Revisiting Electron Ionisation

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Electron ionisation (EI) is important in a variety of naturally-occurring and man-made plasmas, including the Earth's upper atmosphere, interstellar gas-clouds, gas discharges, and industrial and fusion plasmas. It is also widely used as an ionisation technique in mass spectrometry, and plays a key role in radiation damage to biological tissue. In contrast to photoionisation, EI is a collisional process. As such, it does not obey optical selection rules, and the amount of energy transferred from the electron to the molecule is often unknown. This leads to considerable uncertainty as to which electronic state or states the ion is formed in, and whether these are the same states accessed during photoionisation. Recent experimental advances [1-4] have made it possible to study the dynamics of EI by multi-mass velocity-map imaging. This approach yields complete scattering distributions for the ionic products of an electron-molecule collision as a function of the incident electron kinetic energy, providing considerable insight into the detailed dynamics of the EI process and subsequent dissociation of the molecular ion.

While the majority of parent ions formed by EI are singly-charged, at higher energies it also becomes possible to form multiply charged ions, which dissociate to give two or more charged products. In such cases covariance analysis of the data set provides further insight into the dynamics by revealing correlations between pairs of ions formed in the same event.

This talk will provide an overview of velocity-map imaging and covariance-map imaging as applied to the study of EI processes. We will summarise our current working knowledge of the initial ionisation process, as well as illustrating how these new techniques can be used to unravel the complex multi-step dissociation mechanisms that ensue.

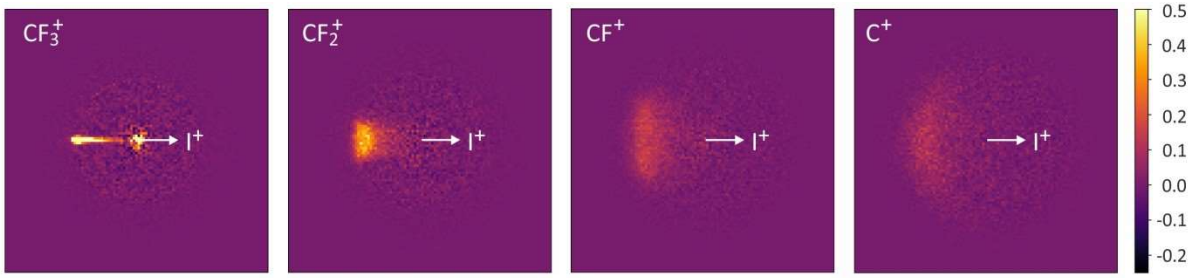

Figure 1: Covariance-map images for some of the ionic fragmentation products of CF_3I^{2+} dications formed by electron ionisation of CF_3I. Each image shows the relative velocity distribution of a given fragment pair, and the images can be analysed to gain detailed information on the fragmentation pathways leading to each pair of products.

[1] H. Köckert *et al.*, *Phys. Chem. Chem. Phys.*, **21**, 14296-14305 (2019).
[2] C. Vallance, *Chem. Comm.*, **55**, 6336 – 6352 (2019).
[3] H. Köckert *et al.*, *Mol. Phys.*, **119**, e1811909 (2021).
[4] C. Vallance *et al.*, *J. Phys. Chem. A*, **125**, 1117-1133 (2021).