

The Ionisation of Pyrimidine

Sasha Kroon, Dr Lily Ellis-Gibbings, Professor Stephen D Price



About the Project

Abstract

The aim of this project was the analysis of a portion of existing coincidence Electron Impact Time of Flight Mass Spectroscopy (EI TOFMS) pyrimidine ($C_4H_4N_2$) data to determine relative partial ionisation cross sections (PICS) for the production of daughter ions, by single and multiple ionisation. The ions analysed had masses of 20 ($NCN^{2+}/C_3H_4^{2+}/CNCH_2^{2+}$), 38 ($C_3H_2^+/CNC^+$), 39 ($C_3H_3^+/CNCH^+$), 40 ($NCN^+/C_3H_4^+/CNCH_2^+$) across the electron ionisation energy range 40 – 200 eV.

These ion cross sections can be used to better understand how pyrimidine is ionised.

As pyrimidine is an analogue of the DNA bases thymine and cytosine and the RNA base uracil, this knowledge can be applied to these bases and by extension DNA, to try to reduce healthy cell damage/death during radiotherapy treatments.



Figure 1 – pyrimidine structure¹

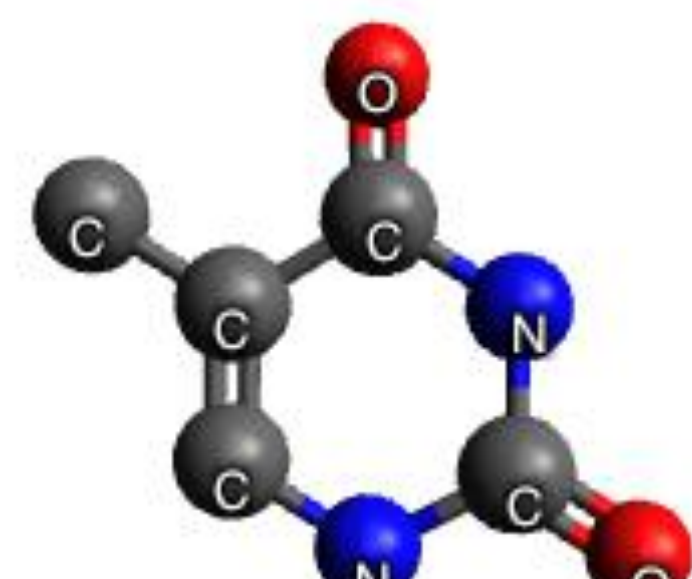


Figure 2 – thymine structure¹

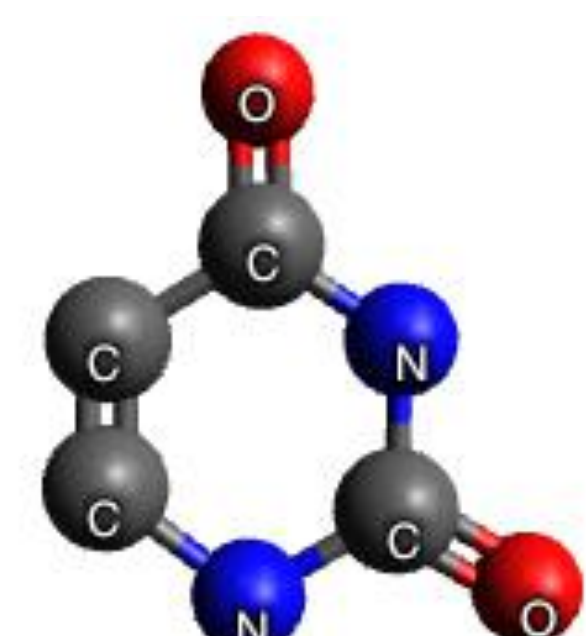


Figure 3 – uracil structure¹

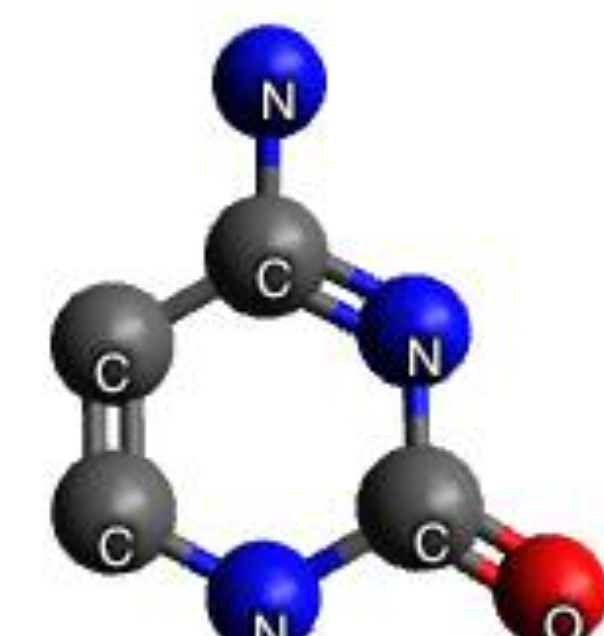


Figure 4 – cytosine structure¹

Experimental Details - pulsed electron impact time of flight mass spectroscopy.

In the EI TOFMS (Wiley McLaren type time of flight mass spectrometer) experiment pyrimidine molecules are ionised by electron impact.

The ions are then accelerated to the detector plate using an electric field (which means all the ions will have the same kinetic energy). The heavier mass ions will have a lower velocity (longer time of flight). Ions, therefore, can be identified by their mass to charge ratio.

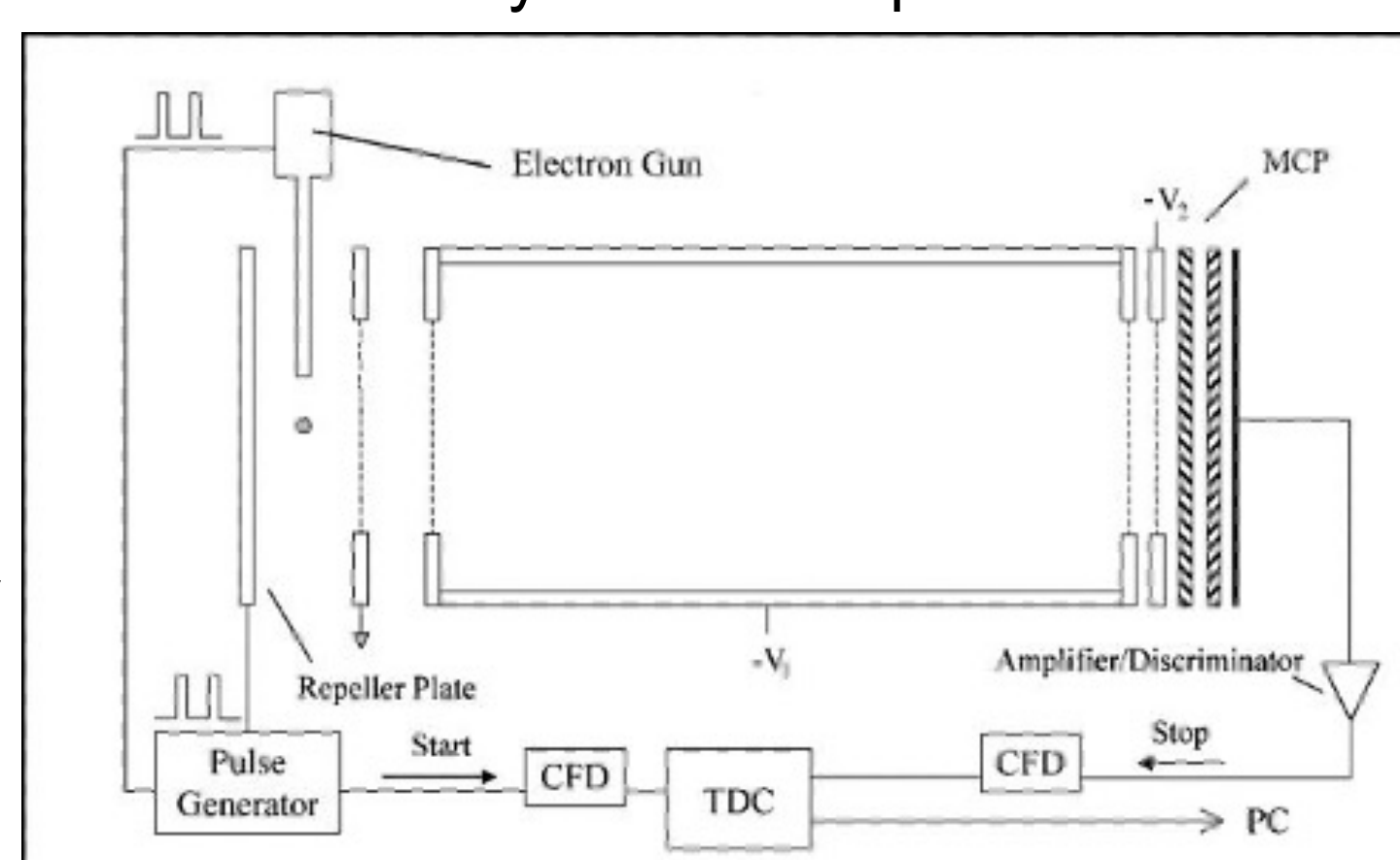
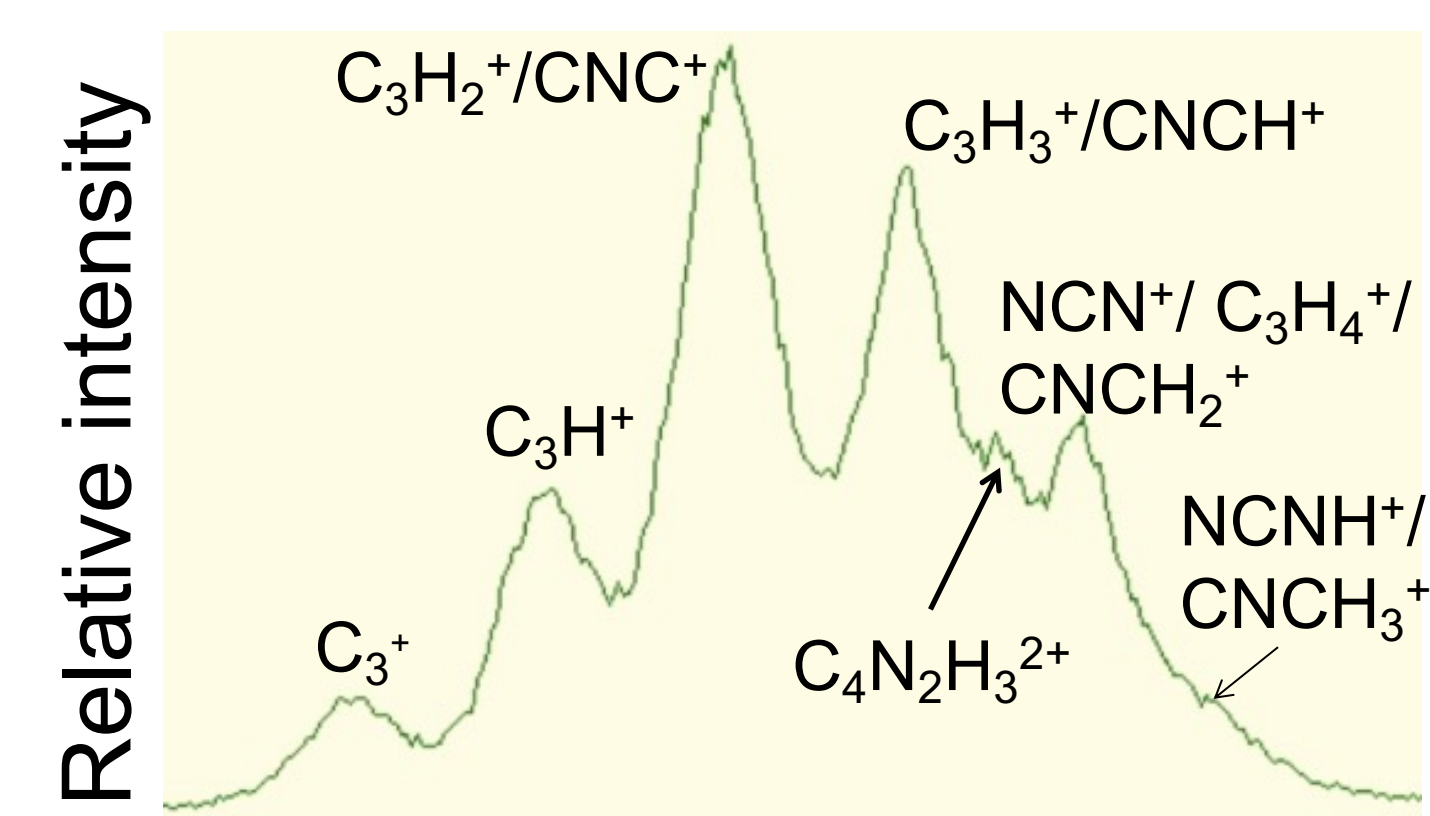


Figure 5- Experimental set up²

Analysis

Singles - A single count is recorded when an ion hits the detector.



Ions detected one at a time are shown in figure 6. Their relative intensities are measured, then the background counts are removed.

Figure 6 – TOF spectrum 200 eV with possible ions labeled

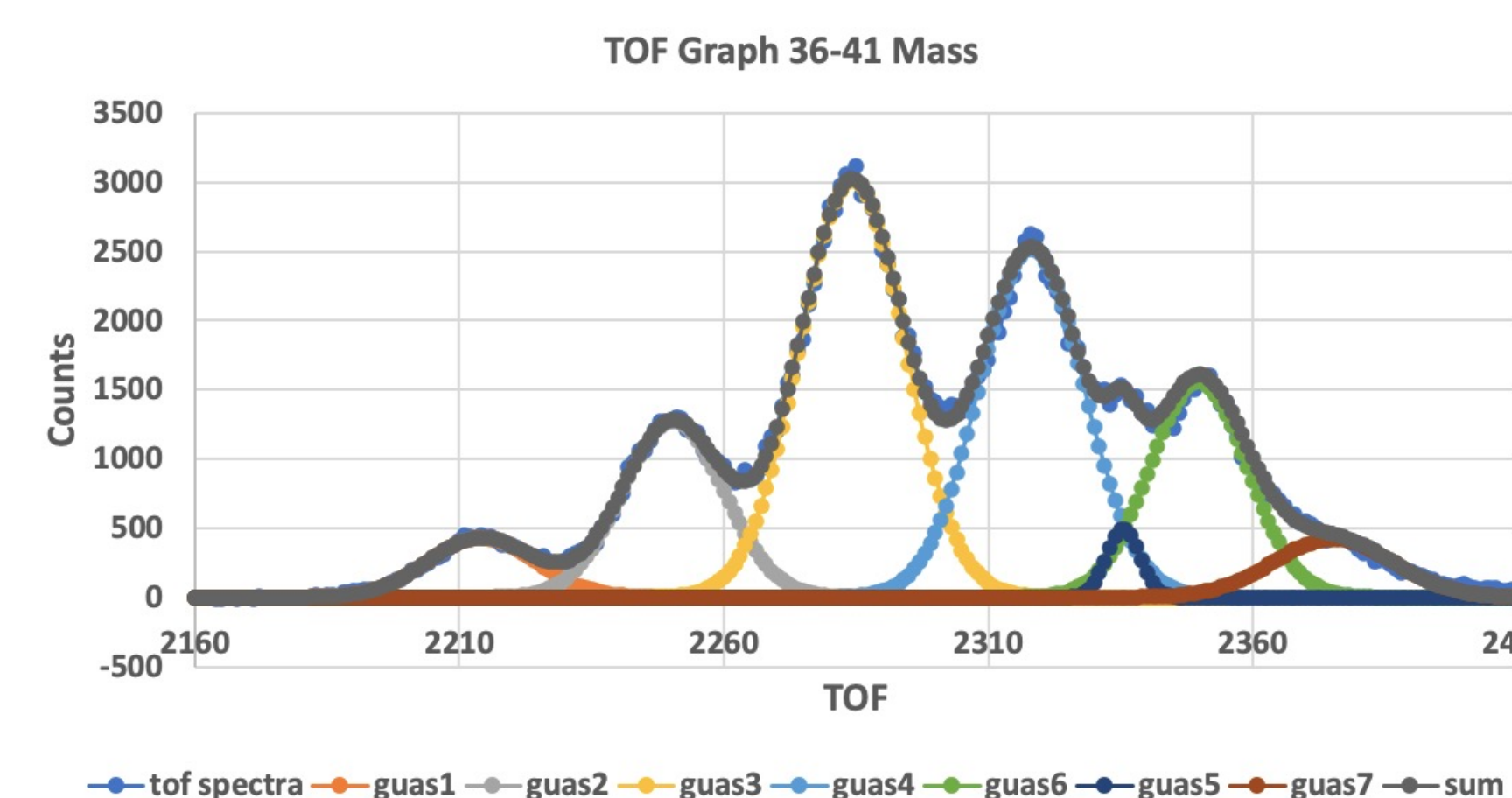
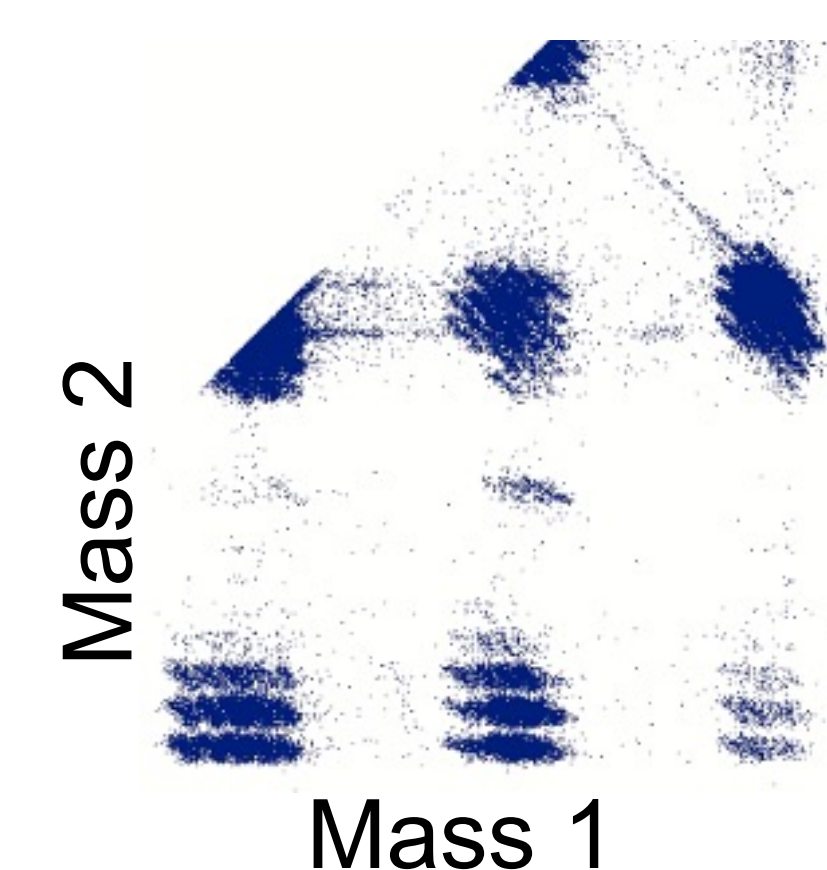


Figure 7 – TOF gaussian graph

If the peaks are merged, gaussians are fitted to peaks to resolve individual intensities.

Pairs - A pairs count is recorded when two ions hit the detector in coincidence, after the dissociation of double or triple ionisation of the parent ion.



The pairs spectrum consists of 1 dot per count. The pairs counts are recoded using diagonal boxes and counting the dots inside the box. There are real pairs and false pairs (where the two ions did not come from the same parent ion). The false pairs and missing counts due to detector dead time are identified and accounted for in the data analysis.

Figure 8 – pairs spectrum 200 eV

False pairs are circular. The masses of the peak may add up to over 80. Real Pairs are lozenge shaped.

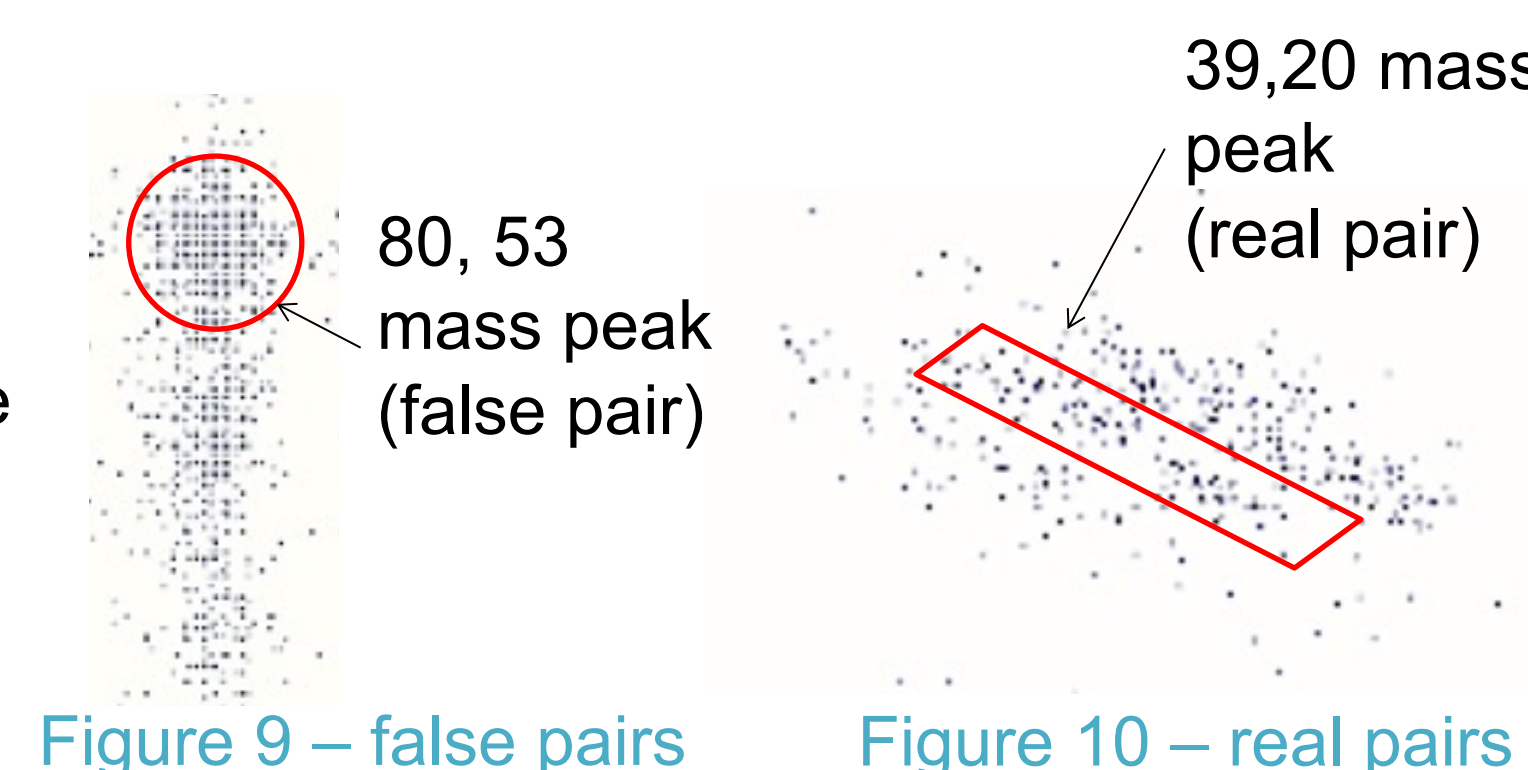


Figure 9 – false pairs

Figure 10 – real pairs

Results

Partial Ionisation Cross Sections (PICS) - a measure of the probability that a specific ion will form.

After all background corrections the cross sections are calculated where:

- The relative PICS (rPICS) are a measure of how likely a certain ion is to form.

$$\text{rPICS equation for the } 1^+ \text{ ions: } \sigma_r[X^+] = \frac{I_1[X^+] + P_2[X^+] + P_3[X^+] + T[X^+]}{I_1[\text{parent}^+]}$$

- The precursor specific PICS (PSrPICS) are a measure of how likely an ion is to form from a specific parent ion with a specific charge.

$$\text{PSrPICS equation for a } 1^+ \text{ ion forming from a } 1^+ \text{ parent ion: } \Sigma_1[X^+] = \frac{I_1[X^+] - \left(\frac{1-f_1}{f_1}\right)(P_2[X^+] + P_3[X^+]) + \left(\frac{1-f_1}{f_1}\right)^2 T[X^+]}{I_1[\text{parent}^+]}$$

Final graphs - the characteristic shape of the graphs begins at threshold, rises to a maximum at approximately 30 eV above this threshold, and then slowly decreases.

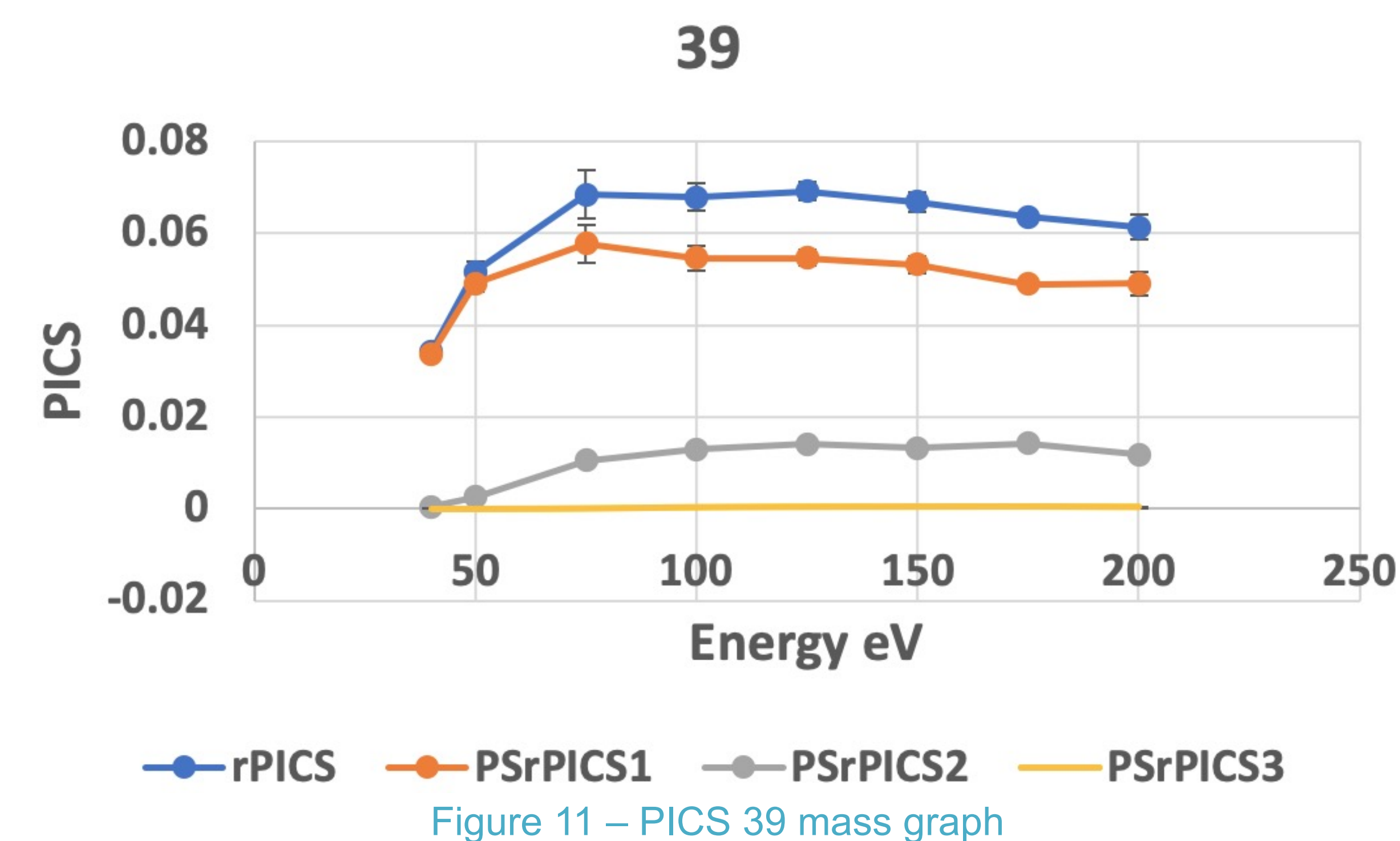


Figure 11 – PICS 39 mass graph

The PSrPICS show a high level of double ionisation. Most of the graphs fit the same pattern, with a few dips/peaks in the 14 and 15 mass graphs.

Conclusion

The knowledge of how pyrimidine is ionised from these ion production cross sections can be used to try to reduce healthy cell damage/death during radiotherapy treatments.