Stability of PAH clusters

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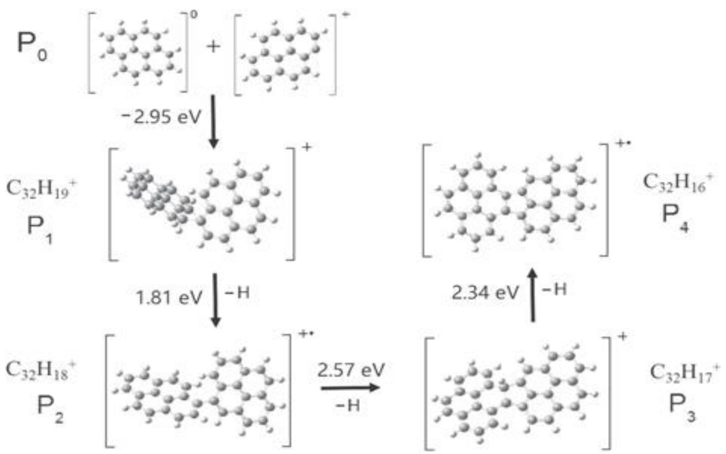
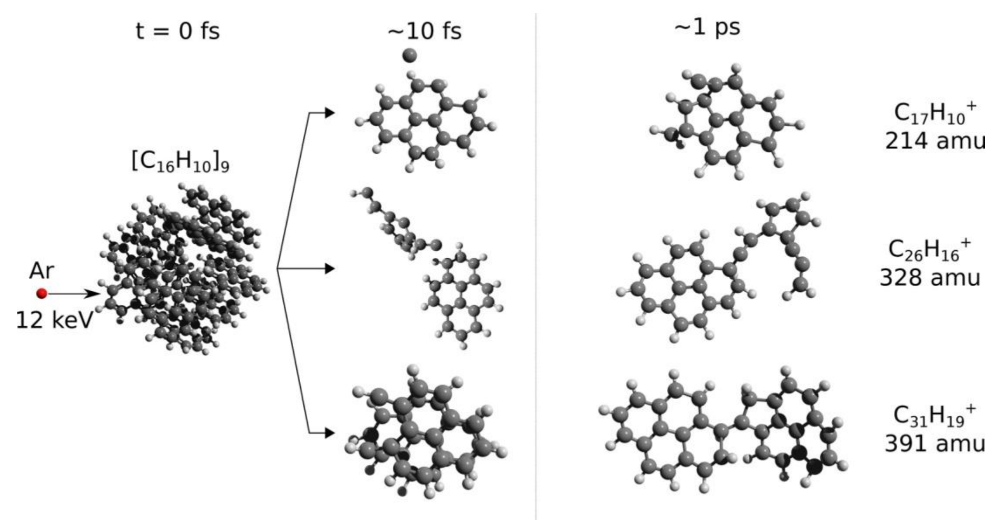
Stability of PAH clusters

PAH clusters as models for carboneous nanograins.

Destruction of such nanograins: route for formation of large complex PAHs?



Zhen et al. *ApJ* 863 128 (2018)



Delaunay et al, *J. Phys. Chem. Lett.*, 6, 1536-1542 (2015)

Are these PAH clusters stable?

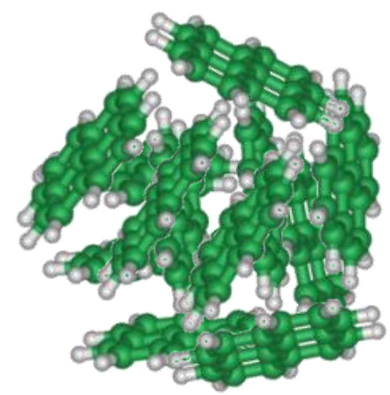
Stability of PAH clusters

- Cationic pyrene clusters $(\mathrm{Py})_n^+$

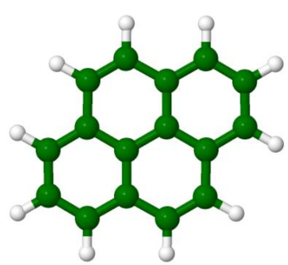
  studied using
- Mass spectrometry techniques

  and
- Phase Space Theory

  to deduce
- Dissociation energies



Pyrene : $C_{16}H_{10}$

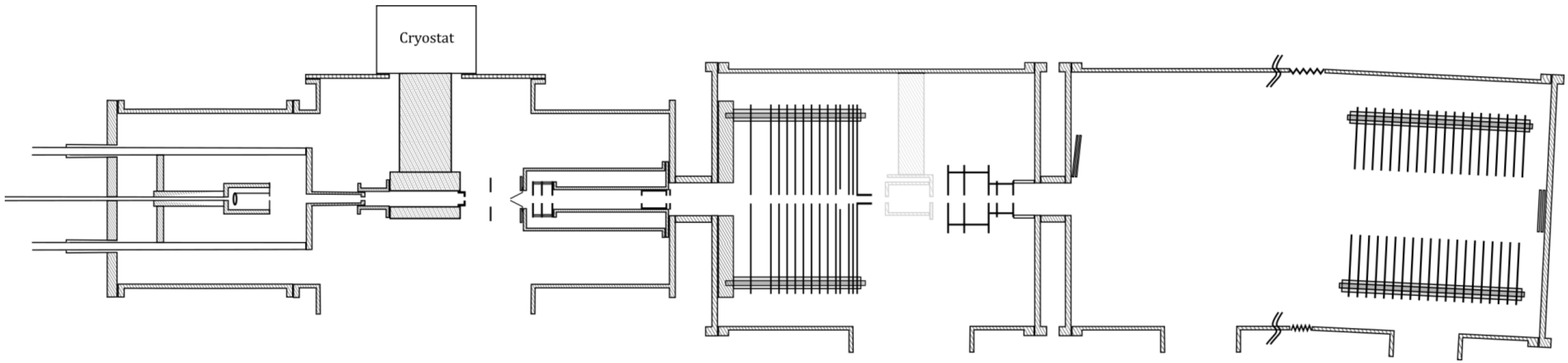


PAH = polyaromatic hydrocarbons

Outline

- Experimental setup
- Experimental results
- Phase Space Theory
- Dissociation energies
- Conclusion

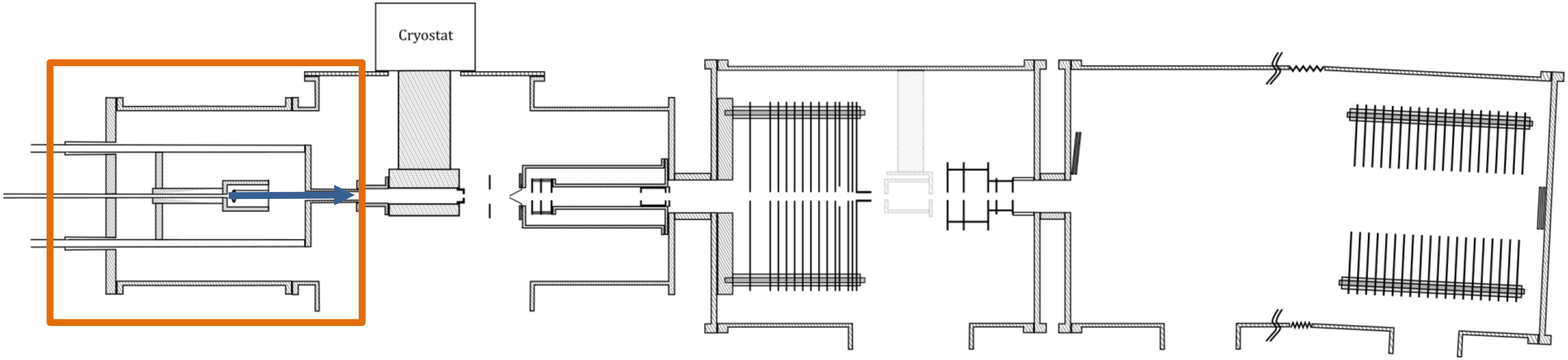
Experimental setup



Experimental setup initially designed to perform collisions between mass selected clusters and atomic or molecular vapor (attachment cross-section, fragmentation cross-section, nanocalorimetry, …).

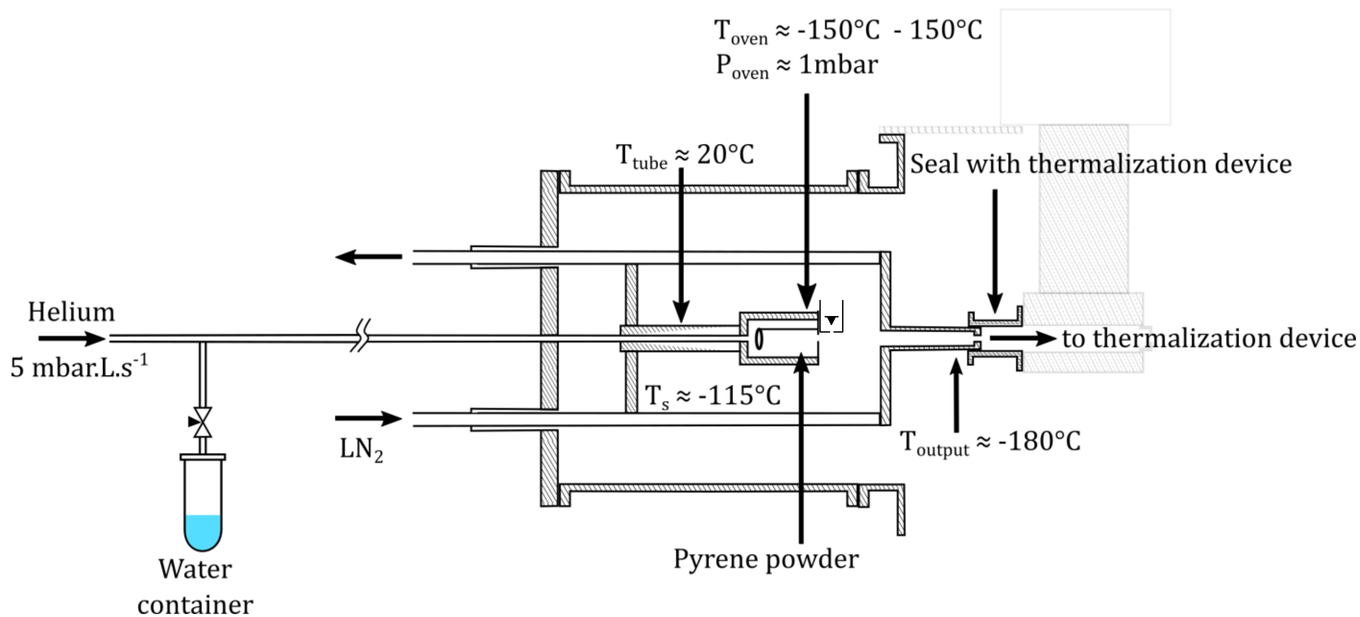
Can also be used to observe the **spontaneous thermal evaporation of mass selected clusters**.

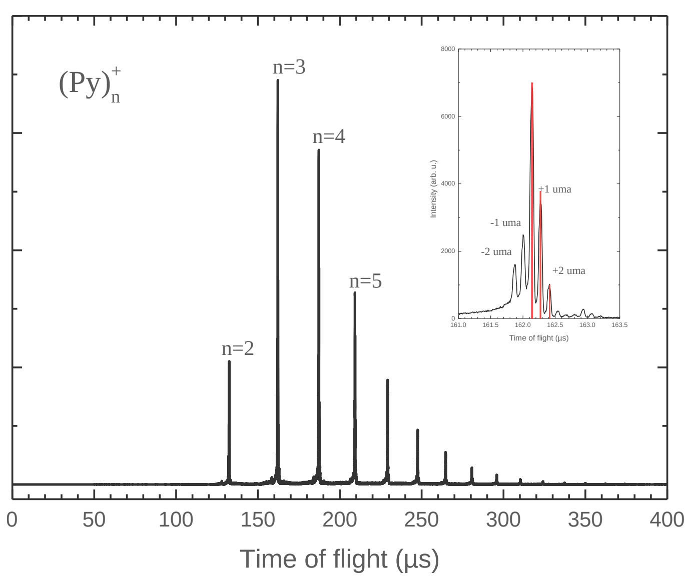
Experimental setup



- Gaz aggregation source

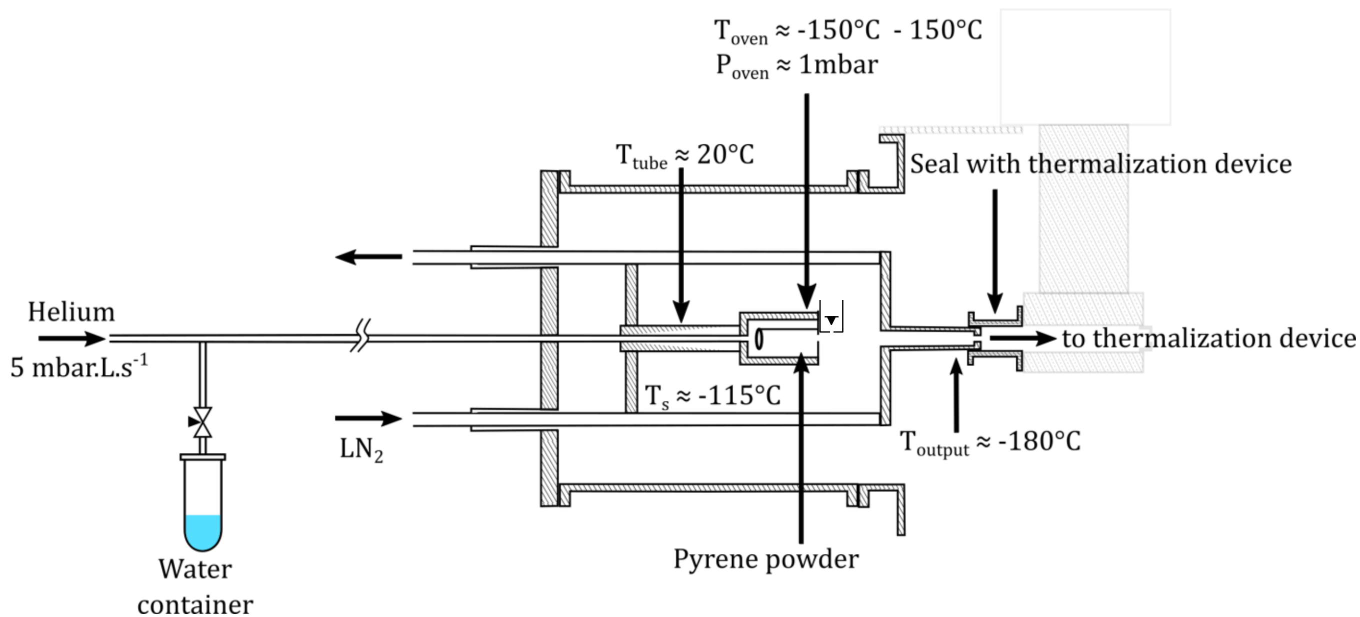
Cluster production

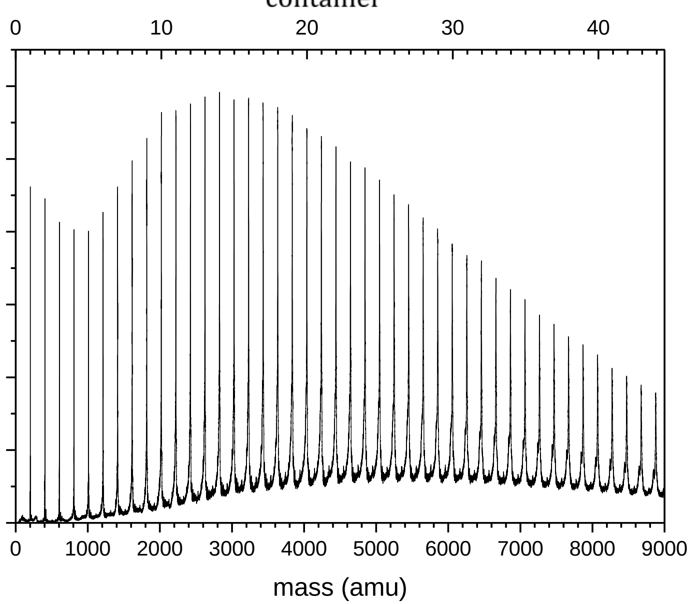




Small pure Pyrene clusters

Cluster production

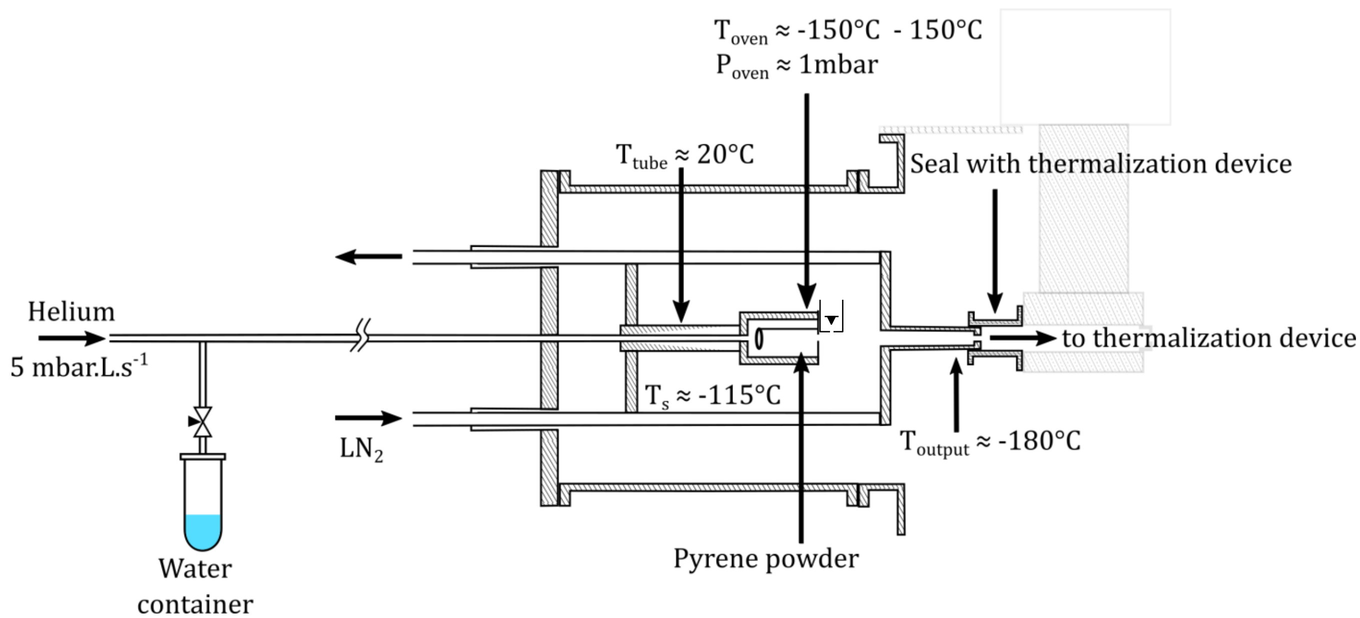


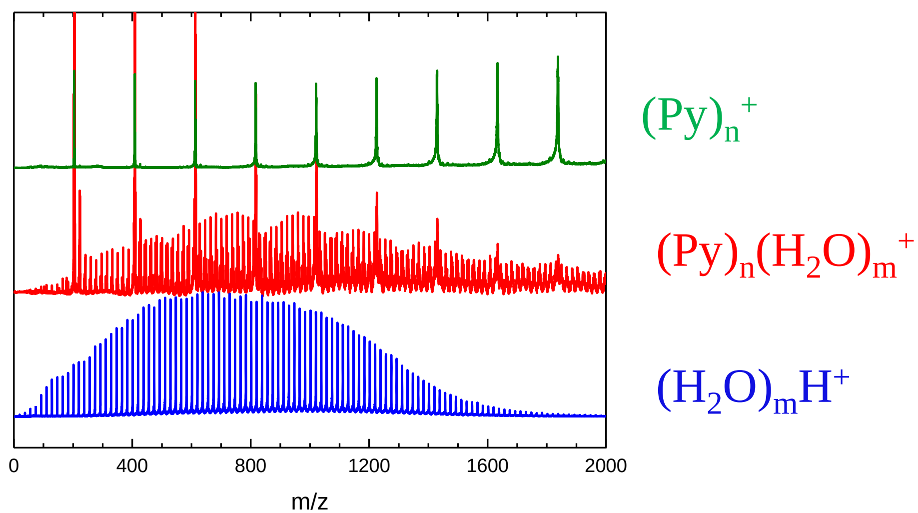


Small pure Pyrene clusters

Large pure pyrene clusters

Cluster production



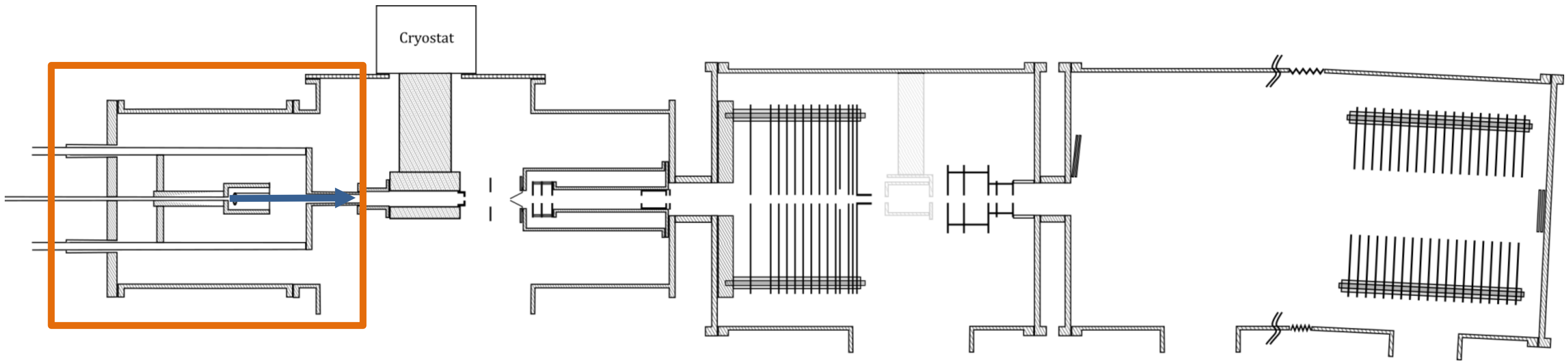


Small pure Pyrene clusters

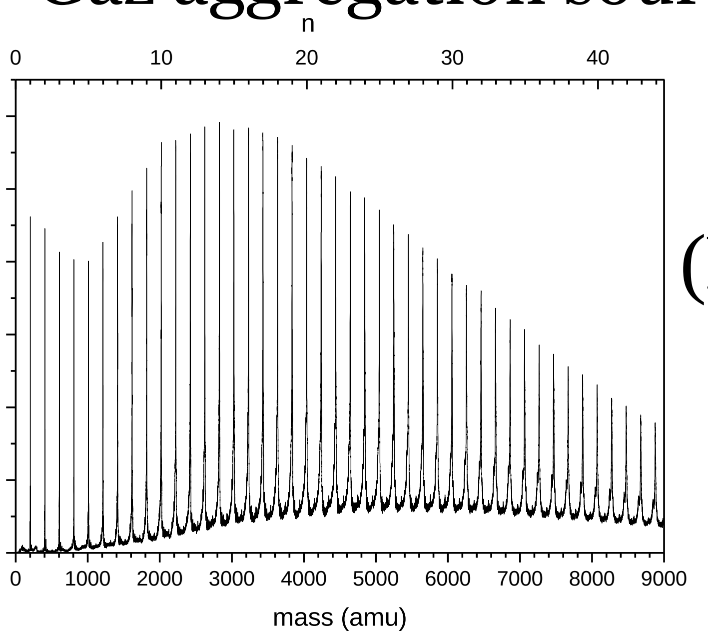
Large pure pyrene clusters

Mixed water-pyrene clusters

Experimental setup

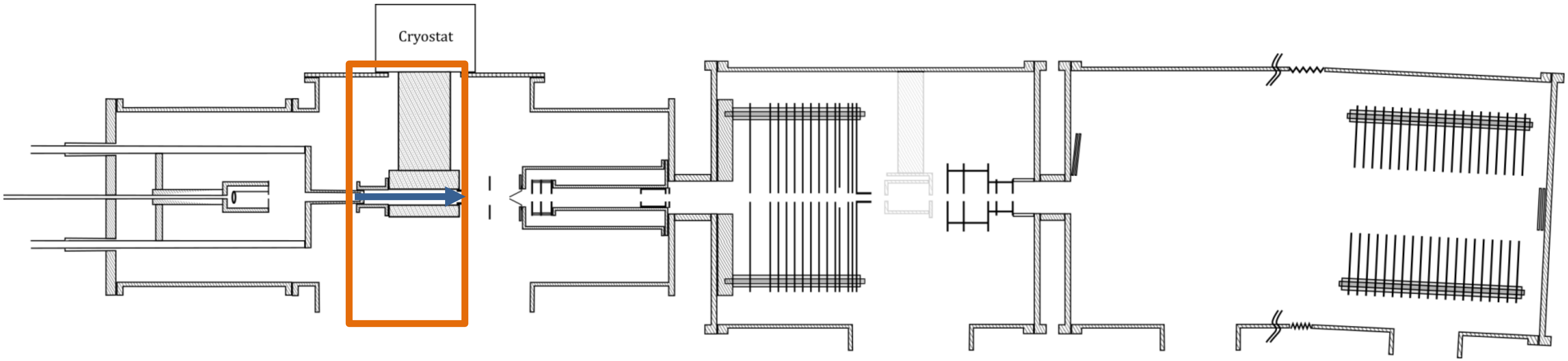


- Gaz aggregation source, n = 1-40

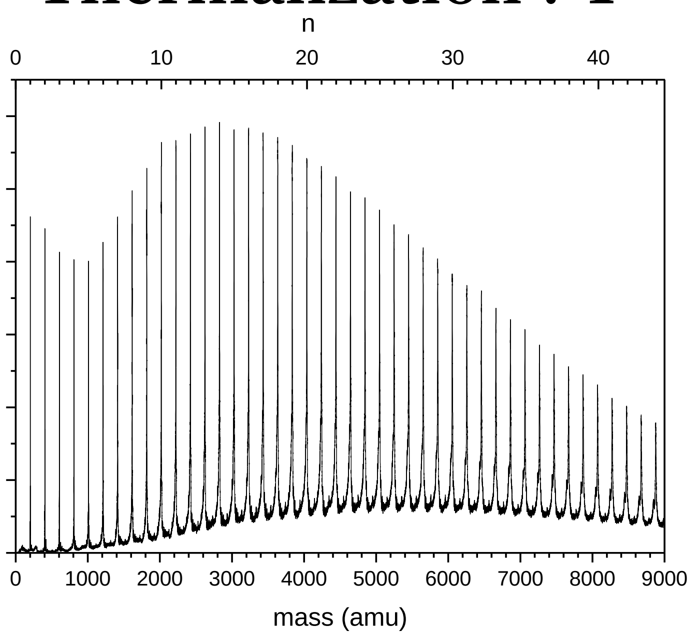


$(Py)_n^+$

Experimental setup



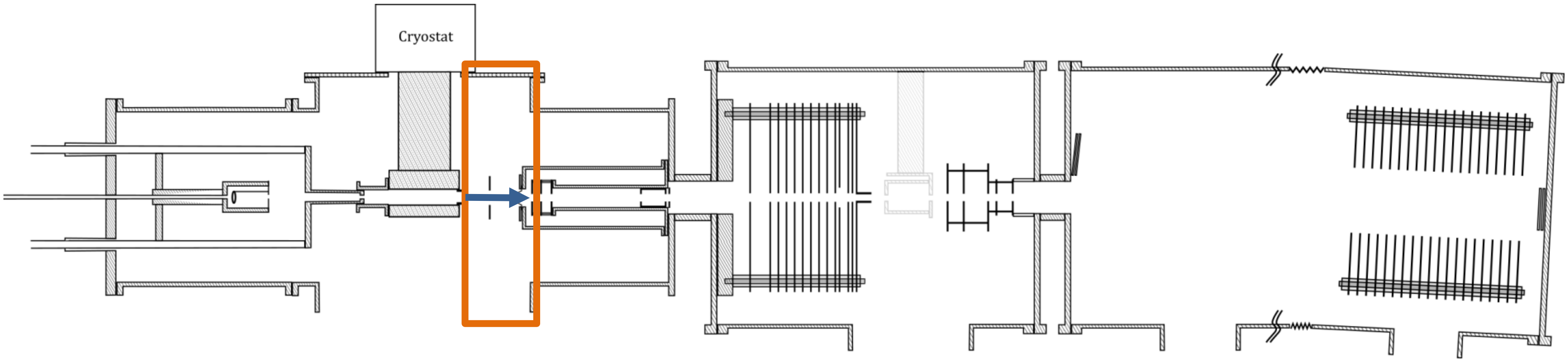
- Thermalization : T = 25-300 K



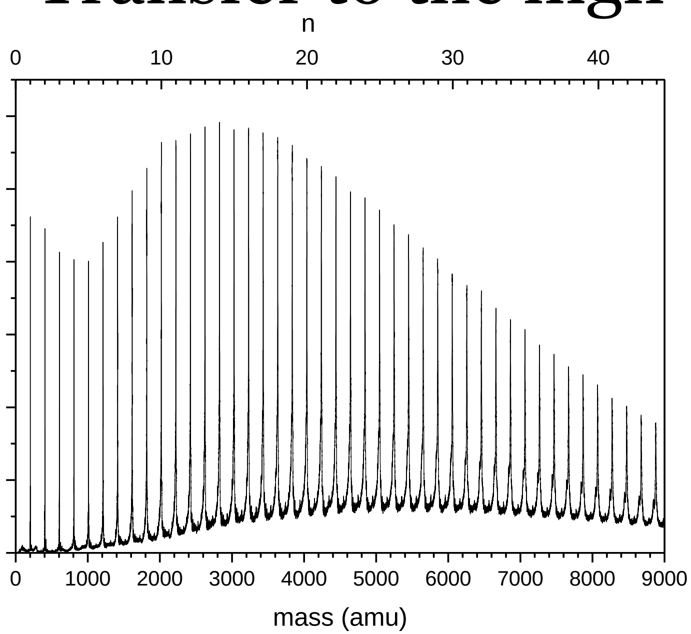
Large number of collisions with the helium buffer gaz

Canonical distribution of internal energies E_i

Experimental setup

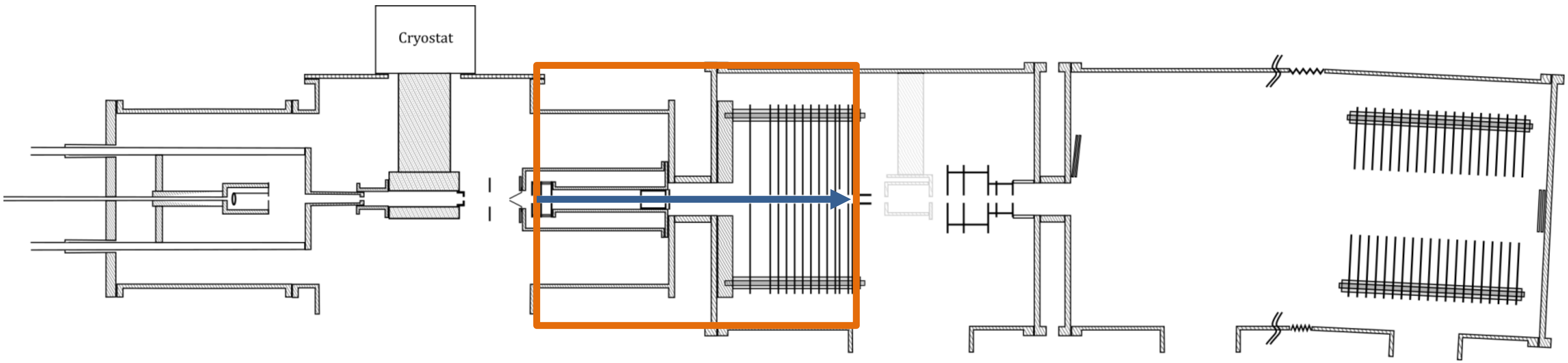


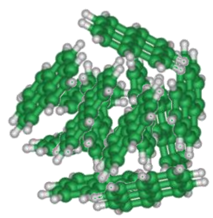
- Transfer to the high vacuum part



Internal energies E_i, microcanonical evolution

Experimental setup



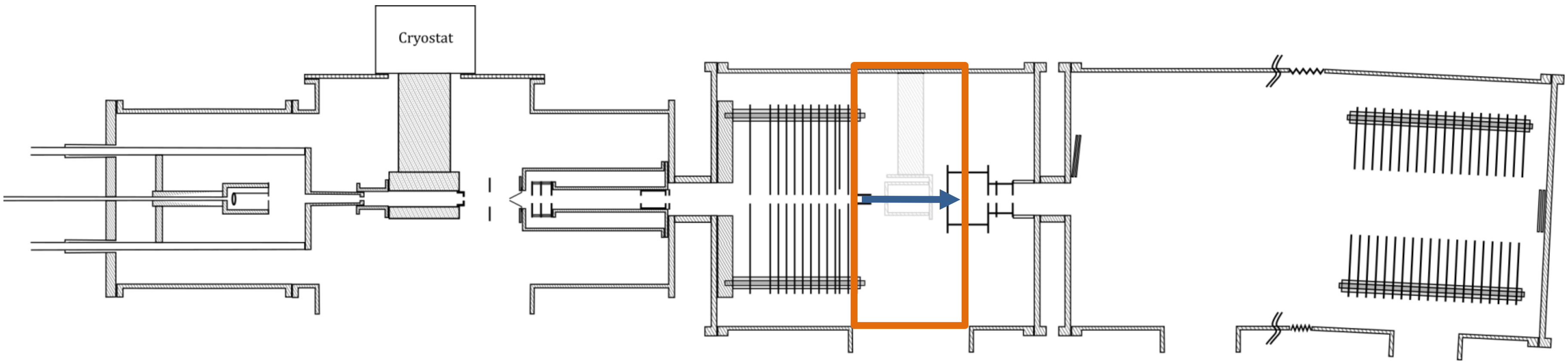


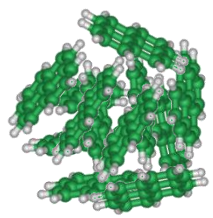
n

- Mass selection and slowing down

Internal energies E_i, microcanonical evolution

Experimental setup



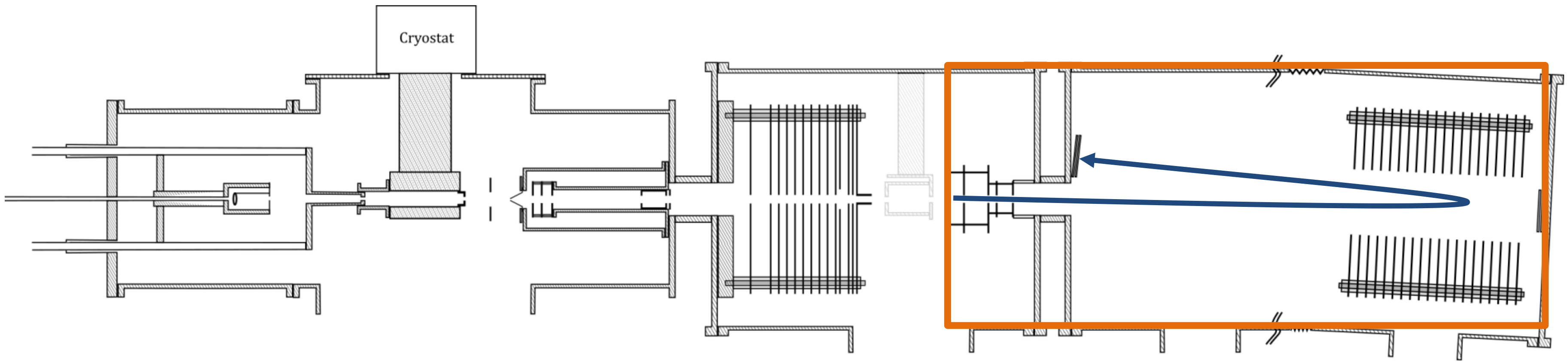


$\boldsymbol{n}$

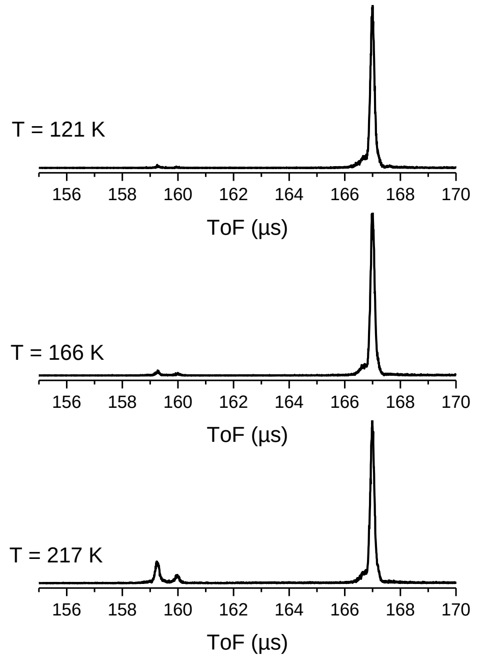
- Free flight

Internal energies E_i, microcanonical evolution

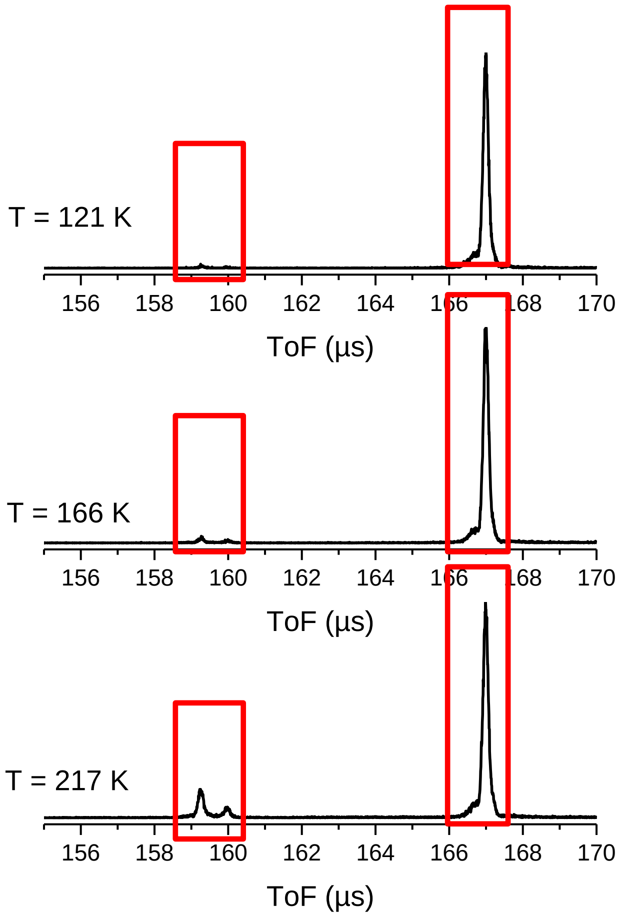
Experimental setup



- Products analyzed by TOF mass spectrometry



Experimental results



Example: $(Py)_{11}^{+}$ **@ 22 eV**

Evolution of the mass spectra of mass selected clusters with initial temperature.

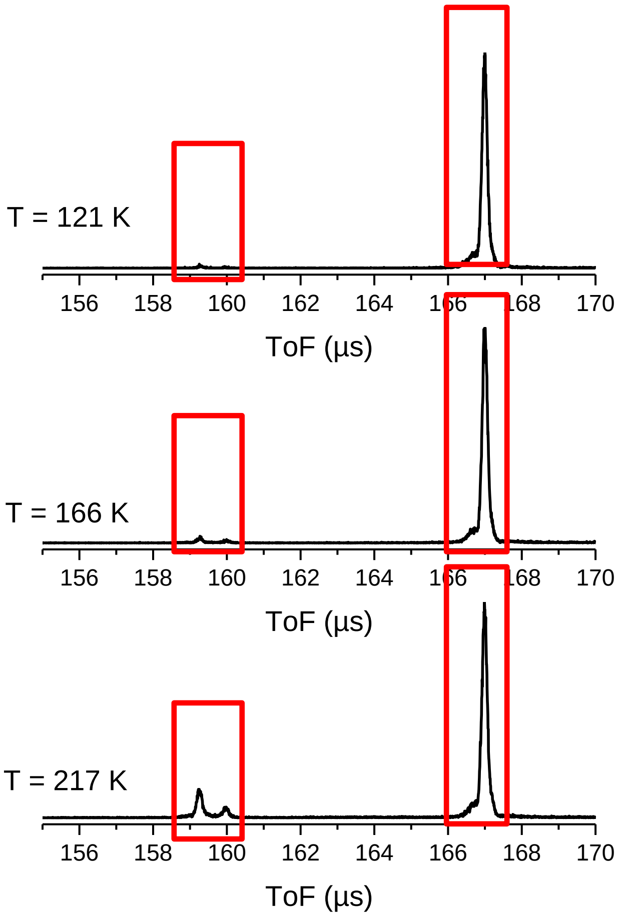
As the temperature is raised, appearance of fragments due to evaporation

Ratio I/I_o

I = parent peak intensity

I_o = sum of parent + fragment peaks

Experimental results



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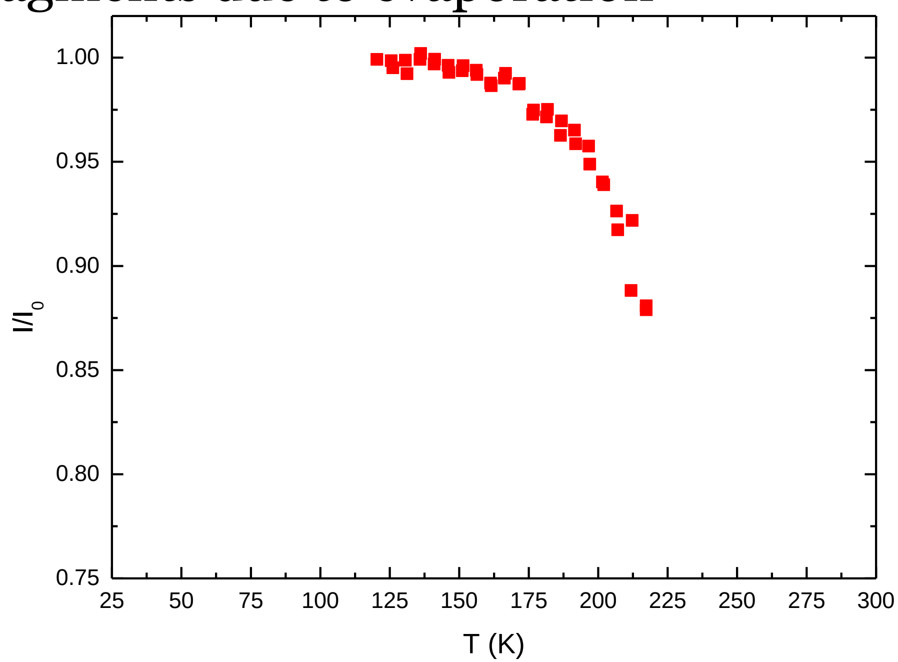
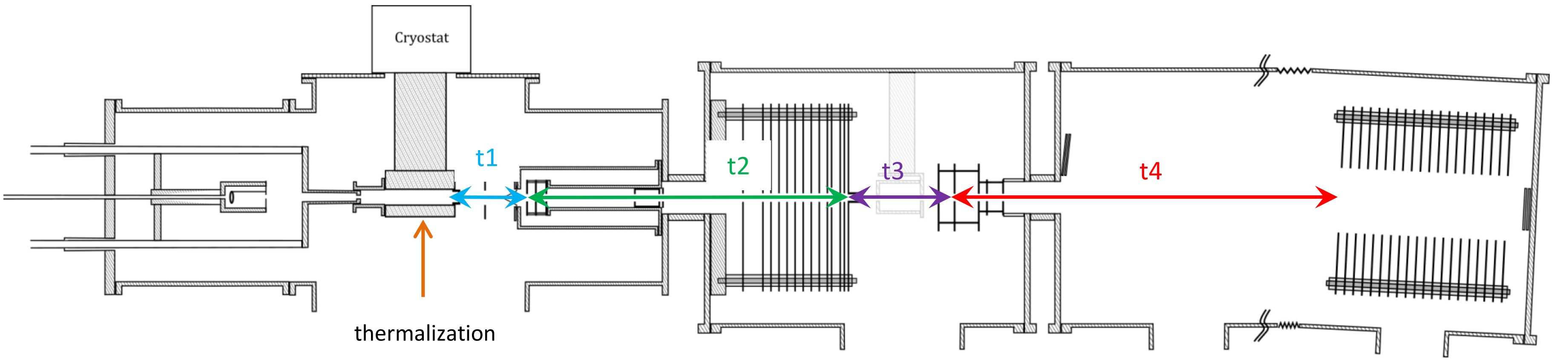


Example: $(Py)_{11}^{+}$ @ 22 eV

$I = I_o e^{-W(T)t}$?

Experimental results



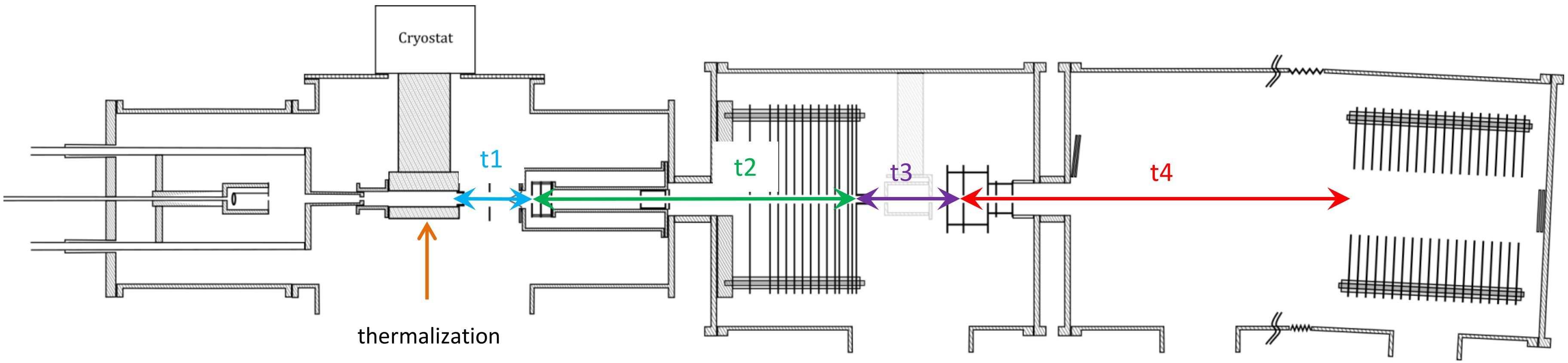
At the thermalizer exit:

- Cluster size distribution
- Canonical distribution of internal energies E_i

After the propagation time t1, the population of size n will have contributions from the evaporation of larger sizes:

$$n+1, E_i \quad \rightarrow \quad n, E_i'$$

Experimental results



At the thermalizer exit:

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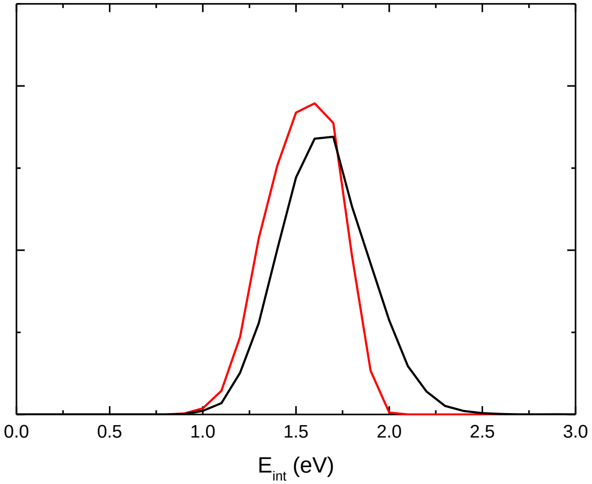
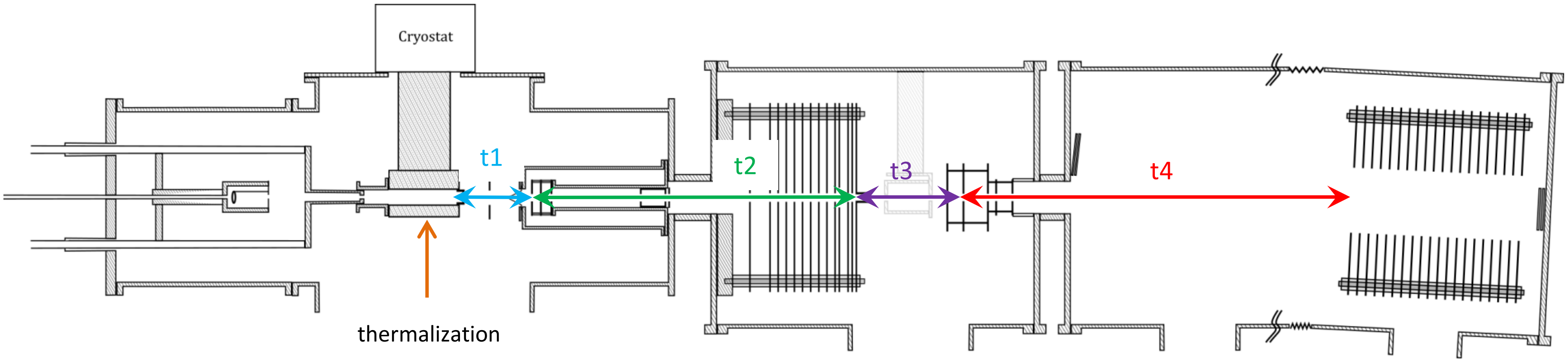


After t1, population of size n might no longer be at temperature T

⇒new, non-canonical, distribution of internal energies

Experimental results



At the thermalizer exit:
- Cluster size distribution
- Canonical distribution of internal energies E_i

Depending on where evaporation takes place, it might not be observed.

Experimental results reproduced by simulating the propagation in the setup with evaporation probabilities evaluated at each time step

$\Rightarrow$ Model for evaporation rates

PST evaporation rates

Ingredients of the Phase Space Theory:

- initial internal energy of the parent E_i
- density of states of the parent *N(E)*
- total number of states of the fragments *G(E,J)*
- conservation of angular momentum

$$W(E_i, J) = \frac{G(E_f, J)}{h(2J+1)N(E_i)}$$

$$E_f = E_i + E_{rot} - D$$

$$E_{rot} = B_0 J(J+1)$$

Approximations:

- only vibrational harmonic frequencies considered
- all species considered as spherical tops
- ion-polar interaction between the neutral fragment and the charged cluster

Energy partition among the fragments

Harmonic frequencies and moments of inertia from DFTB calculation (cf Rapacioli *et al.*)

PST evaporation rates

Ingredients of the Phase Space Theory:

- initial internal energy of the parent E_i
- density of states of the parent $N(E)$
- total number of states of the fragments $G(E,J)$
- conservation of angular momentum

Only one adjustable parameter

$$W(E_i, J) = \frac{G(E_f, J)}{h(2J+1)N(E_i)}$$

$$E_f = E_i + E_{rot} - D$$

$$E_{rot} = B_0 J(J+1)$$

Approximations:

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Energy partition among the fragments

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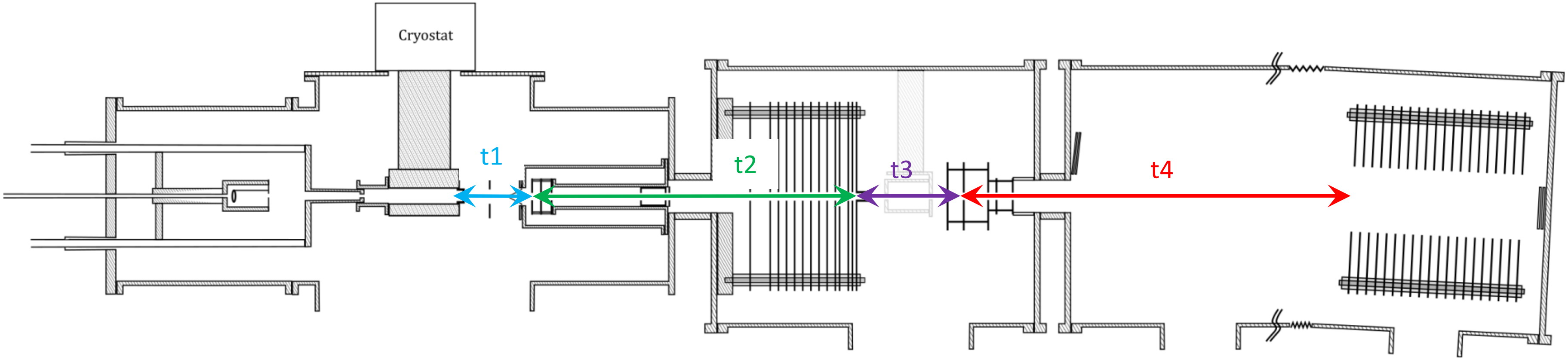
PST evaporation rates

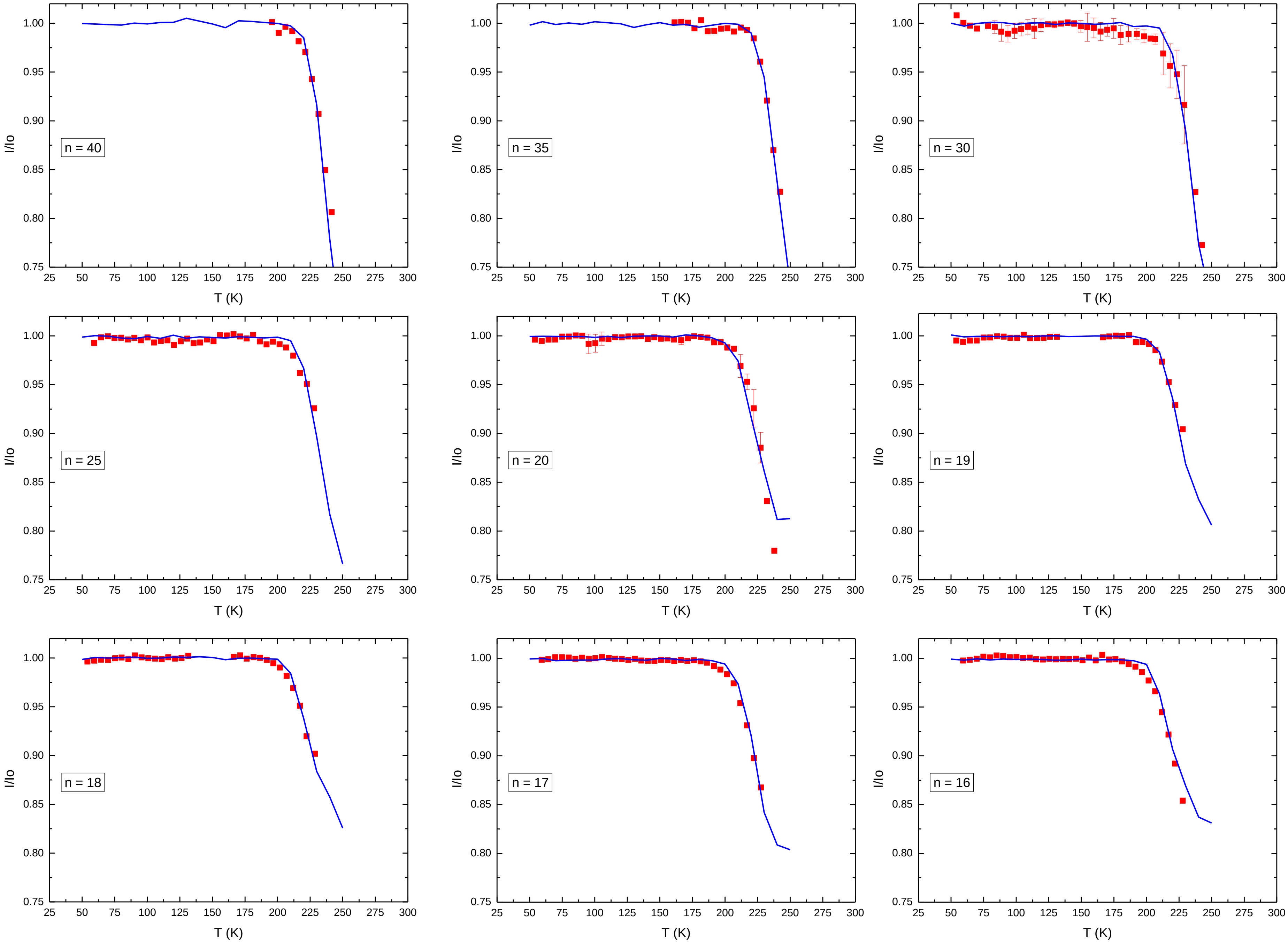


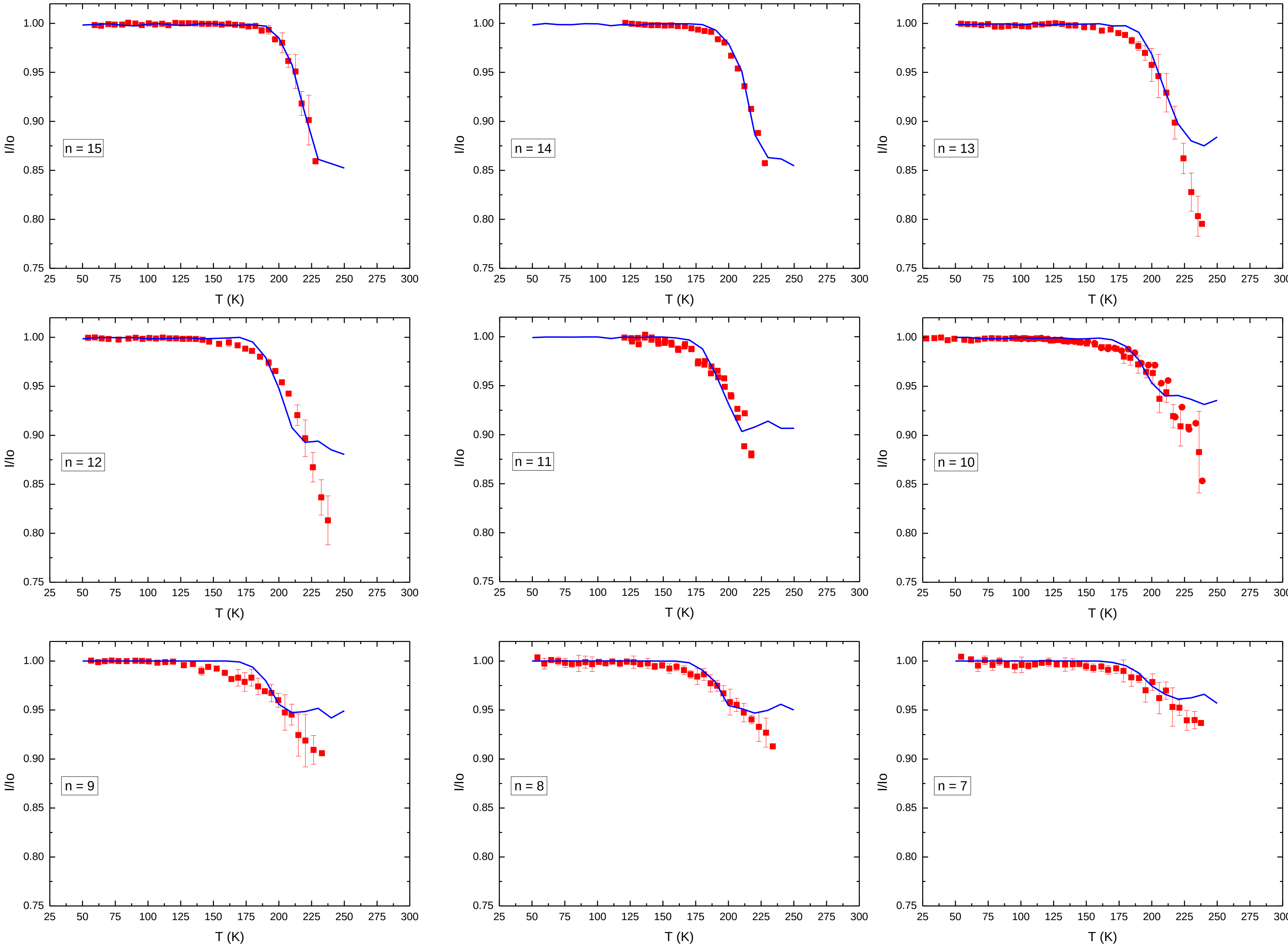
Generate initial population of size n (cascaded evaporations ⇒ use of dissociation energies of sizes n+1, n+2, …) (t1)

Calculate clusters trajectories with evaporation probabilities (t2, t3, t4)

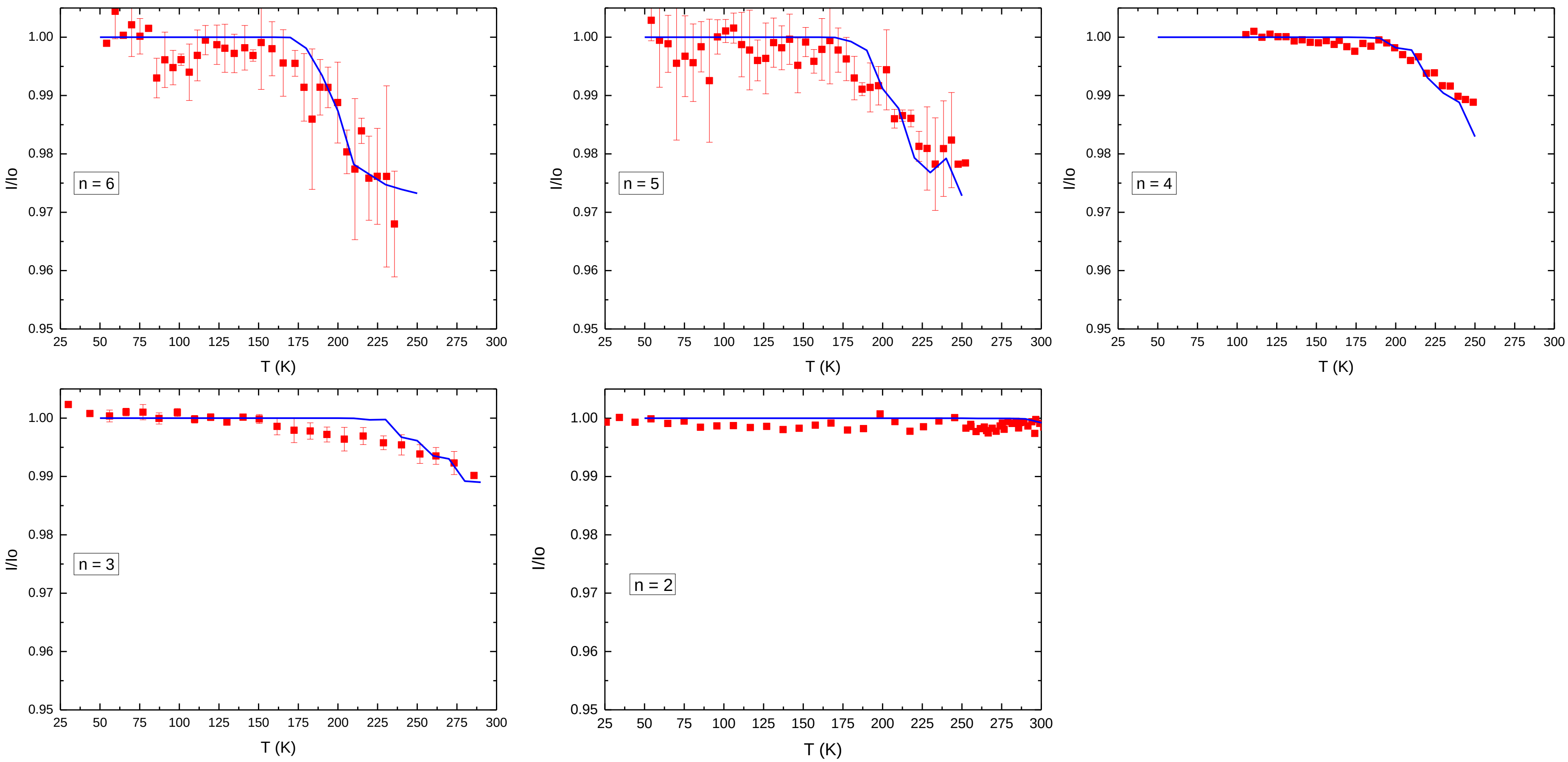
Generate TOF mass spectra *vs* initial temperature

Compare with experiment, adjust dissociation energy

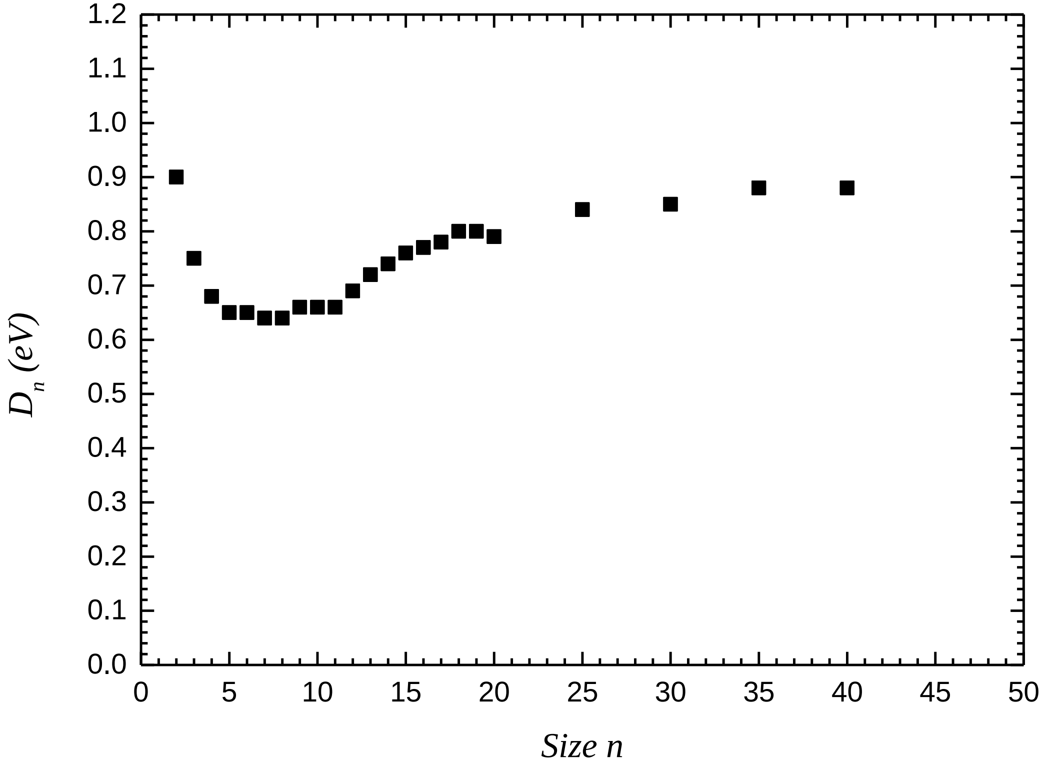

n = 40
n = 35
n = 30
n = 25
n = 20
n = 19
n = 18
n = 17
n = 16
I/Io
T (K)
0.75
0.80
0.85
0.90
0.95
1.00
25
50
75
100
125
150
175
200
225
250
275
300



n = 15
n = 14
n = 13
n = 12
n = 11
n = 10
n = 9
n = 8
n = 7
I/Io
T (K)
0.75 0.80 0.85 0.90 0.95 1.00
25 50 75 100 125 150 175 200 225 250 275 300

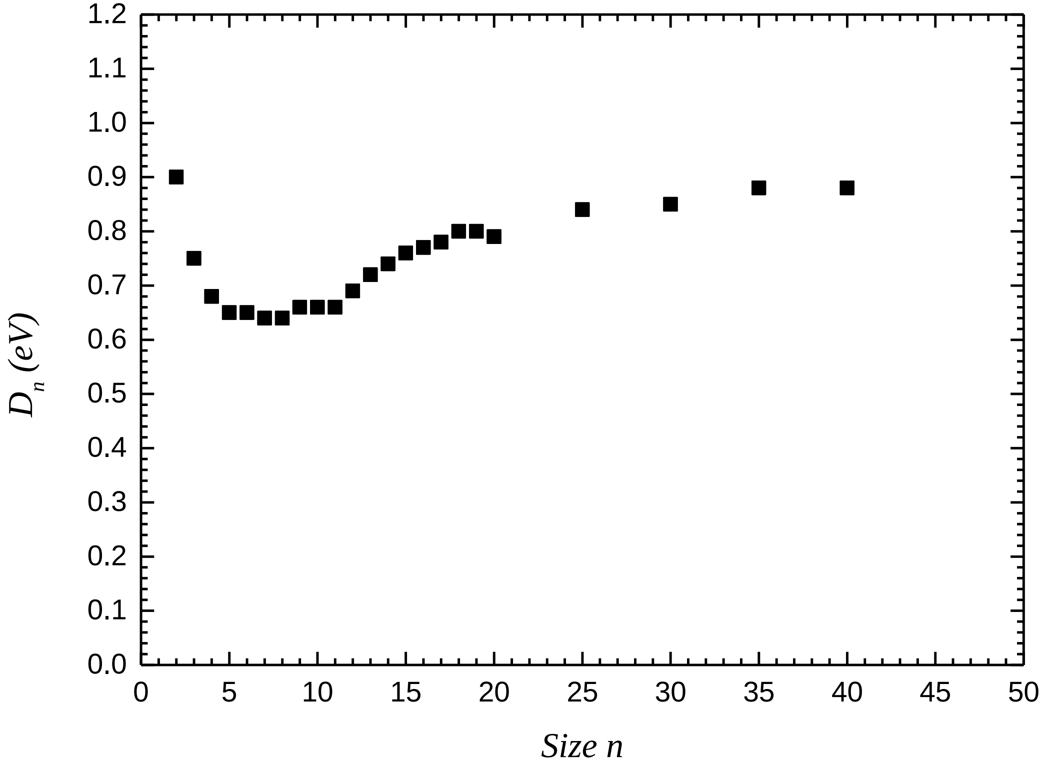

I/Io
T (K)
n = 6
n = 5
n = 4
n = 3
n = 2
1.00
0.99
0.98
0.97
0.96
0.95
25
50
75
100
125
150
175
200
225
250
275
300

Dissociation energies



Black squares: values deduced from the reproduction of the experimental curves using PST

Dissociation energies



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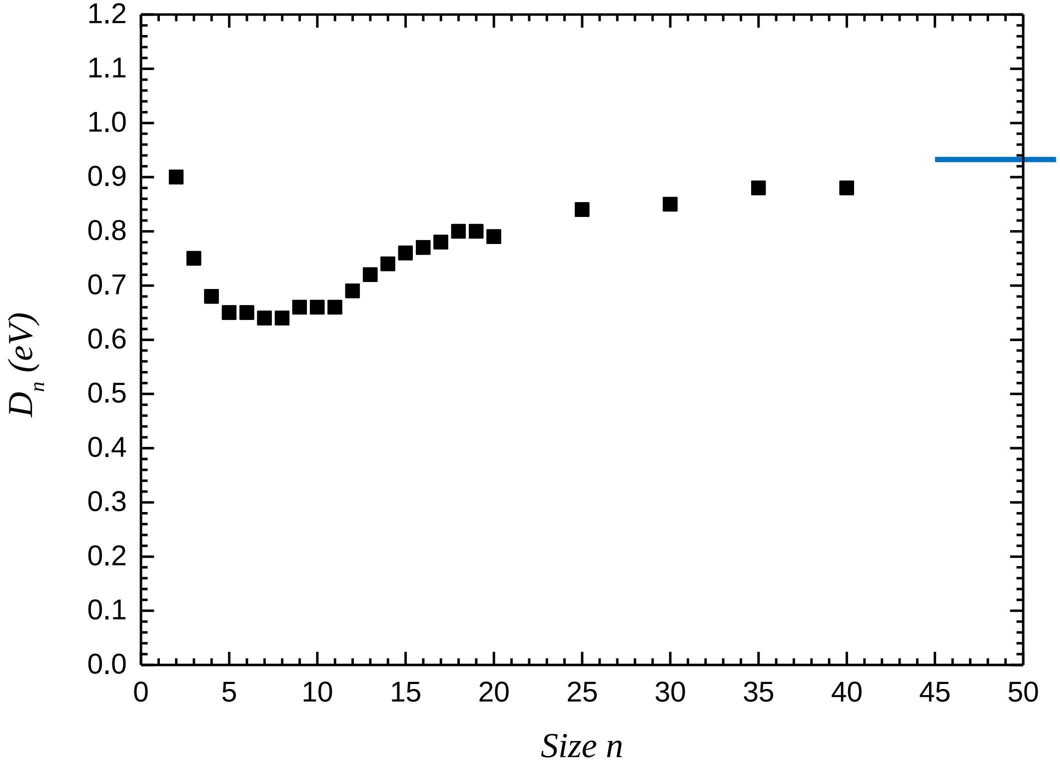
Only lower limit for n=2

Dissociation energies

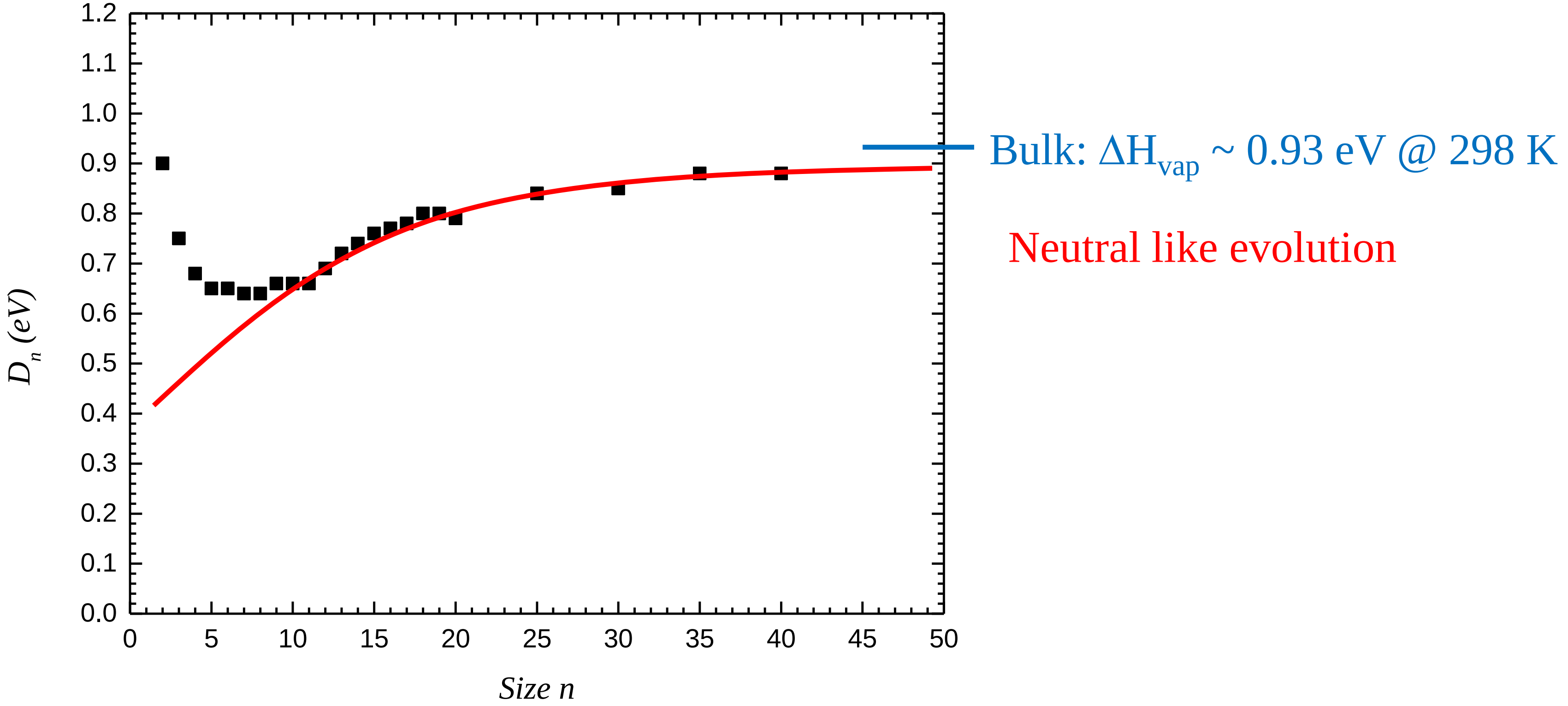


Bulk: ΔH_{vap} ~ 0.93 eV @ 298 K

Black squares: values deduced from the reproduction of the experimental curves using PST

Only lower limit for n=2

Dissociation energies



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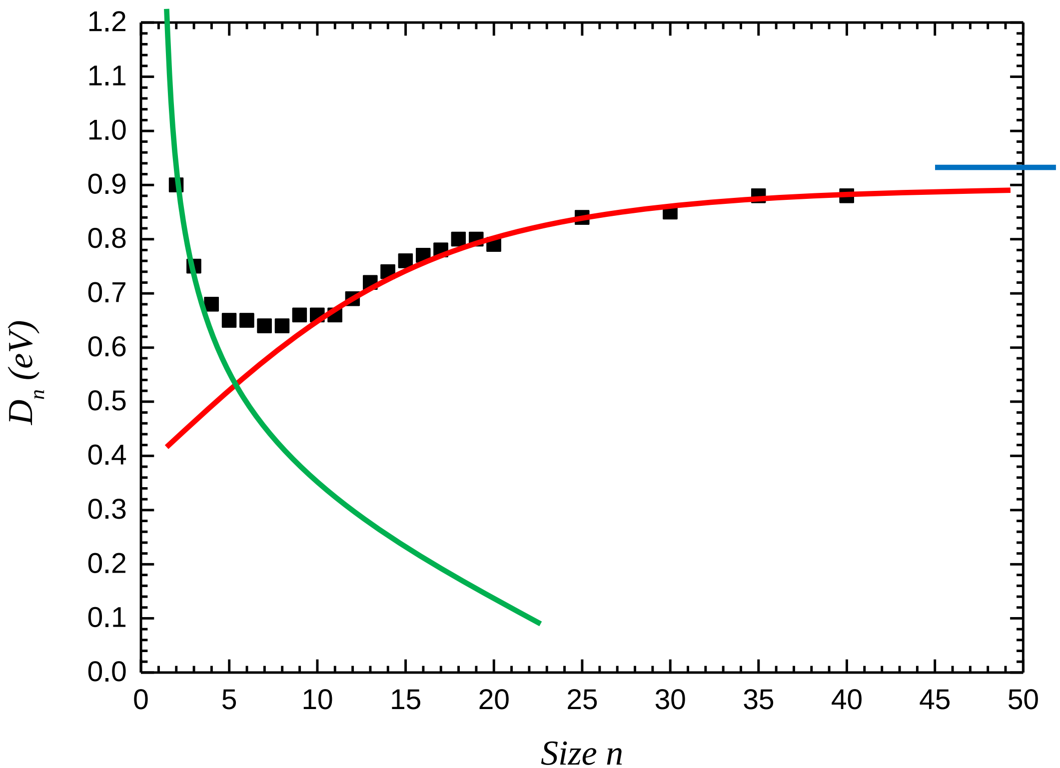

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Neutral like evolution

Dilution of
charge resonance stabilization
as size increases

Black squares: values deduced from the reproduction of the experimental curves using PST

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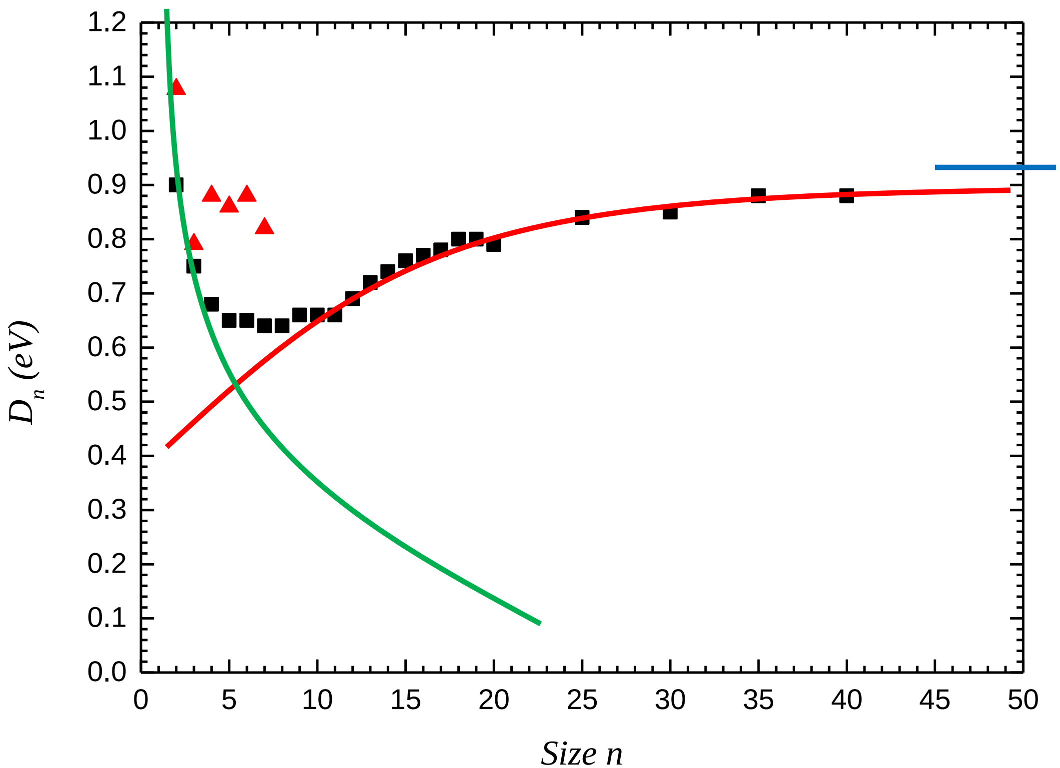
Dissociation energies



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Only lower limit for n=2

Red triangles: DFTB calculation (cf Rapacioli *et al.*)

Conclusion

- We have observed the thermal evaporation of pyrene clusters, n=2-40
- Experimental results successfully reproduced using PST
- Dissociation energies deduced, in good agreement with theory and bulk value

Conclusion

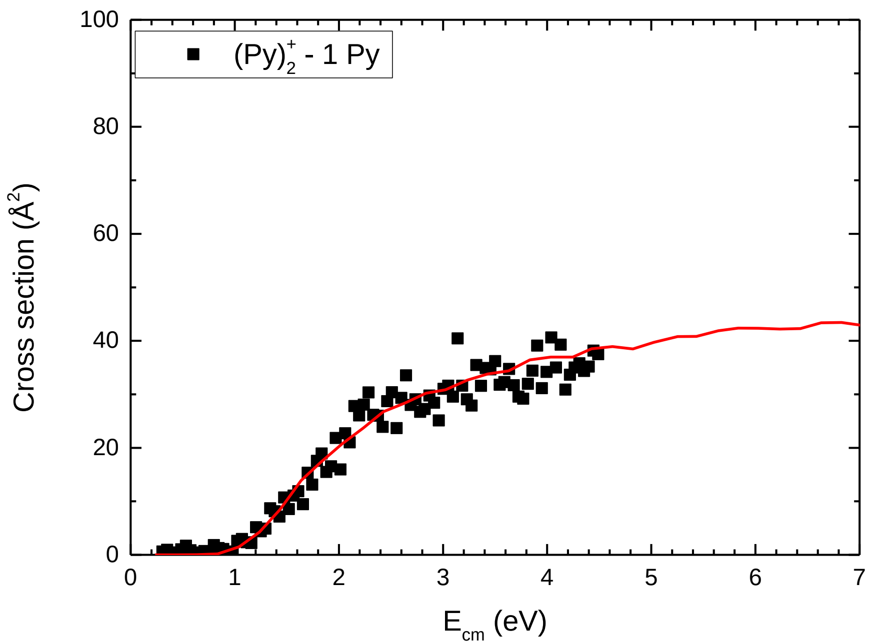
- Apart from the dissociation energy, no free parameters for the PST.

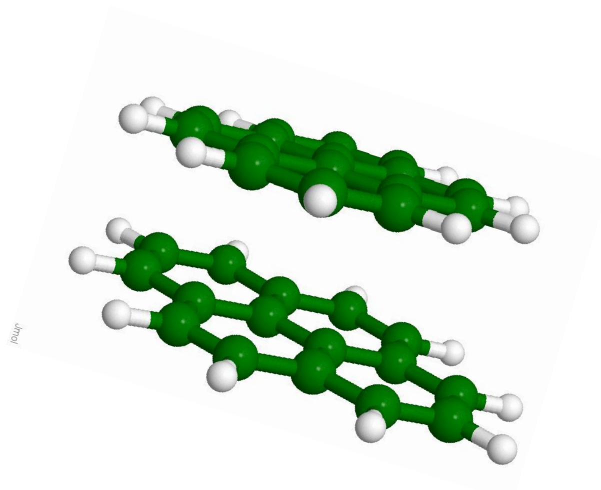
  Too good to be true?

- At least, effective evaporation rates are obtained

Conclusion

- Preliminary data on CID cross-section measurements: dissociation energies compare well with evaporation data.





PIRENEA 2 Setup

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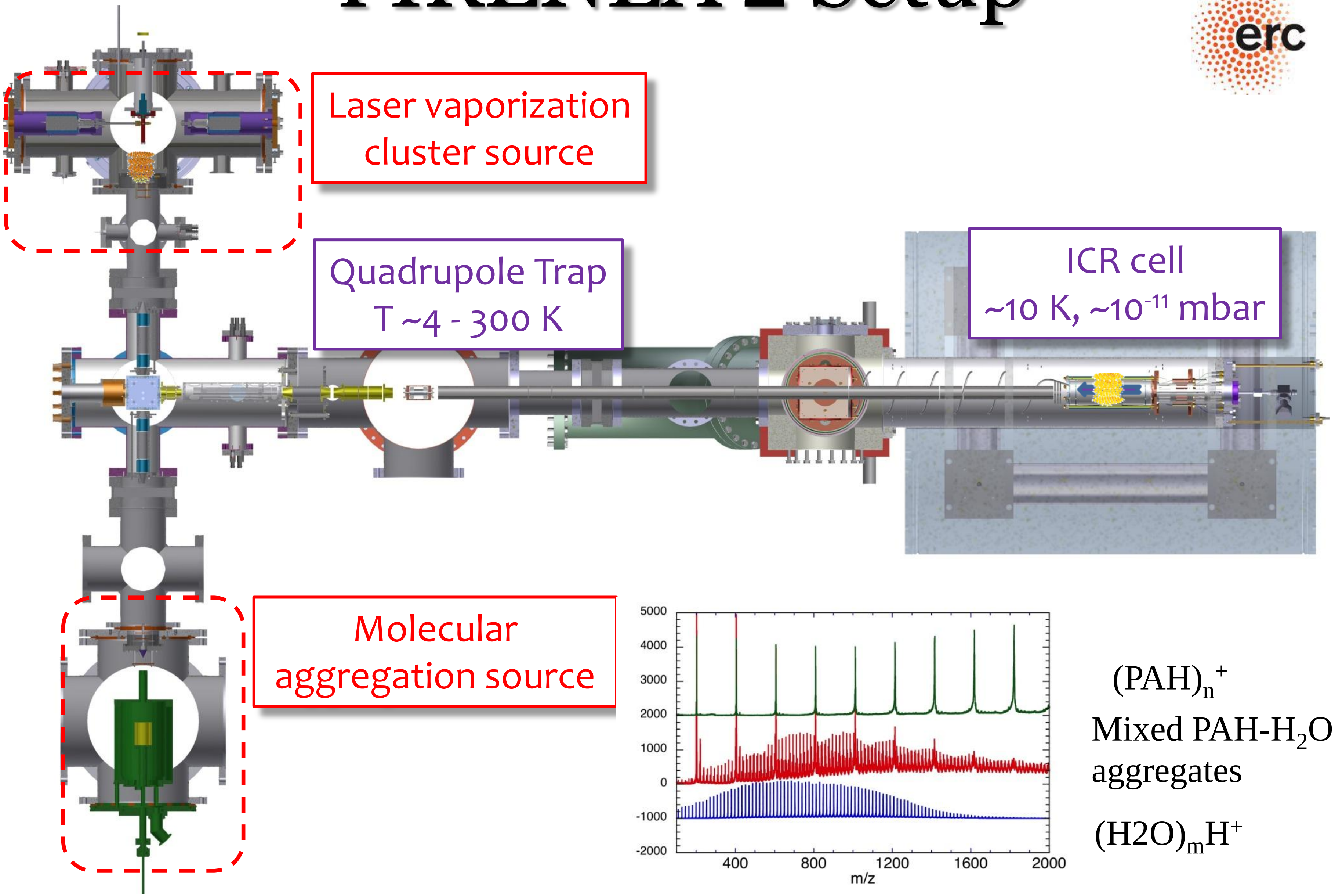
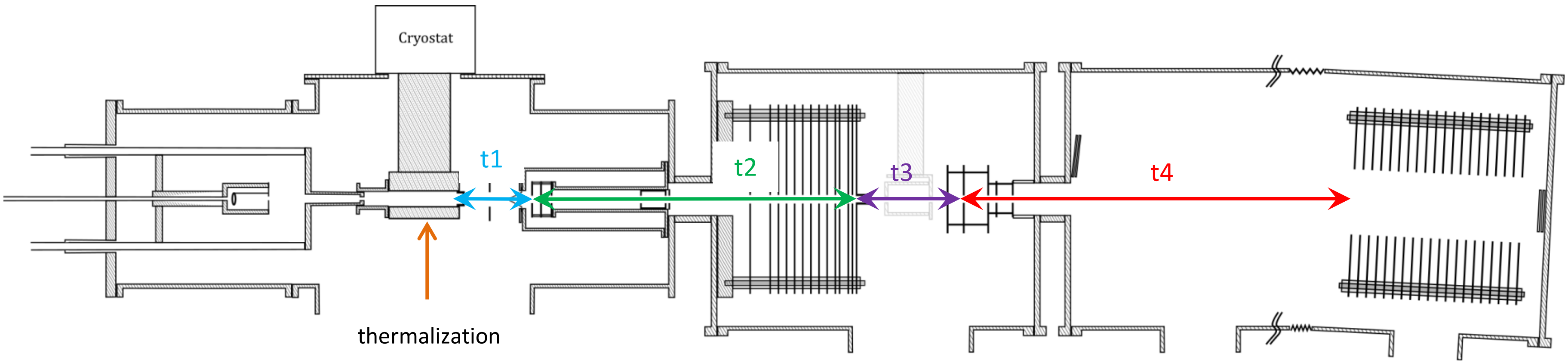


$(PAH)_n^+$

Mixed PAH-H_2O aggregates

$(H2O)_mH^+$

Experimental results



For a size n @ 22 eV, we have:

$t1 = D/v_0$ = 20 µs @ 200 K

$t2 = 24\times\sqrt{n}$ µs

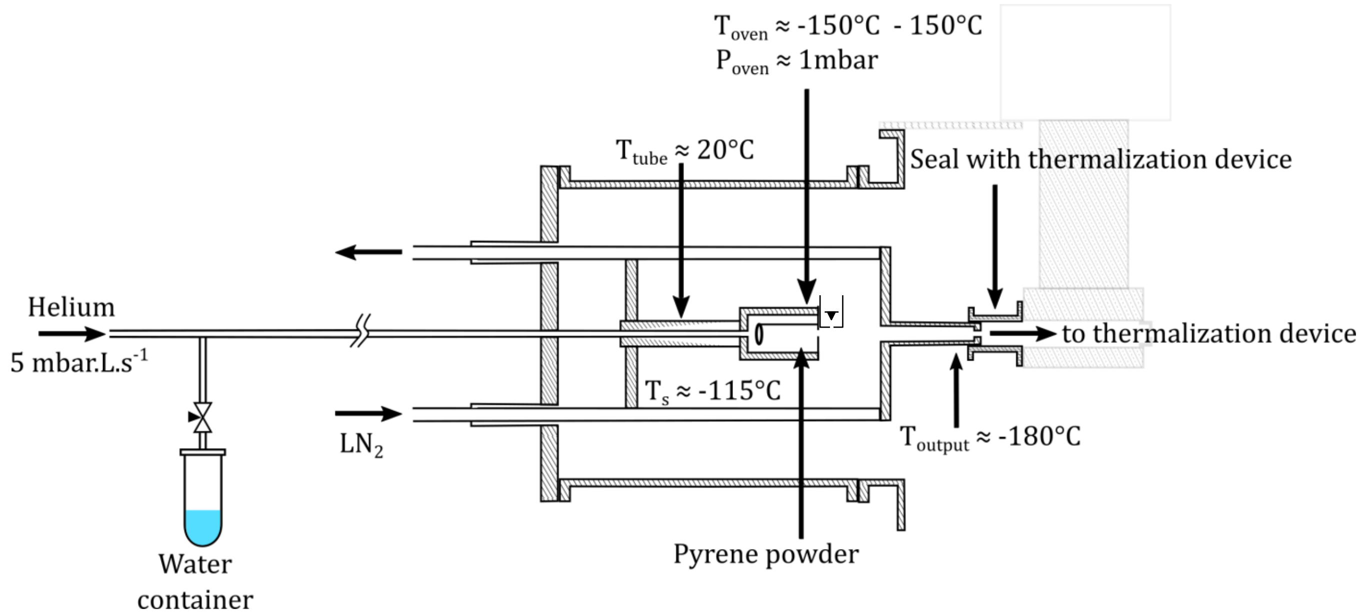
$t3 = 25 \times\sqrt{n}$ µs

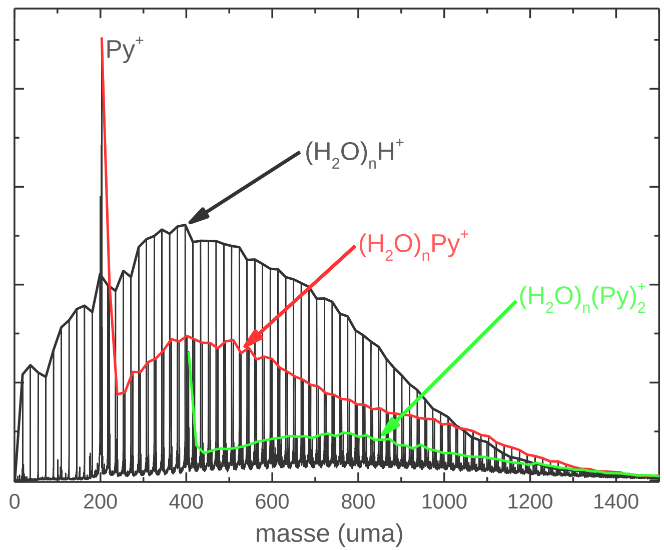
$t4 = 25 \times\sqrt{n}$ µs

D = distance between the exit of the thermalizer and the first Wiley-McLaren = 8 cm
v_0 = thermal velocity of helium

Similar time spent in the different parts of the setup
⇒ Similar evaporation probability at each experimental stage

Cluster production





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PST evaporation rates

The version of PST used here contains the constraint that total angular momentum is conserved, and that in the reverse process the associating product must overcome the maximum of the centrifugal barrier which defines the position of the transition state (loose transition state).

The interaction between the products is represented by an effective central potential of the form:

$$V_{eff}(r) = -\frac{C_4}{r^4} + \frac{L^2\hbar^2}{2\mu r}$$

PST evaporation rates

Ingredients of the Phase Space Theory:

- initial internal energy of the parent E_i
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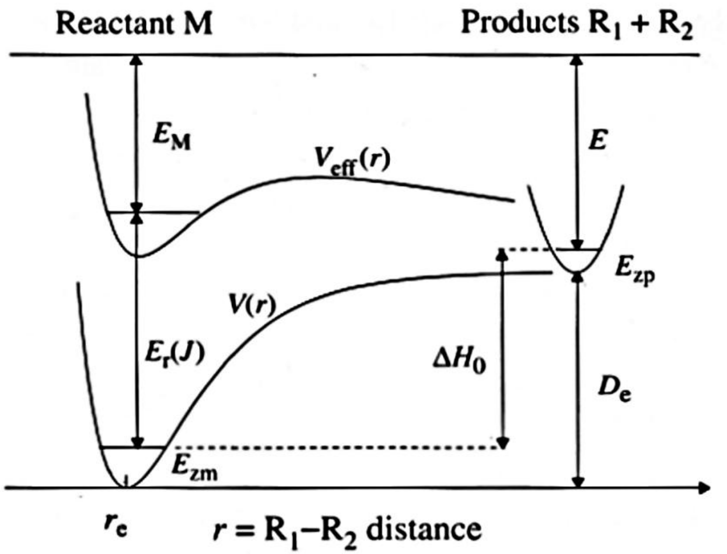
- conservation of angular momentum



$$W(E_i, J) = \frac{G(E_f, J)}{h(2J+1)N(E_i)}$$

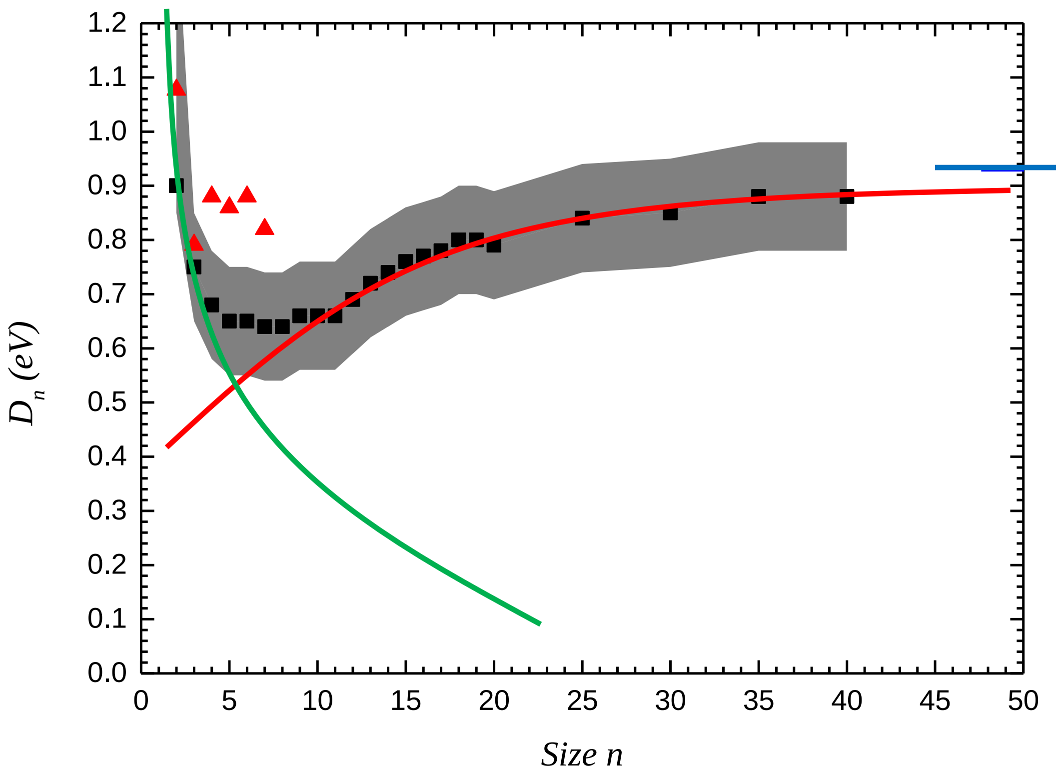
$$E_f = E_i + E_{rot} - D$$

$$E_{rot} = B_0 J(J+1)$$

From the PST we also get the probability of energy partition among the fragments:

$$P(E_v, E_{rel}, E_r)dE_v dE_{rel} dE_r = \frac{N_1(E_v)N_2(E_f - E_v - E_{rel} - E_r)N_x(E_r, E_{rel}, J)}{G(E_f, J)} dE_v dE_{rel} dE_r$$

Dissociation energies



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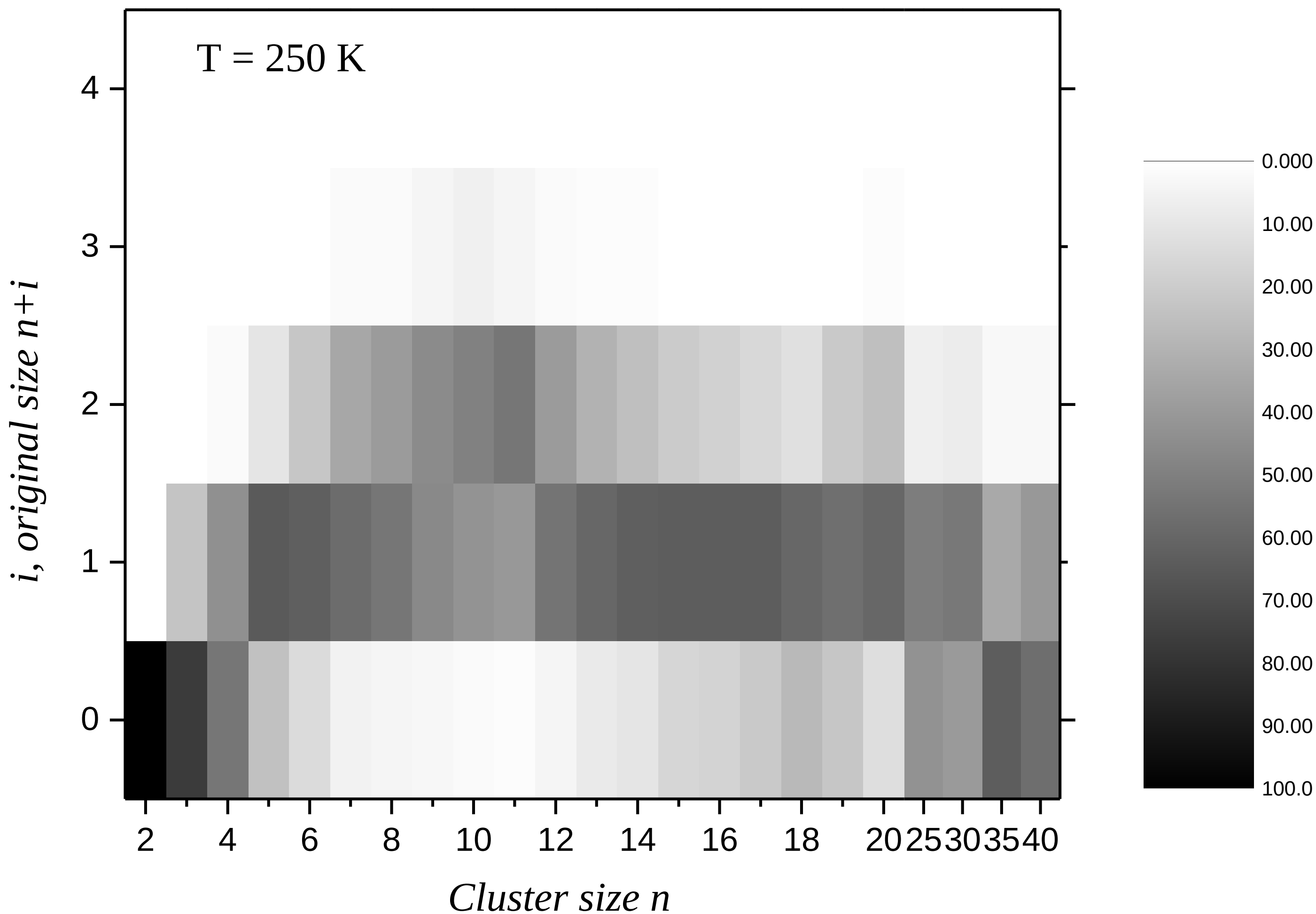
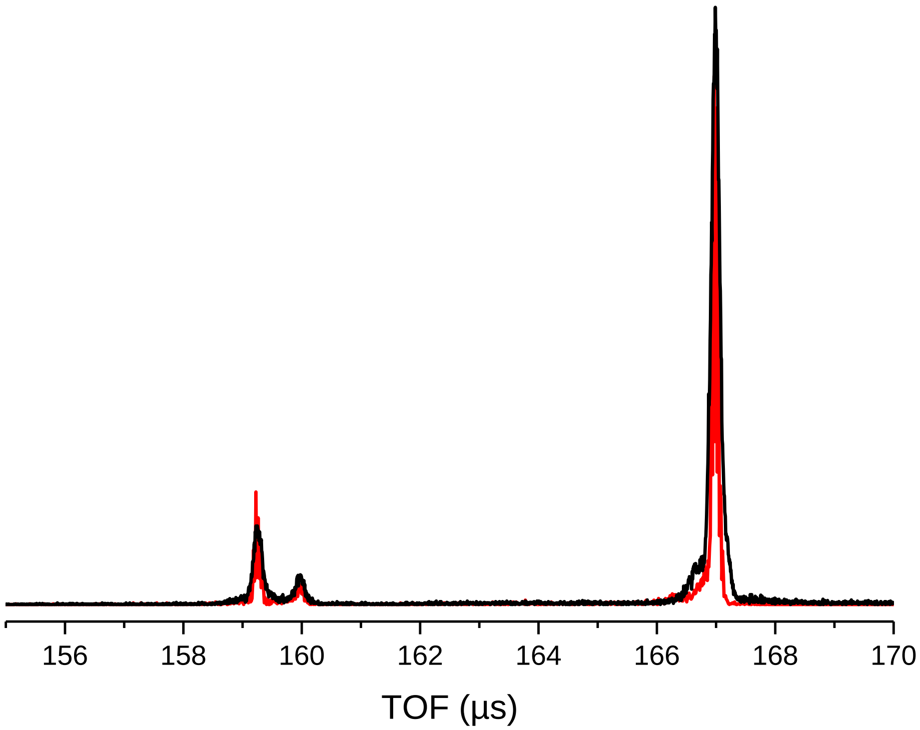
Initial size contributions



Simulated TOF mass spectra



Monte Carlo integration

To compare with the experiment we need to integrate over distributions:

$$\sum_J \int P(E,T)P(J,T)dE$$

P(E,T) = probability to have an internal energy E in the parent cluster.
Number occupation n_i of each vibration randomly picked up so that on average we have:

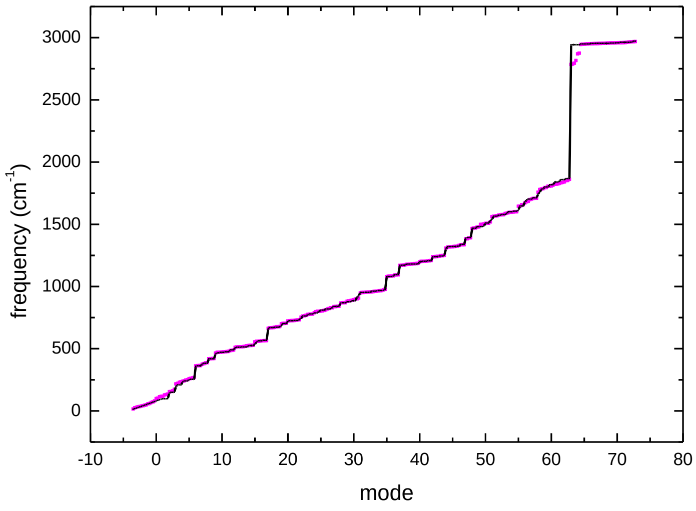
$$E = \sum_i \frac{\hbar\omega_i}{e^{\frac{\hbar\omega_i}{k_B T}} - 1}$$

P(J,T) = probability to have the total angular momentum J in the parent cluster.

$$P(J) = \frac{4}{\sqrt{\pi}}\left(\frac{B}{k_B T}\right) J^2 e^{-\frac{BJ^2}{k_B T}}$$

High temperature or low B limit used

Vibrational harmonic frequencies

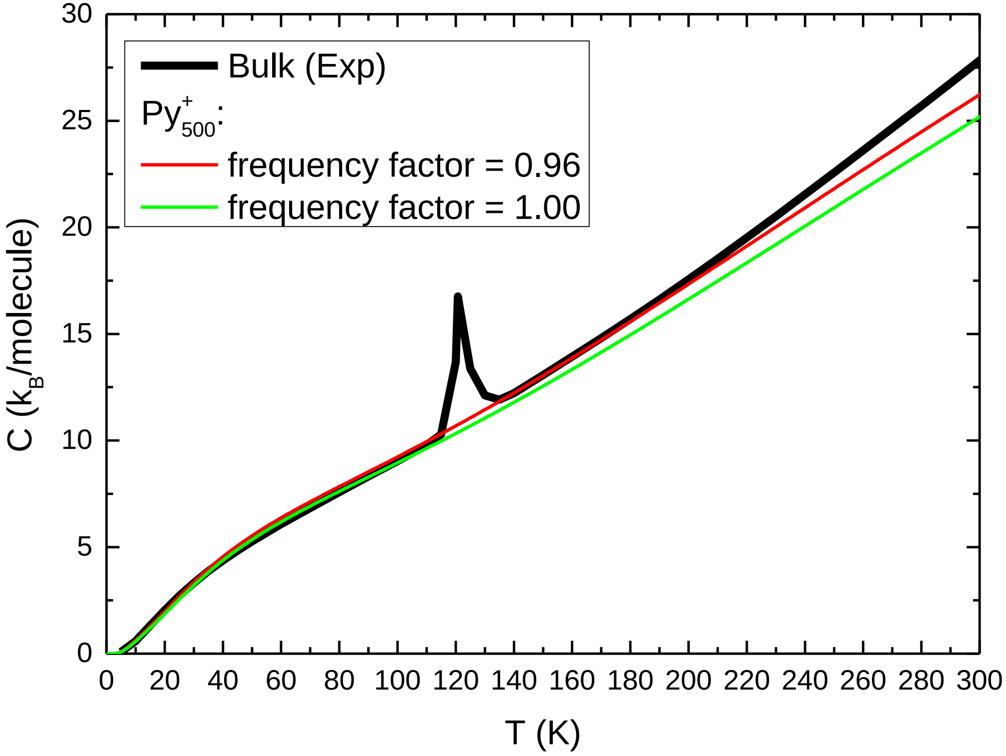


harmonic frequencies from DFTB for the tetramer

Vibrational harmonic frequencies calculated for neutral pyrene and cationic clusters of sizes 1, 2, 3 and 4.
To extrapolate for larger sizes n:
Intramolecular frequencies = cation + (n-1) neutrals
Intermolecular frequencies = linear interpolation between 13 cm^{-1} and the lowest cationic frequency.

Vibrational harmonic frequencies

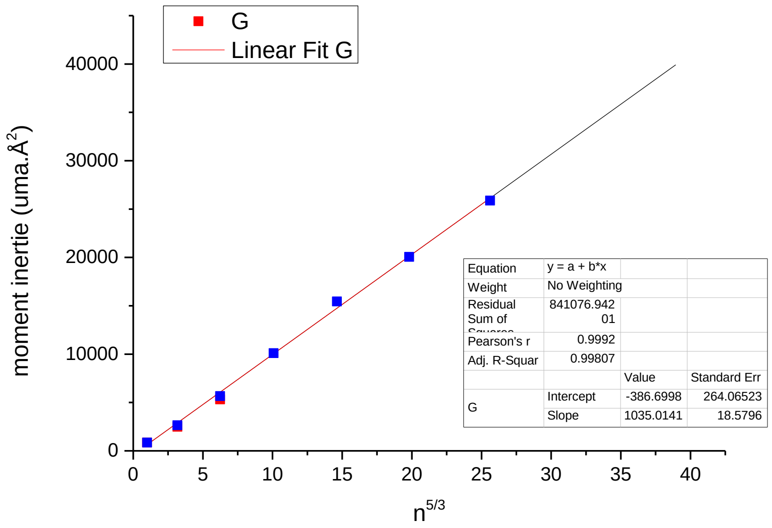
Using these, the heat capacity of bulk pyrene can be reproduced:



Moments of inertia and rotational constants

For the PST calculation the rotational constant B is needed. $B = \dfrac{\hbar^2}{2I}$

The moment of inertia are taken as the geometrical average of the 3 main moments: $$I = \sqrt[3]{I_1 I_2 I_3}$$

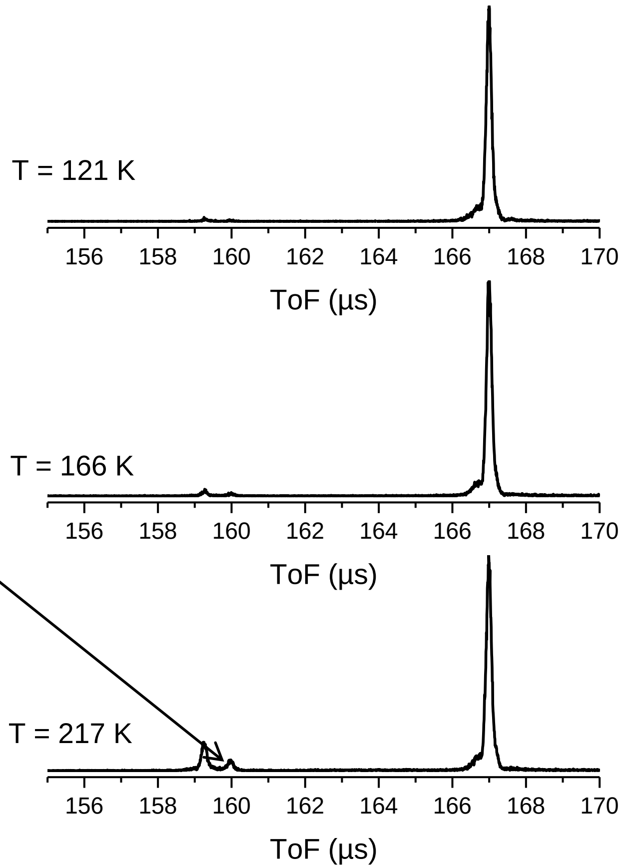


Squares: DFTB calculation

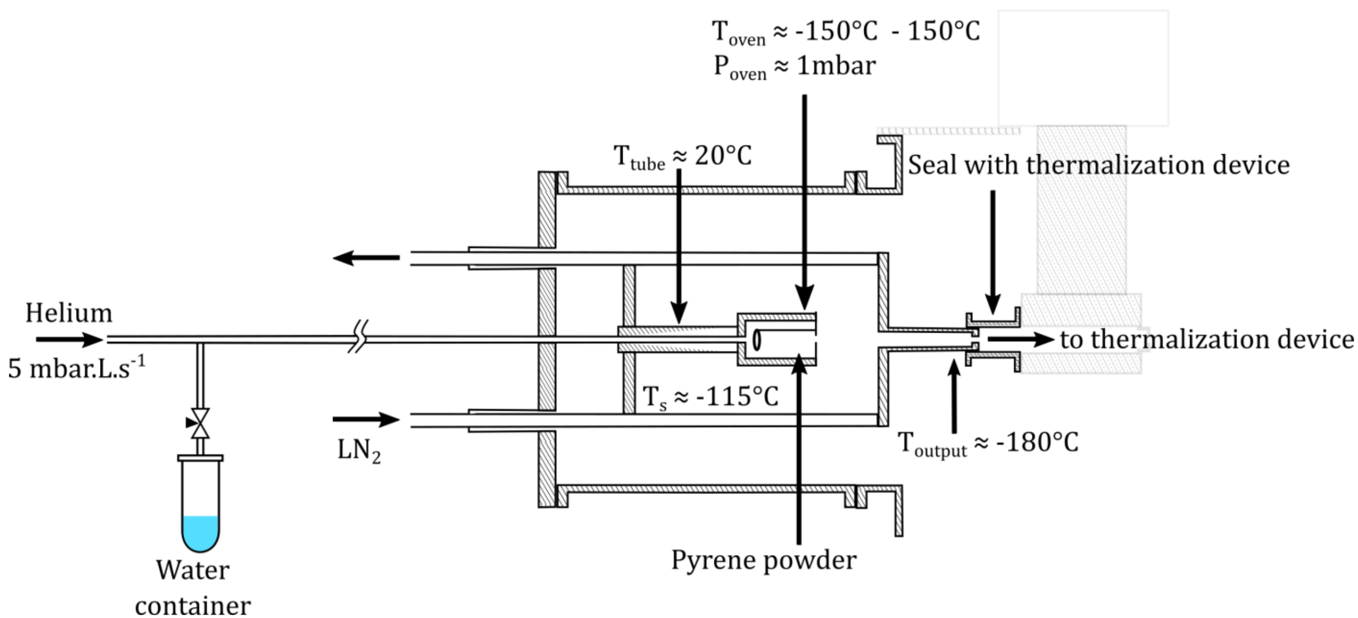
Line : $I(Py_n) \propto I(Py_1) n^{5/3}$

If clusters evaporate after the second Wiley McLaren acceleration and before the reflectron (t4), they end up in the "secondary" fragment peak.

If they evaporate after the reflectron they can not be distinguished from the parent peak.

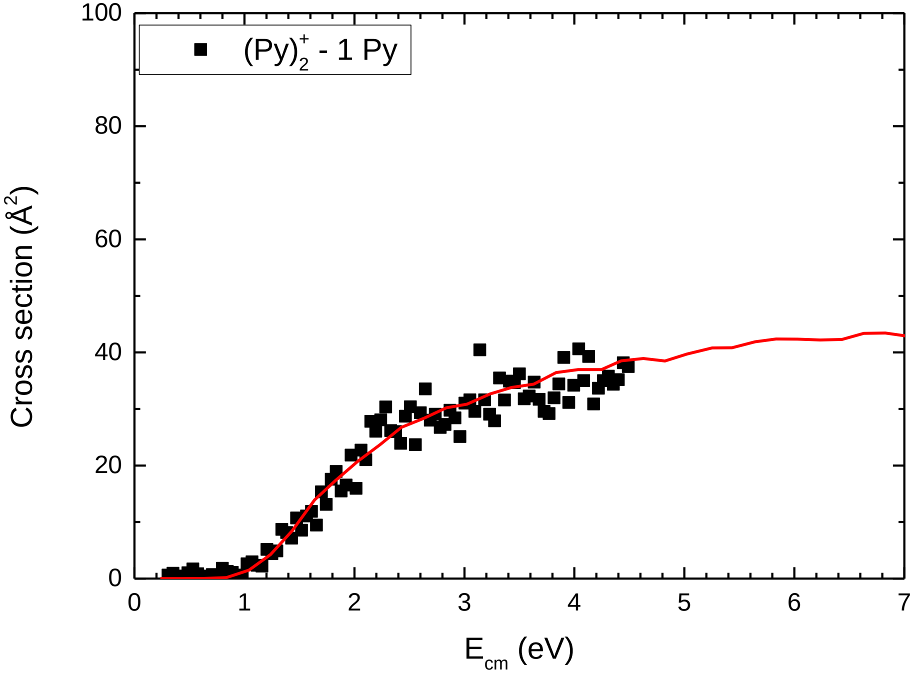


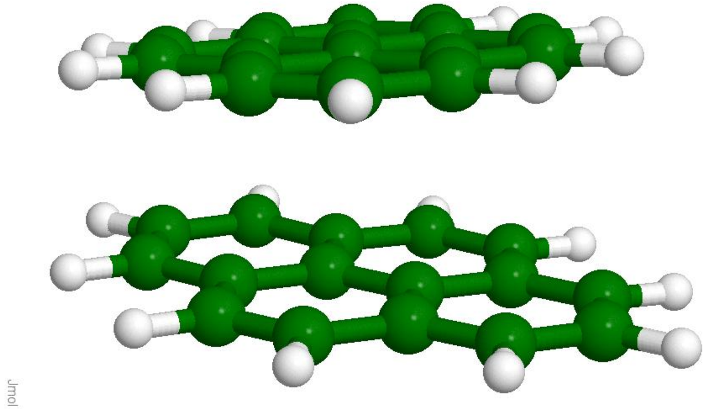
Clusters production



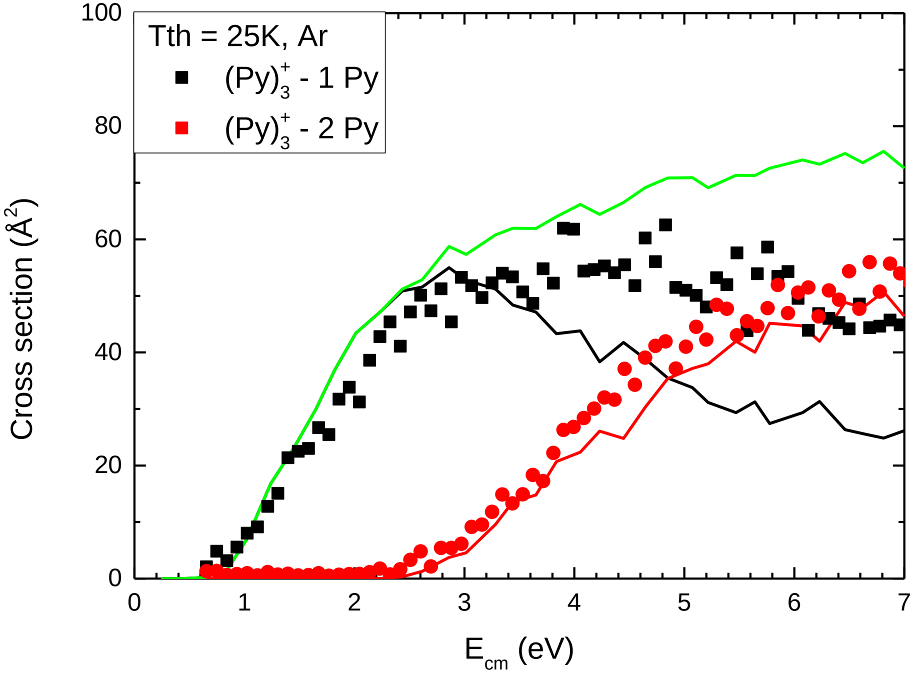
Clusters are produced in a gas aggregation source.
Ionization by either :
- a discharge electrode, I ≈ 100µA, V ≈ 1 kV
- an electron gun, I = 2.5 A, V = -100 V

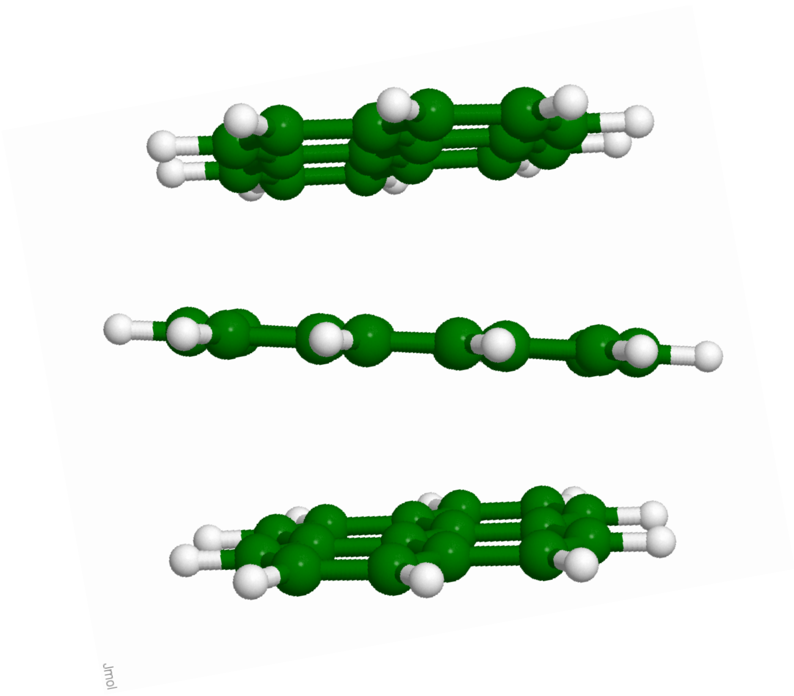
Experimental results



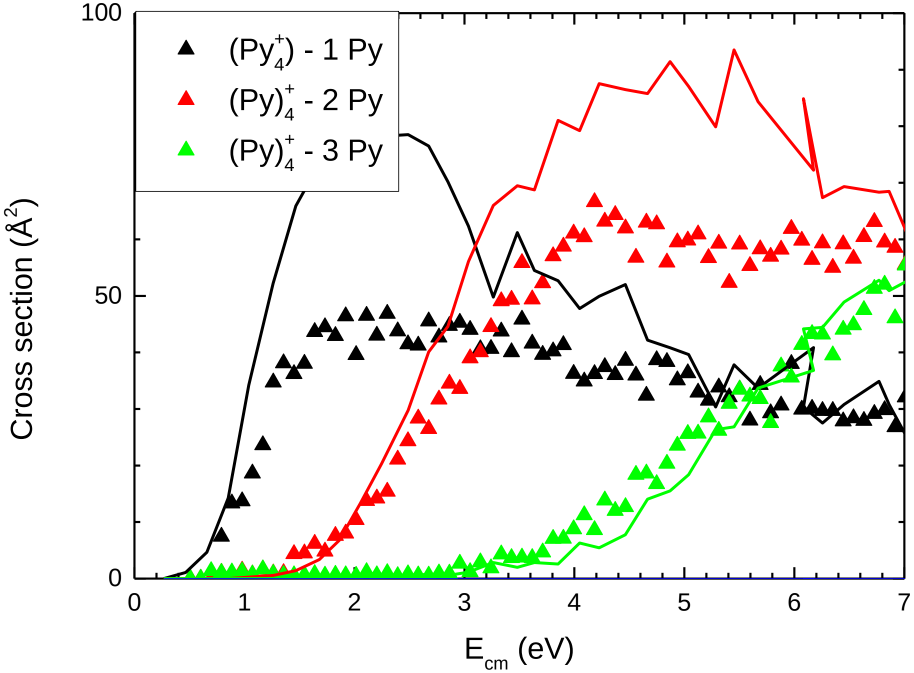


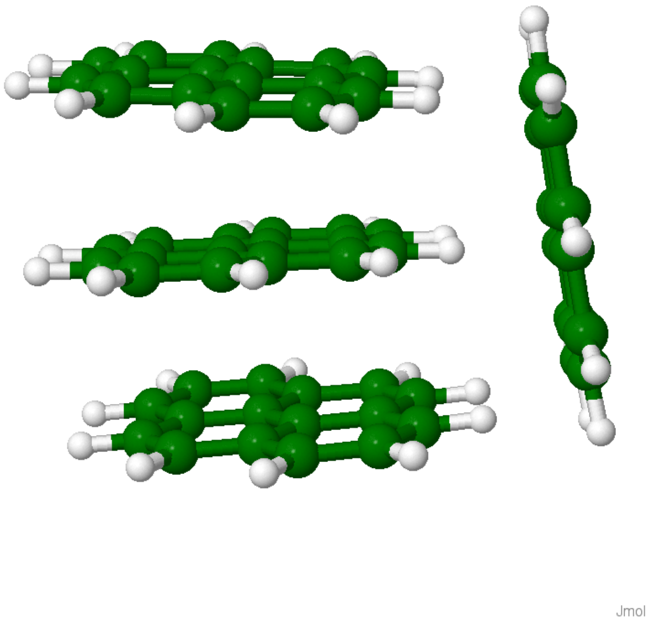
Experimental results

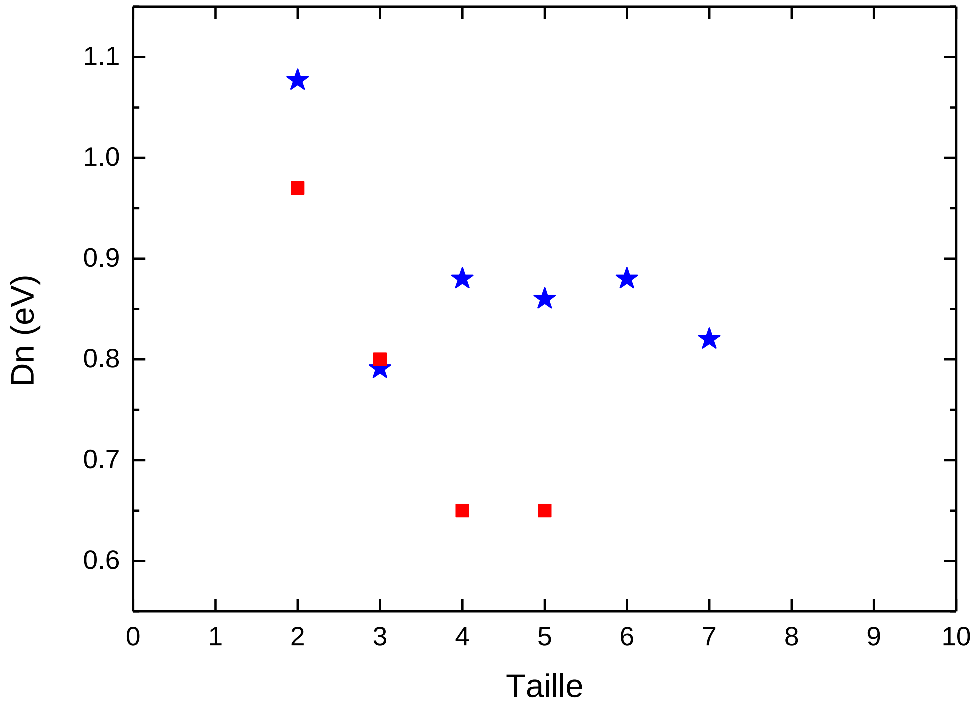




Experimental results







Blue stars: theory

Red squares: values deduced from the reproduction of the experimental curves using PST (CID).