Experimental studies of decays at long timescales

Patrick Rousseau

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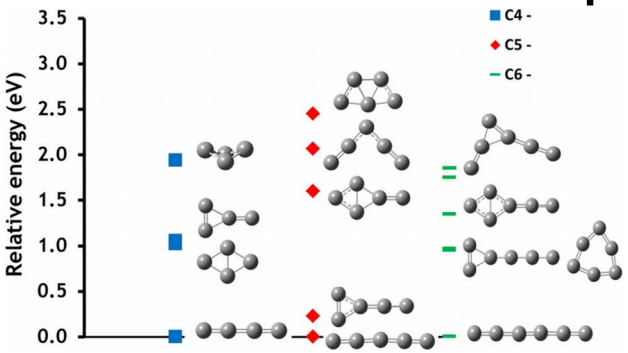

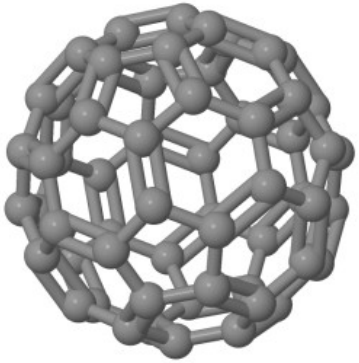

Introduction

Instrumentation

Metastable dissociation

Radiative cooling

Vibrational electron detachment

Slow isomerisation

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Complex systems

They posses a large number of degrees of freedom:

$$s = 3N - 6$$

→ numerous relaxation channels are expected

- in competition
- at different timescales

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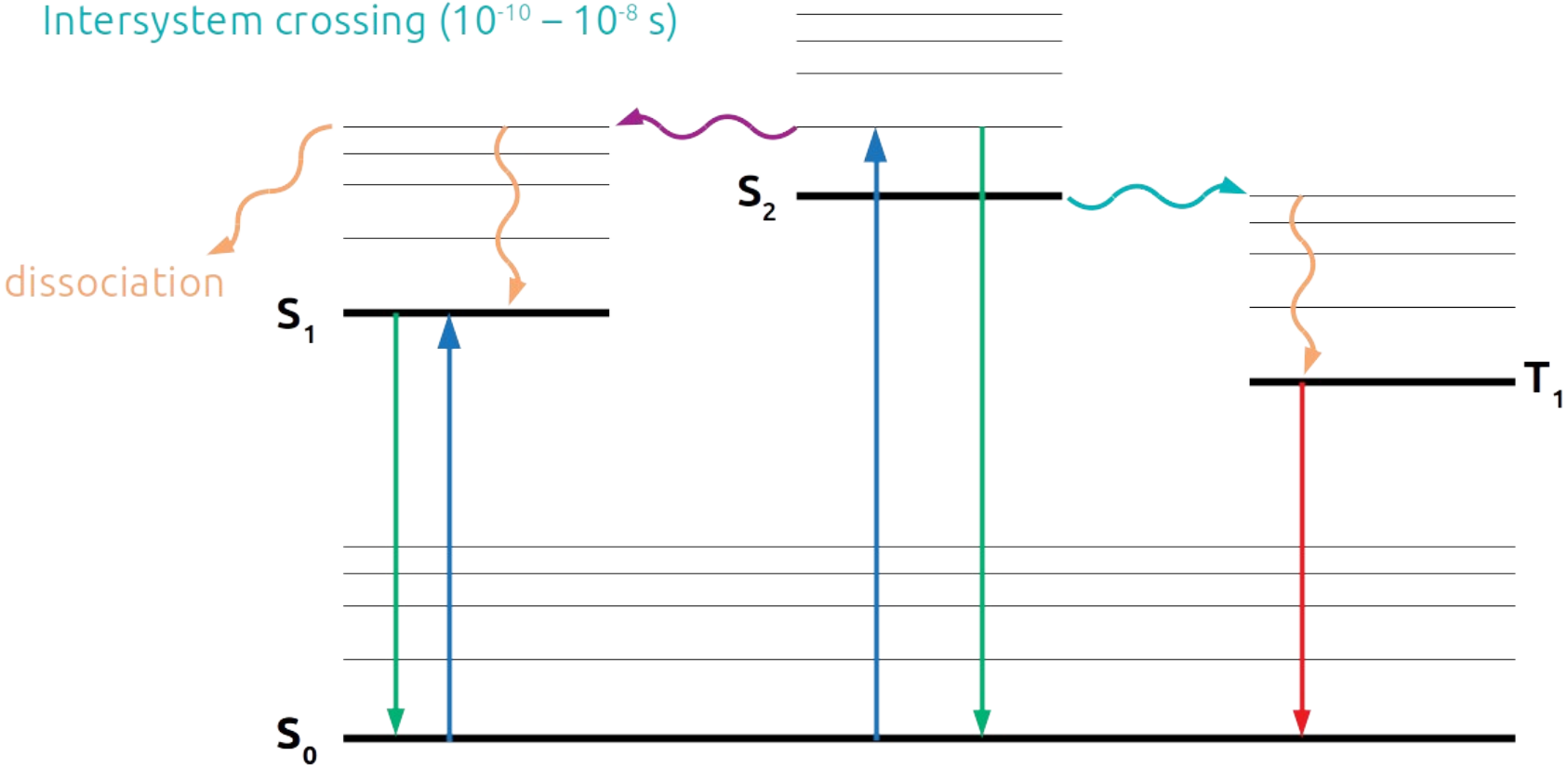
Jablonski diagram

Absorption (10^{-15} s)
Fluorescence (10^{-10} – 10^{-7} s)
Phosphorescence (10^{-6} – 10 s)
Internal conversion (10^{-11} – 10^{-9} s)
Vibrational relaxation (10^{-12} – 10^{-10} s)
Intersystem crossing (10^{-10} – 10^{-8} s)



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Complex systems

They posses a large number of degree of freedom:

$$s = 3N - 6$$

→ numerous relaxation channels are expected

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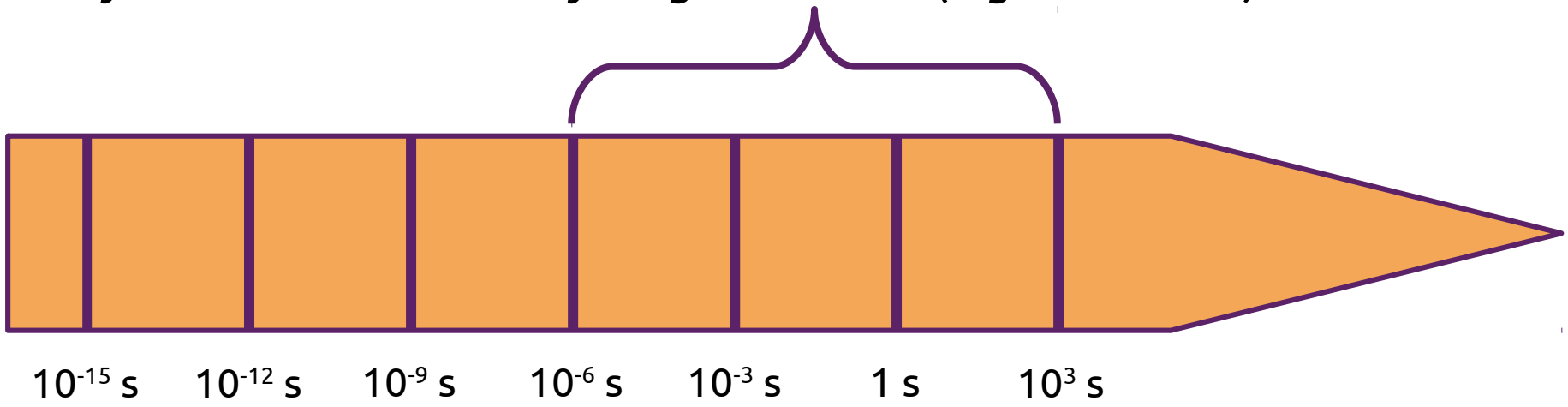
- at different timescales

Today we will focus on really long timescales (higher than ns).



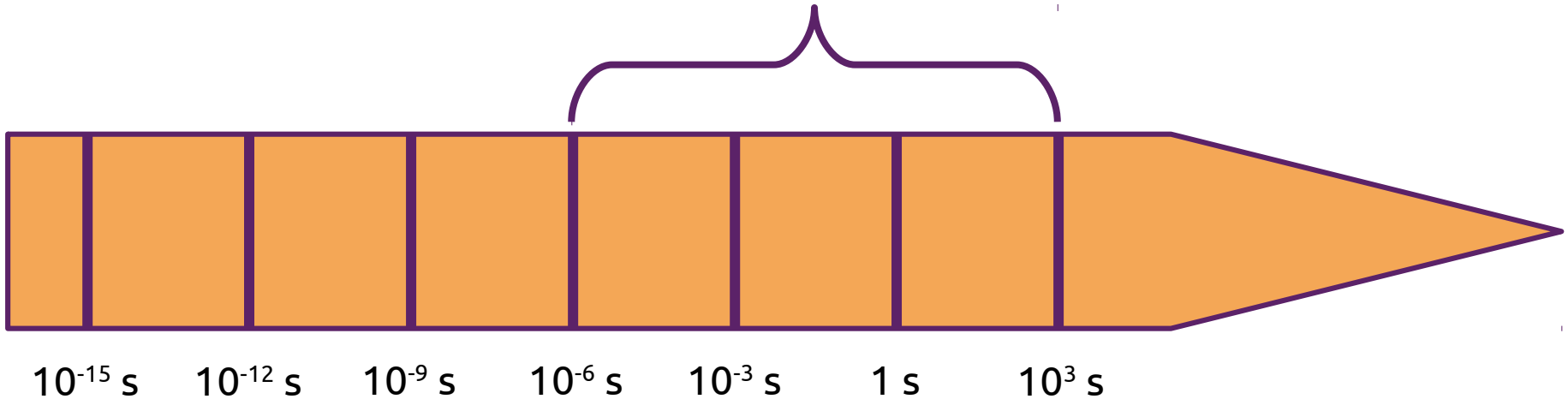
Long timescale

At such long timescale, the system can be described by statistical physics.

From the experimental point of view, we need to keep the control on the system

BUT in 1 µs, a thermal water molecule runs through about 1 mm.

One need to store the molecular system in order to study longer timescales.



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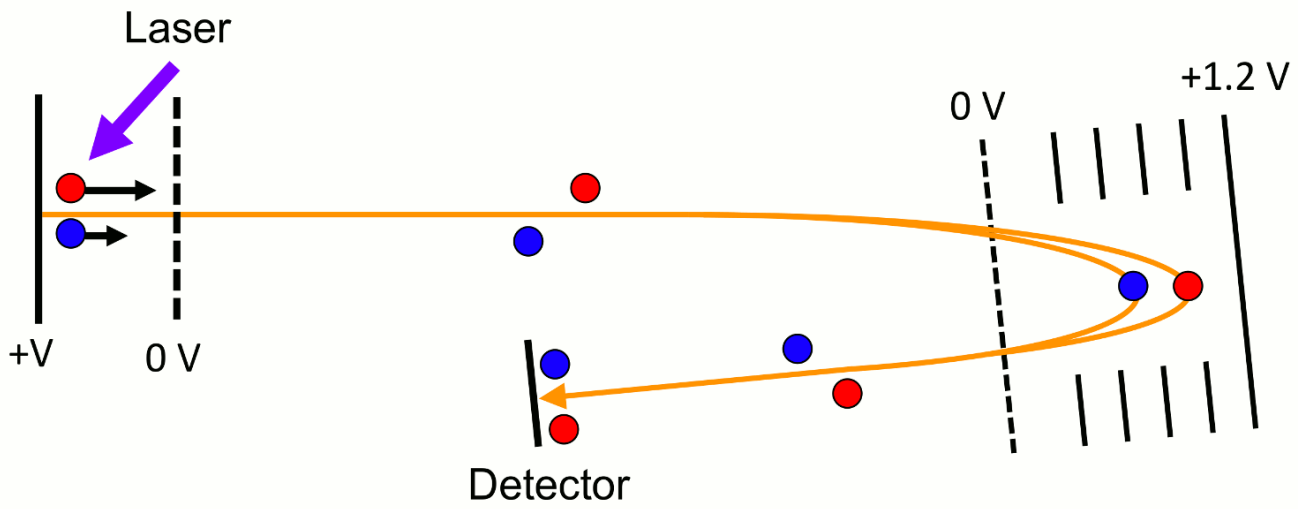
Time-of-flight spectrometer

Indeed for relatively “short” timescales (µs range), one may study the so-called delayed fragmentation using time-of-flight mass spectrometer.



With reflectron configuration, one can observe decays occuring in the first field-free region.

prompt: $AB^+ \rightarrow A^+ + B^0$

delayed: $AB^+ \rightarrow A^+ + B^0$

Storage devices

For longer timescales, the field-free region length required is too high.

→ one needs to consider alternative configurations

(multiple reflections, ring…)

Storage rings based on magnetic field existed since several decades.
However, as the molecular system can be heavy, it is important to consider instead electrostatic device with no mass limitation.

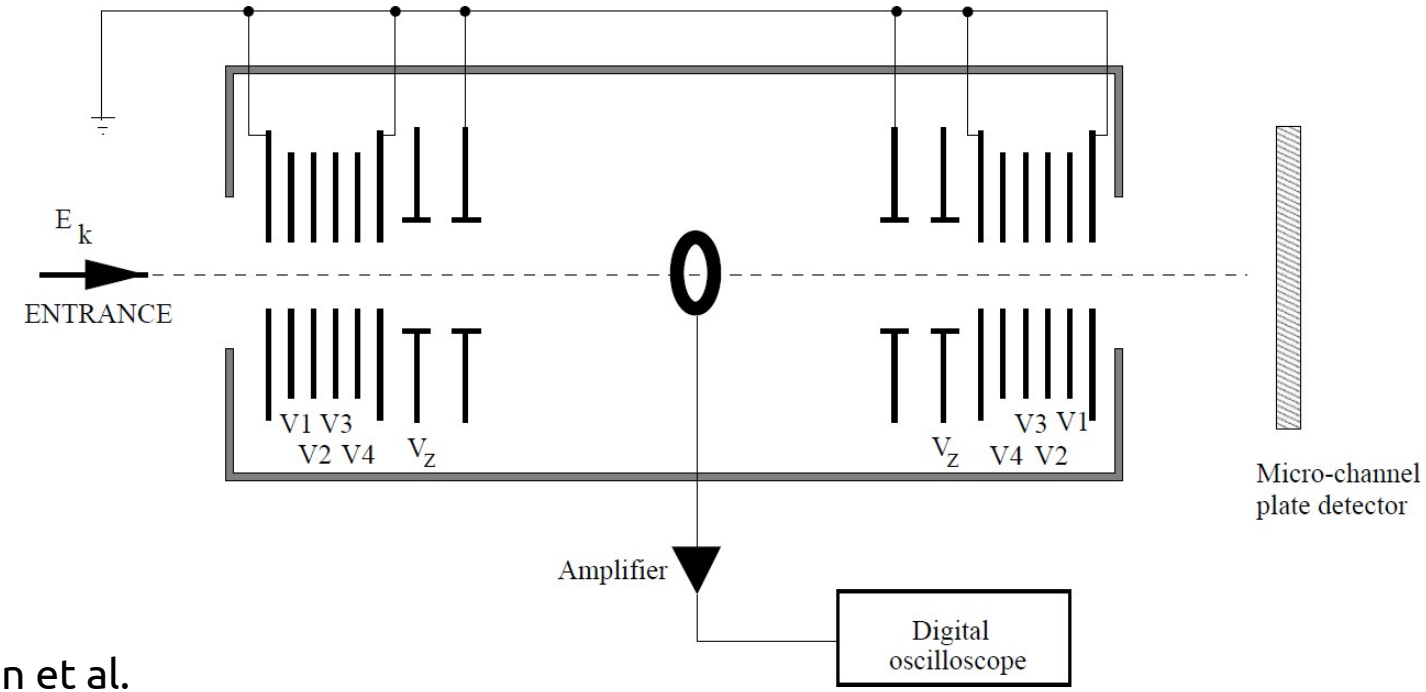
In 1997, two families of electrostatic storages devices emerge:

- electrostatic ion beam trap, D. Zajfman et al. in Israel
- electrostatic storage ring, L. H. Anderson et al. in Danmark

Electrostatic ion beam trap

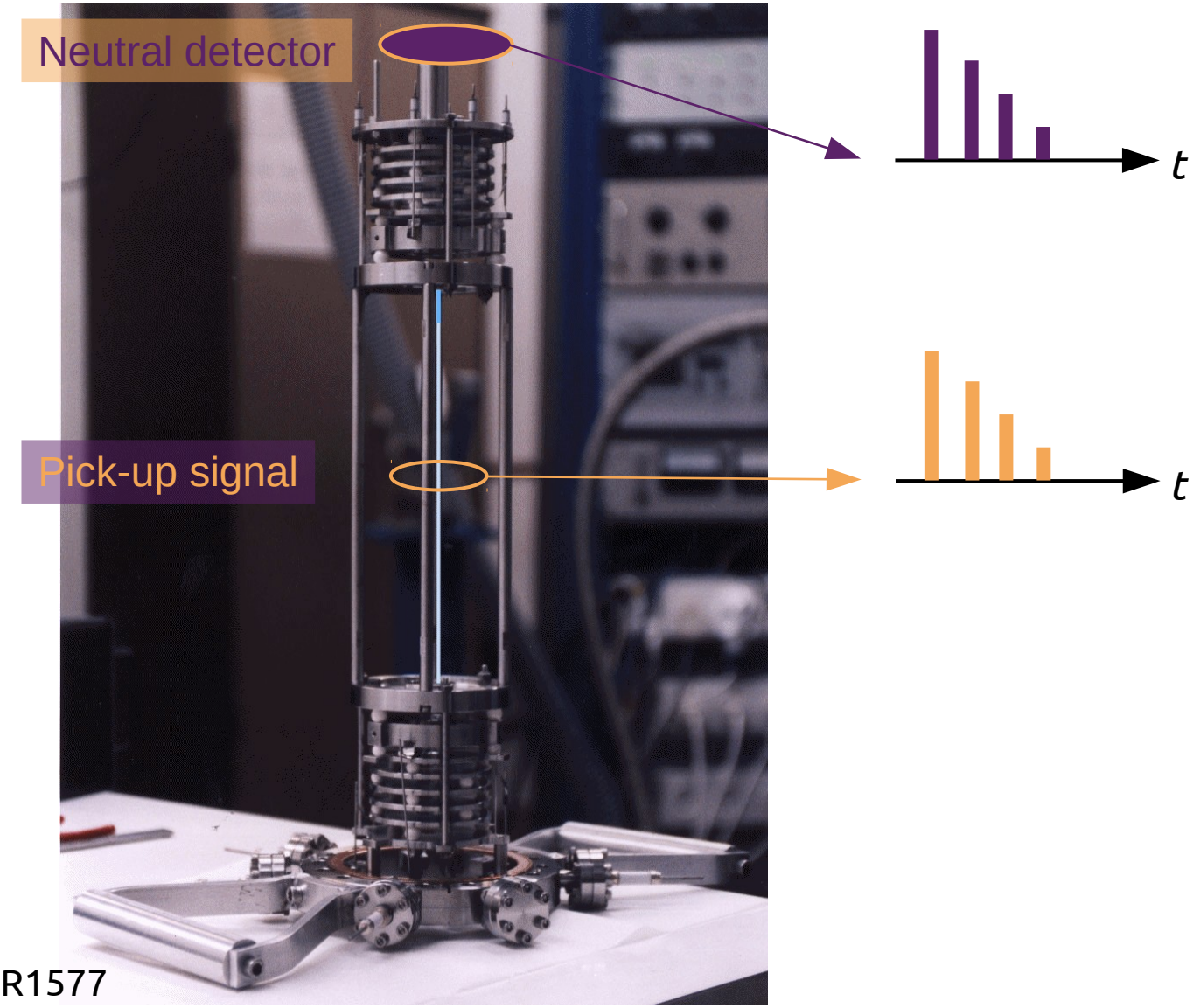
The idea is to use two electrostatic mirrors in order to obtain multiple reflection of the beam.

- compact design (~ 1m)
- long storage time in UHV condition (100 ms to s)



D. Zajfman et al.
Phys. Rev. A **55** (1997) R1577

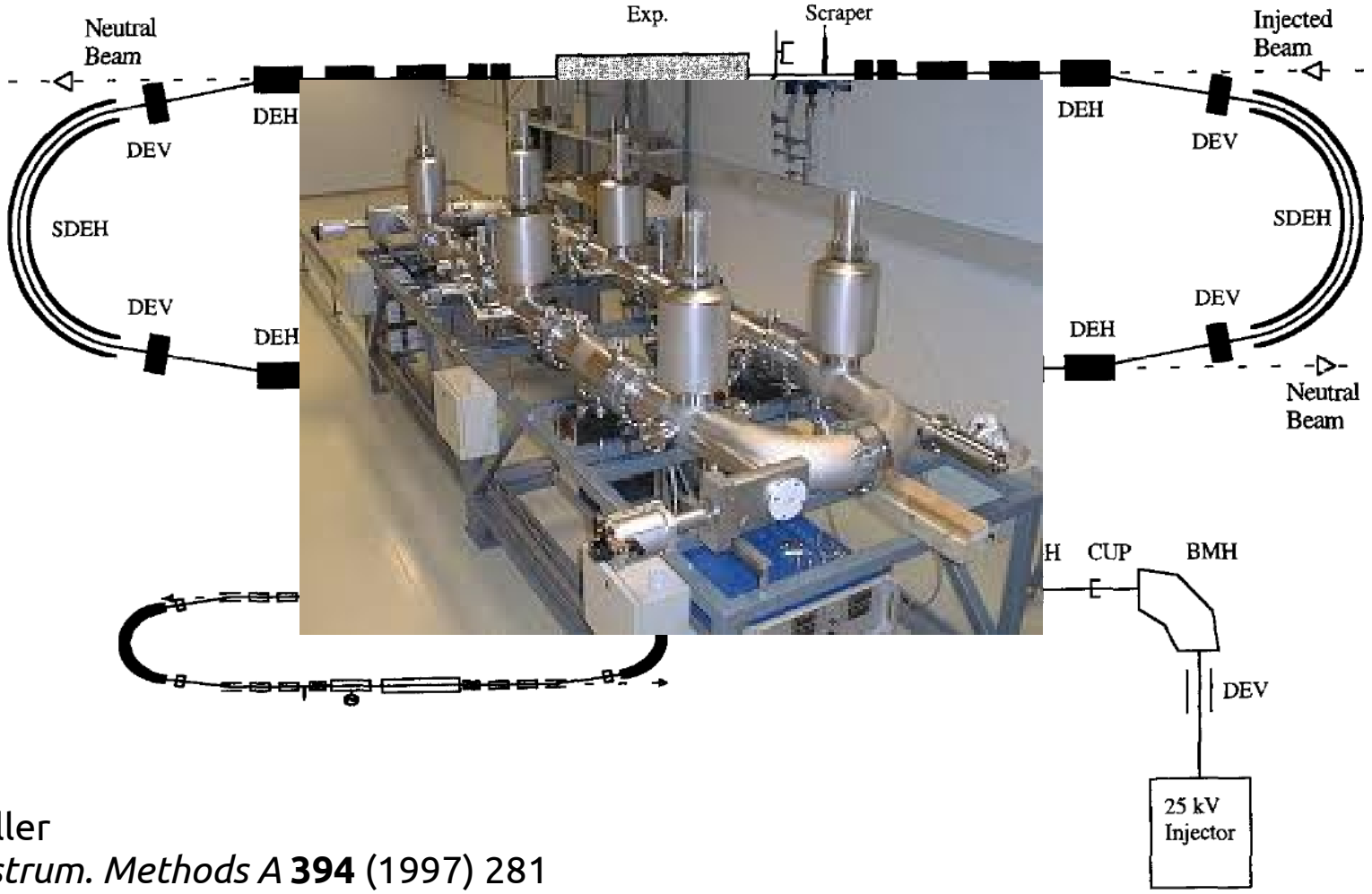
Electrostatic ion beam trap (2)



D. Zajfman et al.
Phys. Rev. A **55** (1997) R1577

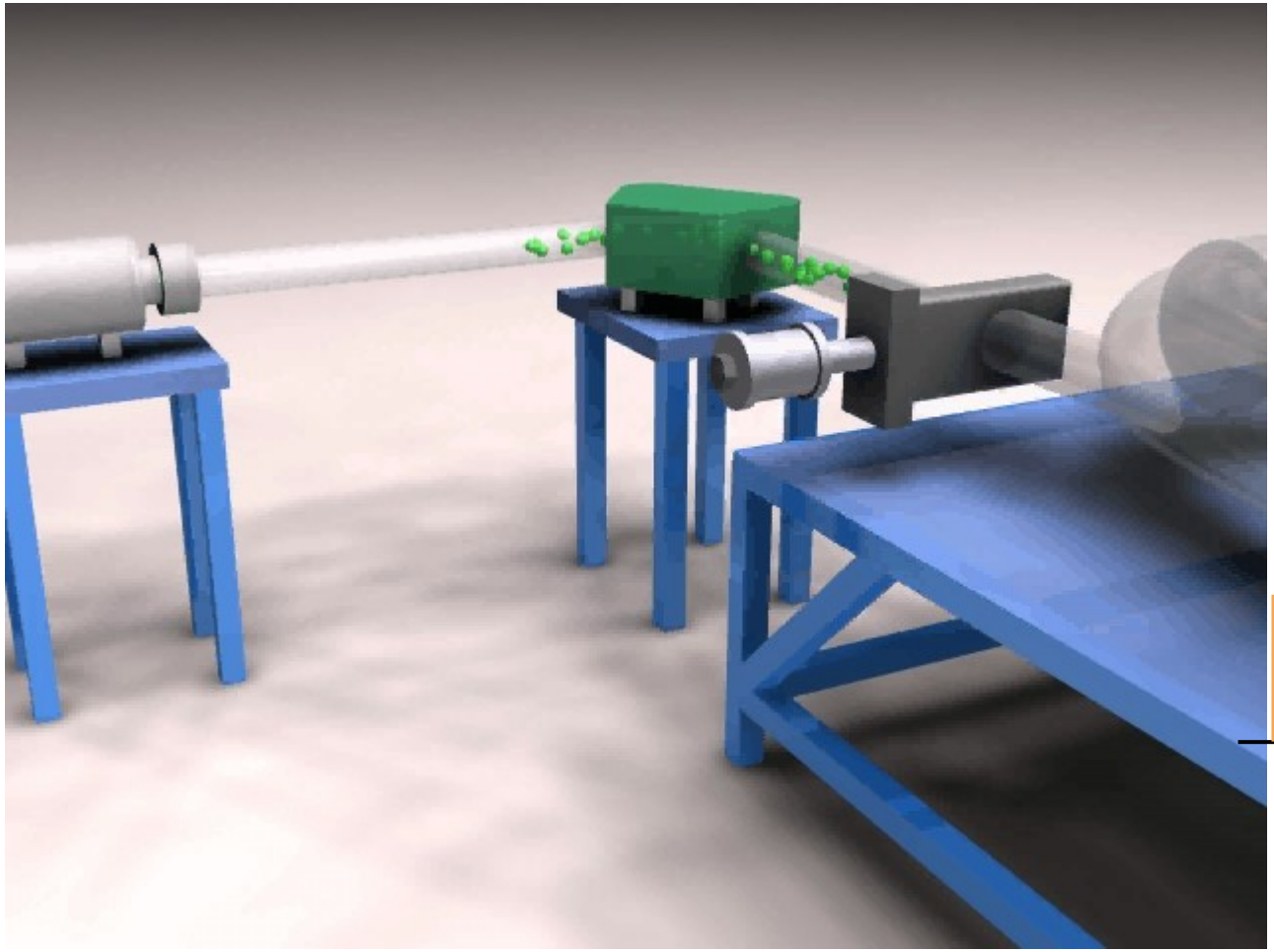
Electrostatic storage ring

The use of electrostatic steering elements removes the mass limitation.



S. P. Moller
Nucl. Instrum. Methods A **394** (1997) 281

Electrostatic storage ring (2)



S. P. Moller
Nucl. Instrum. Methods A **394** (1997) 281

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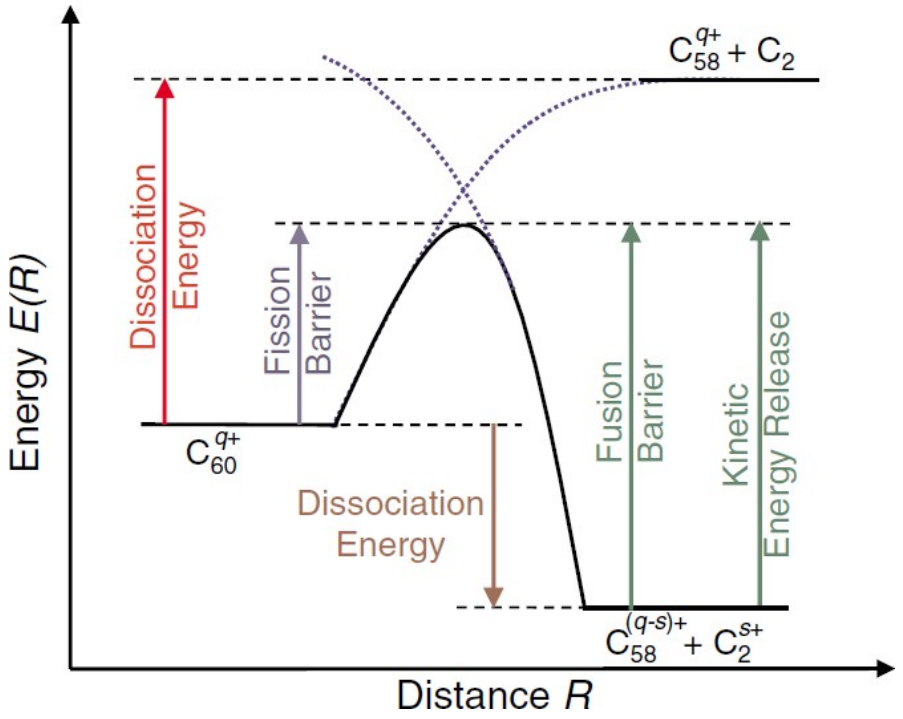
Metastable fragmentation

Multiply charged fullerene can accomodate the charge excess.
→ they are metastable on the µs timescale.

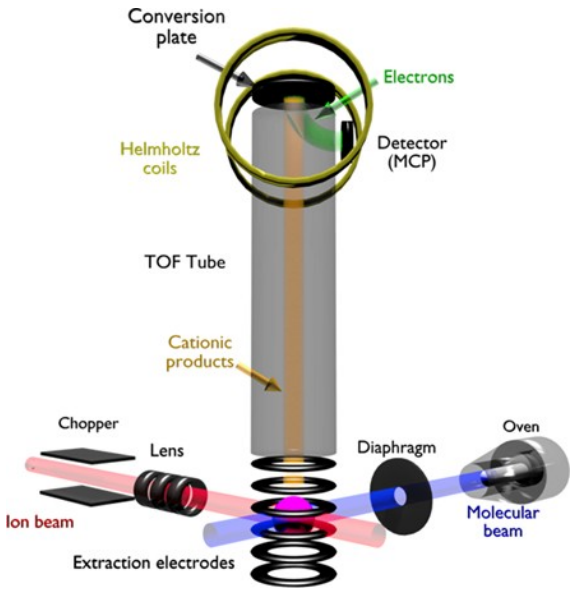
This is due to the presence of a fission barrier associated with a transition state during the dissociation.



Theoretical predictions stated that C_{60}^{15+} is stable while the dissociation energy is favourable from C_{60}^{6+}.
[S. Díaz-Tendero et al., *Phys. Rev. Lett.* **95** (2005) 013401]

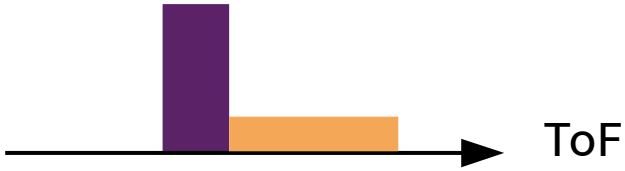
Metastable decay of C_{60}^{q+}

Using a long extraction region (several cm), it is possible to observe decays on the µs range.

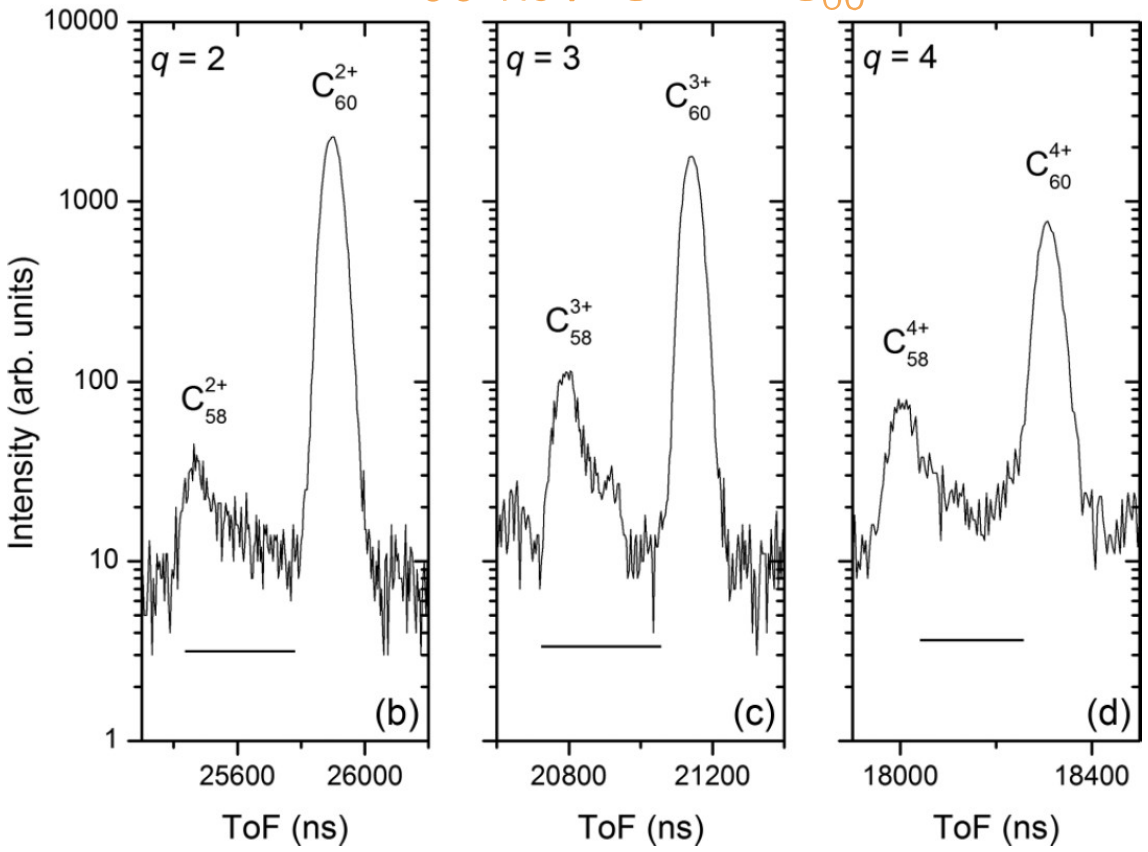


prompt: $C_{60}^{q+} \rightarrow C_{58}^{q+} + C_2^0$

delayed: $C_{60}^{q+} \rightarrow C_{58}^{q+} + C_2^0$



60 keV $C^{6+} - C_{60}$



H. da Silva et al.
Phys. Rev. A **90** (2014) 032701

Metastable decay of C_{60}^{q+}: theory

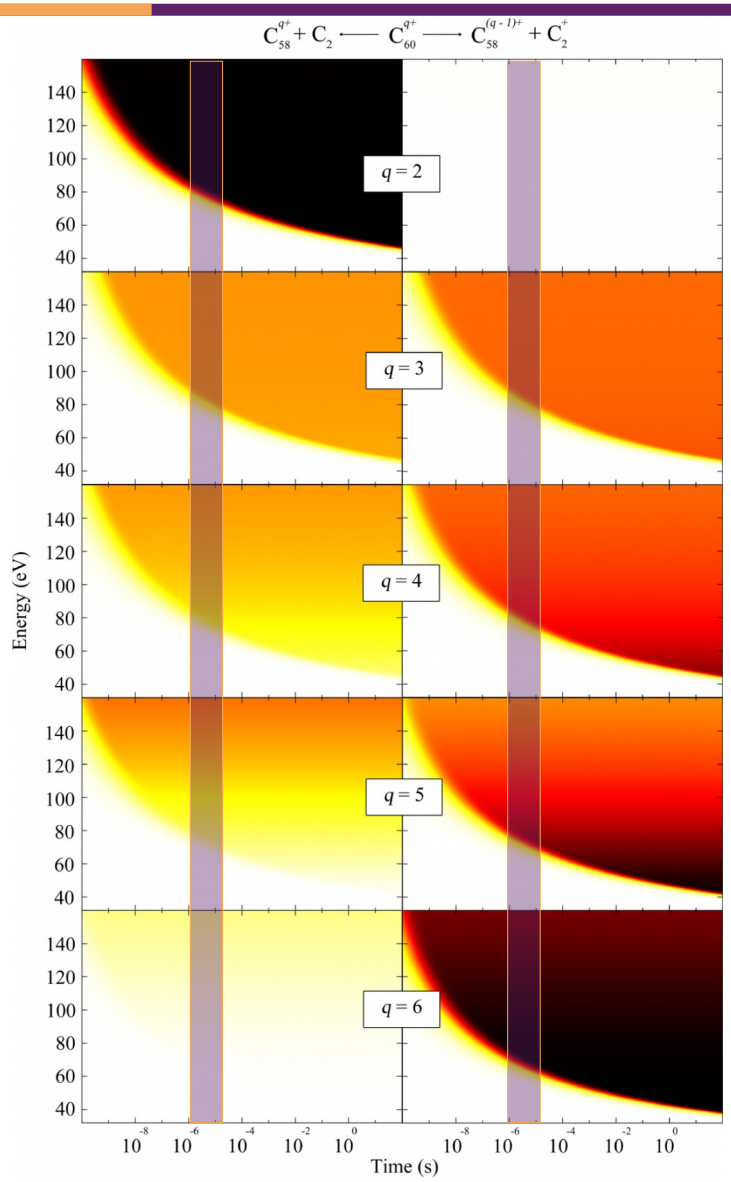
Based on the Weisskopf theory, a fragmentation model is obtained.

The dissociation rate depends on the dissociation energy and fission barrier energy.

Competition between dissociation by emission of neutral/charged C_2.

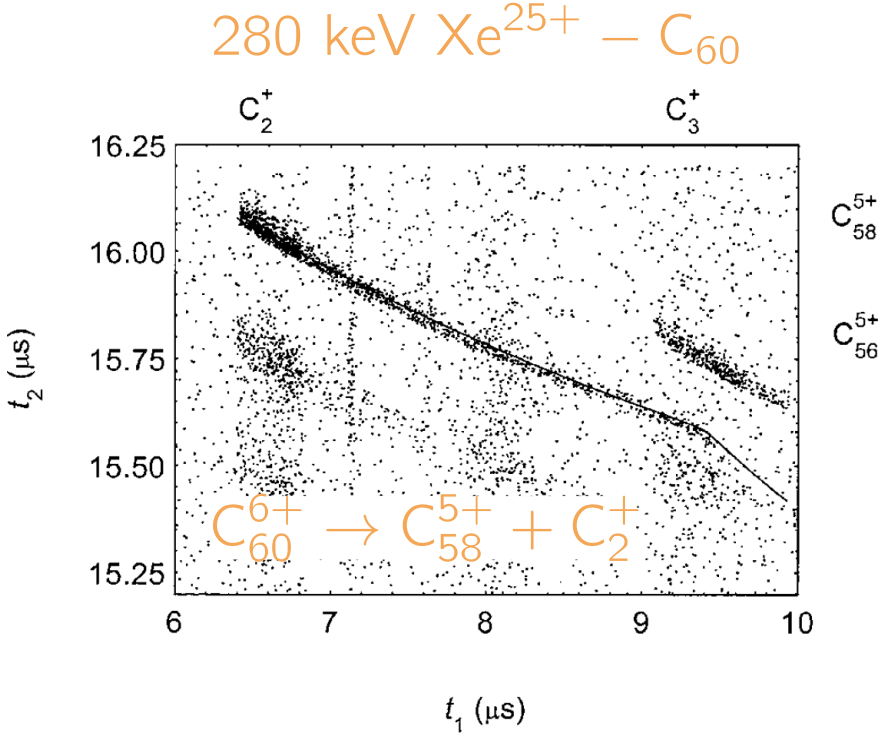
For higher charged states ($q \geq 4$), one can expect a delayed fission.

$$C_{60}^{q+} \rightarrow C_{58}^{(q-1)+} + C_2^+$$

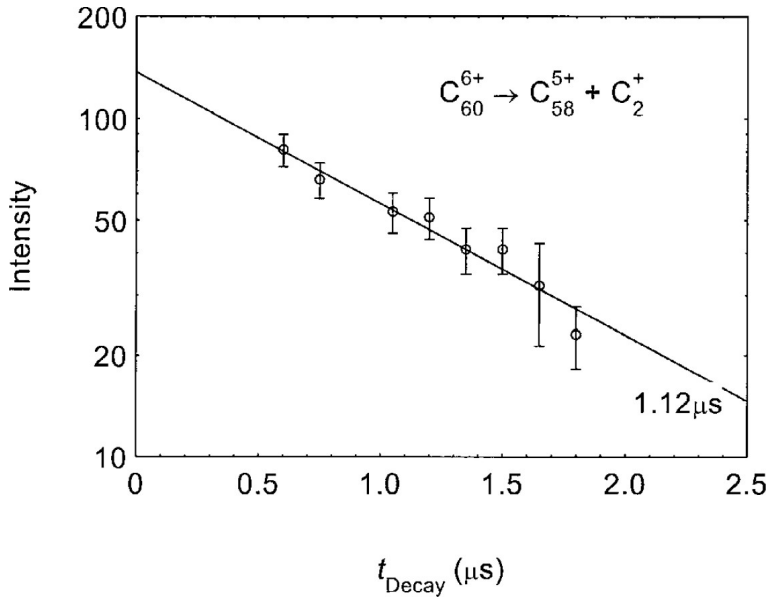


H. da Silva et al.
Phys. Rev. A **90** (2014) 032701

Metastable fission of C_{60}^{q+}



H. Lebius et al.
Phys. Scr. **T80** (1999) 197



It is possible to deduce the lifetime of the metastable states studying their delayed fragmentation.

Power law decay

Complex molecules with a broad energy distribution

→ population of many initial excited states

→ many different exponential decays

The emission rate is given by $R(t) = N_0 \int g(E,t) k_{\text{diss}}(E) dE$

Considering that the energy distribution decays exponentially from an initial one broad enough to be considered as constant

$$R(t) \propto g/t \int k_{\text{diss}}(E) t e^{-k_{\text{diss}}(E)t} dE$$

If $k_{\text{diss}}(E) t e^{-k_{\text{diss}}(E)t}$ is strongly peaked at its maximum

$$R(t) \propto 1/t$$

It may be necessary to include a second term to the exponent

$$R(t) \propto t^{-1+\delta}$$

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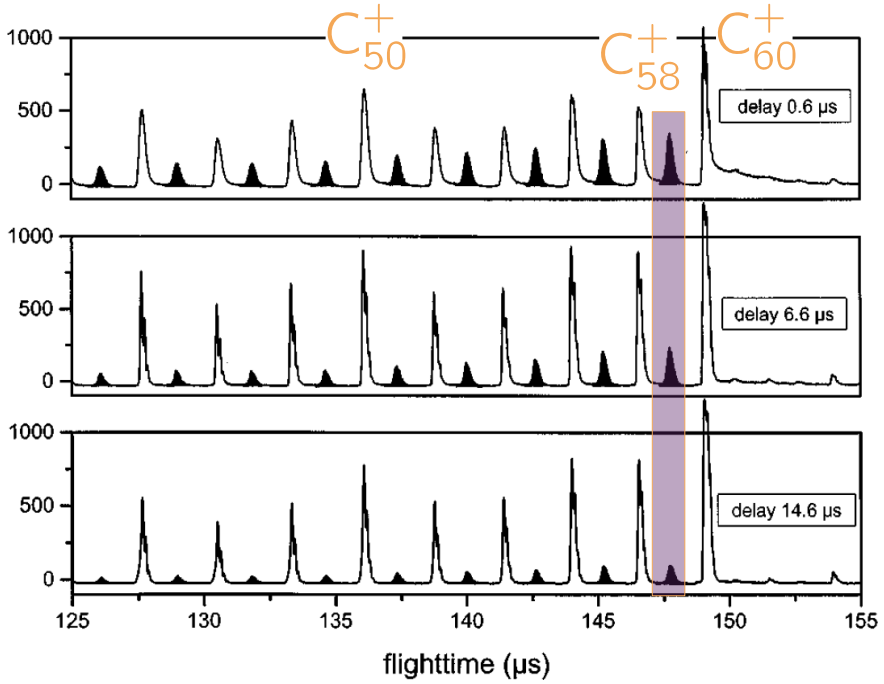
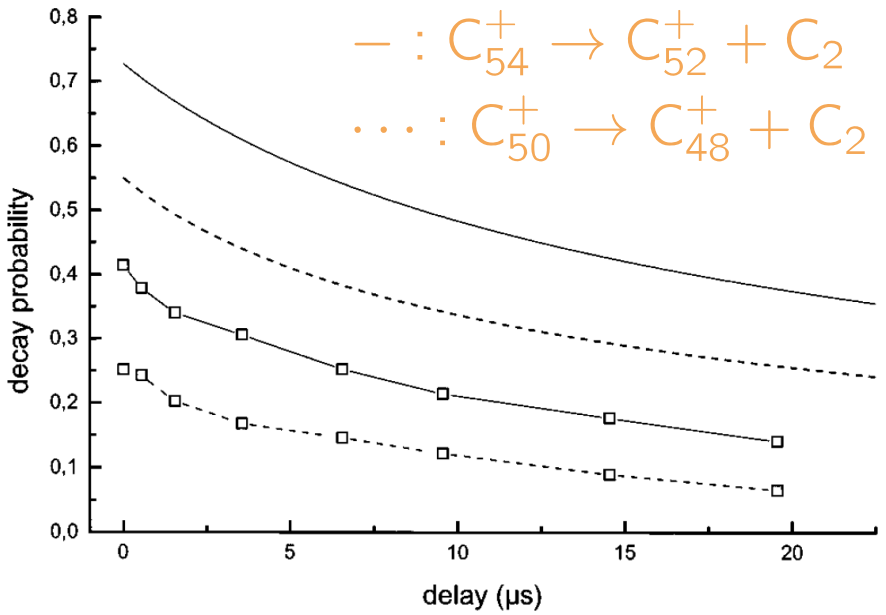
Metastable decay of C_{60}^{q+}: higher *E*

Delaying the extraction of the ion into the ToF, one can study longer timescale.

ns UV laser — C_{60}





K. Hansen and E. E. B. Campbell
J. Phys. Chem. **104** (1996) 5012

Evaporation model fails to fit data
→ competitive process

Take home message #1

Coupling between electronic and vibrational degrees of freedom by internal conversion.

→ hot species are produced

Decay through:

- Dissociation
- thermoionic electron emission

Evaporative model may be applied

power law decay if broad initial energy distributions

However some discrepancies may appear

→ competitive process

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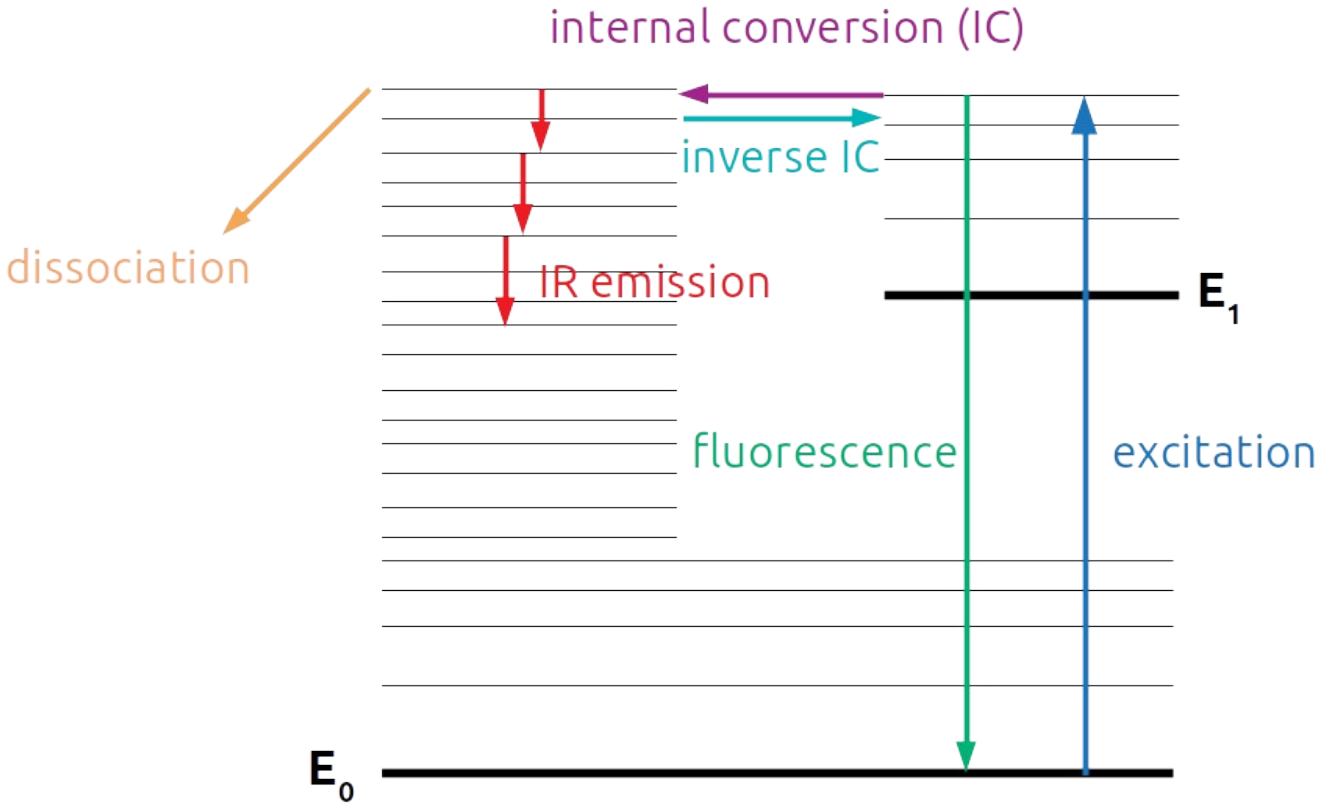
Radiative cooling

Beside the dissociation, the internal energy can be lowered via electronic, vibrational and/or rotational transitions

→ emission of one photon

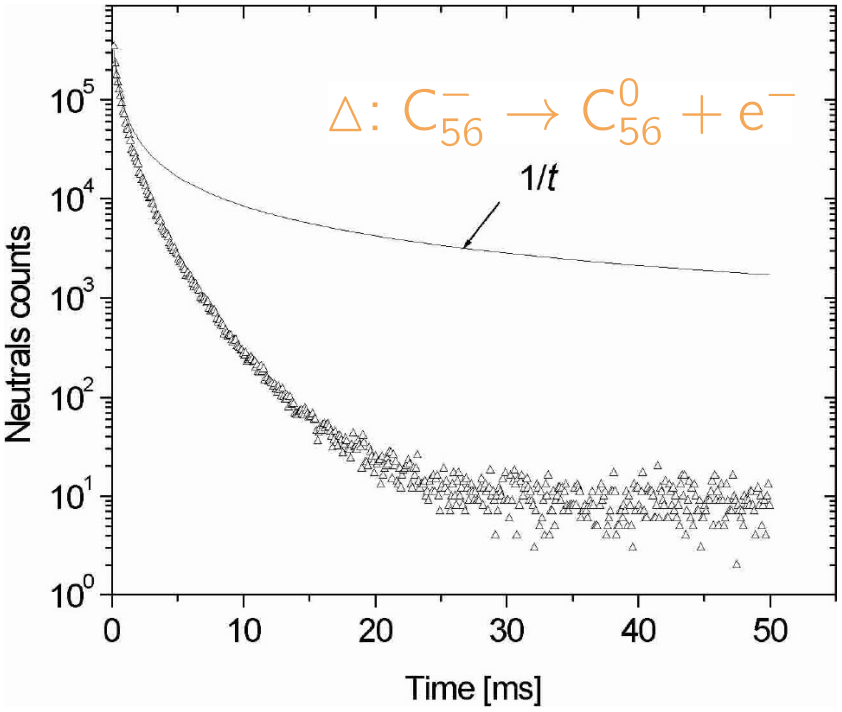
→ radiative cooling

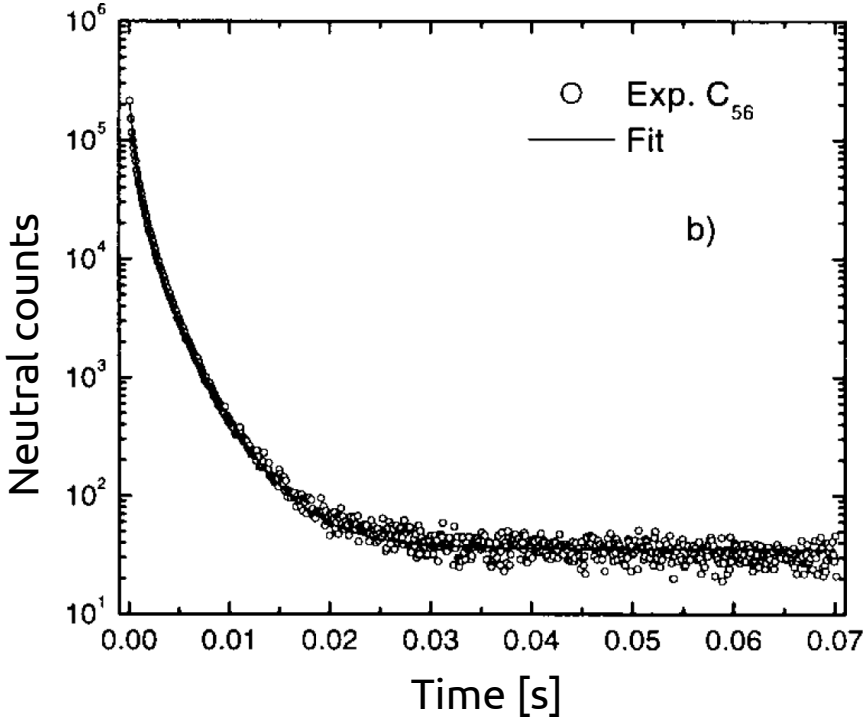


Radiative cooling of fullerene

The radiative cooling quenches the thermoionic electron emission.

$$R(t) \propto t^{-1+\delta} e^{-t/\tau}$$



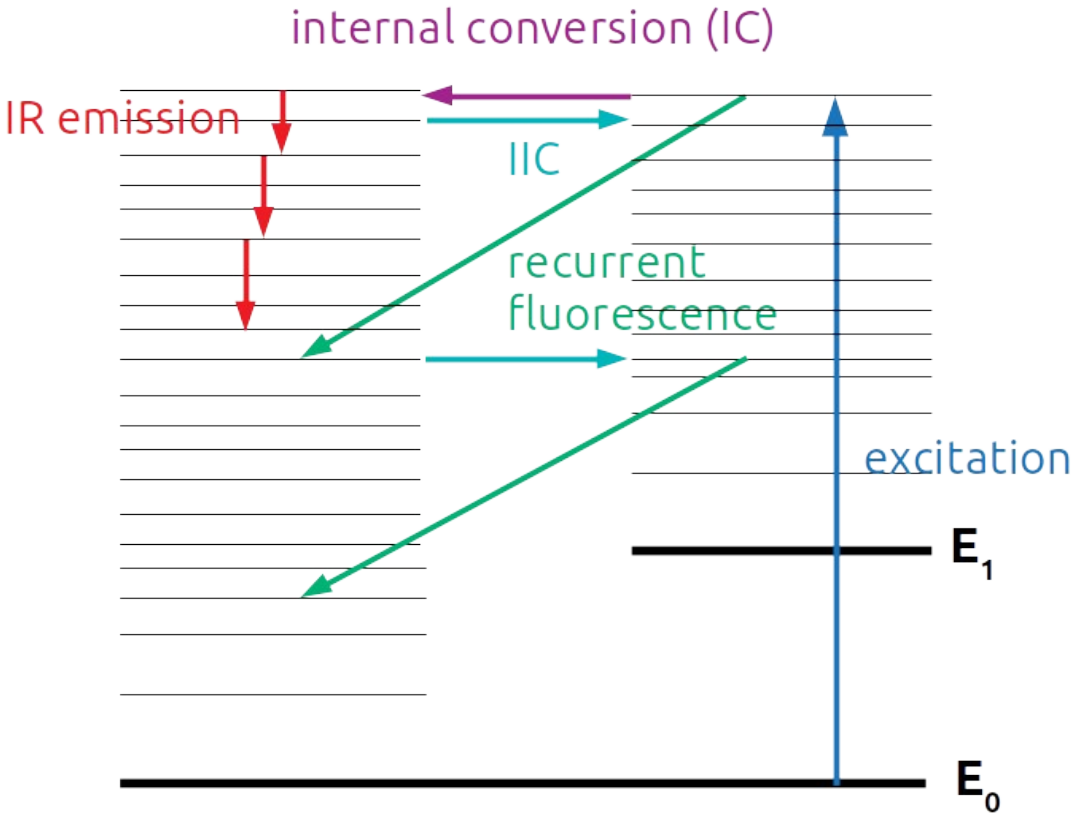


J. U. Andersen et al.
Eur. Phys. J. D **17** (2001) 189

Poincaré fluorescence

The radiative cooling via vibrational transitions is associated with IR photons and long timescale (ms).

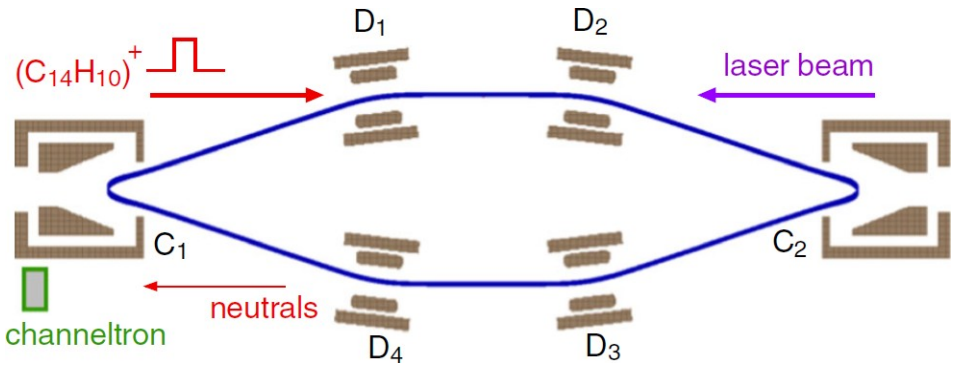
It was proposed that inverse internal conversion (IIC) can lead to a fast radiative cooling by recurrent fluorescence.



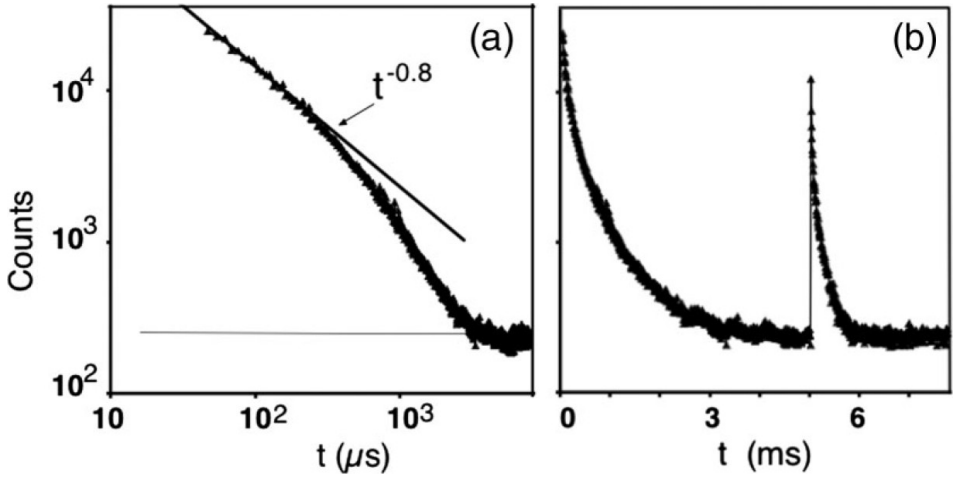
A. Léger, P. Boissel, L. d'Hendecourt
Phys. Rev. Lett. **60** (1988) 921

Fast radiative cooling of anthracene

Using a compact storage ring, the MINI-RING in Lyon, short revolution times (few µs) are accessible.



A fast quenching of the dissociation of anthracene cation is observed.

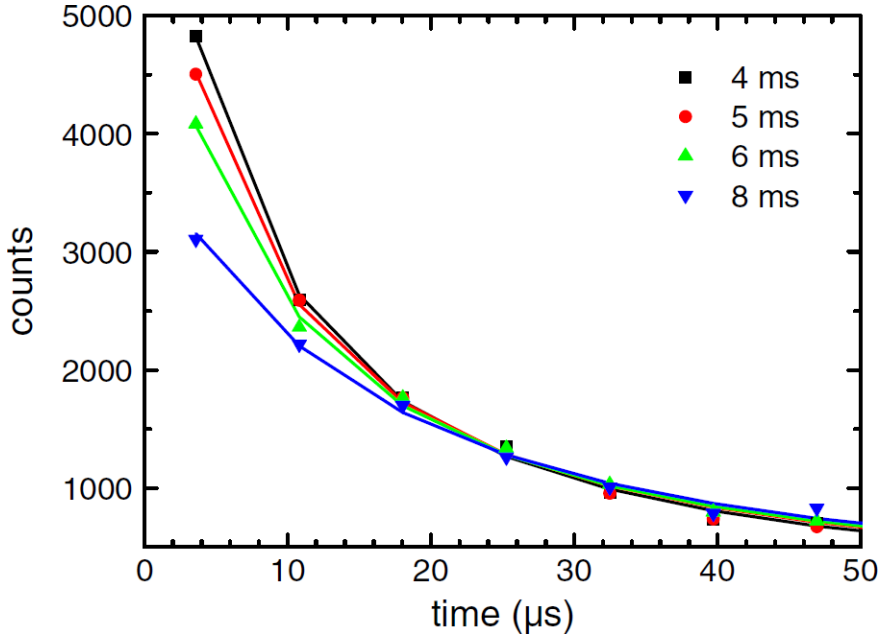


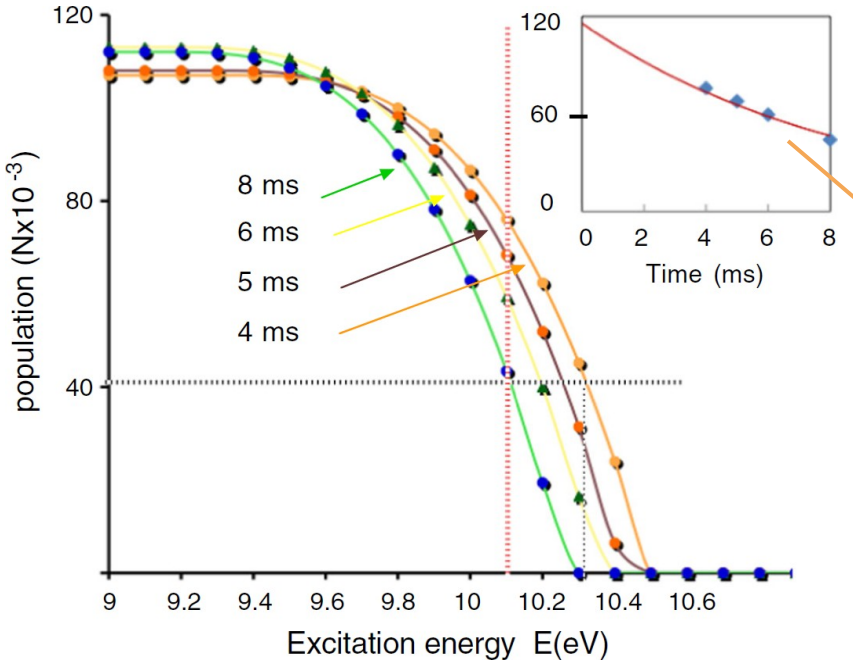
S. Martin et al.
Phys. Rev. Lett. **110** (2013) 063003

Fast radiative cooling of anthracene (2)

Decay as a function of the cooling time shows that the anthracene population cools down on the ms timescale.

→ internal energy distribution





Fast radiative cooling: $k_{rad} \approx 200 s^{-1}$

IR cooling rate: $k_{IR} \approx 2 s^{-1}$

→ Poincaré fluorescence

S. Martin et al.
Phys. Rev. Lett. **110** (2013) 063003

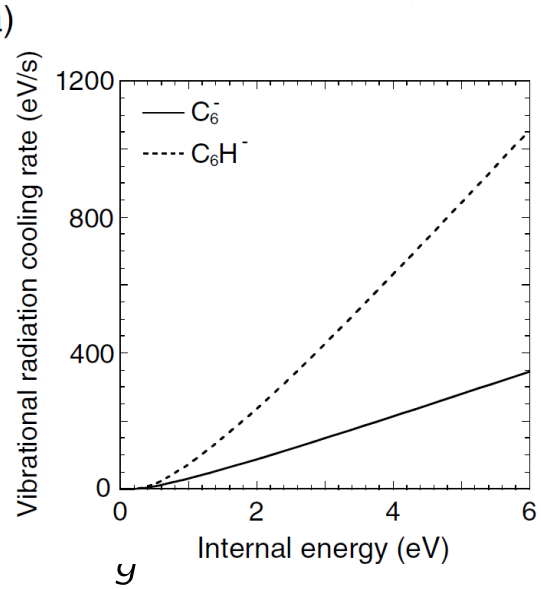
Recurrent fluorescence : excited state

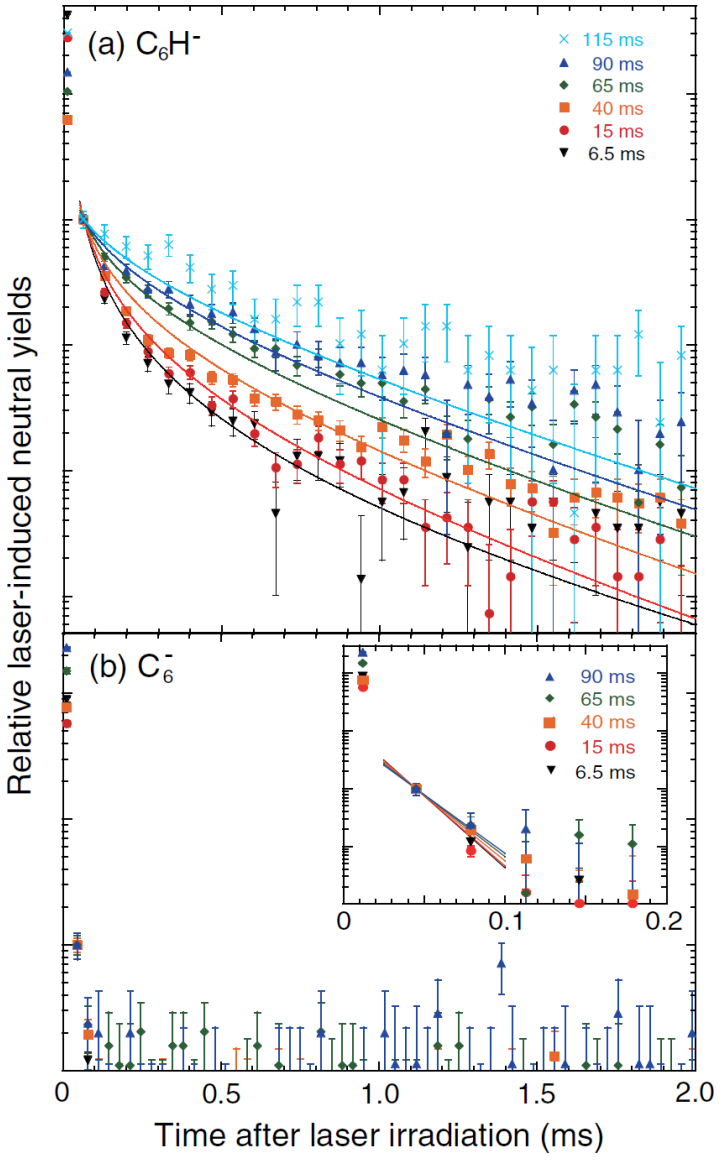
C_6H^-: decay in ms time range

C_6^- : decay below 0.1 ms.

Poincaré fluorescence requires excited states for inverse internal conversion.

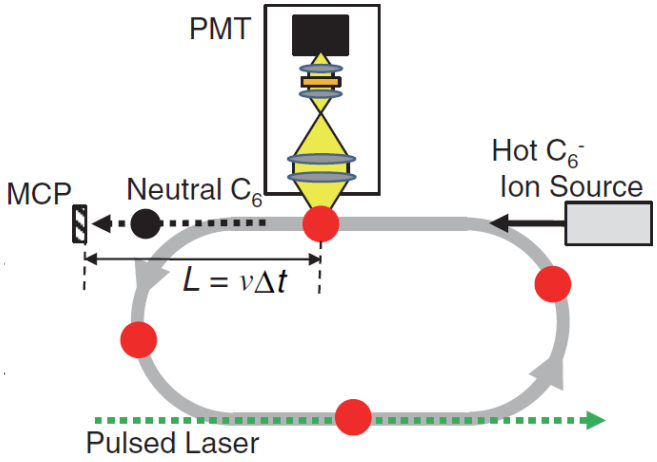
anion	population
C_6H^-	≈ 1
C_6H^-	$< 10^{-12}$
C_6^-	0.94
C_6^-	0.035
C_6^-	0.020
C_6^-	0.0013
C_6^-	3×10^{-5}



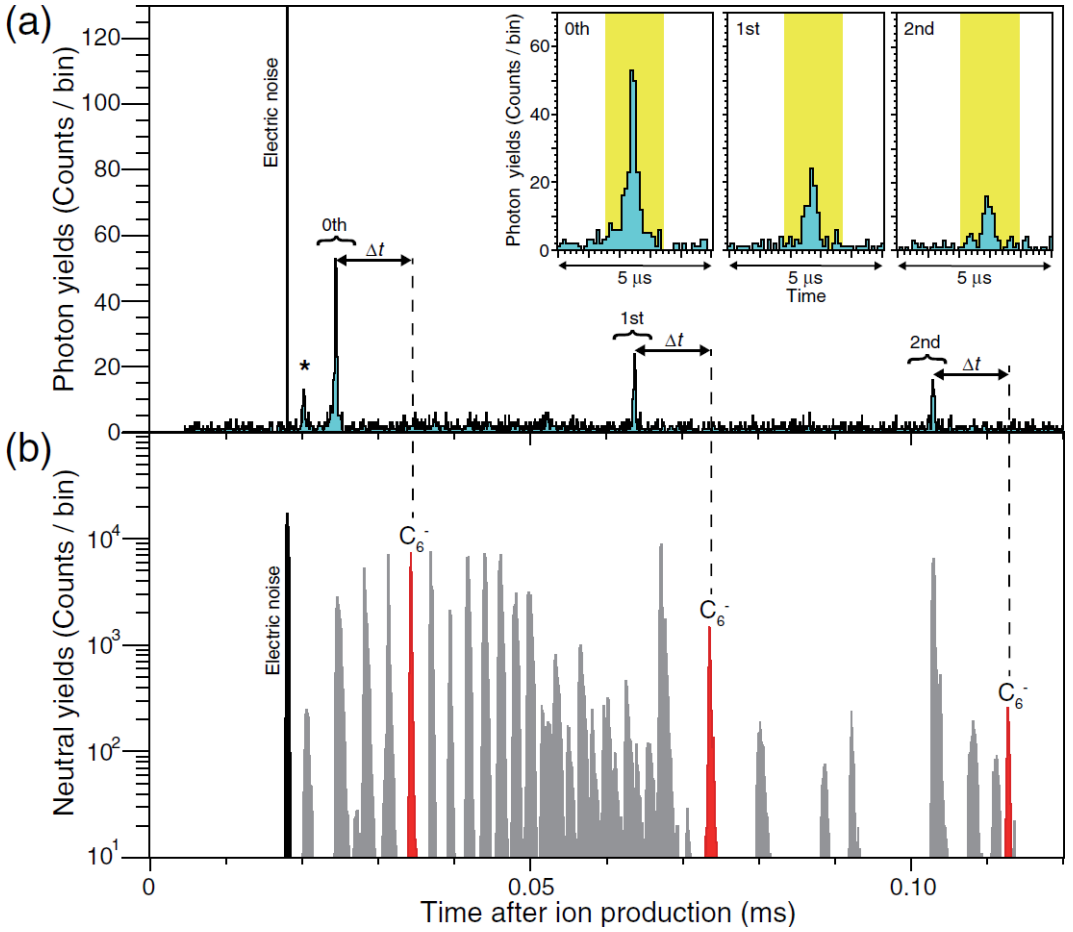


G. Ito et al.
Phys. Rev. Lett. **112** (2014) 183001

Recurrent fluorescence : photon detection



Detection of 607 nm photon correlated with C_6^- revolution



Y. Ebara et al.
Phys. Rev. Lett. **117** (2016) 133004

Take home message #2

The emission of one photon allows to dissipate some excess energy.

→ radiative cooling

This may occur through both electronic and vibrational transitions.

Vibrational transition:

- IR photons
- slow process (typically ms)

Electronic transition:

- through inverse internal conversion
- presence of excited states
- recurrent fluorescence of near-IR/visible photons

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Electron attachment to SF_6

The excess energy due to electron attachment can induce vibrational excitation:

$$SF_6 + e^- \rightarrow SF_6^{-*}$$

Further decays include:

- dissociation (DEA)

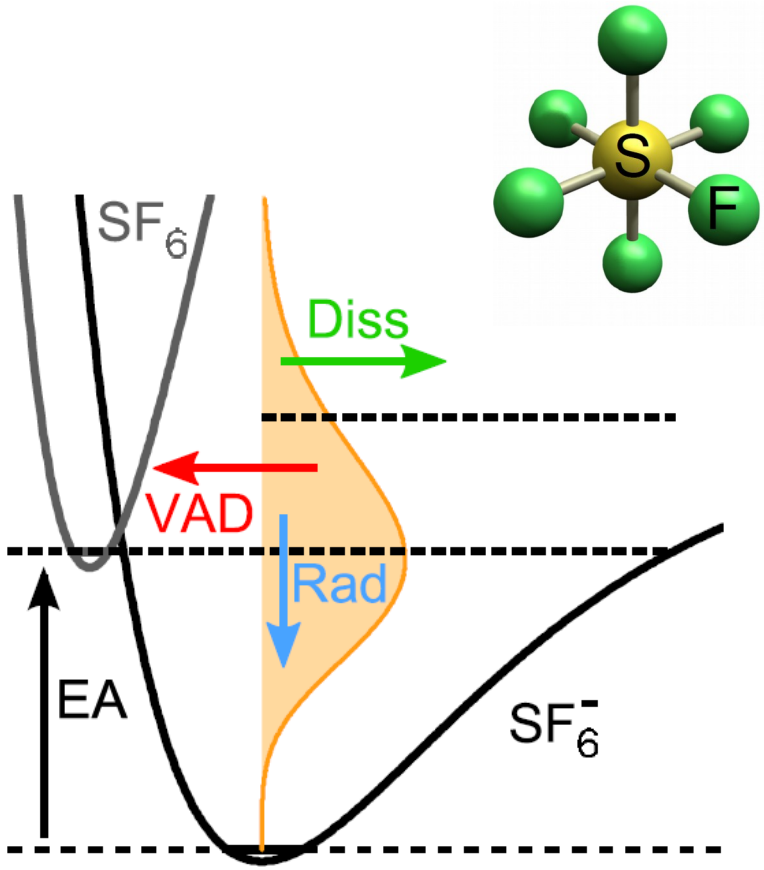
$$SF_6^{-*} \rightarrow SF_5^- + F^0$$

- radiative cooling

$$SF_6^{-*} \rightarrow SF_6^- + h\nu$$

- vibrational auto-detachment (VAD)

$$SF_6^{-*} \rightarrow SF_6^0 + e^-$$



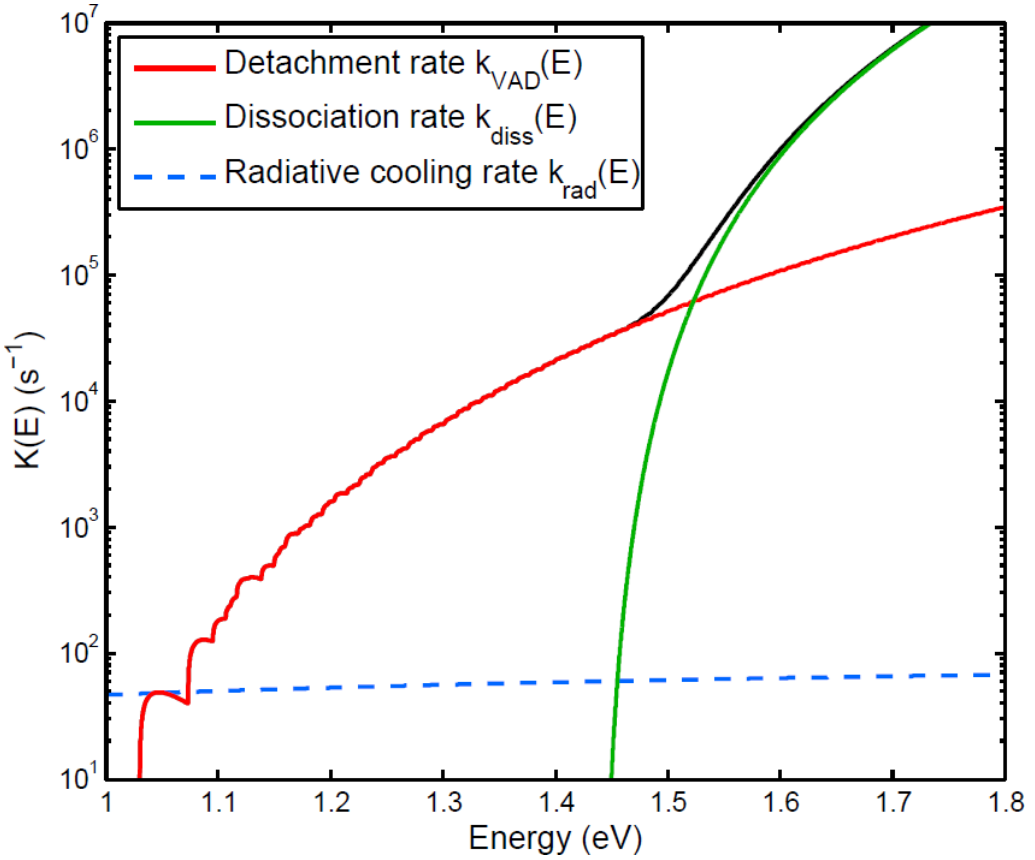
VAD of SF_6^- : rates

One may take into account the rotation of excited SF_6^{-*} molecules.

$$k_{VAD}(E,J) = \frac{\mu}{\pi^2\hbar^3}\int_0^{E_v - EA(J)} \frac{\sigma(\epsilon)\epsilon\rho_0(E_v^0(\epsilon))}{\rho_-(E_v)}d\epsilon$$

In order to observe the VAD, long storage time (several 100 ms) are required.

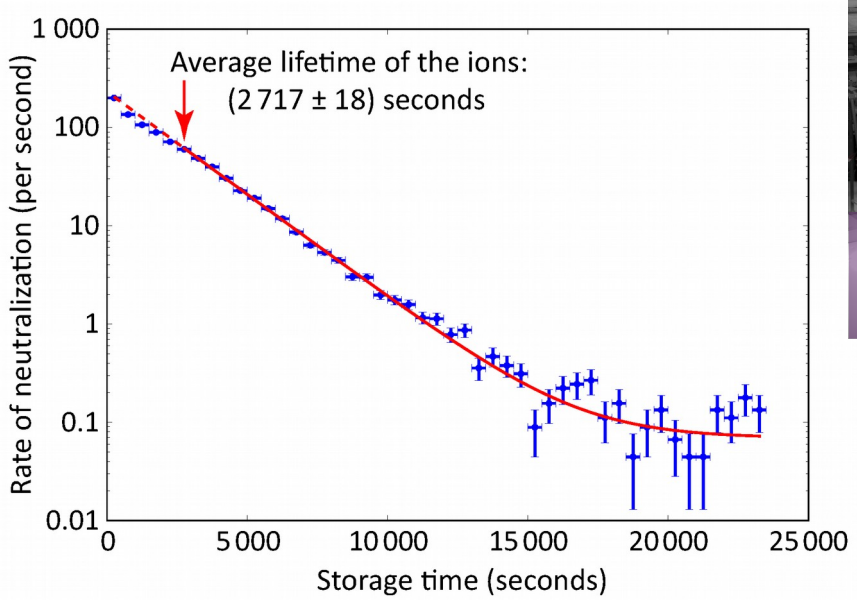
→ cryogenic storage device



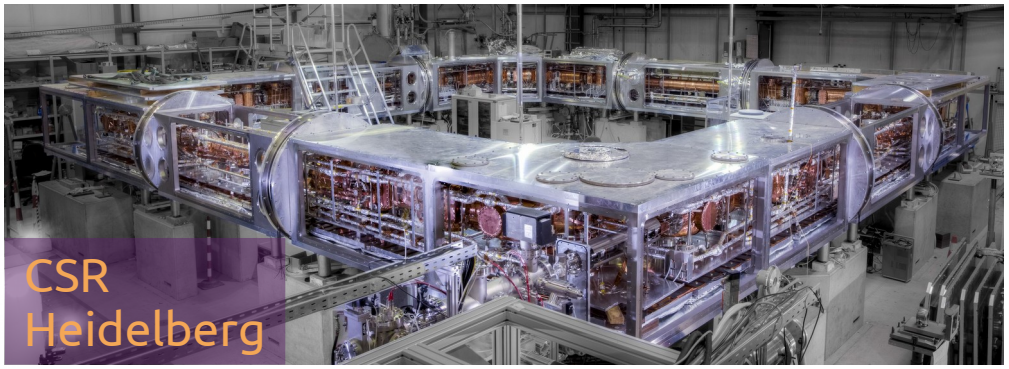
PhD of S. Merk
Heidelberg University (2013)

Cryogenic electrostatic storage devices

Cryogenic environments allow to increase the lifetime of the stored beam.

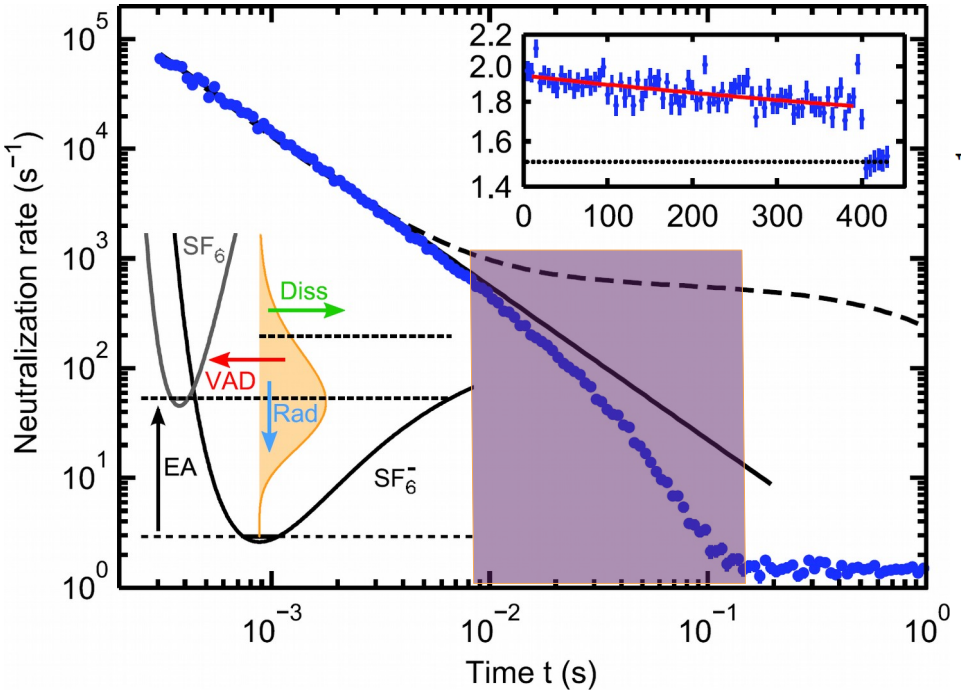


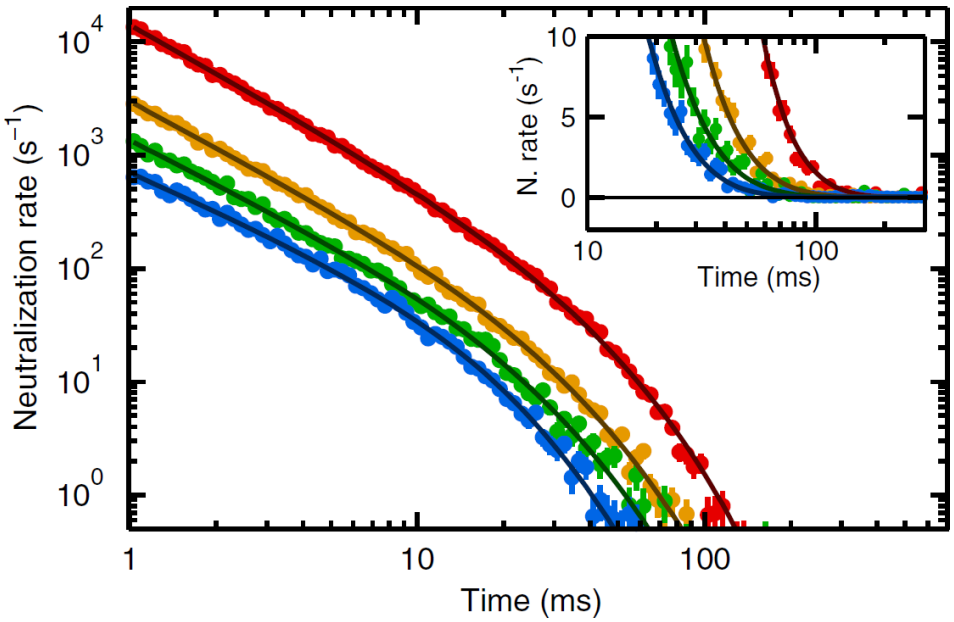
Storage of Ag_2^- at CSR
MPIK webpage



SF_6^- Storage in CTF

Using a cryogenic EIBT it is possible to observe the VAD otherwise hidden by the depletion due to the background pressure.
Model fits well the data for different source parameters.



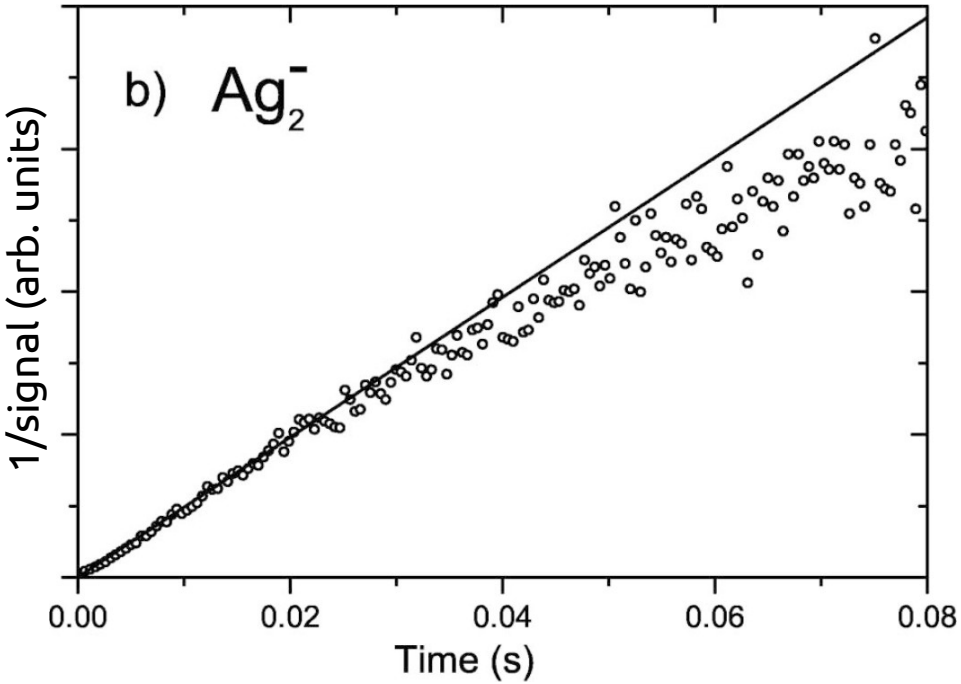


S. Merk et al.
Phys. Rev. A **89** (2014) 022502

Decay of Ag_2^-

Similarly to SF_6^{-*}, metal dimer such as Ag_2^{-*} can decays through dissociation or VAD.

$$Ag_2^{-*} \rightarrow Ag^- + Ag^0$$
$$Ag_2^{-*} \rightarrow Ag_2^0 + e^-$$



J. Fedor et al.
Phys. Rev. Lett. **94** (2005) 113201

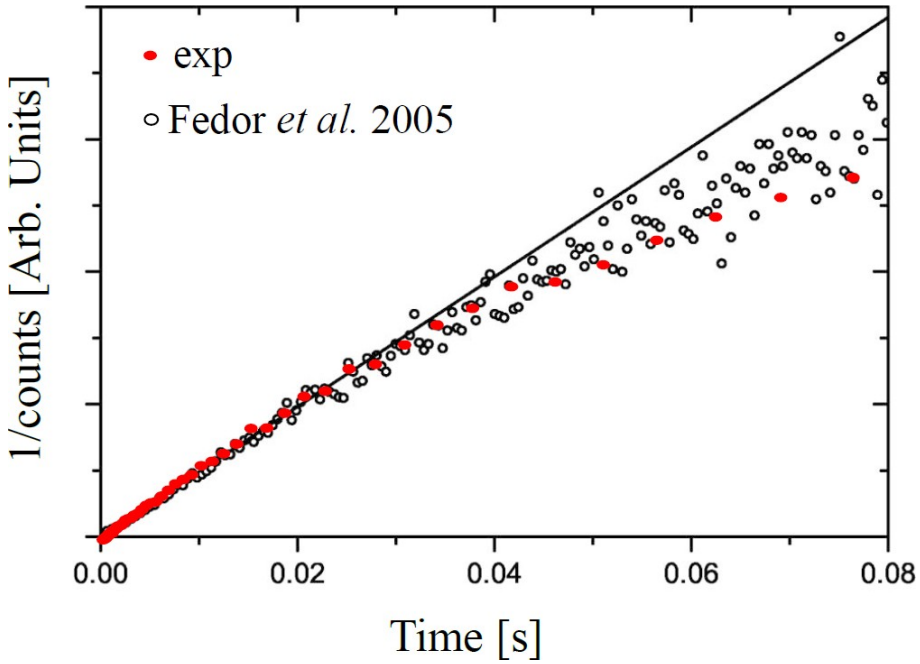
Using room temperature storage device, the decay rate is well described (below 100 ms) by a power law assuming the fragmentation from high rotational levels.

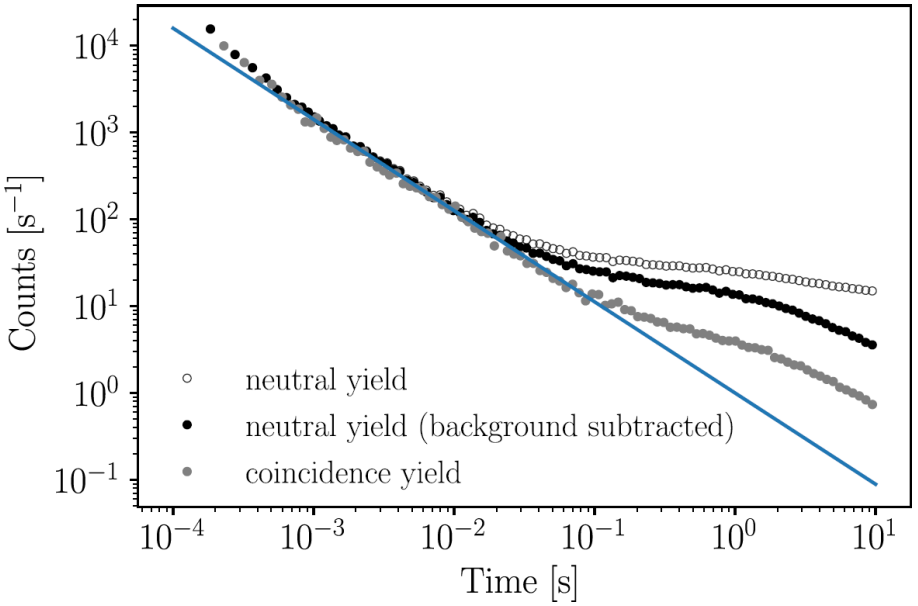
Decay at further time range is associated with the depletion of the beam due to collision with the residual gas.

Decay of Ag_2^- in cryogenic ring

Longer storage time are obtained with the DESIREE cryogenic ring.
Deviation from the power law decay is not anymore due to depletion of the beam.

→ contribution from the VAD





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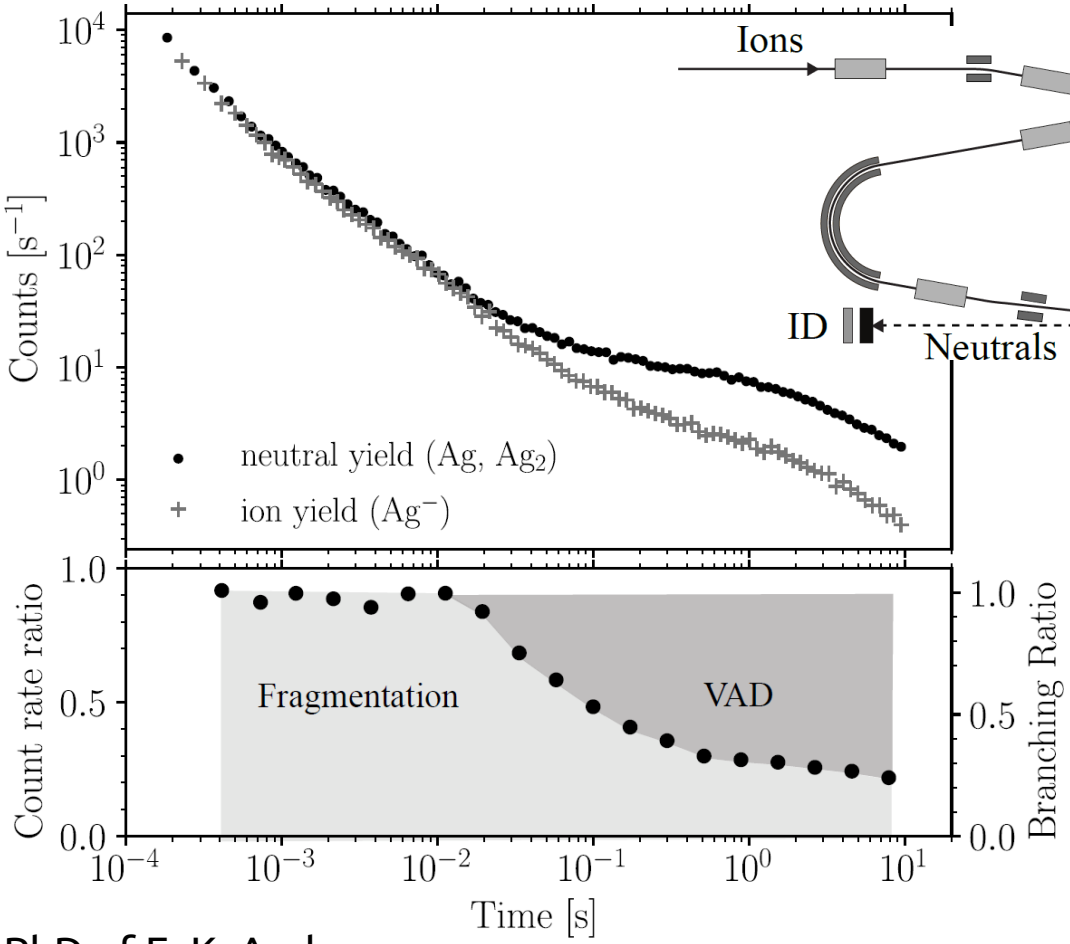
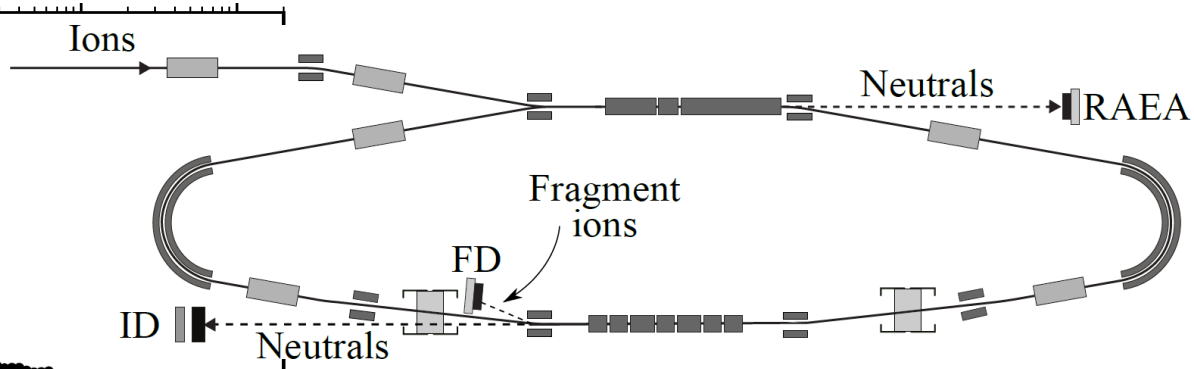
Stockholm University (2019)

VAD vs. dissociation of Ag_2^-

Coincidences between detectors disentangle the two contributions.





For Ag_2^-:

high J level → fragmentation

high vibrational levels → VAD

no J - v exchange

- VDE = 1.06 eV
- D_0 = 1.37 eV

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Stockholm University (2019)

Take home message #3

Vibrational auto-detachment (VAD)

→ transfer from the vibrational energy to the electronic excitation

→ electron emission

Timescale can be very long (ms range)

→ VAD “hidden” by beam depletion

→ need of cryogenic device

As the radiative cooling, VAD may be used to determine the internal energy distribution.

Introduction

Instrumentation

Metastable dissociation

Radiative cooling

Vibrational electron detachment

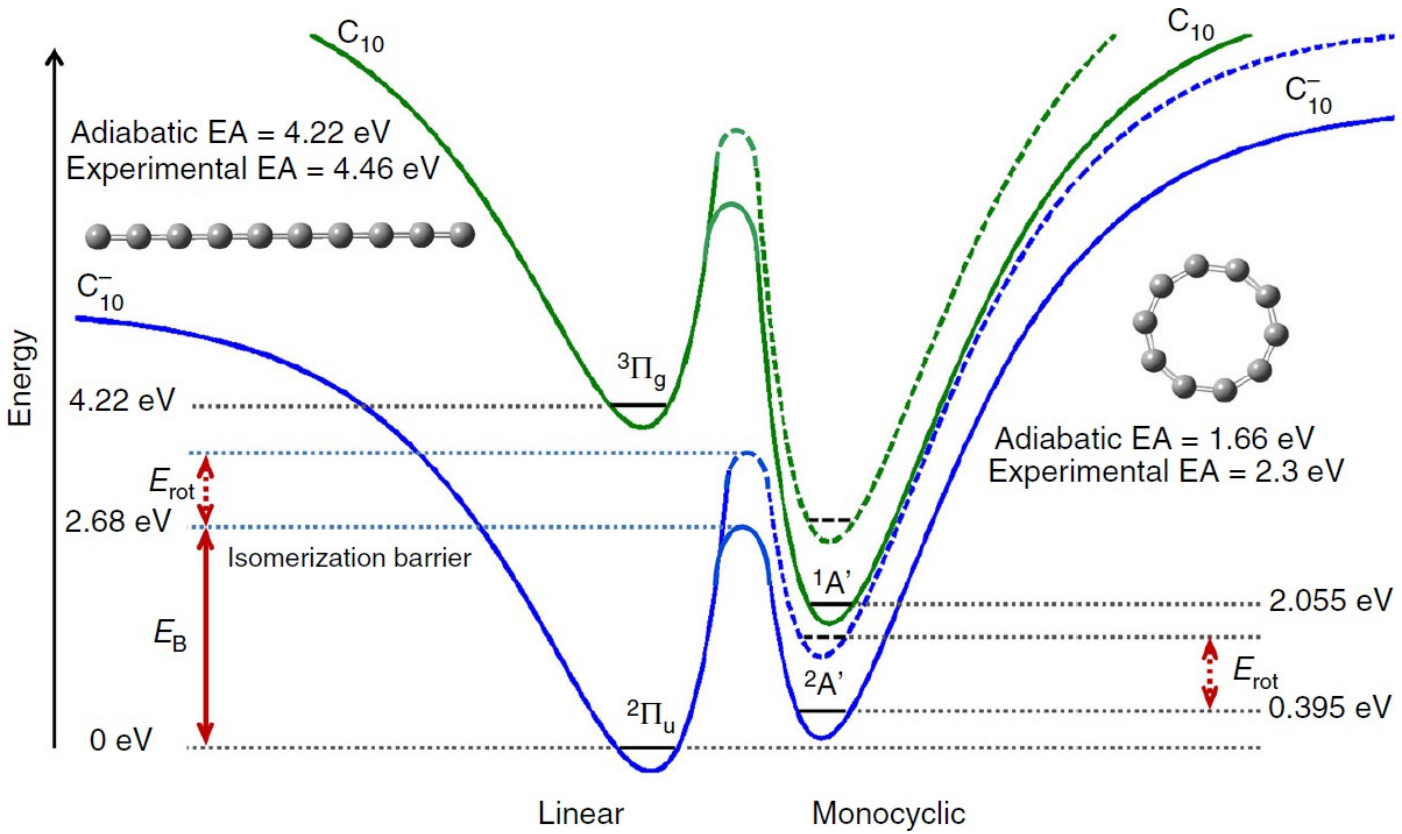
Slow isomerisation

patrick.rousseau@unicaen.fr

Isomerisation of C_{10}^-

Passage from linear isomer to cyclic isomer

→ isomerisation barrier: 2.68 eV



K. Saha et al.
Nature Comm. **9** (2018) 912

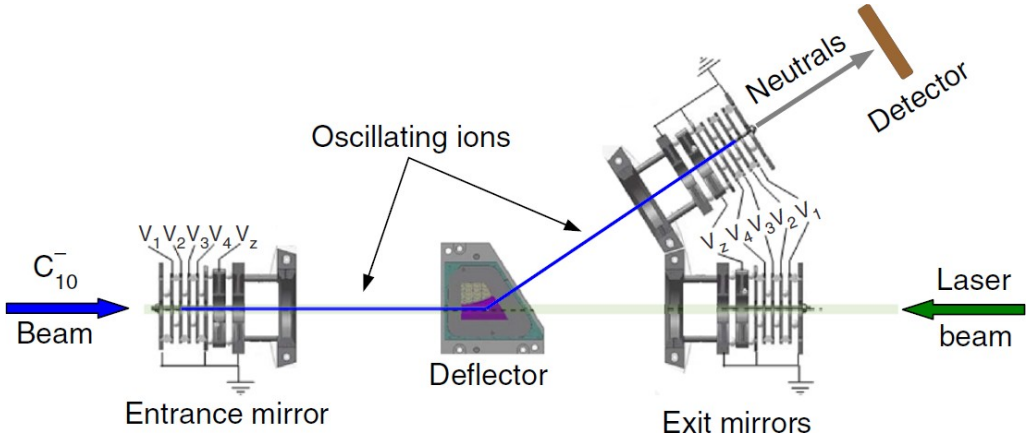
Preparation of C_{10}^-

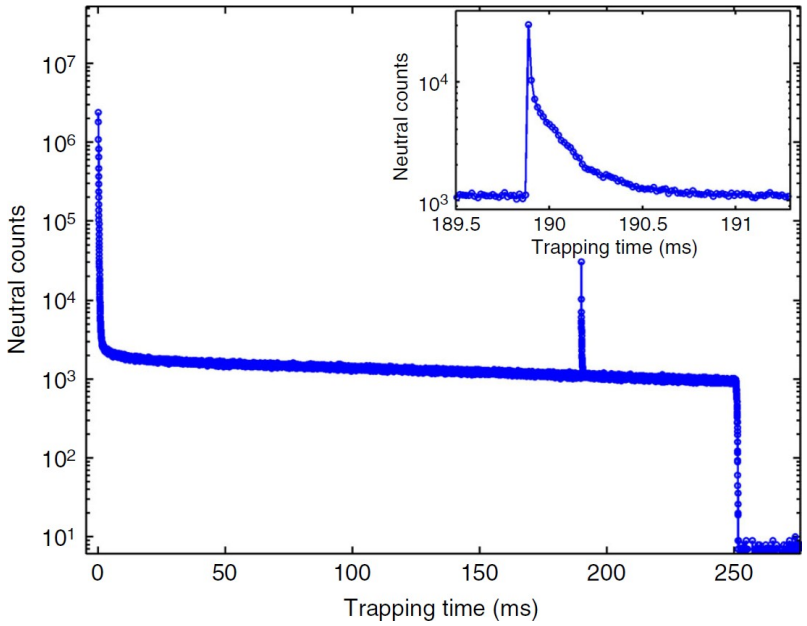
Trapping:

- vibrationnaly cold
- some rotational excitation

Laser excitation:

- after 190 ms
- hv = 2.48 eV – 2.92 eV
  → below and above E_B
  → no VAD from linear C_{10}^-





K. Saha et al.
Nature Comm. **9** (2018) 912

Competitive processes

VAD:

$$k_{\mathrm{VAD}_{I,c}}(E) = f_{\mathrm{VAD}_{I,c}} \int_0^{E_v - \mathrm{EA}(I,c)} \frac{2\mu G_{I,c} e}{\pi \hbar^3} \sqrt{2\alpha_{I,c}} \sqrt{\epsilon} \frac{\rho_{I,c}(E - EA_{I,c} - \epsilon)}{\rho^-_{I,c}(E)} d\epsilon$$

IR radiative cooling:

$$k_{\mathrm{IR}_{I,c}}(E) = f_{\mathrm{IR}_{I,c}} \sum_S A_S(h\nu_S) \sum_{n \geq 1} \frac{\rho^-_{\mathrm{I,c}}(E - nh\nu_S)}{\rho^-_{I,c}(E)}$$

Recurrent fluorescence from linear isomer:

$$k_{\mathrm{RF}_I}(E) = f_{\mathrm{RF}_I} \sum_{j=1-4} A_j(E_j) \frac{\rho^-_I(E - E_j)}{\rho^-_I(E)}$$

Isomerisation

$$k_{\mathrm{iso}}(E) = f_{\mathrm{iso}} \frac{N_{\mathrm{ts}}(E - E_{\mathrm{B}})c}{\rho^-_I(E)}$$

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Nature Comm. **9** (2018) 912

Neutralisation rates

Neutralisation by VAD from linear isomer after 1 and 2-photon excitation

$$R_{l_{1,2}}(t) = N_{1,2} \int_{EA_l}^{\infty} f_0(E = E_i + E_{\mathrm{phot}_{1,2}}) k_{\mathrm{VAD_l}}(E) e^{-k_{\mathrm{tot}_l}(E)t} dE$$

Neutralisation of cyclic isomer after isomerisation

$$R_{\mathrm{iso}_{1,2}}(t) = N_{1,2} \int_{E_B}^{\infty} f_0(E = E_i + E_{\mathrm{phot}_{1,2}}) \times \frac{k_{\mathrm{iso}}(E) k_{\mathrm{VAD}_c}(E)}{k_{\mathrm{tot}_c}(E) - k_{\mathrm{tot}_l}(E)} (e^{-k_{\mathrm{tot}_l}(E)t} - e^{k_{\mathrm{tot}_c}(E)t}) dE$$

For one-photon excitation: $R_1(t) = R_{l_1}(t) + R_{\mathrm{iso}_1}(t)$

For two-photon excitation: $R_2(t) = R_{l_2}(t) + R_{\mathrm{iso}_2}(t)$

Total neutralisation rate: $R(t) = R_1(t) + R_2(t)$

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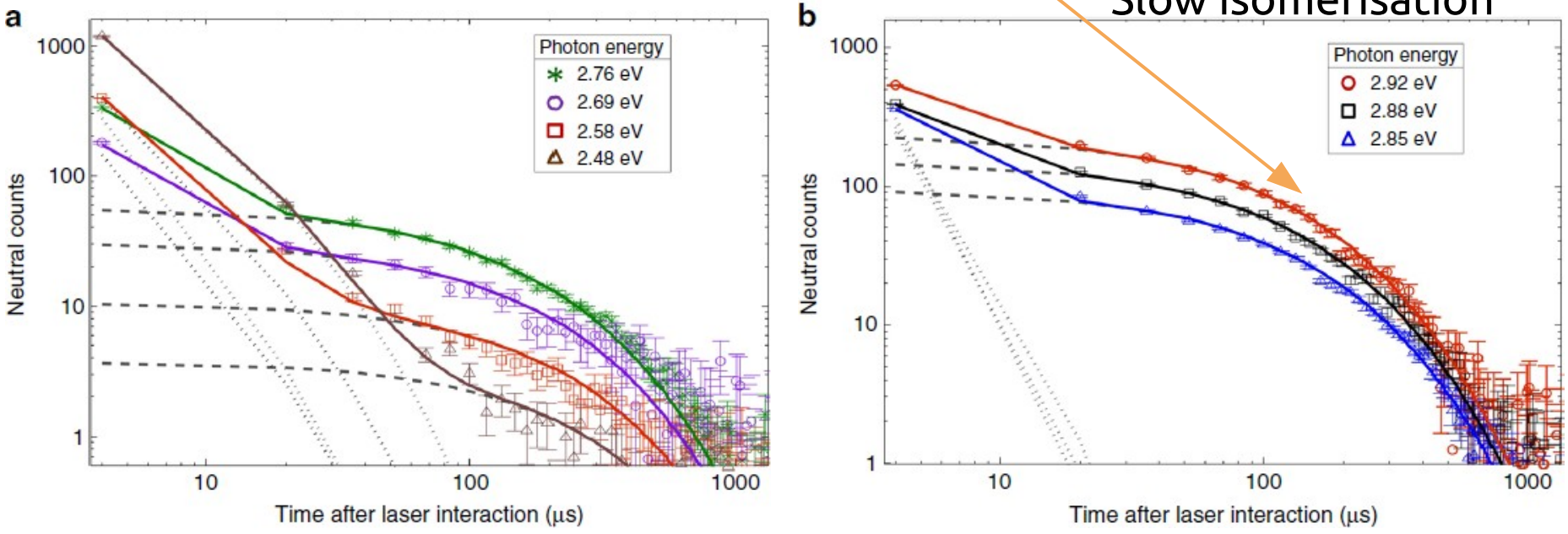
C_{10}^- decay curves

Model fits well the experimental data.

Two-photon excited molecules promptly decay.

One-photon excitation: $R_1(t) = R_{\text{[illegible]}}(t) + R_{\text{iso}_1}(t)$

Slow isomerisation



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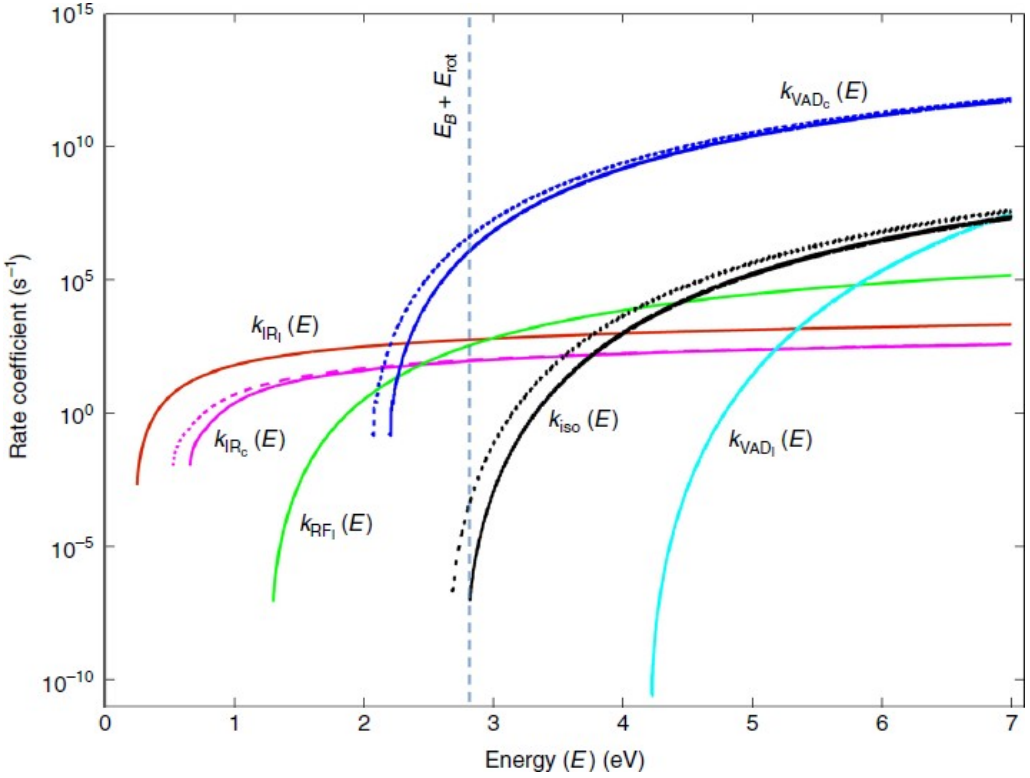
C_{10}^- Rate coefficients

Isomerisation is slow due to the barrier to pass

BUT

promptly after isomerisation, the cyclic isomer decays via VAD



K. Saha et al.
Nature Comm. **9** (2018) 912

Final take home message

Excited molecular system de-excites via various processes

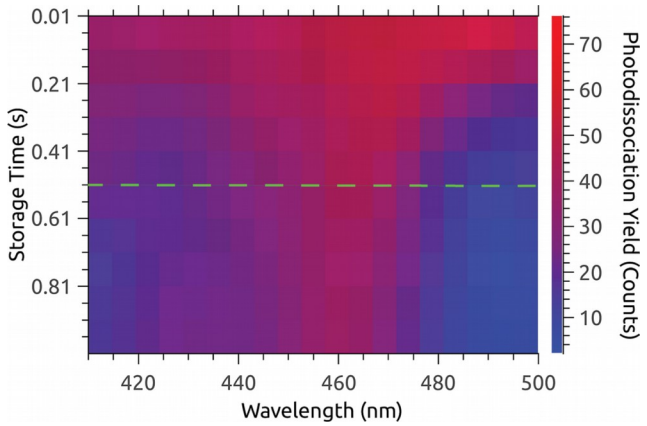
→ statistical physics

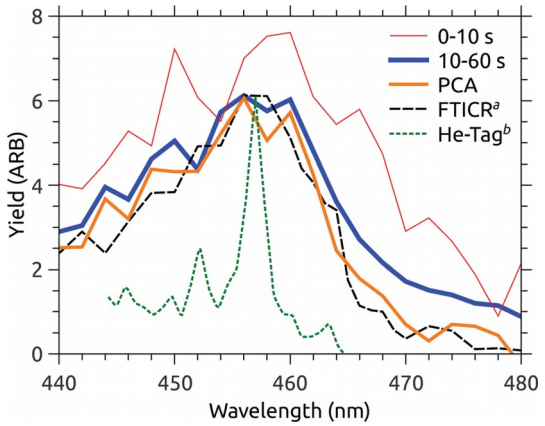
Both electronic and vibrational dynamics observed in the range µs – s

→ coupling between electronic and vibrational degrees of freedom

(dissociation, isomerisation, radiative cooling, VAD)

(Cryogenic) storage devices allow to prepare a well-defined system





Action spectroscopy
of stored coronene cation
M. H. Stockett et al.
Faraday Discuss. **217** (2019) 126

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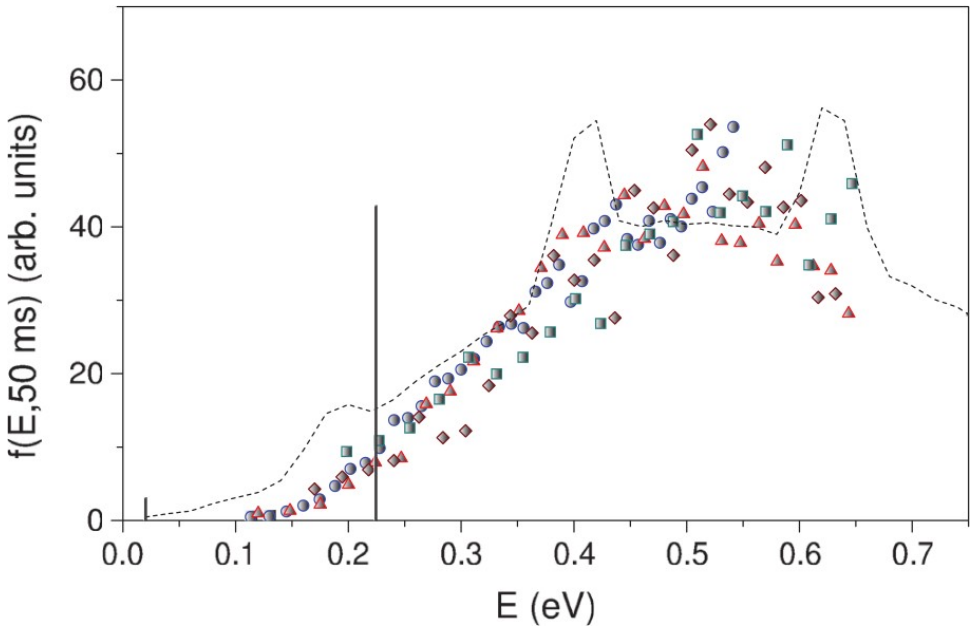
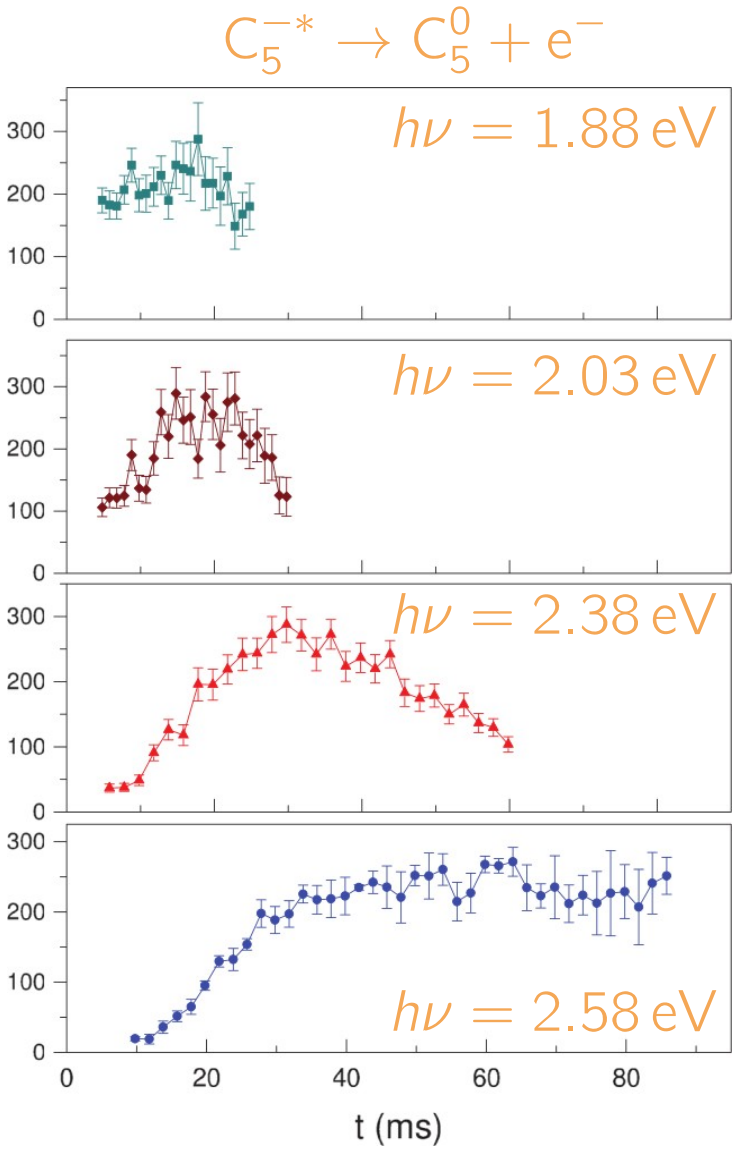
Internal energy distribution

Photo-enhanced electron emission allows to determine the internal energy distribution.

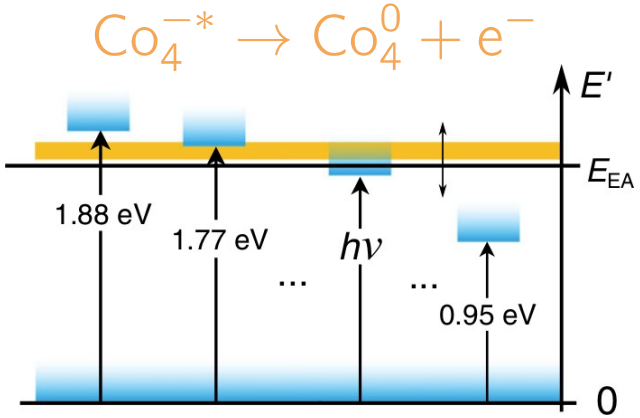


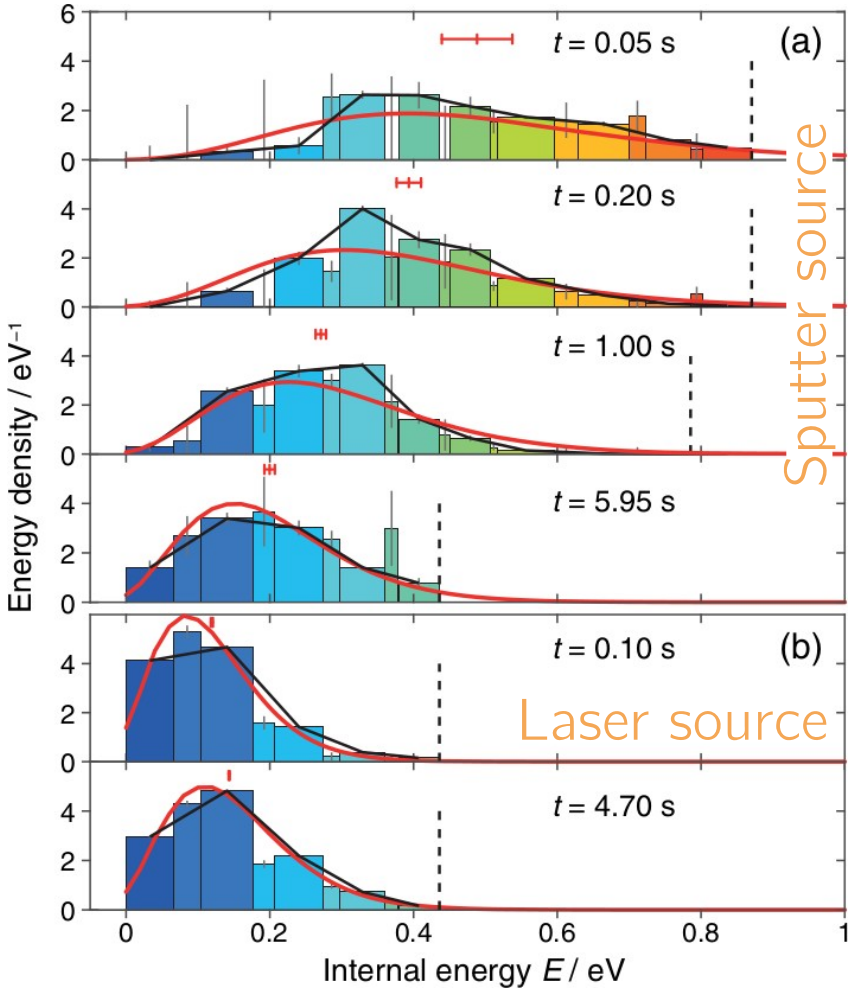


M. Goto et al.
J. Chem. Phys. **139** (2015) 054306

Internal energy distribution (2)

Vertical auto-detachment can also give the internal energy distribution.





C. Breitenfeldt et al.
Phys. Rev. Lett. **120** (2018) 253001