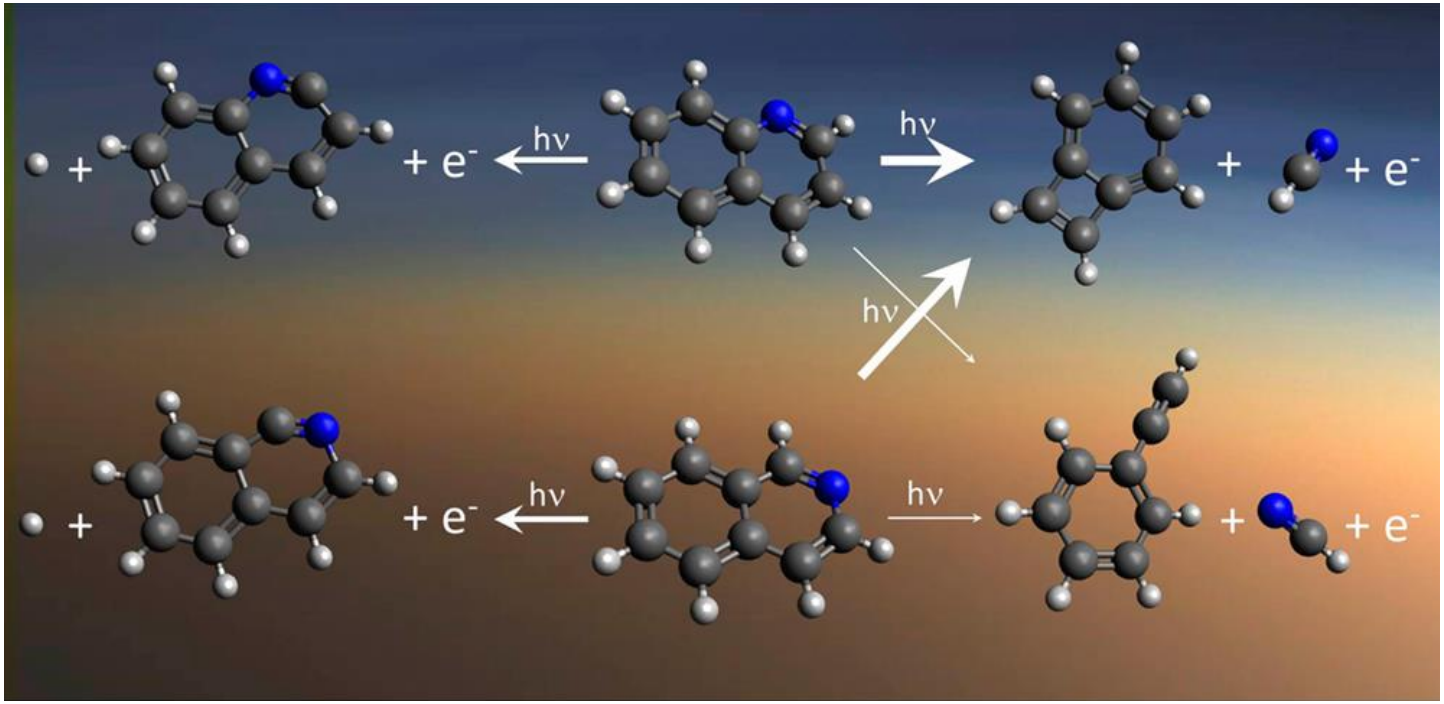
Dissociative Photoionization of Nitrogen-Containing Polycyclic Aromatic Hydrocarbons



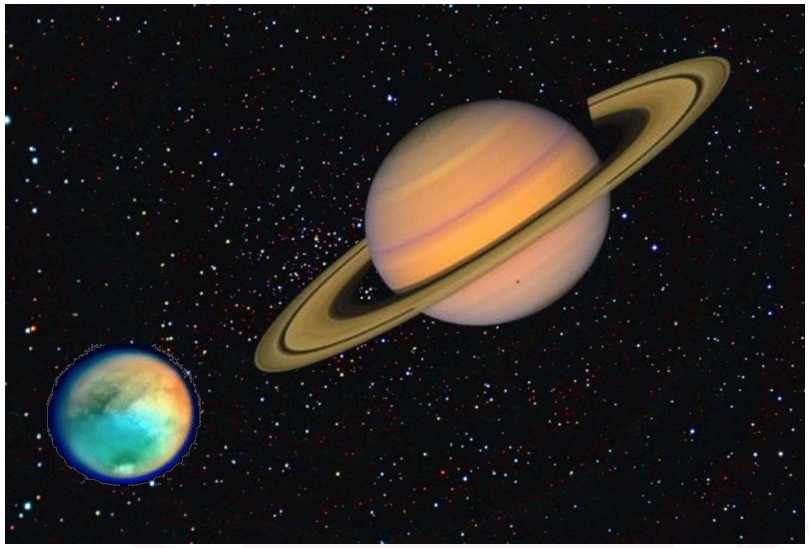
Jordy Bouwman

Radboud University

Motivation

- Titan's atmosphere
- Active N & C chemistry
- Evidence for aromatics

Waite, J. H. *et al. Science* **316**, 870-875, 2007



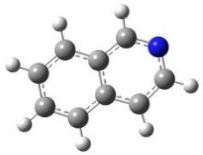
- Interstellar medium
- PAH mid-IR emission bands
- 6.2 μm band shift by N-inclusion

Mattioda *et al. J. Phys. Chem. A* **107**, 1486, 2003

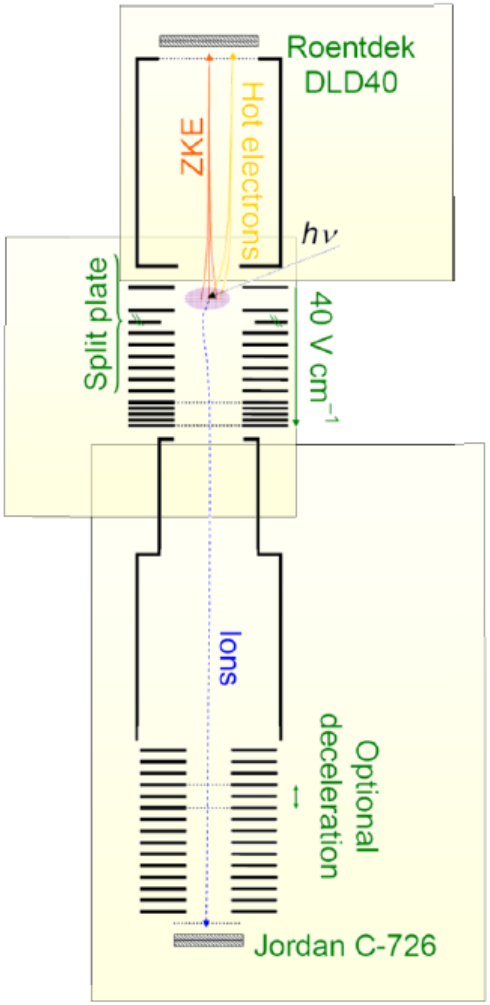
iPEPICO Experiments

- i-PEPICO: imaging Photoelectron Photoion Coincidence Spectrometer
- VUV beamline of Swiss Light Source (5-21 eV)
- High E resolution electron imaging; Threshold electrons
- Slow extraction of ions; kinetics of slow dissociations

Quinoline

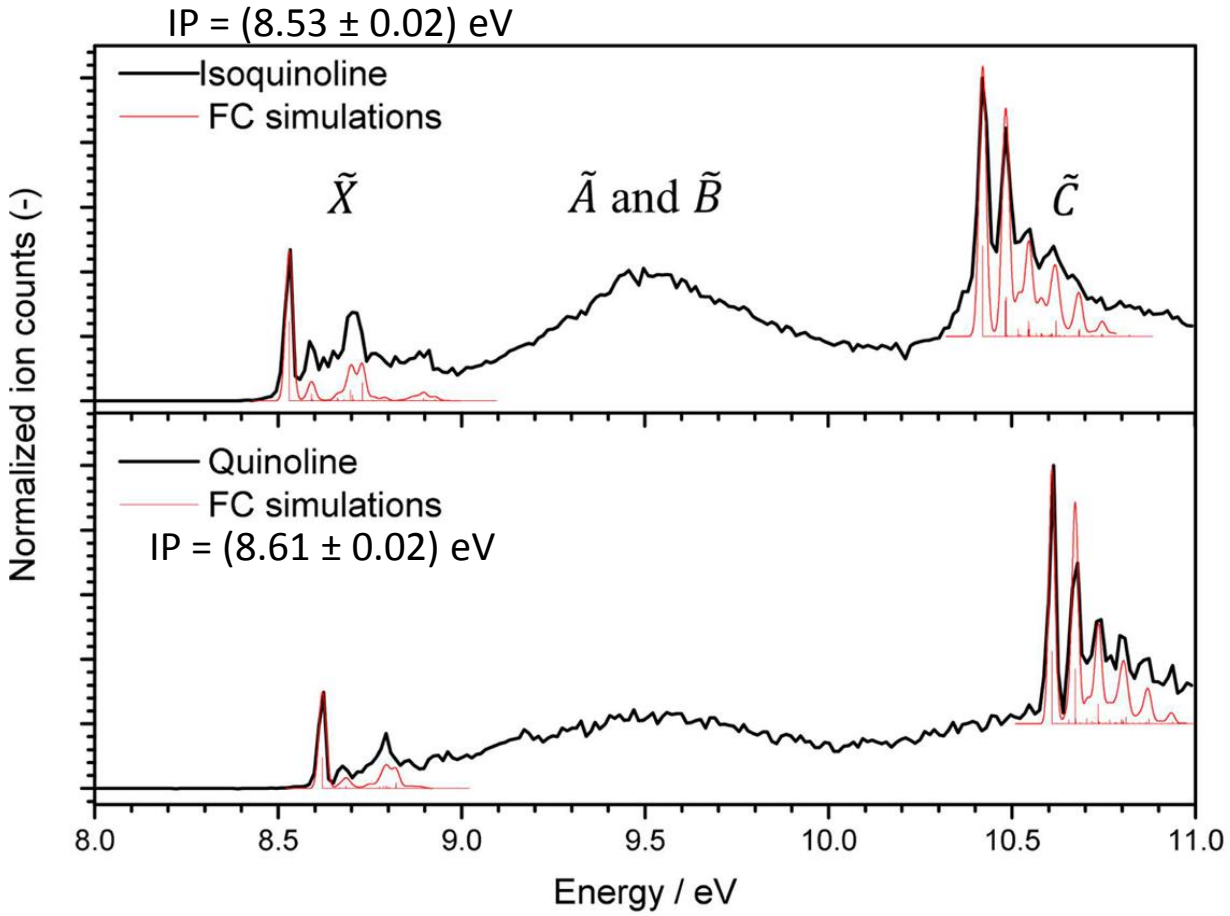


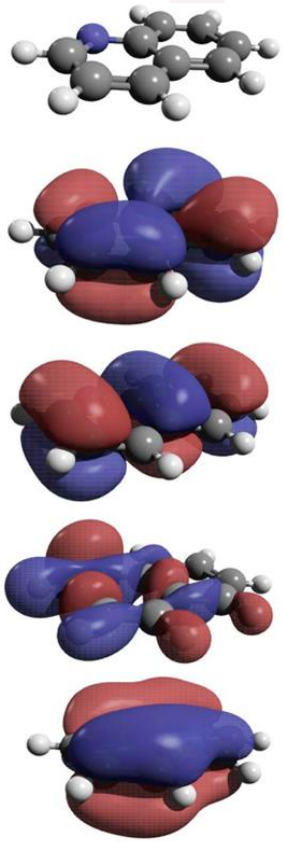
Isoquinoline



Bodi *et al. Rev. Sci. Instrum.* **80**, 034101, 2009

Threshold Photoelectron Spectra





HOMO (A″)

HOMO–1 (A″)

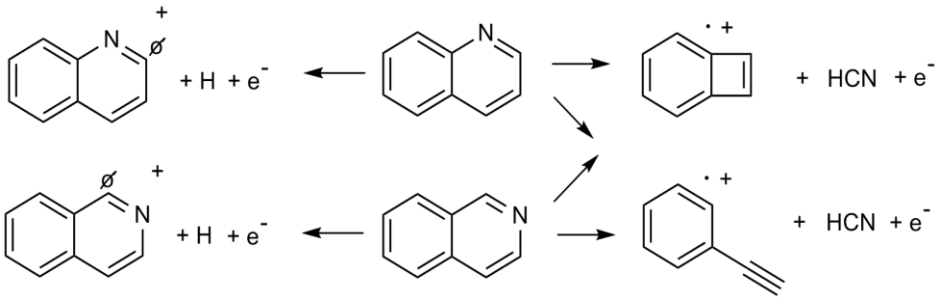
HOMO–2 (A′)

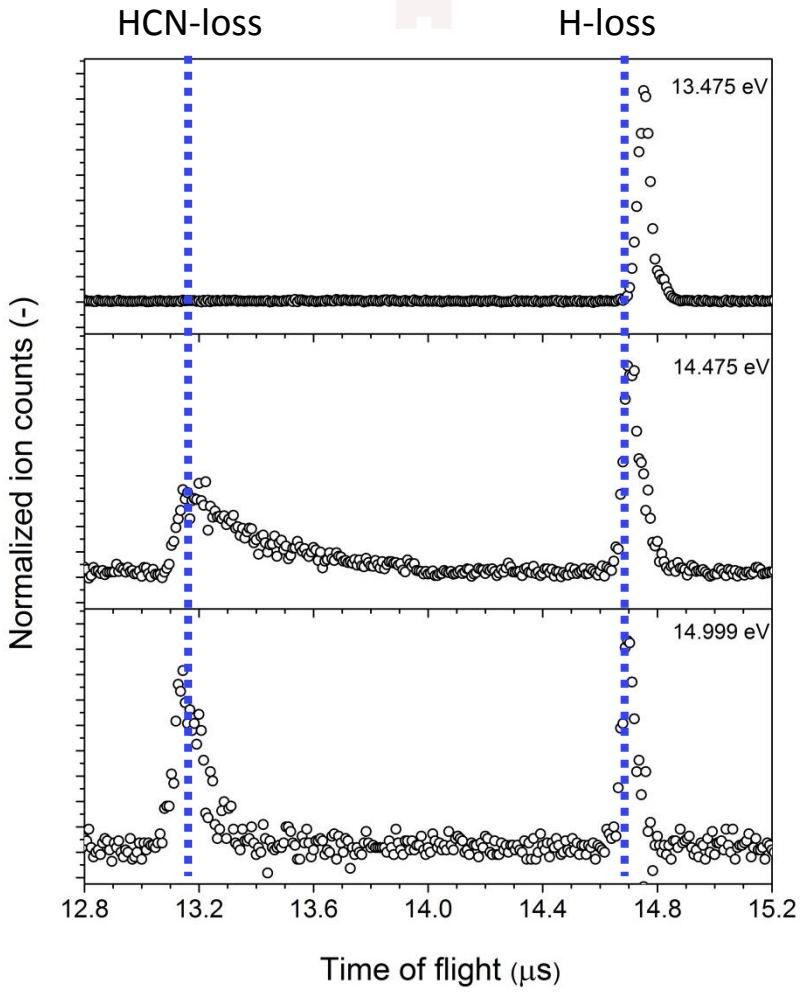
HOMO–3 (A″)

Franck-Condon simulations using “ezSpectrum”

Bouwman *et al. J. Phys. Chem. A.* accepted 2015

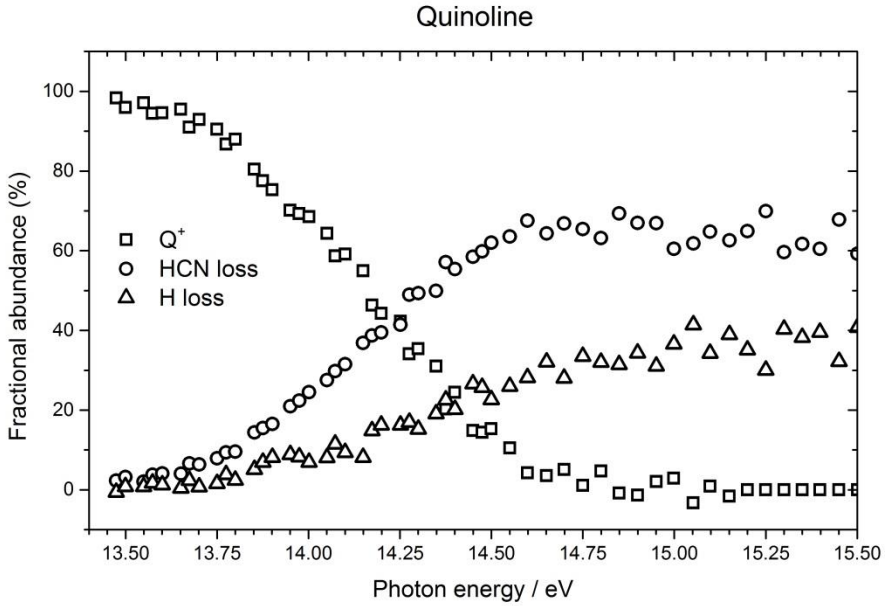
Mass Spectra

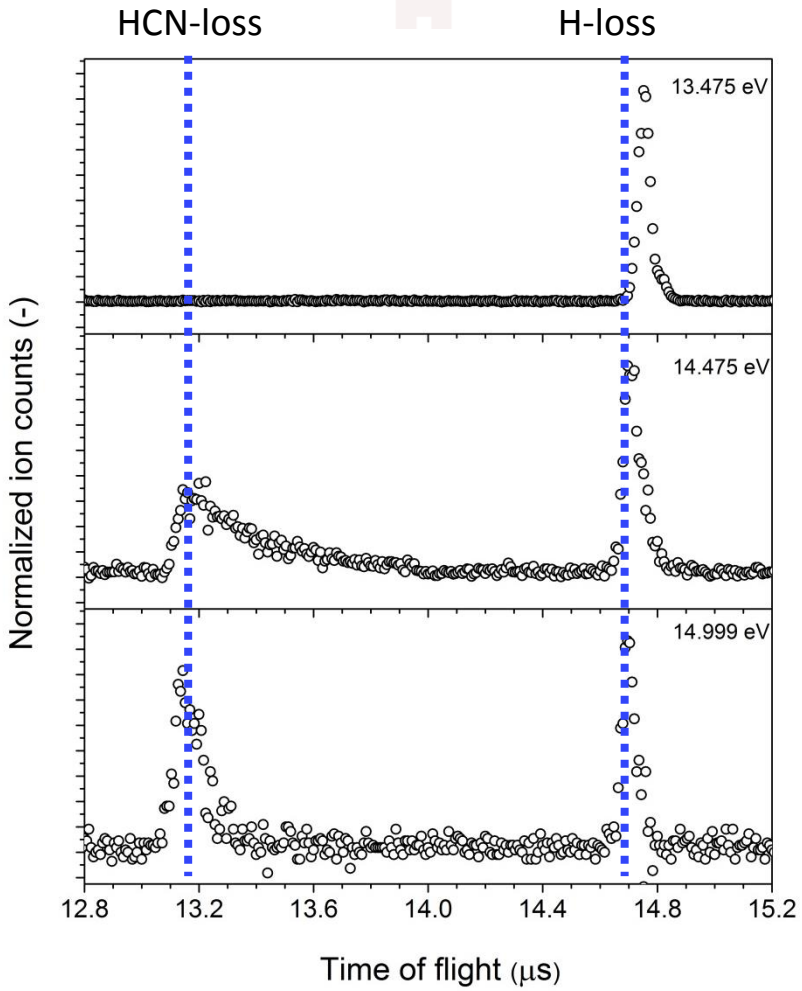




Bouwman *et al. J. Phys. Chem. A.* accepted 2015

Breakdown Diagram



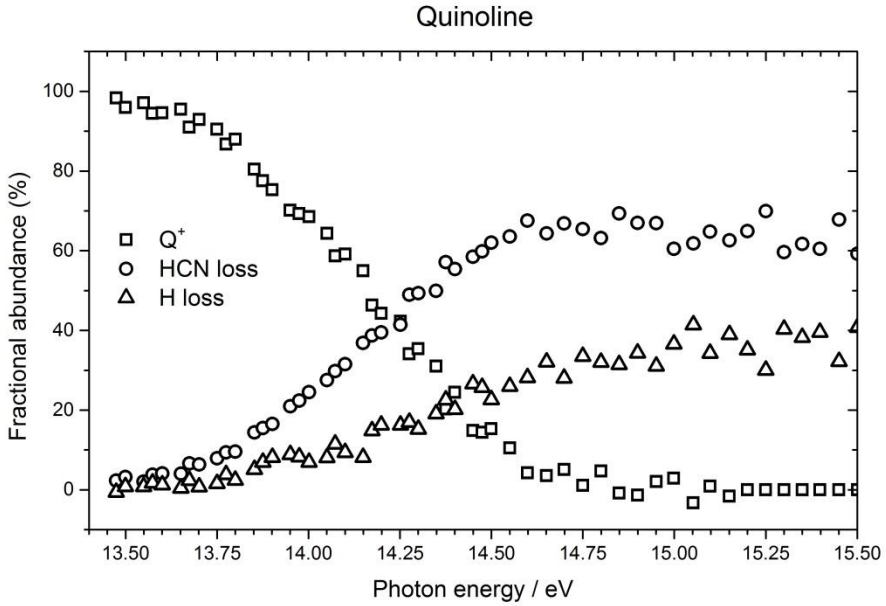


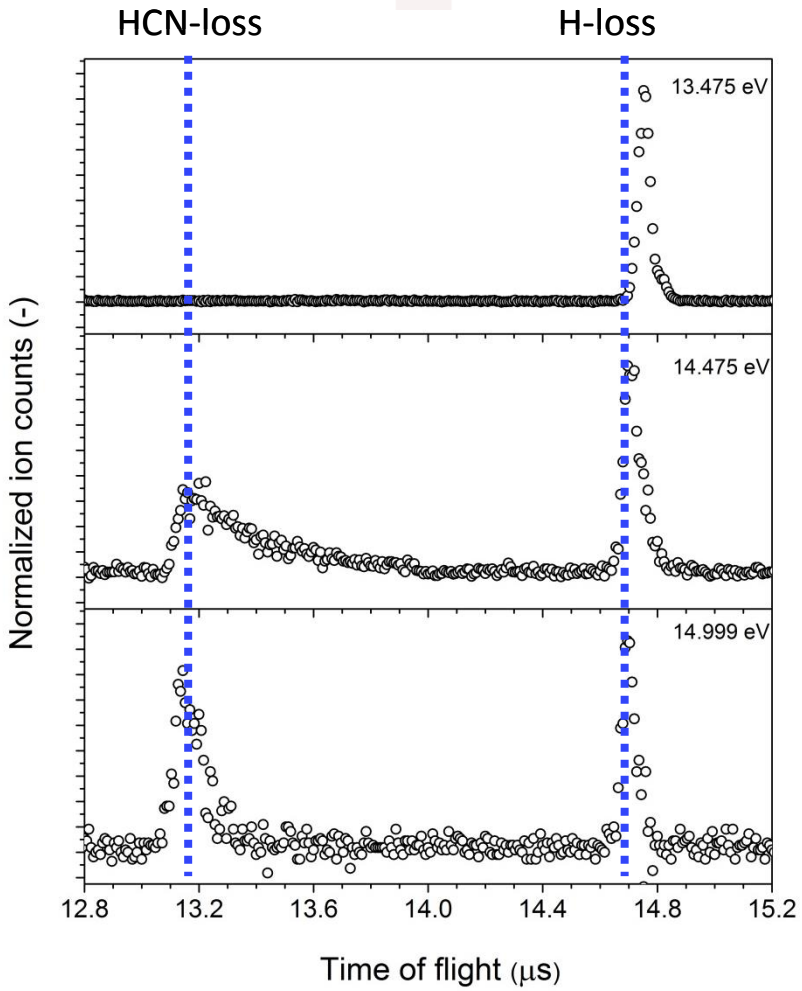
Bouwman *et al. J. Phys. Chem. A.* accepted 2015

Appearance Energies

- RRKM model fit: $$k(E) = \frac{1}{h}\frac{G(E^{\ddagger})}{N(E_v)}$$

Sztaray *et al. J. Mass Spectrom.* **45**, 1233, 2010



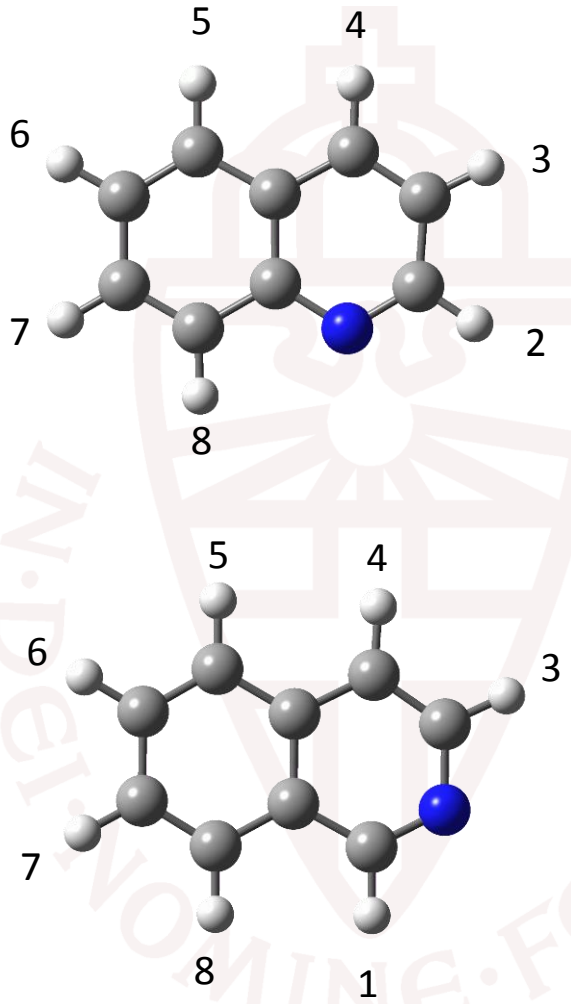


Bouwman *et al. J. Phys. Chem. A.* accepted 2015

Hydrogen Loss Channel

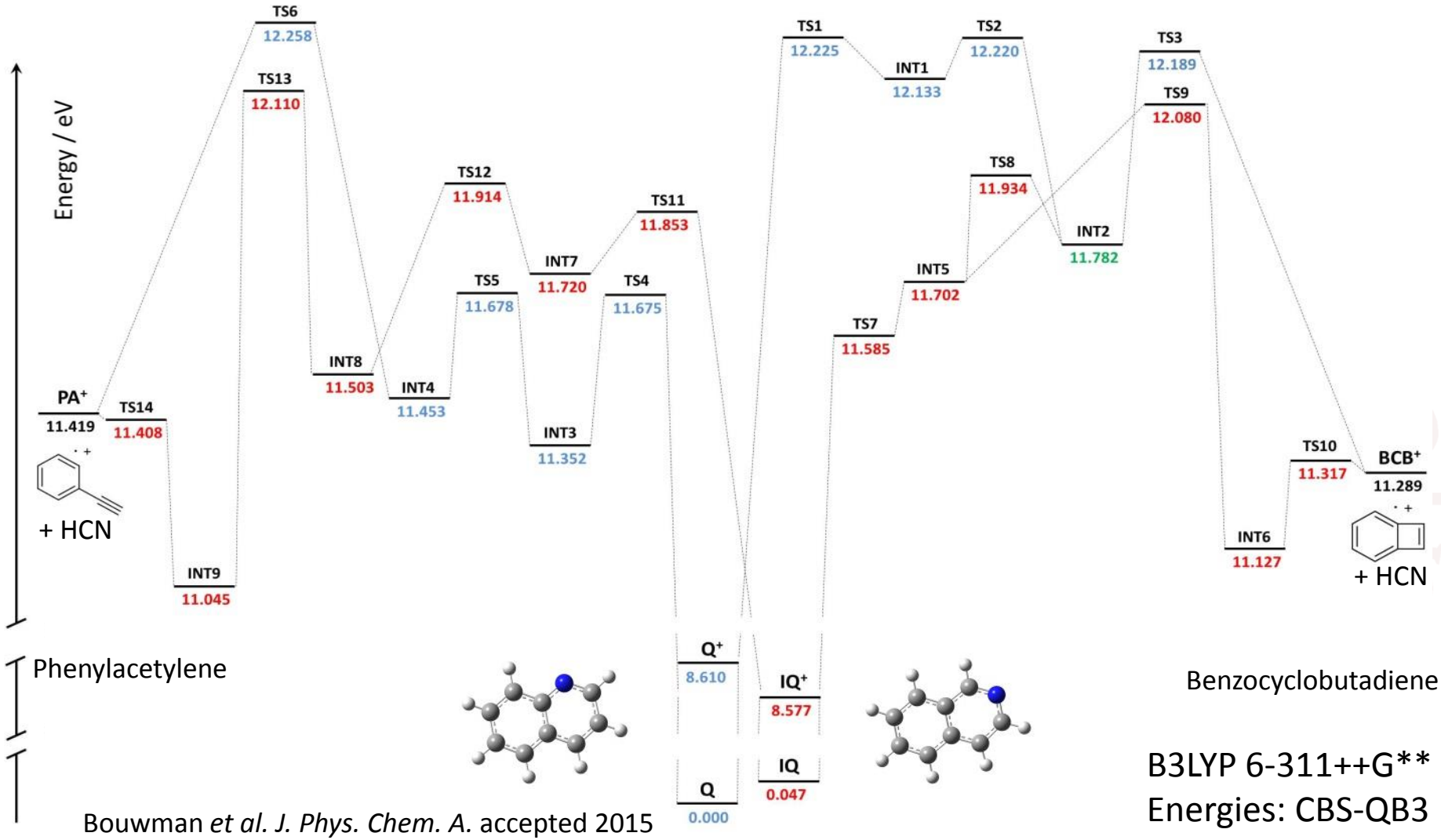
Q	E_0 / eV	IQ	E_0 / eV
H2	11.914	H1	11.903
H3	12.819	H3	12.126
H4	12.888	H4	12.728
H5	12.870	H5	13.209
H6	13.099	H6	13.209
H7	13.024	H7	13.164
H8	13.115	H8	13.208

Energies calculated using CBS-QB3



Bouwman *et al. J. Phys. Chem. A.* accepted 2015

$C_9H_7N^+$ Potential Energy Surface



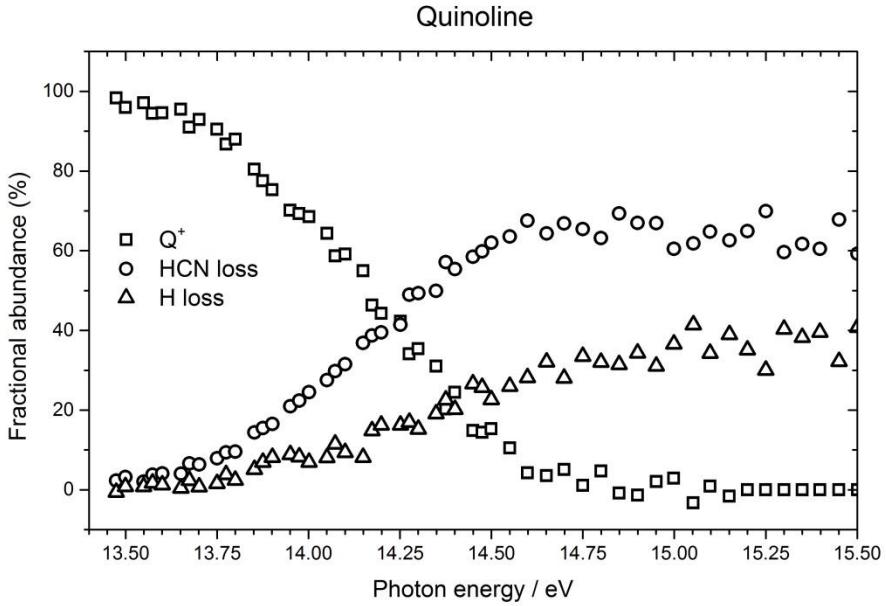
Bouwman *et al. J. Phys. Chem. A.* accepted 2015

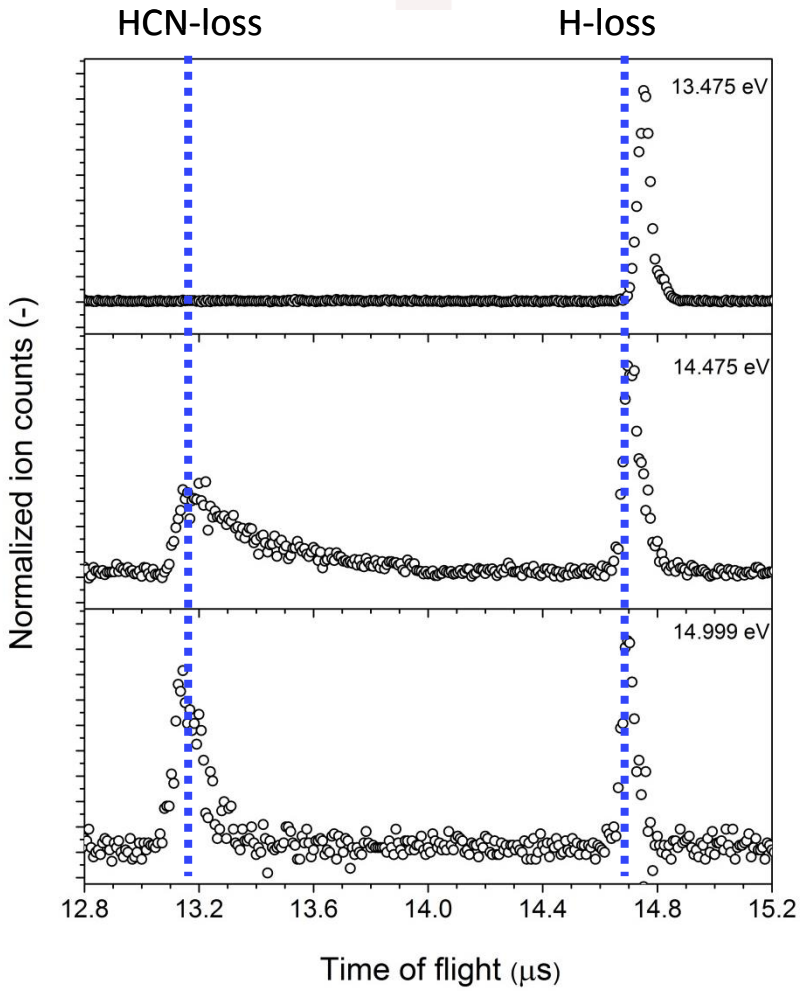
B3LYP 6-311++G**
Energies: CBS-QB3

Appearance Energies

- RRKM model fit: $$k(E) = \frac{1}{h}\frac{G(E^{\ddagger})}{N(E_v)}$$

Sztaray *et al. J. Mass Spectrom.* **45**, 1233, 2010





Bouwman *et al. J. Phys. Chem. A.* accepted 2015

Appearance Energies

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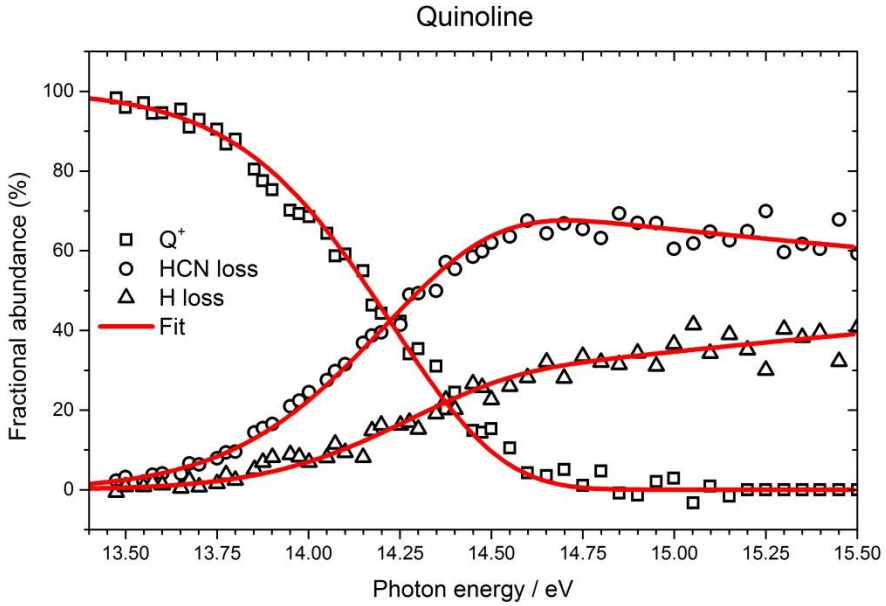
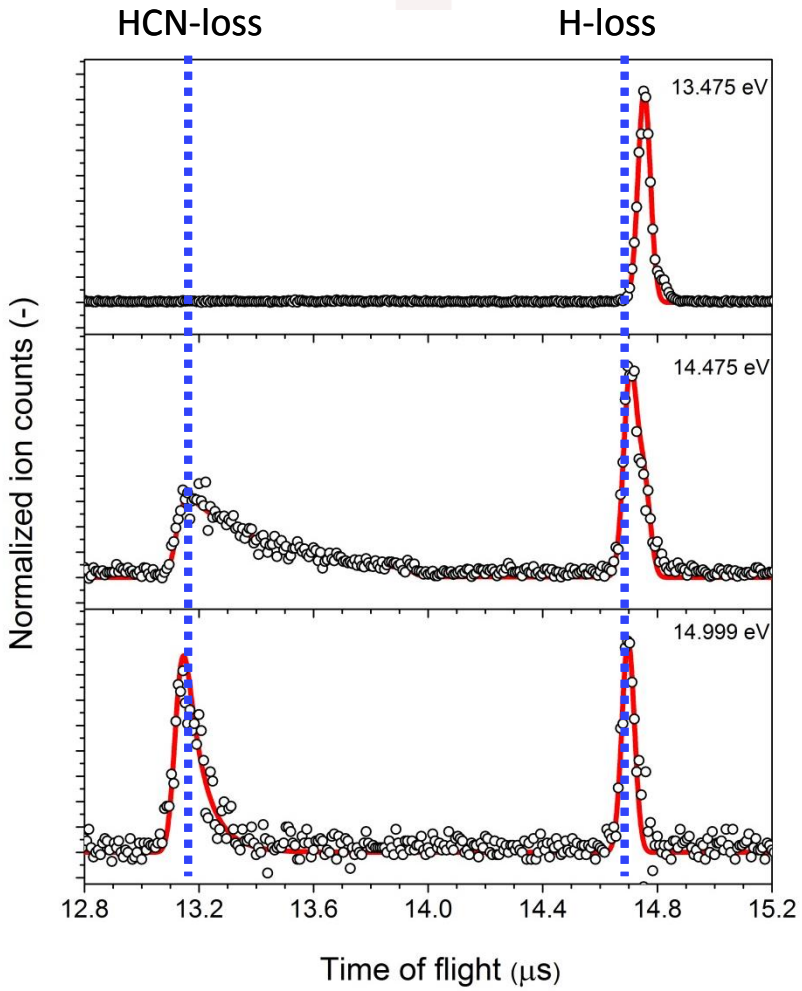
Sztaray *et al. J. Mass Spectrom.* **45**, 1233, 2010





Bouwman *et al. J. Phys. Chem. A.* accepted 2015

Appearance Energies

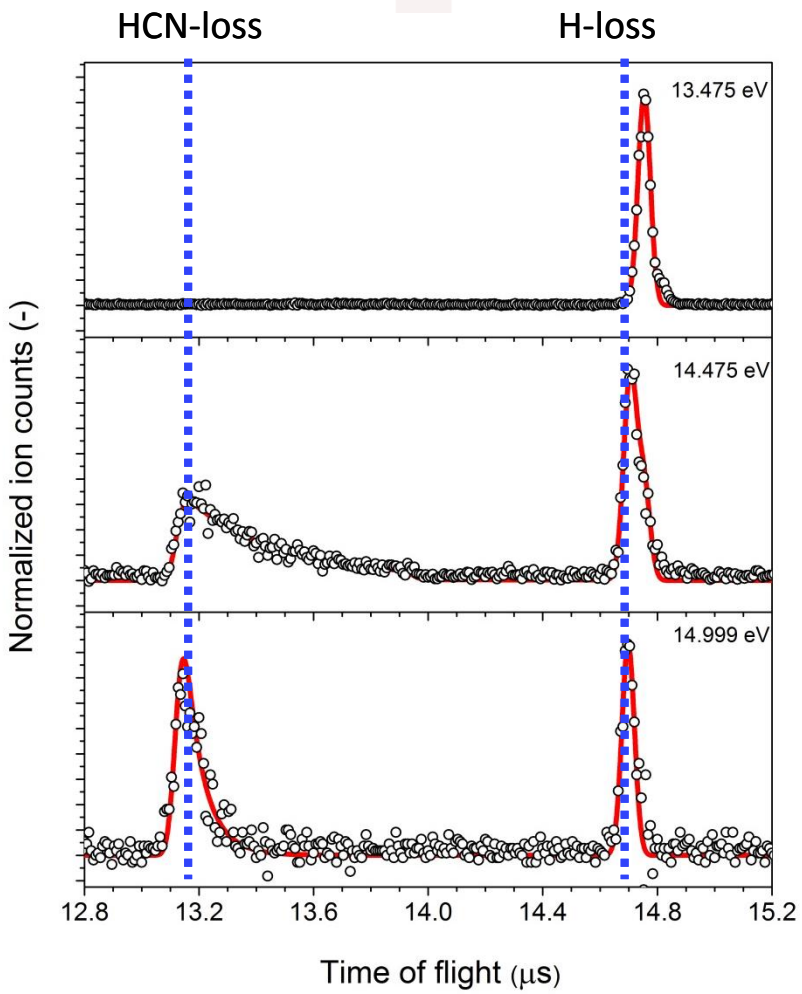
- RRKM model fit: $$k(E) = \frac{1}{h}\frac{G(E^{\ddagger})}{N(E_v)}$$

Sztaray *et al. J. Mass Spectrom.* **45**, 1233, 2010

- Appearance energies

Channel	Quinoline	Isoquinoline
HCN-loss	11.9 ± 0.1	11.6 ± 0.1
H-loss	12.0 ± 0.1	12.1 ± 0.1

Energies in eV



Bouwman *et al. J. Phys. Chem. A.* accepted 2015

Conclusions

- Main dissociation pathway <15 eV is HCN-loss (~60%)
- Appearance energies (AE in eV) for HCN and H-loss:

Channel	Quinoline	Isoquinoline
HCN-loss	11.9 ± 0.1	11.6 ± 0.1
H-loss	12.0 ± 0.1	12.1 ± 0.1

- C_2H_2 loss from naphthalene (AE = 12.26 eV)

West *et al. J. Phys. Chem. A* **118**, 7824-7831, 2014

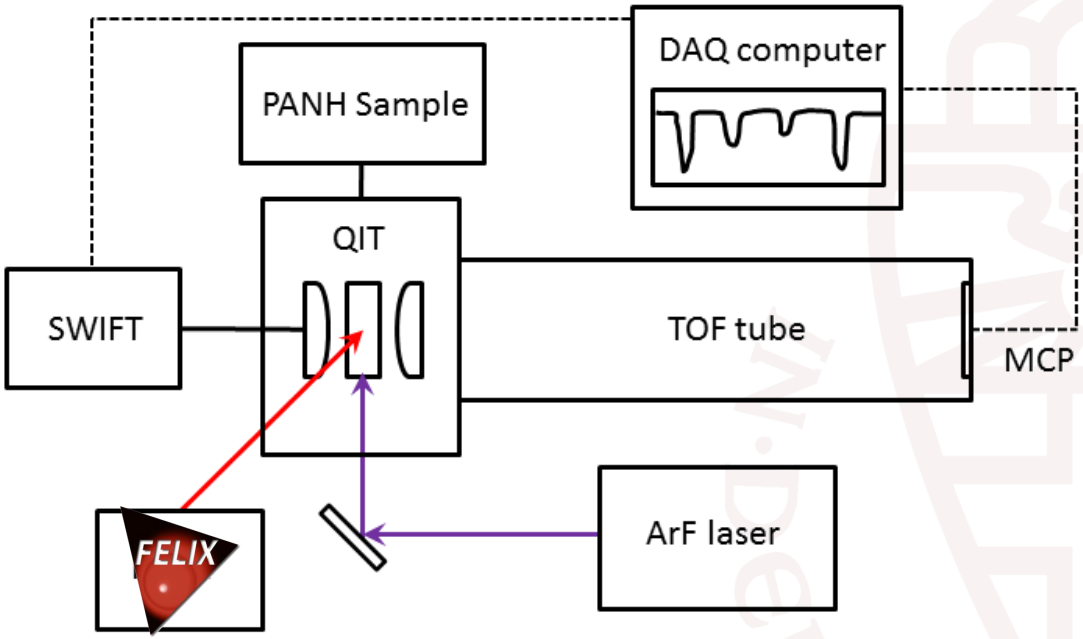
- Reverse: Large barrier for the addition of HCN to $PA^{\bullet+}$ / $BCB^{\bullet+}$

Hamid *et al. Chem. Phys. Lett.* **543**, 23-27, 2012

- No unambiguous identification of product species ($PA^{\bullet+}$ / $BCB^{\bullet+}$)

Outlook: Structural Information

- Structural determination using IRMPD @ FELIX



- Isomer specific detection of photodissociation products

- Isomer specific detection of ion-neutral reaction products

Acknowledgement

Funding:

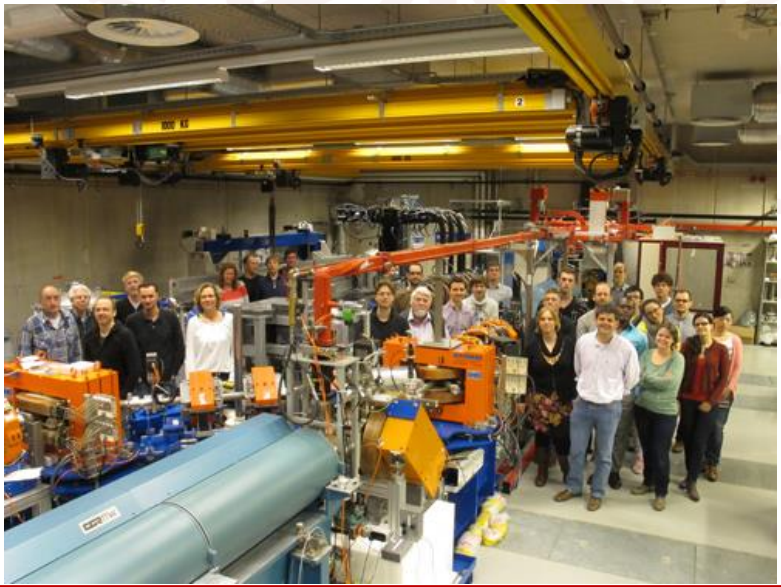
Veni

MSD and FELIX:

Jos Oomens

Collaborations:

Andras Bodi
Patrick Hemberger



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