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Pixel Imaging Mass Spectrometry with fast silicon detectors

A.Nomerotski^{a*}, S.Adigun-Boaye^b, M.Brouard^b, E.Campbell^b, A.Clark^c,
J.Crooks^c, J.J.John^a, A.J.Johnsen^b, C.Slater^b, R.Turchetta^c, C.Vallance^b, E.Wilman^b,
W.H.Yuen^b

^a *Department of Physics, Oxford University, Oxford, OX1 3RH, United Kingdom*

^b *Department of Chemistry, Oxford University, Oxford, OX1 3QZ, United Kingdom*

^c *Rutherford Appleton Laboratory, Didcot, OX11 0QX United Kingdom*

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Abstract

We report on ‘proof of concept’ experiments in Pixel Imaging Mass Spectrometry (PimMS) using an ultra-fast frame-transfer CCD camera. The fast framing CCD camera is capable of recording and storing on-chip up to 16 separate images corresponding to different mass fragments, with a time resolution of 10 ns. In addition to the standard mass spectrum, the technique allows recording of the spatial or velocity distributions of the ions at their point of formation within the instrument. Our results unambiguously demonstrate the feasibility of technique, but it is also clear that the CCD camera restricts the total number of masses that may be imaged to an unacceptably small number. We describe possible CMOS pixel detectors capable of considerably improving the achieved performance in order to meet the demanding requirements for complete recording of mass spectra of complex organic molecules. © 2001 Elsevier Science. All rights reserved

Keywords: mass spectroscopy; ion imaging; CCD ; CMOS; pixel sensor; INMAPS; PimMS;

1. Introduction

Time Of Flight Mass Spectrometry (TOF-MS) is an invaluable and widely used tool in analytical chemistry.

It is based on the principle that when molecular fragment ions are accelerated through an electric potential, since all ions receive the same kinetic energy from the field, heavier fragments reach a lower velocity than lighter fragments. Ions can therefore be separated according to their mass by recording their arrival times at a detector

* Corresponding author. Tel.: +44 1865 273400; fax: +44 1865 273417; e-mail: A.Nomerotski@physics.ox.ac.uk

following passage through a flight tube. In a commercial mass spectrometer, the range of ion flight times is of the order of 100 – 200 μ s. Traditionally, TOF-MS instruments simply measure ion current as a function of arrival time. The technique of velocity/spatial-map ion imaging has the potential to take mass spectrometry beyond this single dimension by associating positional information on the ions within each mass peak. This method is widely used in physical chemistry for analysis of simple molecules [1].

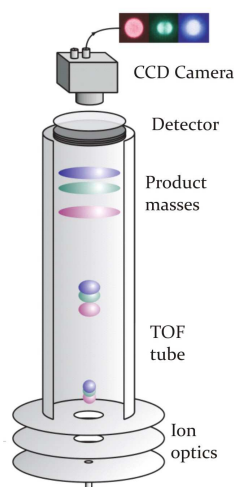


Fig.1 Schematic of an ion imaging apparatus

A schematic view of an ion imaging apparatus is shown in Fig.1. For photofragment velocity imaging, the parent molecule is prepared in a molecular beam, which passes through a small orifice in the repeller plate of the ion optics assembly. The beam is intercepted by a pair of laser pulses, the first of which fragments the molecule, and the second of which ionizes the resulting fragments. The nascent ions have speed and angular distributions characteristic of the specific fragmentation process in which they were formed. A carefully tuned electrostatic field maintained within the ion optics assembly accelerates the ions along a flight tube towards a position sensitive detector consisting of a pair of microchannel plates (MCPs) coupled to a phosphor screen. All ions of a given mass with a given velocity component in the image plane are mapped onto the same point on the detector, regardless of the position at which they were formed. The image on the phosphor is captured by a camera and transferred to a PC for processing and analysis. To record an image for a single mass, either the MCPs or the camera are gated to the

flight time of the ion of interest. Until very recently it has not been possible to image more than one mass per laser pump-probe cycle due to slow image transfer times.

In velocity imaging mode, the ion velocities are mapped regardless of their initial positions. By adjusting the ion lens potentials, the instrument is also capable of operating in spatial mapping mode, in which the ion positions are mapped independently of their velocities. The two types of mapping are illustrated in Fig. 2.

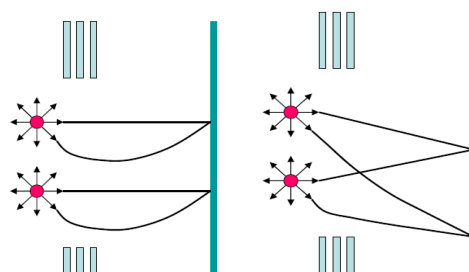


Fig.2 Left: spatial mapping; right: velocity mapping.

2. Pixel Imaging Mass Spectroscopy (PIImMS)

With recent progress in silicon technologies, several novel types of fast, position sensitive detectors are becoming available. These overcome the single mass peak limitation and allow imaging of multiple masses in a single acquisition. This approach, named by us Pixel Imaging Mass Spectrometry (PIImMS), gives access to new information and provides scope for a range of new and exciting techniques. The PIImMS mass resolution is largely determined by the speed of the imaging sensor and the decay lifetime of the phosphor. Below we describe two different technologies appropriate for this application: fast framing CCD cameras and CMOS cameras.

2.1. Fast Framing CCD camera

The technology currently in use in our experiments is the Zenith fast framing CCD camera from Dalsa [2], which allows recording of 16 sequential images at 64x64 resolution with 100x100 μ m² pixels. The maximum frame rate, 100 MHz, allows for adjustable image exposure in the range from 10 ns to 1.2 ms in 5 ns increments. The camera is based on the principle of local charge storage in a CCD register at imaging pixel level [3]. After all 16 register cells are full, the recorded information must be read out before image acquisition

can continue. The main limitation of the DALSA camera is the small number of frames, aggravated by the fact that in our application approximately half of the frames must be used to integrate charge between mass peaks and, hence, are not useful. The future development of this technology may allow a somewhat larger number of frames but will always be limited by the pixel area. A typical single frame shot taken with the DALSA camera is shown in the left image of Fig.3. Each bright pixel on the image corresponds to detection of a single ion. The image on the right shows the signals from two ion hits recorded under similar experimental conditions with a standard CCD camera (Photonic Science) with pixel size $12 \times 12 \mu\text{m}^2$. The white square overlaid on the image corresponds to the DALSA pixel dimensions demonstrating that the cluster size in the experiment was smaller than the DALSA pixel area. It should be noted that the pixel size is not the ultimate figure of merit for this application. Normally the full phosphor screen image is projected onto the sensor using lenses and it is the number of pixels in the sensor that is most important for the spatial resolution of the apparatus.

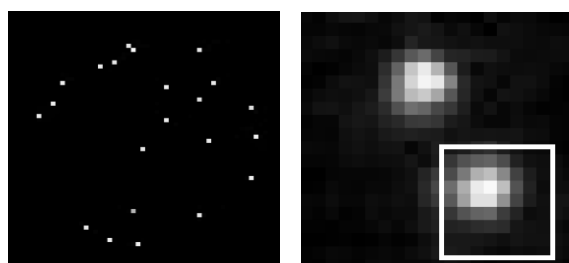


Fig. 3. Left: A typical single frame shot taken with the DALSA camera. Right: two clusters recorded with a slow CCD camera with pixels $12 \times 12 \mu\text{m}^2$. White square is $100 \times 100 \mu\text{m}^2$.

The first PImMS proof-of-concept experiments were successfully performed in 2008 using the Dalsa Zenith camera. Images were recorded of several photofragments from the 193 nm photolysis of dimethyldisulphide, a small organic molecule [4]. The ion spatial distributions from these experiments are presented in Fig.4., which shows all four detected fragments separated by empty frames. The typical separation in arrival times between consecutive fragments in this experiment was about $1 \mu\text{s}$. The spatial distributions recorded at the detector were used to reconstruct associated speed and angular distributions separately for each TOF mass peak. In addition to providing information on the fragmentation dynamics,

the method may potentially also be used to enhance mass fingerprinting, and to deconvolute multiple contributions to a single mass peak.

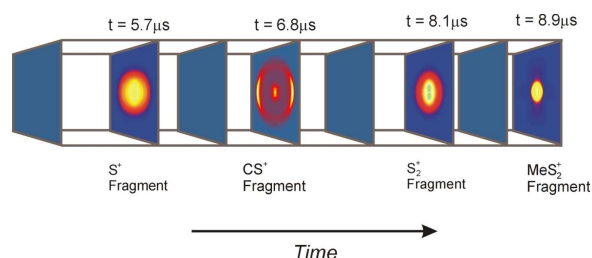


Fig. 4. Velocity maps of fragment ions from the photolysis of dimethyldisulfide resolved for each mass peak.

Two other promising applications of the PImMS technique lie in surface imaging and coincidence imaging. Spatial imaging allows the measurement of separate images of a surface for each mass peak. While this has been possible for some time using a technique known as MALDI imaging [5], PImMS would allow images to be obtained in a single laser shot, rather than by rastering a focused laser across the surface as in existing approaches. Coincidence imaging reveals correlations between ions of different masses, allowing them to be assigned unambiguously to the same fragmentation event [6]. Experiments to demonstrate both of these applications are currently in progress.

2.2. CMOS based sensors

Technology in CMOS-based image sensing is a rapidly growing area. CMOS approach allows enhanced in-pixel signal processing and more flexible readout architectures when compared with CCD sensors. For example, a considerable data reduction can be achieved by incorporating 'time stamping' into each pixel, in which time information is recorded only if a pixel registers a light pulse. At low event intensities the time stamp approach provides the same information as full frame readout, while generating much less data. In addition, the intensity requirement can be relaxed if each pixel can record several time stamps. The experimental parameters for PImMS are a good match for time stamping.

In a CMOS pixel sensor (MAPS or monolithic active pixel sensor) the light is detected in a thin epitaxial layer near the surface, producing charge which is normally collected by diffusion to an $n+$ node. Though the signal is small, good signal-to-noise is achieved due to the

small capacitance of the node. Traditionally, the pixel has limited functionality, as only NMOS type transistors are allowed [7]. The INMAPS process developed at the Rutherford Appleton Laboratory, UK, shields the PMOS type transistors with a deep p^+ implant, resulting in better charge collection efficiency and enabling the full CMOS capability [8]. The INMAPS process has already been used in a number of projects in particle physics and for other applications [9].

The INMAPS process described above is currently being used to produce a new specialized sensor for PImMS. At present we are formulating the sensor specifications and performing ion imaging measurements with an existing sensor, VANILLA [10], made using the CMOS technology. Fig.5 shows a single cluster (left) and a single image (right) recorded with the VANILLA sensor. The VANILLA pixel size is $25 \times 25 \mu\text{m}^2$. VANILLA does not have sufficient time resolution to resolve individual mass peaks, but these measurements show that CMOS-based sensors have sufficient sensitivity for our application.

The new PImMS sensor is likely to have specifications similar to the following:

- 512×512 pixels
- Pixel size $70 \times 70 \mu\text{m}^2$
- 12 bit counter, time resolution < 100 nsec
- Four storage elements per pixel
- Power $30 \mu\text{W}/\text{pixel}$
- 20 acquisition cycles/sec

It is worth mentioning that the 12-bit counter will effectively correspond to 4096 time slices. This will dramatically increase the potential number of mass peaks that may be recorded compared to the fast framing CCD camera currently in use, and will allow to apply the sensor to studies of complex organic molecules.

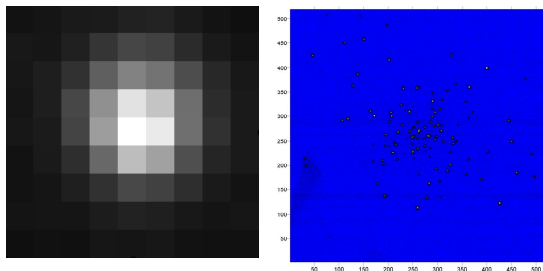


Fig. 5. Single cluster (left) and single image (right) recorded with the VANILLA sensor.

3. Summary

We have described a novel technique, Pixel Imaging Mass Spectrometry, which combines features of TOF-MS and ion imaging, and have presented proof-of-concept results obtained using an off-the-shelf fast framing CCD camera. A specialized CMOS sensor for PImMS is in development at the Rutherford Appleton Laboratory, with the first prototype expected in 2010.

Acknowledgements

The support of the EPSRC through Grant EP/G00224X/1, of the STFC through PNPAS award, of the RC-UK through MI-3 programme (GR/S85733/01) and a 'proof of concept' grant from ISIS Innovation Ltd. are gratefully acknowledged. This work is protected in patents PCT/GB2008/004085 and PCT/GB2004/02014.

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