A Next-Generation Ultrafast Detector for Imaging Mass Spectrometry: the Pixel Imaging Mass Spectrometry (PImMS) Sensor

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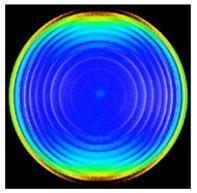
1. The Need for a Fast Multi-Mass Detector

- In time-of-flight (TOF) experiments, the ion flight time, *t*, is proportional to the mass-to-charge ratio, *m*/*q*:

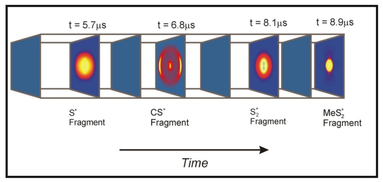
$$t = k\sqrt{\frac{m}{q}}$$

- Imaging Mass Spectrometry (IMS) experiments, such as velocity-map imaging (VMI) and surface imaging, record an image for each ion mass.[1]



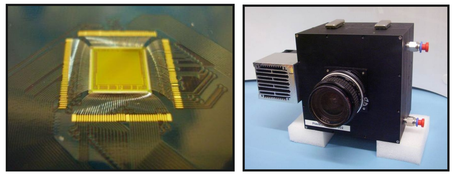
Left: a VMI image of laser dissociation of O^+ from fragmentation from O_2. The rings correspond to products formed in different quantum states.
Right: CS_2 dissociates into four fragments, each with a characteristic spatial distribution and arrival time.

- As the achievable time-of-flight resolution determines mass resolution, IMS studies of large molecules with extensive fragmentation require an ultrafast multi-mass imaging detector.
- In the conventional approach, ions of different masses are imaged in separate experiments; this is both time consuming and potentially susceptible to experimental drift.



2. The Pixel Imaging Mass Spectrometry Sensor (PImMS)

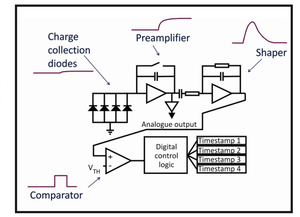
- The PImMS sensors are event-triggered image sensors that record ion events as a series of timestamps within each pixel. The sensors have been developed in collaboration with the CMOS Sensor Design Group at the Rutherford Appleton Laboratory (RAL), and was designed to address the limitations of other sensors used in IMS.
- We have developed and characterised the prototype first-generation sensor, PImMS1. This consists of a 72 x 72 array of 70 µm pixels. The sensor is designed to detect light pulses from a conventional MCP/Phosphor detector.
- The achievable time resolution of the sensor is 12.5 ns, corresponding to an equivalent frame rate of 80 million frames per second. The time codes are stored as 12 bit integers, allowing data to be recorded for 51.2 µs each acquisition cycle.
- The next generation sensor, PImMS2, has been completed and deployed in experiments. The resolution has been improved to 324 x 324 pixels, while maintaining the time-resolution of 12.5 ns.



Left: a close-up view of the PImMS1 sensor, measuring 7.2 mm x 7.2 mm.
Right: the complete camera assembly, with housing, cooling fan and lens.

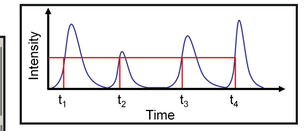
3. Pixel Architecture

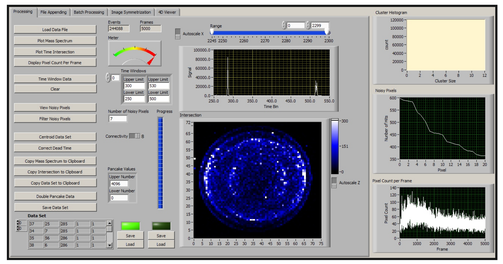
- A global clock (≤ 40 MHz) controls all pixels. Within each pixel, four photodiodes are connected to shaping and amplification circuits followed by a comparator. When a signal reaches a predefined threshold, the corresponding timecode value is written to one of four 12-bit memory elements contained within the pixel.
- The four memory registers in each pixel allow four independent time codes to be recorded before the data set is read from the camera. Consequently, signals arising from ions with different arrival times can be detected by the same pixel within a single time-of-flight cycle. An analogue signal is also acquired, which can be used for camera focussing and debugging.
- The pixel architecture is identical for the PImMS1 and PImMS2 sensors, maintaining the time resolution of 12.5 ns for an increased array size of pixels.



Above: Schematic of the PImMS pixel architecture.

Below: the thresholding sequence in the digital logic control. The shaped charge is compared to a user specified threshold, with time stamps recorded in one of four memory registers each time a rising edge is detected.

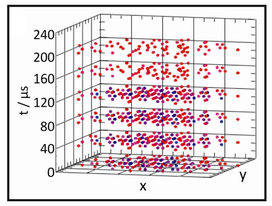


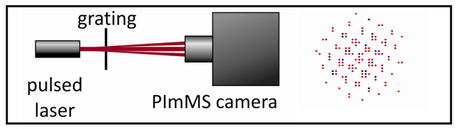


Left: Software written for acquisition and analysis of data from the PImMS sensor. Data is saved in x,y,t format and can be post-processed with relative ease and speed, with operations such as noise filtering, centroiding, mass spectra extraction and image processing and visualisation. Specific masses can be selected by applying an appropriate time-window to the data.

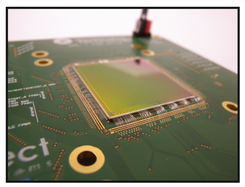
4. Preliminary Experiments

- To test the operation of the camera, a 405 nm laser was passed through a diffraction grating, creating a diffraction pattern. The laser created 25 ns pulses every 40 µs.
- By triggering the camera at certain delay relative to a laser pulse, an intensity profile over several shots could be built up. The resulting distribution showed excellent agreement with the expected result.

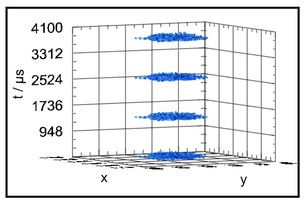




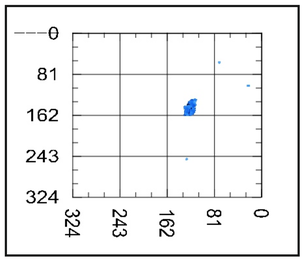
Left: The laser setup with the diffraction pattern from the grating shown on the right of the camera.
Above: The resulting data recorded by the PImMS sensor - data is accumulated over 3000 experimental cycles. The colour represents the intensity of a particular time value recorded by a single pixel.

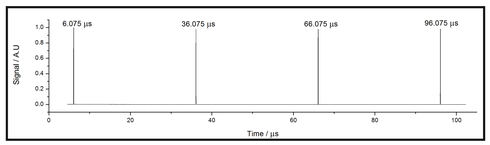


- Similar experiments were used to characterise the PImMS2 sensor behaviour, with 25 ns laser pulses, every 30 µs. The resulting data was found to agree perfectly with the expected values.



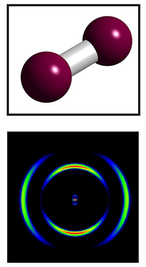
Above: The PImMS2 sensor, measuring 25 mm x 25 m, mounted on a sensor board, with the bond wires visible.
Right: The resulting data recorded by the PImMS sensor - data is accumulated over 200 experimental cycles. The colour represents the intensity of a particular time value recorded by a single pixel.
Below: The time data recorded by the PImMS2 sensor, matching the expected timings of the laser pulses.

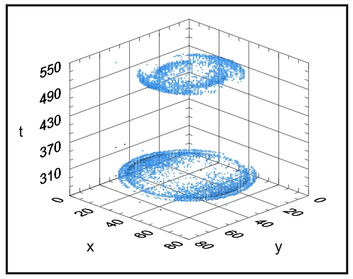


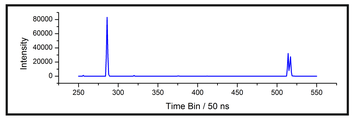


5. Application to Chemical Sytems

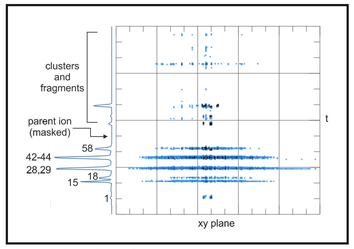
- The images show the velocity distributions of fragment ions formed at the intersection of a molecular beam with a laser beam. The images may be analysed to gain insight into the molecular fragmentation dynamics.
- Photolysis of molecular bromine yields both Br^+ ions and electrons, which can be detected consecutively during the same experimental cycle. The electrons are detected first and thus appear at an earlier flight time than the ions.
- The two bromine isotopes are clearly resolved in the mass spectrum and images.

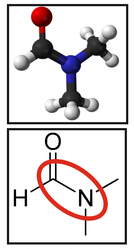






Upper left: molecular bromine, a diatomic. Upper right: a three-dimensional representation of the electron and fragment ion velocity distributions recorded following photolysis of Br_2 at 446.32 nm, integrated over 20,000 laser shots. Lower right: the mass spectrum extracted from the recorded PImMS data, bromine isotopes resolved. Lower left: an inverse Abel transformed image of the extracted two-dimensional distribution of the bromine ions.



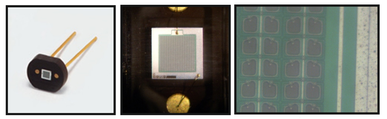


- *N,N*-Dimethylmethanamide (DMF) is a model for the peptide bond. It is a much more complex molecule than Br_2, and has a complicated fragmentation pattern.
- The many different ions formed in the 193 nm photolysis of DMF were recorded using the PImMS1 sensor, demonstrating the multi-mass imaging capabilities.

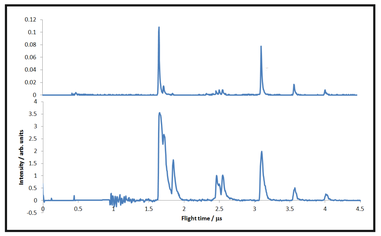
Above left: a three-dimensional representation of the ion velocity distributions recorded following 193 nm photolysis of DMF, integrated over 4000 laser shots. All fragments were recorded on each laser shot. The mass spectrum extracted from the recorded data is shown to the left of the graph. Above right: N, N-Dimethylmethanamide. Below right: the prototypical peptide bond

6. Single Photon Avalanche Diode (SPAD) Arrays

- SPADs are a new detection technology offering single photon detection sensitivities and sub-nanosecond time resolution, offering intriguing possibilities for future image sensors.
- We have recently performed proof of concept measurements demonstrating that a SPAD coupled with a scintillator may be used as a detector for mass spectrometry.[3]



The photodiode module and a detail of the 1 mm^2, 25 µm pitch diode array.



- Our results demonstrate direct detection of low energy (<5 keV) ions. SPAD-based sensors are much more rugged than existing MCP-based sensors for mass spectrometry, and may be operated at high pressure.
- We are now working on developing a SPAD-based image sensor for direct ion detection.

Left: Mass spectra of butanone acquired using (top) an MCP detector with a 10 ns time gate, and (bottom) a SPAD-scintillator combination. Spectra were acquired over 512 time-of-flight cycles. The time resolution in the lower trace is limited by the ~40 ns scintillator decay lifetime, and our groups have developed a more suitable scintillator with a faster decay.

7. Collaboration Opportunities

- The versatility of the PImMS sensor allows it to be applied to a wide range of imaging applications that require both spatial and temporal resolution. If you have a possible application, please get in touch! The current facility deployments include:

- Deutsches Elektronen-Synchrotron (DESY), Germany
- ISIS, Rutherford Appleton Laboratory (RAL), United Kingdom
- Academic laboratories; Bristol, Oxford, Leeds, Aarhus, Brookhaven, Ottawa, Waterloo

Acknowledgements

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- Oxford Chemistry - Lee, Burt, Wilman, Halford, Slater, Winter, Yuen, Gardiner, Lipciuc, Brouard and Vallance
- Oxford Physics - John, Hill, Pisarczyk, Nomerotski, Nickerson
- The Rutherford Appleton Laboratory - Clark, Crooks, Sedgwick, Turchetta

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