

CRESUSOL : un instrument pour déterminer la cinétique et des rapports de branchement des collisions réactives entre espèces neutres aux basses températures

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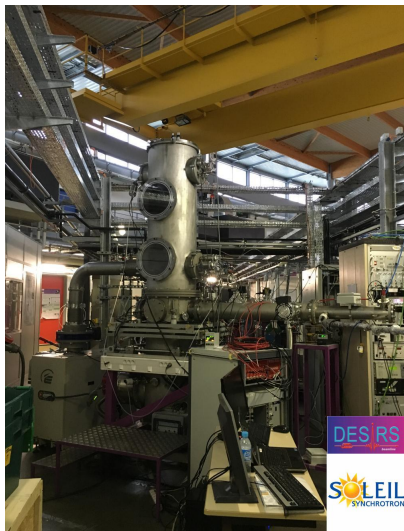
GDR EMIE, 12-15 novembre 2018, Nouan-le-Fuzelier



Context

- ▶ More than 200 molecules detected in interstellar media, revealing a rich chemistry
- ▶ Kinetics of many collisional processes remain poorly known, especially at low temperature
- ▶ Study of collisional processes provides also information on reaction mechanisms, including first steps of nucleation
- ▶ We develop an instrument to determine the rate coefficient and branching ratio of collisional processes at low temperature

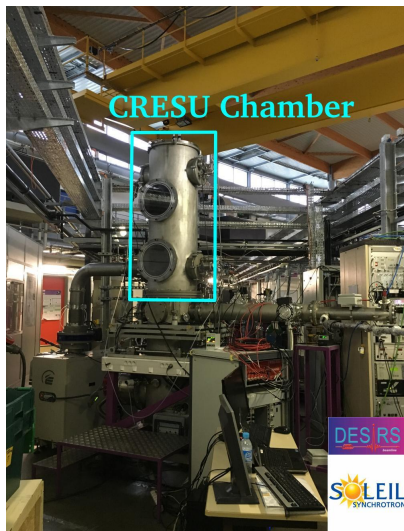
Our experimental approach : uniform supersonic flow coupled with photoionization mass spectrometry



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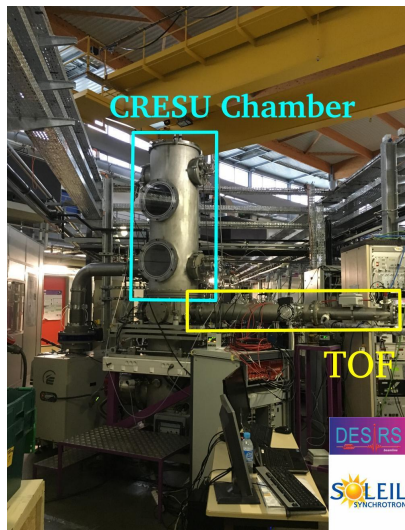
SOLEIL
SYNCHROTRON

Our experimental approach : uniform supersonic flow coupled with photoionization mass spectrometry



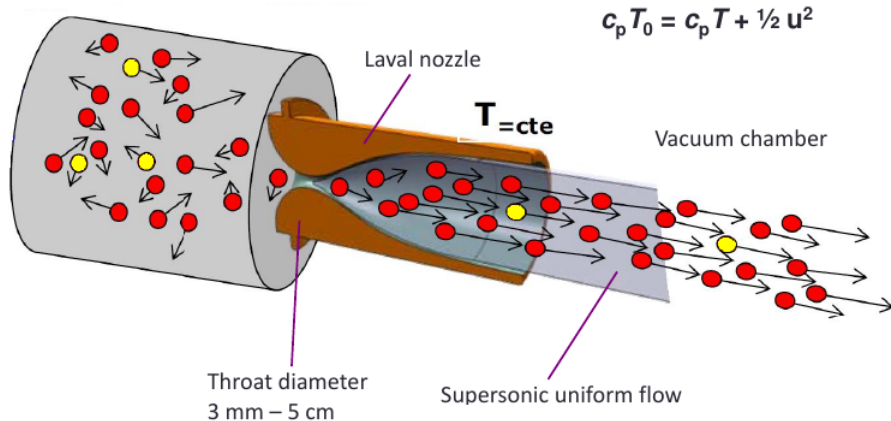
▷ $\left. \begin{array}{l} \text{The CRESU technique} \\ \text{uniform supersonic flow} \end{array} \right\} \text{reactor}$

Our experimental approach : uniform supersonic flow coupled with photoionization mass spectrometry



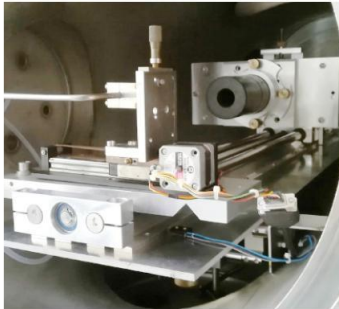
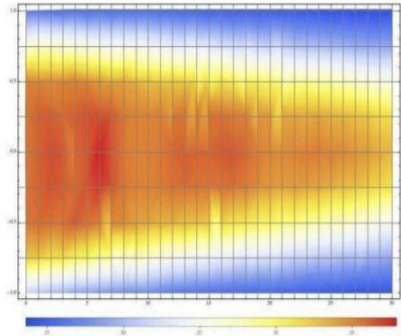
- ▷ The CRESU technique
uniform supersonic flow
 - ▷ Mass Spectrometer
photoelectron-photoion coincidence
 - ▷ Synchrotron radiation
tunable ionization source
- } reactor
 } detector

The reactor : a uniform supersonic flow



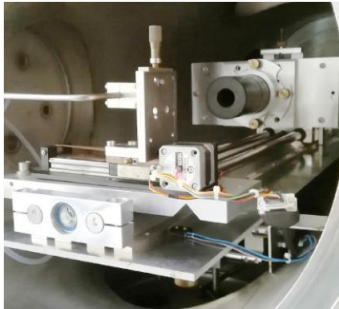
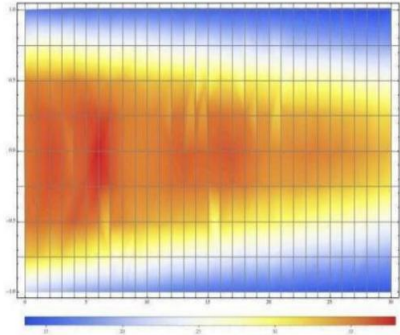
- ▷ Abiabetic expansion
- ▷ Thermal equilibrium
- ▷ $T = 10\text{K} - 250\text{K}$, $n = 10^{16} - 10^{17} \text{ cm}^{-3}$
- ▷ Uniformity lenght : 20-60 cm (200 – 900 μsec)

The reactor : a uniform supersonic flow



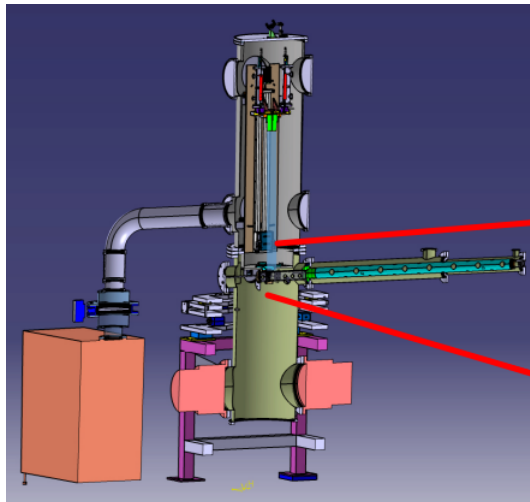
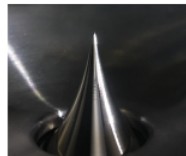
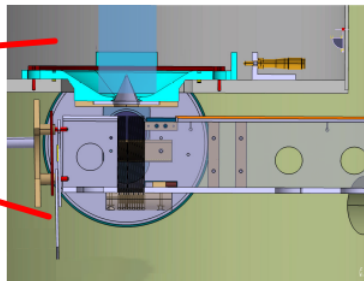
- ▷ numerical resolution (J.B. Marquette)
- ▷ spectroscopy or pitot measurement

The reactor : a uniform supersonic flow

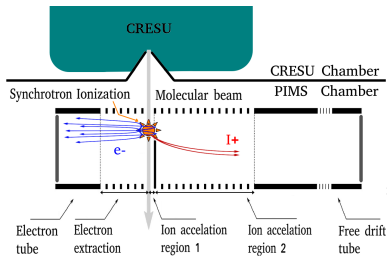


- ▷ numerical resolution (J.B. Marquette)
- ▷ spectroscopy or pitot measurement
- ▷ hydrodynamic chopper or piezoelectric stack
- ▷ CFD simulation
- ▷ 3D printing

The detector : a continuous time of flight mass spectrometer

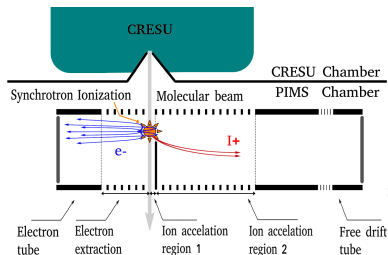


Photoelectron photoion coincidence spectrometry (PEPICO)



- ▷ Current sensitivity
 $\sim 10^{11} \text{ molecule} \cdot \text{cm}^{-3}$
- ▷ Current resolution
 $m/\Delta m \sim 800$
- ▷ Continuous measurement
- ▷ Robust
- ▷ Possible evolution : VMI

Photoelectron photoion coincidence spectrometry (PEPICO)

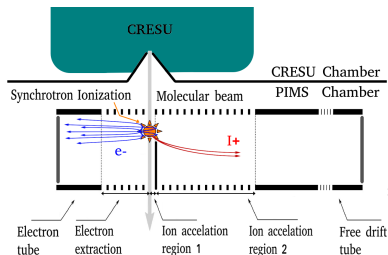


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Ionization source : synchrotron radiation

- ▷ Tunability allows :
 - Threshold ionization to minimize fragmentation
 - Isomer discrimination through photoionization spectra
- ▷ Great brilliance and very thin beam section

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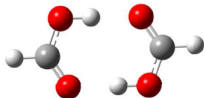
- ▷ Tunability allows :
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But the synchrotron is not readily accessible ...

Experimental results

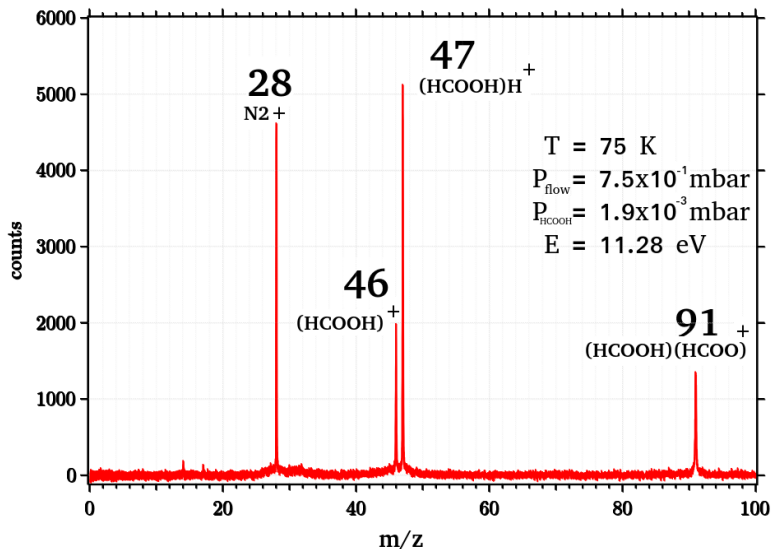
- Kinetics of formic acid dimerization at 52K and 75K
- Reaction products detection at 95K : $\text{C}_2\text{H} + \text{C}_2\text{H}_2 \longrightarrow \text{C}_4\text{H}_2 + \text{H}$

Kinetics of formic acid dimerization at 52K and 75K

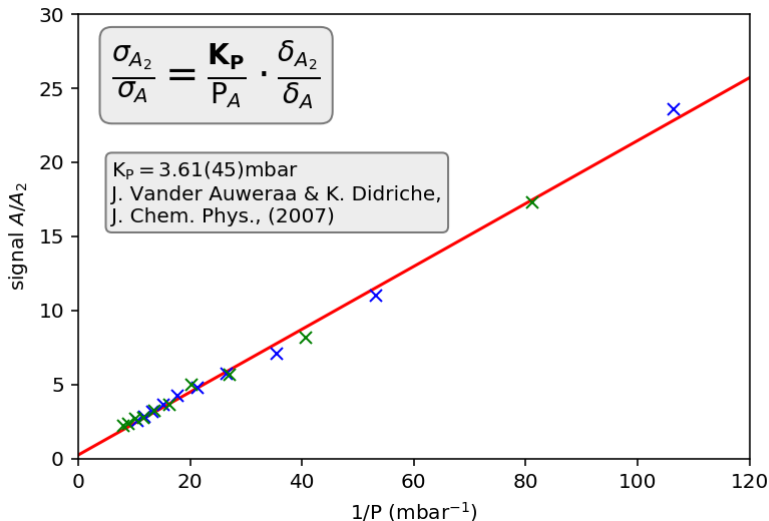


- ▷ First steps in a fundamental mechanism of nucleation
- ▷ Many studies in the literature about this system but few about kinetics and less at low temperatures
- ▷ Formic acid has been very recently observed in planetary disks, and this simplest acid stands as a basis for synthesis of more complex carboxylic acids used by life on Earth (C. Favre & al.)
- ▷ How fast is the dimerization process ?
- ▷ Is the equilibrium between monomers and dimers reached along the CRESU flow in our experimental conditions or do larger clusters also form ?

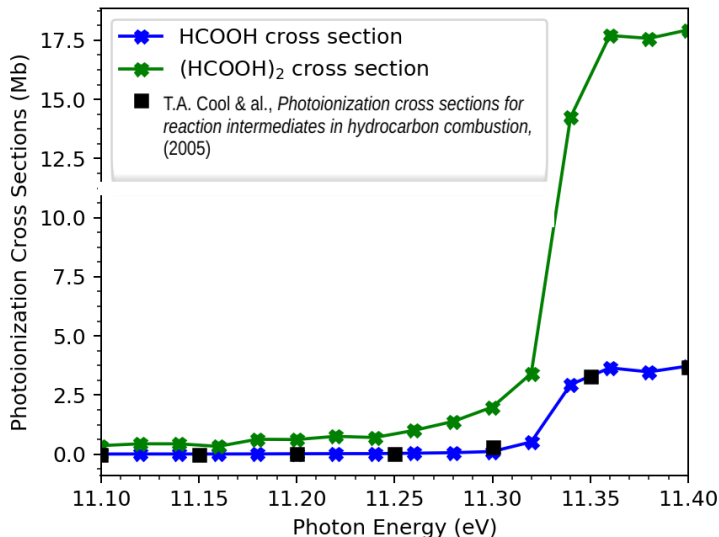
Mass spectrum in the CRESU flow



Experiment at room temperature

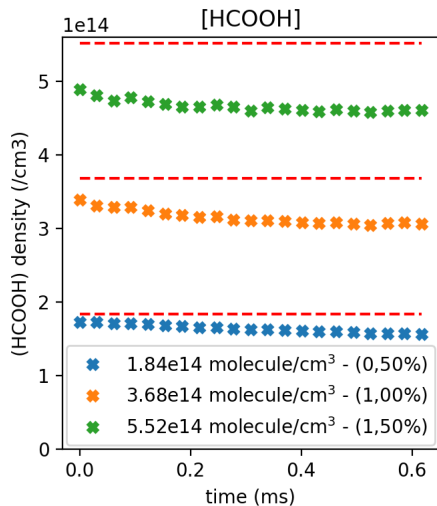
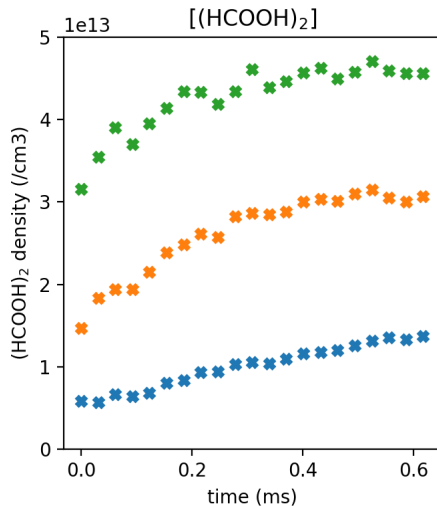


Photoionization Absolute Cross Section (at room temperature)

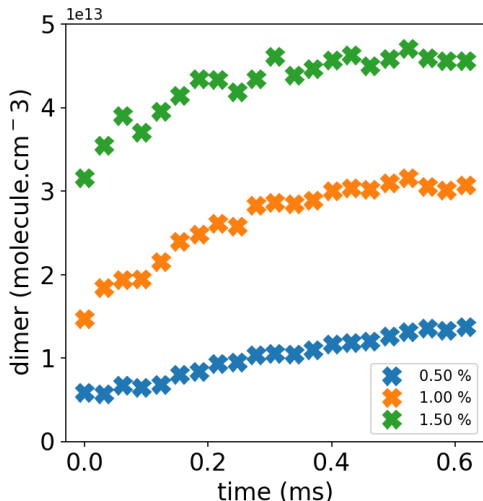


Kinetic traces of monomer and dimer

temperature 52K, density $3.7 \times 10^{16} / \text{cm}^3$



Kinetic model



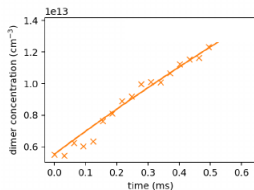
Far from the equilibrium :



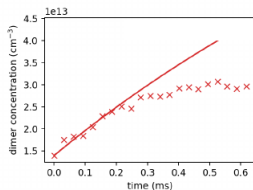
$$\frac{d[A_2]}{dt} = k_1[A]^2$$

- ✱ 1.84e14 molecule/cm³ - (0,50%)
- ✱ 3.68e14 molecule/cm³ - (1,00%)
- ✱ 5.52e14 molecule/cm³ - (1,50%)

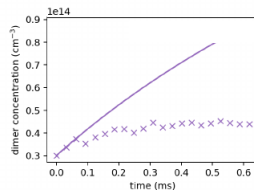
Kinetic model



(a) Concentration 0,5 %

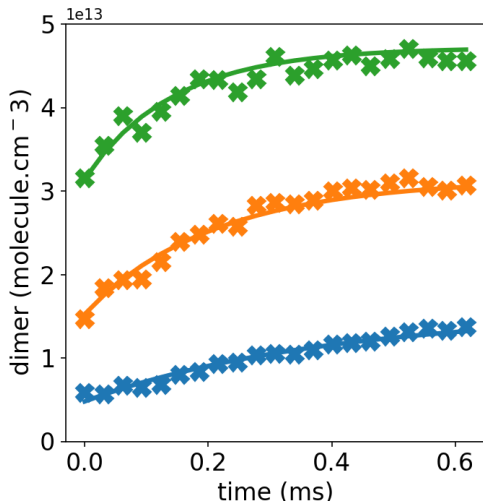


(b) Concentration 1,0 %



(c) Concentration 1,5 %

Kinetic model

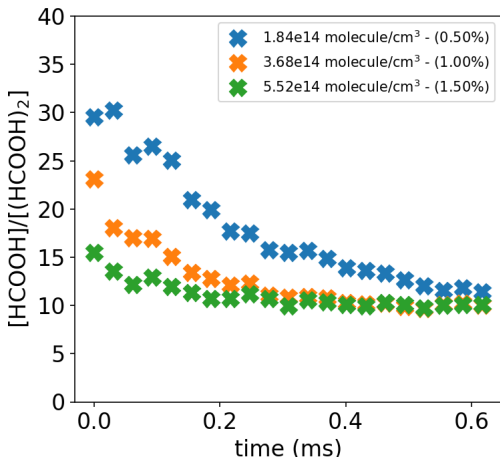


$$\frac{d[A_2]}{dt} = k_1[A]^2 - \text{Loss}$$

Bimolecular rate coefficient :

$$k_1 = (1.2 \pm 0.6) \times 10^{-12} \text{ cm}^3/\text{s}$$

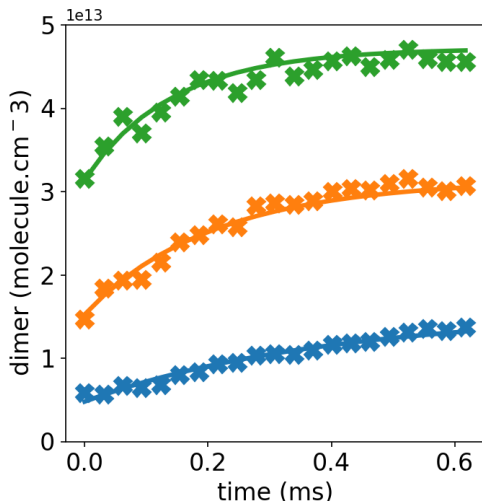
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$$\text{Loss} = \alpha \times [\text{A}] \times [\text{A}_2]$$

$$\alpha = 9.7 \times k_1$$

Kinetic model



$$\frac{d[A_2]}{dt} = k_1[A]^2 - \alpha[A][A_2]$$

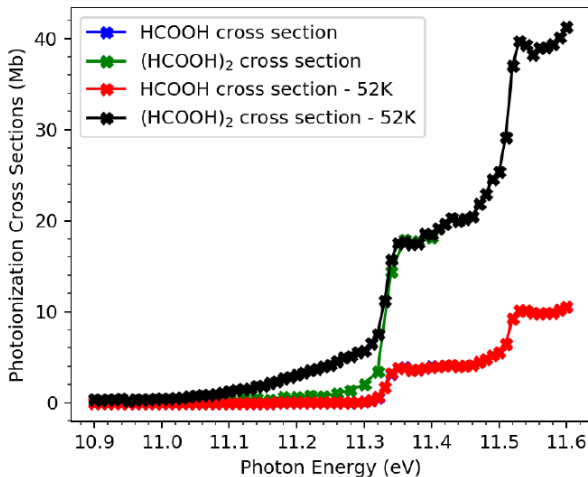
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Kinetic model / PIE



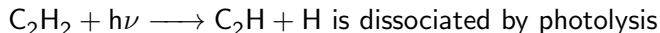
Dimerization of Formic Acid

- ▷ At low temperatures, the system is not as simple as it looks
- ▷ Possible formation and dissociation of trimers
- ▷ At 52K, $P_{\text{flow}} = 0.26$ mbar :
 $k_1 = (1.2 \pm 0.6) \times 10^{-12} \text{ molecule.cm}^3/\text{s}$
- ▷ At 75K, $P_{\text{flow}} = 0.68$ mbar :
 $k_1 = (0.8 \pm 0.4) \times 10^{-12} \text{ molecule.cm}^3/\text{s}$

Reaction products detection at 95K :



- 1 C_2H_2 is introduced in the reservoir (10^{15} cm^{-3})
- 2 With an excimer laser ArF at 193 nm :

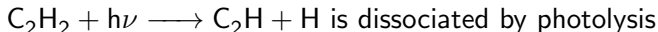


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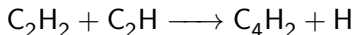
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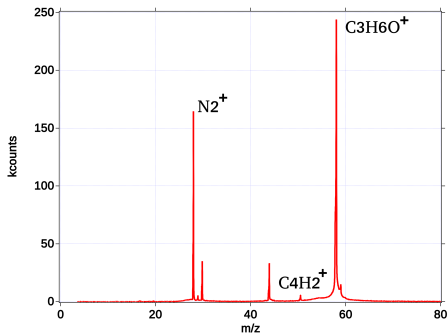
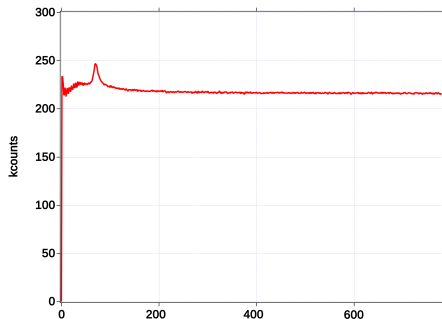


③ C_2H radical is produced all along the CRESU flow ($3.5 \times 10^{11} \text{ cm}^{-3}$)

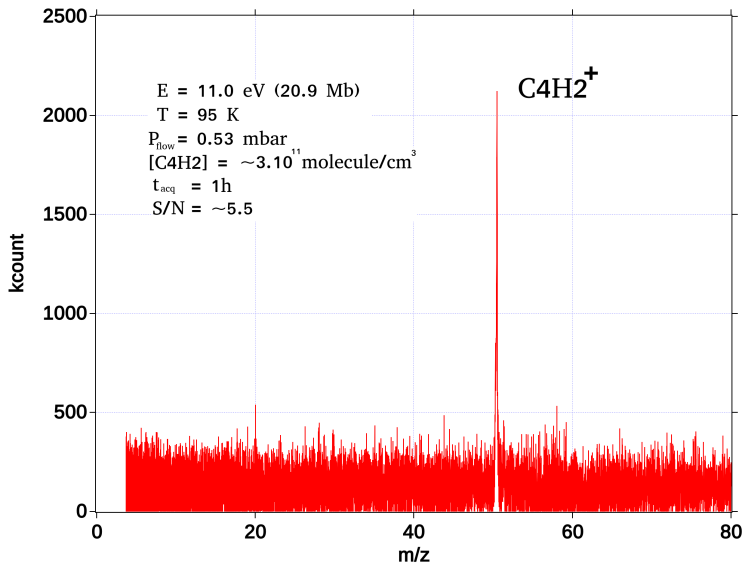
④ The following takes place :



Ion and electron spectrum



Background subtracted mass spectrum at 95K



Conclusion

Many possibilities with CRESUSOL !

- ▶ An experimental challenge to combine the CRESU reactor with the synchrotron, and it works !
- ▶ Unique apparatus to investigate kinetics of nucleation
- ▶ Brings knowledge about neutral-neutral reactions playing a key role in the astrophysical environments
- ▶ Low temperature favors quantum effects
- ▶ In the coming months and years : studies of reactions involving other radicals down to 10K

Acknowledgements

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- I.R. Sims
- J. Thiévin
- Technical Staff

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- J.F. Gil
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