Threshold photoelectron and electron-ion coincidence spectroscopies: past, present and future

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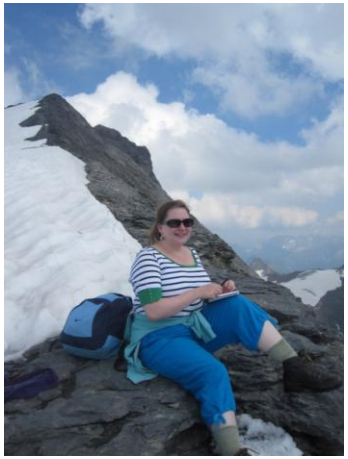
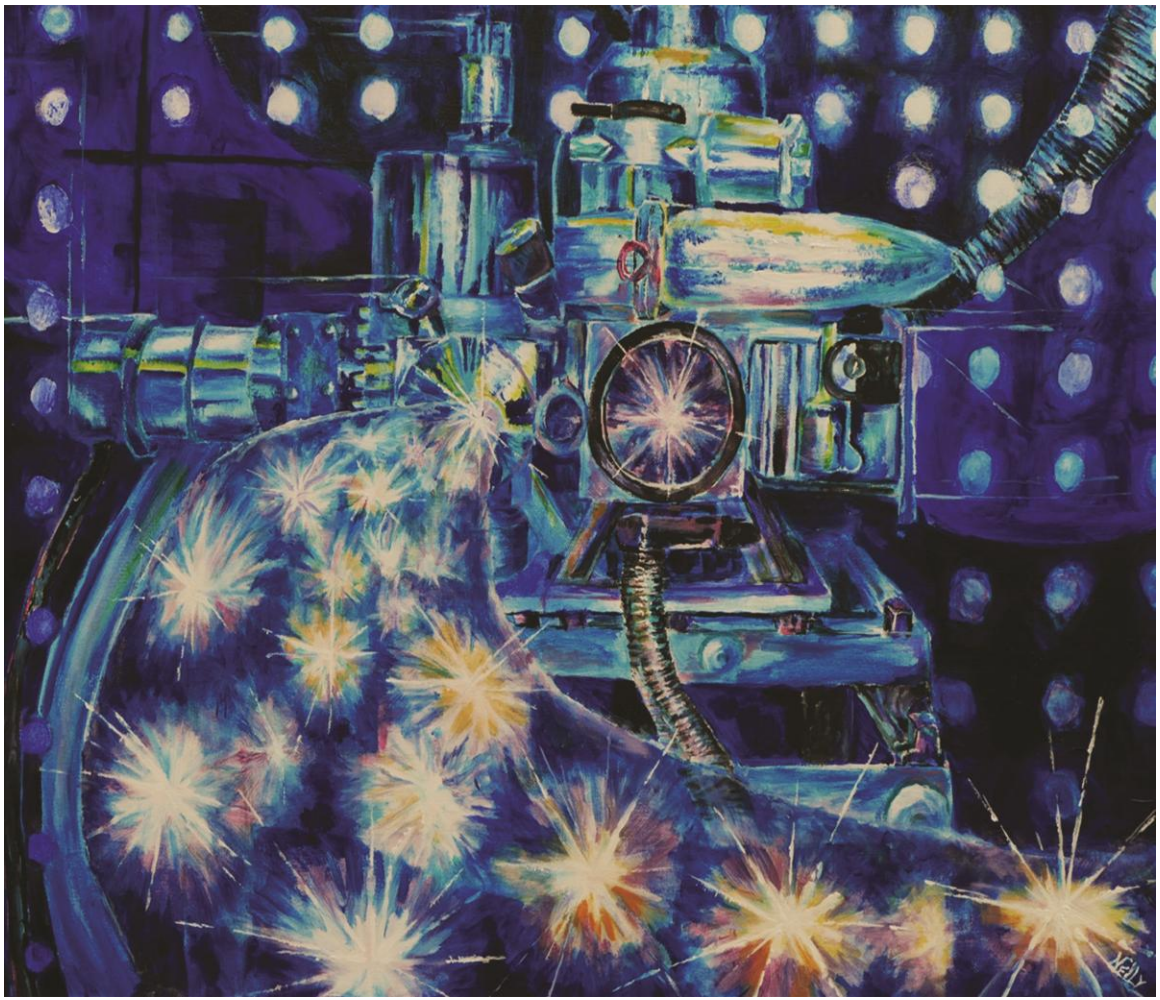
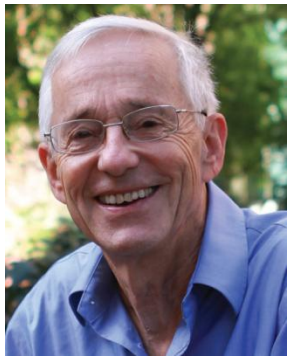
Phys. Chem. Chem. Phys., (2017) 19, 9698–9723. DOI: 10.1039/c7cp00144d

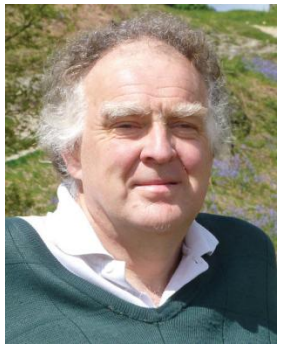
Dublin Sept 2017 & Beatenberg January 2019



Jonelle Harvey







Story how this paper evolved

Freak bike accident, July 2016, Good weather.
Traumatic Brain Injury (TBI).

Hospitals, Cambridge and Birmingham, for 2 months

Could not swallow or speak for 7 weeks

Many MRI scans. Foix-Chavany-Marie Syndrome

Nothing in medical literature about outcome for TBI patients

Extensive Therapy as Outpatient for 2 years, mostly Speech & Language.
Advice early on: 'Speak slowly, …' Still on-going.

Huge help from family, *Tom Baer*, and piano playing. Care with food and drink.

One year on: 'We would not have put money on this [good] outcome a year ago'

***Acta Neurochirurgica* (2018) 160, 2303-2305 DOI: 10.1007/s00701-018-3702-x**
The Patient's Perspective (*i.e.* thoughts of RT) submitted 8.1.19, now in press.

The Past (1970) : the basic photoelectron equ $h\nu = IE + E_{ion} + KE_{electron}$

***Advantages of* detecting threshold *or* zero electrons** (*i.e.* $KE_{electron} = 0$)

Improved electron energy resolution

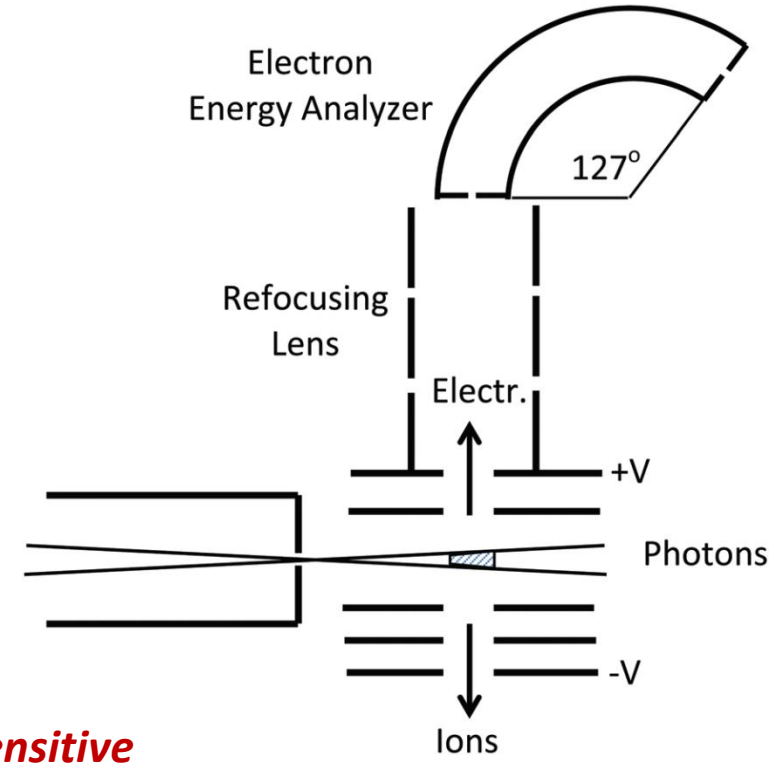
Coincidences of energy-selected ions with electrons: (T)PEPICO experiments:
needs good collection efficiency of electrons *and* ions

Collection efficiency of threshold electrons (c. 95%)
much greater than energetic electrons (c. 0.1%)

Autoionisation effects

Ion imaging

High resolution synchrotron radiation,
providing tunable vacuum-UV photons



Early TPEPICO apparatus (RPT, Daresbury UK, c. 1990 – 2008). Many aspects of later position-sensitive imaging detectors. 127° post-analyser needed to solve the 'hot electron' problem

Meas. Sc. Tech., (1992) 3, 891-896

Velocity focussing techniques

Achromatic lens for electron extraction
(Baer, c. 1975; Tuckett, c. 1990)

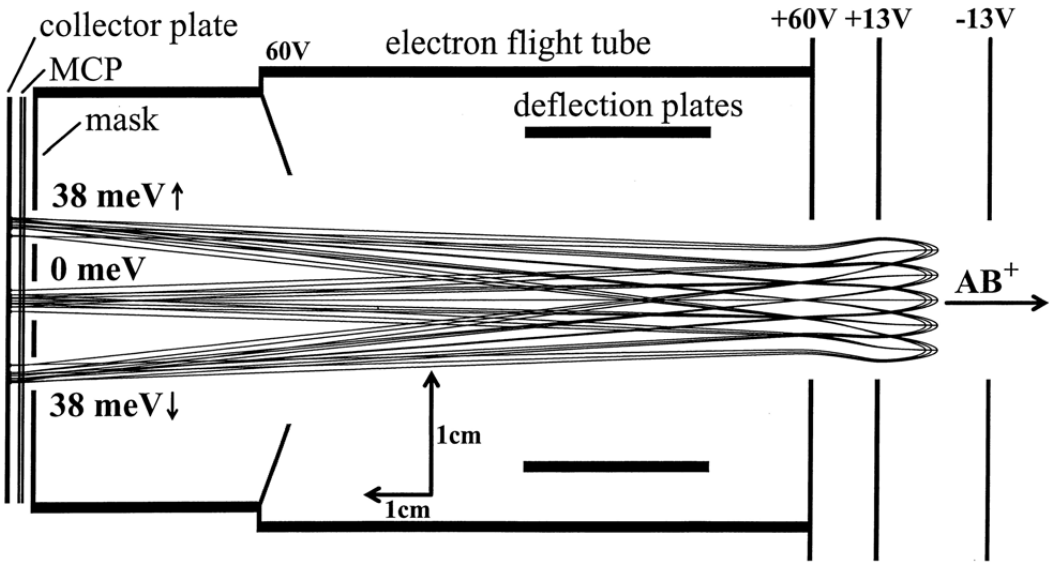
Velocity map imaging (Eppink and Parker, 1997)

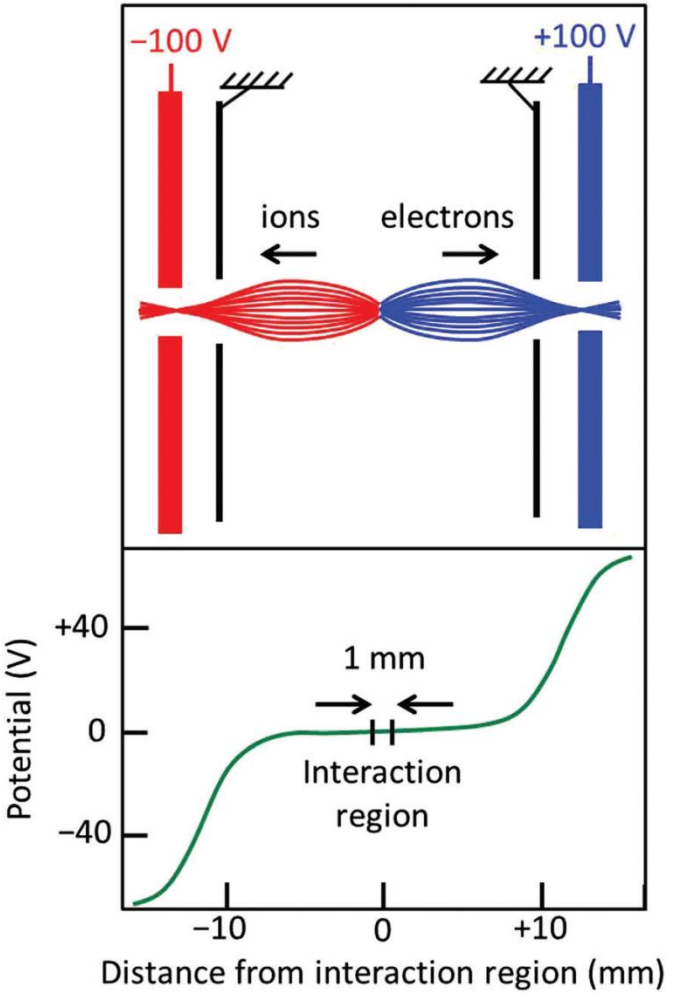
Weak penetrating field (King, 1987 on) : electrostatics

Excellent for spectroscopy, not for coincidences / dynamic studies. No 'hot electron' issue.
Extension to spectroscopy of *doubly-charged* cations

Elimination of the hot electron problem

Baer and Sztaray (*Rev. Sci. Inst.* (2003) 74, 3763)





J. Phys. E. (1987) 20, 440

Three (and a half?) huge advances from the years 1970 to c. 2017: PAST to PRESENT

[Development of very high resolution in Zero Energy Kinetic Energy (ZEKE) laser-based spectroscopy, as the technique turned from a synchrotron- to a laser-based study [c. 1990] (c. 1 meV to 0.01 meV, *or* 5 cm^{-1} to 0.05 cm^{-1}) (Tuckett, c. 1990 on)]

1. Evolution from a spectroscopic to a unimolecular dynamic study of molecular ions: moved from studies of autoionisation to much more interaction with Theory of how molecular ions dissociate (and their timescale) (Baer, c. 1975 on)

2. Velocity focussing of threshold electrons onto an position sensitive imaging detector: this led to the solution of the hot-electron problem [c. 1995] (Eppink&Parker, Baer&Sztaray)

3. Multi-start multi-stop detectors for both electrons and ions: all electrons and ions collected are timed *wrt* a Master Clock. Can now use the full intensity of modern synchrotrons, improving signal-to-noise ratios of coincidence expts [c. 2005] (Boedi, *Rev. Sci. Inst.* (2007) 78, 084102)

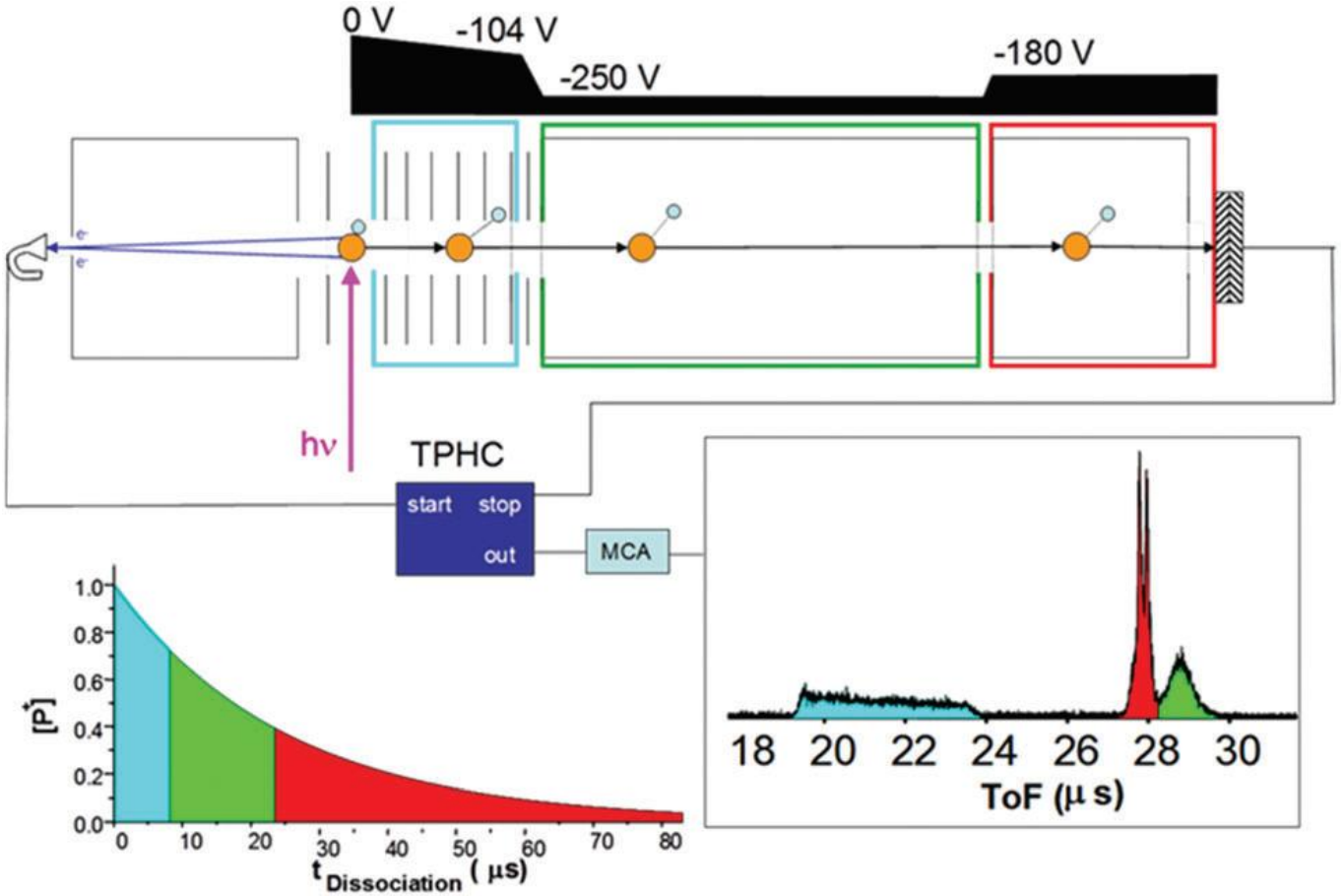
PRESENT to FUTURE: 2017 onwards

1. Image ions and electrons over a range of energies on *separate* position-sensitive detectors: improvement of collection sensitivity so that low-density samples can be investigated.

2. Investigate isomeric mixtures, free radicals in pyrolysis, discharge and combustion processes.

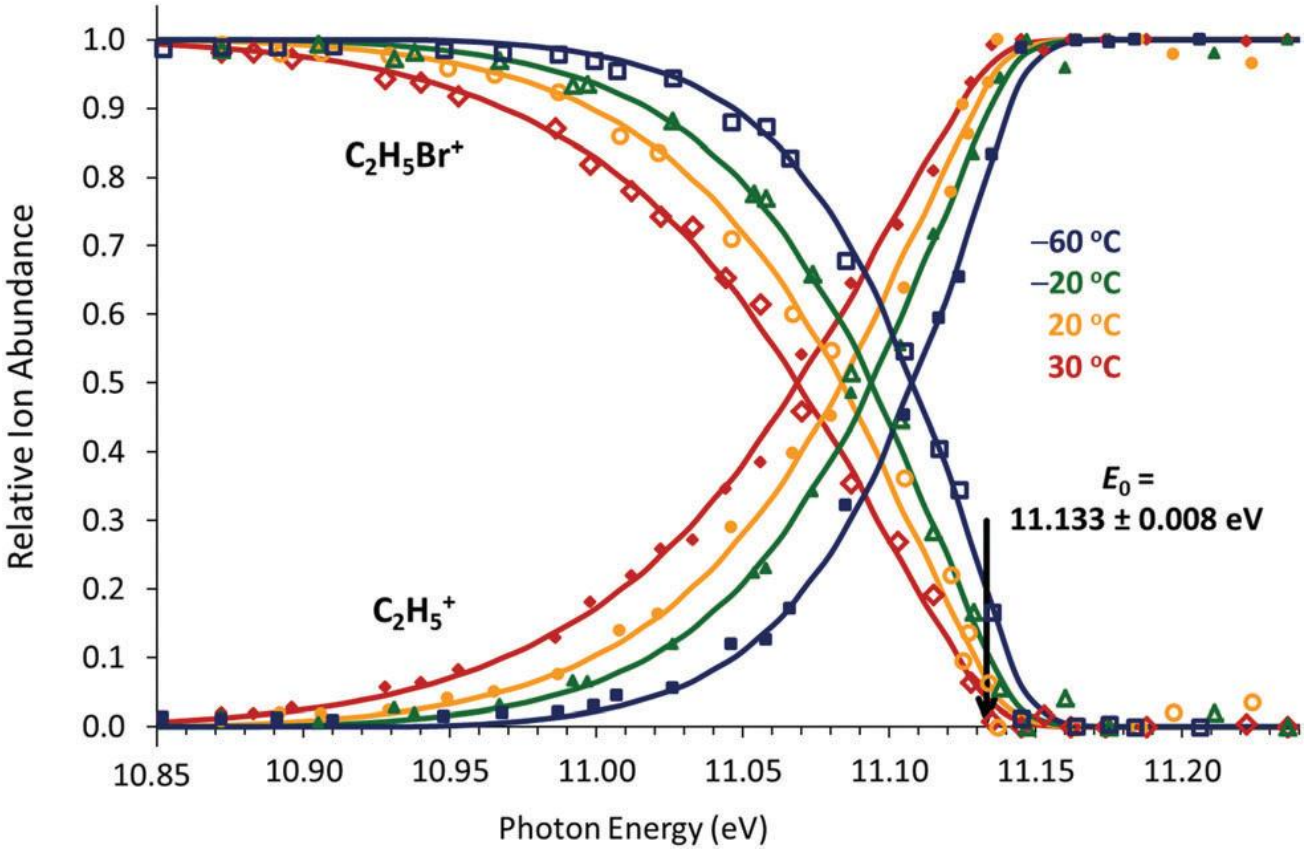
3. (T)PEPICO spectroscopy may become a truly quantitative and analytical technique.

Unimolecular dynamics: Dissociation of bromobenzene cations



Imaging **PEPICO experiment to measure an ion dissociation rate constant. The blue section is the first ion acceleration region, followed by a short acceleration region to bring the ions to 250 V. The ions then drift at this energy through the green region. They then decelerate and enter the final red drift region. Ions that dissociate in the blue region (0–8 μs) appear as the dispersed blue peak in the TOF spectrum. Fragment ions that decay in the green region appear as the green peak in the TOF spectrum. Finally, undissociated ions or those that decay in the red region appear as the red peak. (Baer *et al. J. Phys. Chem. A.* (2009) 113, 573)**

Rapid (> 10^7 s^{-1}) loss of Br atoms from $C_2H_5Br^+$: high-accuracy thermochemistry



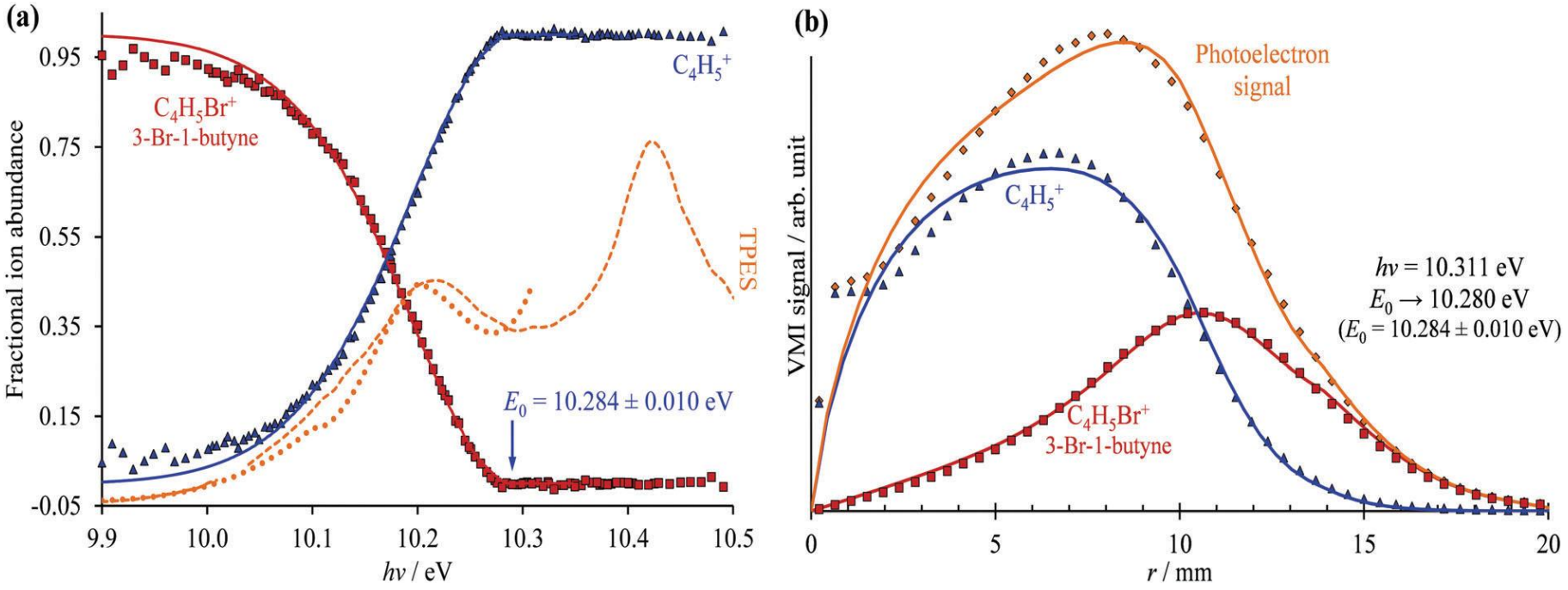
$$C_2H_5Br \rightarrow C_2H_5^+ + Br + e^-$$

Solid lines through the breakdown diagram obtained using a dissociation limit of 11.133 (8) eV, and varying only the temperature of the source

(Borkar and Sztaray, *J. Phys. Chem. A.* (2010) 114, 6117)

(Moral: Beware of supersonic beams, they are *NOT* the panacea, as scientists believed in their early days.)

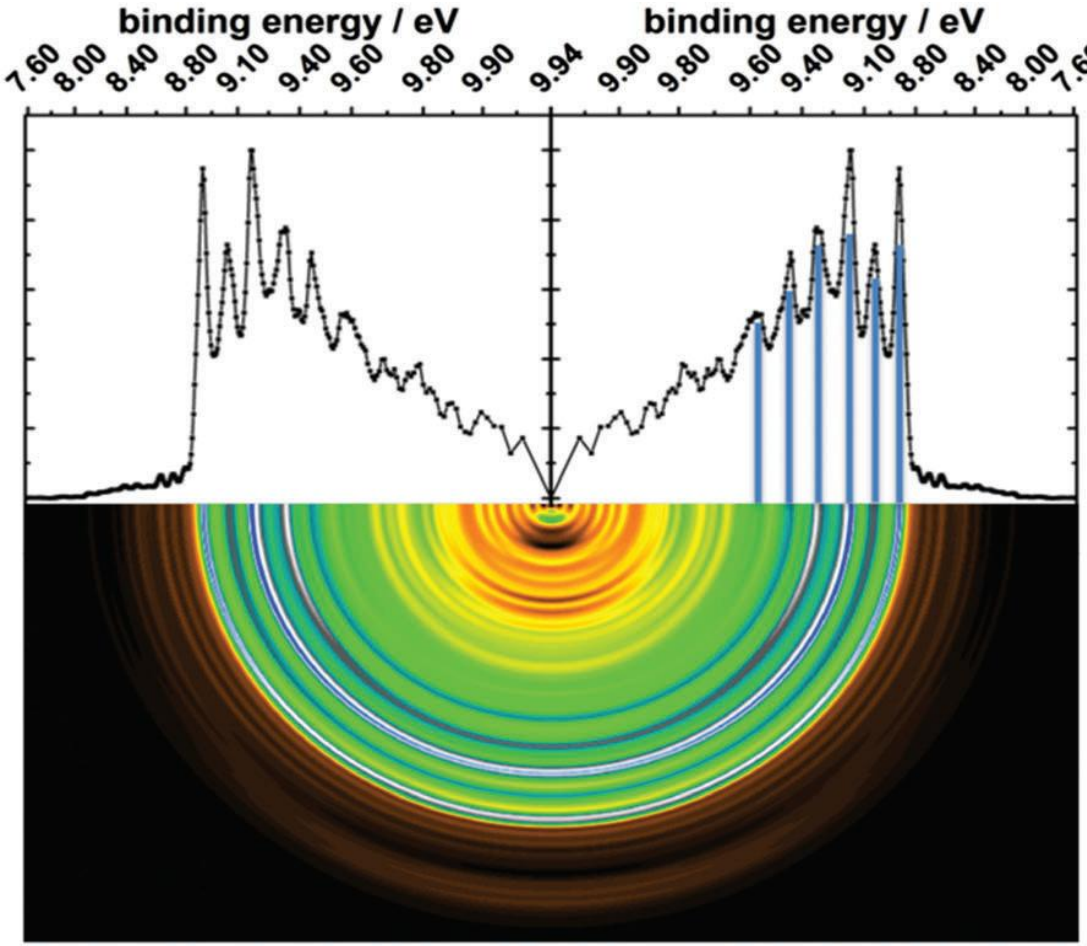
Use of parts of an image that show threshold electrons (a) and energetic electrons (b)

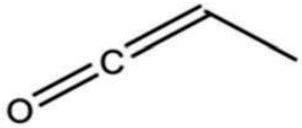


Breakdown diagrams for 3-Br-1-butyne and loss of Br. (a) shows the traditional breakdown diagram (ions as a function of photon energy) obtained by ion threshold coincidence (TPEPICO), along with the high resolution TPES. (b) shows the data obtained by collecting *all* electrons on the image in coincidence with the ions at a photon energy of 10.311 eV; this displays ions as a function of radial electron signal. The 0 K dissociation onset energies obtained from the two methods are 10.284 ± 0.010 eV and 10.280 eV, in good agreement.

(Boedi, *Phys. Chem. Chem. Phys.* (2014) 16, 505)

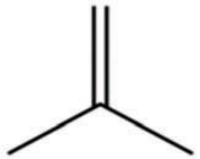
Isomeric identification from a flame: Felsmann et al. *Z. Phys. Chem.* (2016) 230, 1067





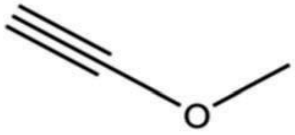
methylketene
IE 8.95 eV

2-butene
trans: IE 9.10 eV
cis: IE 9.11 eV



i-butene
IE 9.22 eV

1-butene
IE 9.55 eV



methoxyacetylene
IE 9.48 eV

Photoelectron spectrum at hν = 9.94 eV collected in coincidence with ions of mass 56 recorded fom a methyl propionate / oxygen flame at a fixed height above the flame burner. The upper 2-D spectrum is the reconstructed PES of the lower image using the *p*Basex inversion procedure. Isomers of mass 56 that can contribute to the total signal are shown.