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Ion pair dissociation of highly excited carbon clusters

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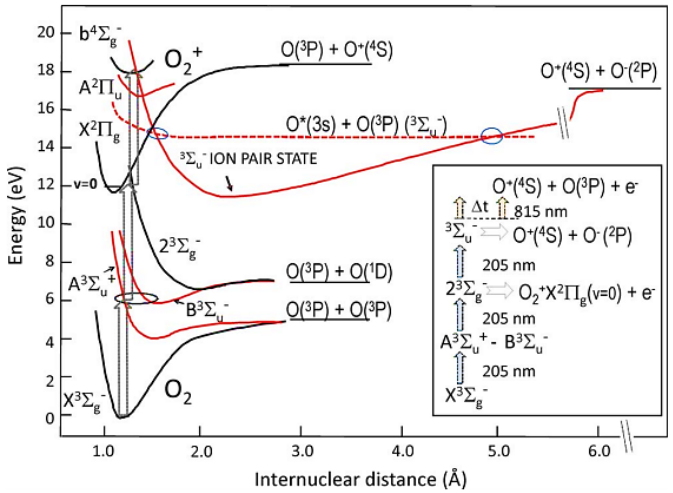
Plan

- Introduction
- Experimental setup
  - Results of ion-pair dissociation of C_n^{q+} clusters
- Theoretical methodologies
  - *Ab initio* calculations
  - Statistical approach
- Conclusions and perspectives

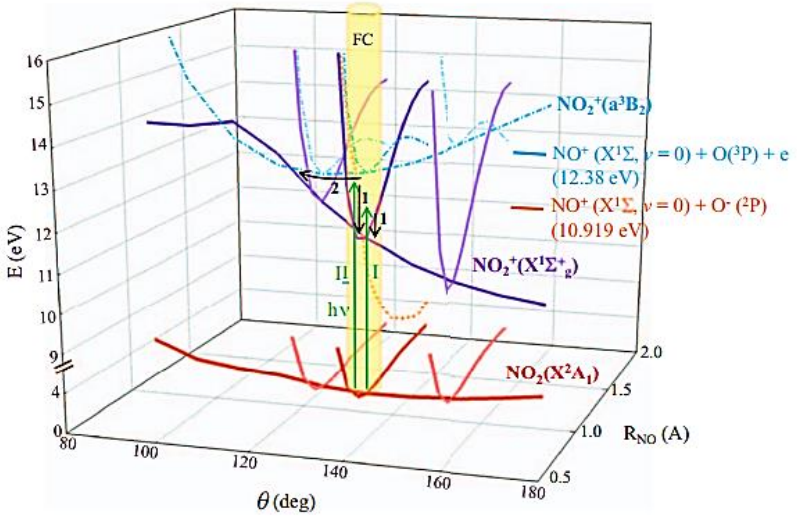
Ion pair dissociation mechanisms

- Relaxation of an excited molecule into a **cation** – **anion pair** of fragments
- Various processes leading to ion pair dissociation/formation :

- O_2 into O^+ (^4S) + O^- (^2P) by photo-dissociation :
  - Baklanov *et al.* 2008



- NO_2 into NO^+ ($X\ ^1\Sigma^+$) + O^- (^2P) by pre-dissociation :
  - Poullain *et al.* 2013



➢ Direct population of an ion pair state with 3 photons

➢ Indirect population via Rydberg states by pre-dissociation

➢ Ion pair states generate **avoided crossings** with neutral states in the inner and outer regions

Ion pair dissociation

- Little information on ion pair dissociation from cations:
  - First observation of an ion pair from a cation : $SO_2^+ \rightarrow SO^{++} + O^-$ by Dujardin *et al.* 1989
  - No potential energy curves for those multi-charged systems
  - No quantitative interpretation of the measurements

- Competition between the ion pair and other relaxation processes:
  - Ionisation (dissociative or not)
  - Radiative relaxation
  - Dissociation without anion emission : « Normal » fragmentation
  - …

➢ Our work: Comparison between ion pair dissociation and « normal » dissociation

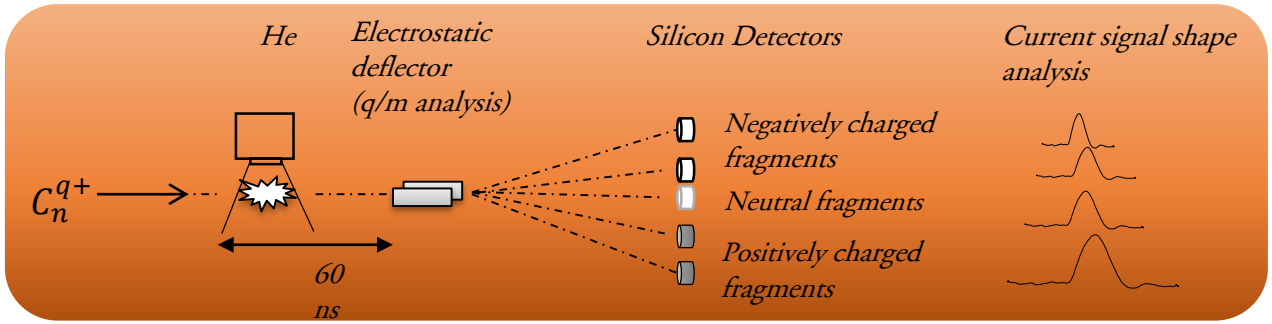
The AGAT setup

- High velocity collisions (v=2.25 a.u / 5.10^6 m s^{-1}) :

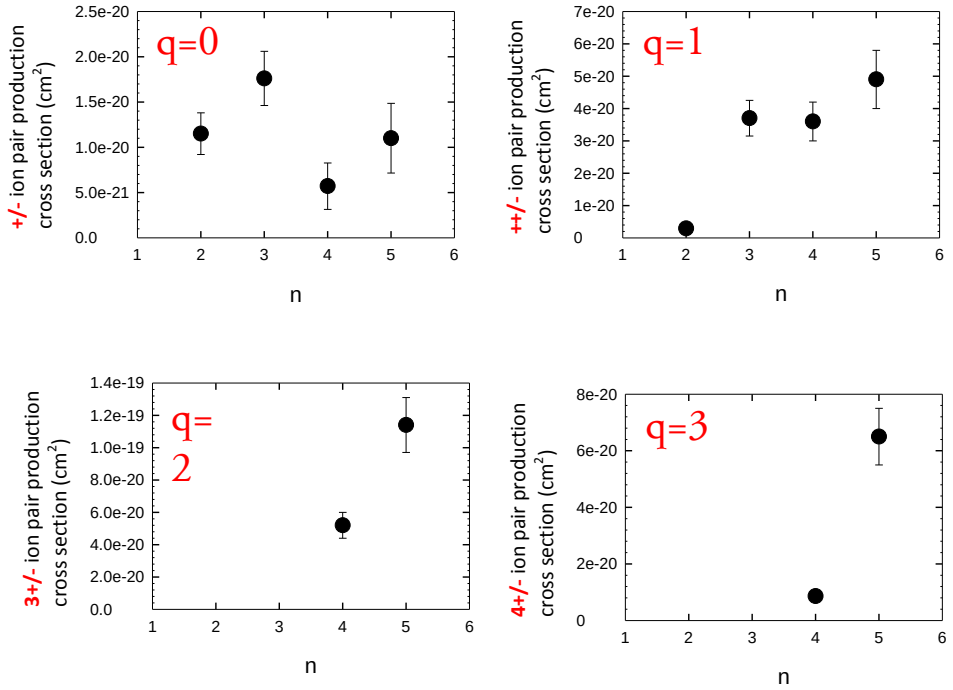
$$C_n^{q+} + \{He\} \rightarrow C_p^- + C_{n-p}^{(q+1)+}$$

  - C_n^- projectiles :
    - graphite sputtering source
    - accelerated and sent to the Tandem facility (Orsay, France)
    - by a stripper gas : $C_n^- \rightarrow C_n^+$
  - In the AGAT (AGrégat-ATome) : C_n^+ clusters collide with helium atoms.
  - Deflection of the fragments according to their charge over mass ratio and sent to silicon detectors.

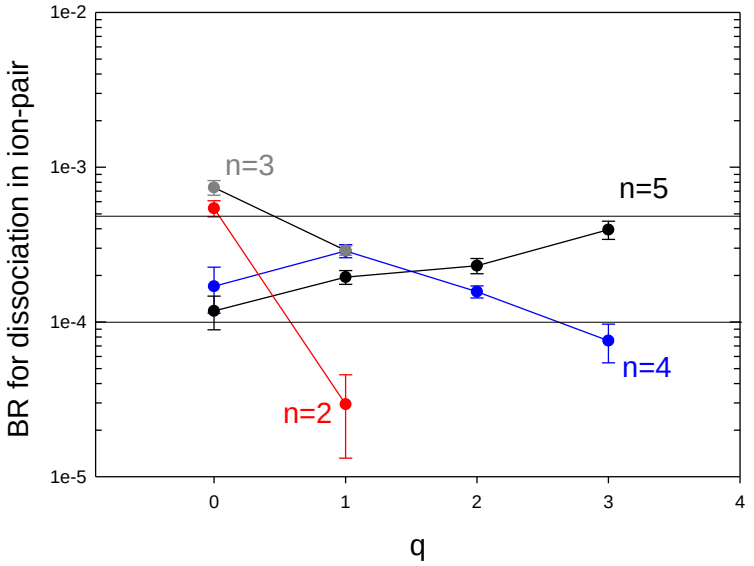
- Coincidence measurements of all fragments emitted from the collision allowing the unambiguous identification of the ion pair relaxation.



Measured cross section and Branching ratio



- Ion pair dissociation compared to dissociation without anion emission



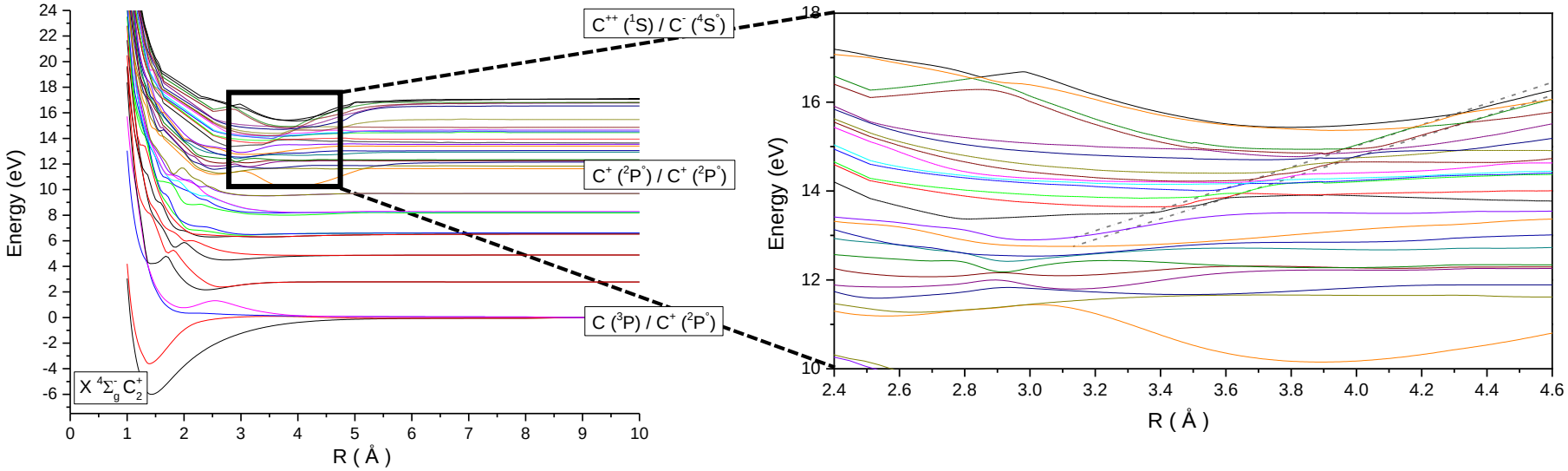
- First results concerning ion pair dissociation of C_n species
- First results of ion-pair dissociation into 3+/- and 4+/-

- For some clusters : the dissociation into ion pair is weakly dependent on the cluster size and charge
- Exception for C_2^+

- Can we understand the difference between C_2^+ and C_3^+ ?
- Can we theoretically predict these branching ratios ?

Ab initio calculations

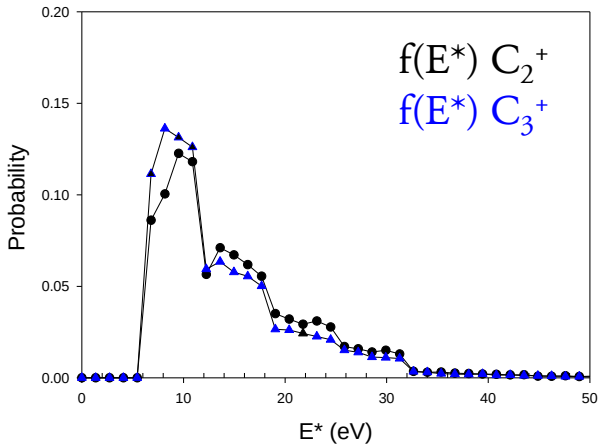
- Lowest dissociation limits : MRCI (+Davidson correction) with ACV6Z basis set
- Excited dissociation limits : CASSCF method with VTZ basis set due to convergence problems.



- ✓ 50 low-lying $^4A_2$ electronic states arising from various molecular dissociation channels : Σ^-, Δ and Γ molecular symmetry.
- ✓ Mulliken population analysis : the ionic channels of C^{++} (^1S) / C^- ($^4S^\circ$).
- ➢ **Number of states and avoided crossings is enormous : the use of traditionnal methodologies for BR and cross sections is almost impossible**

Statistical approach

- Rate of ion pair dissociation at internal energy E* : $\frac{nb\ of\ ion\ pair\ states}{nb\ of\ other\ dissociation\ states}$
  - All final dissociative states are considered based on the atomic NIST database and calculated using Wigner and Witmer correlation rules.
- Populated states in the collision depend on the dipole excitation selection rules.
  - $\Delta S = 0\ ;\ \Delta\Lambda = 0, \pm 1\ ;\ u \leftrightarrow g$
- Branching ratio is based on the internal energy E* of the carbon cluster and the normalized probability $f(E^*)$ to produce this energy E* during the collision (Béroff *et al.* 2013):
  - $BR = \int_0^\infty BR(E^*) f(E^*) dE^*$
- The excited states lying near the ground state of C_n^+ are taken into account :
  - Removing electrons from the incident beam C_n^- produced ground and excited states of C_n^+.



1) Count the number of dissociative states below excited energy E*
2) Count the number of states that could be populated by selection rules
3) Count the number of states emerging from the ion pair channels
4) Integrate over the internal energy distribution $f(E^*)$

➢ Branching Ratio

Statistical approach: results

C_2^+

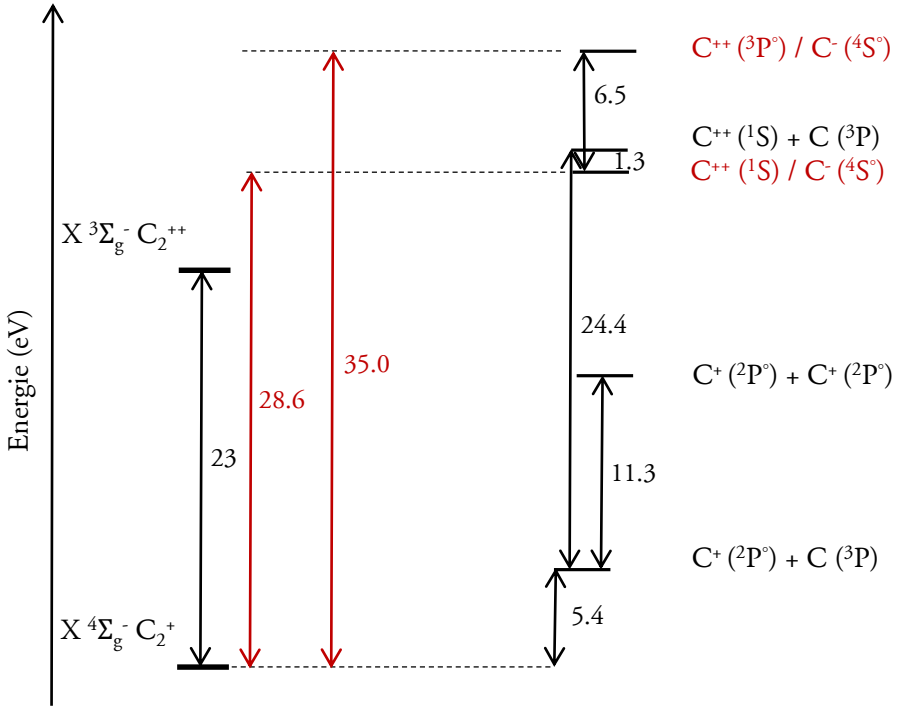
- ✓ Theoretical value:
  - From C_2^+ (GS) : $BR = 4.7\ 10^{-5}$
  - From C_2^+ (excited) : $BR = 1.0\ 10^{-5}$
- ✓ Experimental value:
  - $BR = 3.0\ 10^{-5}\ (\pm 60\%)$

C_3^+

- ✓ Theoretical value:
  - From C_3^+ (GS) : $BR = 2.6\ 10^{-4}$
  - From C_3^+ (excited) : $BR = 2.0\ 10^{-4}$
- ✓ Experimental value:
  - $BR = 5.3\ 10^{-4}\ (\pm 30\%)$

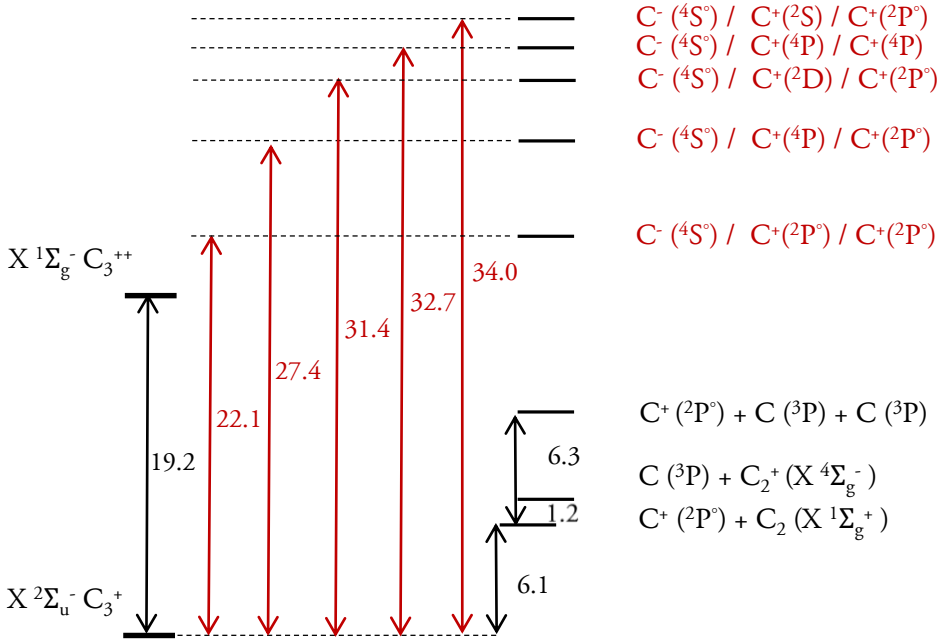
Energetics involved

❑ C_2^+



- ❑ Ion pair dissociation requires 28.6 eV
- ❑ Only **two** dissociation channels

❑ C_3^+



- ❑ Ion pair dissociation requires only 22 eV
- ❑ **5** ion pair channels

CCSD(T) calculations by Diaz-Tendero *et al.* (2005)

Conclusions - Perspectives

$$C_n^{q+} + \{He\} \rightarrow C_p^{-} + C_{n-p}^{(q+1)+}$$

- Experimental
  - ✓ Cross section and Branching ratio for ion pair dissociation in highly excited C_n^{q+} clusters ($n \leq 5$, $q \leq 3$)
    - Difference between C_2^+ and C_3^+
- Theoretical
  - ✓ *Ab initio* :
    - Potential energy curves of molecular C_2^+
    - C^{++} / C^- channel visible
  - ✓ Simple Statistical model:
    - Branching ratio in agreement with experiments
    - Explanation of the difference between C_2^+ and C_3^+
- Apply the same approach for $C_nN^{(q+)}$ systems
  - Predict the BR value?
- Experiments on other carbon clusters

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