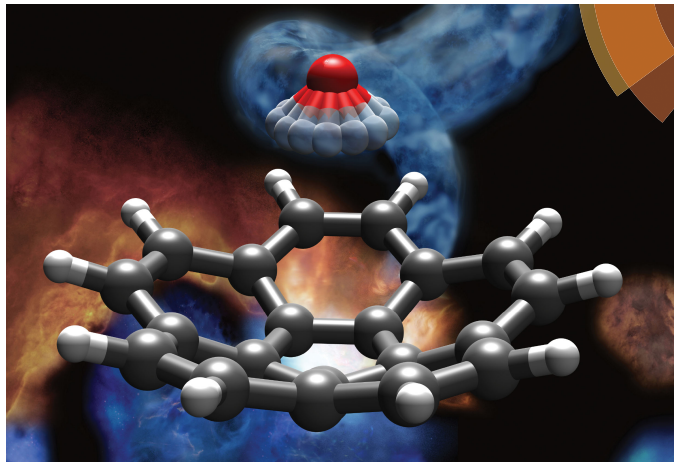
A multi-spectroscopic approach to reveal the astrochemistry of polycyclic aromatic hydrocarbons

ISMS mini-symposium: Spectroscopy at large-scale facilities

Melanie Schnell

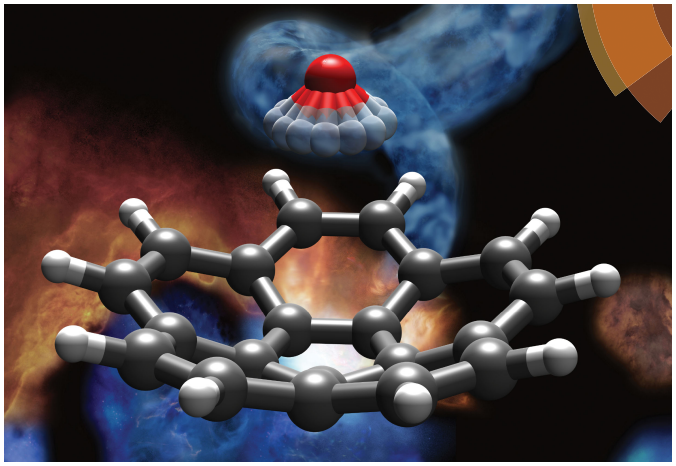


HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

C A U

DESY.

Melanie Schnell



HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

C | A | U

DESY.

Astrochemistry

- Chemistry under extreme conditions: low temperatures, low densities, and **harsh radiation**
- Rich chemistry (more than 280 molecules so far, including **chiral and aromatic** ones).

Astrochemistry and PAHs

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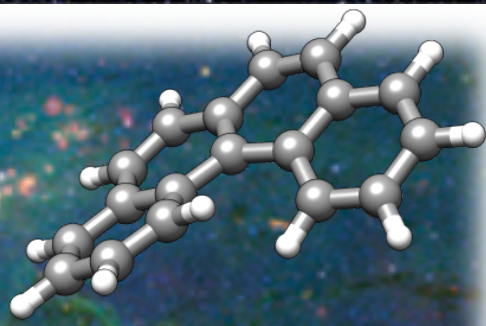
Polycyclic aromatic hydrocarbons: abundances



Green: emission from PAH molecules (Image taken by Spitzer looking towards the plane of the Milky Way)

- present in many extreme chemical environments:
  combustion, atmosphere, interstellar medium, also in charged states
- an estimated 10-20% of the total galactic carbon is locked in PAHs
- “relatives” of fullerenes

Astrochemistry and PAHs

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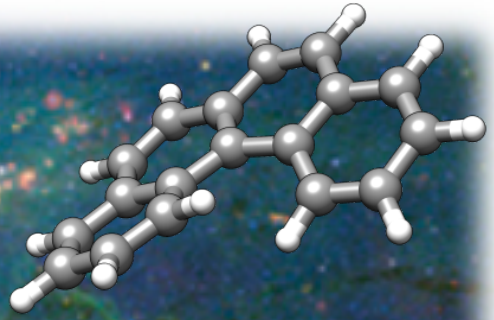
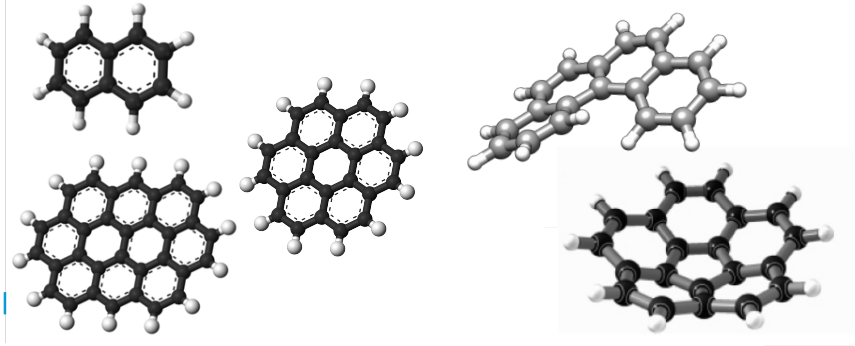
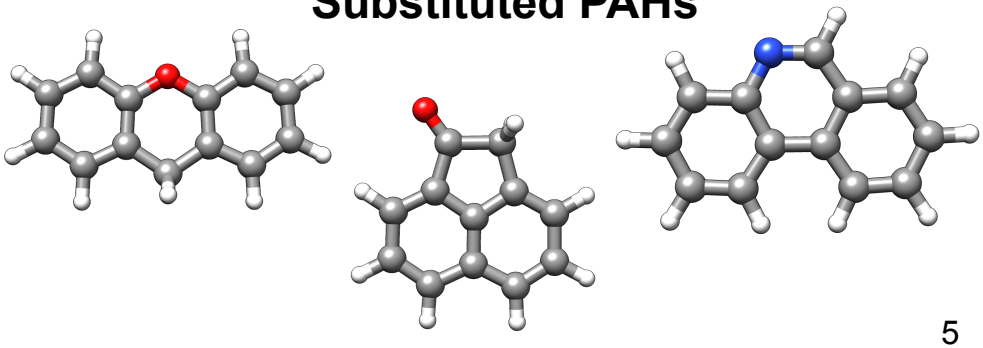


Green: emission from PAH molecules (Image taken by Spitzer looking towards the plane of the Milky Way)

Planar, curved, and helical PAHs

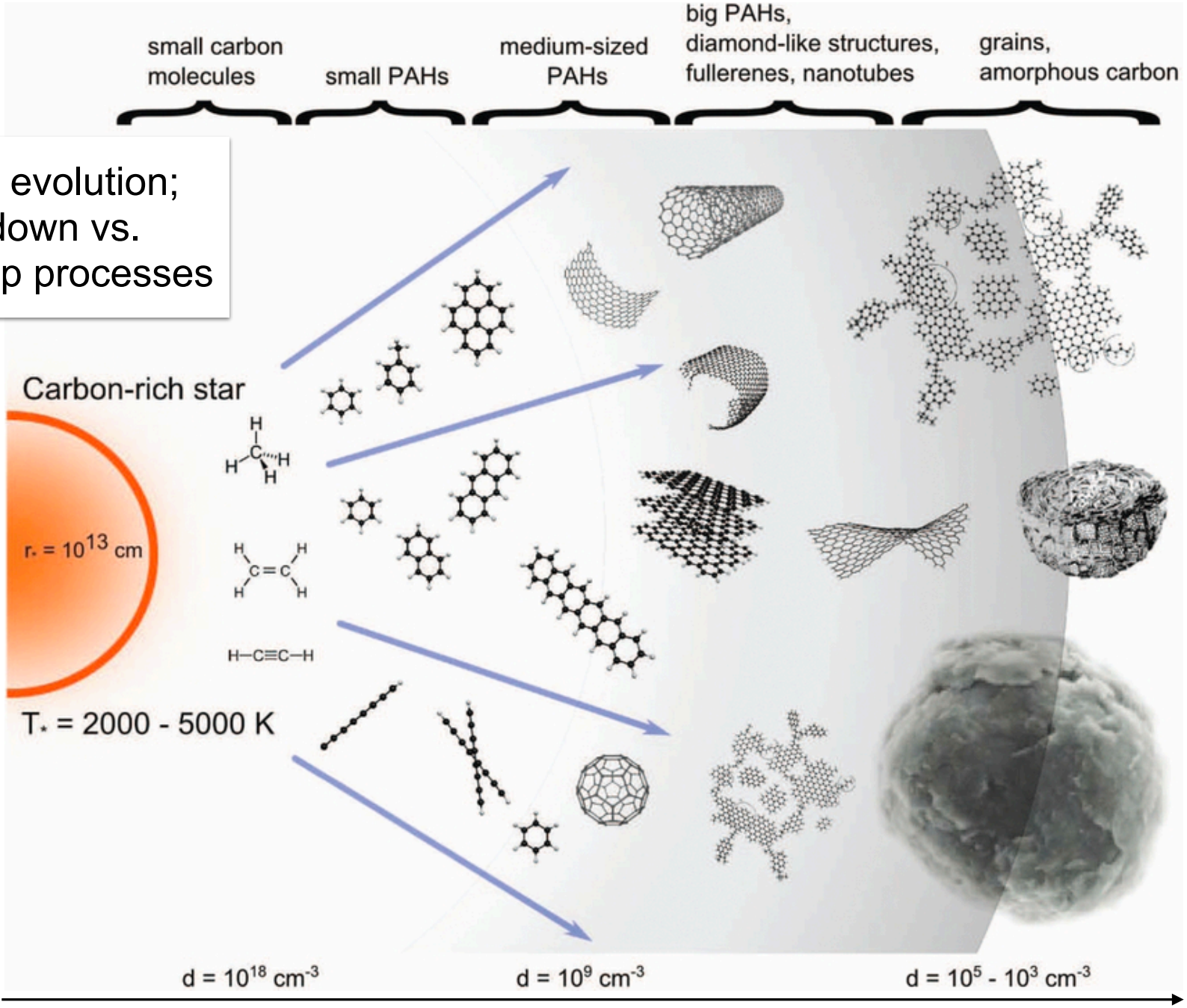


Substituted PAHs



Grains, fullerenes, and polycyclic aromatic hydrocarbons (PAHs)

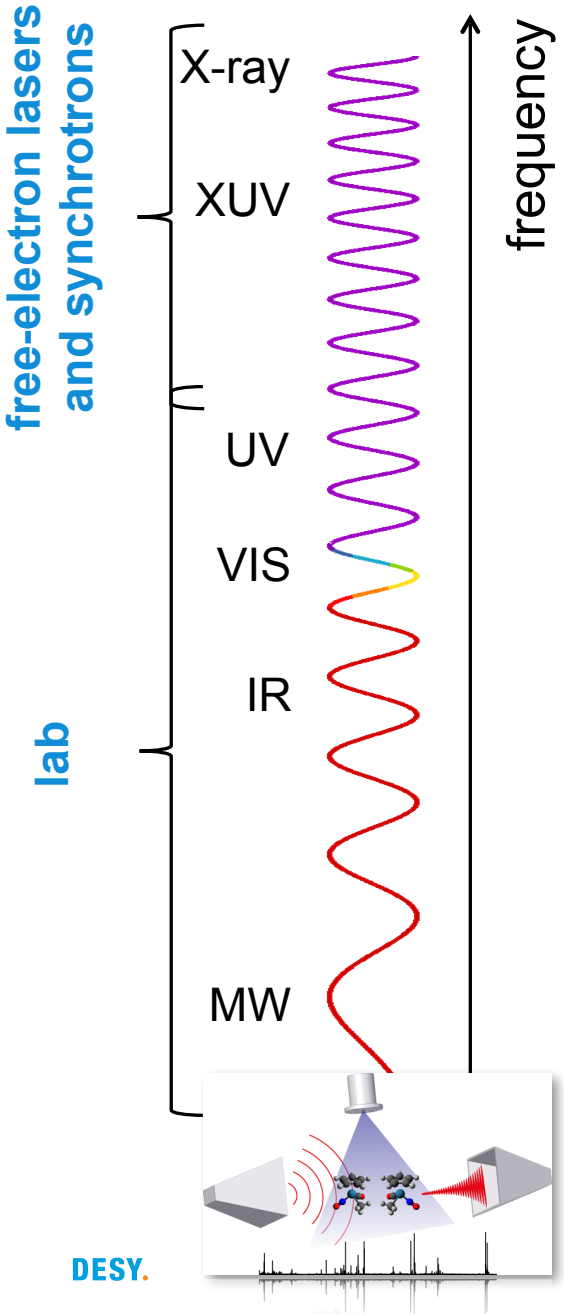
carbon evolution;
top-down vs.
bottom-up processes



Adapted from Pascoli & Pollux (2000)

Unraveling the role of PAHs in astrochemistry

A multi-spectroscopic approach



Response to harsh radiation; extreme states of matter

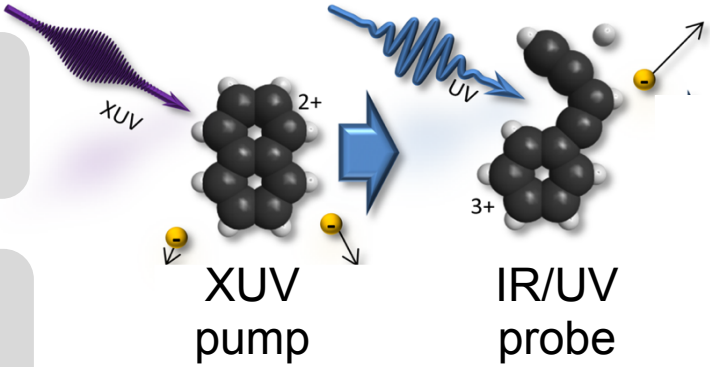
Photochemistry
Bottom-up vs. top-down

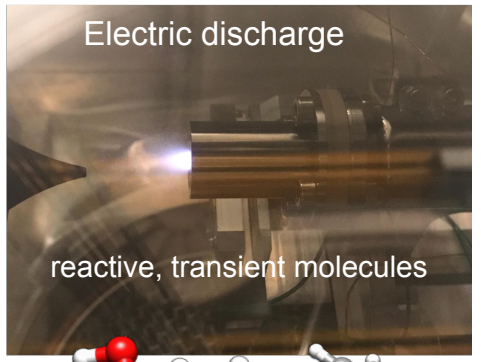
“Exotic” PAHs

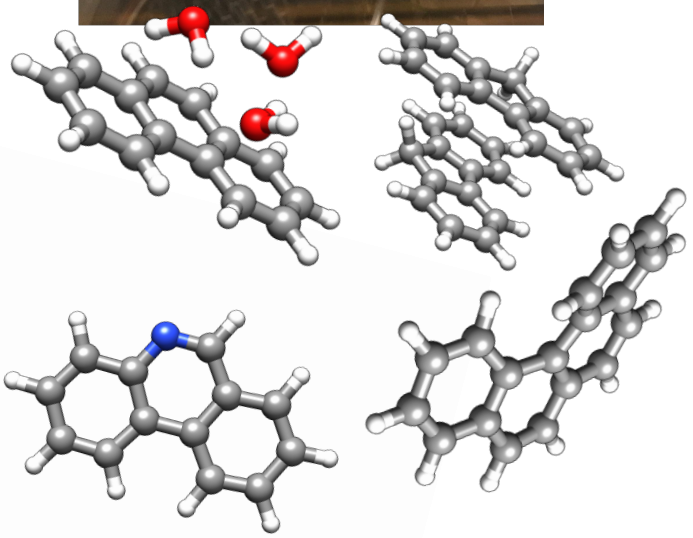
Complexes;
Role in grain formation

Molecular fingerprints

Structures







Unraveling the role of PAHs in astrochemistry

A multi-spectroscopic approach

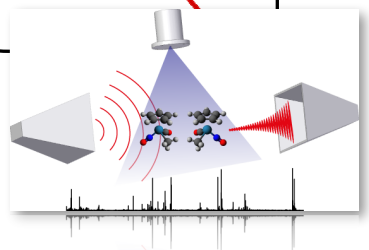
free-electron lasers and synchrotrons

X-ray
XUV
UV
VIS
IR
MW

frequency

lab

FELIX Free Electron Lasers for Infrared eXperiments



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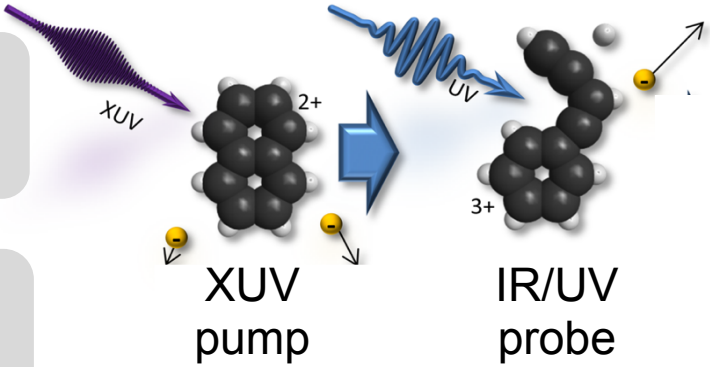

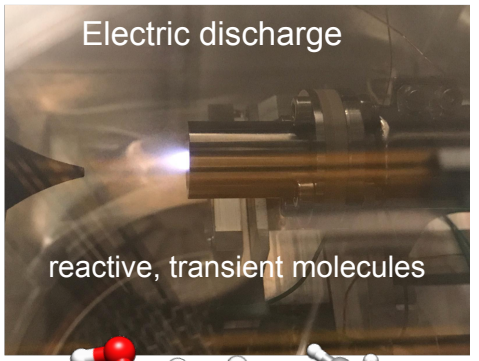

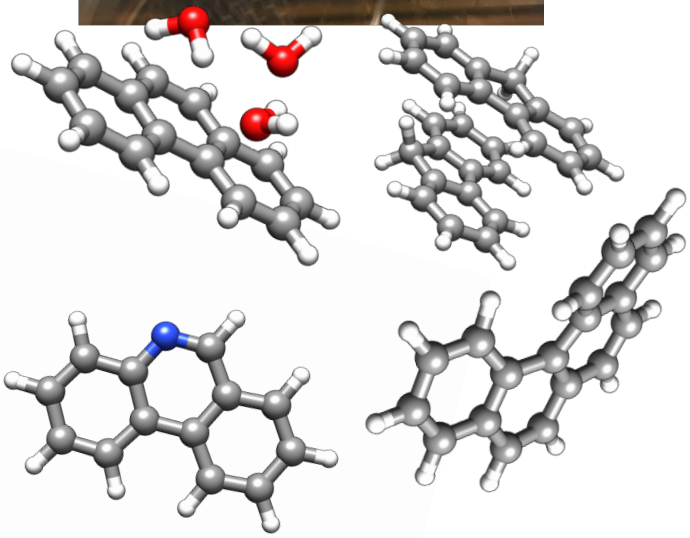

Unraveling the role of PAHs in astrochemistry

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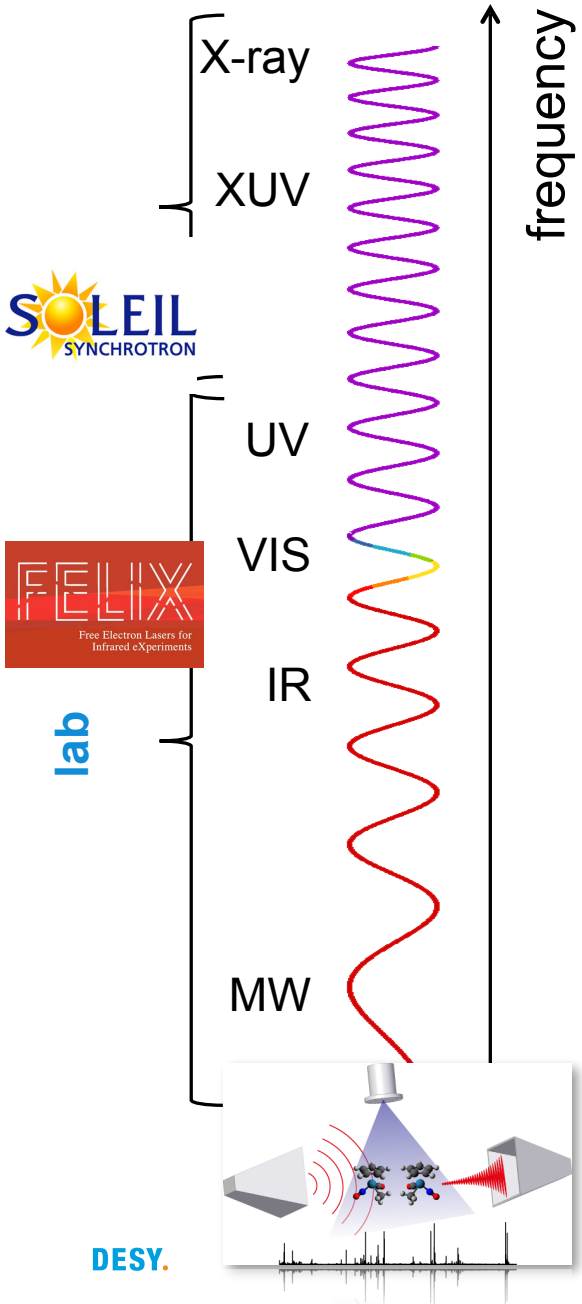

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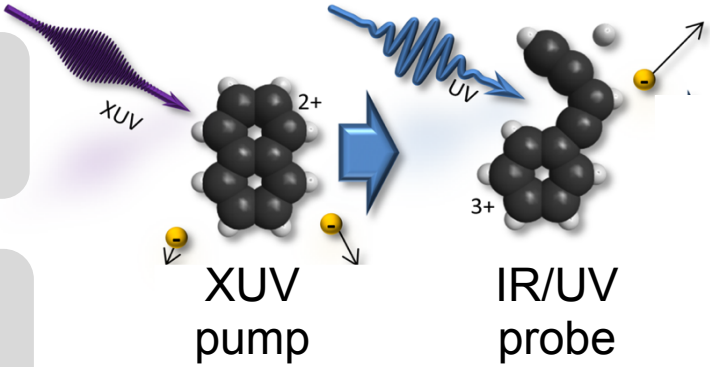

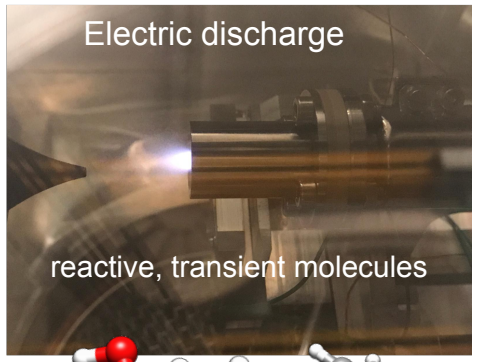

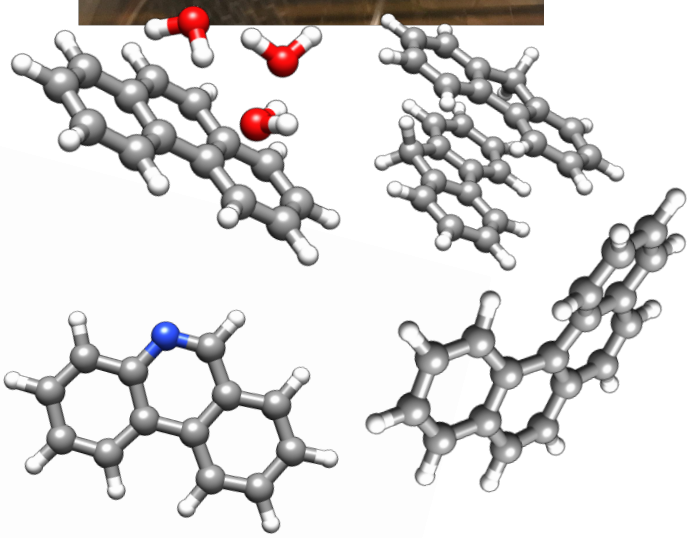

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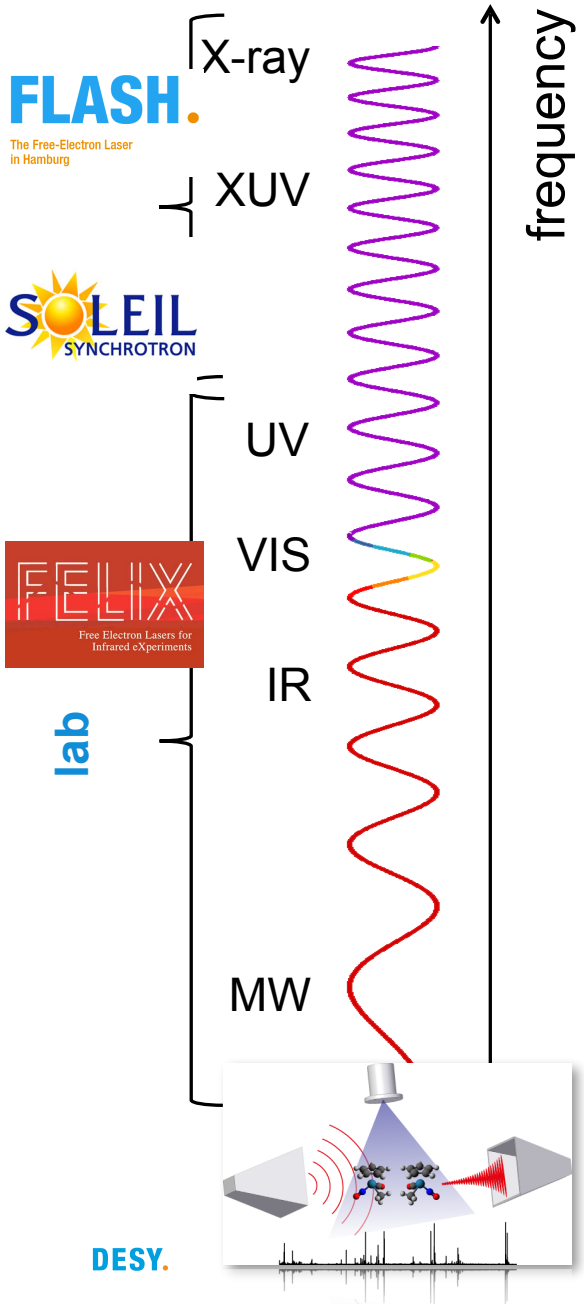

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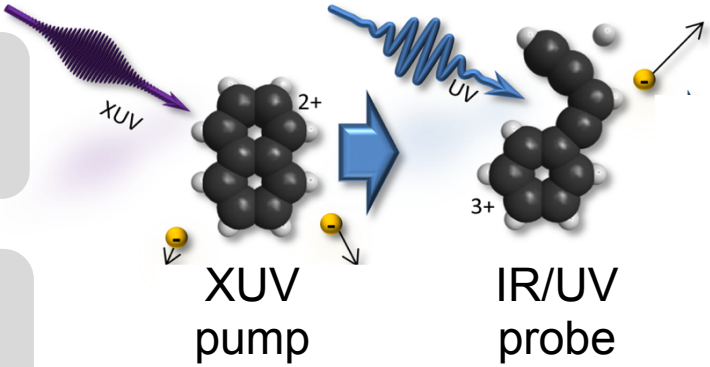
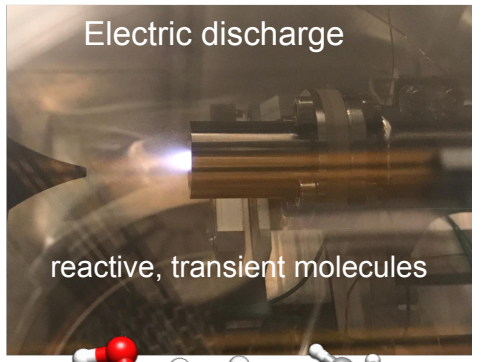
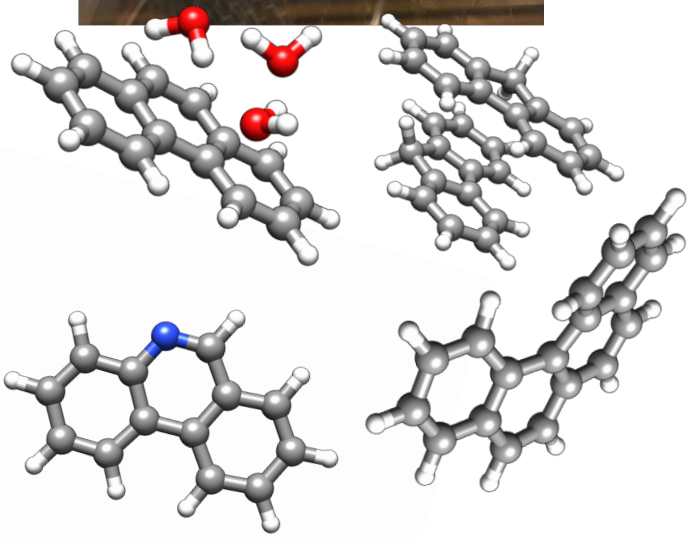




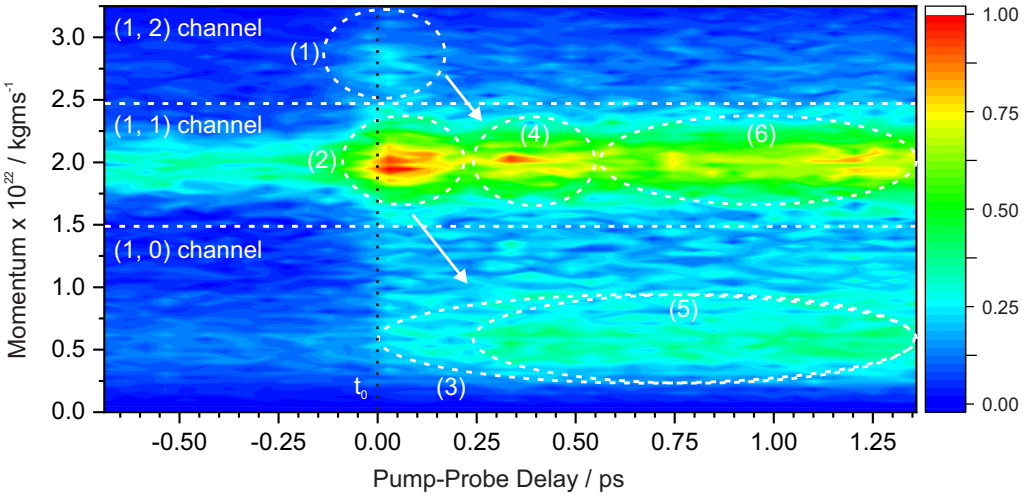


Outline

- **IR-UV ion-dip spectroscopy @ FELIX**
  - PAH growth (and other processes) in a plasma (and a comparison with CP-FTMW measurements)
  - IR fingerprints of PAH clusters

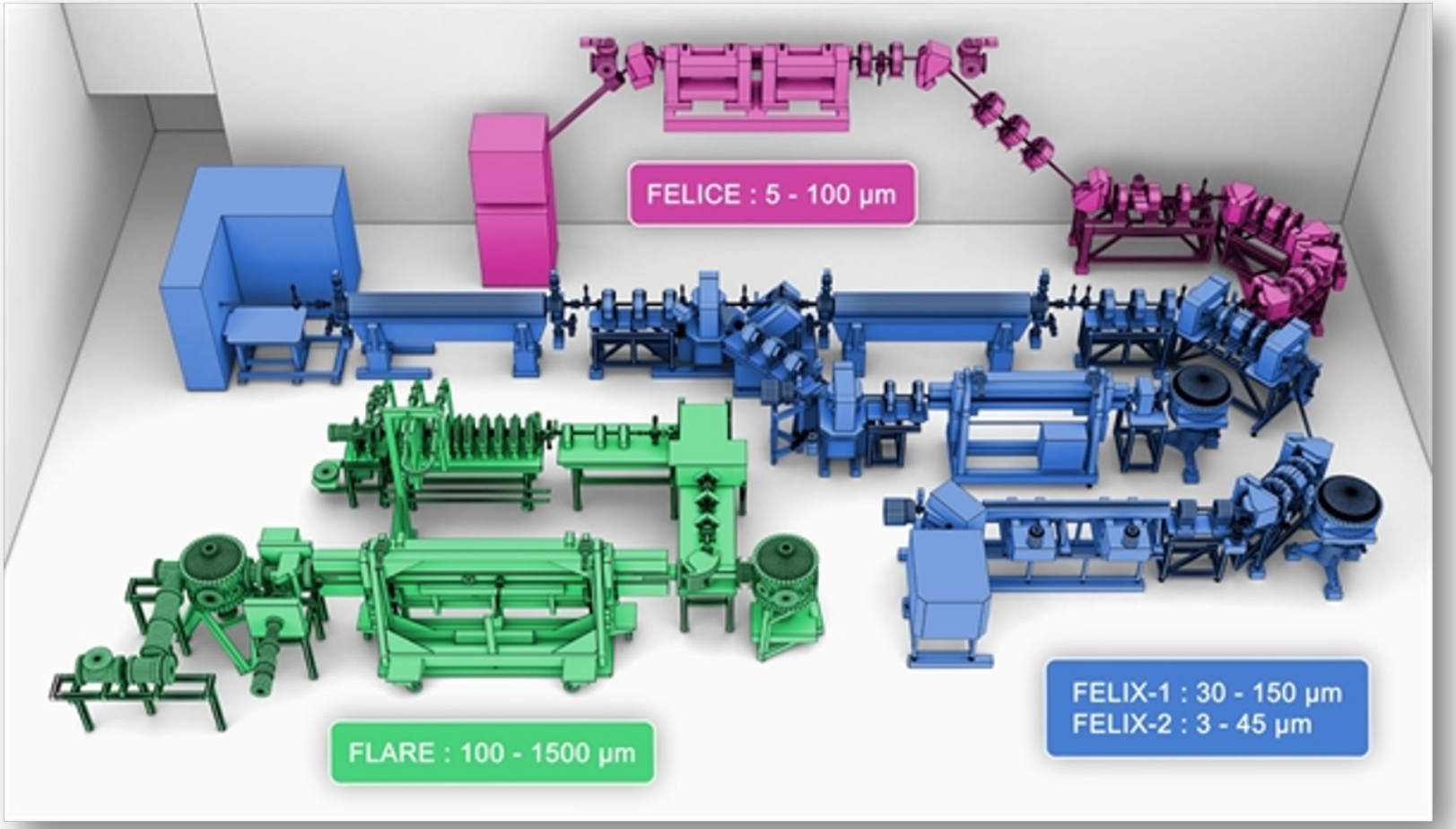
- Time-resolved pump-probe experiments using FLASH
  - interplay between ionisation & fragmentation of PAHs
  - life times of electronically excited states in different charge states

- Conclusions



FELIX

Free-Electron Laser for Infrared eXperiments at the Radboud U Nijmegen



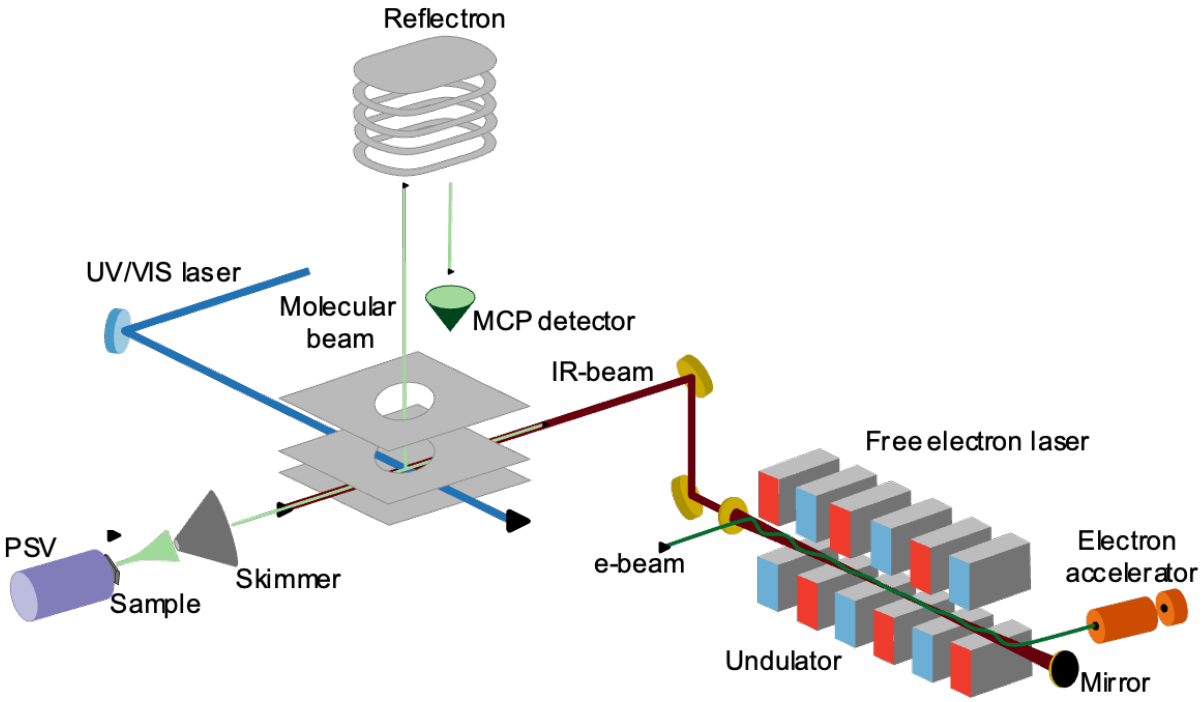
- Four lasers:
  - FELIX-1
  - FELIX-2
  - FLARE
  - FELICE
- Tuning range:

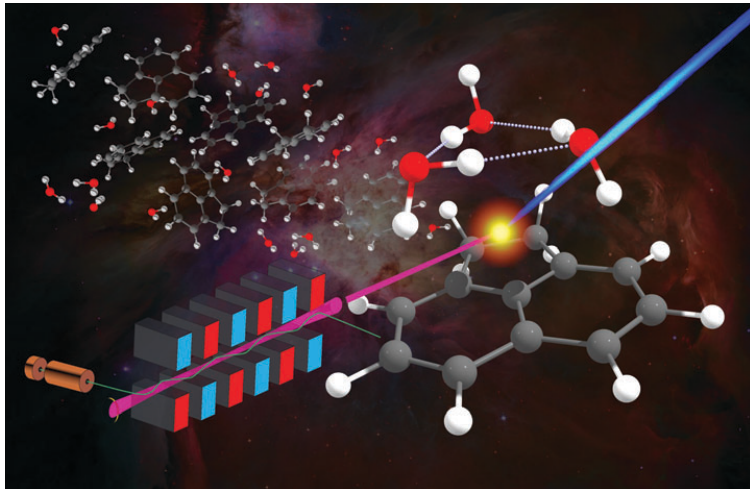
  6 – 3600 cm^{-1}

- IR-UV double-resonance experiments
- fingerprint region

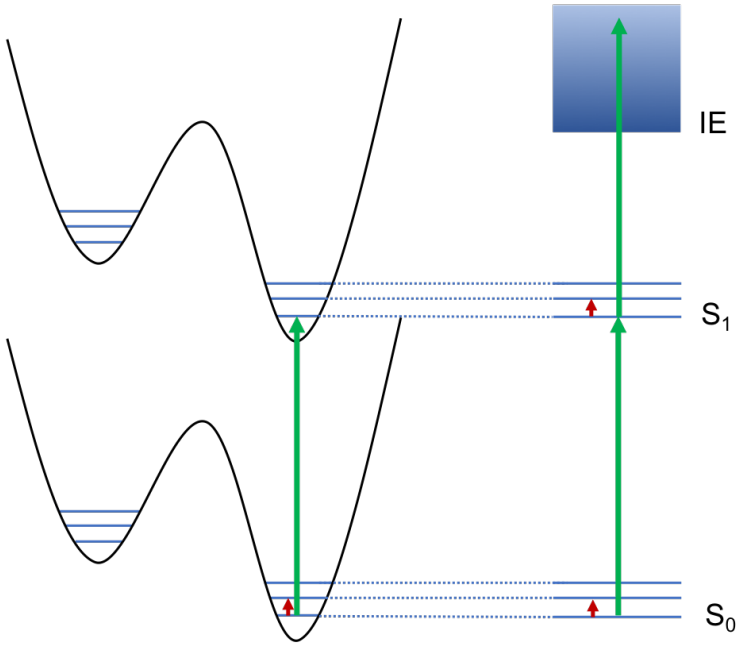
in collaboration with A. Lemmens, P. Ferrari, A. Rijs, B. Redlich

IR-UV ion-dip spectroscopy at FELIX

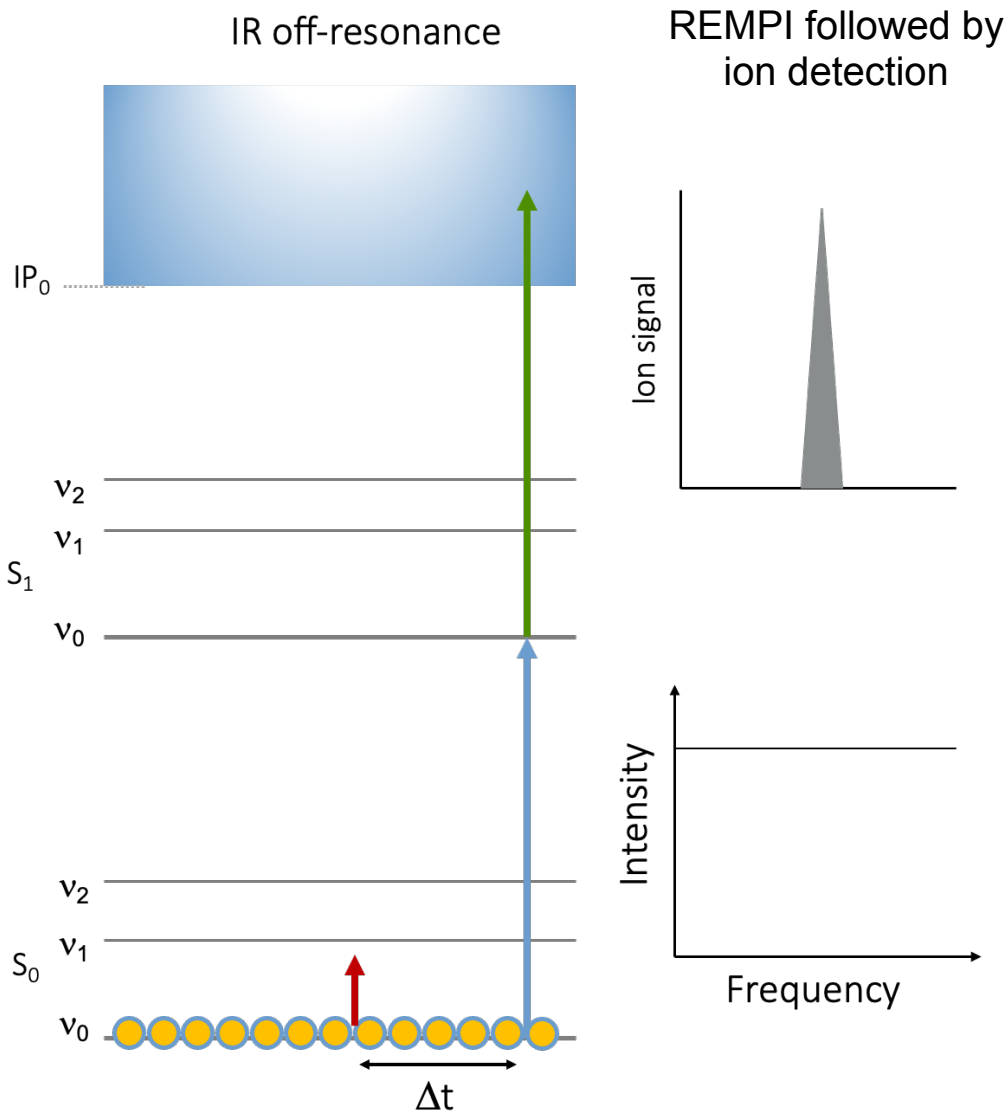




Resonance-enhanced multi-photon ionisation (REMPI)



IR-UV ion-dip spectroscopy at FELIX



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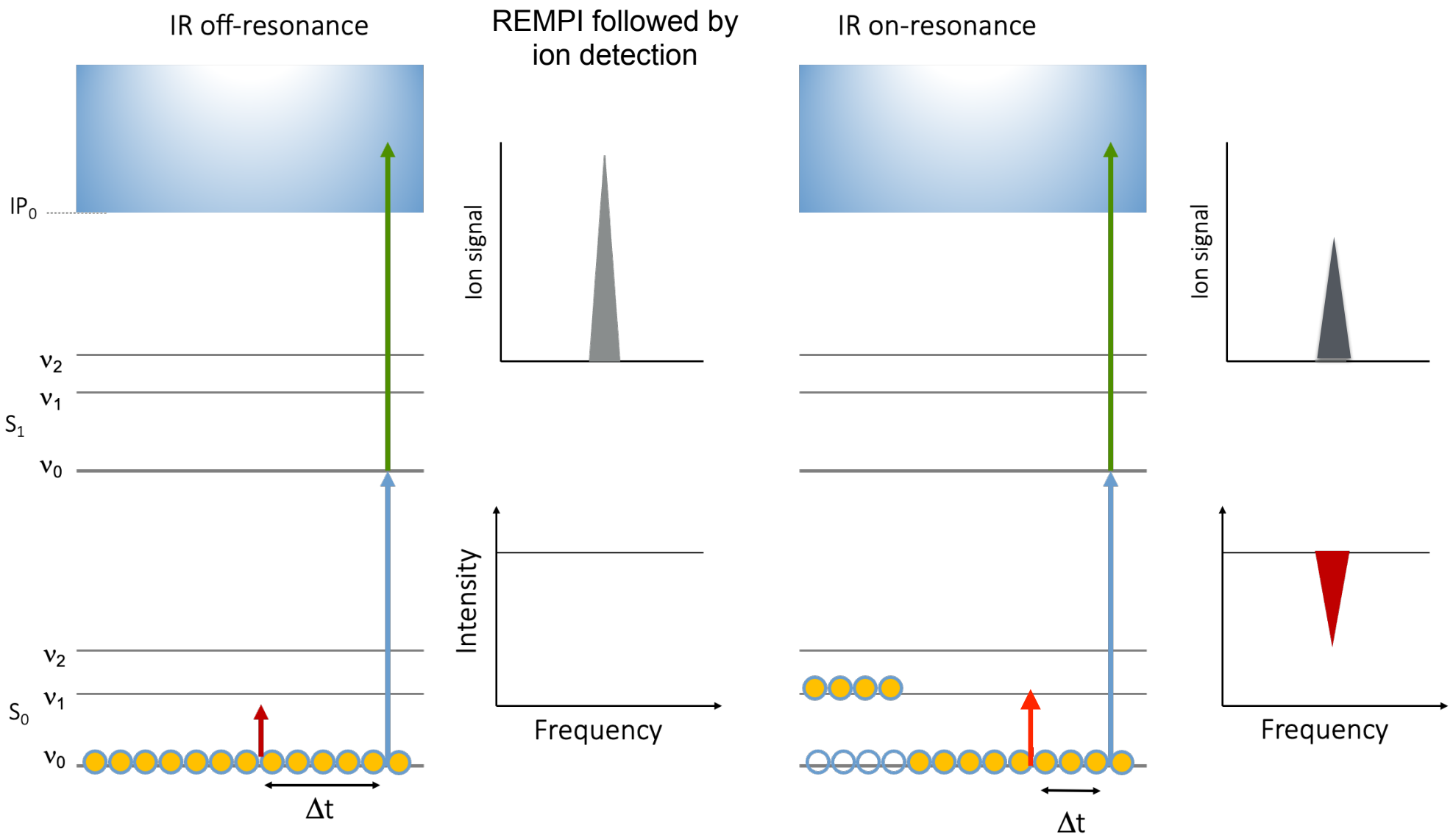


IR-UV ion-dip spectroscopy at FELIX

Experimental conditions

T = 135 °C

Ar @ 5 bar

U = 0.5-0.6 kV

[1 + 1'] REMPI

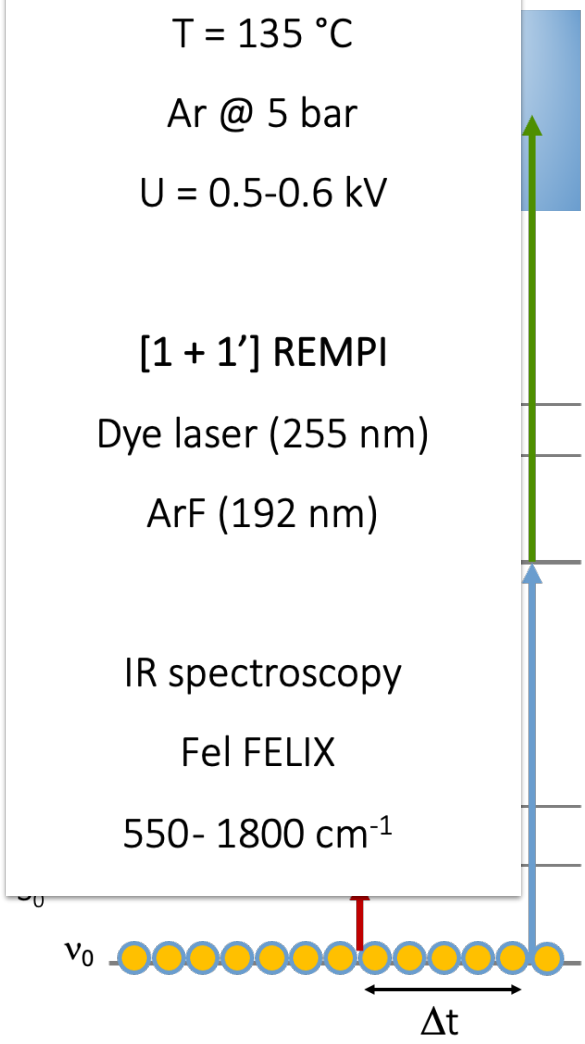
Dye laser (255 nm)

ArF (192 nm)

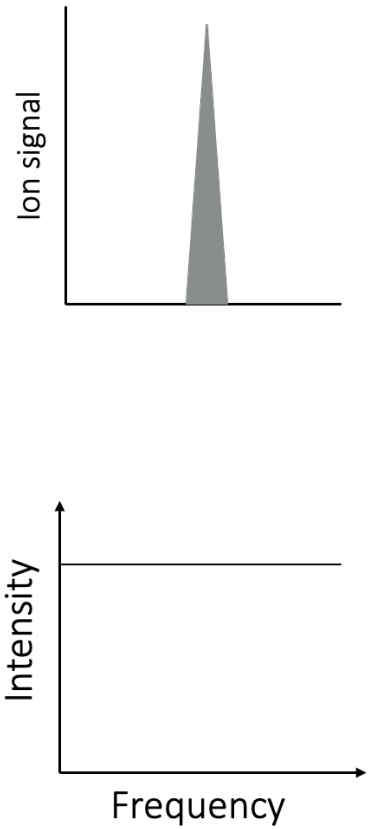
IR spectroscopy

FEL FELIX

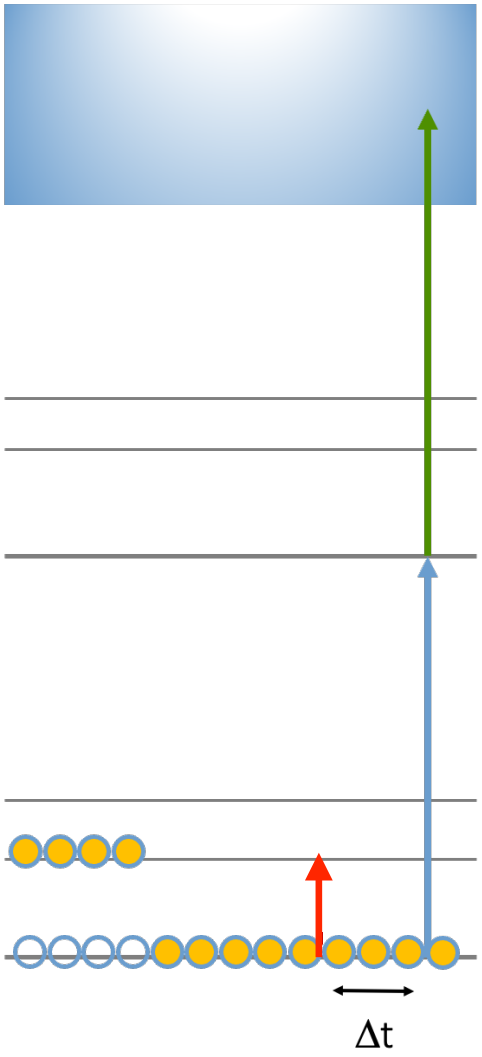
550- 1800 cm^{-1}

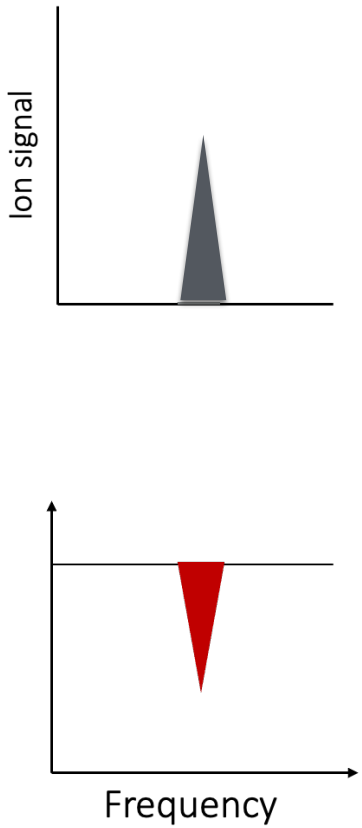


REMPI followed by ion detection



IR on-resonance

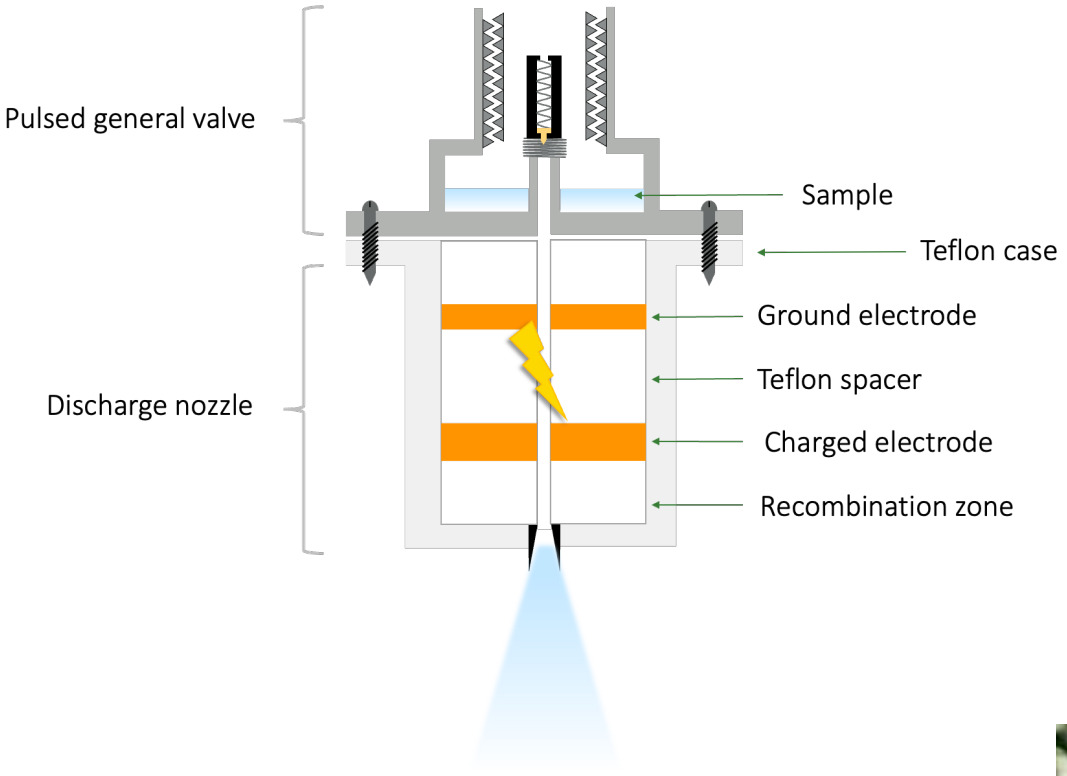


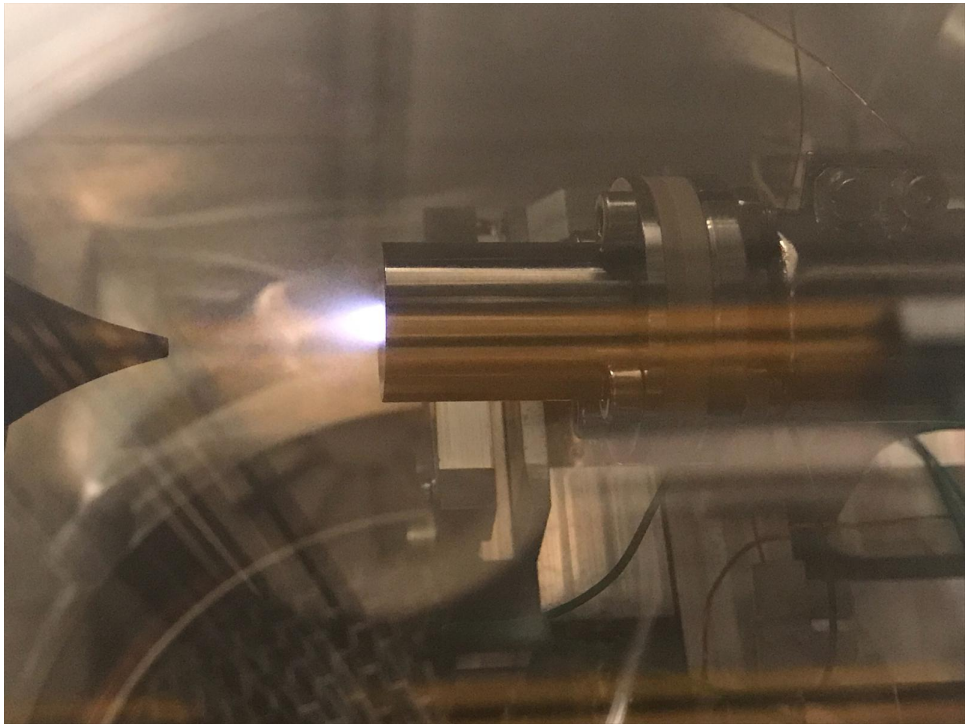


PAH chemistry

Formation of reactive, transient species under electric discharge plasma conditions

DC discharge pulsed valve





Amanda Steber (now at U Valladolid, Spain)

Donatella Loru

FELIX Free Electron Lasers for Infrared eXperiments

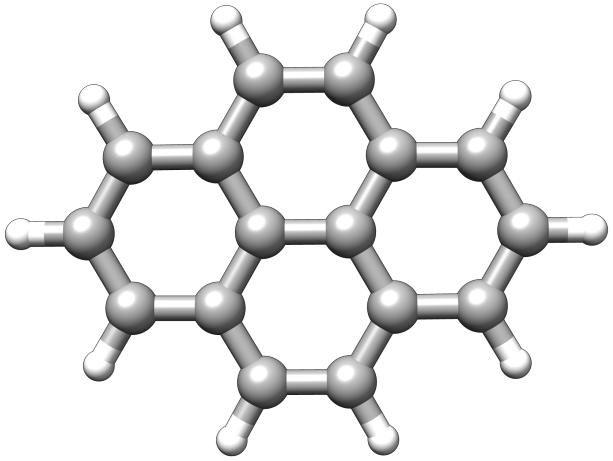
DESY.

The precursor molecules

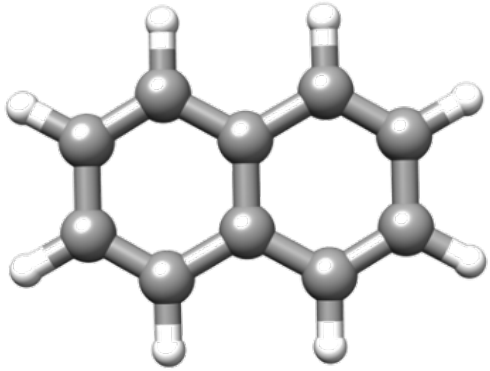
WH01
Gayatri Batra

WH02
Donatella Loru

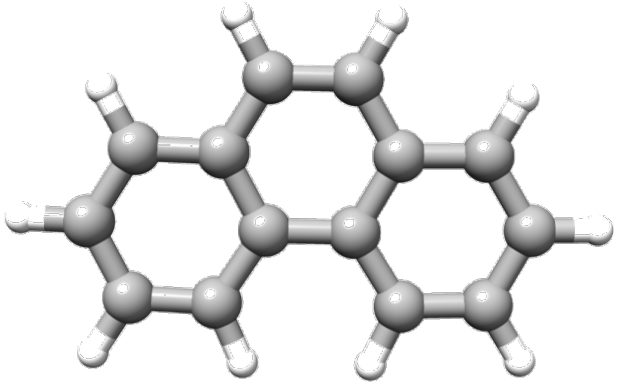
Examples of PAHs



Pyrene ($C_{16}H_{10}$)



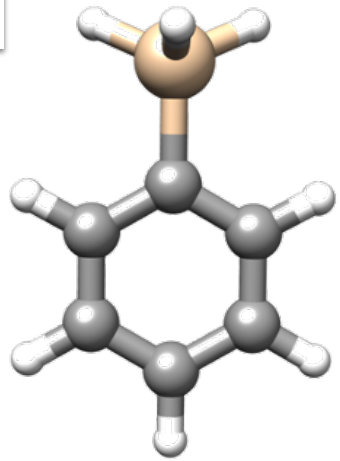
Naphthalene ($C_{10}H_8$)



Phenanthrene ($C_{14}H_{10}$)

PHE

partner molecules



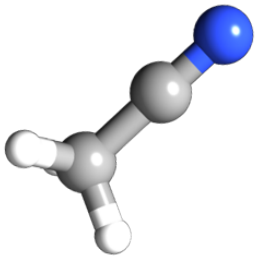
Phenylsilane (C_6H_8Si)

METHODS

IR-UV ion-dip

FELIX
Free Electron Lasers for Infrared eXperiments

CP-FTMW spec

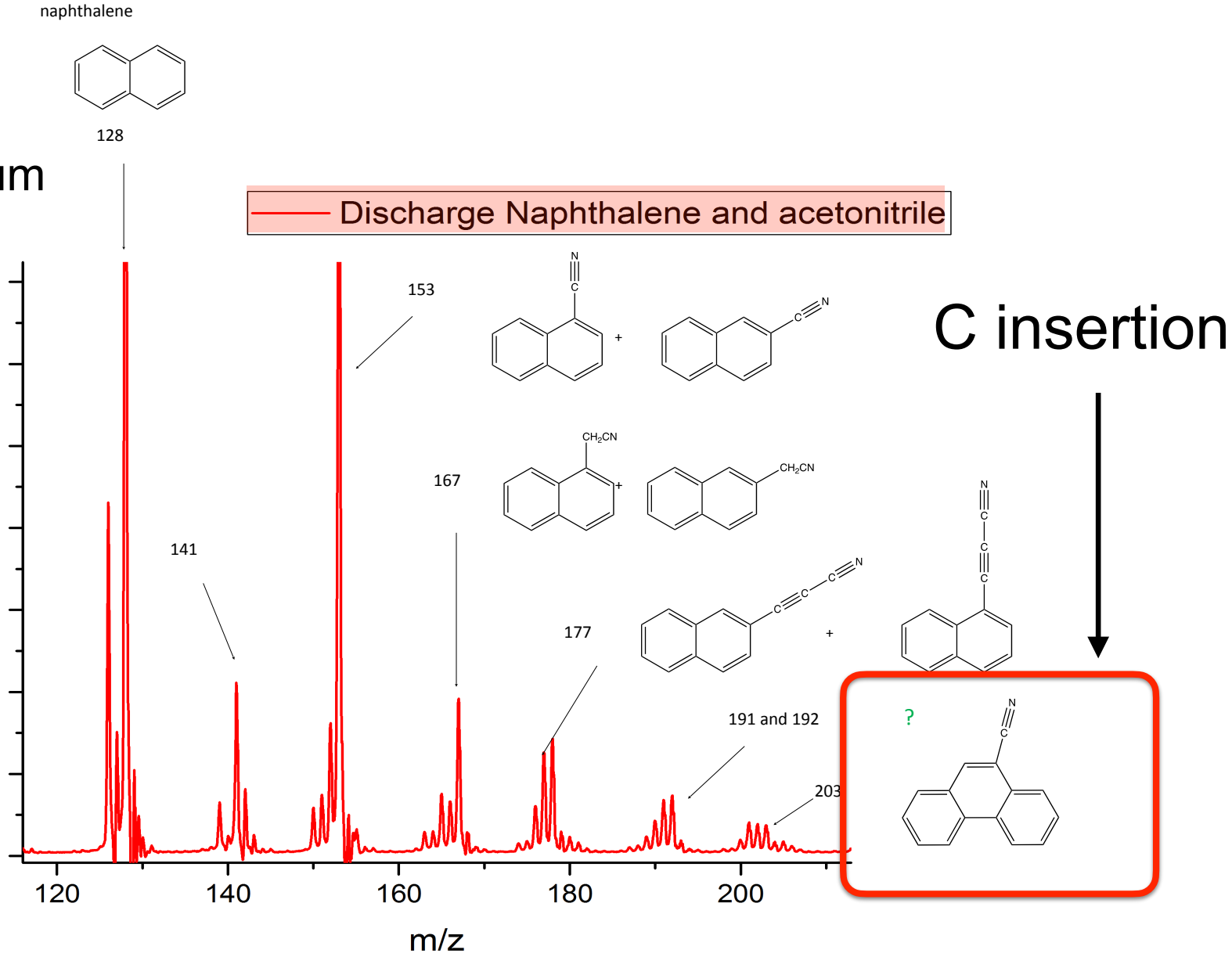


Acetonitrile (CH_3CN)

Electrical discharge of PAHs

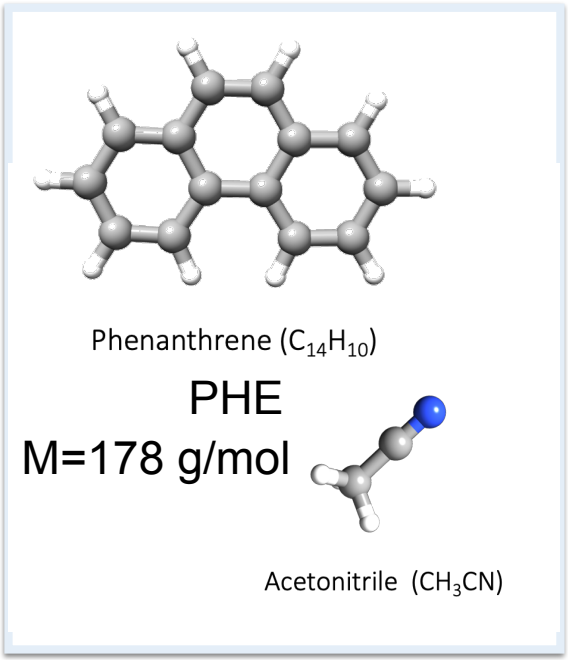
Chemical processes under electric discharge plasma conditions

TOF
mass spectrum

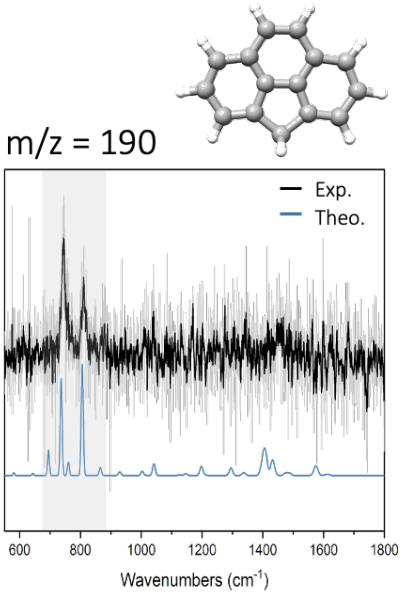


A. K. Lemmens *et al.* “Polycyclic aromatic hydrocarbon formation chemistry in a plasma jet revealed by IR-UV action spectroscopy.” *Nat Commun* **11**, 269 (2020).

Electrical discharge of PHE with acetonitrile



C insertion



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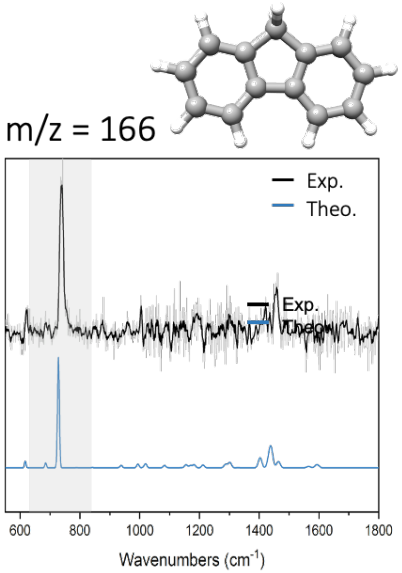
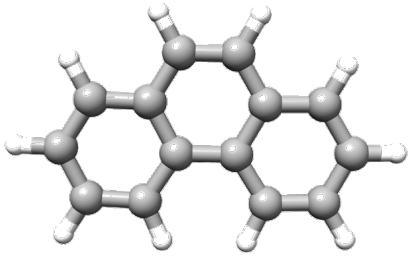


Theoretical calculations: B3LYP/def2-TZVP

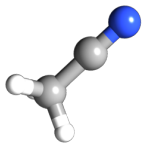
Electrical discharge of PHE with acetonitrile



Phenanthrene ($C_{14}H_{10}$)

PHE

M=178 g/mol



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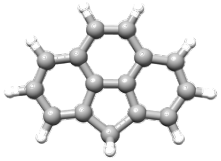
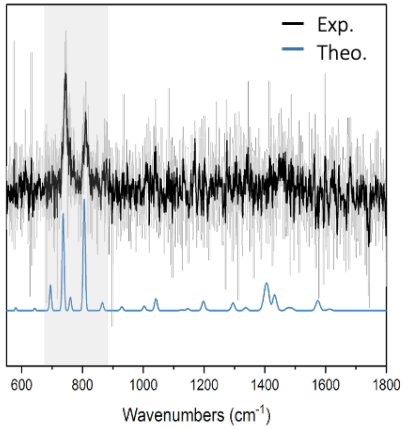
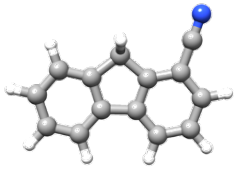


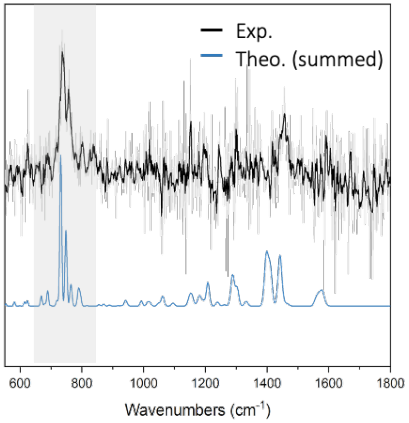
m/z = 190

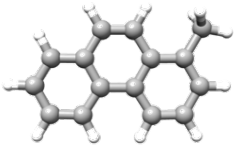


substitution

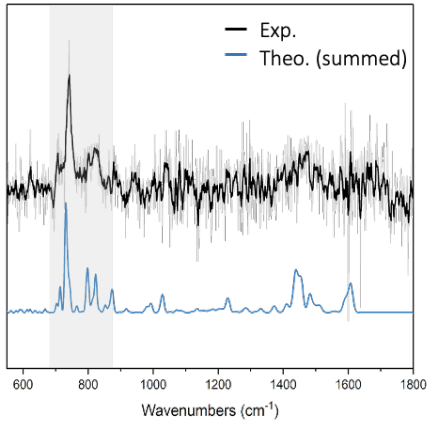


m/z = 191

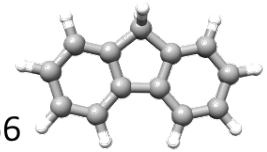




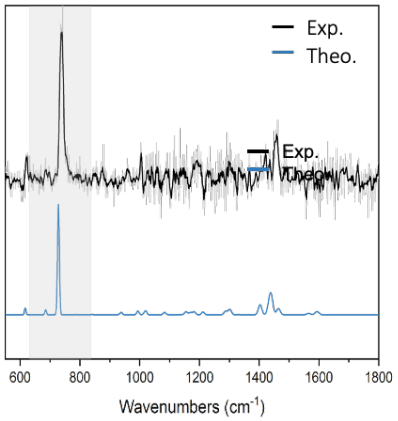
m/z = 192



C elimination

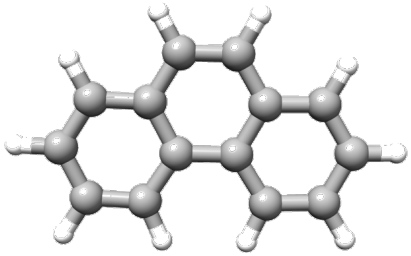


m/z = 166



Theoretical calculations: B3LYP/def2-TZVP

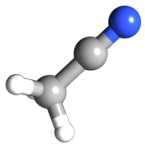
Electrical discharge of PHE with acetonitrile



Phenanthrene ($C_{14}H_{10}$)

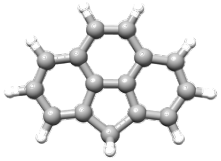
PHE

M=178 g/mol

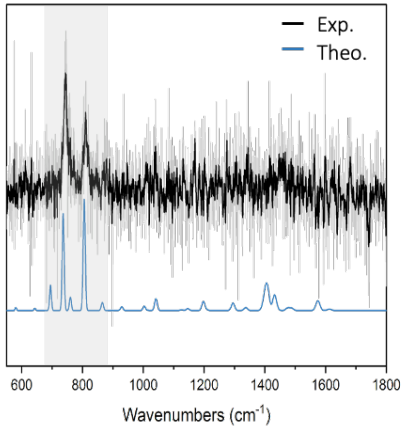


Acetonitrile (CH_3CN)

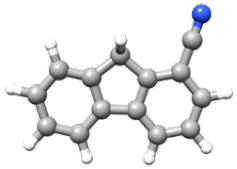
C insertion



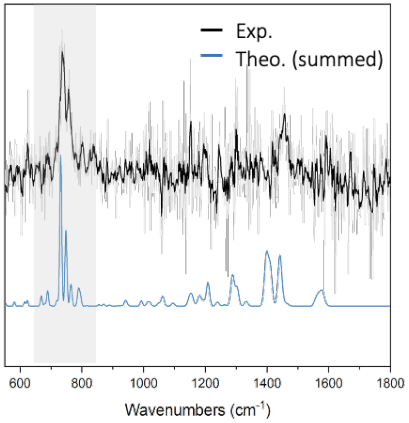
m/z = 190

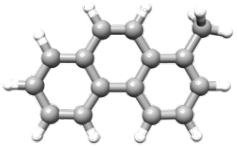


substitution



m/z = 191





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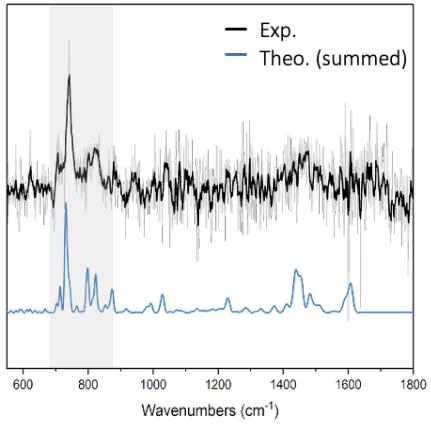
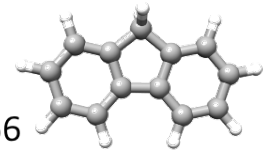


C elimination



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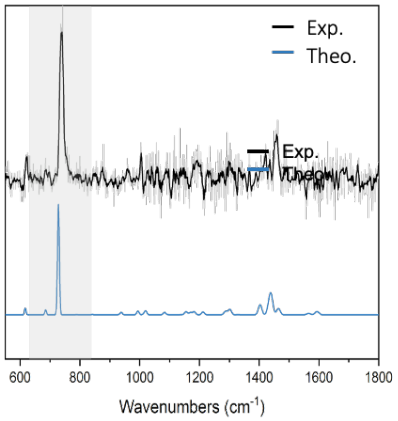

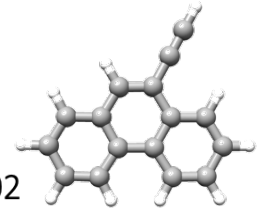

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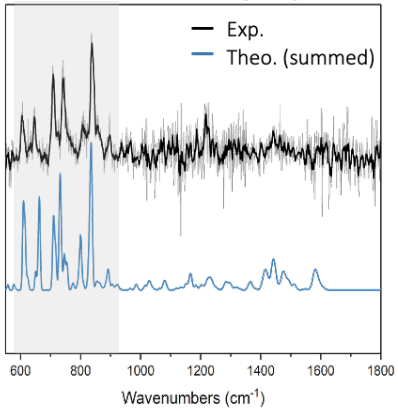
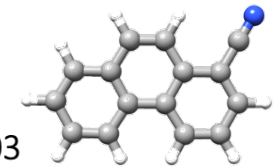
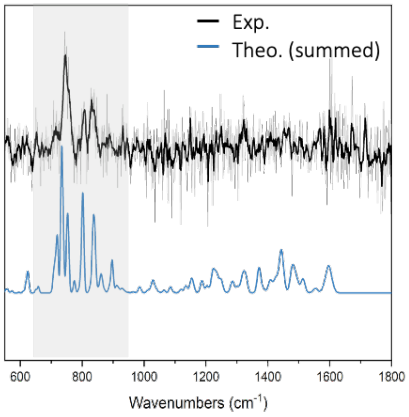
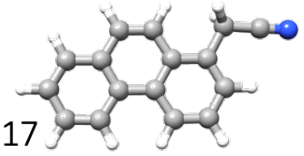


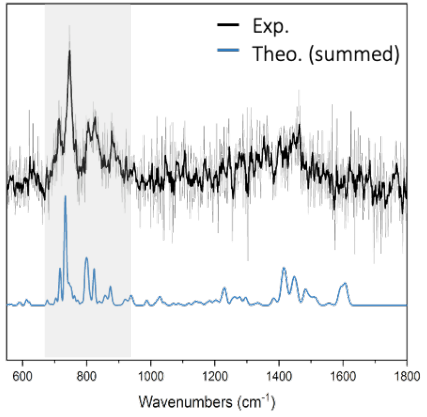


m/z = 203



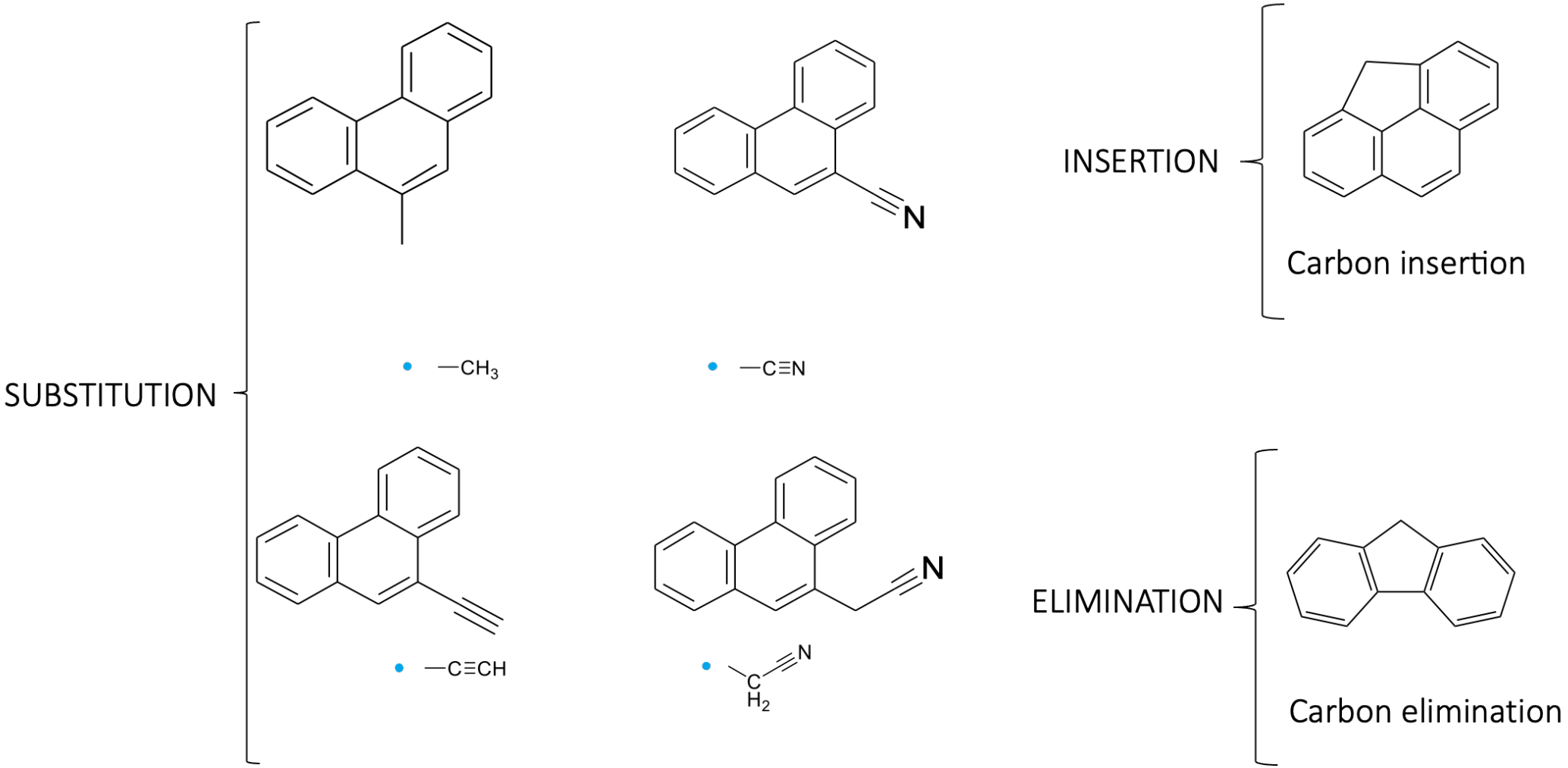


m/z = 217



Theoretical calculations: B3LYP/def2-TZVP

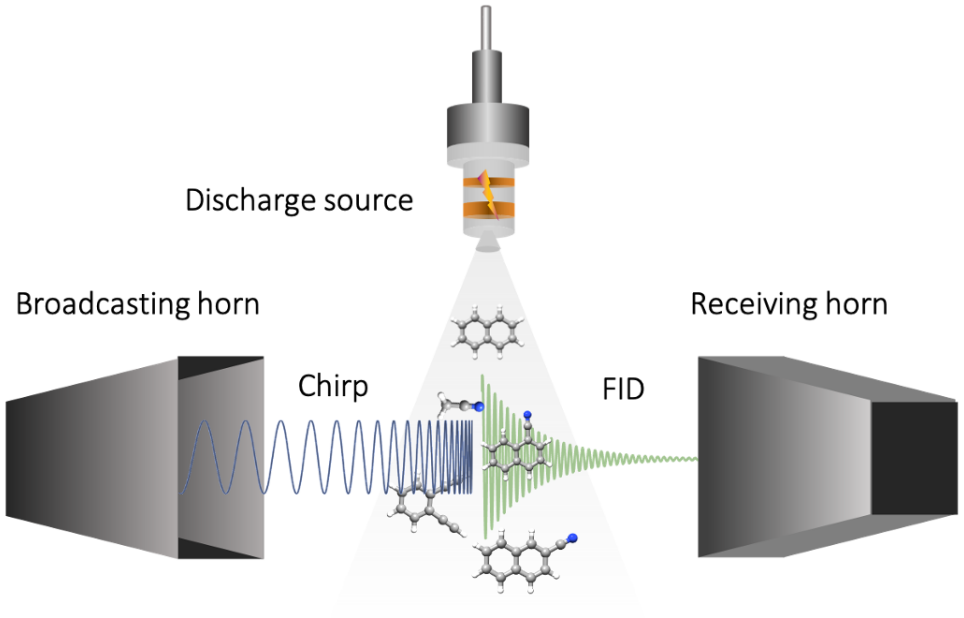
Observed processes



- Similar outcomes observed for pyrene, fluorene, naphthalene…
- Important for discussions regarding bottom-up vs. top-down chemical processes.

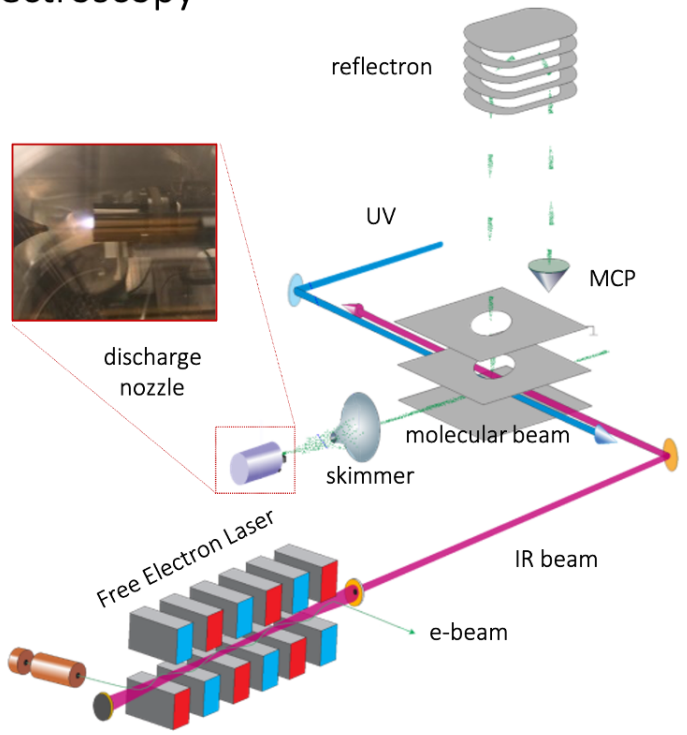
Complementary spectroscopy approaches

Broadband rotational spectroscopy



- Molecules must possess a permanent dipole moment
- Molecules are identified via unique **microwave spectra**.

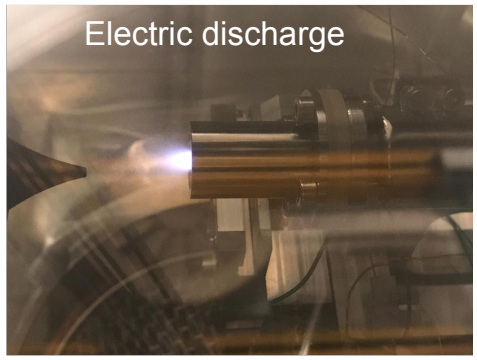
IR-UV spectroscopy



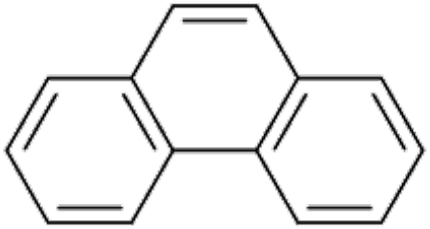
- Molecules must have a suitable **UV cross section**.
- Molecules are identified via a combination of their **mass** and their **IR signatures**.

Electrical discharge of PAHs

CP-FTMW spectroscopy



Precursors

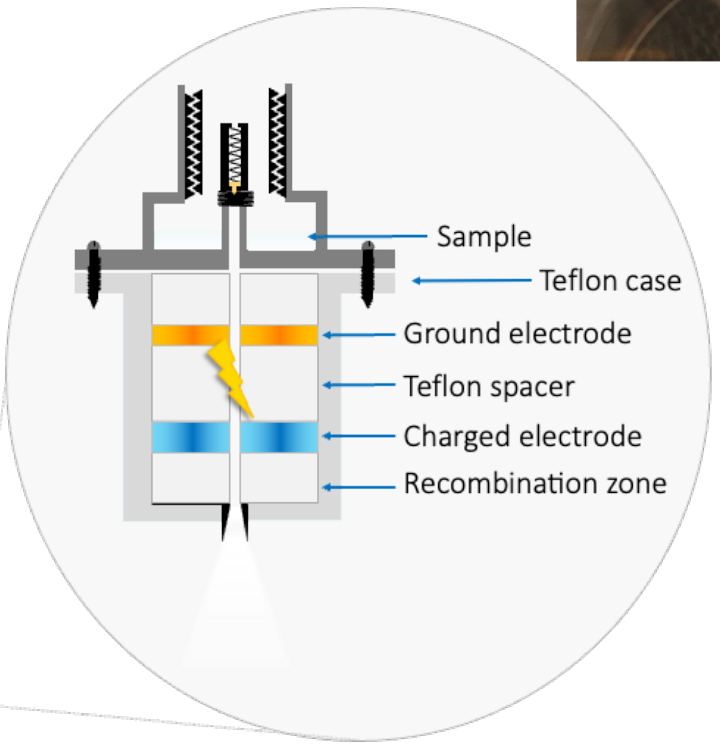


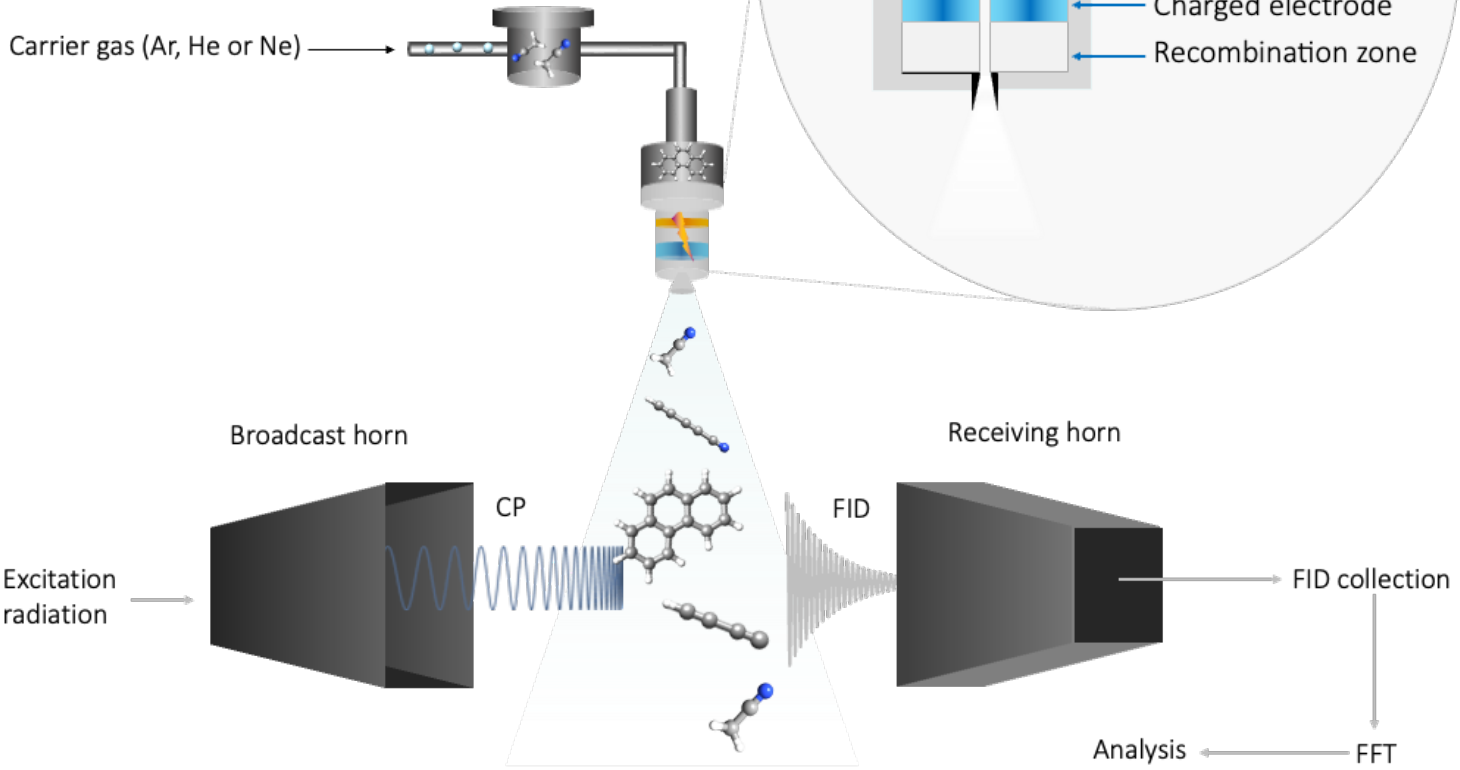
Phenanthrene ($C_{14}H_{10}$)

with & without

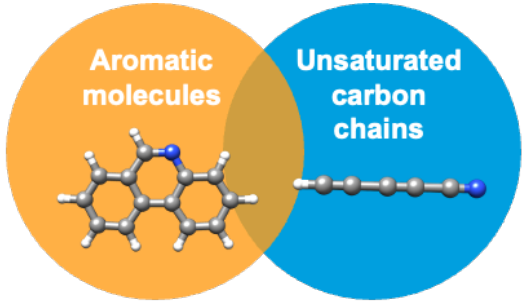
\+ $H_3C-C\equiv N$

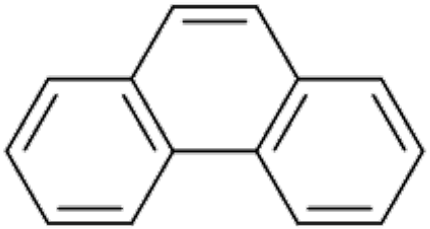
Acetonitrile (CH_3CN)





Phenanthrene & acetonitrile





Phenanthrene ($C_{14}H_{10}$)

+

Acetonitrile (CH_3CN)

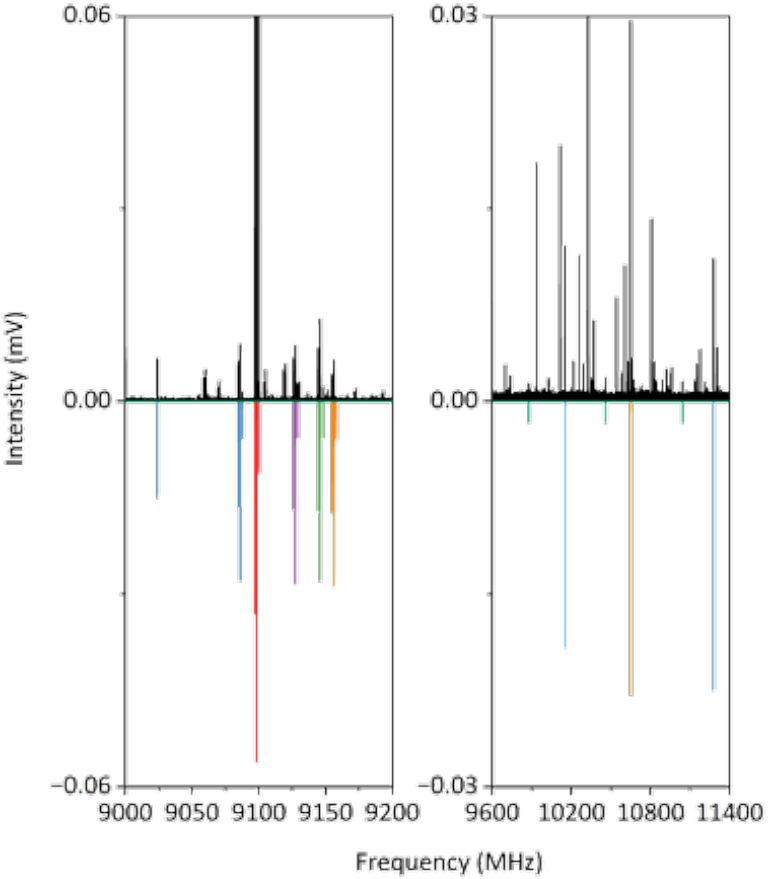
Electrical discharge

Experimental conditions

T = 135 °C

Ne @ 2.5 bar

V= 1.0 kV



HC_3N

($\nu_4 = 1$, $\nu_6 = 1 + \nu_7 = 1$, $\nu_7 = 1$, $\nu_7 = 2$)

HC_5N

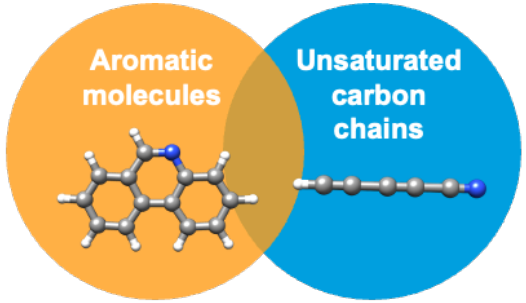
HC_7N

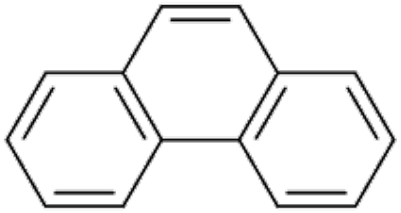
HC_9N

cyanopolyynes

Phenanthrene

No additional precursor





Phenanthrene ($C_{14}H_{10}$)

Electrical discharge

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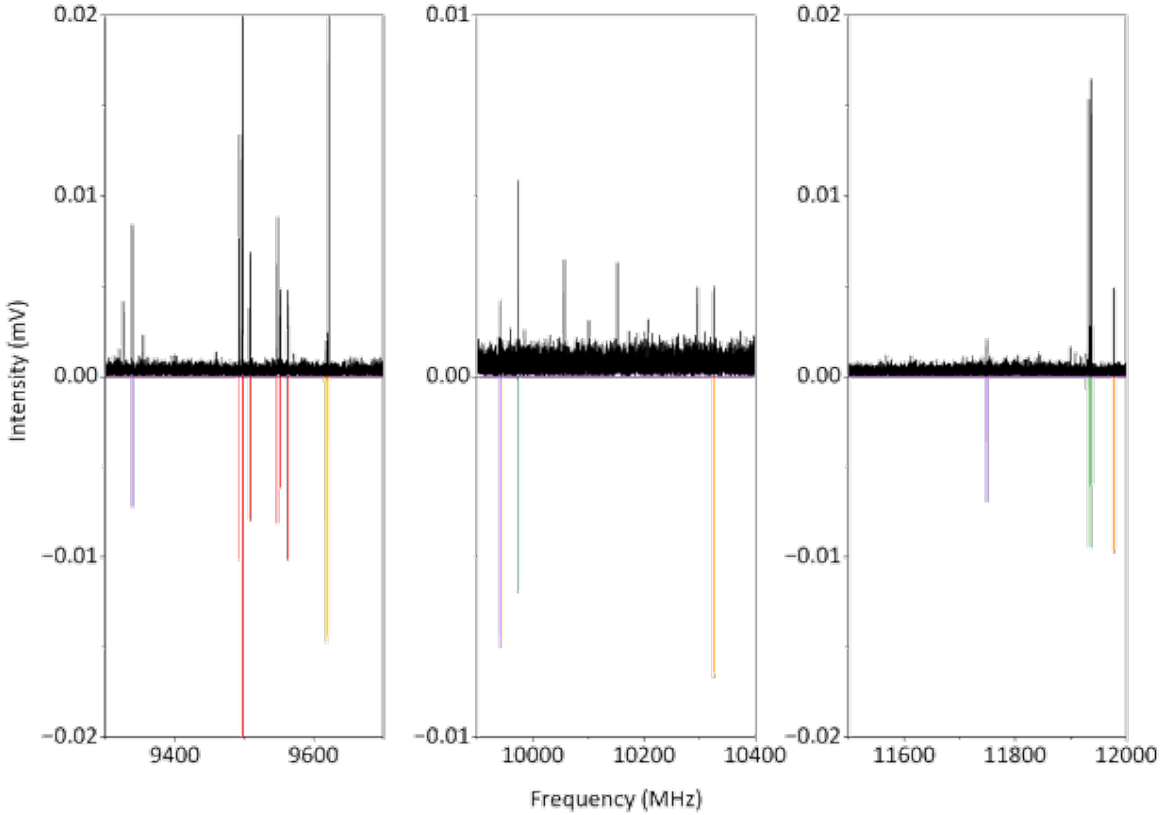
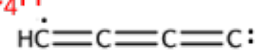
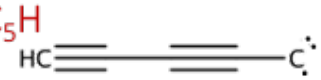


C_4H

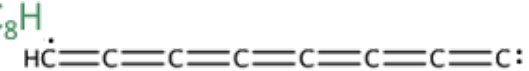


C_5H

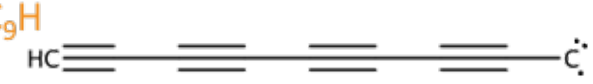


C_7H

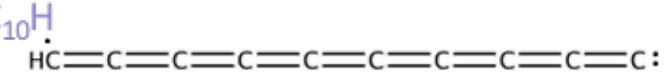
C_8H



C_9H

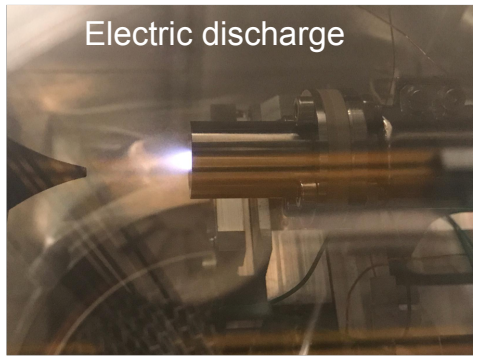


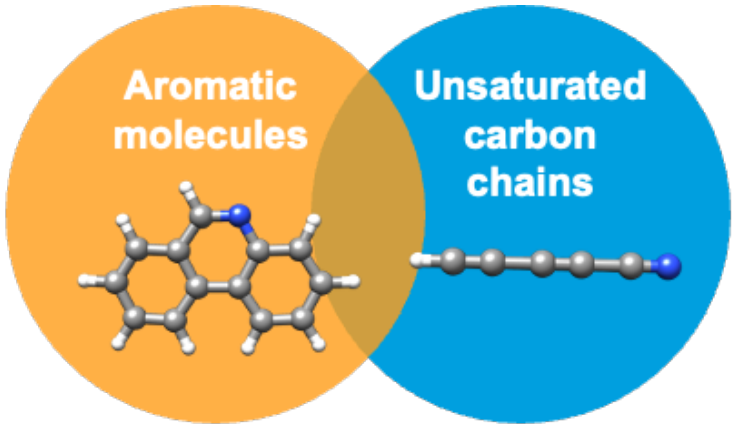
$C_{10}H$



linear radicals

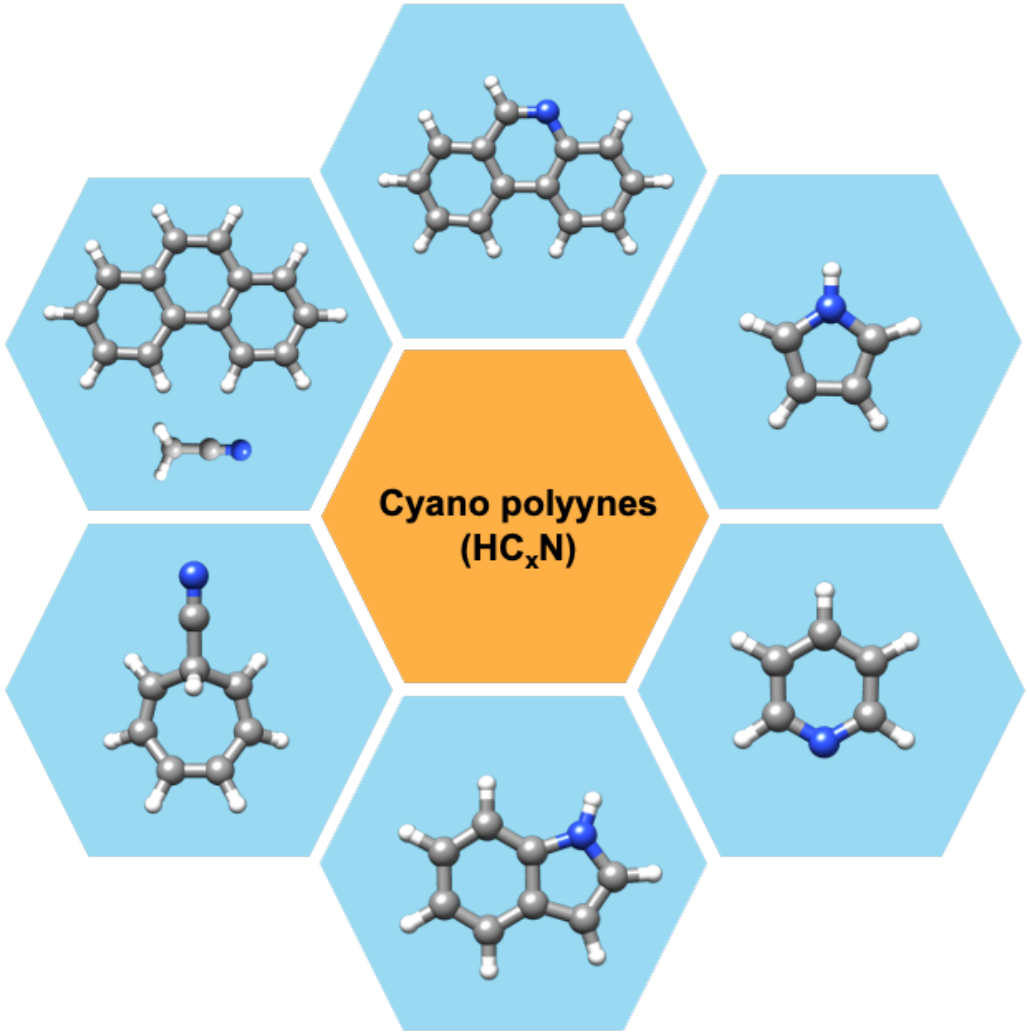
Polyynes are omnipresent





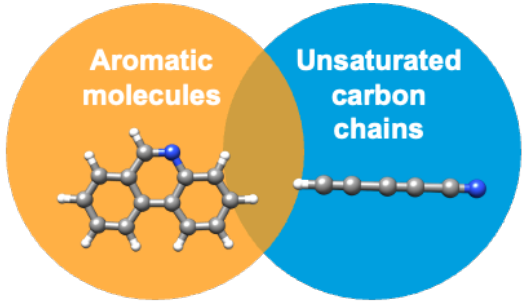
The formation of highly unsaturated (cyano-)polyynes is a common observation.

A variety of precursors

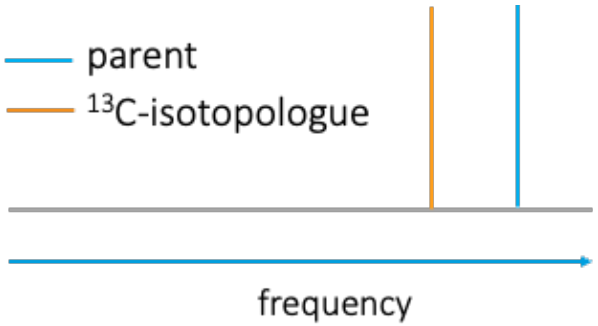


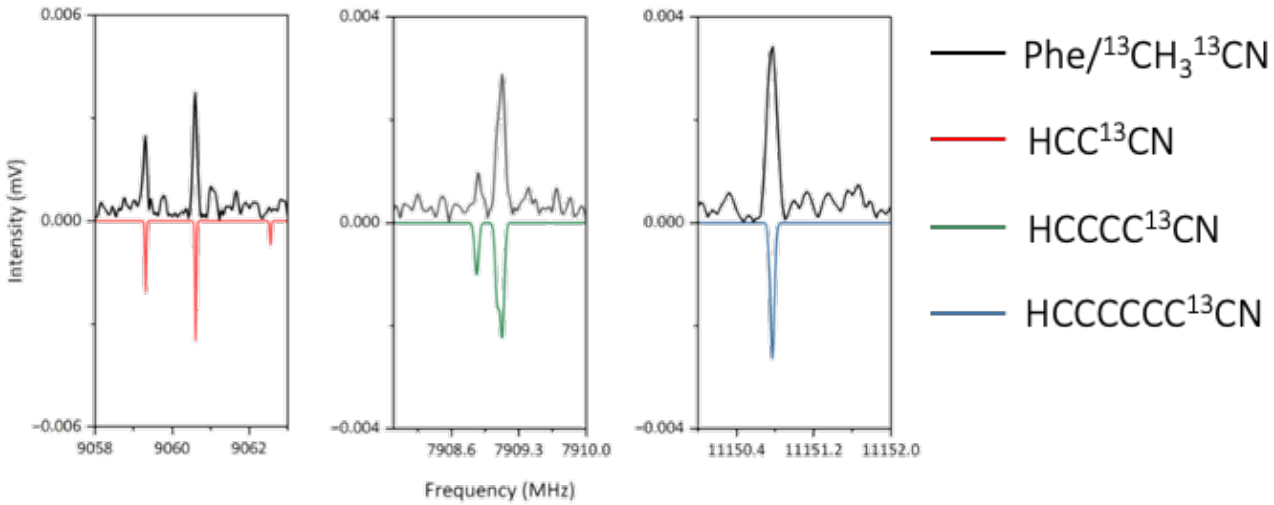
Isotopic labelling with $^{13}CH_3{}^{13}CN$

Phenanthrene-acetonitrile discharge



$$B = \frac{h}{8\pi^2 I_b} \longleftrightarrow I = \sum_{i=1}^{n} m_i r_i^2$$

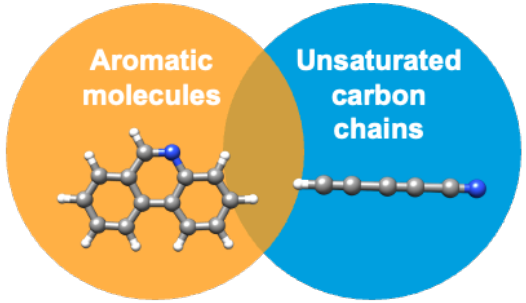




Representative rotational transitions of $HCC^{13}CN$, $HCCCC^{13}CN$ and $HCCCCCC^{13}CN$ identified in the electrical discharge experiment of phenathrene and $^{13}CH_3{}^{13}CN$.

Isotopic labelling with $^{13}CH_3{}^{13}CN$

Phenanthrene-acetonitrile discharge



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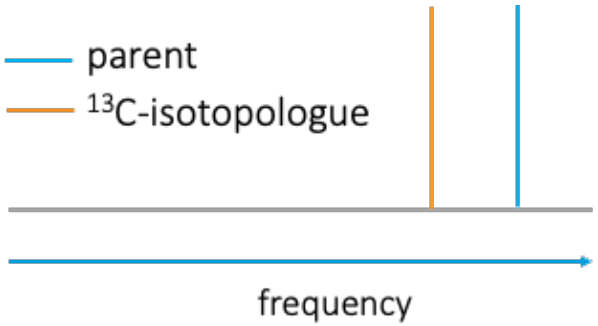
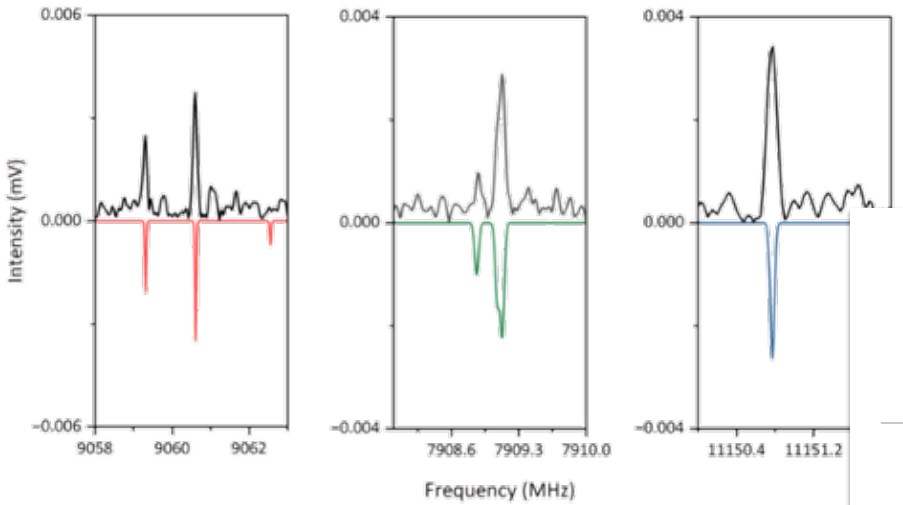
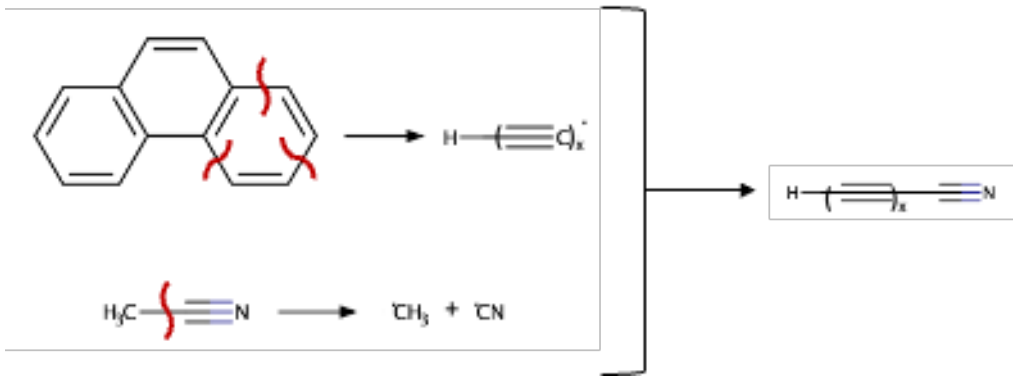




Representative rotational transitions of $HCC^{13}CN$, $HCCCCCC^{13}CN$ identified in the electrical discharge phenathrene and $^{13}CH_3{}^{13}CN$.

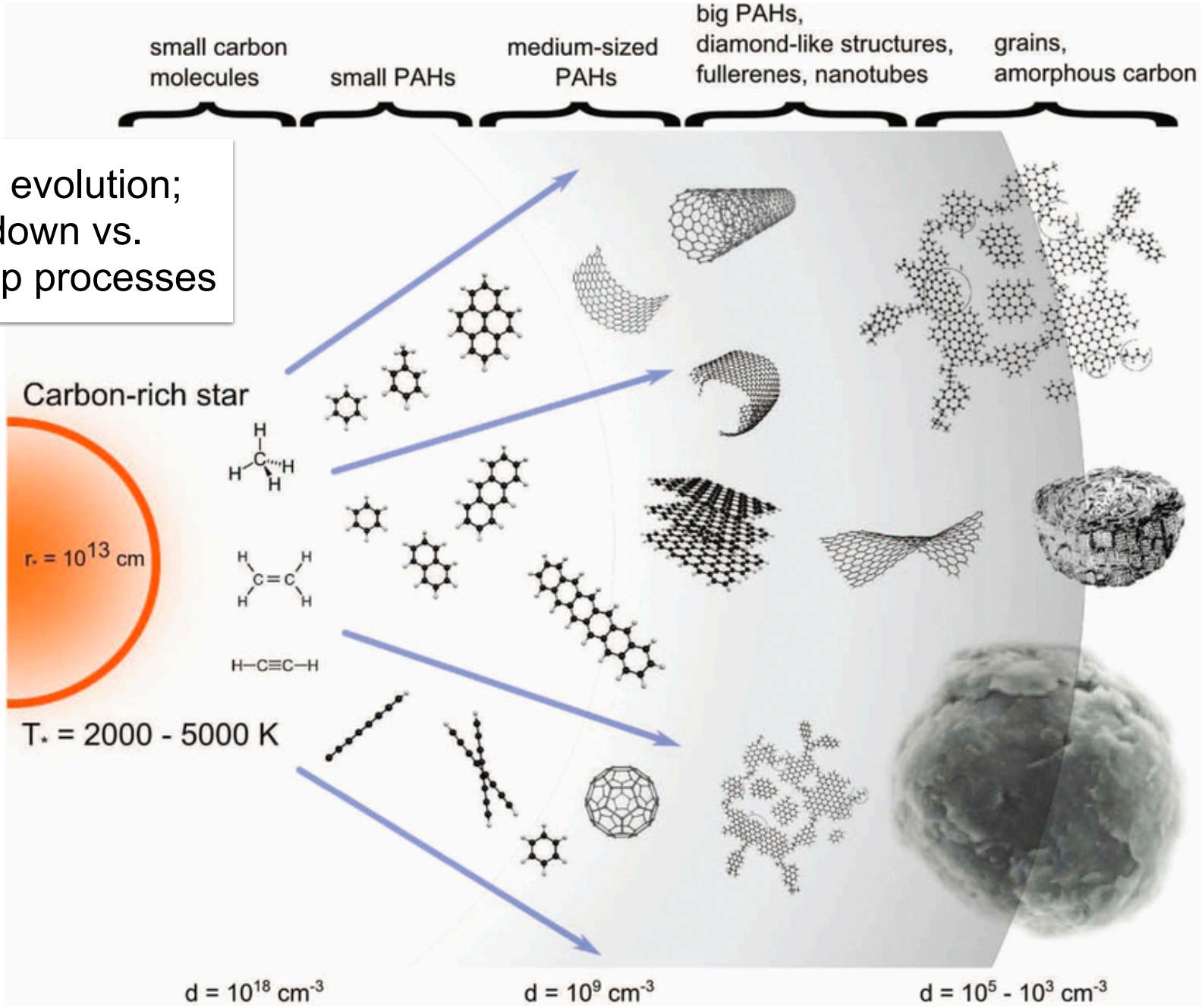
Proposed mechanism

1. Fragmentation
2. Recombination



Grains, fullerenes, and polycyclic aromatic hydrocarbons (PAHs)

carbon evolution;
top-down vs.
bottom-up processes

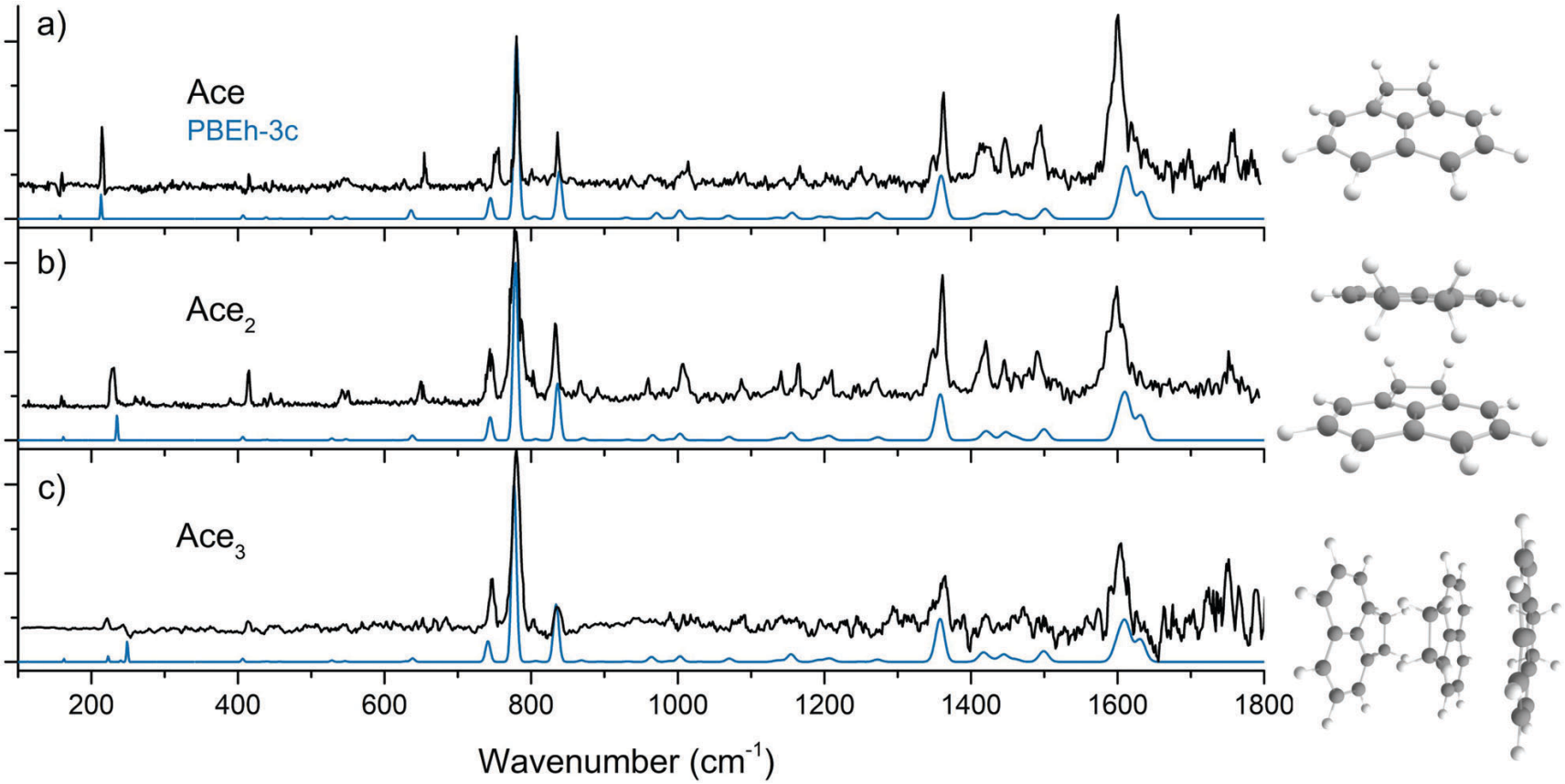


Adapted from Pascoli & Pollux (2000)

Far-IR spectral signatures of PAH complexes

Collaboration with Sander Lemmens, Anouk Rijs and the Grimme theory group (U Bonn)

Acenaphthene



- spectra are very similar for the clusters
- only small differences visible in the far-IR
- weak interactions between the moieties

DESY.

A.K. Lemmens, S. Gruet, A. L. Steber, J. Antony, S. Grimme, M. Schnell, A.M. Rijs, PCCP (2018).

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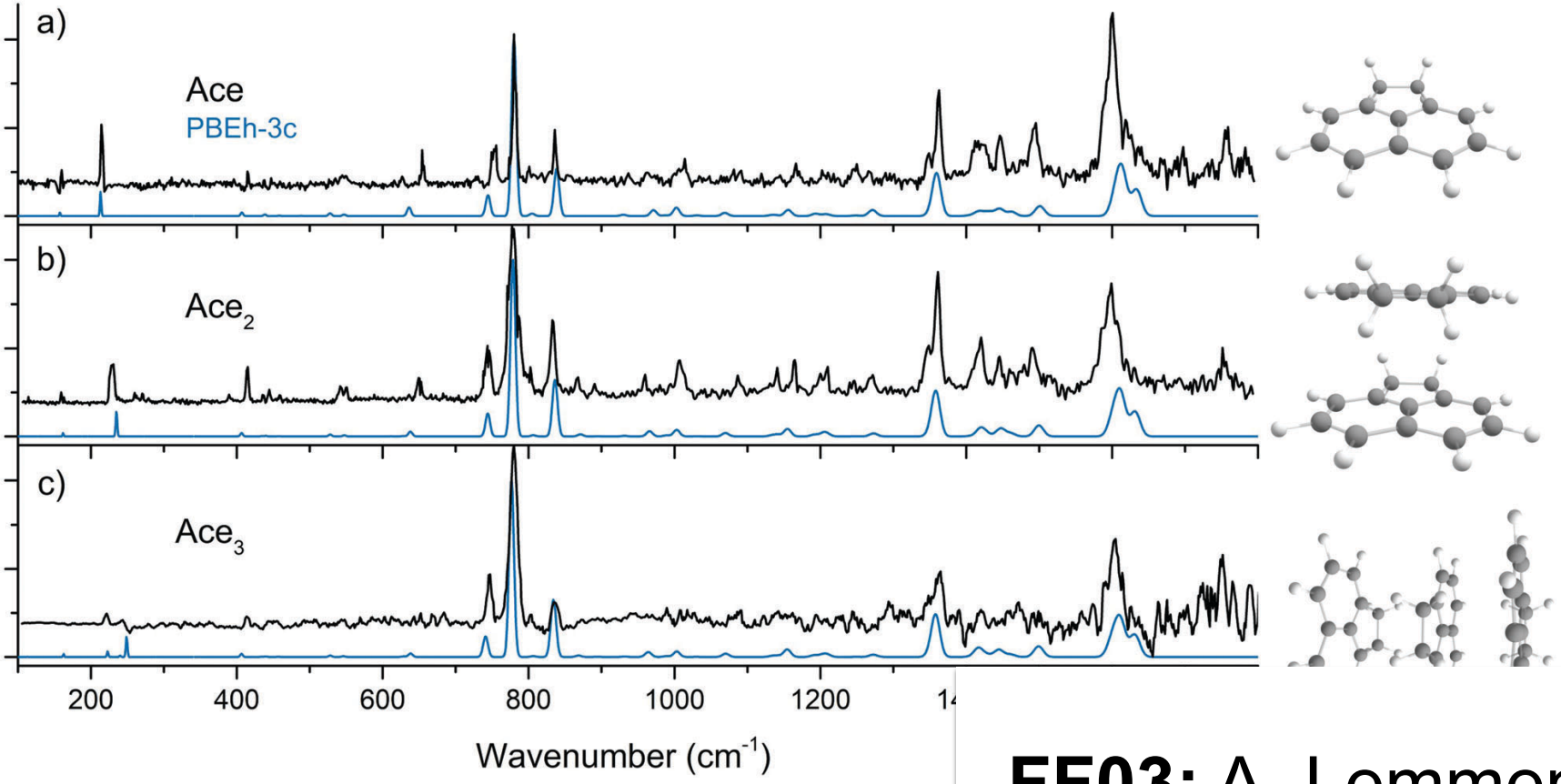

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FF03: A. Lemmens - PAH-water clusters

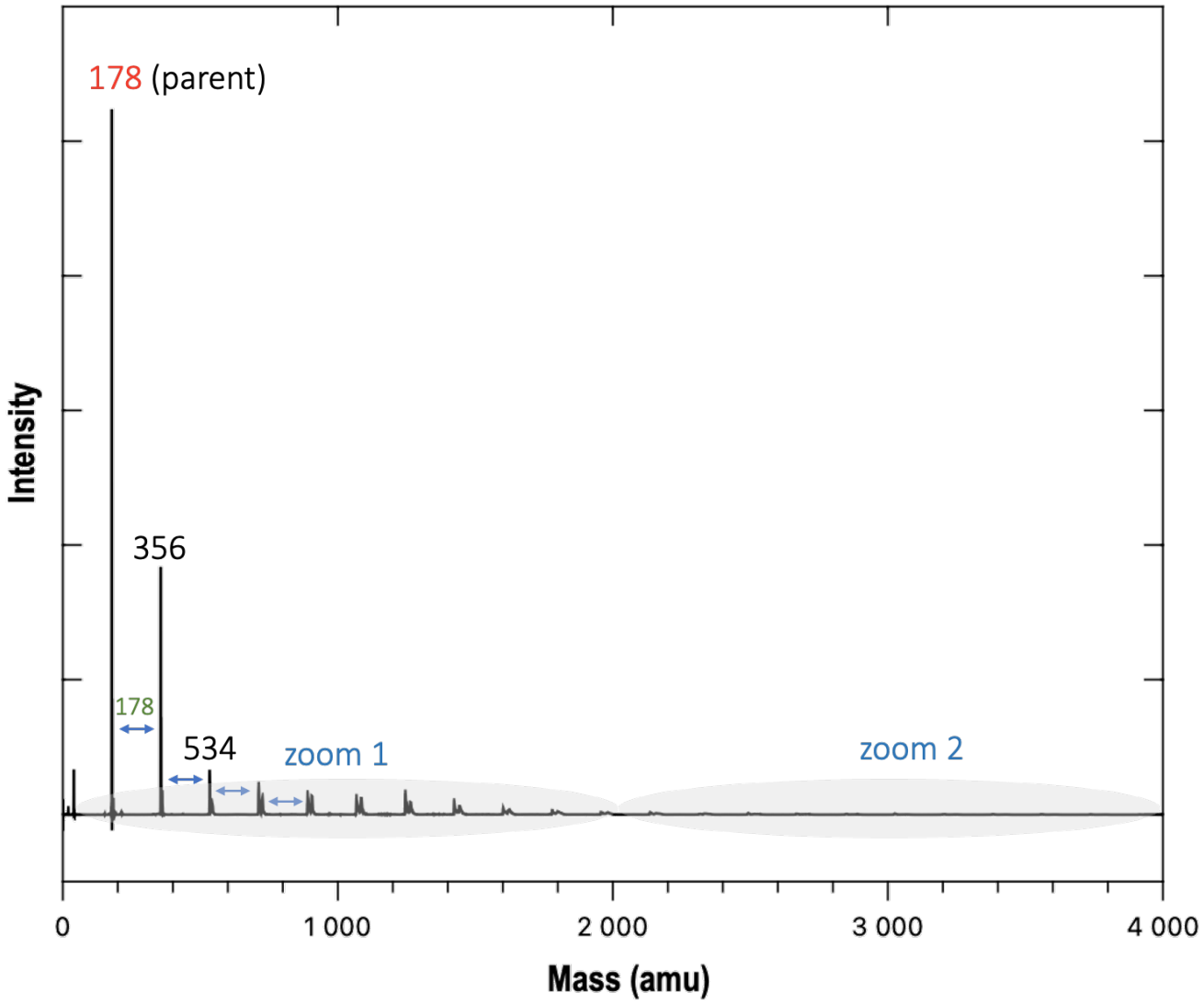
FELIX Free Electron Lasers for Infrared eXperiments

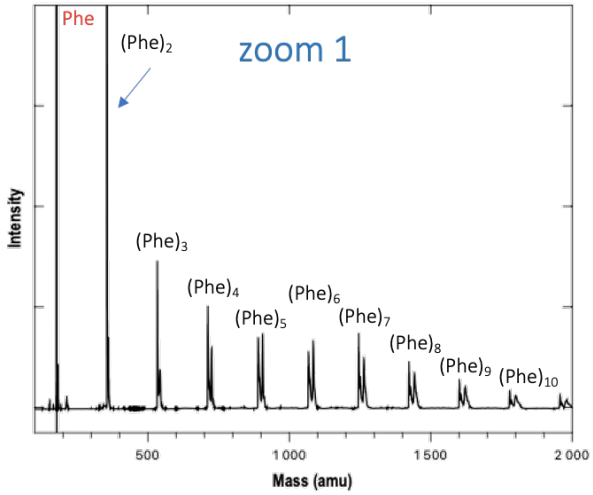
DESY.

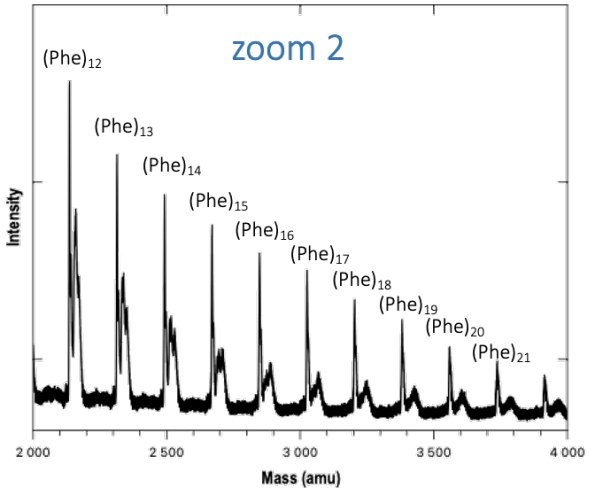
A.K. Lemmens, S. Gruet, A. L. Steber, J. Antony, S. Grimme, M. Schnell, A.M. Rijs, PCCP (2018).

Phenanthrene and its (many) clusters

Mass spectrum



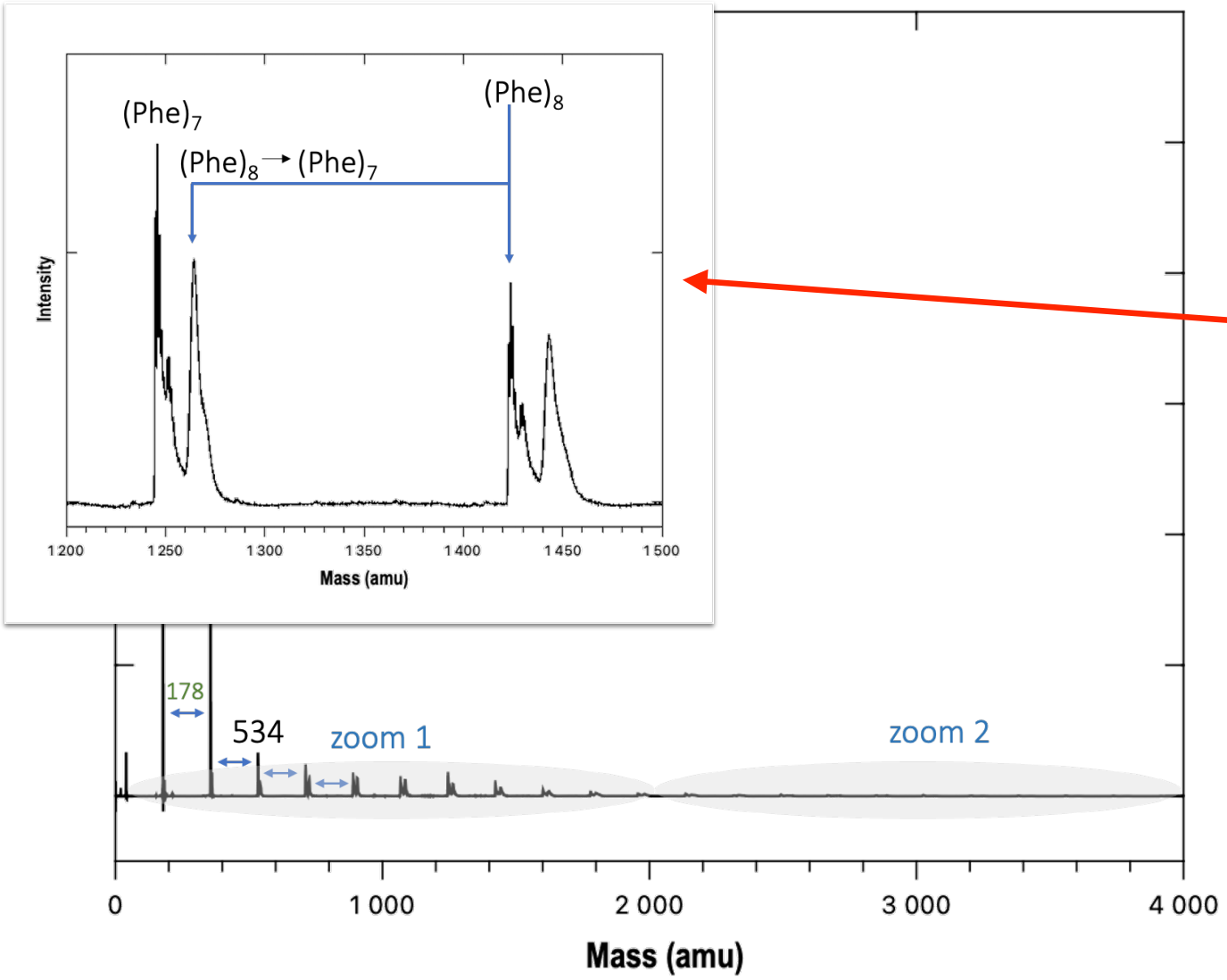


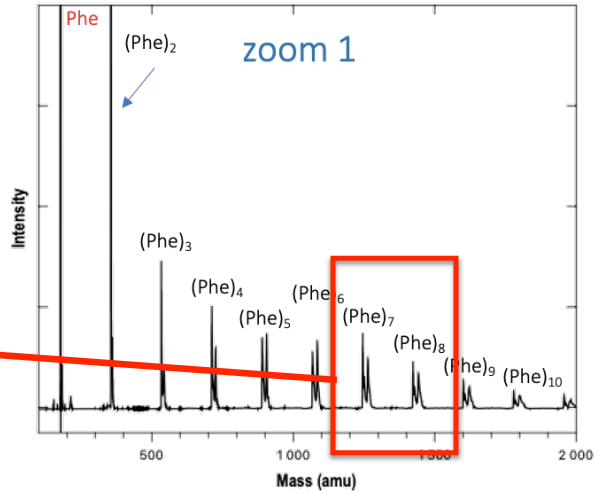


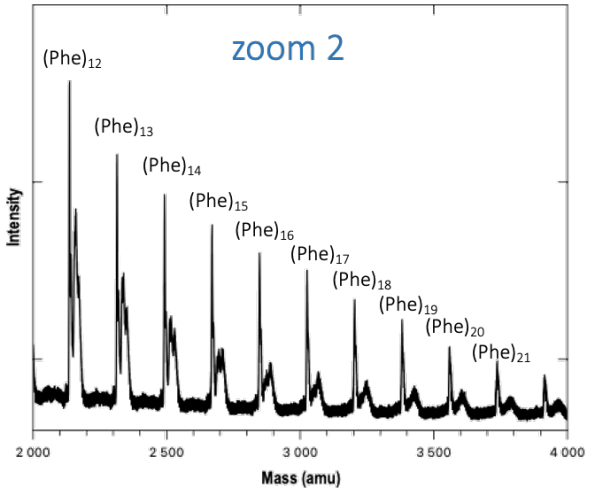
… work in progress…

Phenanthrene and its (many) clusters

Mass spectrum



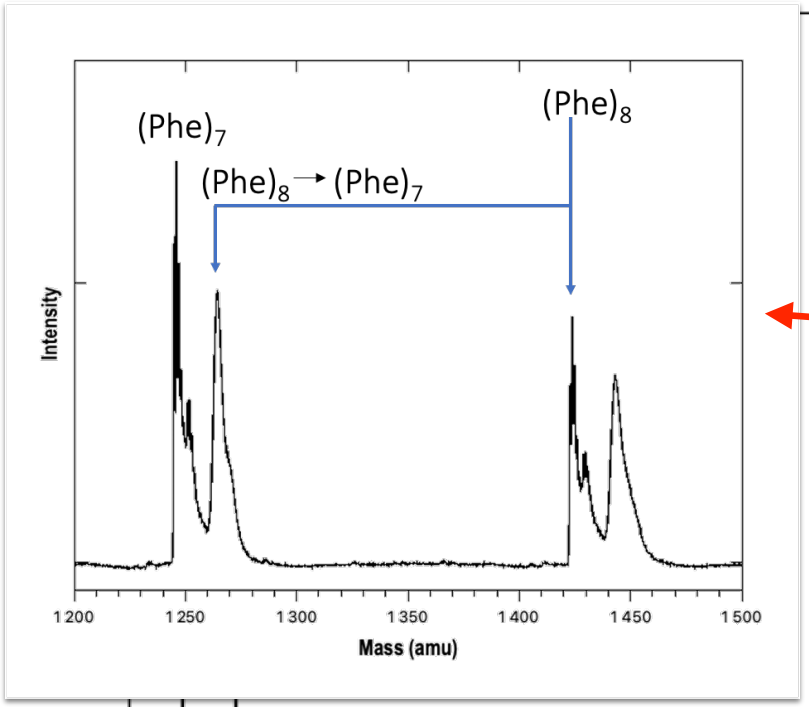


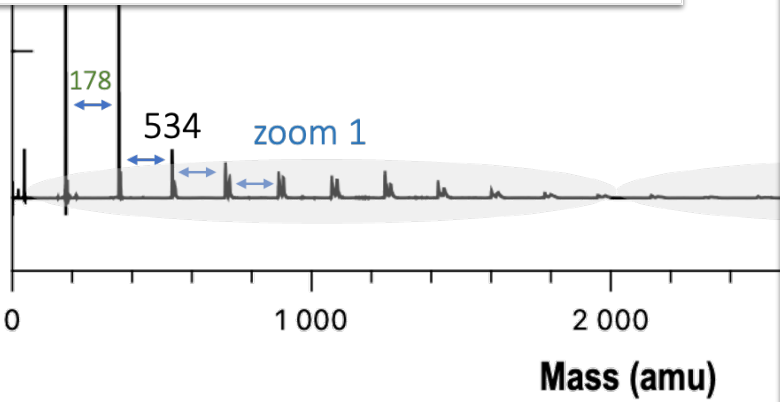


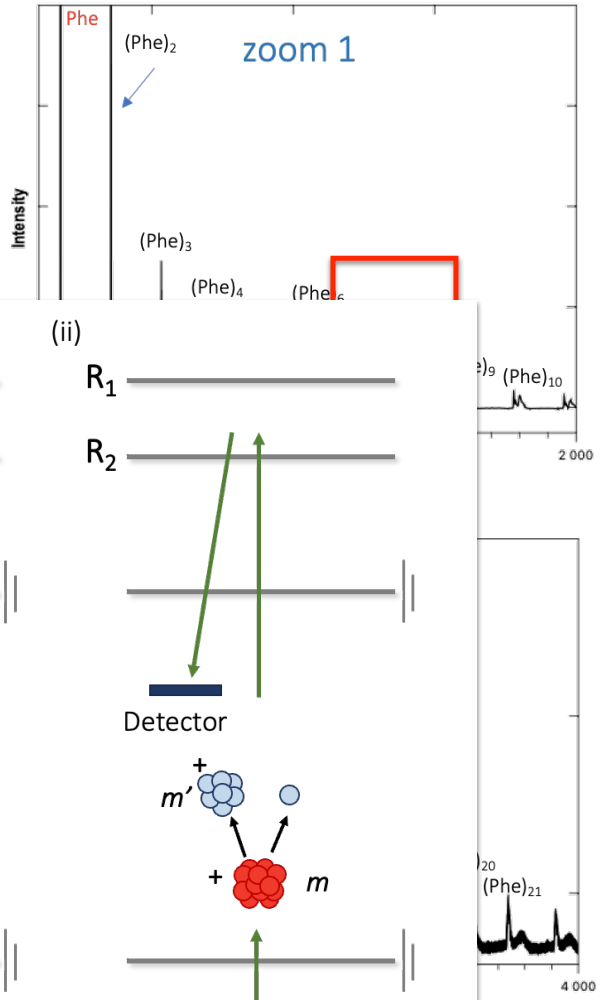
… work in progress…

Phenanthrene and its (many) clusters

Mass spectrum

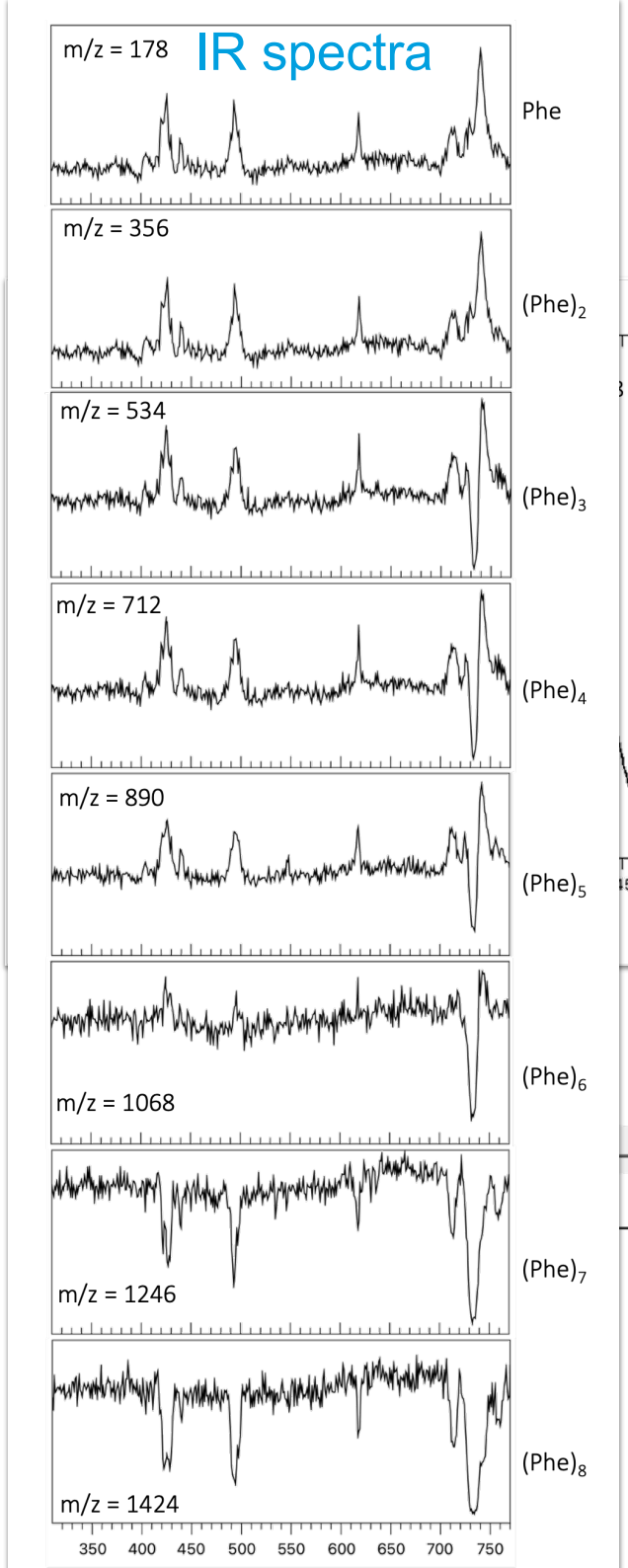


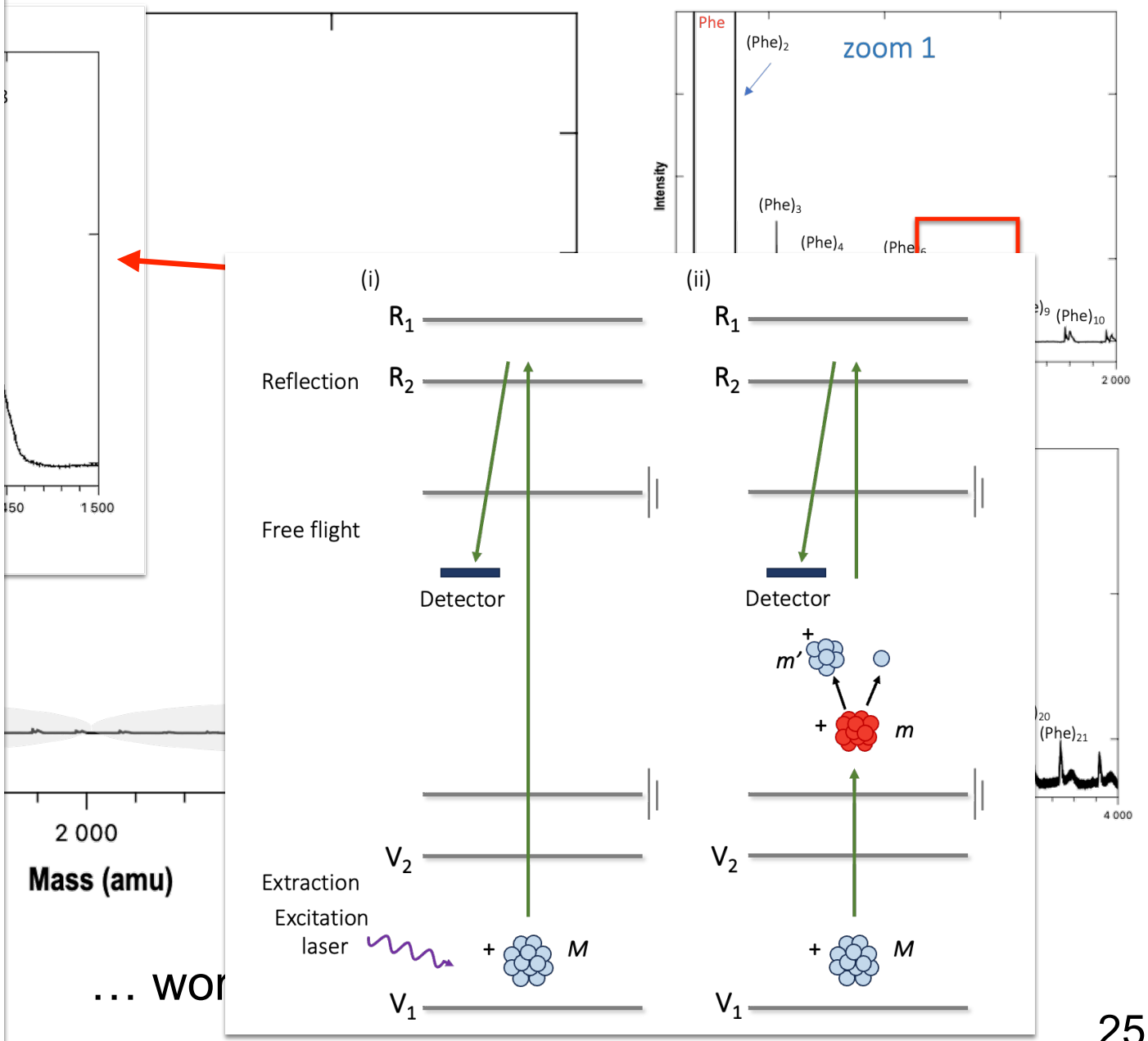




… wor

and its (many) clusters



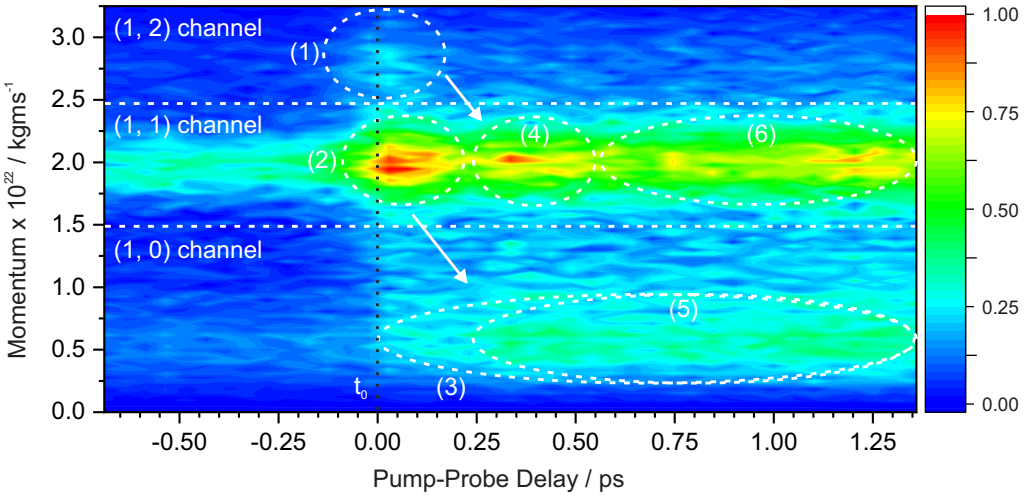


Outline

- IR-UV ion-dip spectroscopy @ FELIX
  - PAH growth (and other processes) in a plasma (and a comparison with CP-FTMW measurements)
  - IR fingerprints of PAH clusters

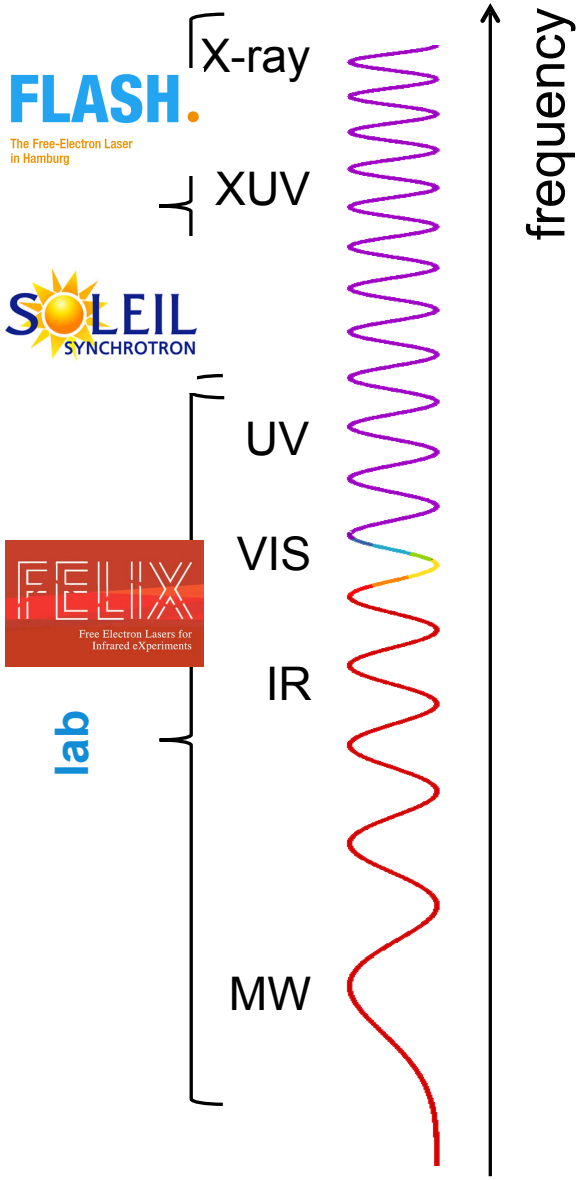
- **Time-resolved pump-probe experiments using FLASH**
  - interplay between ionisation & fragmentation of PAHs
  - life times of electronically excited states in different charge states

- Conclusions



Unraveling the role of PAHs in astrochemistry

A multi-spectroscopic approach



Response to harsh radiation; extreme states of matter

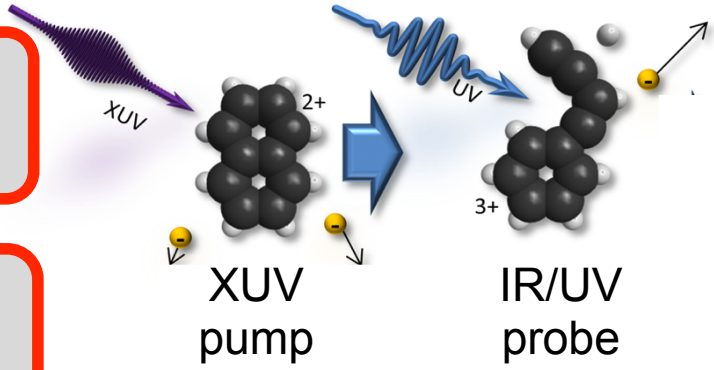
Photochemistry Bottom-up vs. top-down

"Exotic" PAHs

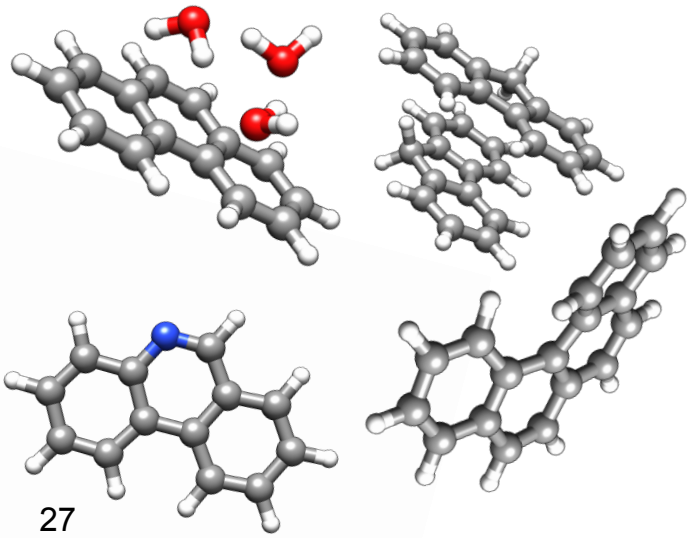
Complexes; Role in grain formation

Molecular fingerprints

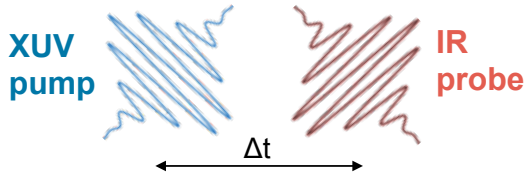
Structures

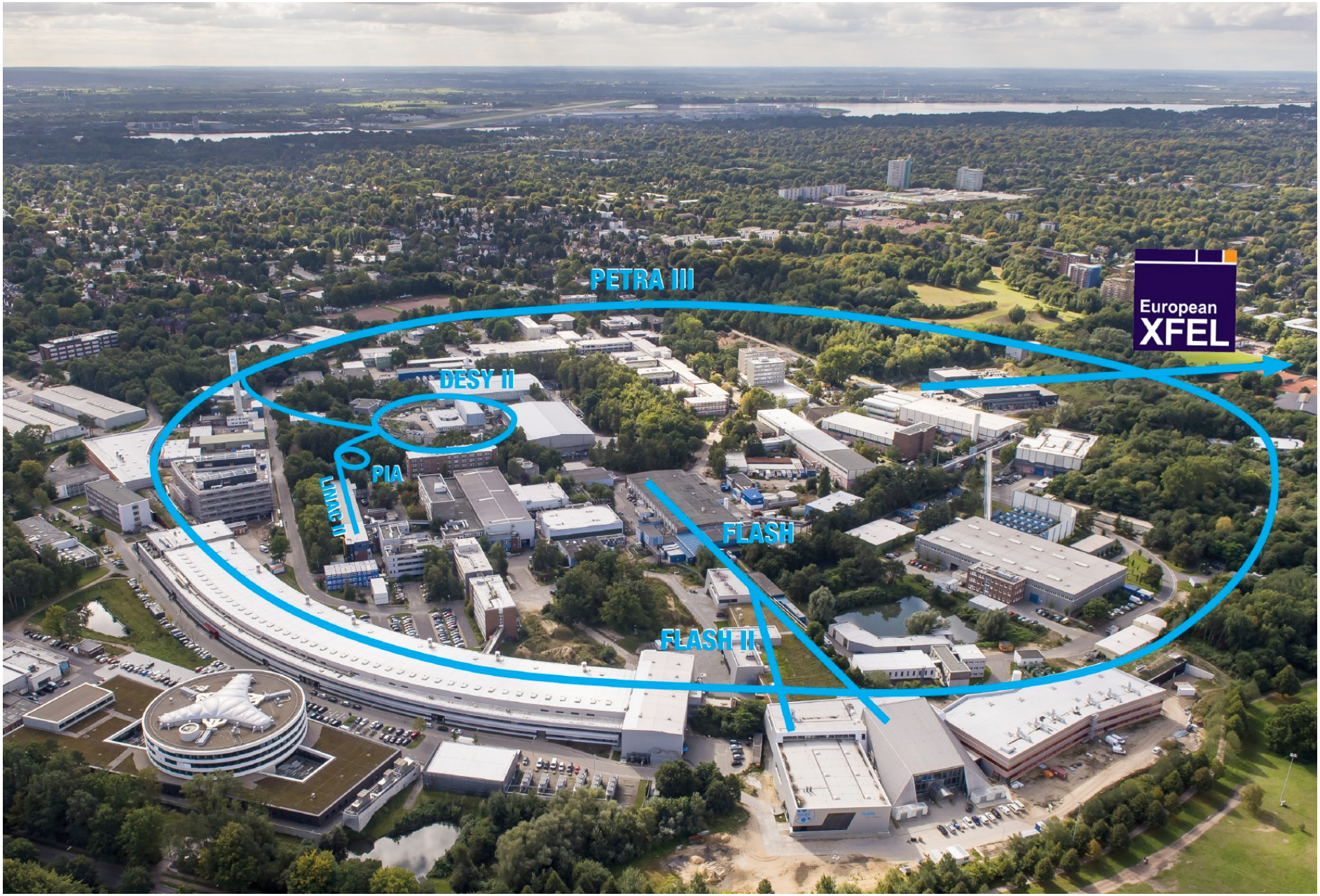


mechanistic insight after photo-excitation



The Bahrenfeld campus - DESY





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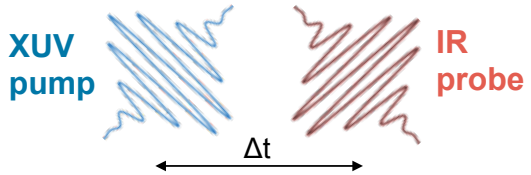

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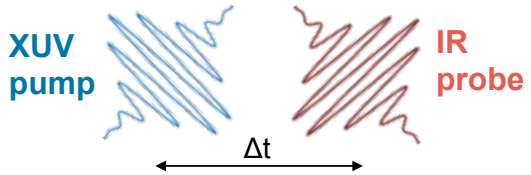
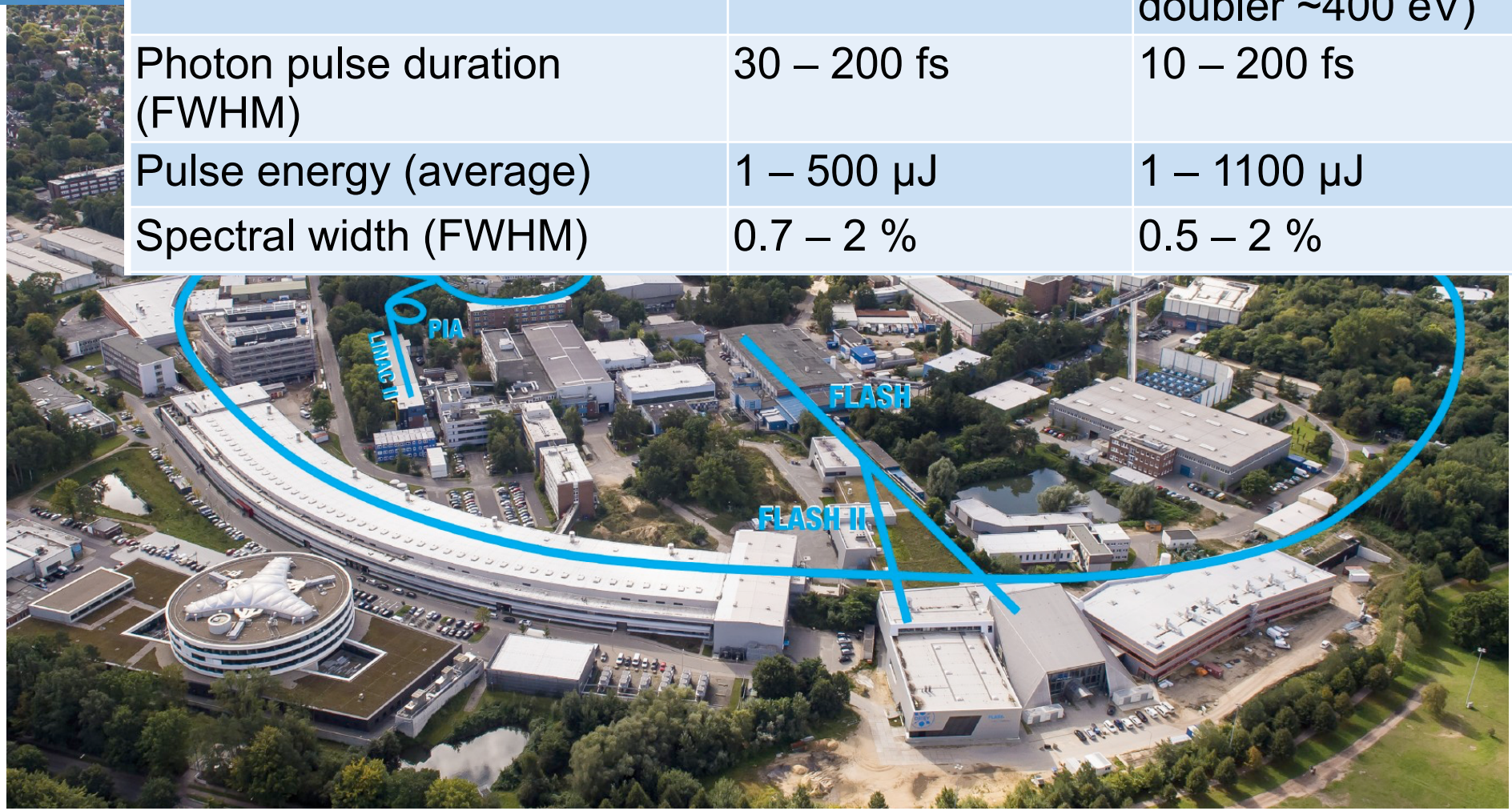
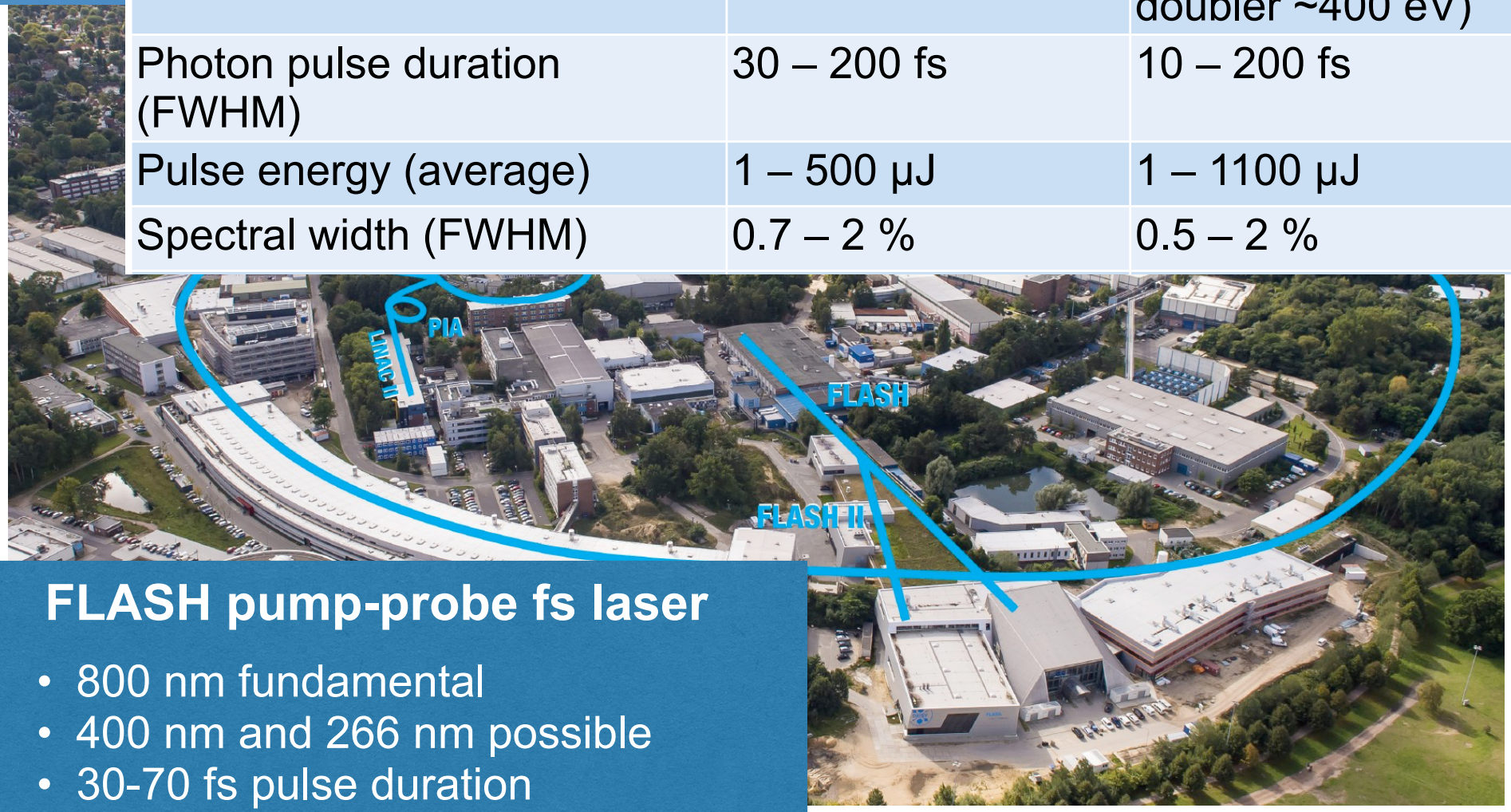


FLASH Key parameters	FLASH1	FLASH2
Photon energy fundamental	24 – 295 eV (3rd harm. ~900 eV)	14 – 310 eV (with Frequency doubler ~400 eV)
Photon pulse duration (FWHM)	30 – 200 fs	10 – 200 fs
Pulse energy (average)	1 – 500 µJ	1 – 1100 µJ
Spectral width (FWHM)	0.7 – 2 %	0.5 – 2 %



The Bahrenfeld campus - DESY



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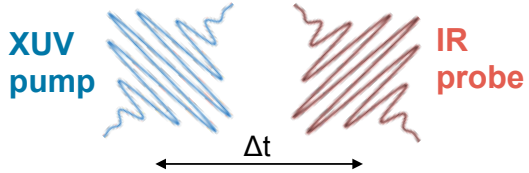
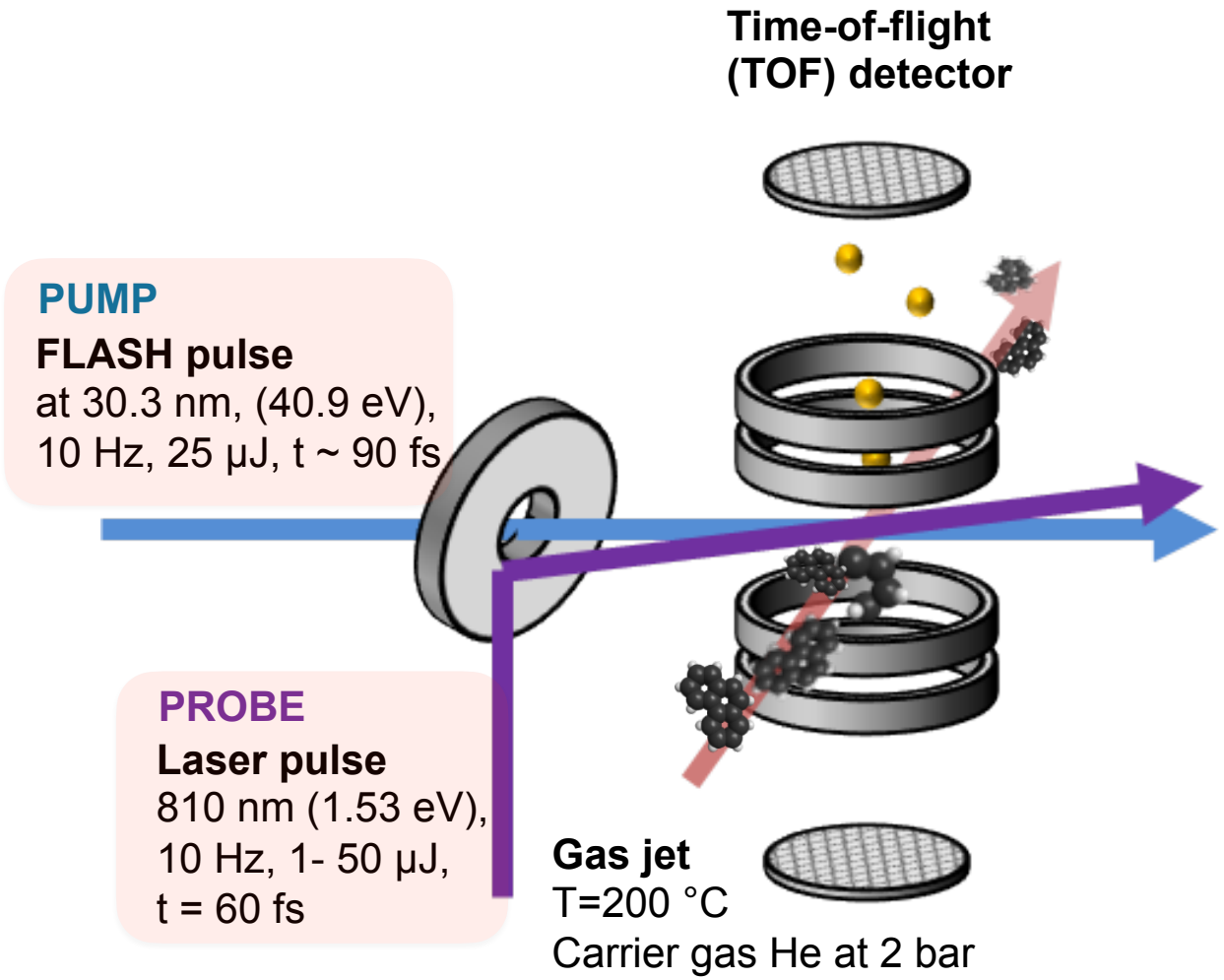
FLASH pump-probe fs laser

- 800 nm fundamental
- 400 nm and 266 nm possible
- 30-70 fs pulse duration



CAMP@FLASH

Packets of internally cold PAHs using an Even-Lavie valve



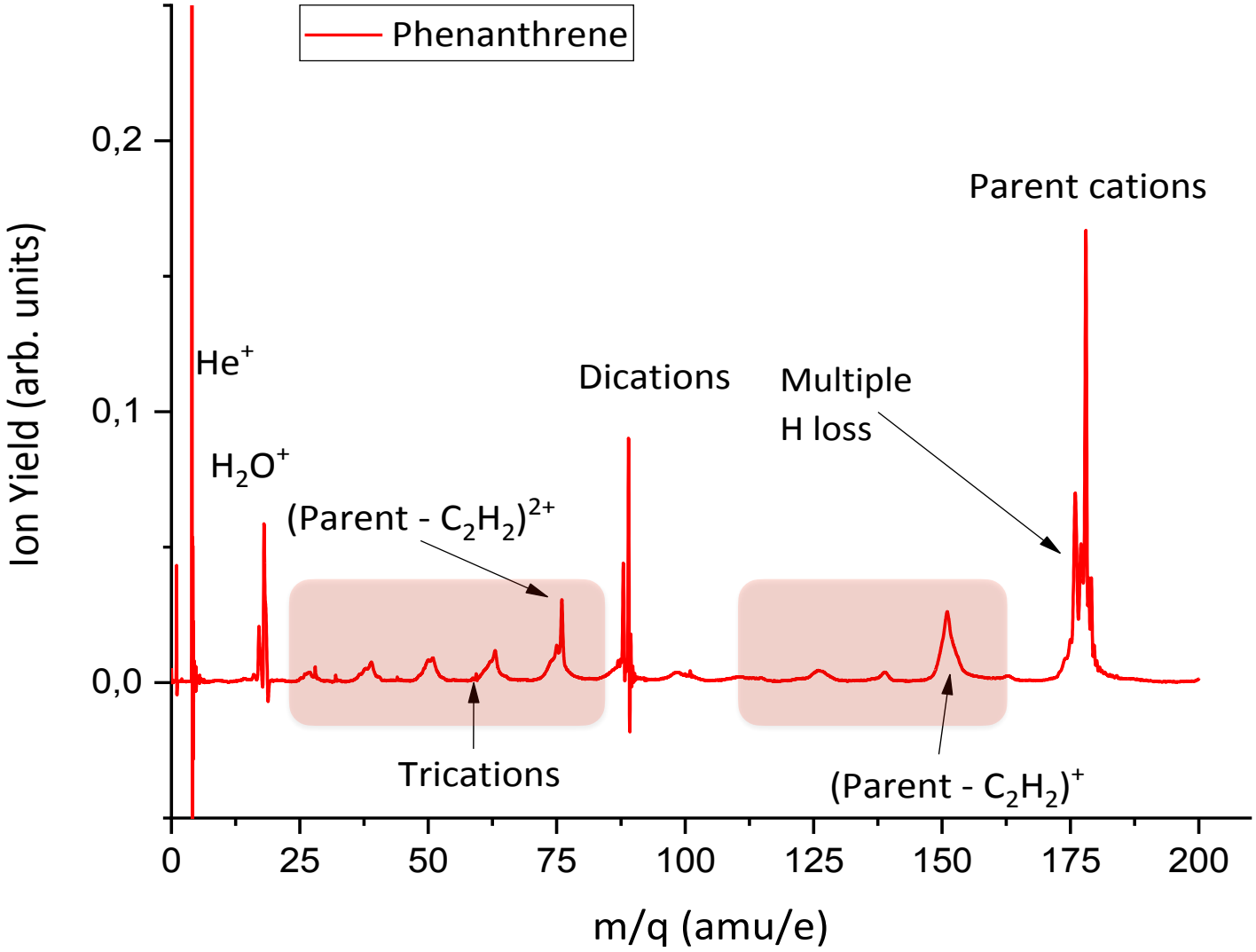
- TOF mass spectrometry of ion species
- Velocity map imaging spectrometer for electrons and ions
- **P**ixel **Im**aging **M**ass **S**pectrometry (PImMS) camera for parallel acquisition of the ion kinetic energy release and angular distribution of different fragments. Installed and operated by collaborators from Oxford University

Co-PIs Bastian Manschwetus, Jason Lee, Denis Tikhonov
the Bari, Küpper, Rolles, Johnsson teams,
as well as the FS-LA and CAMP@FLASH teams;
PImMS camera Oxford (Brouard, Vallance, Burt)

Lee *et al. Nature Communications* **12** (2021) 6107.

Ion-TOF mass spectra (FLASH: 40.9 eV)

Ionisation and different fragmentation channels



- Formation up to the parent trication
- Characteristic fragmentation pattern

CAMP@FLASH

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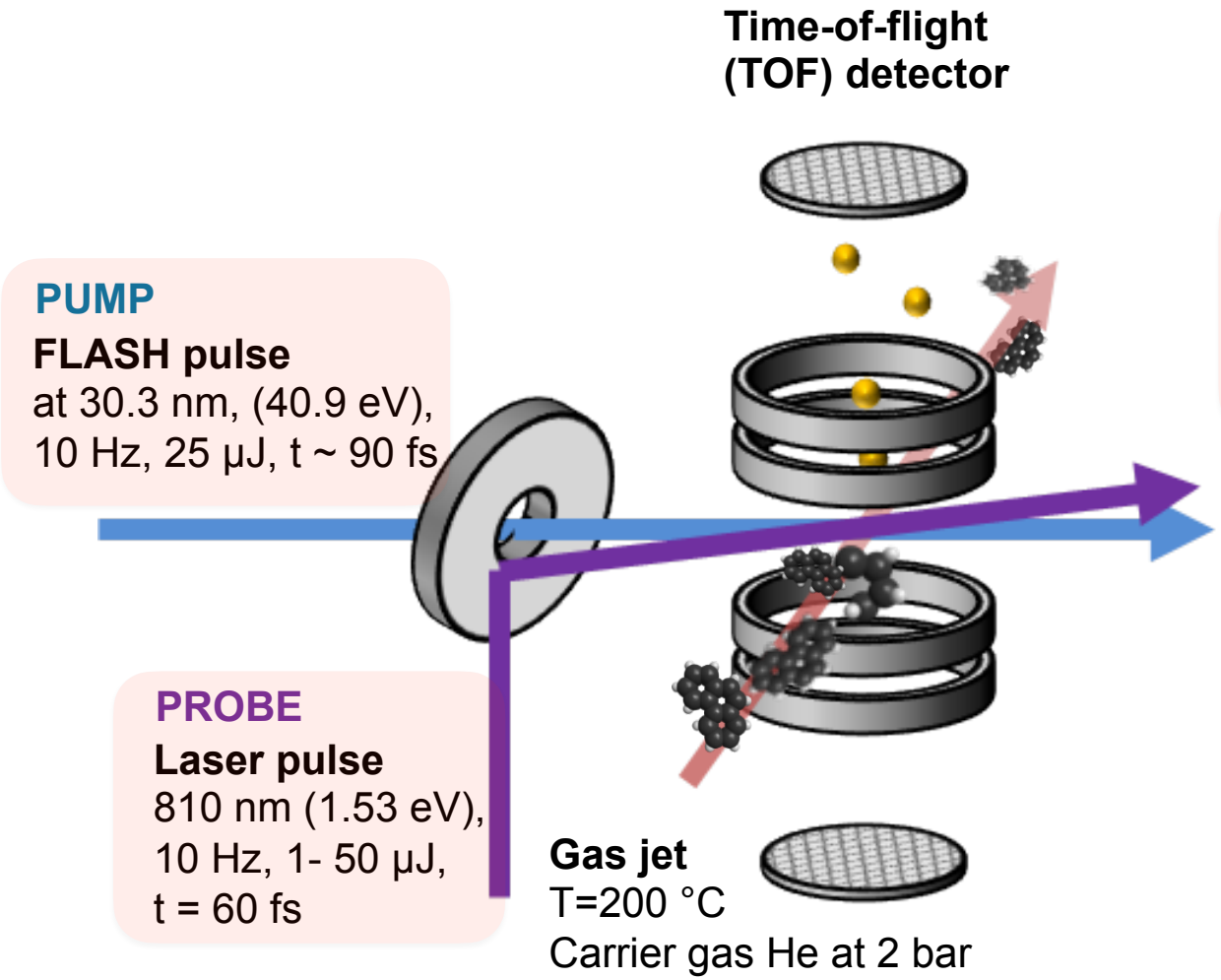

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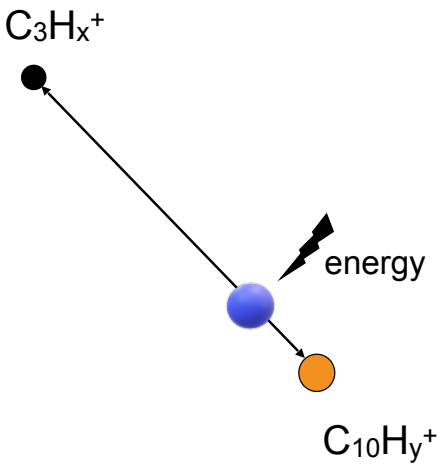
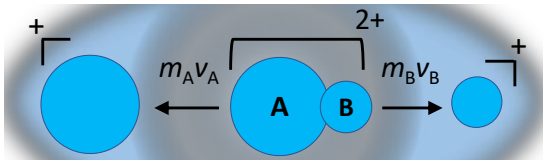
Recoil-frame covariance analysis

Fluorene
$C_{13}H_{10}$

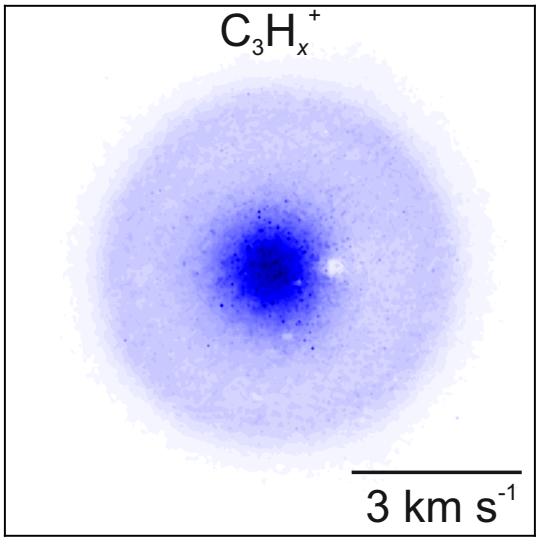
all fragments recorded simultaneously per laser pulse

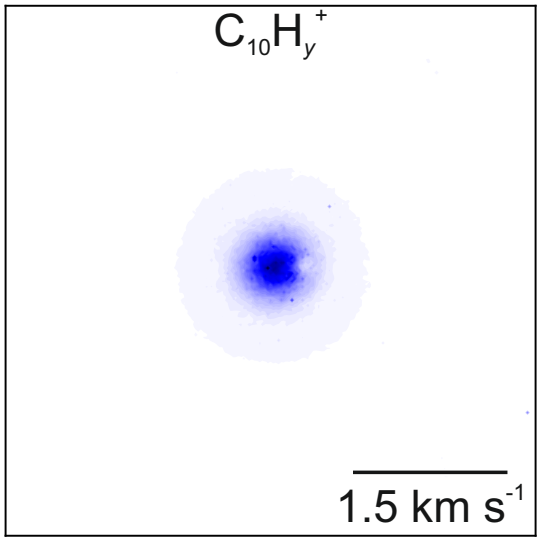
—> determine statistical correlation

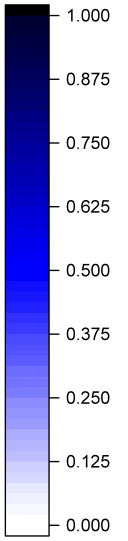




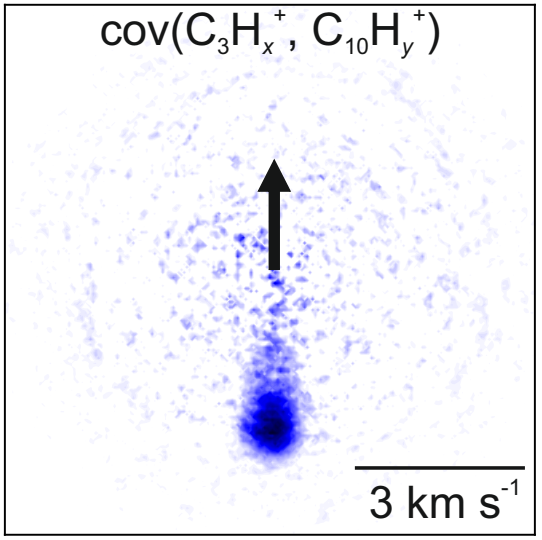
(a) velocity-map images

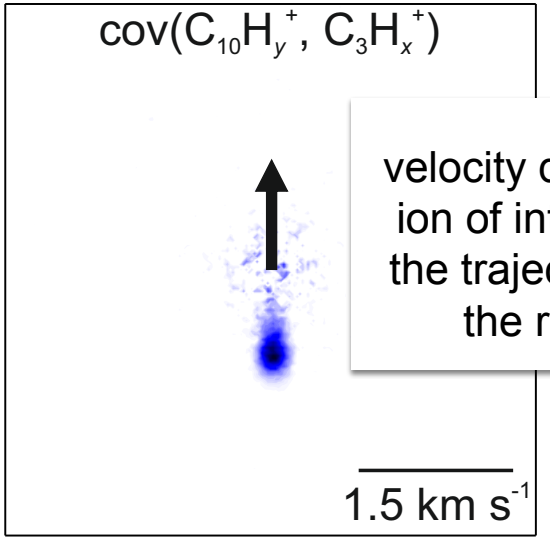






(b) recoil-frame covariance images



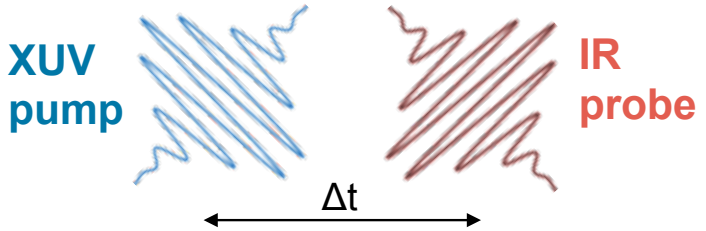


velocity distribution of the ion of interest relative to the trajectory direction of the reference ion

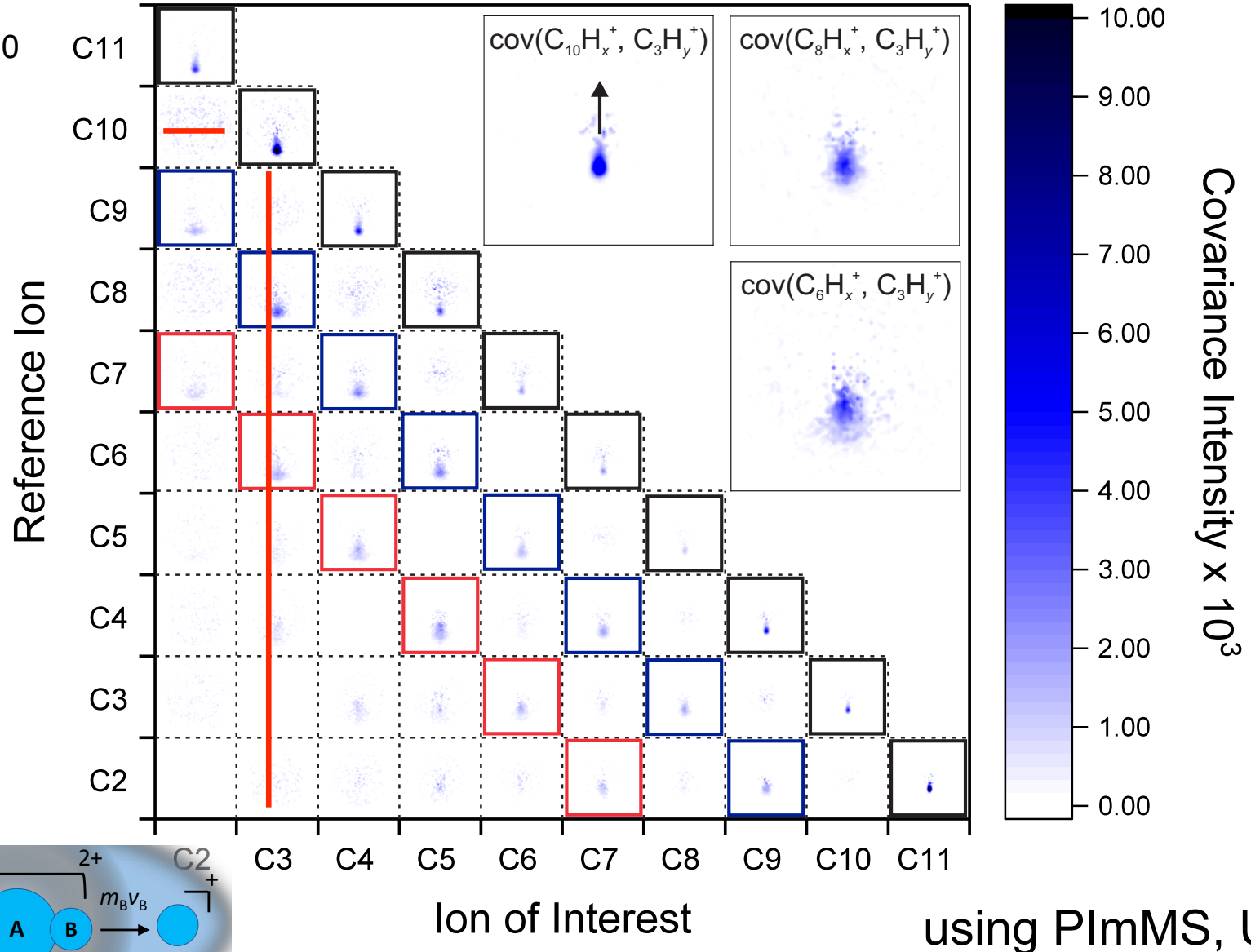
$$\mathrm{cov}(X,Y) = \langle (X - \langle X \rangle) \cdot (Y - \langle Y \rangle) \rangle = \langle XY \rangle - \langle X \rangle \langle Y \rangle$$

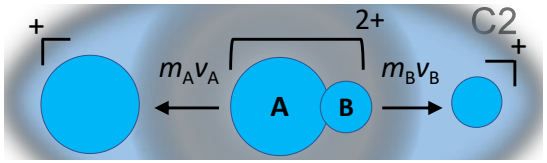
Breakup of PAH^{2+}

Recoil-frame covariance analysis



Fluorene
$C_{13}H_{10}$

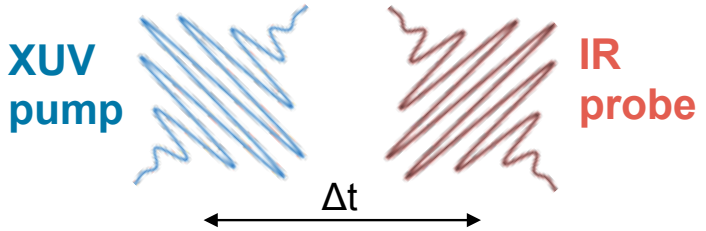




using PImMS, U Oxford

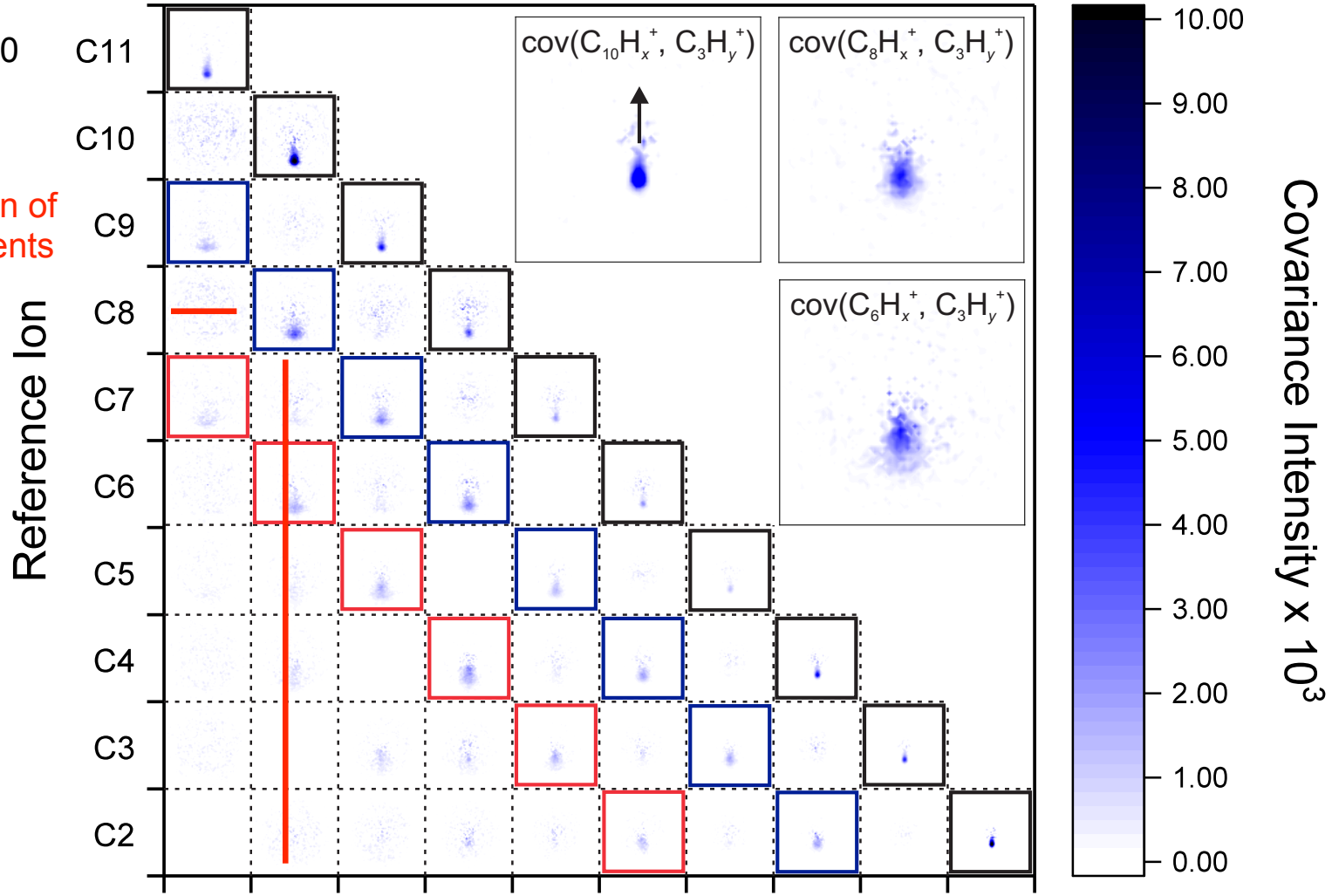
PAH breakup

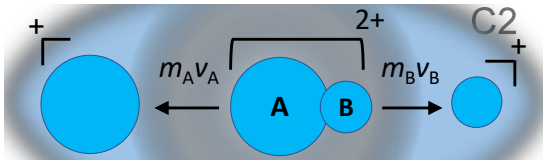
Recoil-frame covariance analysis



Fluorene
$C_{13}H_{10}$

also generation of neutral fragments

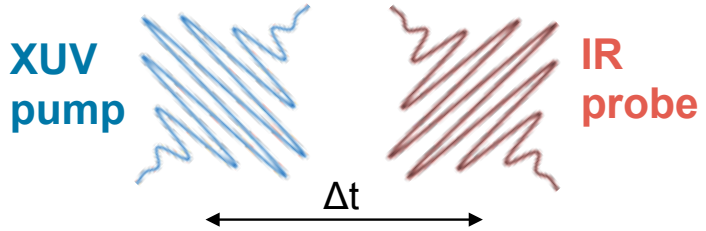


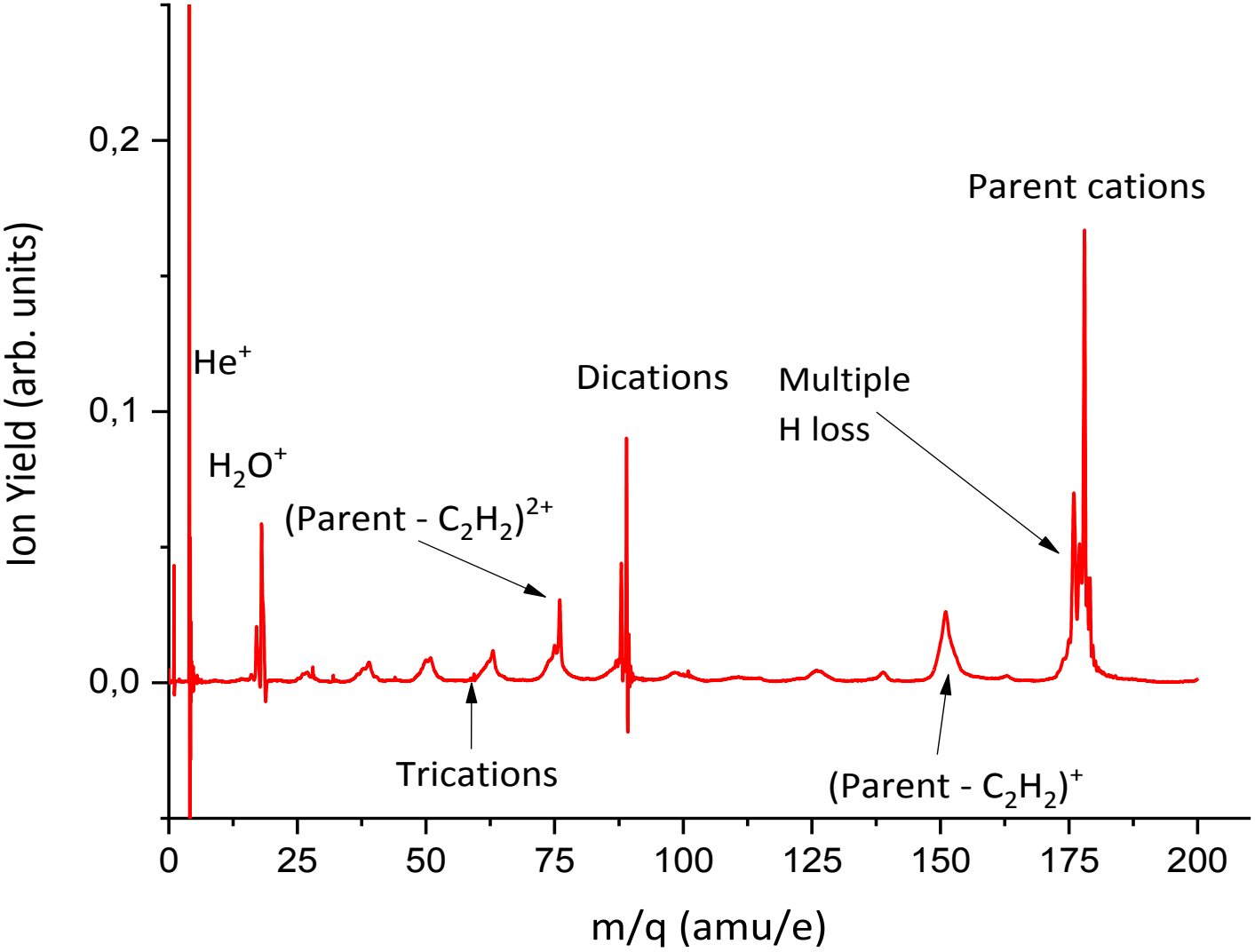


using PImMS, U Oxford

Ion-TOF mass spectra

Ionisation and different fragmentation channels

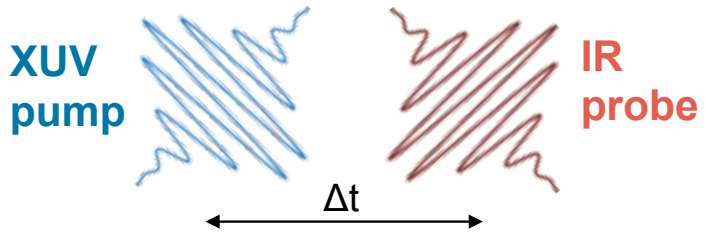


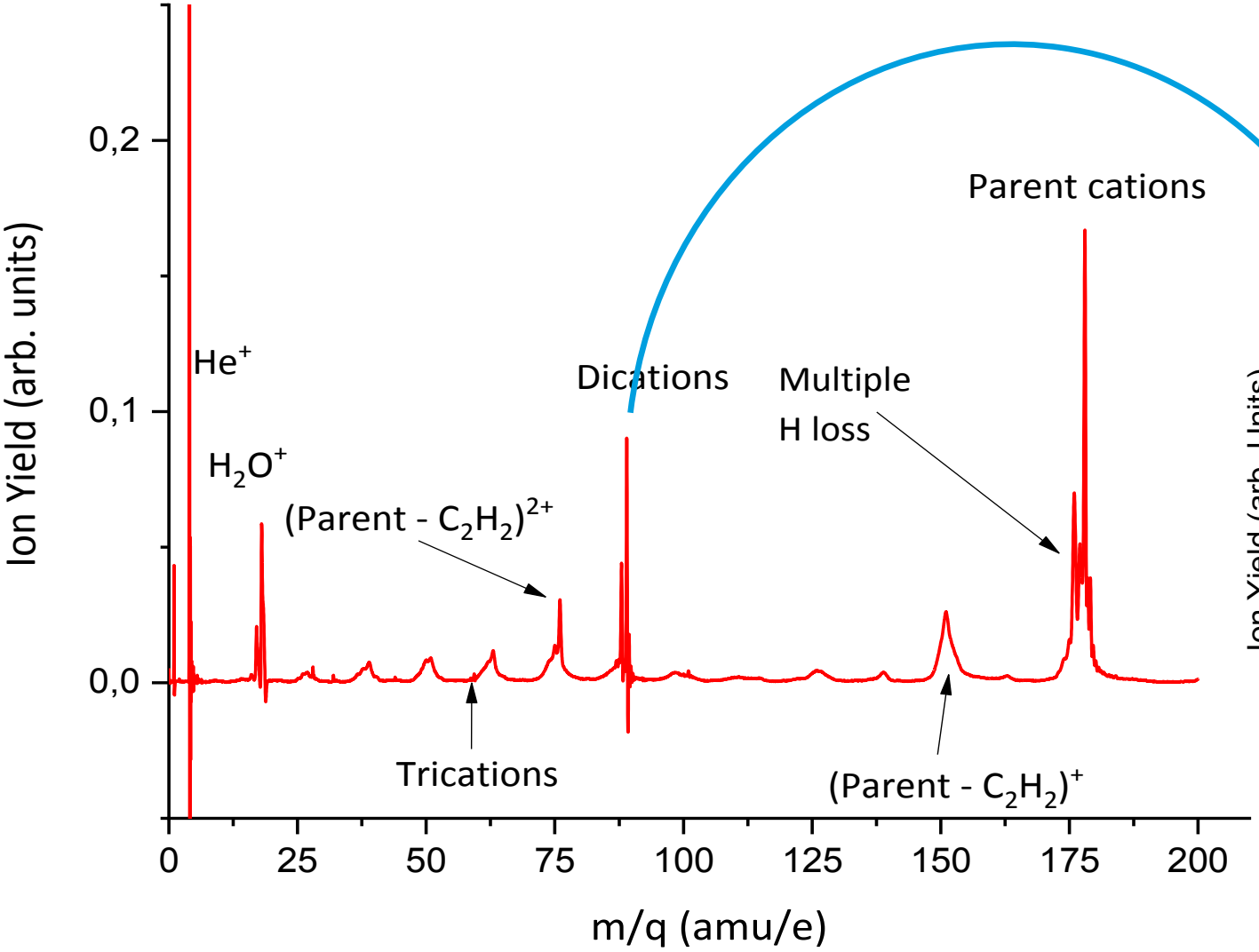


- Formation up to the parent trication
- Characteristic fragmentation pattern

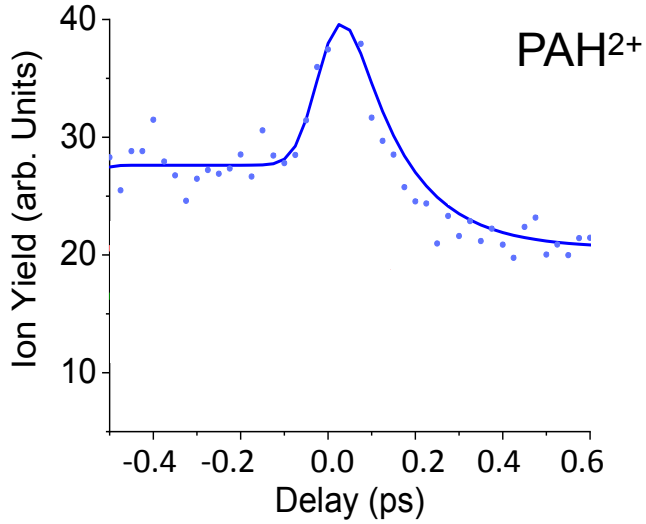
Ion-TOF mass spectra

Ionisation and different fragmentation channels



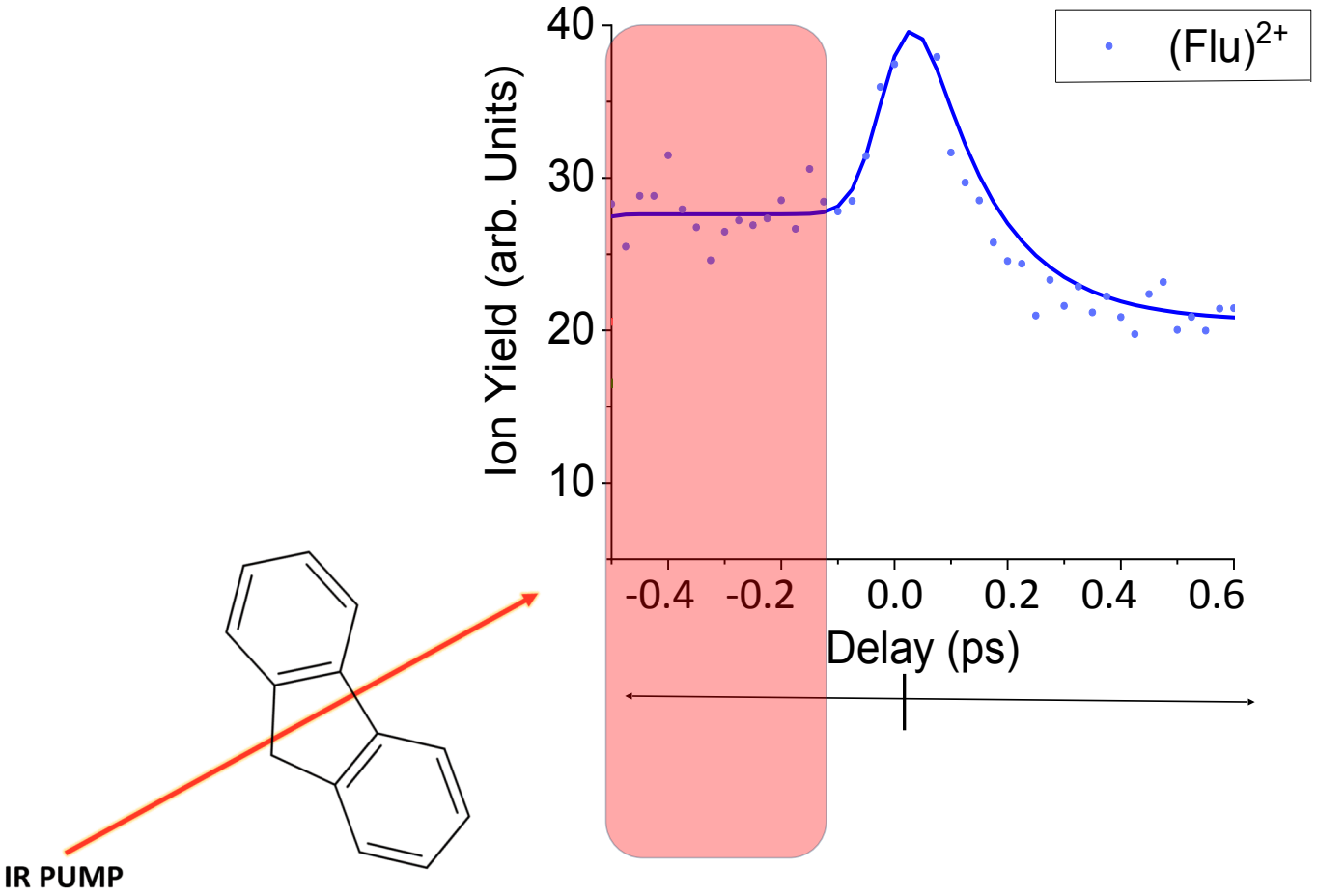


integrate and plot over all time delays



- Formation up to the parent trication
- Characteristic fragmentation pattern

Pump-probe delay curve

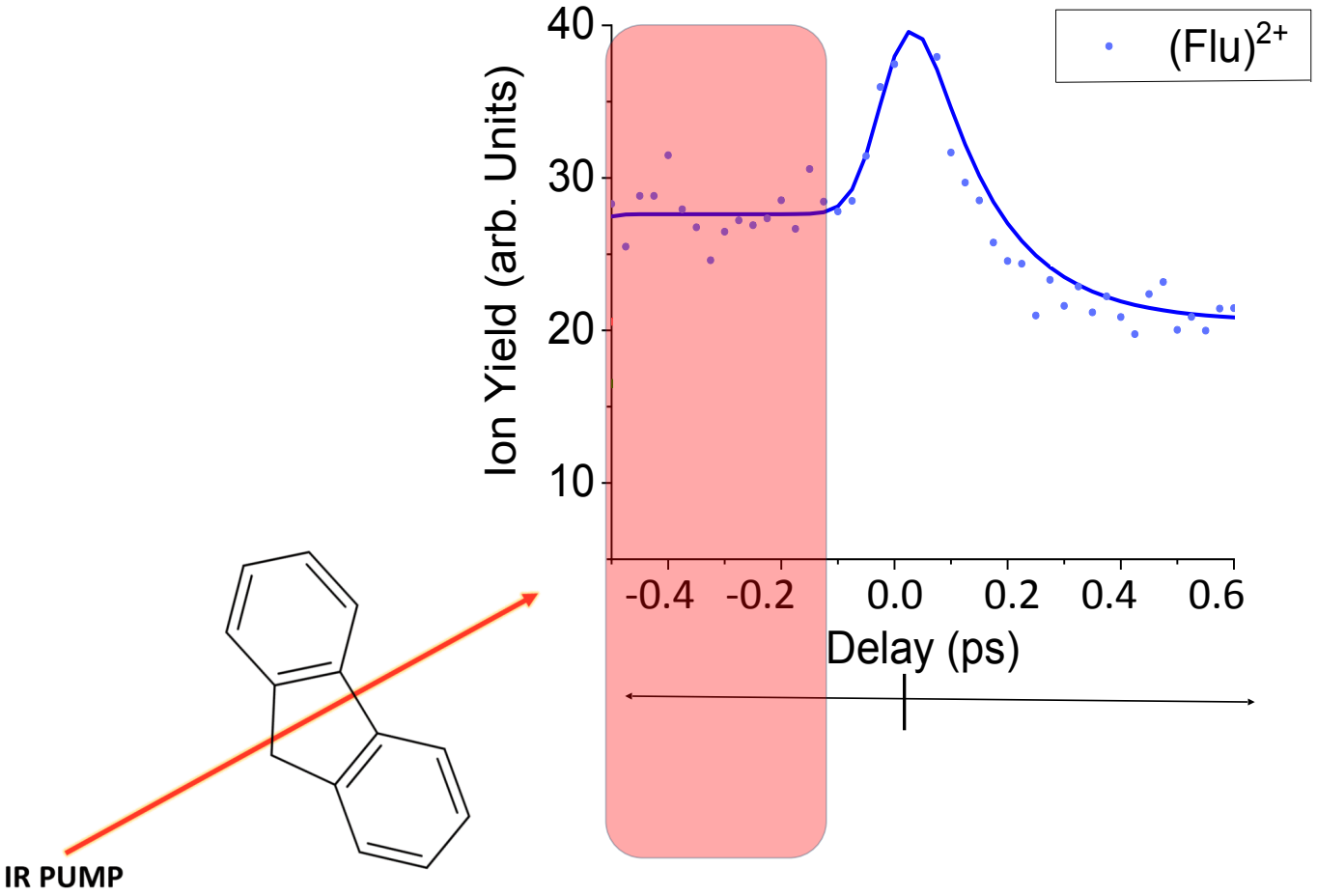


$t < t_0$

IR as pump

XUV as probe

Pump-probe delay curve



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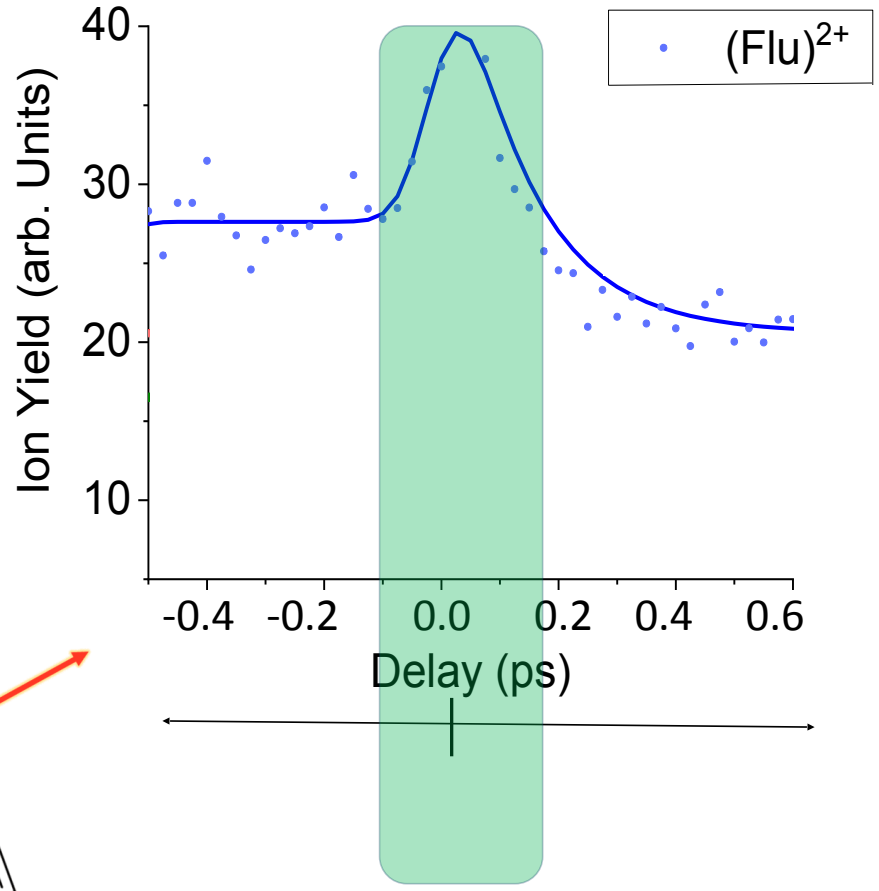
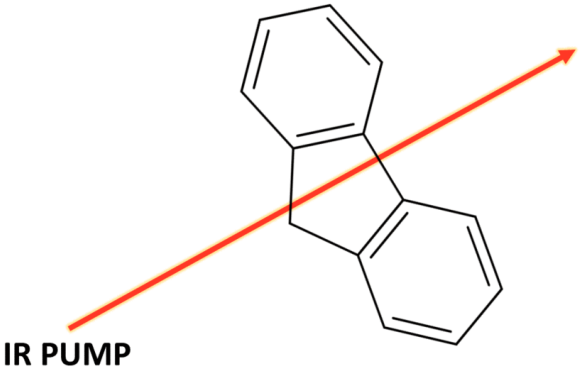
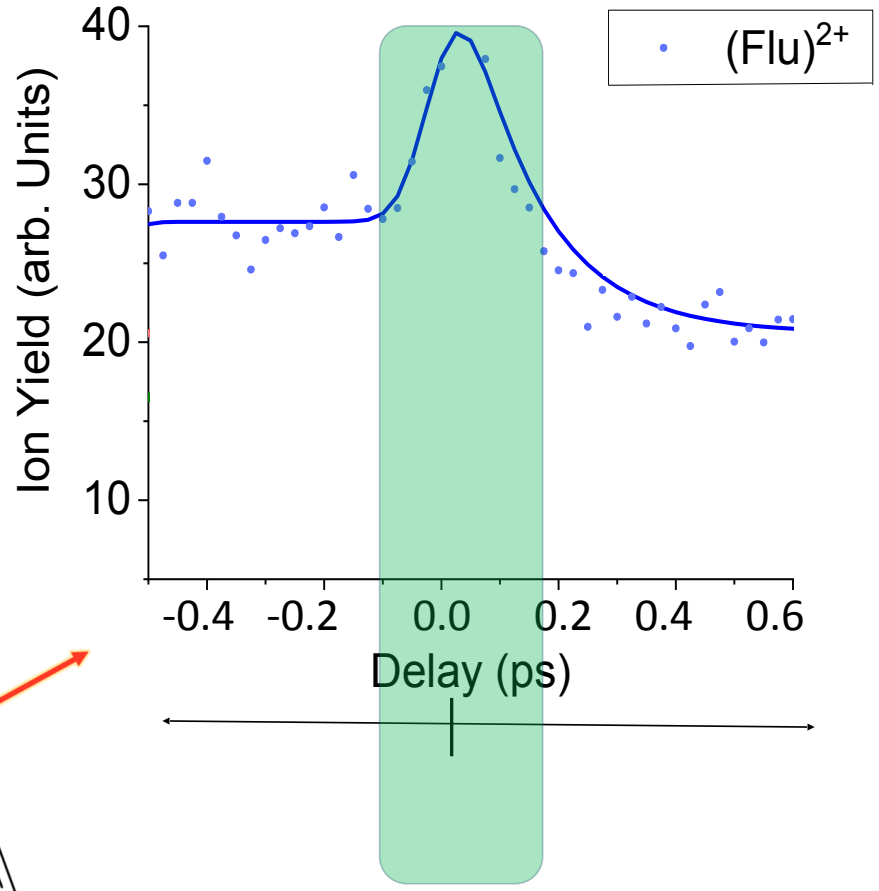


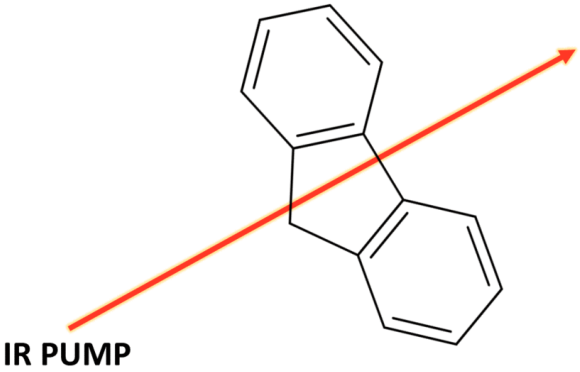


Pulses overlap

$t = t_0$

Pump-probe delay curve





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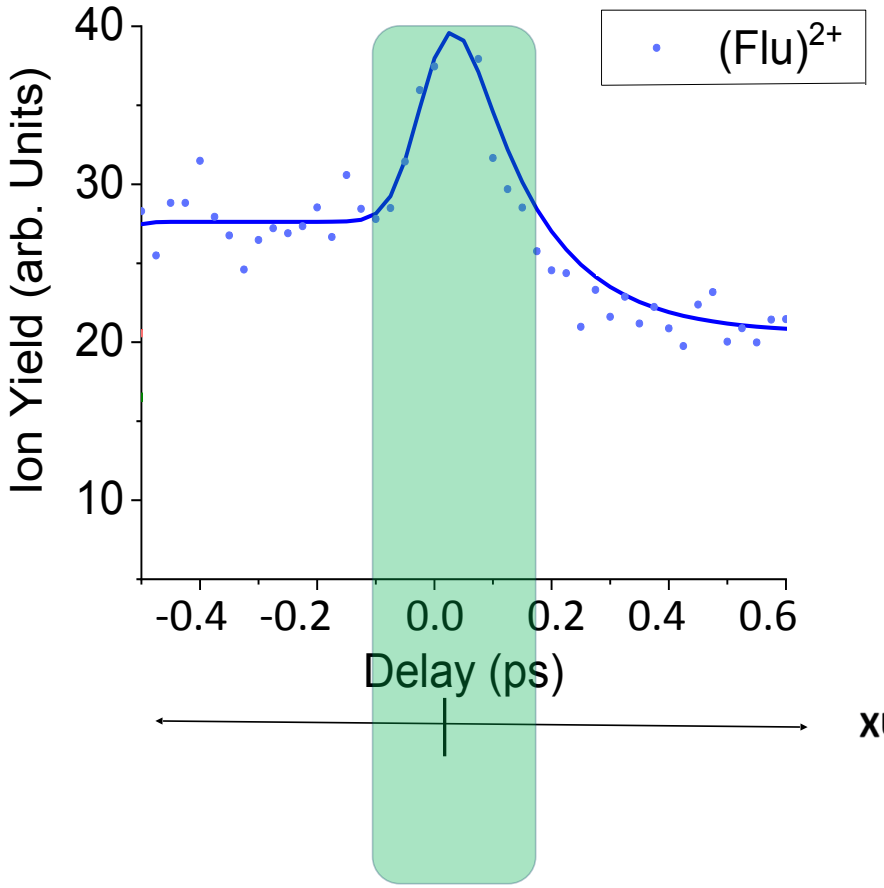
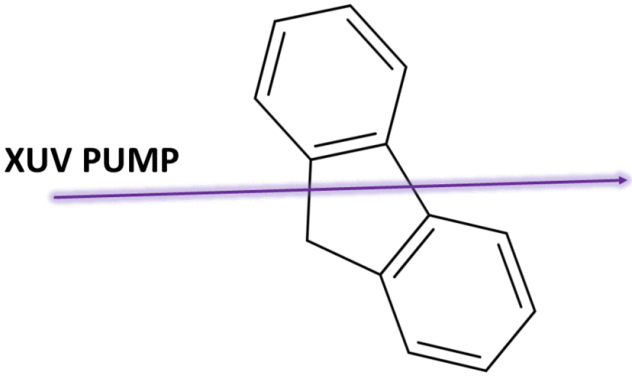


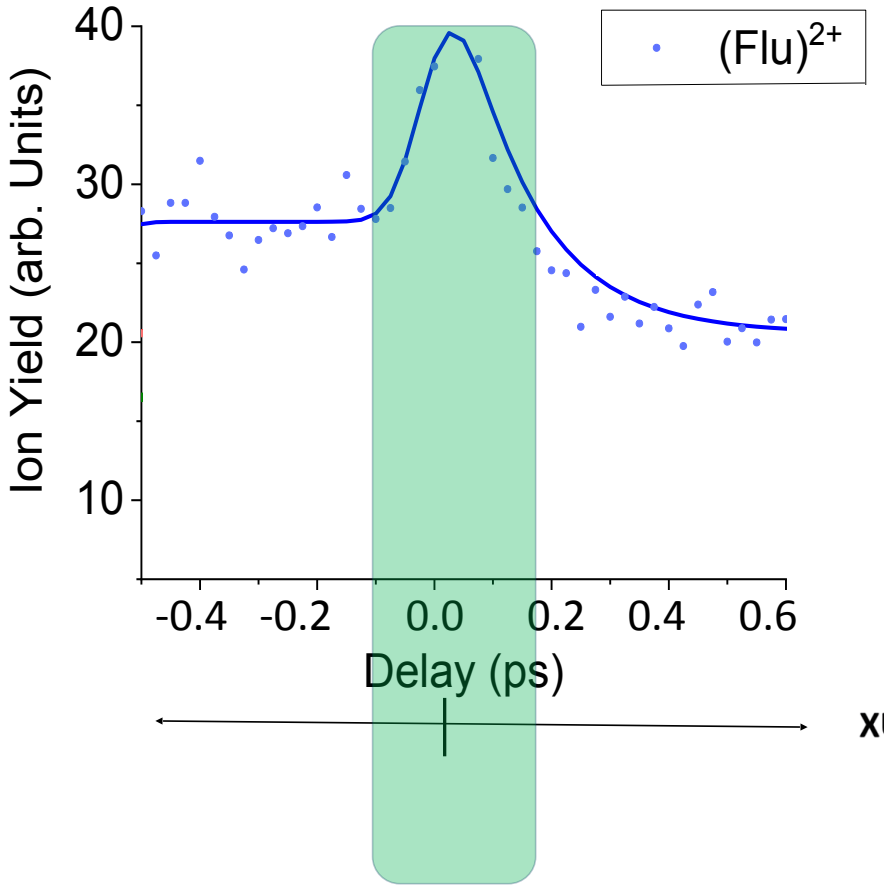


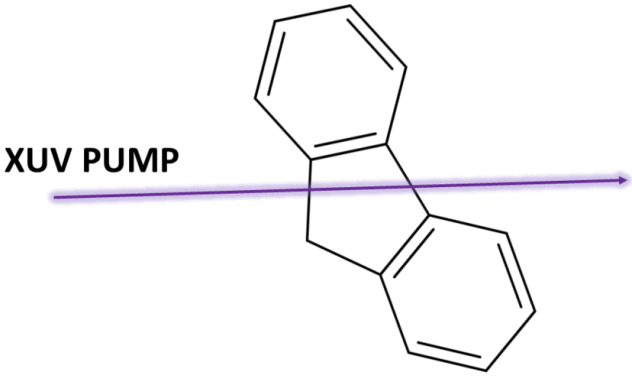
$t > t_0$

XUV as pump

IR as probe

Pump-probe delay curve



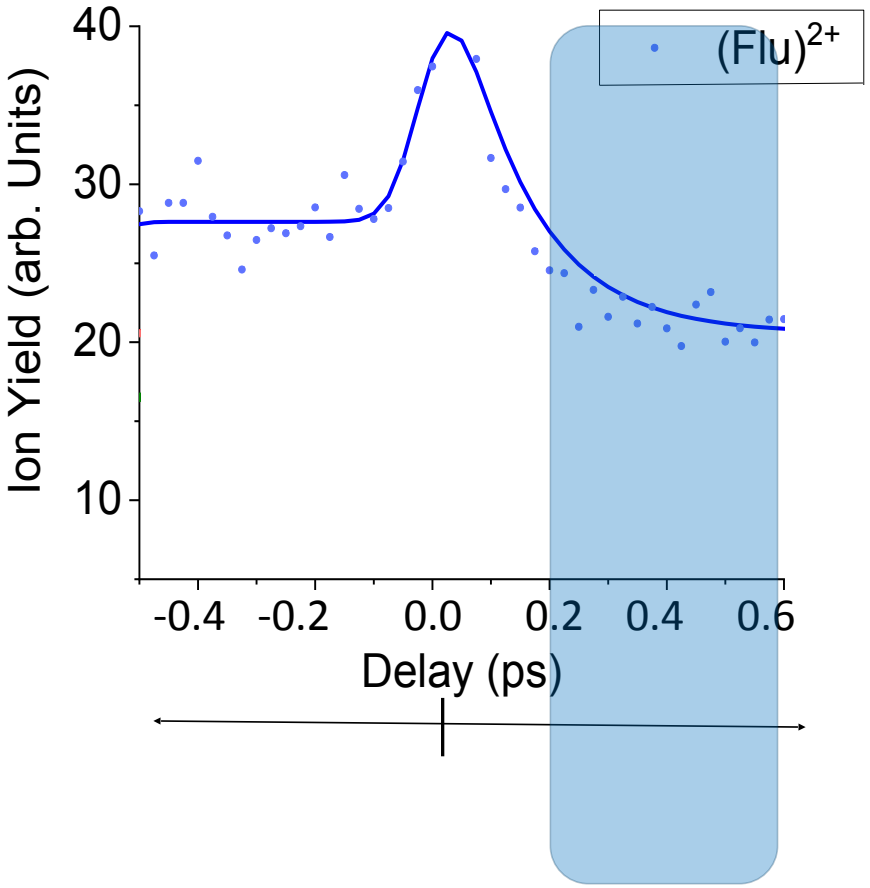


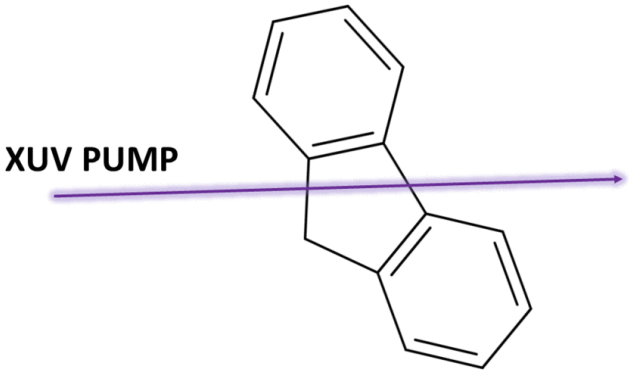
$t > t_0$

XUV as pump

IR as probe

Pump-probe delay curve



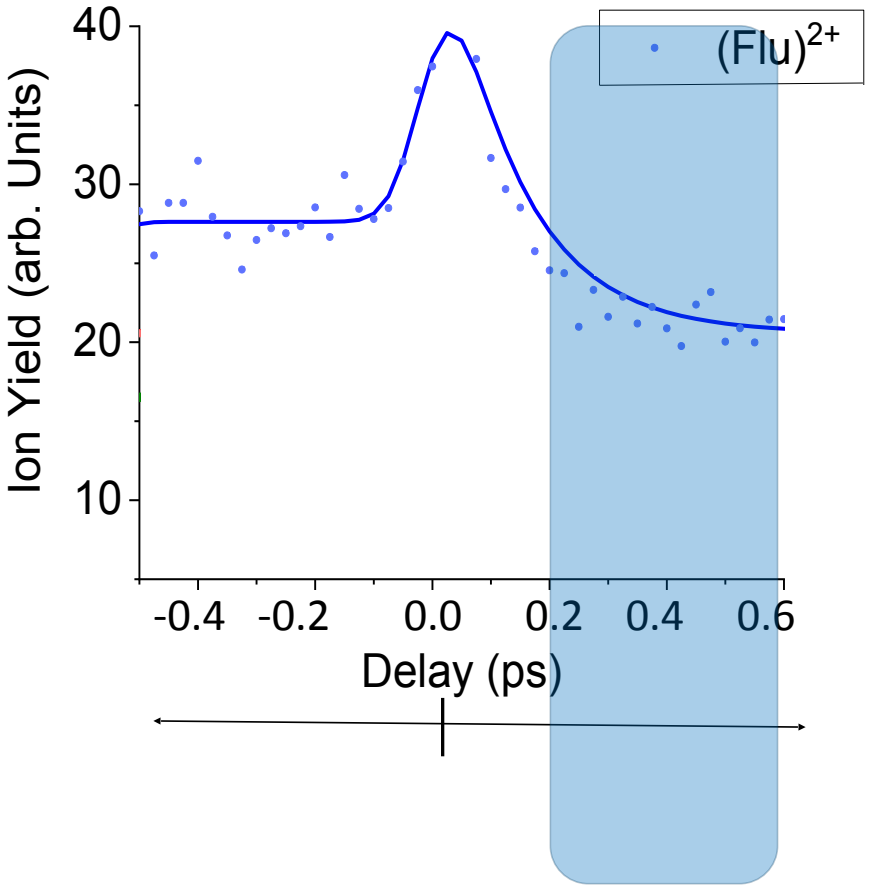


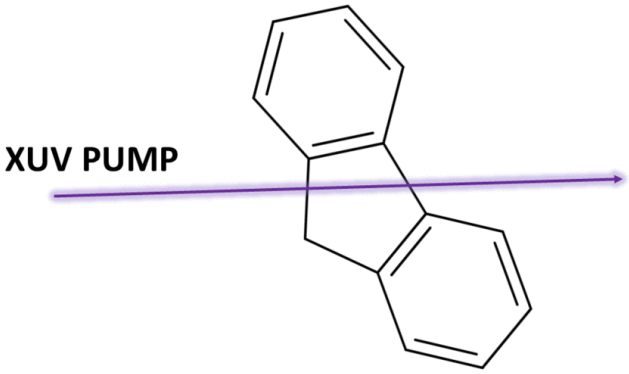
$t > t_0$

XUV as pump

IR as probe

Pump-probe delay curve



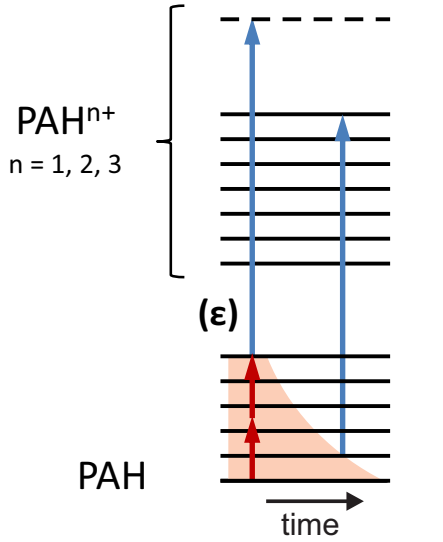


$t > t_0$

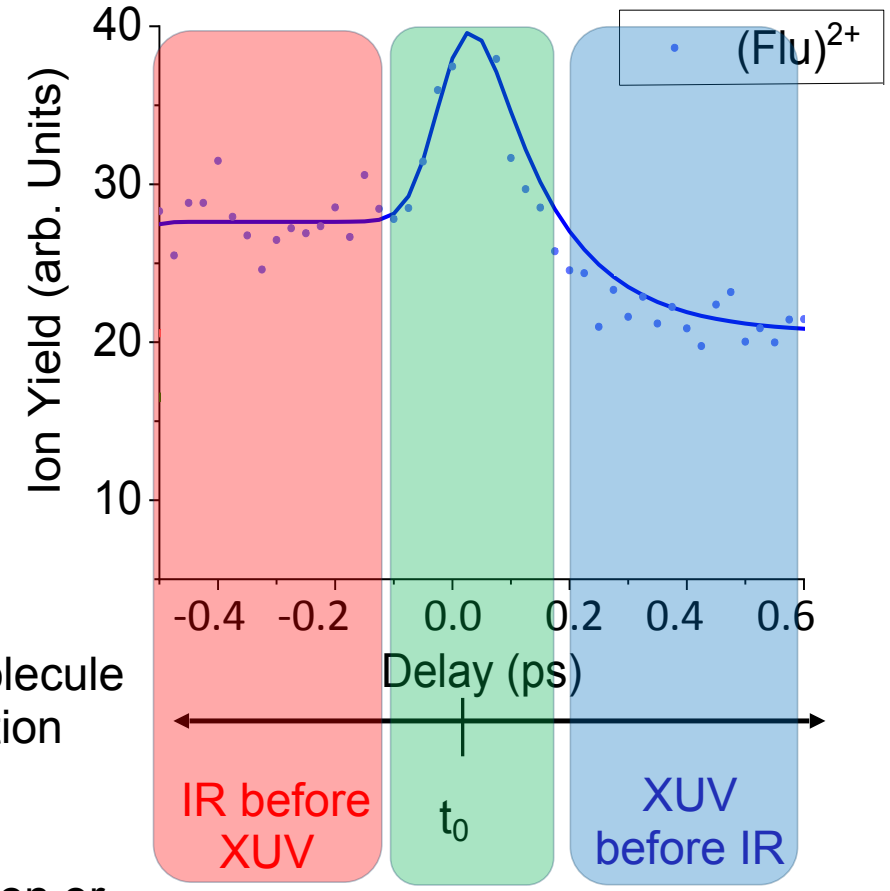
XUV as pump

IR as probe

Schematic of the PAH states

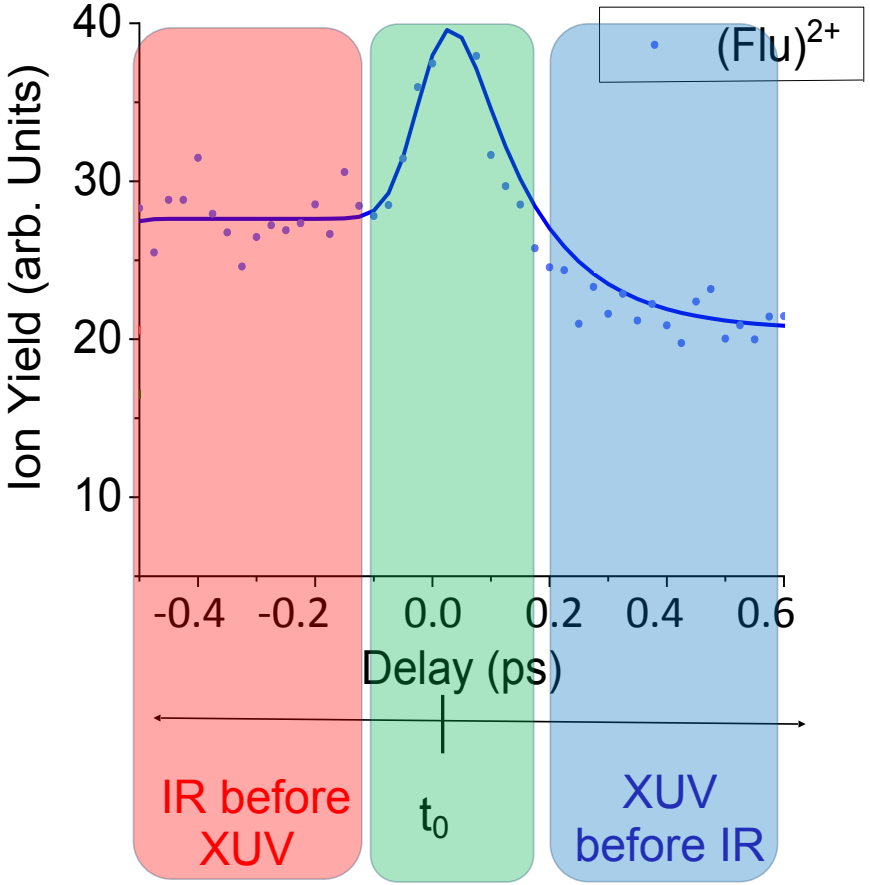


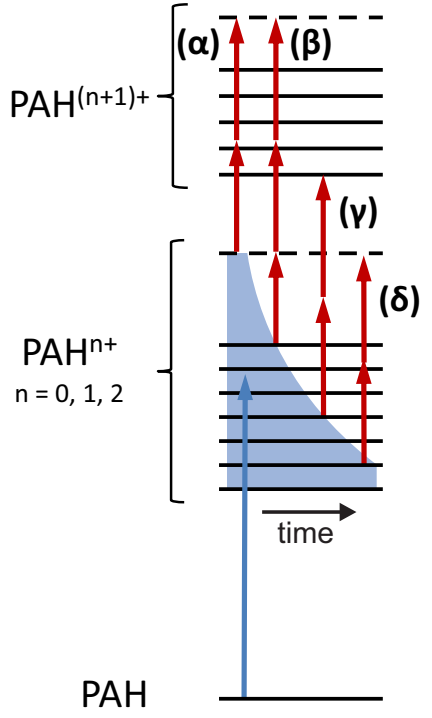
IR pump, XUV probe



- IR: excited neutral molecule by multiphoton excitation (FLU*)
- XUV: leads to ionization or dissociative ionization (FLU^{2+})

Schematic of the PAH states

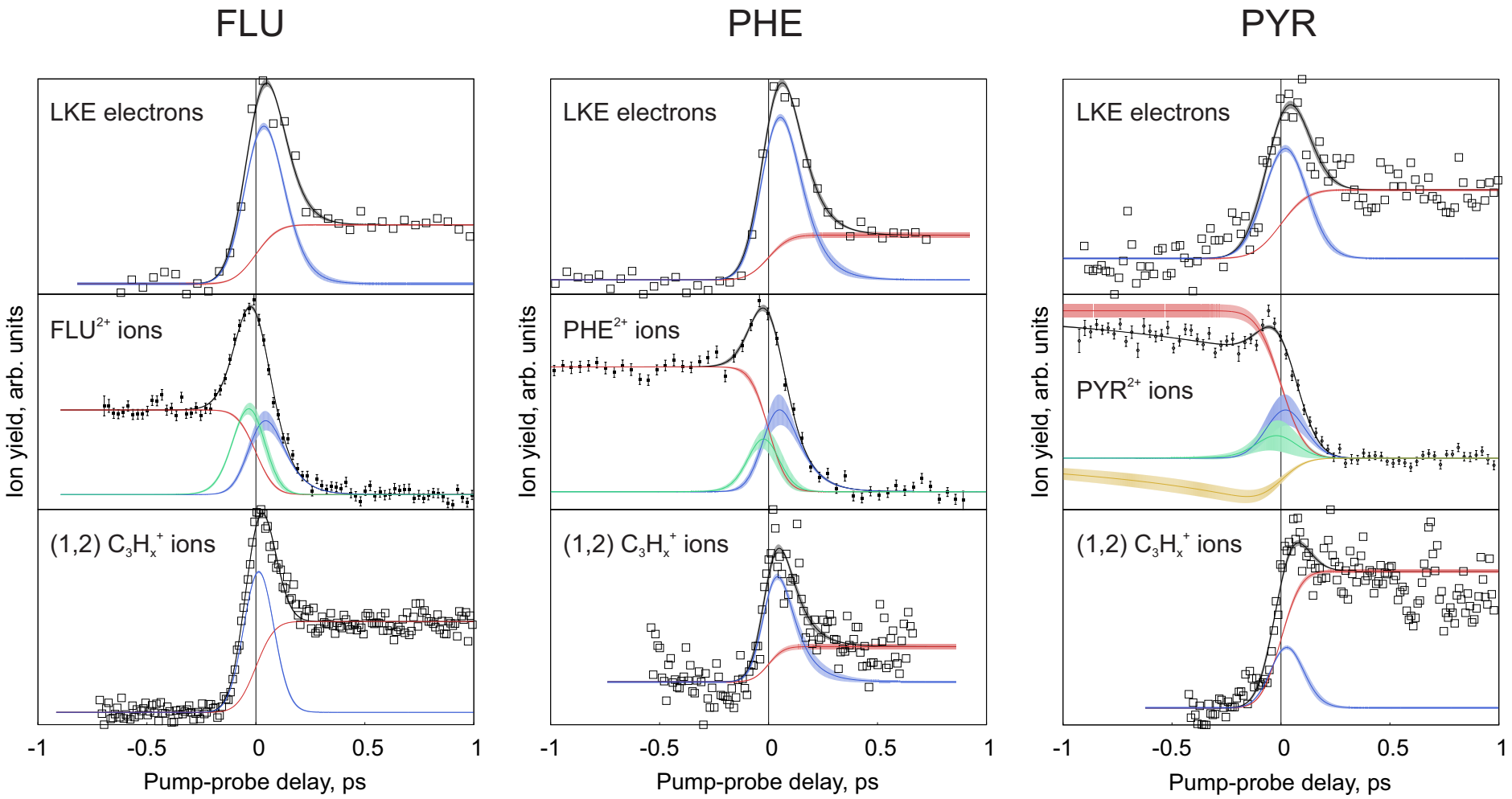




XUV pump, IR probe

- XUV: electronically excited charged molecule (Flu^{+*})
- IR before electronic relaxation: promote to next charged state (FLU^{2+})
- IR after longer delays: molecule electronically relaxes, leads to fragmentation

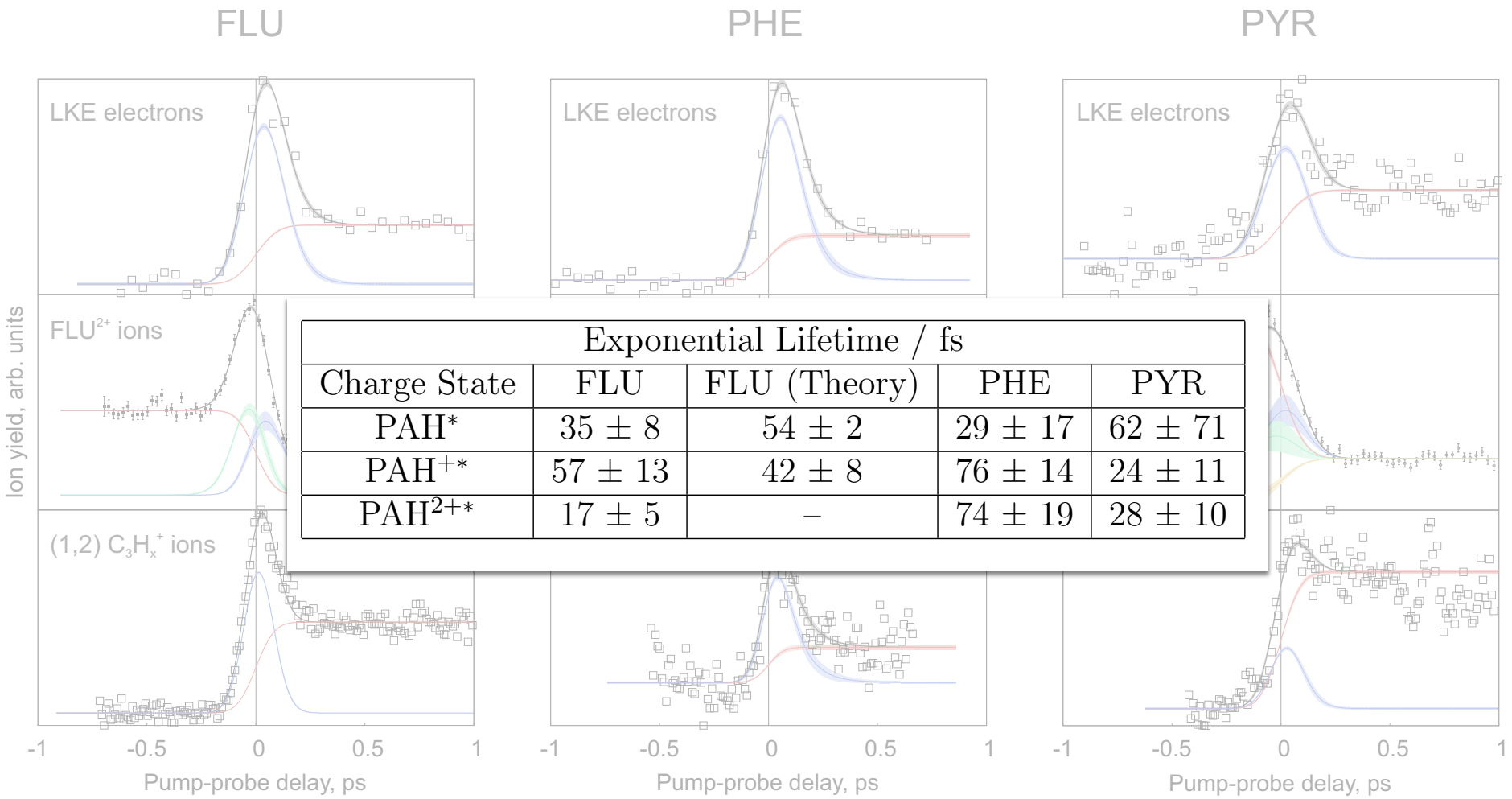
Delay-dependent yields



- green: IR pump — XUV probe
- blue: XUV pump — IR probe
- red: change in signal due to different PAH ionisation rates populated by the pump laser

A Monte Carlo sampling procedure is used to obtain the relaxation times of the PAH^{+*} species.

Delay-dependent yields

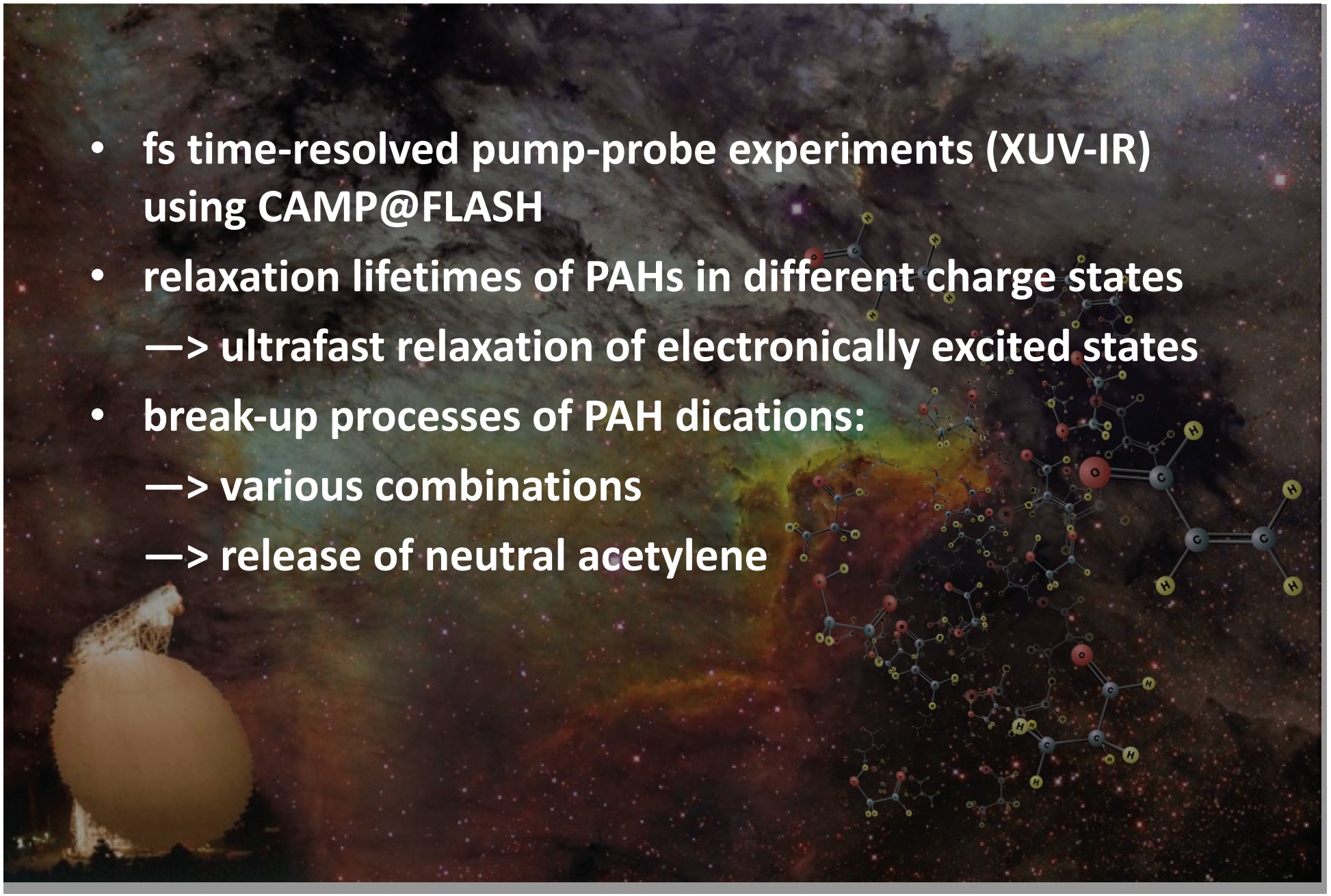


Exponential Lifetime / fs				
Charge State	FLU	FLU (Theory)	PHE	PYR
PAH^*	35 ± 8	54 ± 2	29 ± 17	62 ± 71
PAH^{+*}	57 ± 13	42 ± 8	76 ± 14	24 ± 11
PAH^{2+*}	17 ± 5	–	74 ± 19	28 ± 10

- green: IR pump — XUV probe
- blue: XUV pump — IR probe
- red: change in signal due to different PAH ionisation rates populated by the pump laser

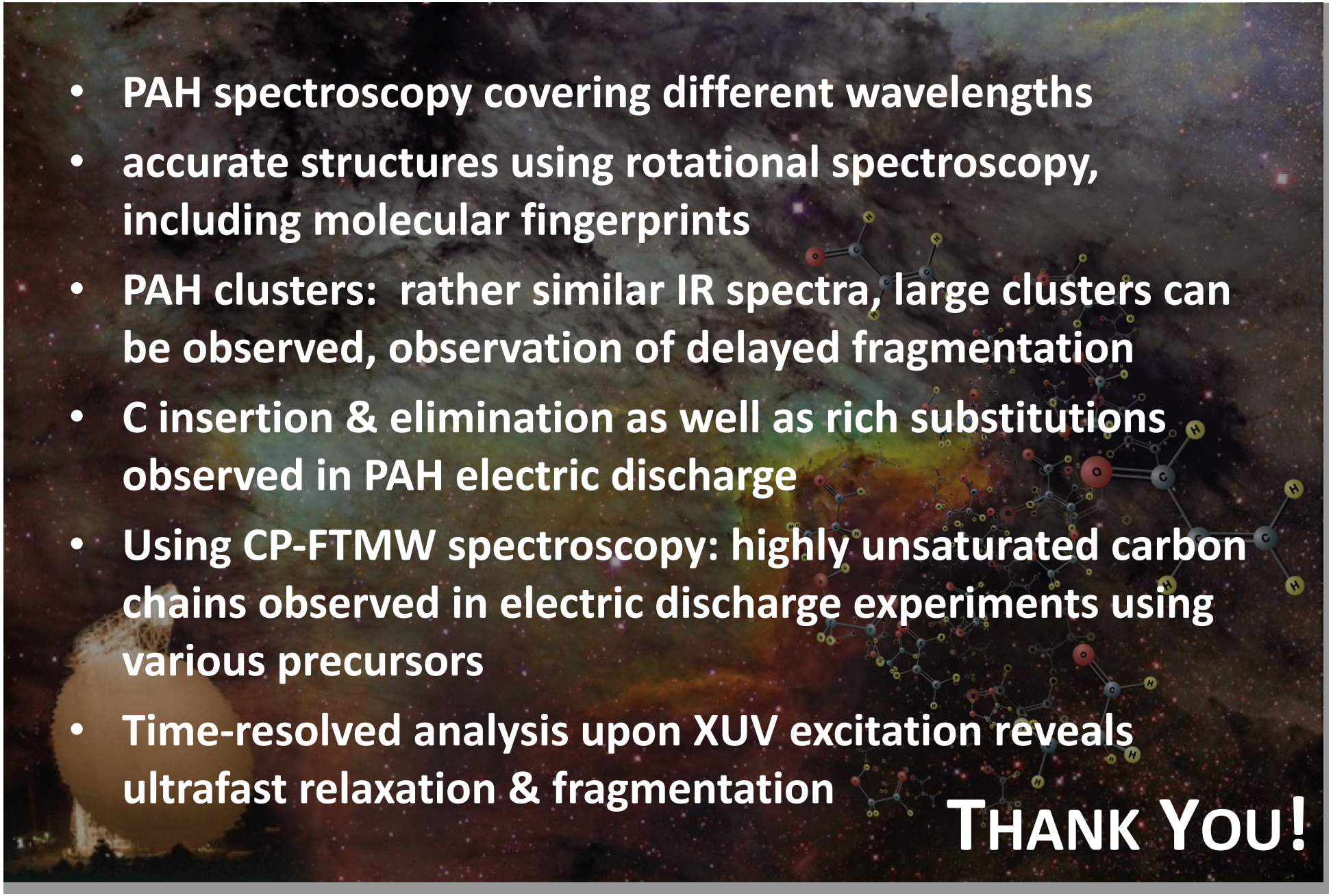
A Monte Carlo sampling procedure is used to obtain the relaxation times of the PAH^{+*} species.

Summary PAH photophysics



- fs time-resolved pump-probe experiments (XUV-IR) using CAMP@FLASH
- relaxation lifetimes of PAHs in different charge states
  —> ultrafast relaxation of electronically excited states
- break-up processes of PAH dications:
  —> various combinations
  —> release of neutral acetylene

Summary and conclusions



- PAH spectroscopy covering different wavelengths
- accurate structures using rotational spectroscopy, including molecular fingerprints
- PAH clusters: rather similar IR spectra, large clusters can be observed, observation of delayed fragmentation
- C insertion & elimination as well as rich substitutions observed in PAH electric discharge
- Using CP-FTMW spectroscopy: highly unsaturated carbon chains observed in electric discharge experiments using various precursors
- Time-resolved analysis upon XUV excitation reveals ultrafast relaxation & fragmentation

THANK YOU!

Acknowledgement

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DFG Deutsche Forschungsgemeinschaft

FCI Fonds der Chemischen Industrie

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erc European Research Council

CMWS Centre for Molecular Water Science

The group (& some guests)

and: Cristobal Perez, Amanda Steber, Sergio Domingos

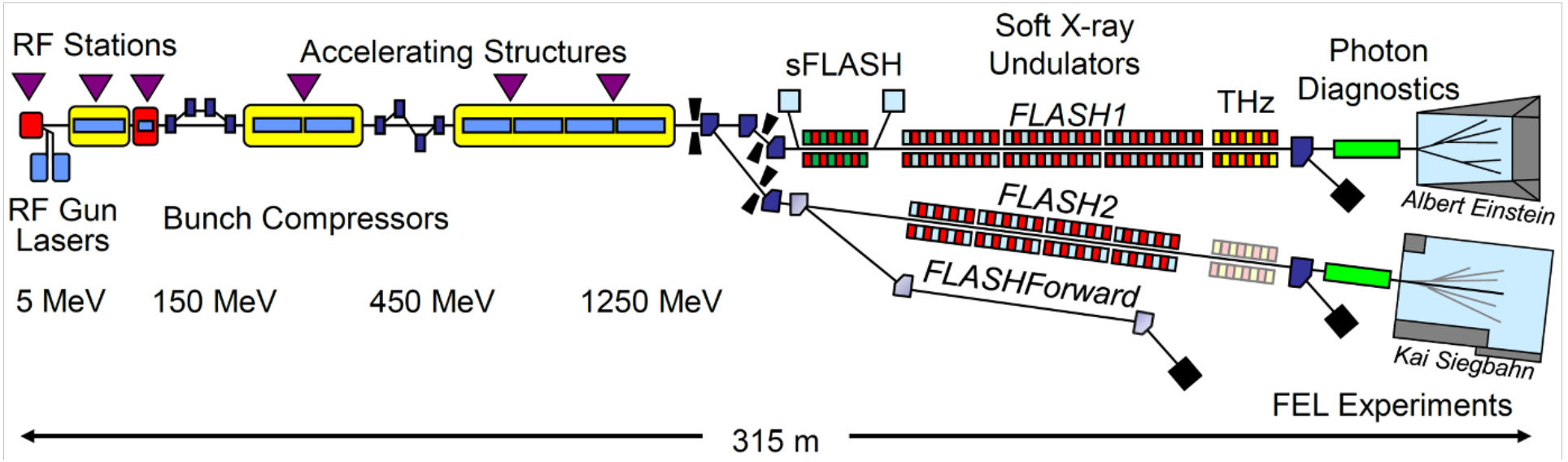
Collaborations

H. Leung, M. Marshall, Amherst College
J.-U. Grabow, Leibniz Universität Hannover
Z. Kisiel, Warsaw, Poland
P. R. Schreiner, Universität Gießen
D. Patterson, UC Santa Barbara

J. C. Lopez, Universidad de Valladolid, Spain
A. M. Rijs, VU Amsterdam
M. Gerhards, TU Kaiserslautern
M. Suhm, Universität Göttingen
N. Mitzel, Universität Bielefeld
L. Nahon, SOLEIL, Orsay

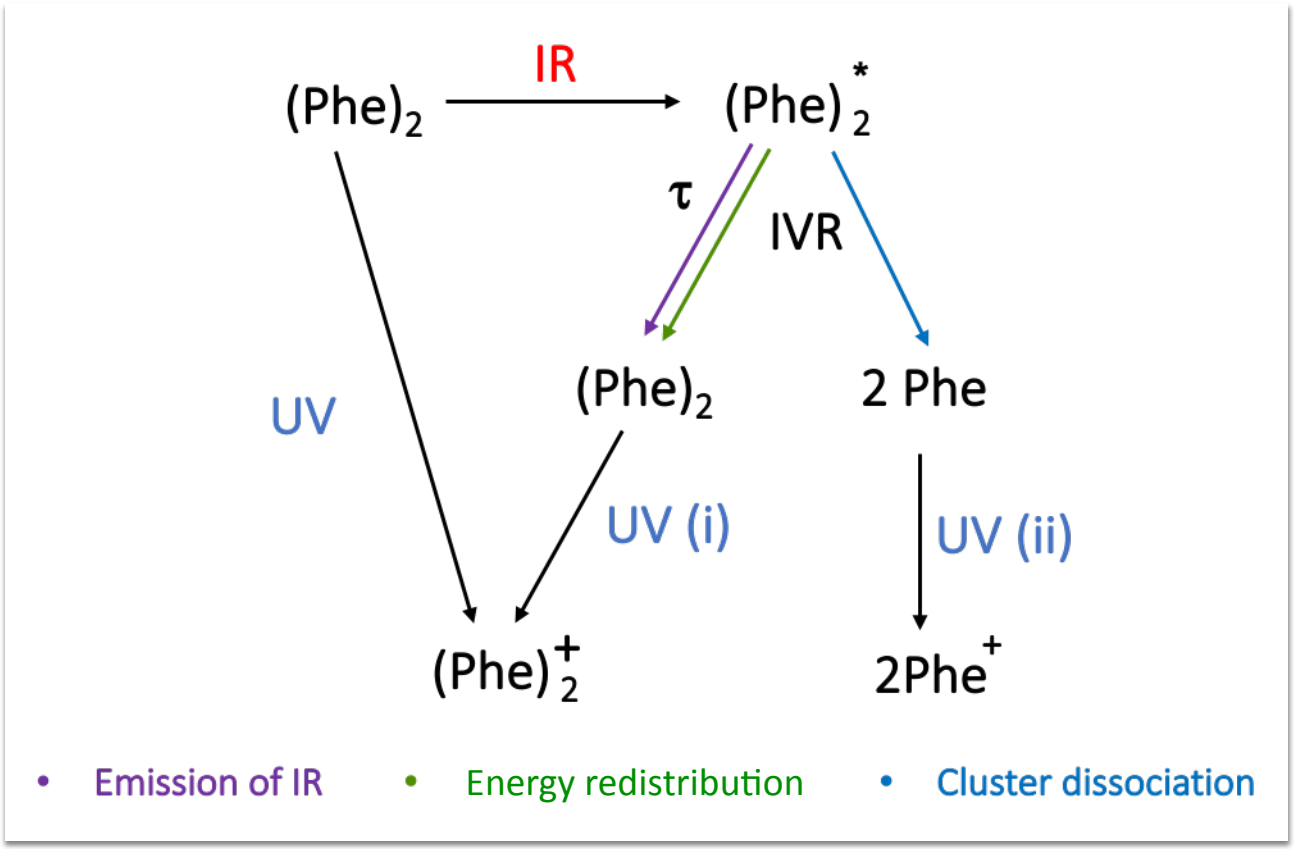
FLASH: The XUV to soft-X-ray FEL in Hamburg

RF electron gun | Accelerator module | Bunch compressor | Undulator assembly | Experimental hall

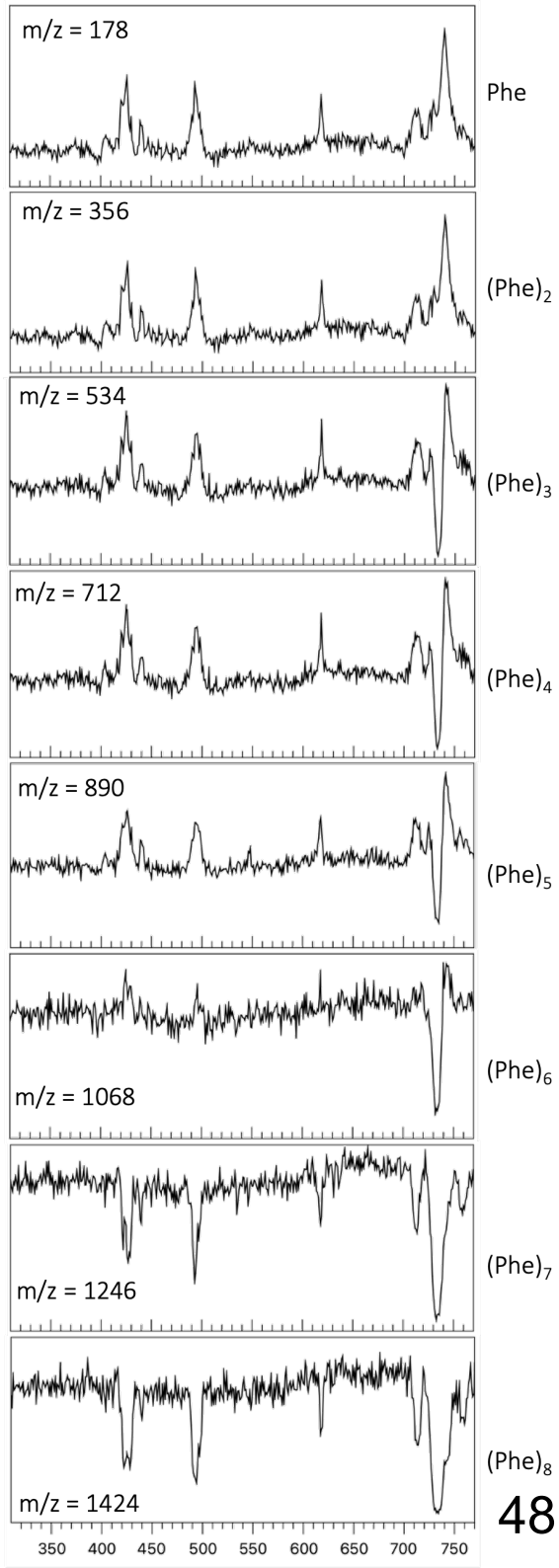


Phenanthrene and its (many) clusters

IR spectra



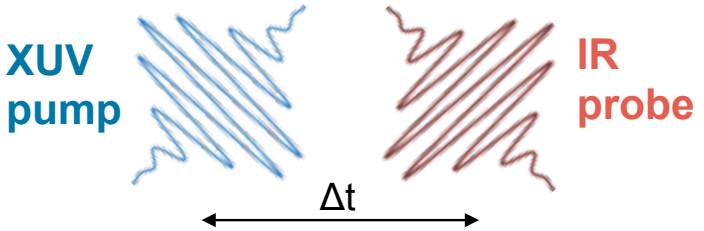
… work in progress…



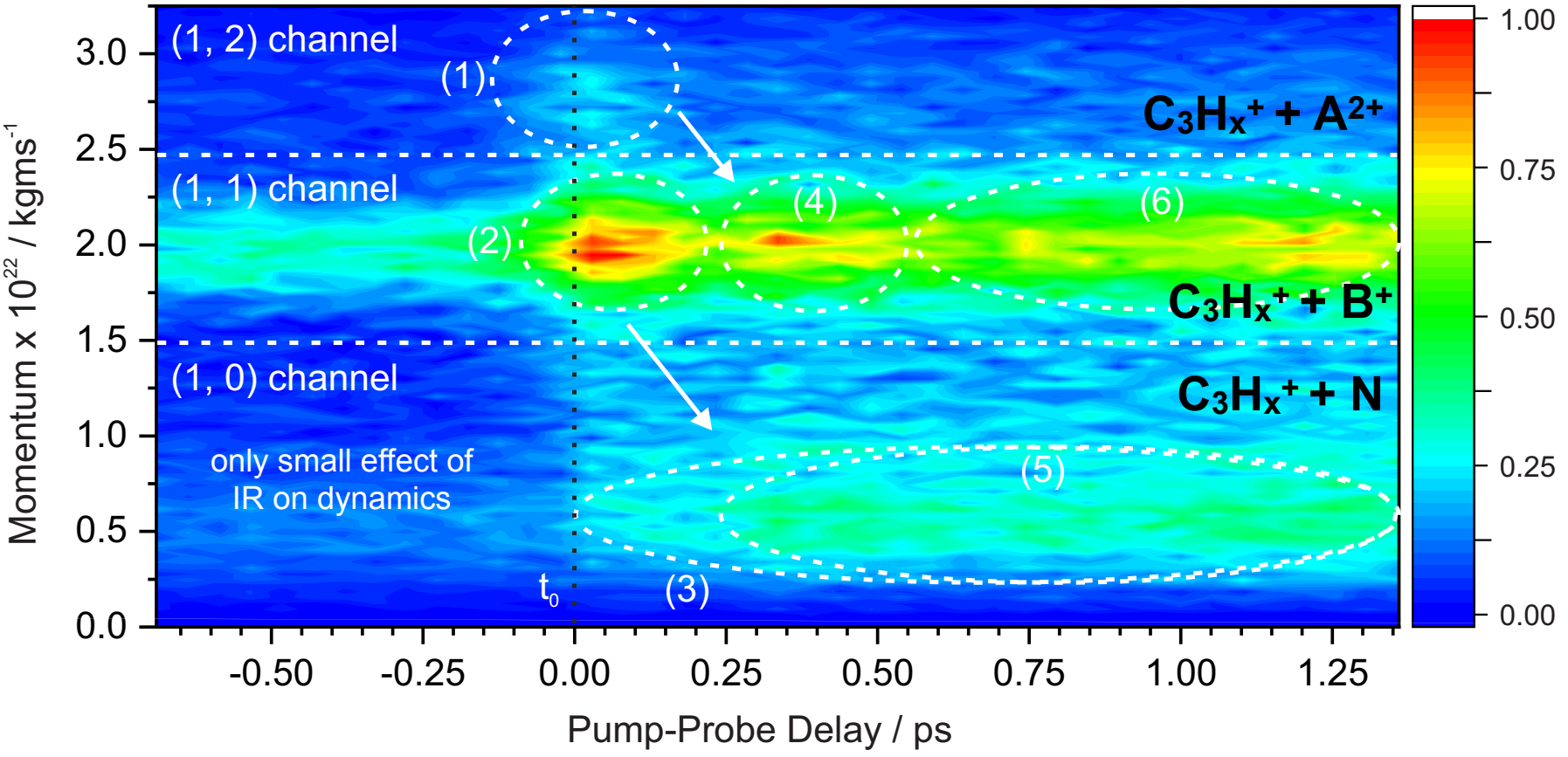
PAH breakup

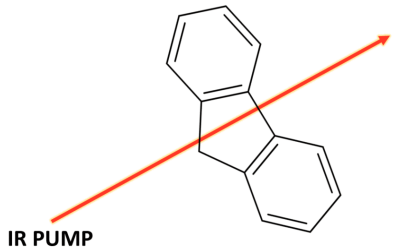
Time dependence

Fluorene
$C_{13}H_{10}$



$C_3H_x^+$ momentum profile





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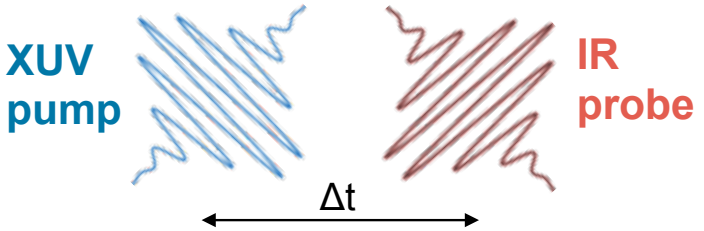

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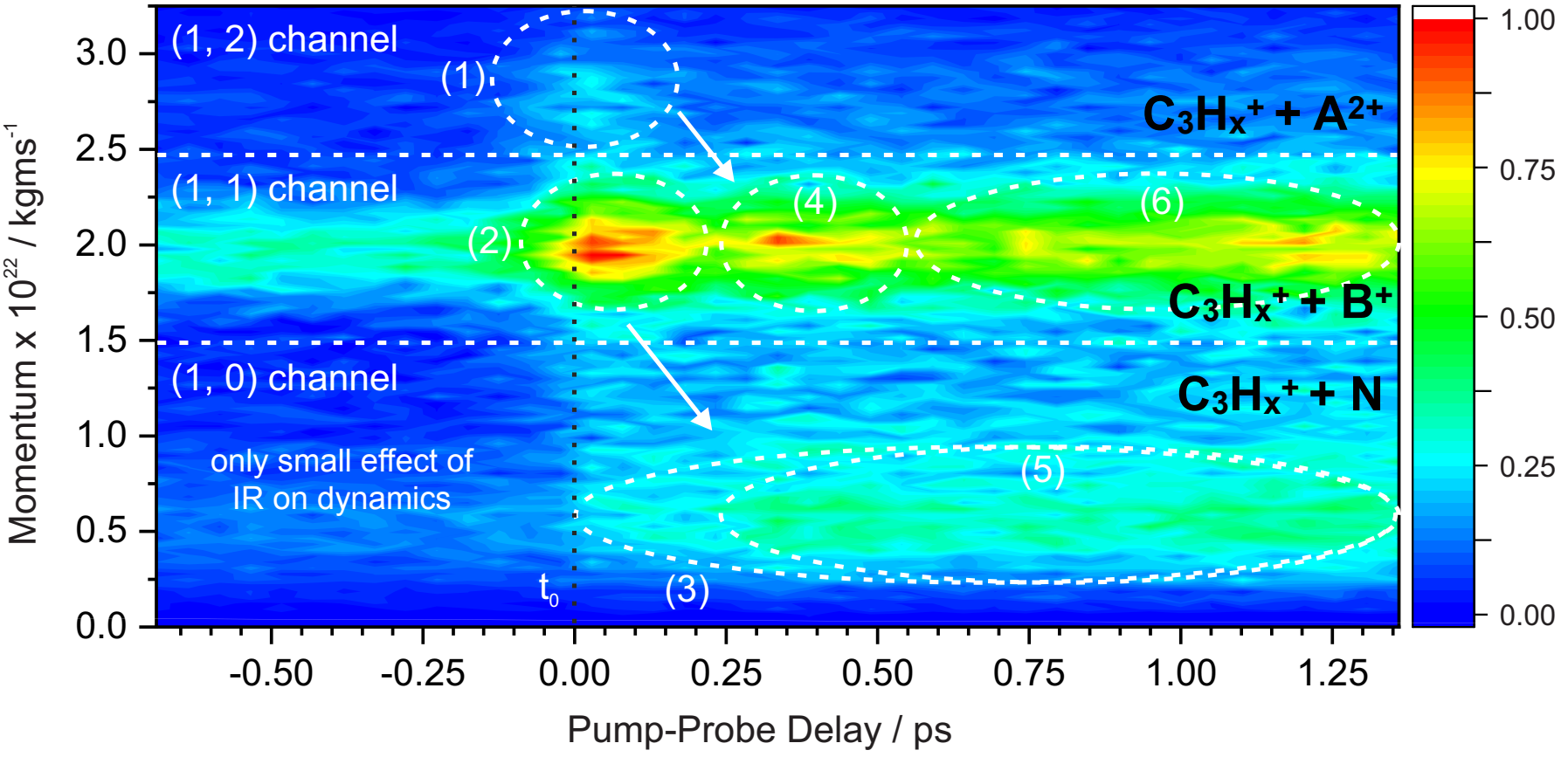

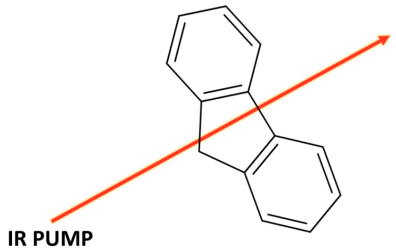

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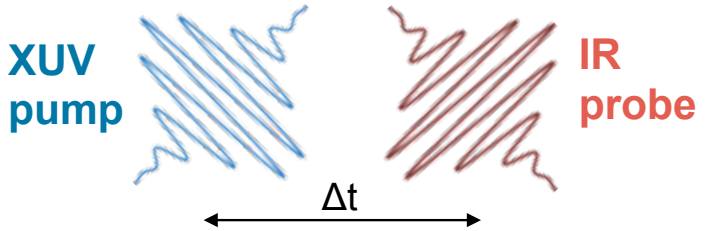
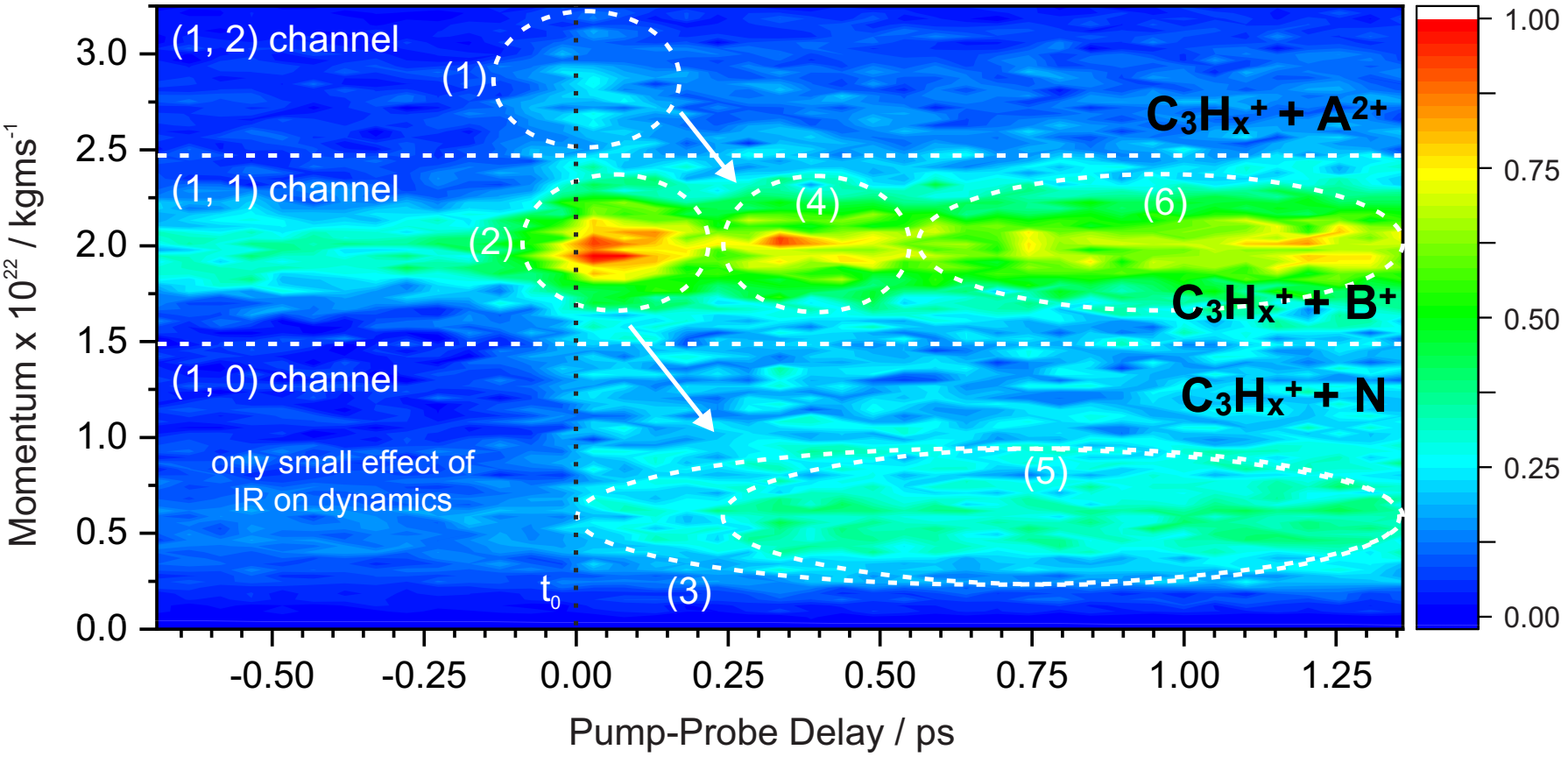
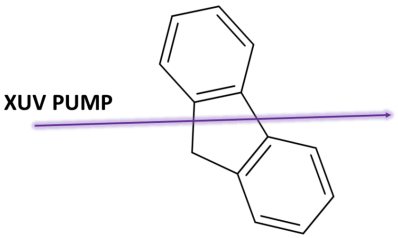


$C_3H_x^+$ momentum profile





PAH breakup

Time dependence

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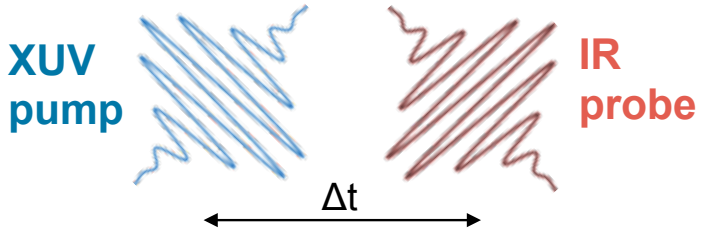

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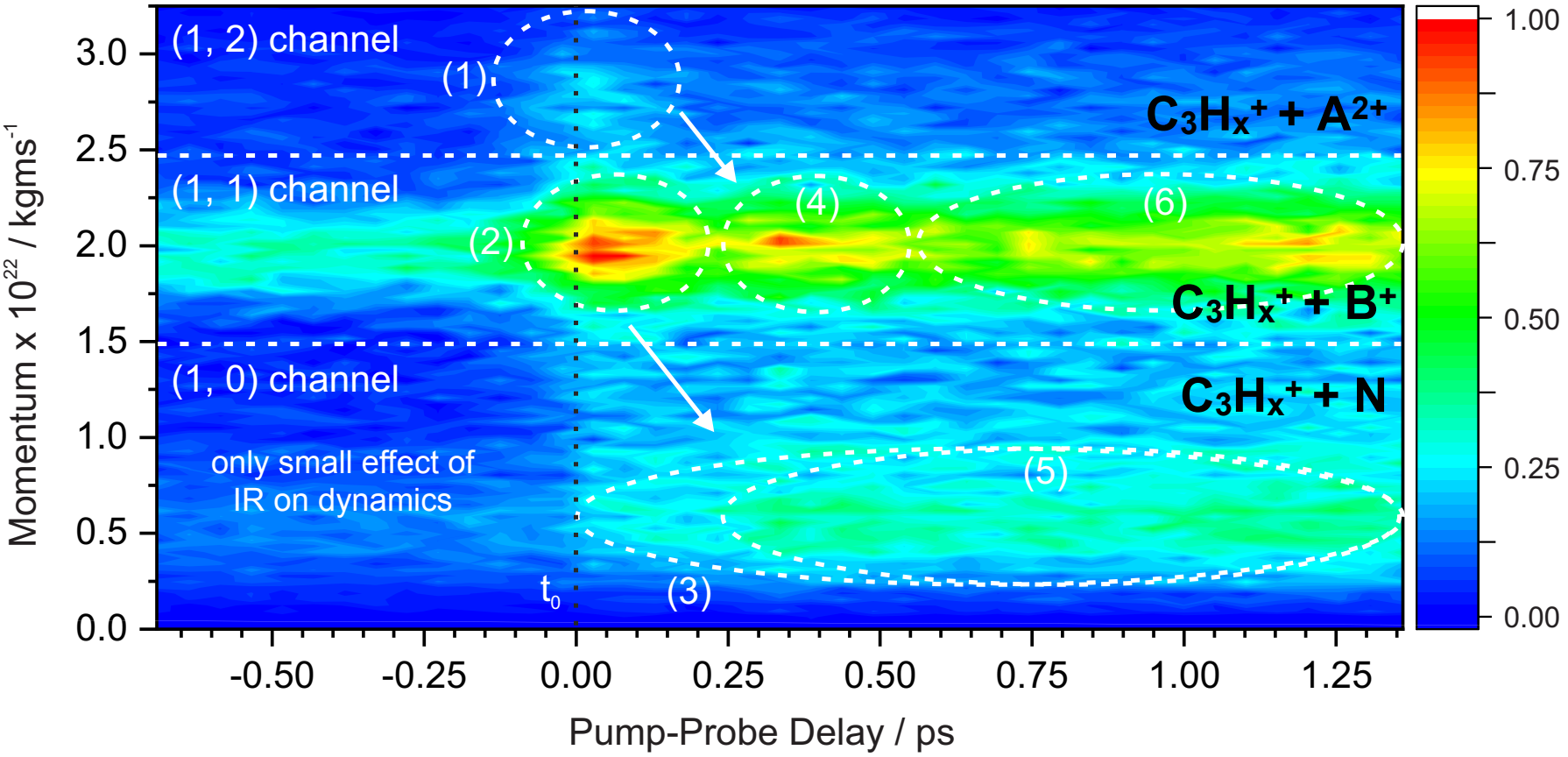

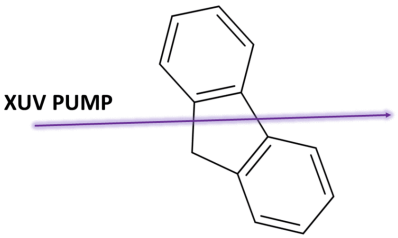

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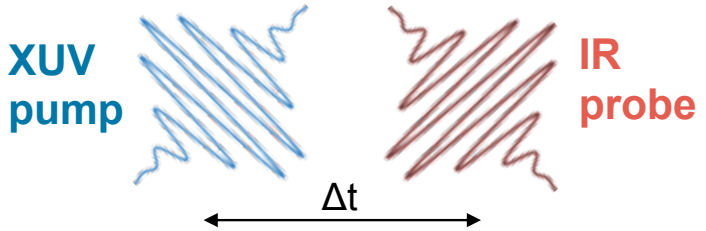

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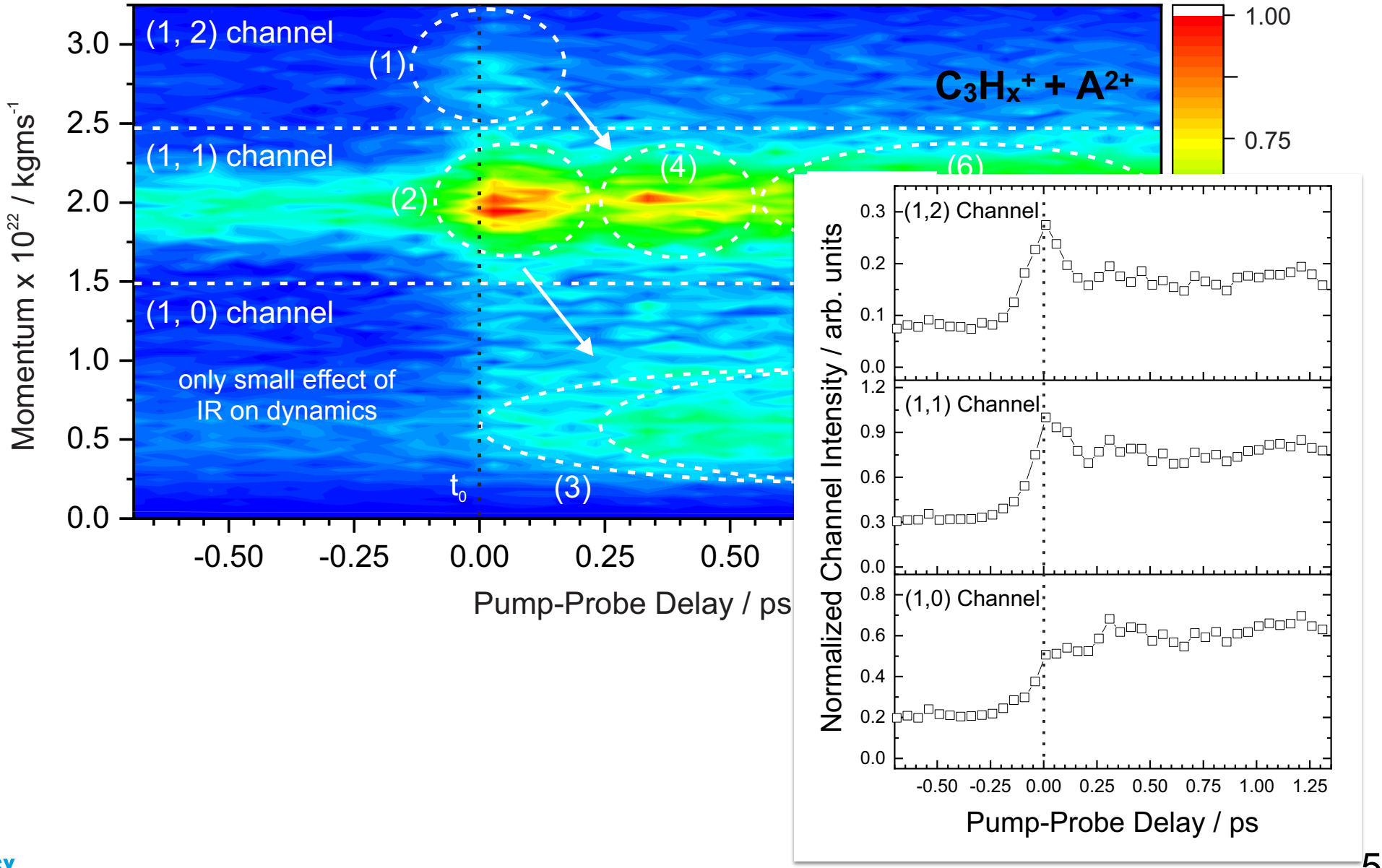

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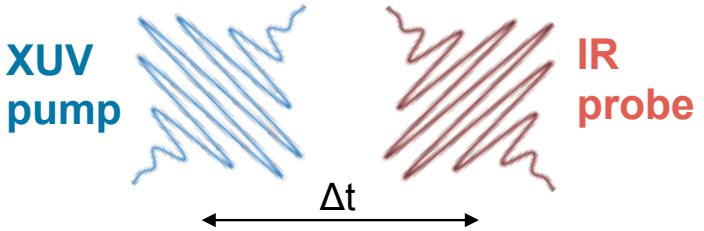

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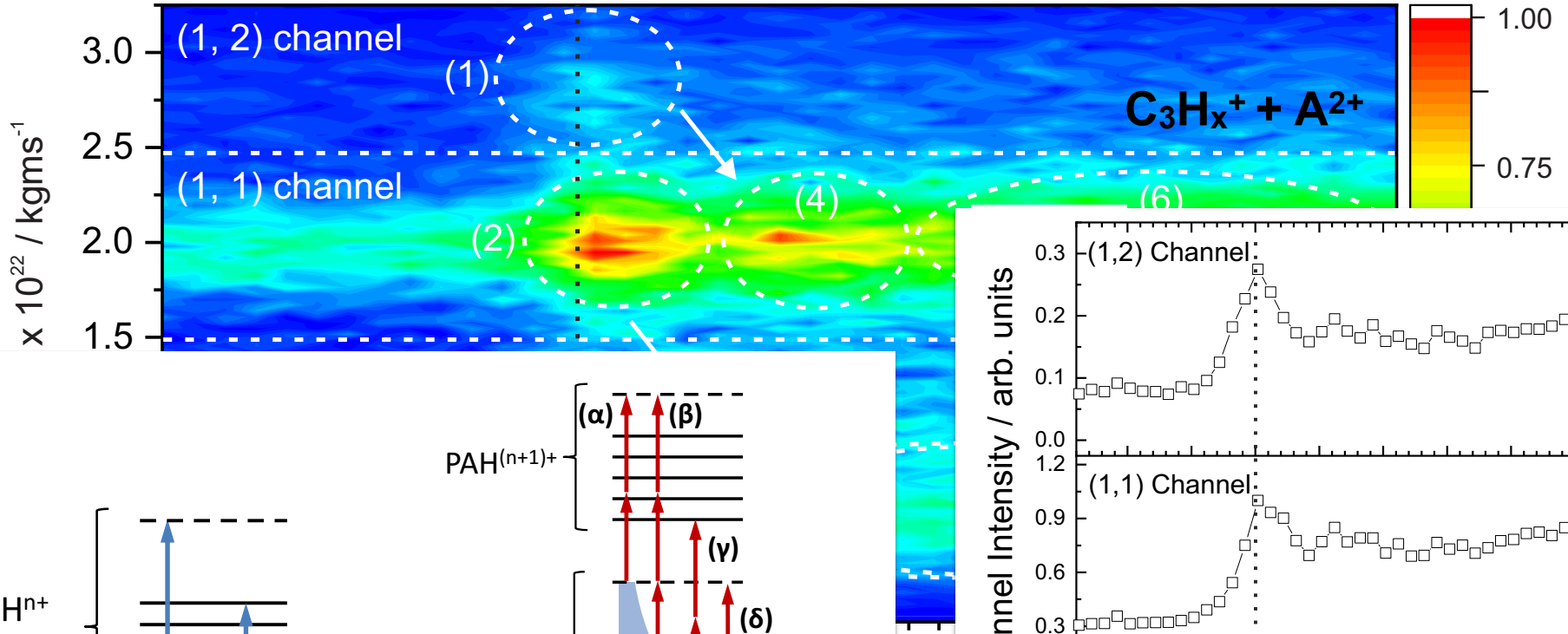
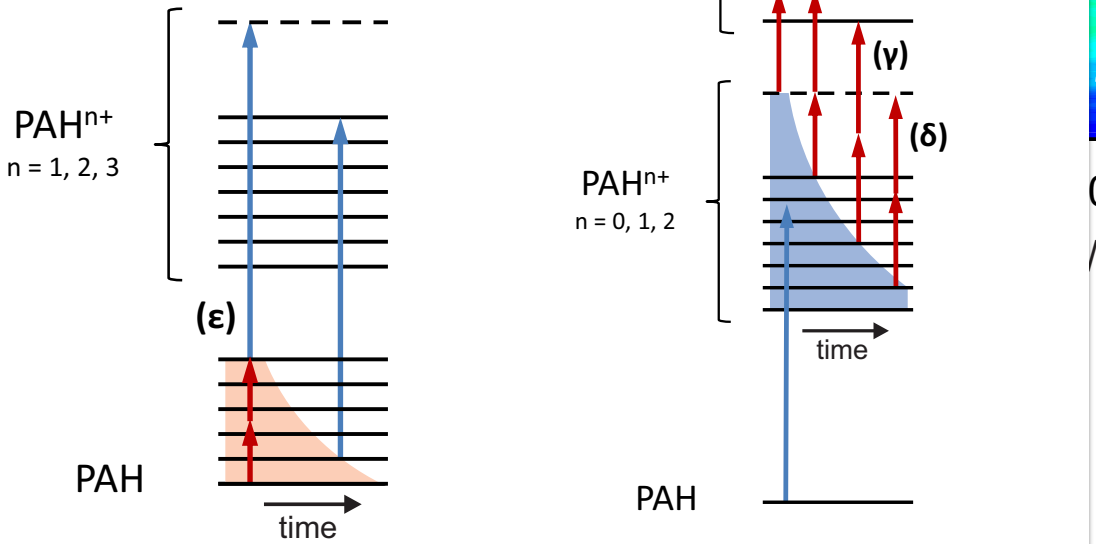
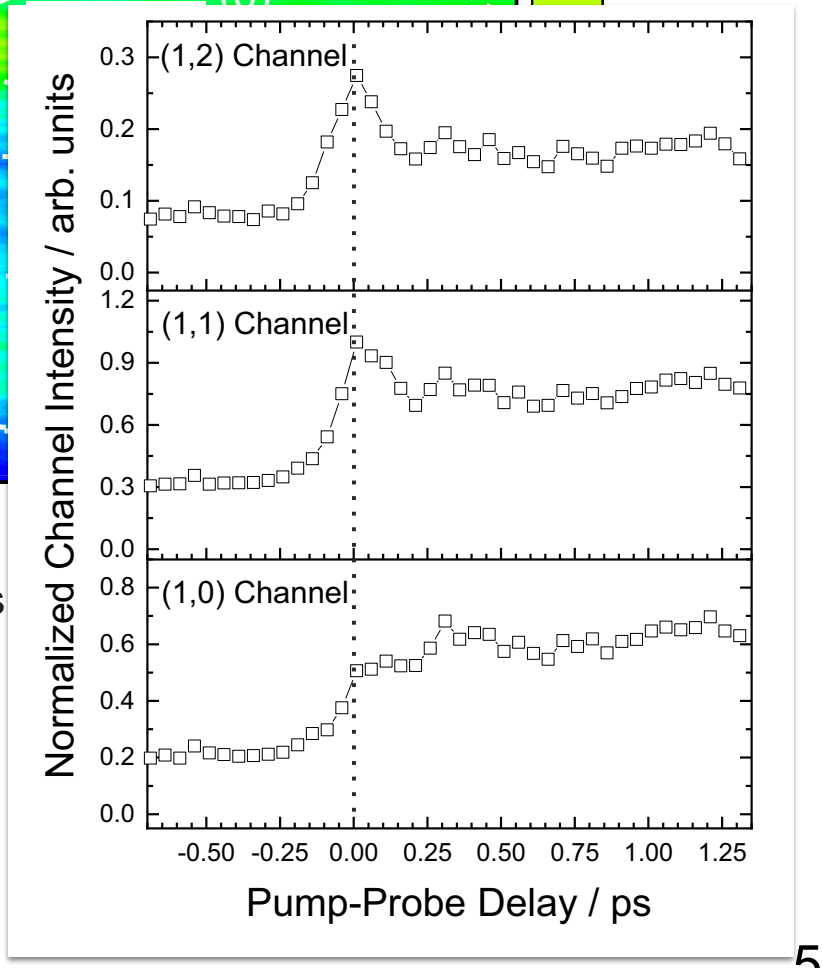
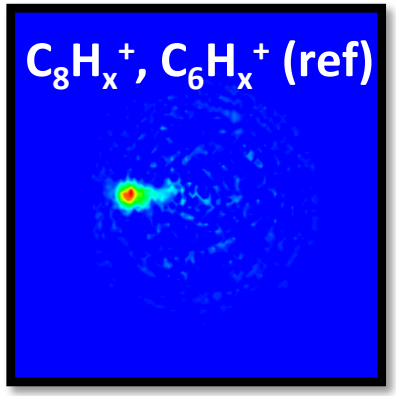
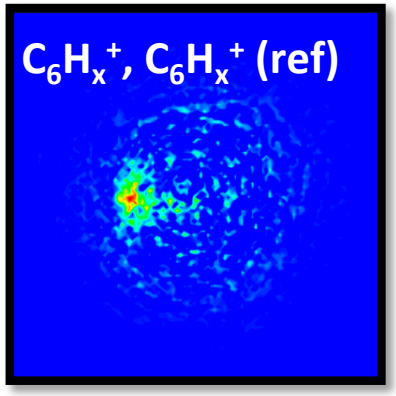


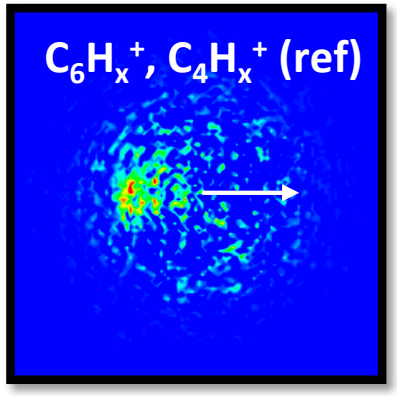




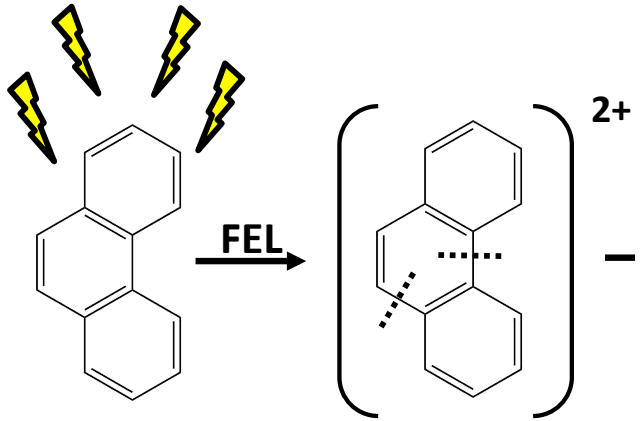
Secondary fragmentation — elucidating mechanisms







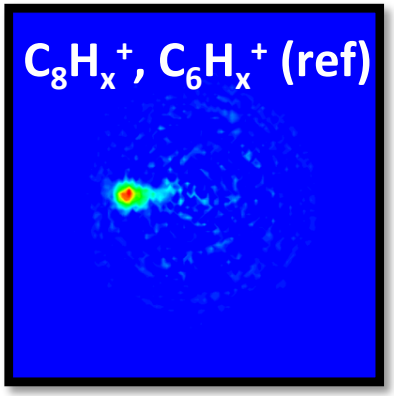
Phenanthrene
$C_{14}H_{10}$

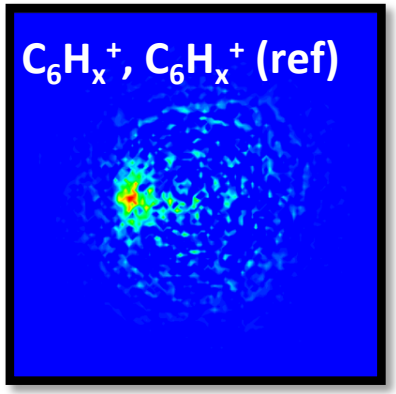


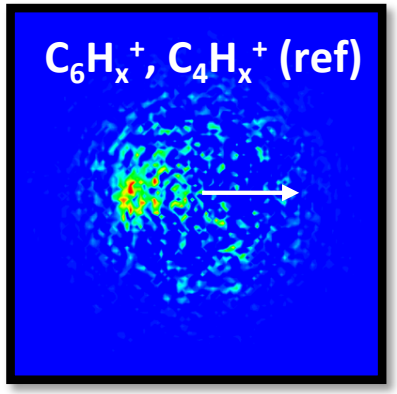
FEL/ IR

$$C_{14}H_{10} \rightarrow C_{14}H_{10}^{2+}$$

Secondary fragmentation — elucidating mechanisms







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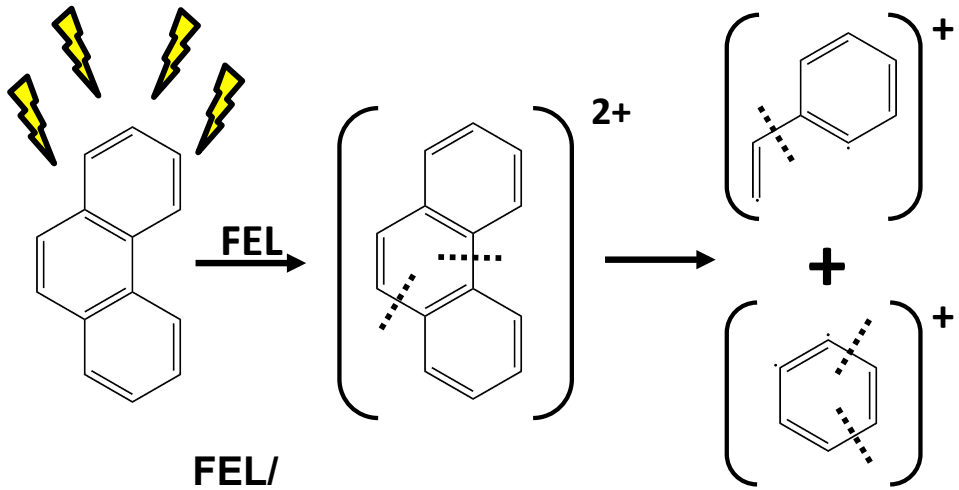
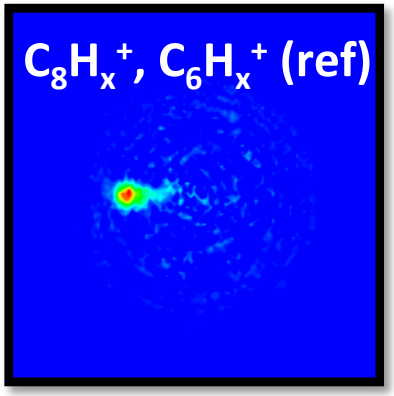
$C_{14}H_{10}$

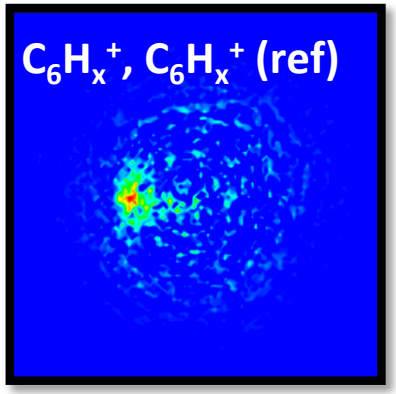


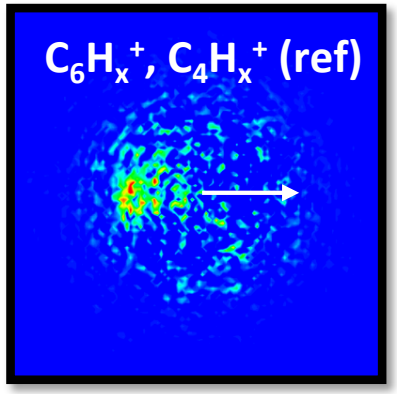
FEL/
IR

$$C_{14}H_{10} \rightarrow C_{14}H_{10}^{2+} \rightarrow C_6H_x^+ + C_8H_x^+$$

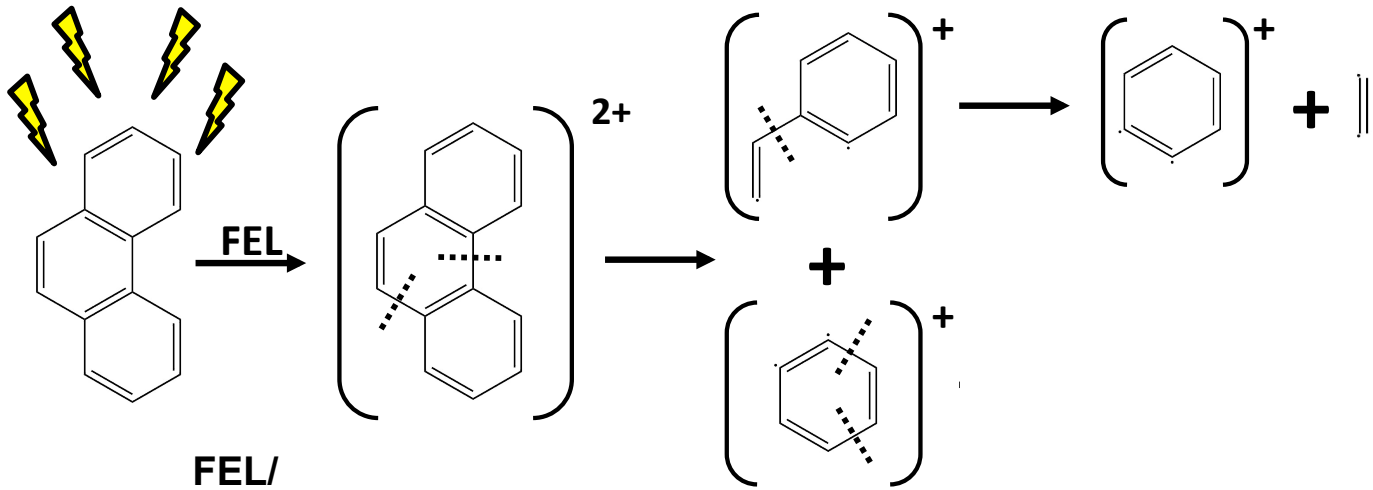
Secondary fragmentation — elucidating mechanisms







Phenanthrene
$C_{14}H_{10}$

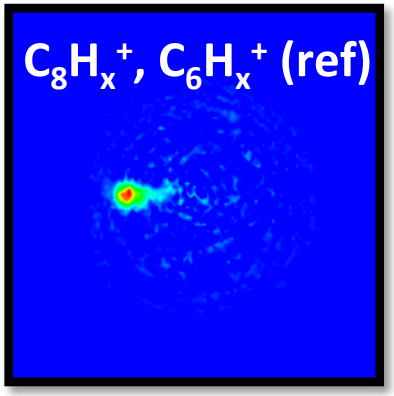


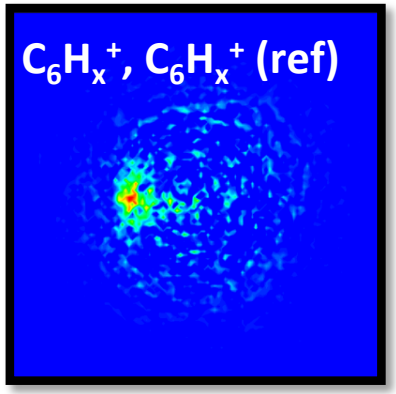
FEL/
IR

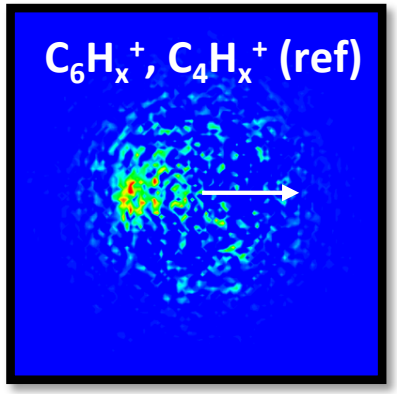
$$C_{14}H_{10} \rightarrow C_{14}H_{10}^{2+} \rightarrow C_6H_x^+ + C_8H_x^+$$

$$C_6H_x^+ + C_6H_x^+ + C_2H_x(neutral)$$

Secondary fragmentation — elucidating mechanisms







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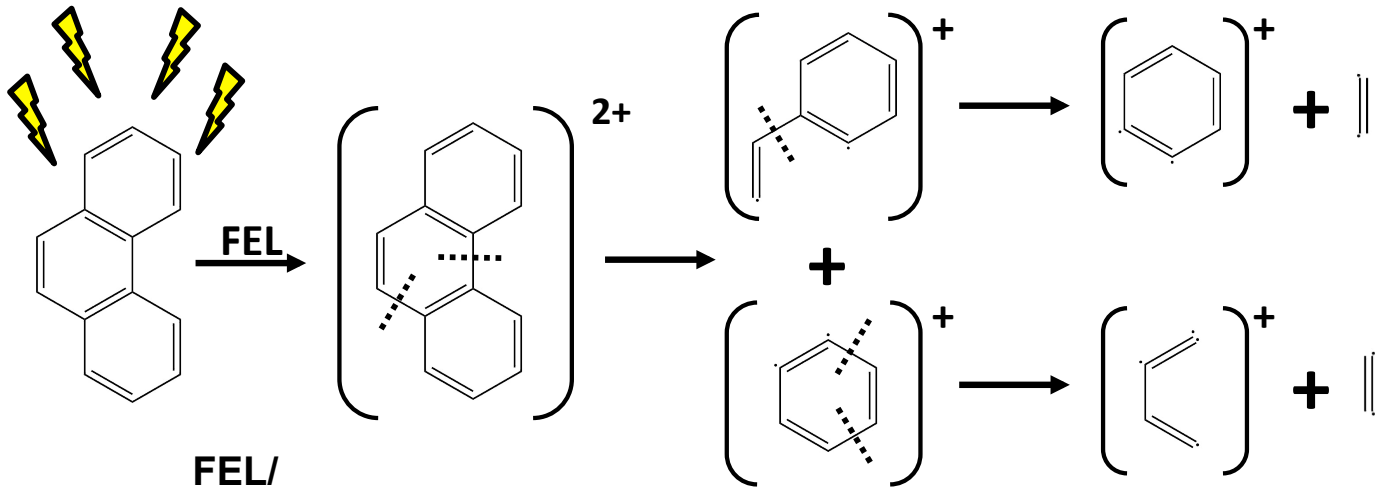
$C_{14}H_{10}$



FEL/
IR

$$C_{14}H_{10} \rightarrow C_{14}H_{10}^{2+} \rightarrow C_6H_x^+ + C_8H_x^+$$

$$C_6H_x^+ + C_6H_x^+ + C_2H_x(neutral)$$

$$C_6H_x^+ + C_4H_x^+ + 2C_2H_x(neutral)$$