant frequency of PAS cell, respectively.

Next, PAS measurement of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ sample in the wavelength region from 8.0 to 9.5 μm with the interval of 0.1 μm . As same as the first experiment, we measured the voltage signal waveform (the PAS signal) 100 times, and take an average. The integral of the voltage signal waveform was calculated at the same range and normalized by the FEL intensity and the PAS signal of Carbon Black. The result is shown in Fig. 8 which is also consistent with the reported IR spectrum (Fig. 4) [5]. In this result, it was confirmed that the small dip at 8.8 μm , which is also visible in the transmittance spectrum shown in Fig. 4, can be recognized in the obtained PAS spectrum.

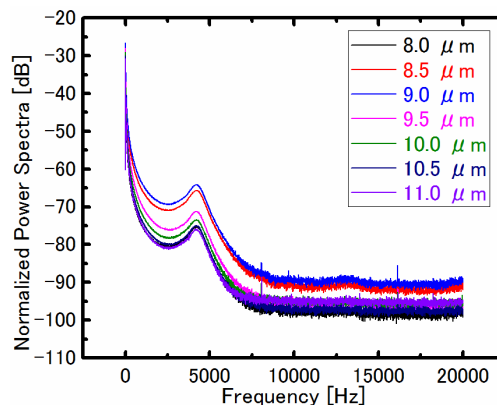


Figure 7: The frequency power spectra of the voltage signal waveforms for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. A strong peak was observed at around 4000 Hz, and small peak was observed at around 13000 Hz.

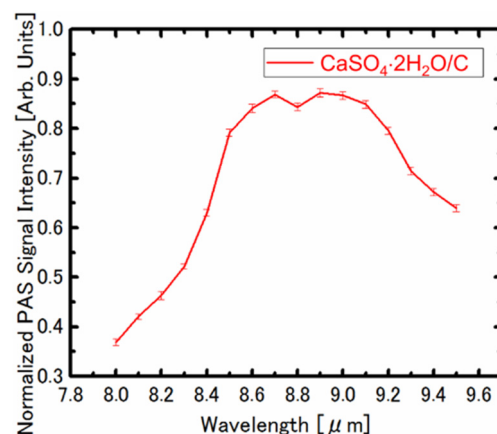


Figure 8: The wavelength dependence of the integrated voltage signal waveforms for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ from 8.0 to 9.5 μm by 0.1 μm step. They are normalized by FEL intensity and Carbon Black. The error bars represent the standard deviation of 100 samples.

In order to confirm whether the developed system has expected resolution (0.15%) or not, we should measure a reference sample which has narrower absorption peak to confirm the resolution of this system. In addition, the S/N ratio of PAS signal is quite high, so we will evaluate the minimum required number of samples for PAS measurement.

CONCLUSION

A high-resolution PAS system for solid samples is under development at Kyoto University Free Electron Laser Facility. We aim to achieve 0.2% resolution in 10 μm . A PAS cell which has a small internal volume with cup type sample holders to exchange the sample easily has been designed and fabricated. In order to evaluate the system performance, two demonstration experiments have been conducted. One was a PAS measurement of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 in wider wavelength region with a 0.5- μm

step. The other was a PAS measurement of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in a narrower wavelength region and with 0.1- μm step. As the result, the PAS signals with high S/N ratio and the reasonable wavelength dependences were observed for both $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 , even though the FEL beam power was reduced to one-eightieth by the monochromator which had the wavelength resolution of 0.15% at 10- μm wavelength.

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