

# Electrostatic trapping of femtosecond laser produced ions for high resolution mass spectrometry

Contact [okelly04@qub.ac.uk](mailto:okelly04@qub.ac.uk) / [j.greenwood@qub.ac.uk](mailto:j.greenwood@qub.ac.uk)

**O. Kelly, J. D. Alexander,  
C. R. Calvert, R. B. King,  
L. Graham, I. D. Williams and  
J. B. Greenwood**

*School of Mathematics and Physics,  
Queen's University Belfast, University  
Road, Belfast, BT7 1NN, UK*

**W. R. Newell**

*Department of Physics and  
Astronomy, University College  
London, Gower Street, London,  
WC1E 6BT, UK*

**W. A. Bryan and G. R. A. J. Nemeth**

*Department of Physics, Swansea  
University, Singleton Park, Swansea,  
SA2 8PP, UK*

**E. Springate, C. A. Froud and  
I. C. E. Turcu**

*Central Laser Facility, STFC, Rutherford  
Appleton Laboratory, HSIC, Didcot,  
Oxon OX11 0QX, UK*

## Introduction

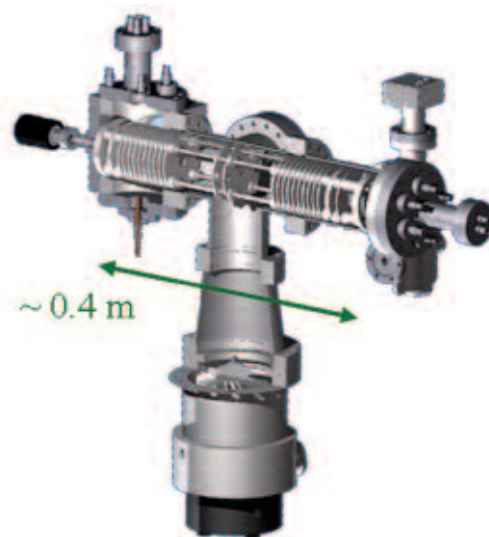
Short pulse, intense IR lasers have a number of features which are desirable in mass spectrometry. Ionisation with femtosecond lasers is very efficient, offering high sensitivity, while fragmentation can also be induced to yield information on the sub-structure of complex molecules<sup>[1,2]</sup>. The ions generated are well defined spatially and temporally, and such an ion source could find application in time-of-flight (ToF) mass spectrometers, microscopy, or in the study of reactive collisions<sup>[3]</sup>.

In this report, we demonstrate the use of the femtosecond (fs) laser in the Artemis facility at the CLF to photoionise a gas target for subsequent analysis in a linear electrostatic ion trap. Once trapped, the ions oscillate on stable trajectories with frequencies inversely proportional to the square root of their mass and are detected non-destructively by a pick-up ring. A Fourier transform of the time dependent signal yields mass spectra which can be of high resolution if the trapping time is long<sup>[4,5]</sup>.

Our results demonstrate that the laser produced ions have a very small energy spread and spatial extent which means that the ions remain bunched for long periods in the trap. In the results presented here, the mass resolution is limited by the background gas pressure of a few  $10^{-7}$  mbar. The trapping conditions in our apparatus are mass-independent and thus this is a promising technique for studying larger biomolecular systems.

## Experimental setup

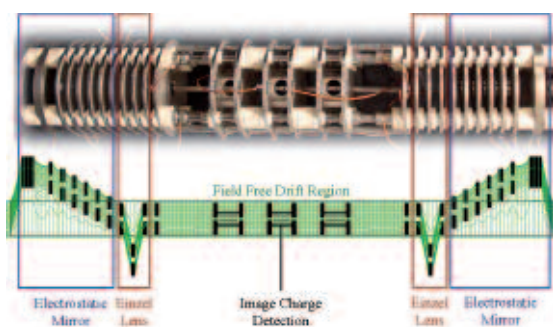
At Queen's University Belfast we have two linear electrostatic traps, where one is used primarily for the study of the photodissociation kinetics of vibrationally cold fundamental molecules, like  $\text{HD}^+$ <sup>[6,7]</sup> and  $\text{D}_3^+$ <sup>[8,9]</sup>. This report focuses on a previously unreported second trap, KEIRA: Kilovolt Electrostatic Ion Reflection Analyser (Figure 1). Although both devices have a similar design, KEIRA has a longer trapping region, consisting of more electrodes with narrower apertures. By applying voltages to these stainless steel electrodes,



**Figure 1. Impression of the Kilovolt Electrostatic Ion Reflection Analyser, inside the vacuum chamber. The electrostatic trapping region is made of a series of stainless steel plates, approximately 400 mm in length.**

a potential energy surface may be created, as shown in Figure 2. At either end, seven electrodes are used to provide an electrostatic mirror, where incremental voltages are applied in order to create a reflective potential hill. This will confine the ions along the trap axis, provided the ion's energy is less than its charge multiplied by the maximum voltage potential. The energy of stored ions is typically on the order of a few kV. Due to the electrostatic nature of the device, it is mass independent – ions of any mass may be trapped simultaneously, under the same conditions, provided they have the same total energy per unit charge.

Adjacent to the mirror regions (Figure 2) are three electrodes that act as an einzel lens, focusing the ions as they oscillate. Choosing the correct voltages will create a suitable saddle potential to confine the ions radially, and in combination with the reflection



**Figure 2.** KEIRA trapping region and corresponding potential energy surface from application of voltages to the individual stainless steel electrodes. Each electrode has a 16 mm aperture, allowing ions to traverse back and forth along the central axis of the trap. The potential surface was generated using SIMION®.

mirrors, an ion beam may oscillate on a stable trajectory along the axis of the instrument and is thus trapped. The centre of the trapping region is field-free, such that ions will traverse it with a constant velocity.

To map the evolution of the trapped ions, a non-destructive detection technique is employed. As the ions pass through a conductive ring located at the centre of the trap, an image-charge proportional to the total charge of the ions is generated. For this detection method to be effective there must be a change in the image charge as a function of time. Therefore the ions must oscillate as a bunch to be observed. To obtain the best resolution from the results, the width of this bunch in time must be much less than the time it takes for one period of oscillation.

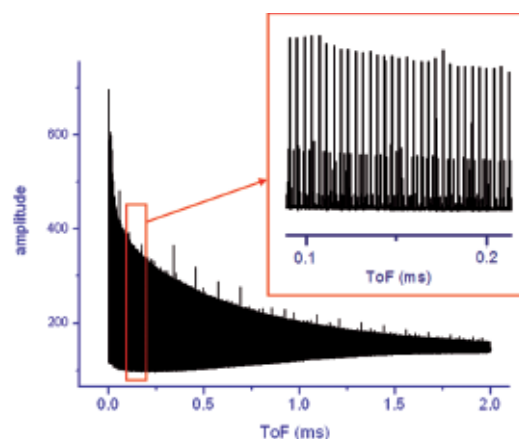
In practice, a bunch of ions consisting of a range of mass-to-charge ratios ( $m/q$ ), all with the same energy, are introduced from a source, allowing simultaneous detection and analysis. Each unique  $m/q$  ratio has a corresponding oscillation frequency that is directly proportional to  $(m/q)^{0.5}$ . Thus the separation of the ion species as they oscillate, and the image-charge detections from the pick-up ring, allows for  $m/q$  identification and quantification of all the confined species.

Multiple passes through the pick-up electrode generates a train of peaks (Figure 3) with successive temporal separations equal to half the period of oscillation of the ions in the trap. Fourier analysis of these results allows the different  $m/q$  to be separated in frequency space, where each  $m/q$  generates a fundamental peak and corresponding harmonics. A large number of these harmonics exist in order to represent the narrow peaks that are obtained in the temporal domain.

## Results

Initial characterisation experiments in KEIRA were conducted by trapping and analysing photoionised atomic species. This was carried out at the CLF Artemis facility where 30 fs pulses of peak intensity  $\sim 10^{15}$  W cm<sup>-2</sup> were used to ionise argon and xenon gas targets.

For the intense fs pulses used here, the high photon flux mediates an intense electric field that drives the ionisation dynamics. In this non-linear regime, electrons are removed via tunnel-ionisation<sup>[10]</sup> on the



**Figure 3.** Typical spectra from fs-ionised argon; decay in signal is due to ion loss through neutralising collisions with the residual gas. Inset: train of peaks from oscillating Ar<sup>+</sup> bunch.

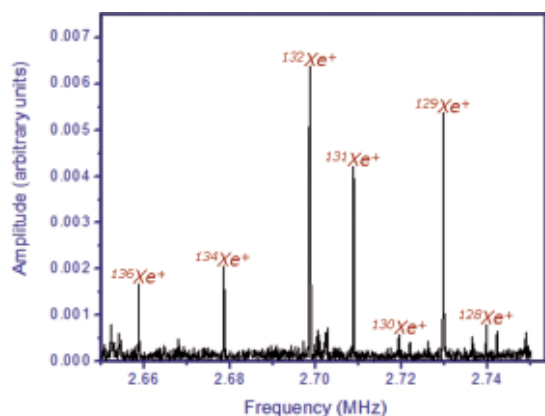
rising edge of the fs-pulse. This constitutes an extremely short femtosecond time-window in which the ions are produced. In this way, the ion bunch is initiated almost instantaneously, providing narrow peaks in the time domain spectrum. This is a significant advantage in using fs laser interactions as an ion source<sup>[3]</sup>, as temporal definition provides increased accuracy in determination of  $m/q$ .

Another advantage is that the high intensity and tuneability of the fs laser means it provides a highly efficient ionisation method. Furthermore, the fs-laser has a waist at the focus on the order of tens of micrometers, which is  $< 0.01\%$  the length of the trapping region, providing a small spatial spread in the created ion bunch.

Typical spectra were recorded for tens of milliseconds, with the main limiting factor being the residual gas in the trap. With an operating pressure of greater than  $10^{-7}$  mbar, there was significant loss of ions from the bunch, where the ions are involved in neutralising collisions with the background gas. In a typical spectrum (Figure 3), after 1 ms of trapping ( $\sim 125$  oscillations for 3 keV argon ions), only  $\sim 30\%$  of the ions remain within the bunch.

As the time spectrum is usually dense with information, a Fast Fourier Transform (FFT) of the temporal spectrum gives an efficient way to separate the different  $m/q$  species in frequency space, for accurate mass identification. Figure 4 shows a section of the FFT spectrum from trapped xenon, corresponding to the 21<sup>st</sup> harmonic, where the masses of the different xenon isotopes are clearly distinguishable. This means the fundamental for the most abundant isotope, xenon-132, occurs at 130 kHz, corresponding to a period of oscillation in the trap of 16  $\mu$ s. The amplitude of the isotopic masses formed via fs photoionisation correlates well with the abundances of the isotopes found naturally. A mass resolution of  $10^4$  was obtained with this particular spectrum.

Assuming the widths of the peaks at half the maximum ( $\Delta f$ ) is the same for all harmonic orders, the mass resolution ( $m/\Delta m$ ) attainable will grow linearly with increasing harmonics.



**Figure 4. The 21st harmonic of trapped xenon isotopes, with clear separation in the different masses providing a mass resolution of  $\sim 10^4$ .**

This may be seen in the equation defining resolution in terms of frequency:

$$\frac{m}{\Delta m} = \frac{nf}{2\Delta f}$$

where  $n$  is the harmonic order and  $f$  is the fundamental frequency. It can thus be seen that resolving power is directly proportional to the frequency of the harmonic ( $nf$ ). In fact, the peak-widths slowly increase with the harmonic order, but this effect is negligible in relation to the increased separation of the peaks at the higher harmonic frequencies.

### Conclusions

Work has been presented using an fs-laser as a tool for ionisation to obtain high resolution mass spectrometry

using our novel electrostatic ion trap. The Artemis facility at the CLF provided 30 fs pulses, generating a well defined bunch in space and time. Using electrostatic potentials, these ions were confined along an axis of  $\sim 400$  mm in length. A non-destructive image-charge detection method was employed to obtain information on the different ion species as they oscillate, without interfering with their trajectories.

High resolving power has been seen for femtosecond ionised xenon. Utilising the higher harmonics available in frequency space, the isotopic masses are well separated providing a resolution of  $10^4$ .

### Acknowledgements

O. Kelly and C. R. Calvert acknowledge funding from the Leverhulme Trust. R. B. King and L. Graham acknowledge funding from the Department for Employment and Learning (NI). J. D. Alexander acknowledges funding from the European Social Fund. G. R. A. J. Nemeth acknowledges funding from the STFC.

### References

1. T. Laarman *et al.*, *J. Phys. B*, **41**, 074005 (2008).
2. C. L. Kalcic *et al.*, *J. Am. Chem. Soc.*, **131**, 940 (2009).
3. C. Hohn *et al.*, *Rev. Sci. Instrum.*, **79**, 053102 (2008).
4. S. Ring *et al.*, *Anal. Chem.*, **72**, 4041 (2000).
5. K. G. Bhushan *et al.*, *Rev. Sci. Instrum.*, **78**, 083302 (2007).
6. P. A. Orr *et al.*, *Phys. Rev. Lett.*, **98**, 163001 (2007).
7. J. D. Alexander *et al.*, *J. Phys. B*, **42**, 154027 (2009).
8. J. D. Alexander *et al.*, *J. Phys. B*, **42**, 141004 (2009).
9. C. R. Calvert *et al.*, CLF Annual Report (2008/09).
10. W. A. Bryan *et al.*, CLF Annual Report (2005/06).