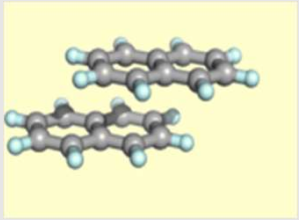
Photodissociation of PAHs dimer cations stored in Electrostatic Storage Rings

Evolution of dimer cations as a function of internal energy of these molecules



Abdulaziz Al Mogeeth
PhD student
Supervisors:
Dr. Jerome Bernard
Prof. Serge Martin
Institut Lumière Matière, Université de Lyon, CNRS

Outline

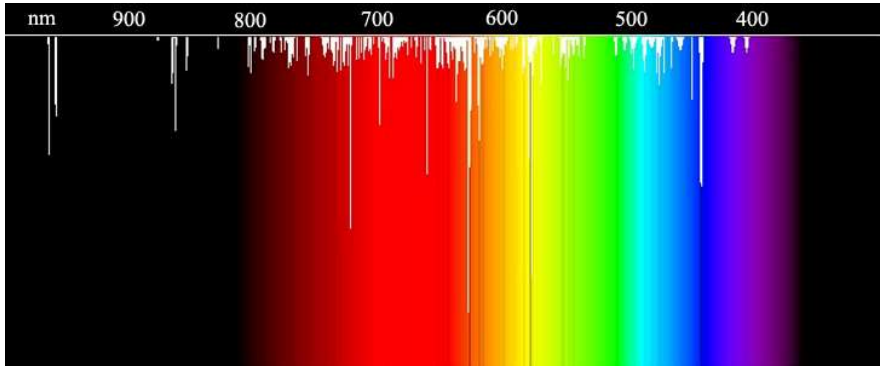
- Introduction
  - PAHs in Space
- Experiment setup
  - General view of Mini-Ring
- Experiment results
  - Optimization of Production of PAHs cationic ion beams
  - Spontaneous decay of Dimer Naphthalene
  - Photo-dissociation Spectrum of Dimer Naphthalene
- Modelling
  - Potential energy curve
- Perspectives

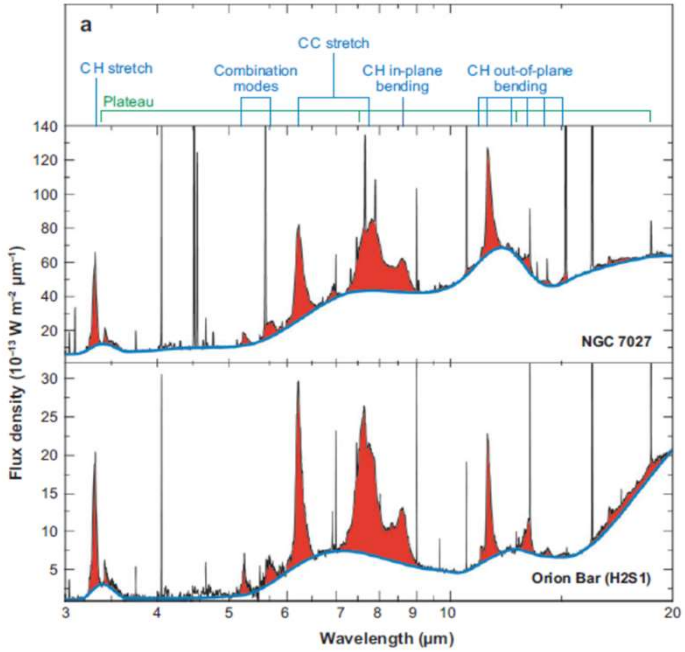
PAHs in Space

- Polycyclic Aromatic Hydrocarbons (PAHs) expected to be abundant free organic molecules in interstellar medium (ISM).
- Unidentified IR emission bands (UIRs) are most likely produced by PAHs.
- PAHs are possible carriers of Diffuse interstellar bands (DIBs) (visible or near-IR).

Expected size in 50-150 C atoms

- How and where do PAH can grow?
- Can clusters play a role in PAH growth?



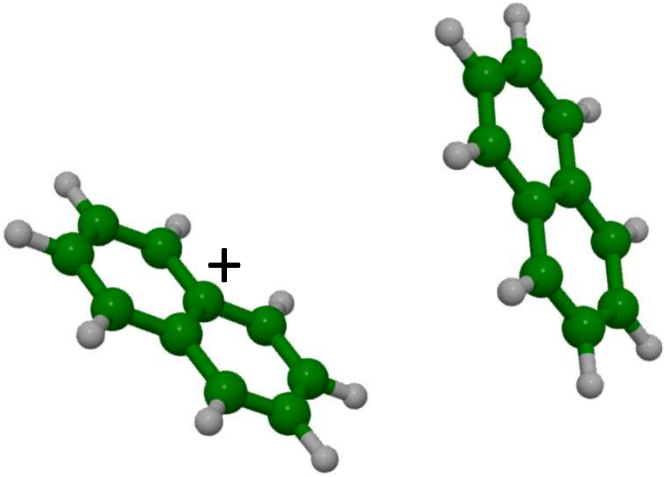


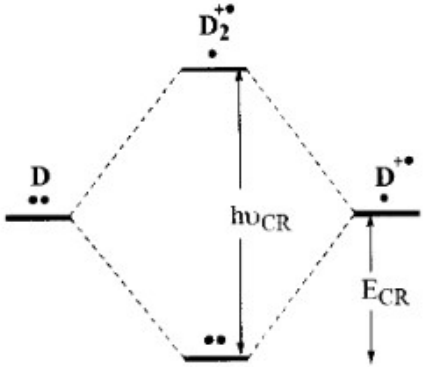
Tielens, A.G.G.M.: Interstellar polycyclic aromatic hydrocarbon molecules. Annu. Rev. Astron. Astrophys. 46,289–337 (2008).

Dimer Cations of PAHs

Attractive force between positively charge monomer and polarized neutral monomer

-> charged dimers more stable than neutrals



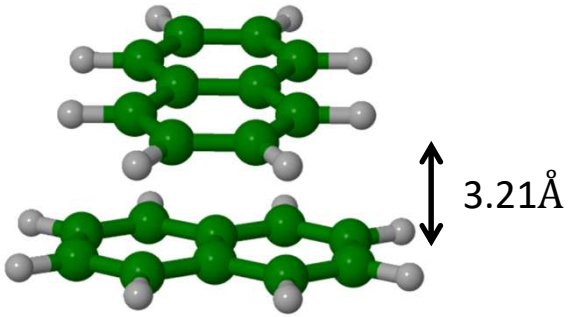


When dimer formed, the charge is shared by the 2 monomers (Charge Resonance)

Charge resonance states : $\Psi_{\pm} = \frac{1}{\sqrt{2}}(\Psi_1^+\Psi_2 \pm \Psi_1\Psi_2^+)$

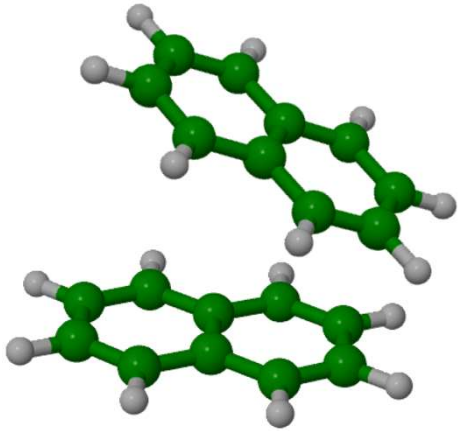
Naphthalene dimer cations - Most stable isomers

L. Dontot et al., ***Phys.Chem.Chem.Phys.,*** 2016, 18, 3545 (ab initio)
A.-R. Allouche, ILM, private comm., (DFT)



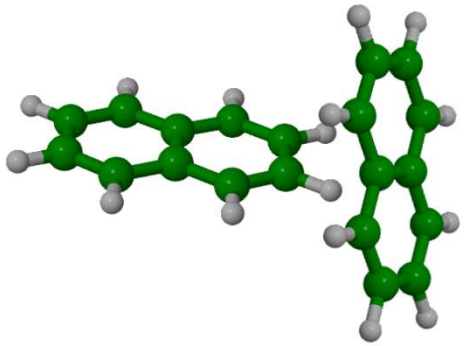
Sandwich

most stable structure
confirmed by ion mobility
(S.P. Platt et al. J. Chem. Phys.142, 191102 (2015)



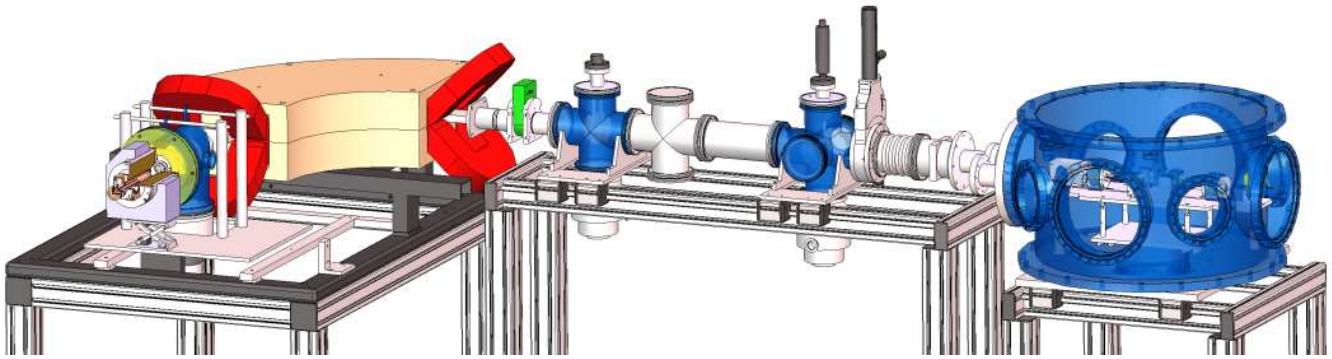
superimposed with an angle (≈ 30°)

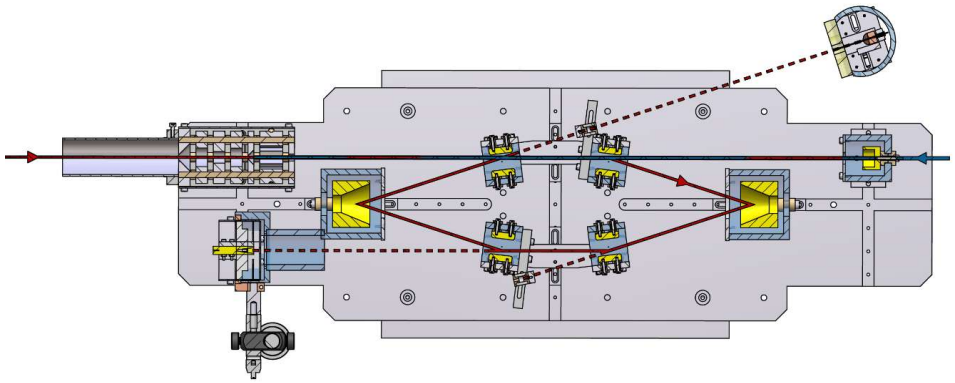
slightly higher energy

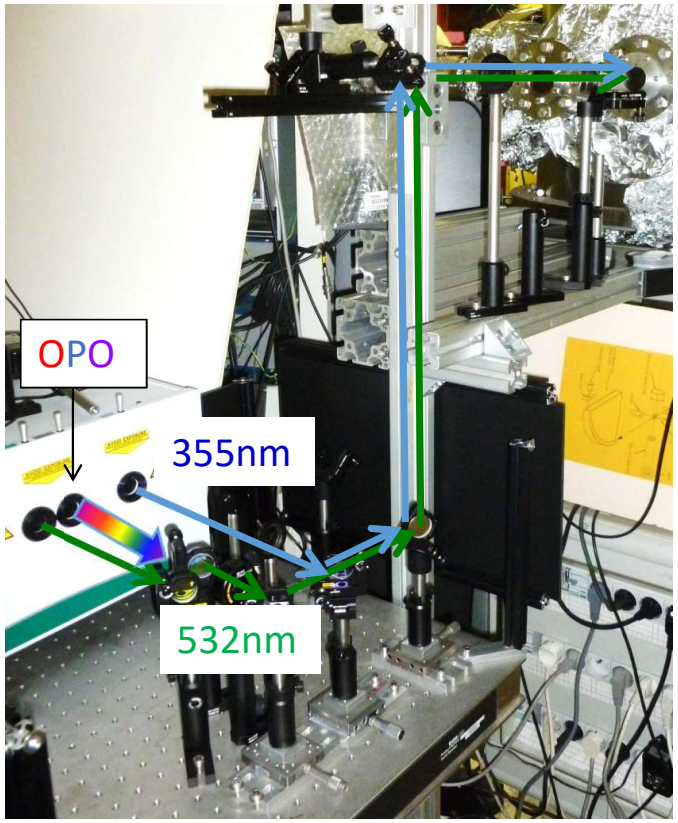


For bigger Monomers (pyrene…)
the T-shape may be rather low energy

Experimental Setup

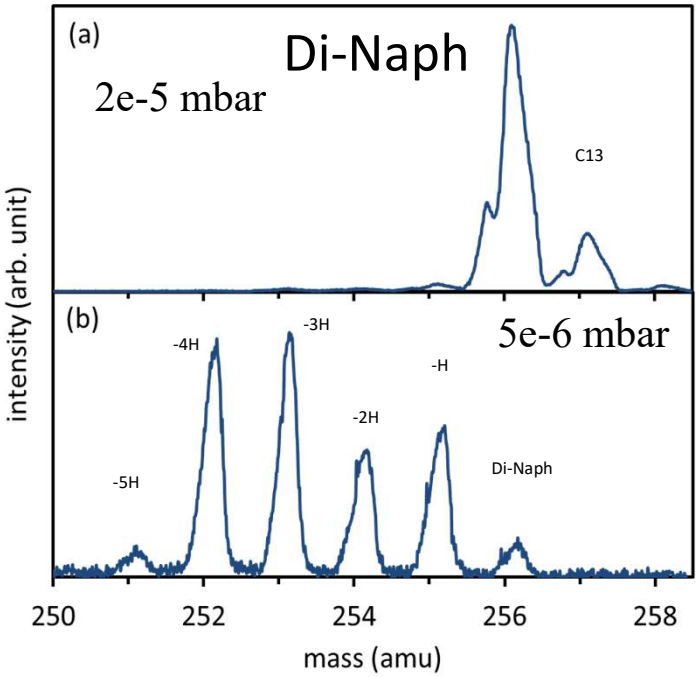


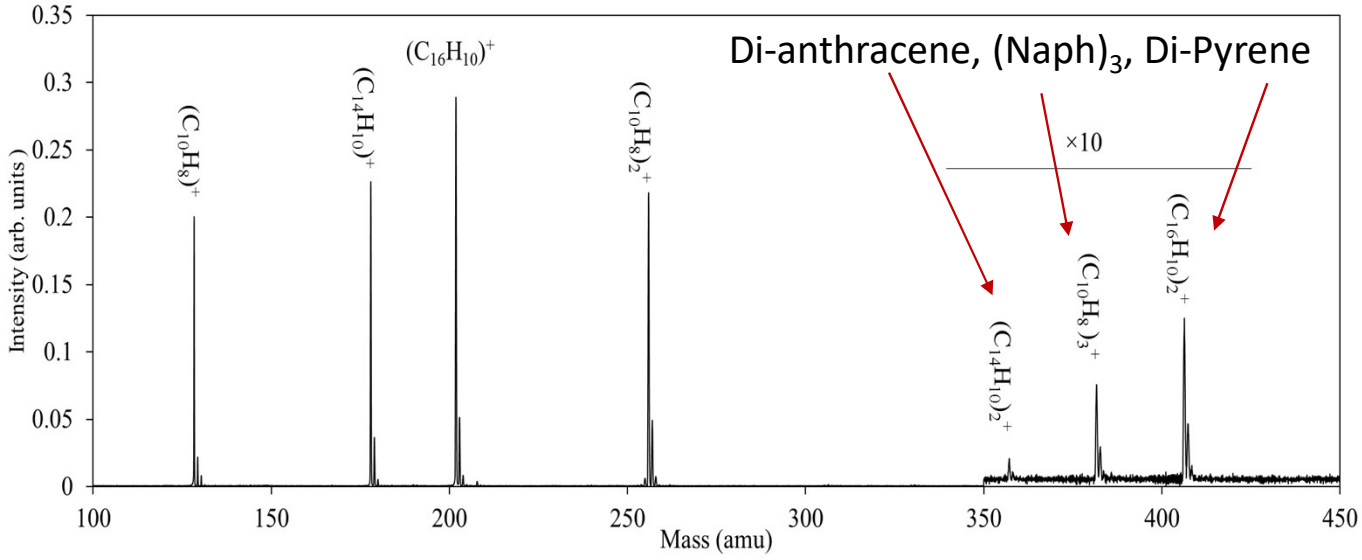




Optimization of production of dimer Cations using Mass spectrometry

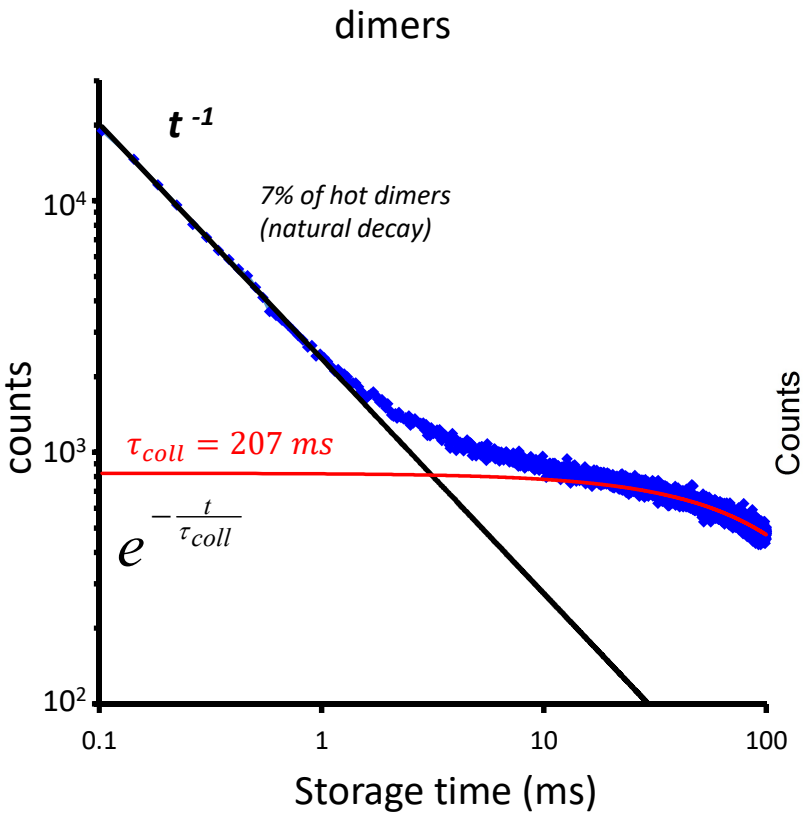
ECR ion Source
NanoGan 1 – Pantechnik (Caen)

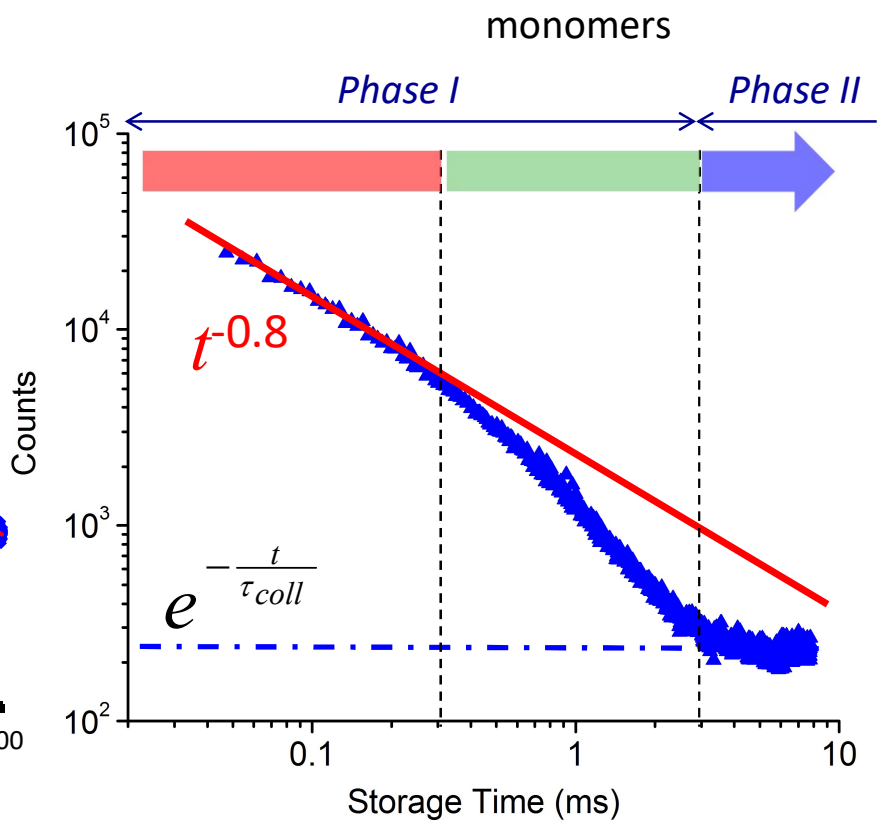




Naphthalene gas pressure allows control of plasma temperature

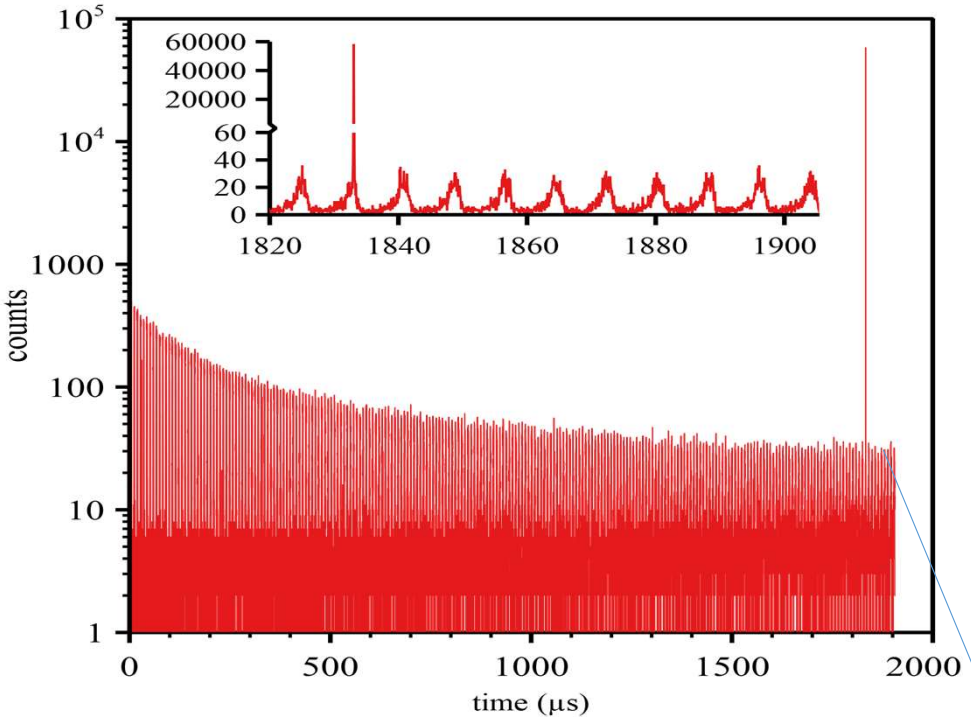
Spontaneous decay of Naphtalene dimer cations



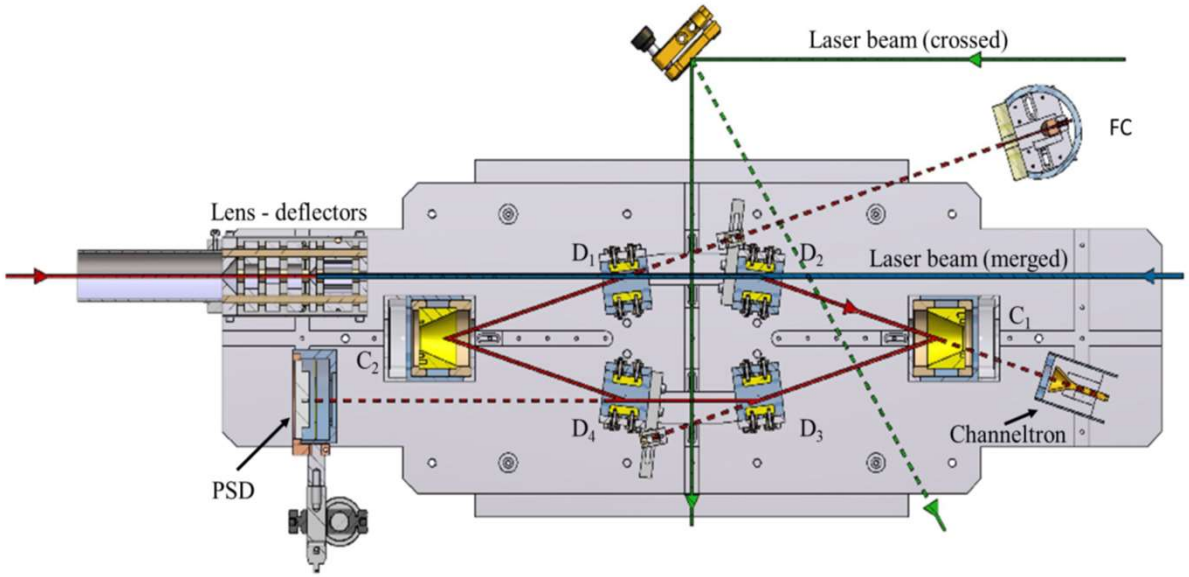


No fast radiative cooling for dimers !
Because no Recurrent Fluorescence

Storage of Dimer Naphthalene



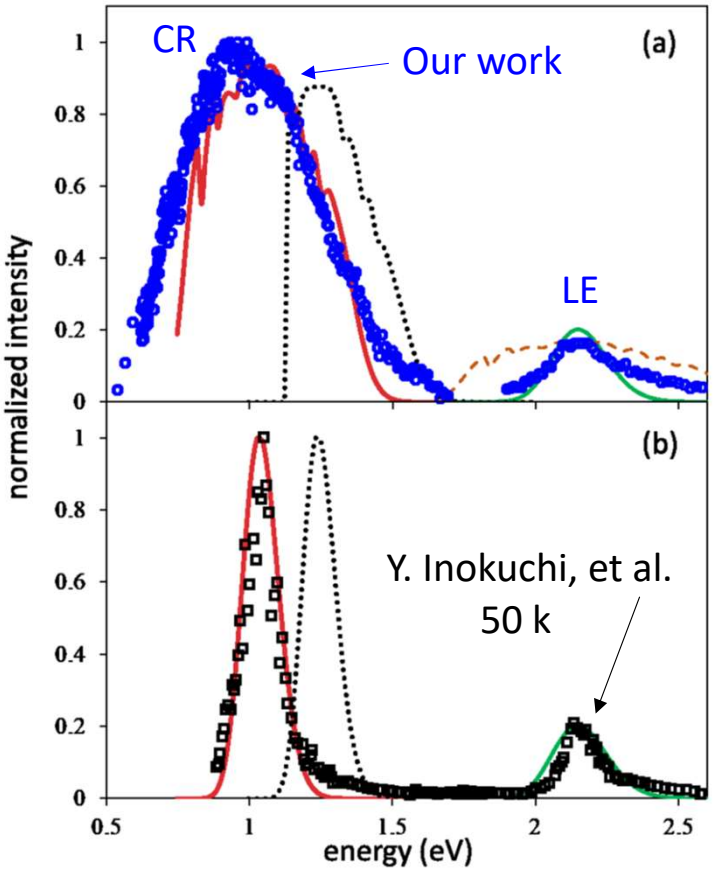
The peak at about 1.8 ms is due to the neutrals produced after laser absorption at 532 nm

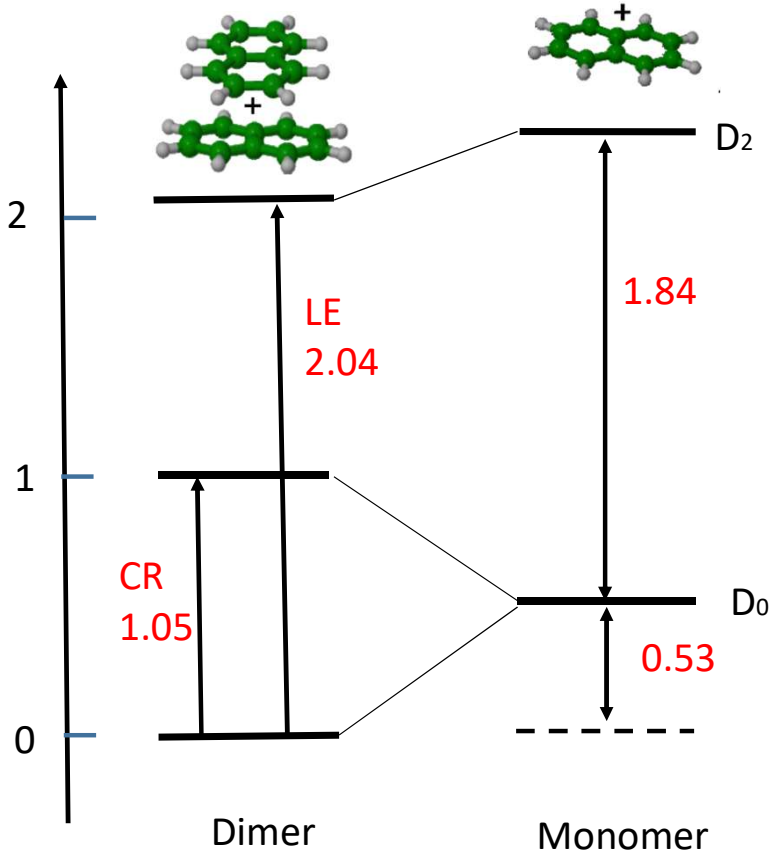


Direct dissociation

Prompt dissociation no delay dissociation
Population of dissociative state

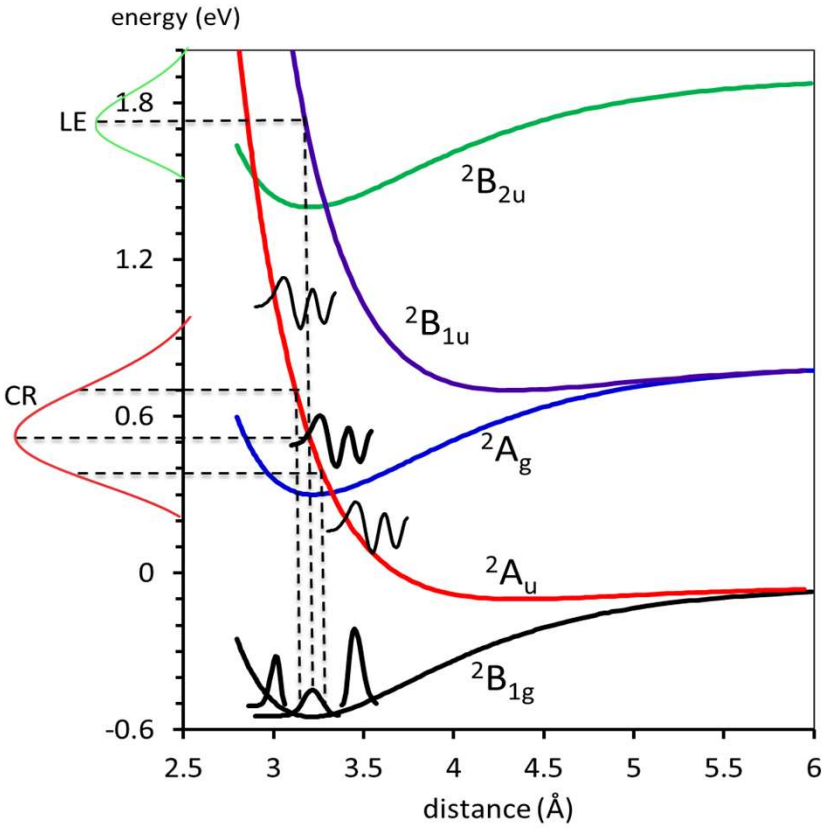
Dimer Naphthalene

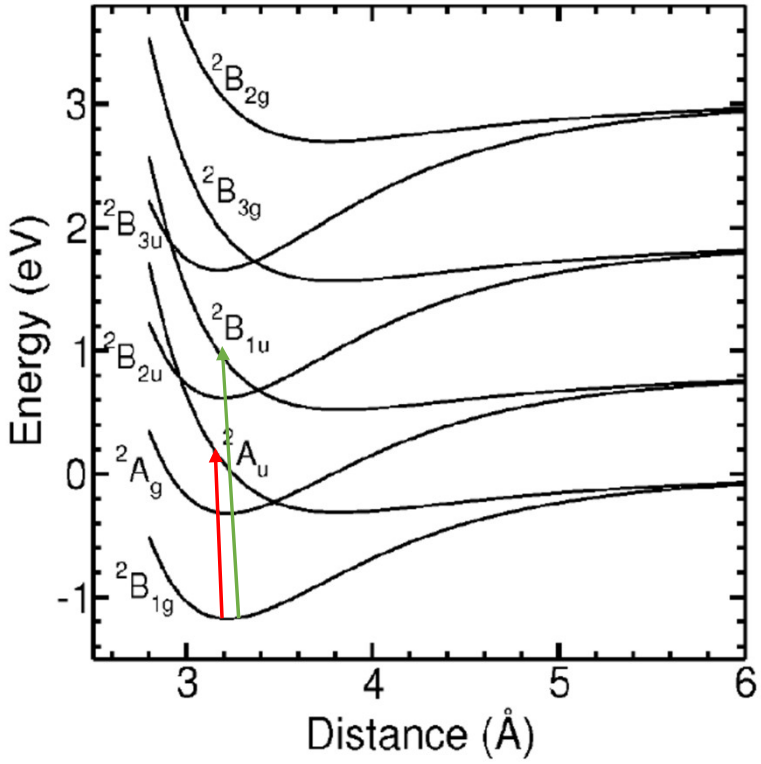




Y. Inokuchi, et al , *J. Phys. Chem.*, vol. 99, no. 11, pp. 3416–3418, Mar. 1995.

Potential energy curve

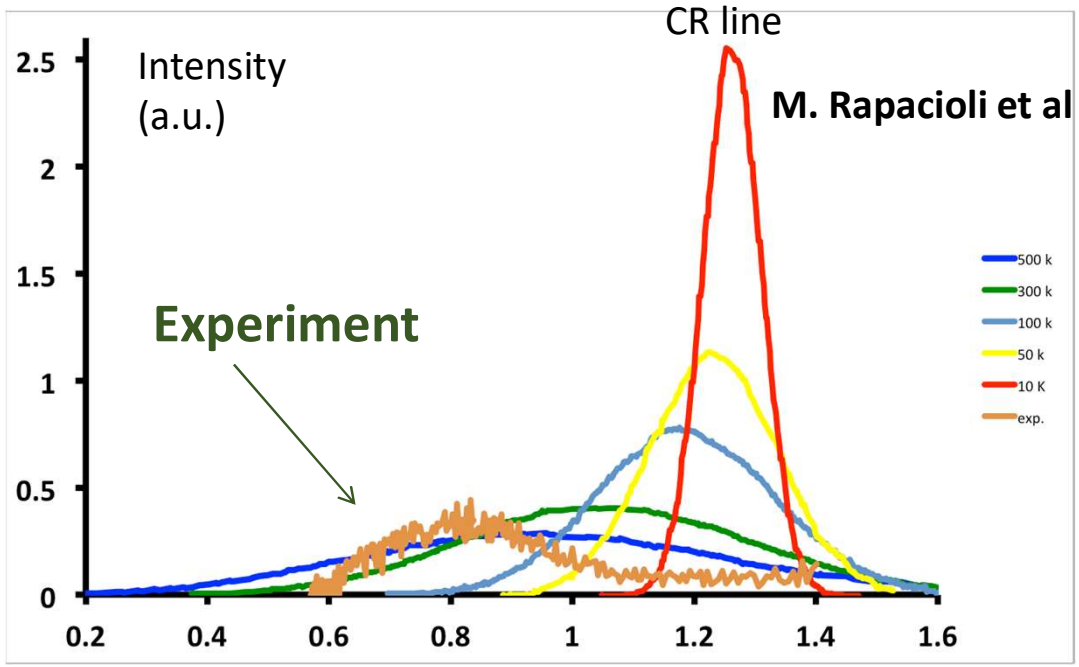




Broad peaks are used to constrain the potential energy curve

Dontot et al, F. An extended DFTB-CI model for charge-transfer excited states in cationic molecular clusters: model studies versus ab initio calculations in small PAH clusters. *Phys. Chem. Chem. Phys.* **18**, 3545–3557 (2016).

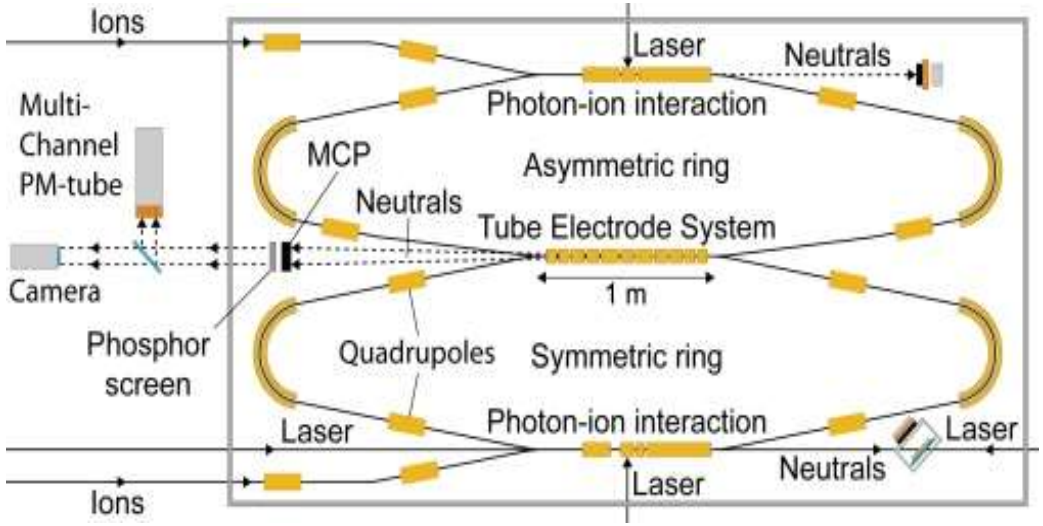
Evolution of the charge resonance with temperature (pyrene)



The vibrational modes which allows to brake the dimer in two equal parts is not only the stretching mode but also the twisting modes of the inter-nuclear axis between two molecules.

Perspectives

- **Evolution of photodissociation spectrum as a function of internal energy**
  - **Experiment planned at DESIREE in Sept. 2019**
  - **Cold Mini-Ring (cryo-cooler)**



Thank you so much for your attention