Electron collision studies on CN^+, CN^-, HCN^+/HNC^+ and C_4^-

by Arnaud Le Padellec

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DR meeting Chicago
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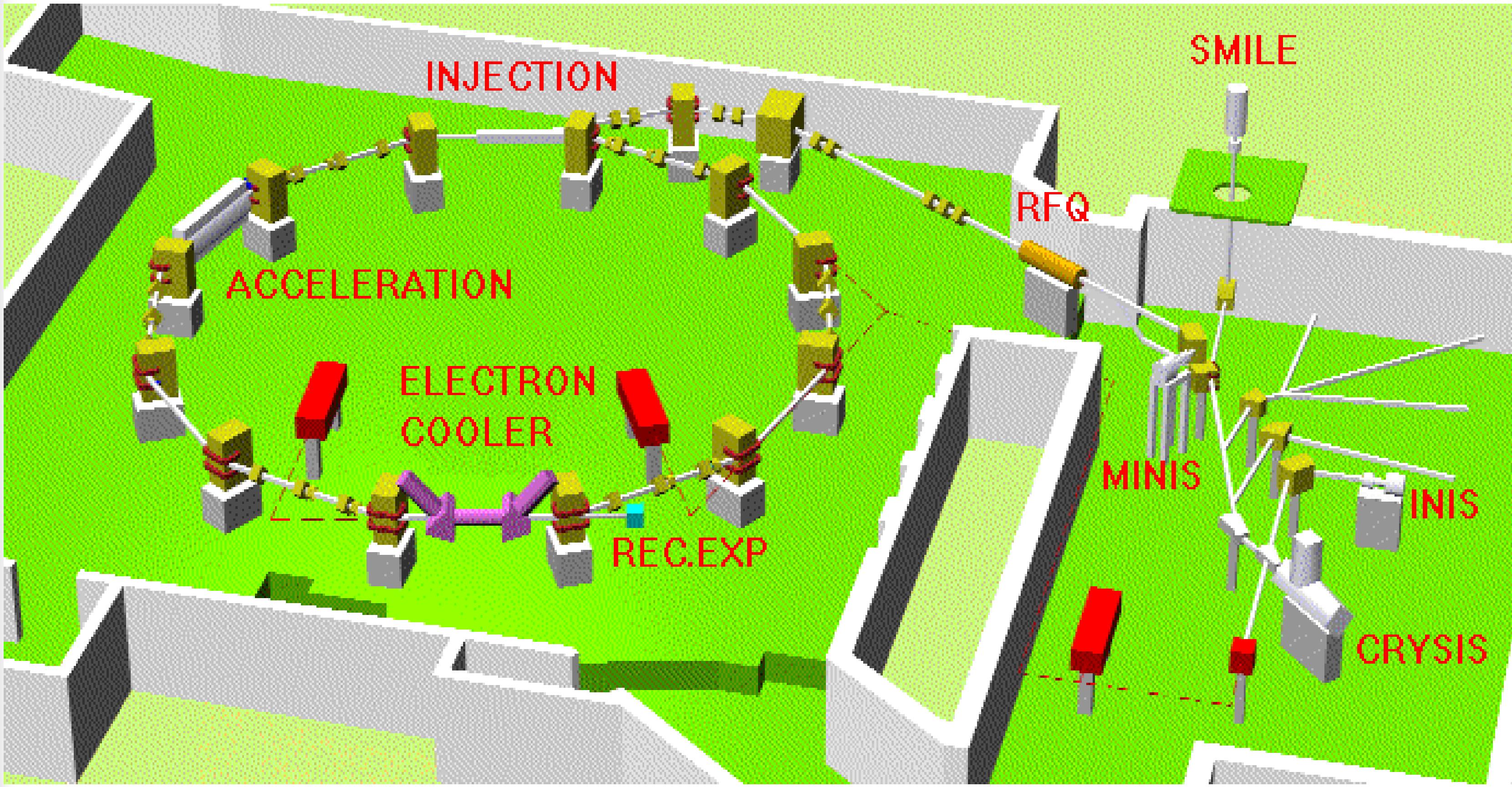
CRYogenicRING (Stockholm Sweden) : an heavy ion storage ring.



$CN^+ + e$

CN^+

-Spectrum first reported by Douglas and Routly (*Astrophys. J.* **119**, 303, (1954)).

-Uncertainty as to the identity of its ground state :

Calculations:

-Wu : $^3\Pi$ state ground state, lying 0.33 eV below the lowest singlet $^1\Sigma^+$ state (*Chem. Phys. Lett.*, **59**, 457, (1978)).

-Shimakura *et al* : $^1\Sigma^+$ state lower than the triplet state by 0.63 eV (*Chem. Phys. Lett.*, **55**, 221, (1978)).

-Murrell *et al* : two states degenerated (*Mol. Phys.*, **38**, 1755, (1979)).

-Bruna *et al*, Roos *et al* and Hirst have firmly established that the singlet state is the ground state lying at an energy of between 0.07 eV and 0.45 eV below the triplet state (*J. Chem. Phys.*,**72**, 5437, (1980), *Chem. Phys.*, **66**, 197, (1982) and *Mol. Phys.*, **82**, 359, (1994)).

Experiments:

-Reid : the singlet state is the ground state with a separation of 0.12 eV from the triplet state.

-CN^+ reported in flames

-CN^+ not reported in interstellar clouds.

formed by: $C^+ + NH \rightarrow CN^+ + H$ — 7.80×10^{-10} cm^{3}s^{-1} (exothermic by 1.9 eV)

$CH^+ + N \rightarrow CN^+ + H$ — 1.9×10^{-10} cm^{3}s^{-1}.

Question of the abundance of the different reactants :
NH a minor component

destroyed by: $CN^+ + H_2 \rightarrow HCN^+ + H$ — 1.24×10^{-10} cm^{3}s^{-1}

$CN^+ + H \rightarrow H^+ + CN$ — 1.9×10^{-10} cm^{3}s^{-1}

CN+ + CO CO+ + CN — 6.3×10^{-10} cm^{3}s-1.

The DR process competes with ion-molecule reactions in the interstellar clouds, at least if the electron fraction is sufficiently large. Is it large enough?

Some experimental facts…

-Nitrogen/methane : 9/1

-$CN^+(X^1\Sigma^+$ and $^3\Pi$ (0.08eV))

with $\tau(^3\Pi)$ >12s $\Rightarrow$ $^1\Sigma^+$ and $^3\Pi$ both populated !

-Vibrational relaxation times of :

38, 58 and 115 ms for the v = 3, v = 2 and v = 1 levels of the $X^1\Sigma^+$ state.

101, 152 and 304 ms for the $a^3\Pi$ state .

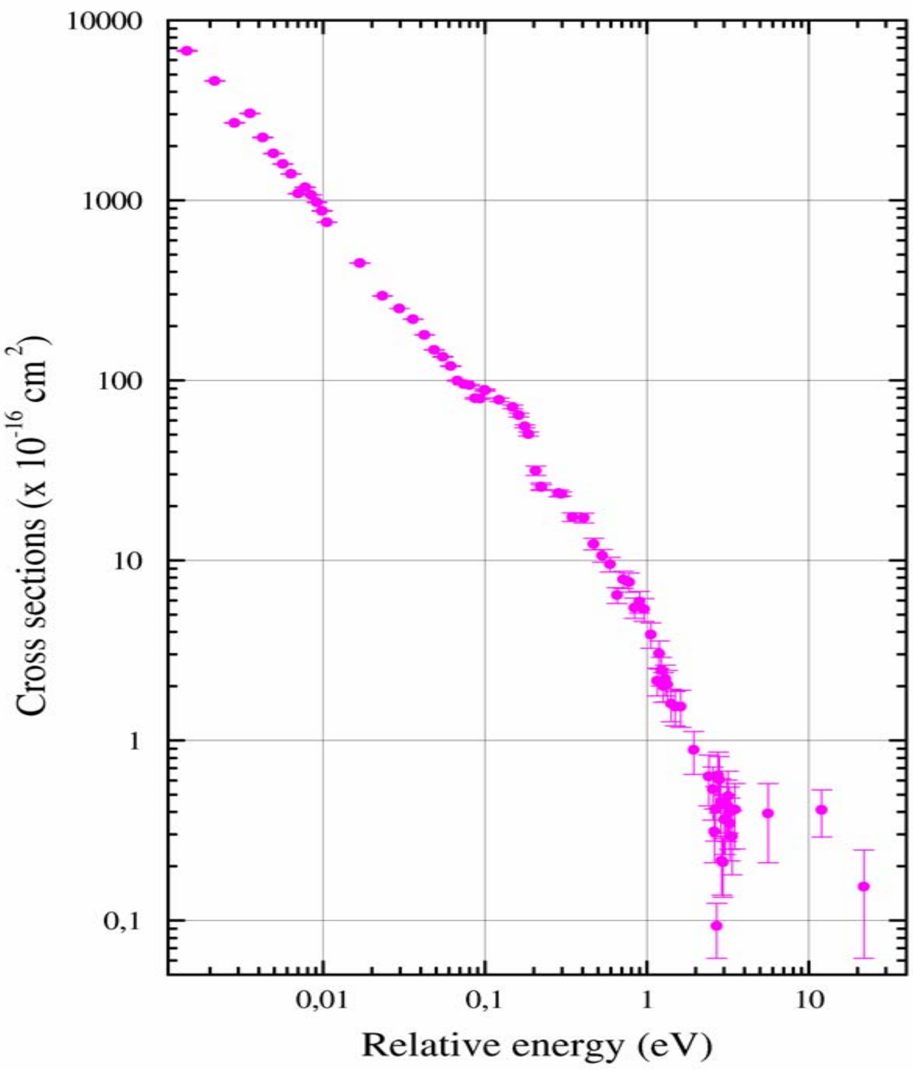
$\Rightarrow$ $^1\Sigma^+$ and $^3\Pi$, v=0 populated !

Many exothermic channels…

$CN^+(X^1\Sigma^+, v=0) + e^-$

$\rightarrow C(^3P) + N(^4S) + 6.3$ eV
$\rightarrow C(^1D) + N(^4S) + 5.0$ eV
$\rightarrow C(^3P) + N(^2D) + 3.9$ eV
$\rightarrow C(^1S) + N(^4S) + 3.6$ eV
$\rightarrow C(^3P) + N(^2P) + 2.7$ eV
$\rightarrow C(^1D) + N(^2D) + 2.6$ eV
$\rightarrow C(^5S) + N(^4S) + 2.1$ eV
$\rightarrow C(^1D) + N(^2P) + 1.4$ eV
$\rightarrow C(^1S) + N(^2D) + 1.2$ eV
$\rightarrow C(^1S) + N(^2P) + 0.0$ eV

+10 more limits coming from $CN^+(a^3\Pi, v=0) + e^-$



CROSS SECTION DETERMINATION

Below 0.1 eV :

$\sigma(E_{cm}) = 8.00\ x10^{-14}(0.01/E_{cm})^{1.05}$

the E^{-1} dependence is observed!

From 0.4 to 3 eV :

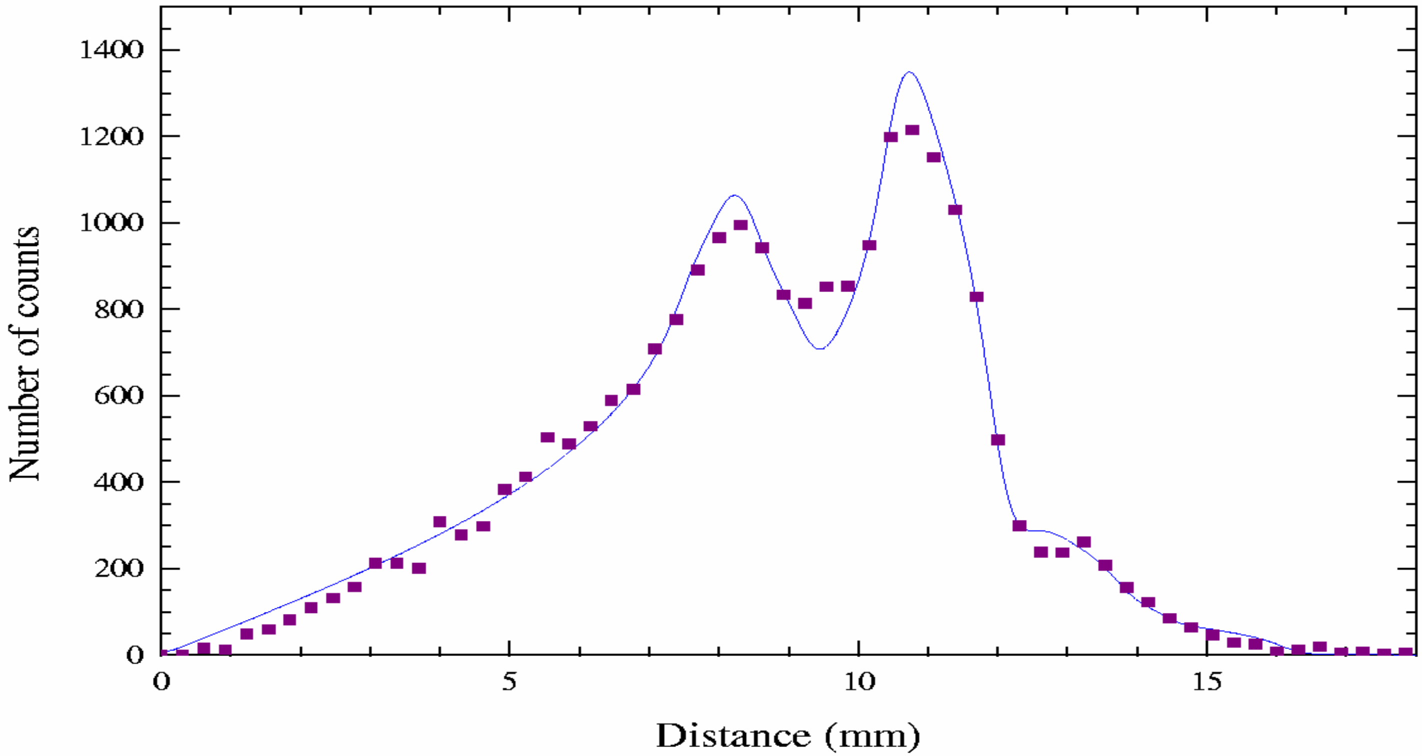
$\sigma(E_{cm}) = 1.49\ x10^{-15}\ (0.4/E_{cm})^{1.41}$

LARGE CROSS SECTIONS :

TYPICAL OF THOSE OF A DIATOMIC

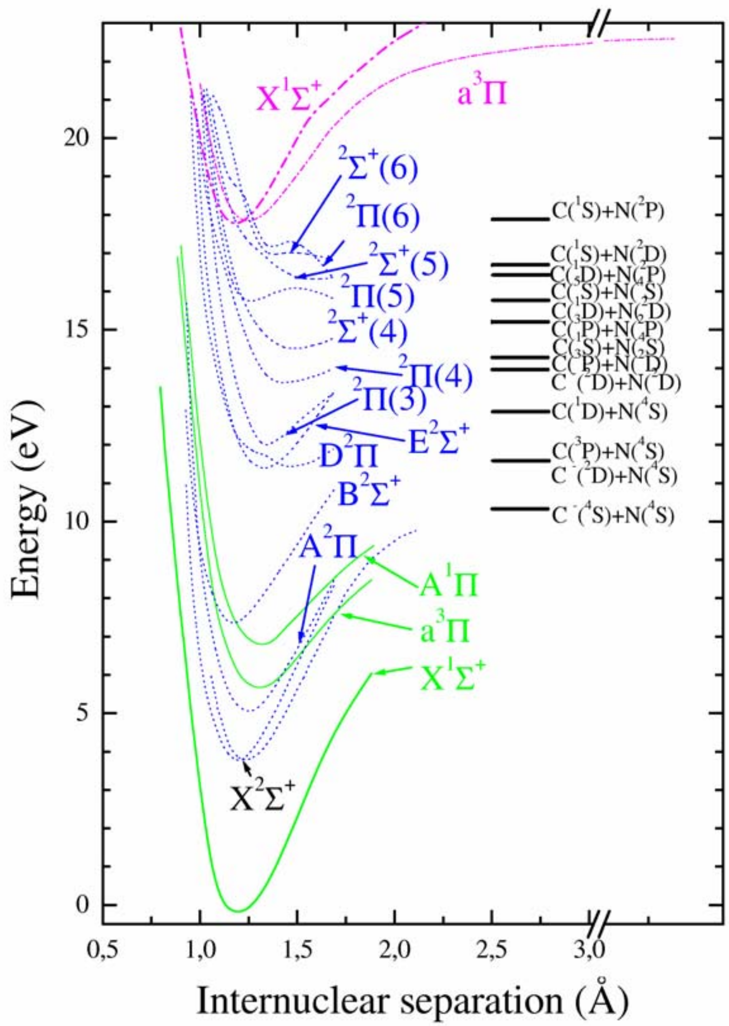
BRANCHING FRACTION DETERMINATION

$$P(D)=\frac{1}{D_{L+1/2}-D_{L-1/2}}\left(\cos^{-1}\left(\min\left(1,\frac{D}{D_{L+1/2}}\right)\right)-\cos^{-1}\left(\min\left(1,\frac{D}{D_{L-1/2}}\right)\right)\right)$$



Branchings at 0 eV…

$C(^3P)+N(^4S)$	<1.8 %
$C(^1D)+N(^4S)$	3.8 %
$C(^3P)+N(^2D)/C(^1S)+N(^4S)$	14.2 %
$C(^3P)+N(^2P)/C(^1D)+N(^2D)$	56.1 %
$C(^1D)+N(^2P)/C(^1S)+N(^2D)$	25.5 %
$C(^5S)+N(^4S)$ and $C(^1S)+N(^2P)$	<1-1.4 %



•$D^2\Pi$, $E^2\Sigma^+$ and $^2\Pi(3)$ do not intersect the ionic curves.

⇒ not suitable drive the DR via the direct process.

⇒ the limits correlating to these states are not populated.

•$CN^+(X^1\Sigma^+)$: best Franck-Condon overlap with $^2\Sigma^+(5)$.

•$CN^+(a^3\Pi)$: best overlap with $^2\Sigma^+(6)$ and $^2\Pi(6)$.

⇒ $C(^3P)+N(^2P)$, $C(^1D)+N(^2D)$, $C(^1D)+N(^2P)$ and $C(^1S)+N(^2D)$ limits represent altogether 81.6 % of the dissociating flux.

•$C(^1S)+N(^2P)$ not significantly populated.

⇒ the corresponding dissociative state converging to this asymptotic limit and displaying a favorable curve crossing near the v = 0 of the ion would have to be extremely shallow!

$CN^- + e$

CN^-

-Structure mainly known from theoretical works.

•Taylor *et al* : construction of the $^1\Sigma^+$ ground state potential by using calculations based on configuration interaction and coupled-pair methods

(J. Chem. Phys., **70(10)**, 4481 (1979)) ⇒ Reliable ro-vibrational data.

▪Ha and Zumofen : spectroscopic constants and potential curves for both the $^1\Sigma^+$ ground state and the $^1\Pi$ and $^3\Pi$ excited states performing CI calculations

(Molec. Phys., **40(2)**, 445 (1980)).

-Little known about the dynamical properties

▪Pulm *et al* : photoionisation study (Chem. Phys., **92**, 457 (1985)).

▪Matti-Maricq *et al* : vibrational product state distribution from reactions of CN^- with hydrogen halides (Cl, Br and I) and hydrogen atoms

(J. Chem. Phys., **74**, 6154 (1981)).

PRACTICAL "APPLICATIONS"

-Readily forms robust complexes with transition metal ions

("Advanced Inorganic Chemistry", Wiley-Interscience, New York, (1972)).

-Can be used to dope alkali halide crystals

("Molecular spectroscopy", Vol 1, Chemical Society, London, (1972)).

Some experimental facts…

-Property : high degree of stability against detachment
-CN^- produced in a cesium sputter ion source (boron nitride cathode)
-Lifetime $\tau(a^3\Pi)$=21 ms $\Rightarrow$ only $CN^-(X^1\Sigma^+)$ populated!
-Vibrational relaxation times of :
700, 930, 1390 and 2790 ms for the levels v = 4, 3, 2 and 1. $\Rightarrow$ $X^1\Sigma^+$, v=0 and 1 populated!

Investigated channels

$CN^- + e^- \rightarrow$	$CN + 2e$	(a)
$\rightarrow$	$C^- + N + e$	(b)
$\rightarrow$	$C + N + 2e$	(c)
$\rightarrow$	$C + N^+ + 3e$	(d)
$\rightarrow$	$C^+ + N + 3e$	(e)
$\rightarrow$	$CN^+ + 3e$	(f)
$\rightarrow$	$C^- + N^+ + 2e$	(g)
$\rightarrow$	$C^+ + N^+ + 4e$	(h)

We recorded the neutral fragments

$\Rightarrow$ (a) and (c) could not be distinguished

$\Rightarrow$ use of a grid in front of the Surface Barrier Detector.

EXPERIMENTAL FINDINGS

At 60 eV :

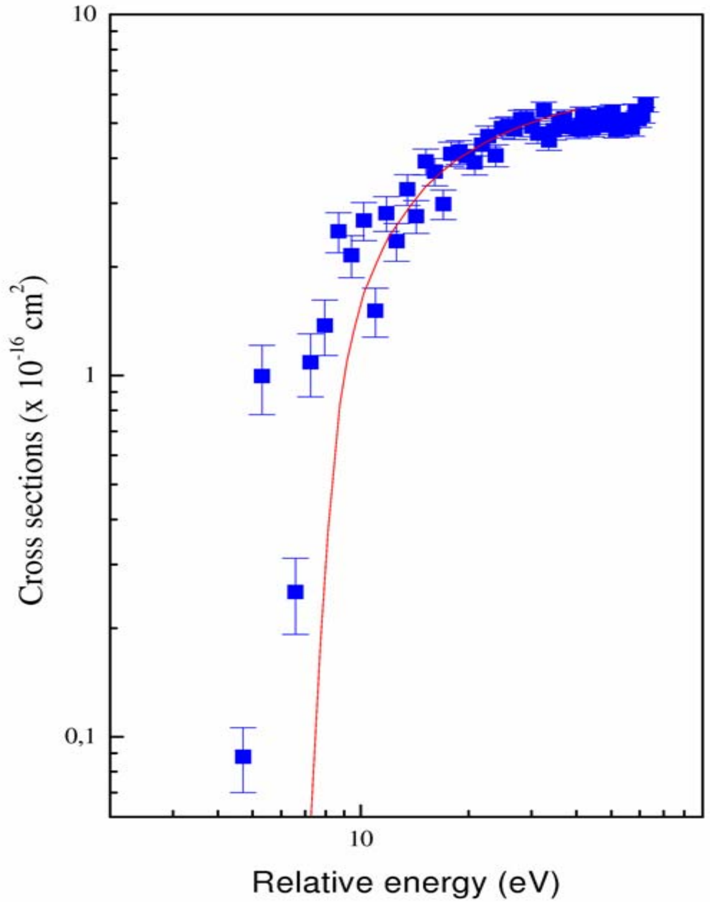
91(±4) % branch into the pure detachment channel CN+2e

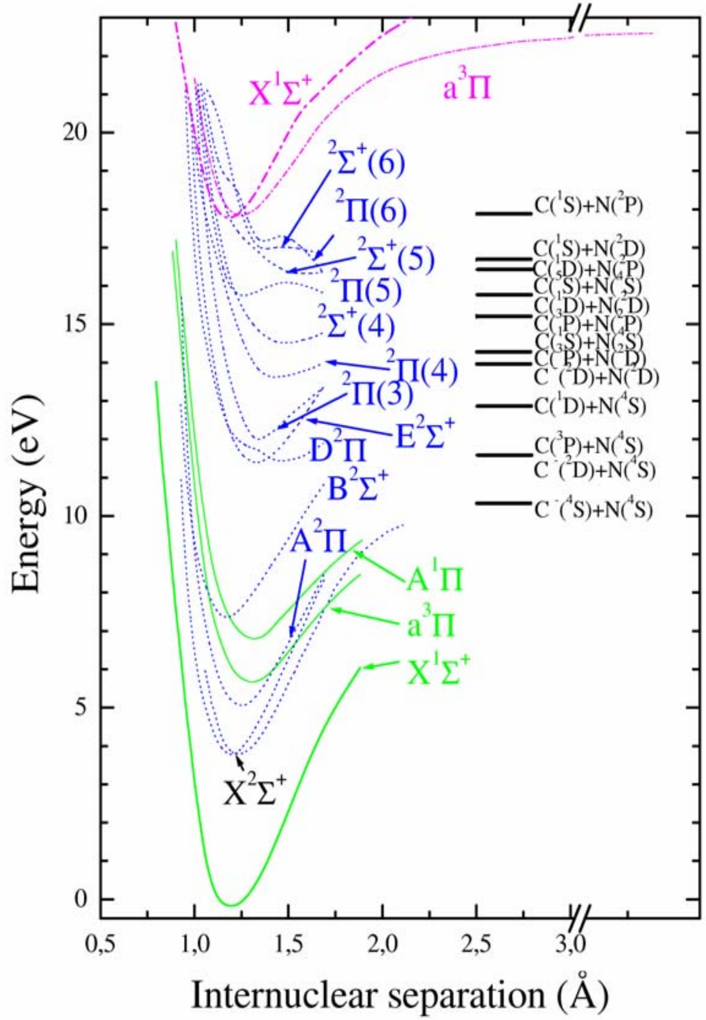
8(±4) % branch into the dissociation channel C^- + N.

The flux into all other open channels represents less than 1 % !

Figure ⇒ PURE DETACHMENT

⇒ Onset at a threshold energy of about 7 eV (fit to our experimental data at medium energy, using a semi-classical formalism developed by Andersen *et al*). ⇒ Threshold = binding energy of the anion (3.8 eV) + finite contribution due to the Coulomb repulsion.





•$C^-(^4S) + N(^4S)$: 4 states do correlate ($^1\Sigma^+$ ground state in green).

•$C^-(^2D) + N(^4S)$ and $C^-(^2D) + N(^2D)$: 36 states do correlate ($^3\Pi$ and $^1\Pi$ states in green).

⇒among these 40 states, some purely repulsive might contribute to the 8(±4) % that branch into the $C^- + N$ channels.

•73 states correlate to the 10 neutral limits

- •Lavendy *et al* : 13 curves of Σ^+ and Π symmetries displayed in blue

  Nine of them are bound states!

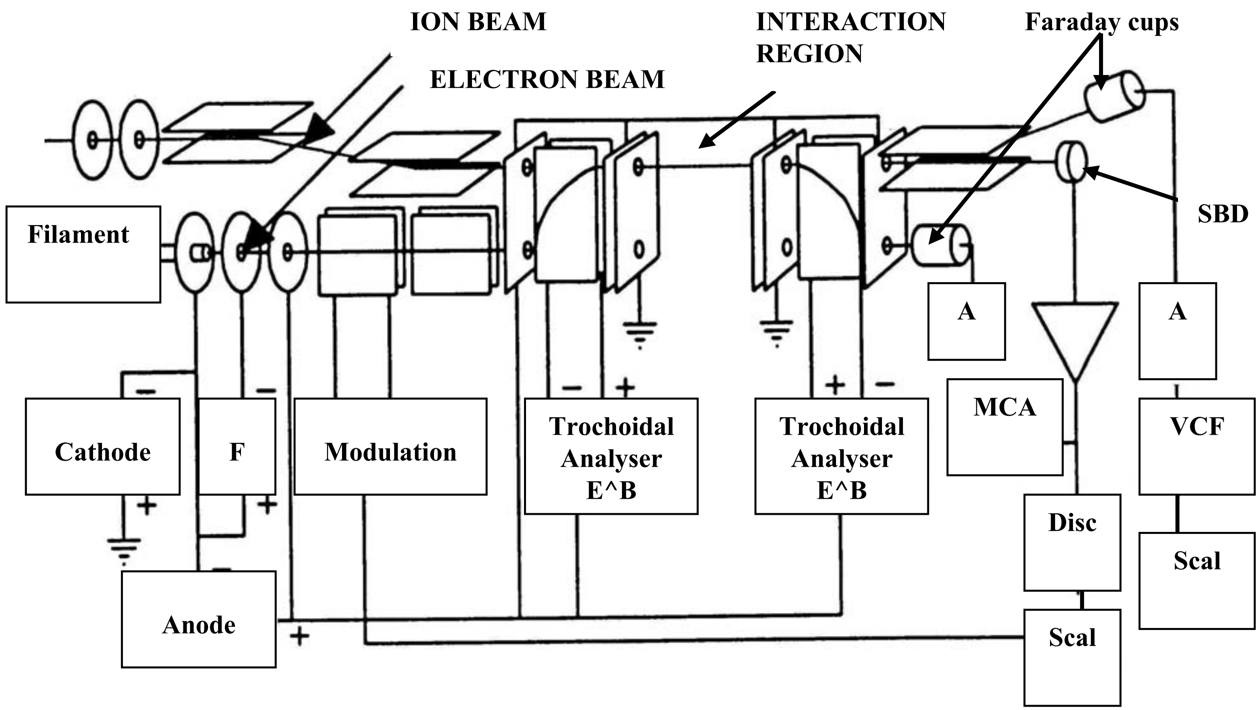
- •States of Σ^-, Δ, Φ and Γ symmetries unknown.

A majority could be associated with bound states !

⇒the pure detachment into CN + 2e is overwhelmingly dominant!

⇒the upper $^2\Sigma^+$ (5, 6) and $^2\Pi$ (6) states could very well contribute to the very weak dissociation C+N channels.

MEIBE (Western-Ontario Canada) : a single pass merged beam setup



HCN^+/ HNC^+ + e

HCN^+

- Well documented in the literature

  ⇒ Ground state : $^2\Pi$.

- Vibrational structures

•CH stretch	3049.9 cm^{-1}	(J. Chem. Phys., 97, 1664, (1992)).
•Bend	760 cm^{-1}	(Chem. Phys. Lett., 23, 472, (1973)).
•CN stretch	1800 cm^{-1}	(J. Electron Spectrosc. Relat. Phenom., 7, 119, (1975)).

…same sort of data for the A and B states…

- Dynamical properties

  - interchange reactions with atoms/molecules

  (ex : J. Chem. Phys., 109, 1743 (1998) or J. Phys. Chem., 99, 12204 (1995)).

- Interstellar chemistry considered by some authors.

HNC^+ : less documented

⇒ Ground state : $^2\Sigma^+$

-Vibrational structures

•NH stretch	3365.0 cm^{-1}	(J. Chem. Phys., 97, 1664, (1992)).
•Bend	577.6 cm^{-1}	(J. Chem. Phys., 97, 1664, (1992)).
•NC stretch	2195.2 cm^{-1}	(J. Chem. Phys., 97, 1664, (1992)).

…little amount of data for the A state…

Some experimental facts…

-Interest in the isomerization chemistry

HNC^+: more stable than HCN^+ (0.98eV).

-Two different gas mixtures within the source

❖ *8.35% N_2 – 8.35% CH_4 – 83.3% CO_2*

⇒ HNC^+ : 96.2%.

⇒ HCN^+ : 3.8%.

❖ *90% N_2 - 10% CH_4* (efficient isomerization reaction of HCN^+/HNC^+ with CH_4)

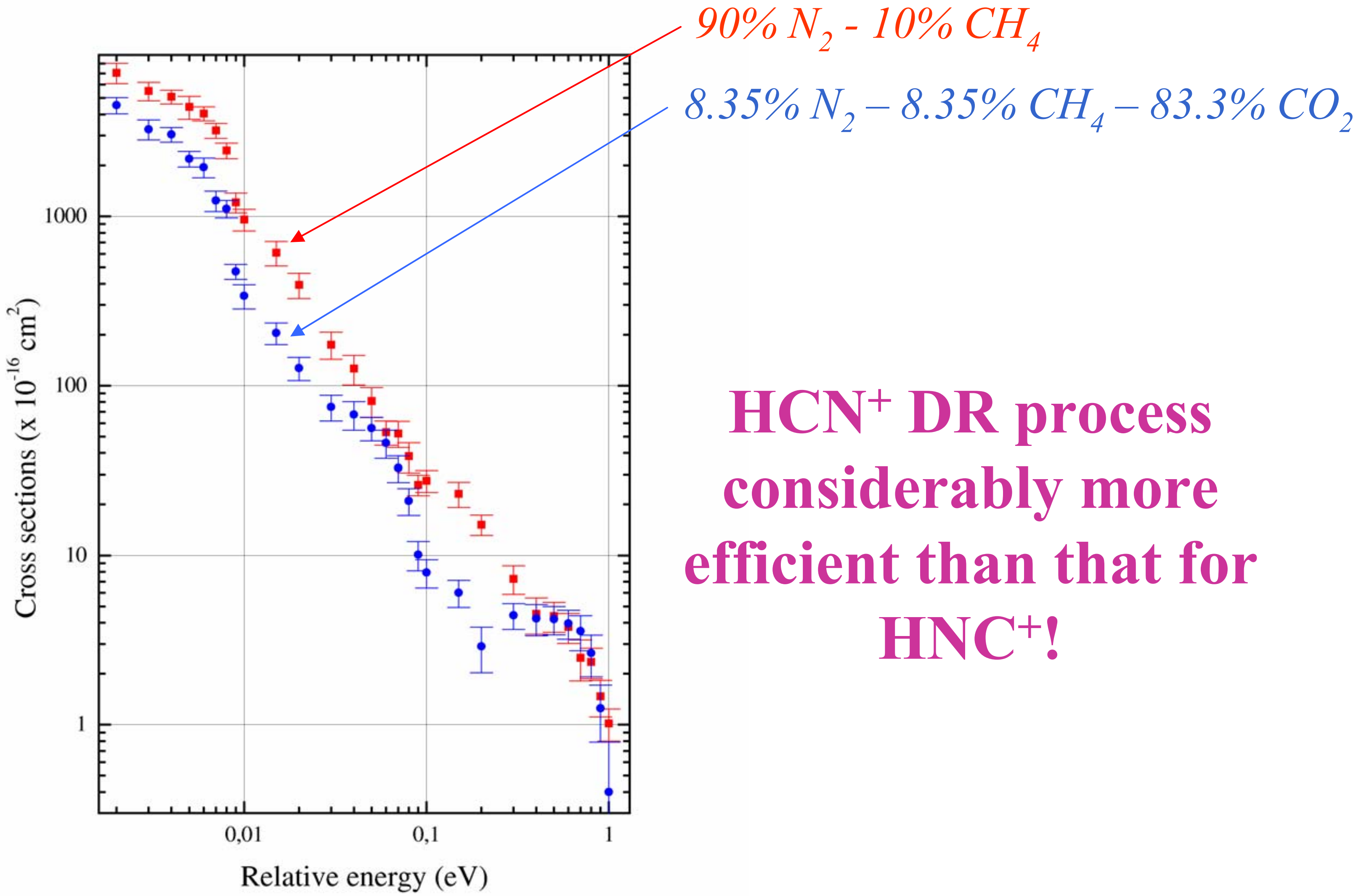
⇒ HNC^+ : 87.5%.

⇒ HCN^+ : 12.5%.

-Internal excitation of the target ions

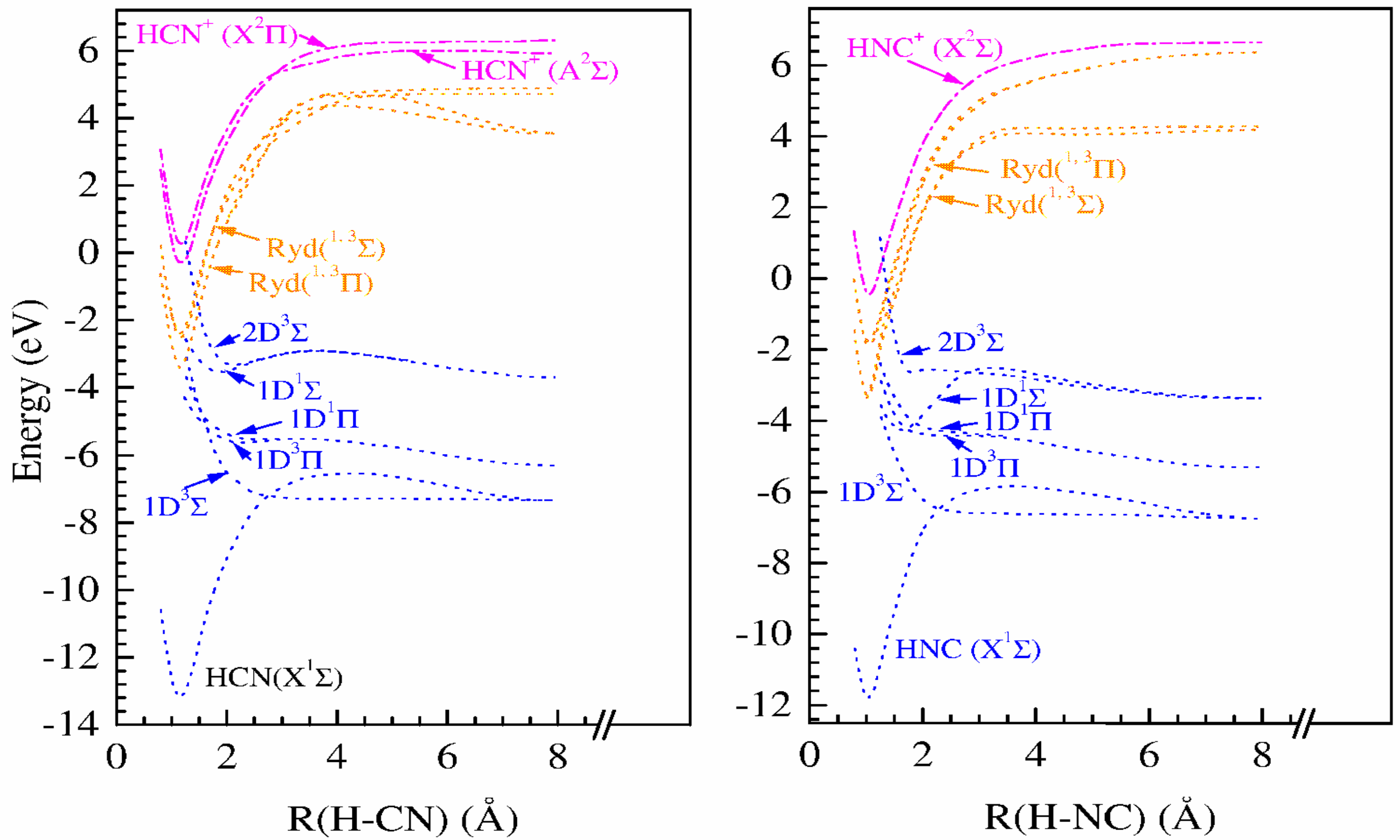
❖ HCN^+: $X^2\Pi$, $A^2\Sigma^+$ (radiative lifetime : 3ms) and $B^2\Sigma^+$ (0.40 and 5.25 eV above X state).

❖ HNC^+: $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ (2.13 and 10.63 eV).



HCN$^+$ DR process considerably more efficient than that for HNC$^+$!

POTENTIAL ENERGY SURFACES IN THE QUASI-DIABATIC REPRESENTATION (see also D Talbi)



Several curve crossings between repulsive states (of different symmetries) and Rydberg states ⇒"Indirect" process.

$C_4^- + e$

Motivations

-Fundamental

❖Collisional properties of the system $C_4^- + e$ (detachment/dissociation) and study of the dianions C_4^{2-} (Structures, energetics…).

-More applied…

❖Possible astrophysical significance of the C_n species as contributors to the formation of the long-chain cyanopolyynes, carbon dust, PAH's and DIB's.

❖Involvement of large C_n clusters in the nucleation of carbon particles and formation of soot in hydro-carbon flames.

Isomeric forms of the C_4^- anion

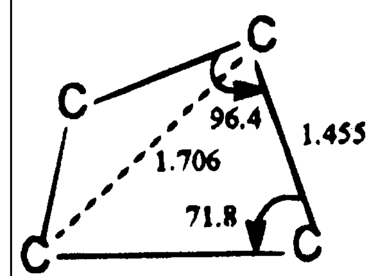
-0.5e -0.5e -0.5e -0.5e Mulliken analysis

Linear structures

-1.0e

-0.5e

-0.5e



Three membered ring

(C_{2v} symmetry)

37.7 kcal mol^{-1}

« Rhombus »

(D_{2h} symmetry)

39.0 kcal mol^{-1}

Non planar diamond shaped

(C_{2v} symmetry)

(57.7 kcal mol^{-1})

Szczepanski *et al*

JPCA, 101, 1841, (1997)

What is known about C_4^-

$C_4^-(X^2\Pi_g)$ ground state

-Schmatz *et al* (Int J Mass Spectrom Ion Proc, 149/150, 621, (1995))

→ symmetric stretch vibrational frequencies predicted to be 2082.7 and 911.3 cm^{-1} for υ1 and υ2, respectively (Ab-initio)

-Maier's group (JCP, 103, 48, (1995))

→ several electronic transitions $C^2\Pi_u$ - $X^2\Pi_g$, $A^2\Sigma^+_g$ - $X^2\Pi_g$, $B^2\Sigma^+_u$ - $X^2\Pi_g$, $(2)^2\Pi_u$ - $X^2\Pi_g$ and $(3)^2\Pi_u$ - $X^2\Pi$ (Experiments in matrix)

→ υ1 and υ2 determined + symmetric bending mode υ4 of 396 cm^{-1}

-Zhao *et al* (JCP, 105, 2575, (1996) – Experiments in gas phase)

→two photon photodetachment techniques: for the $C^2\Pi_u$ - $X^2\Pi_g$ transition, (JPCP, 228, 293, (1998) – Experiments in gas phase)

→ vibrationless origins of the $(2)^2\Pi_u$ - $X^2\Pi_g$ and $(3)^2\Pi_u$ - $X^2\Pi$ bands differ only by 0.3 and 0.5 % to that was found in the matrix work

-Szczepanski *et al* (JPCA, 101, 8788, (1997))

→ υ3 antisymmetric stretch

Various open channels over the energy range…

$C_4 \quad e$

$C_4 \quad 2e \quad 3.9\ eV$

$C_2 \quad C_2 \quad e \quad 6.2\ eV$

$C_3 \quad C \quad e \quad 6.4\ eV$

$C_3 \quad C \quad e \quad 7.2\ eV$

$C_3 \quad C \quad 2e \quad 8.4\ eV$

$2C_2 \quad 2e \quad 9.5\ eV$

$C_2 \quad C \quad C \quad 10.9\ eV$

$C_2 \quad 2C \quad e \quad 12.1\ eV$

$C_2 \quad 2C \quad 12.9\ eV$

$C_2 \quad C \quad C \quad e \quad 14.1\ eV$

$C_2 \quad 2C \quad 2e \quad 15.4\ eV$

$2C \quad 2C \quad 18.8\ eV$

$C_3 \quad C \quad 3e \quad 19.3\ eV$

$C_3 \quad C \quad 3e \quad 19.7\ eV$

$3C \quad C \quad e \quad 20.0\ eV$

$C_2 \quad C_2 \quad 3e \quad 20.9\ eV$

$4C \quad 2e \quad 21.3\ eV$

$C_2 \quad C \quad C \quad 2e \quad 23.0\ eV$

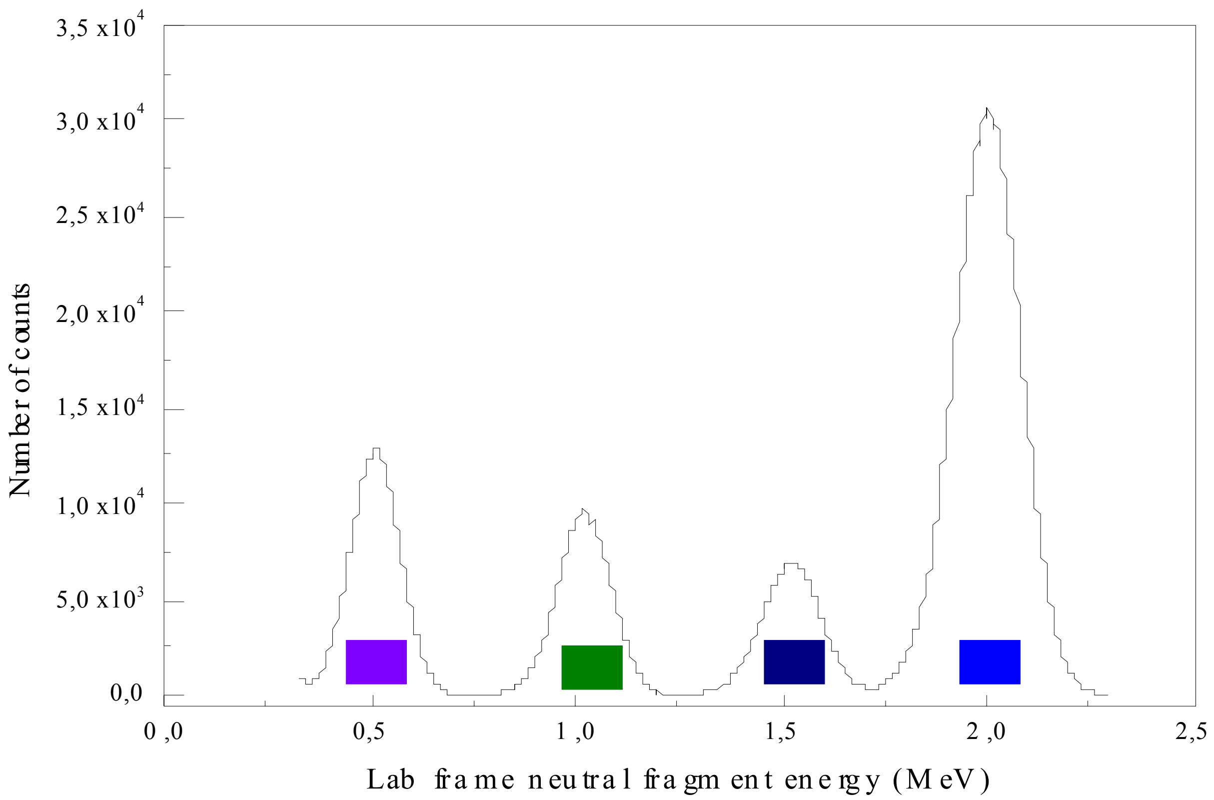
$C_2 \quad C \quad C \quad 2e \quad 25.0\ eV$

$C_2 \quad C \quad C \quad 2e \quad 25.5\ eV$

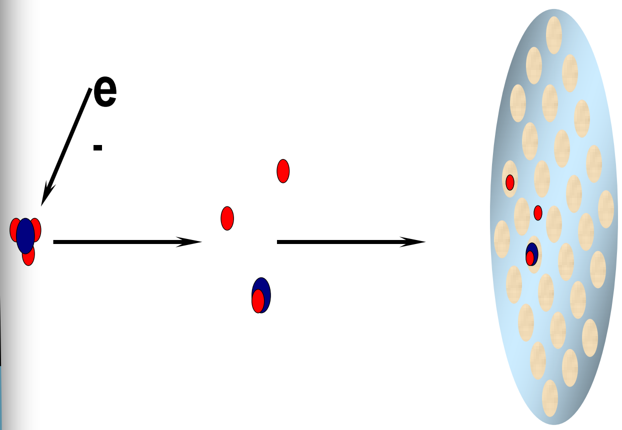
$C_2 \quad C \quad C \quad 3e \quad 26.2\ eV$

$C_2 \quad 2C \quad 3e \quad 26{,}8\ eV$

Detection of the neutral fragments: MCA spectrum



Within one channel, how to get the branching fractions?



N(C)

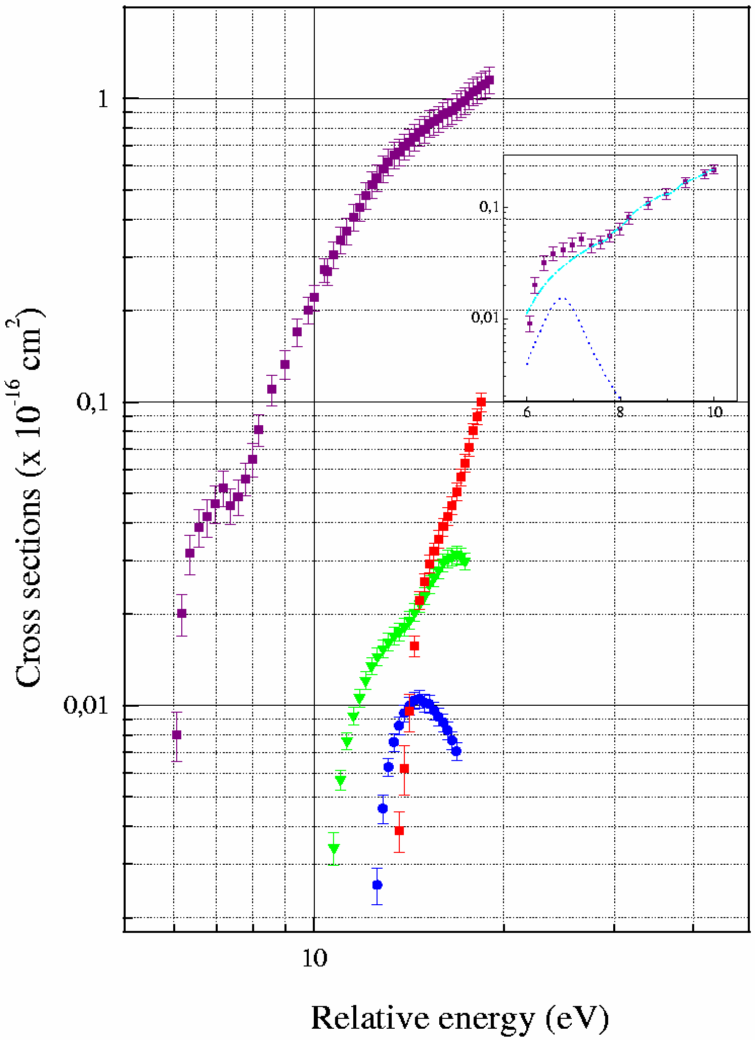
N(2C)

N(3C)

N(4C)

$$=[M]\, N_{i=1-22}$$

Grid inserted in front of the SBD detector



-Apparent threshold : at ~ 6eV

Rhombus ?

Photothreshold at 2.2 eV + contribution due to the Coulomb repulsion

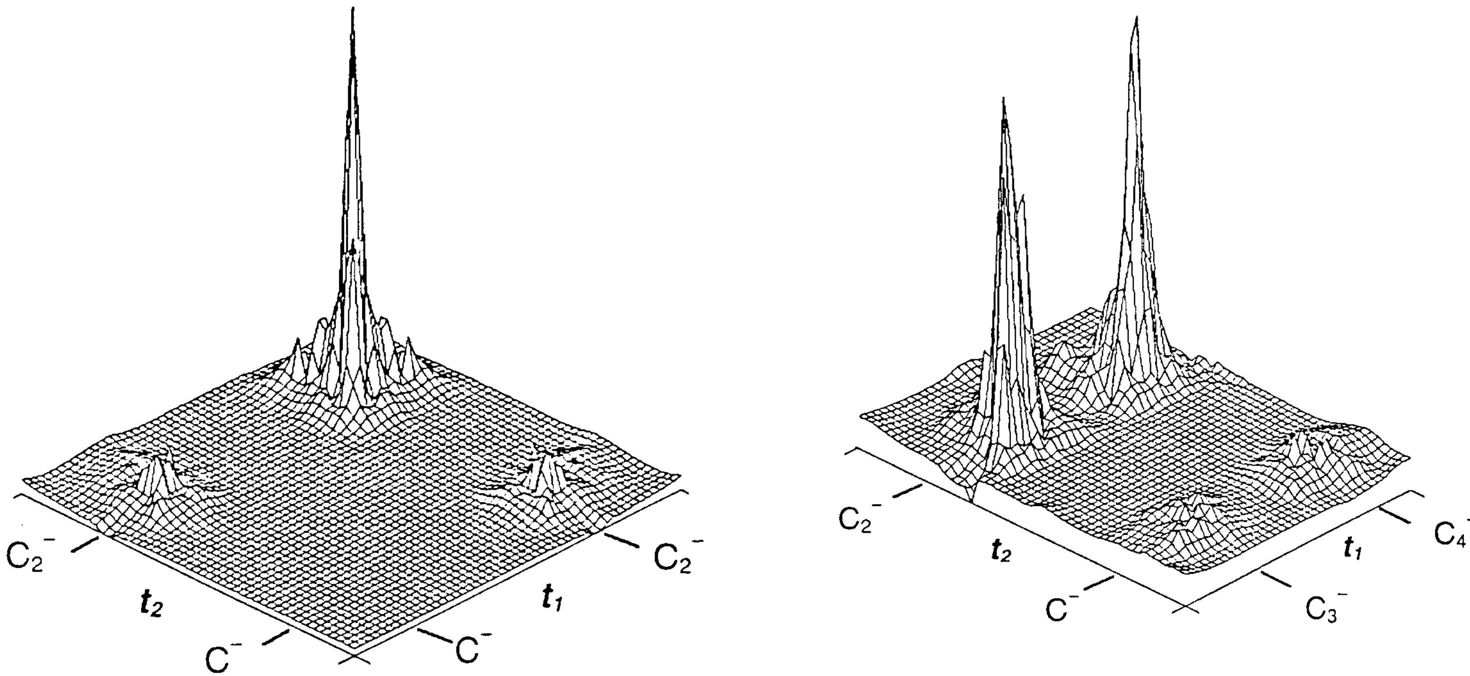
- Cross-section magnitude on top: ~1-2 x10^{-16} cm^2

-Detachment dominant over dissociation (~95%)

-Near threshold resonance due to the dianion (0.7fs)

Dianionic studies of small carbon clusters

(laser ablation of graphite)



Monitoring of the produced ion-pair fragments in dianionic decay: multi-coincidence time-of-flight techniques

Mathur *et al* CPL, 277, 558, (1997).

Conclusion

Results on

- $CN^+ + e$

  -CROSS SECTIONS (Diatomic) +BRANCHING RATIOS (Manifold of exothermic channels)

- $CN^- + e$

  -THRESHOLD, DETACHMENT OVER DISSOCIATION (Grid technique)

- $HCN^+/HNC^+ + e$

  -IZOMERISATION CHEMISTRY, CROSS SECTIONS (Large differences between the two isomers : rationalized)

- $C_4^- + e$

  -THRESHOLD, DETACHMENT OVER DISSOCIATION and DIANION

SPECIAL THANKS !

- **M Larsson and his group** (Stockholm University)
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- **JBA Mitchell** (University of Western Ontario and Rennes 1)