

# 非平衡脱離・イオン化過程観測のための飛行時間型質量分析装置の開発

王健仲<sup>A</sup>、兼松泰男<sup>A</sup>、邨次敦<sup>B</sup>、松田冬樹<sup>C</sup>、松田若菜<sup>A</sup>、河井洋輔<sup>A</sup>、豊田岐聡<sup>A</sup>

大阪大学大学院理学研究科物理学専攻<sup>A</sup>、アトリエ モノトレム、吹田大阪<sup>B</sup>

京都大学物質-細胞統合システム拠点<sup>C</sup>

## Development of a New Femtosecond Laser Mass Spectrometer to Observe Non-equilibrium Desorption Process

J. Z. Wang<sup>A</sup>, Y. Kanematsu<sup>A</sup>, A. Muratsugu<sup>B</sup>, F. Matsuda<sup>C</sup>, Y. Kawai<sup>A</sup>, M. Toyoda<sup>A</sup>

*Department of Physics, Osaka University<sup>A</sup>, Atelier monotrem, Suita Osaka<sup>B</sup>*

*Institute for Integrated Cell-Material Sciences, Kyoto University<sup>C</sup>*

Ultrafast laser interaction with matter triggers various processes depending on the pulse duration and intensity. To investigate the initial process of the non-equilibrium laser desorption/ionization, we have developed a time-of-flight mass spectrometer with a high repetition rate ultrashort laser pulse as the desorption/ionization source. By employing the laser scanning sampling method, the ion counting analyzing method, rapid repeat sampling, and data accumulation, we were able to capture of weak ion signals under low laser pulse energy. We performed experiments while varying the laser power intensity in a range of  $10^{10}\sim 10^{11}$  W/cm<sup>2</sup> and observed the differences in the distribution of the emission ion velocity with different pulse energies preliminarily, and the faster velocity emission ions could be related to the electrostatic ablation process, which can provide extra acceleration effects to the ions.

### 1. Introduction

Femtosecond laser desorption/ionization has gained attention in the last decent as a relatively new ionization technique in mass spectrometry imaging [1]. For femtosecond lasers to achieve sample material transformation the intensity range is typically between  $10^{10}$  and  $10^{16}$  W/cm<sup>2</sup> [2]. Most femtosecond laser applications in mass spectrometry are used as multiphoton absorption ionization methods in a high electric field, and the pulse energy exceeds the sample ablation threshold with an intensity of  $10^{13}\sim 10^{14}$  W/cm<sup>2</sup> [3]. In the ablation regime, the initial non-equilibrium process within 100 fs where an intense femtosecond laser pulse interacts with matter is electrostatic ablation: the target surface electrons absorb the pulse energy and escape, creating a strong electrostatic field that pulls

out a small number of ions from the target and cause ion acceleration. After 100 fs, the interaction process proceeds to a transitional state: electron-phonon and electron-ion collisions occur, and excess laser energy is transferred to the lattice, which causes a large number of ions to be desorbed [4]. In order to minimize damage to the samples, it is necessary to use laser with the lowest possible intensity that below the ablation threshold. Since most current research employees the high-intensity femtosecond laser to enhance the probability of ionization and gain of emission ions, research on the low-intensity femtosecond laser ionization process has not yet been advanced. Therefore, we have developed a time-of-flight (TOF) mass spectrometer using the ultrashort laser pulse as the desorption/ionization source to

observe the non-equilibrium process with extremely low-intensity laser irradiation. We expect to provide new insights into the femtosecond laser desorption/ionization

process and pave the way for low-destructive sampling and high-spatial resolution detection in mass spectrometry imaging.

## 2. System development

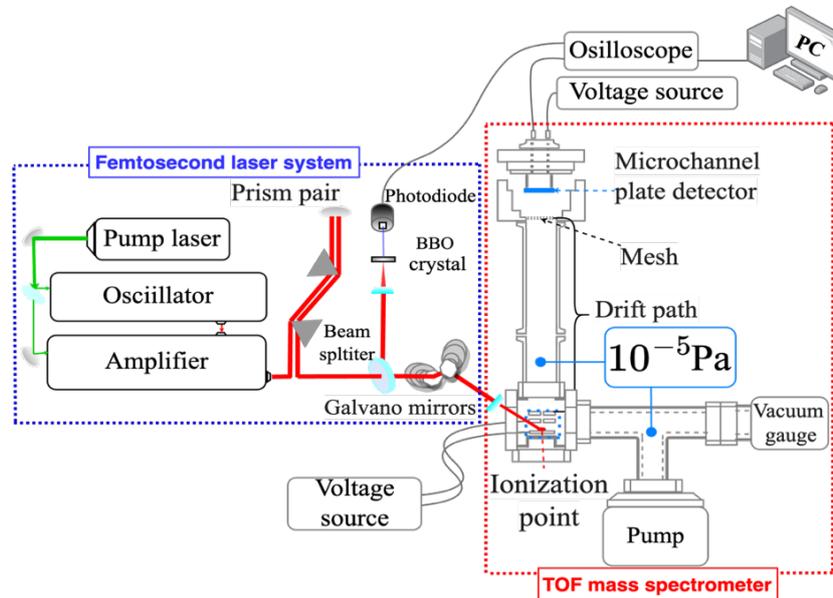


Fig.1. Schematic diagram of developed TOF-MS and femtosecond laser system

The system configuration diagram is shown in Fig. 1, which is composed of a femtosecond laser system and a TOF mass spectrometer. For the femtosecond laser system, the Ti: sapphire laser pulses (wavelength 800 nm, 200 kHz repetition rate, 160 fs duration) are introduced into a prism pair for group velocity dispersion compensation, which can be used to control the laser pulse duration. The shaped pulse train is divided into two parts. One pulse train which passes the focus lens is focused on the nonlinear-optical crystal. The laser pulse intensity peak is detected by the photodiode and transferred to the oscilloscope as the start trigger of the ion TOF spectrum acquisition. The other pulse train will be introduced to the TOF mass spectrometer for sample ionization, which can scan over the entire sample plate by controlling the Galvano mirrors. The ions generated by the laser pulse depart from the sample plate, pass through the aperture-

shaped electrode for acceleration, a drift path for mass separation, and are eventually detected by the microchannel plate detector. Signals from the microchannel plate detector are acquired by the digital oscilloscope and transferred to a PC as waveform data.

## 3. Experiment method

**Sampling method:** we employed a digital oscilloscope (Agilent InfiniVison DSO7104) with 1 ns time resolution. We combined an optical chopper and a shutter to control the irradiation time of the femtosecond pulse train on the sample. Additionally, the laser pulses are evenly distributed on the sample surface by rotating the Galvano mirror. Unlike repeated sampling of a single sample point, scanning sampling reduces damage to the sample.

**Signal analysis:** After the PC received the voltage waveform data from the oscilloscope, we employed the ion counting method setting

an appropriate voltage threshold: When the signal peak exceeds the threshold, the signal is counted, and the signal TOF spectrum is determined by the start trigger obtained from the photodiode. With high-frequency sampling substantial signal data can be quickly analyzed and statistically processed.

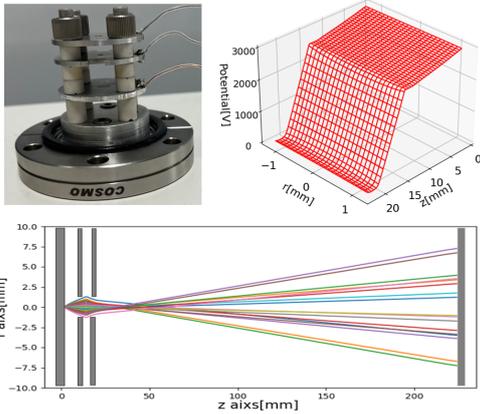


Fig.2. Electrode structure and potential distribution (top), ion trajectory simulation in the system (bottom)

Ion trajectory simulation: To analyze the ion signal under different laser parameters, we simulated the potential distribution and ion trajectory depending on the acceleration electrode arrangement and structure, calculated by the surface charge method [5], as shown in Fig. 2. By simulating the ion trajectory and calculating its time of flight, the distribution of emitted ion's initial velocity can be estimated from the obtained

signal of the TOF spectrum.

#### 4. Experimental results and discussion

We use the deposit CsI as the sample and performed the laser pulse energy dependence experiments. CsI was deposited under  $2 \times 10^{-5}$  Pa, with deposit velocity 0.2-0.4 nm/s for 1000 nm by a physical vapor deposition method using the deposit machine (Knenix KVD-670). We evaluated a  $10 \times 10 \mu\text{m}$  region on the sample surface using the atomic force microscope. The surface height difference was within 1000 nm as shown in Fig. 3, and the TOF difference caused by the height difference is less than 1 ns.

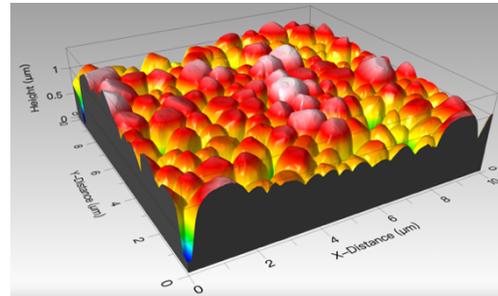


Fig.3. AFM topograph of deposit CsI

We introduced  $6 \times 10^5$  laser pulses to the mass spectrometer for ionization of the deposit CsI, and the laser pulses were evenly distributed over a linear region of 100  $\mu\text{m}$  in length on the sample surface during the Galvano mirrors scanning.  $\text{Cs}^+$  ions were detected for different pulse energies of

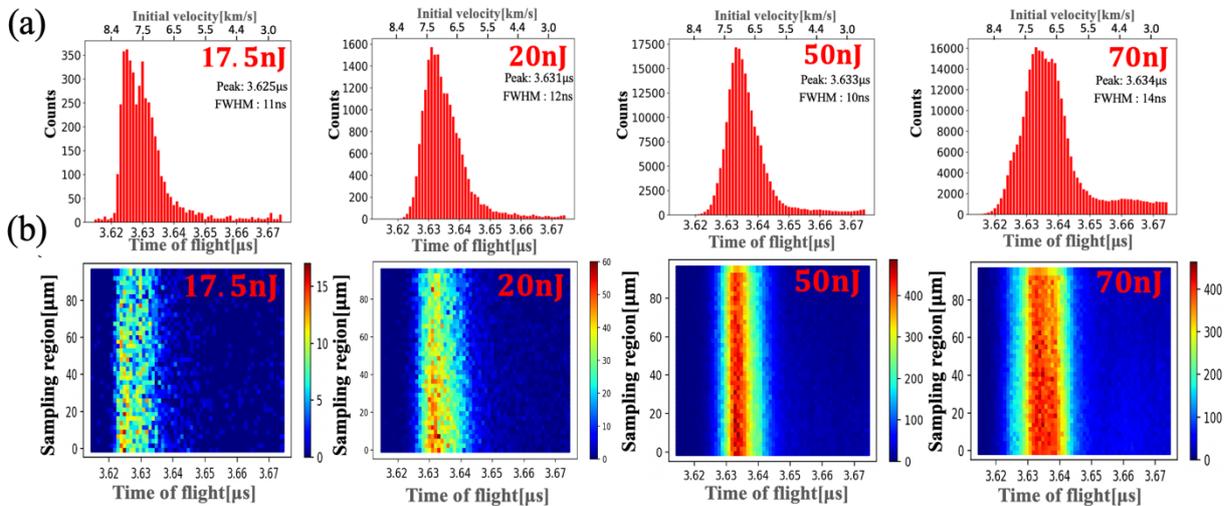


Fig.4. TOF spectrum of  $\text{Cs}^+$  with different pulse energies (a) counts of  $\text{Cs}^+$  (b) laser scanning line region with  $\text{Cs}^+$  emission distribution.

17.5/20/50/70 nJ. Fig. 3 (a) shows the TOF spectra of Cs<sup>+</sup> corresponding to each energy. In Fig. 4 (b), the intensity of the TOF spectrum for the sampling linear region scanned by the laser is mapped. The (a) top x-axis is the initial velocity of Cs<sup>+</sup> calculated from the ion trajectory simulation to fit to the observed TOF spectrum. When the pulse energy is 17.5 nJ, the peak of the Cs is located at 3.625 μs with an initial velocity of 8.2 km/s. When the pulse energy is increased, the peak finally changes to 3.634 μs with an initial velocity of 7.2 km/s, indicating that the initial velocity increases by about 1000 m/s compared to the 17.5 nJ case. Comparing the 50 nJ and 70 nJ TOF spectrum signal shape, the 70 nJ case has a noticeable tail-shaped signal in the 3.65~3.67 μs TOF region. Furthermore, as can be seen in Fig. 4 (b), the Cs<sup>+</sup> TOF spectrum distribution has a good correspondence to sampling linear region.

To investigate the additional pulse energy transfer to the lattice in the emission of a large number of ions, we analyzed the number of the emitted Cs<sup>+</sup> corresponding to each individual laser pulse, as shown in Fig. 5. The

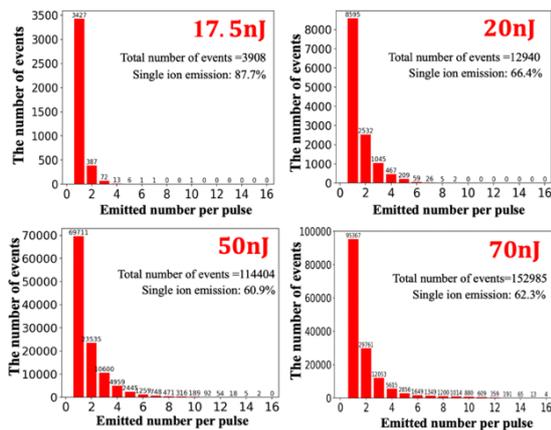


Fig. 5. Cs<sup>+</sup> emitted number per laser pulse and occurrences number of the event with different pulse energies

x-axis represents the number of ions emitted within a single pulse, and the y-axis represents the occurrence number of the event. We can observe that the ion emission is predominantly in the form of single ion

emission with 87.7%, when using low pulse energy. As the energy gradually increases, the total number of ion emission increases, but the proportion of single-ion emission decreases. This suggests that the laser pulse energy is related to the interaction phenomena with the material. Under low energy pulse conditions, electrostatic ablation is the dominant process resulting in a small amount of ion emitted with faster initial velocity. In high-energy pulses, additional energy is transferred to the lattice, resulting in a large amount of ion emission and a relatively slower initial velocity. This is consistent with the correlation between femtosecond laser pulse energy and the size of ion emission described previously.

## 5. Conclusion

We developed a time-of-flight (TOF) mass spectrometer using the ultrashort laser pulse as a desorption/ionization source and achieved signal detection with laser intensity 17.5 nJ ( $2.8 \times 10^{10}$  W/cm<sup>2</sup>). By analyzing the number of emitted ions corresponding to each individual femtosecond pulse, and estimating the initial velocity based on ion trajectory simulation, we have preliminarily observed the phenomenon of electrostatic ablation by reducing the pulse energy. In the future, we will confirm electrostatic ablation with more samples and apply it to mass spectrometry imaging of biological samples.

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