International Symposium and Workshop on Astrochemistry - ISWA 2016

Theoretical/Experimental Investigations of the Effects of Irradiation of Astrophysical ices

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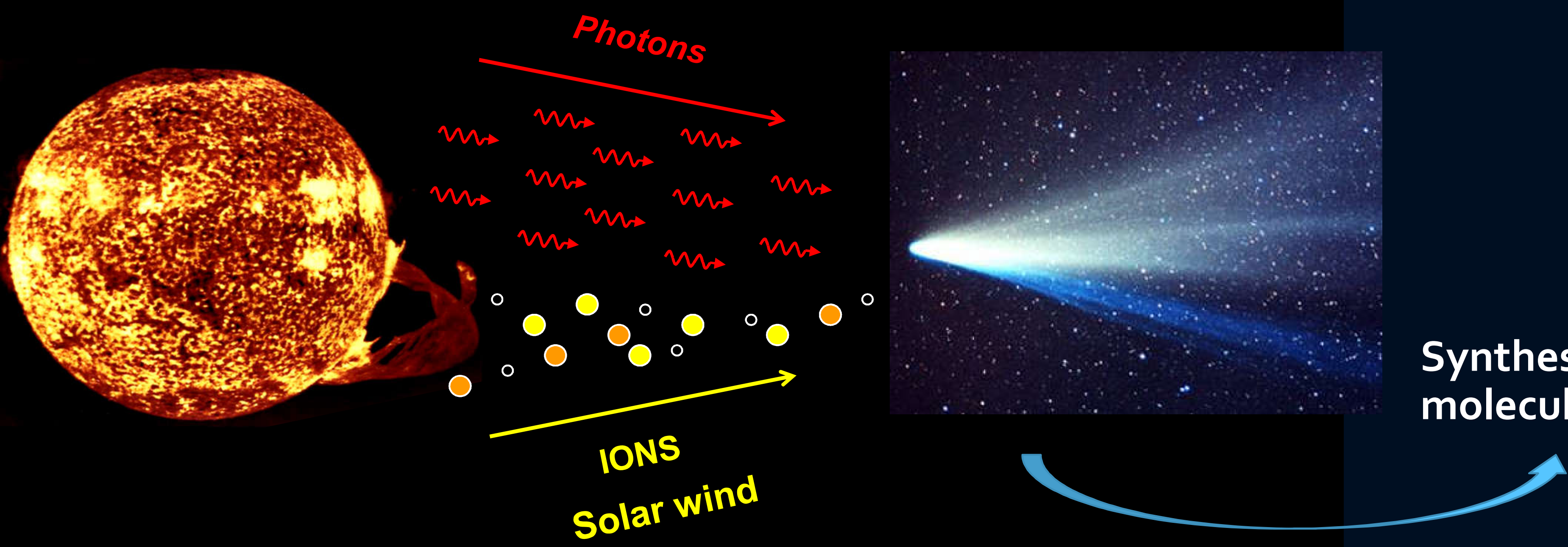
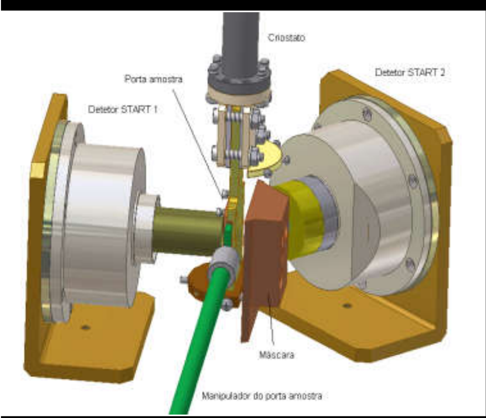
Astrophysical ices are impinged by radiation and solar wind

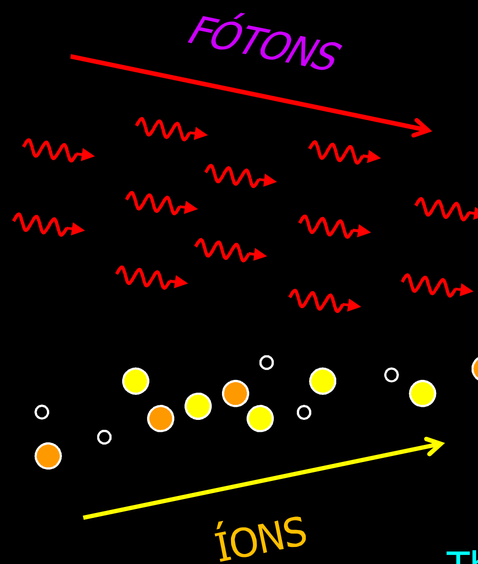


Synthesis of new molecules

Experiments used to reproduce the conditions of interstellar medium



Source of ions (^{252}Cf)



The "astrophysical ice" is obtained in vacuum chambers

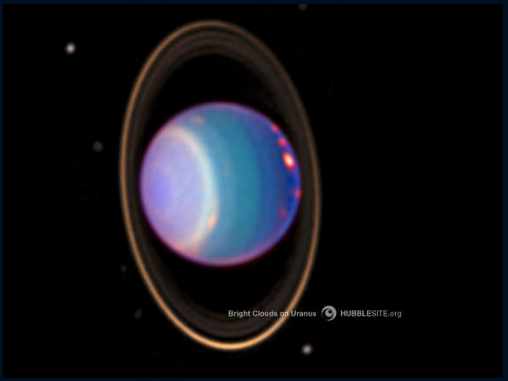
The sun is replaced by a source of ions and photons

Our Goals

- Understand the synthesis of complex molecules in the interstellar medium
- Comprehend the planetary atmospheres formation
- Assist experimental measurements
  - Determination of structural and electronic parameters
  - Evaluation of relative stability of observed species
  - Describe the reactivity of formed species

Systems studied

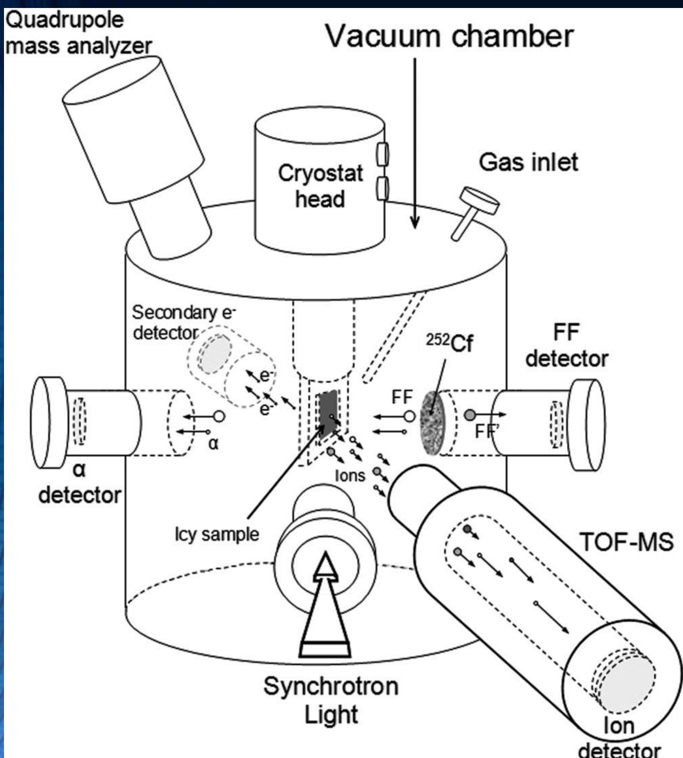
- **Negative and positive formic acid clusters**
  - **Formed due to irradiation of frozen formic acid by ^{252}Cf fission fragments**
- **Negative and positive hydrocarbon clusters**
  - **Formed due to irradiation of frozen hydrocarbons by ^{252}Cf fission fragments and heavy ions**
- **Methane ions reactivity**
  - **Reactivity of such ions should help the knowledge about the synthesis of new molecules after bombardment of icy methane**



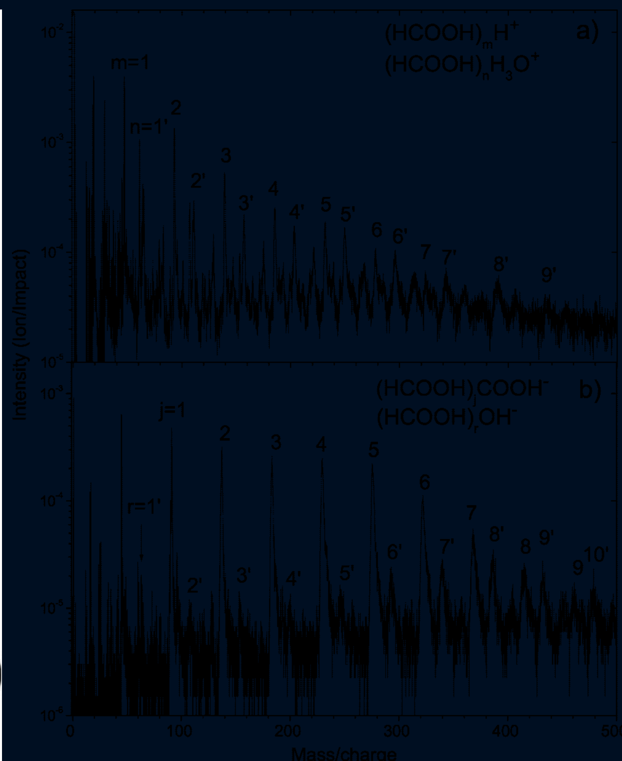
2.4% of CH_4 in the atmosphere

Hydrocarbons and formic acid has been observed in icy comets

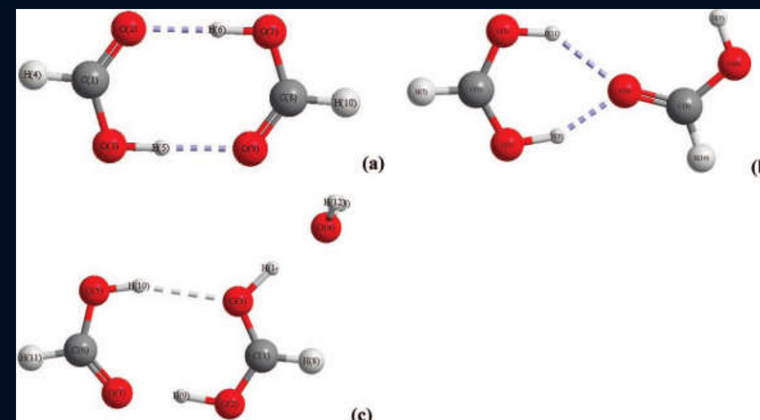
Formic Acid Clusters



Experimental apparatus



Experimental results

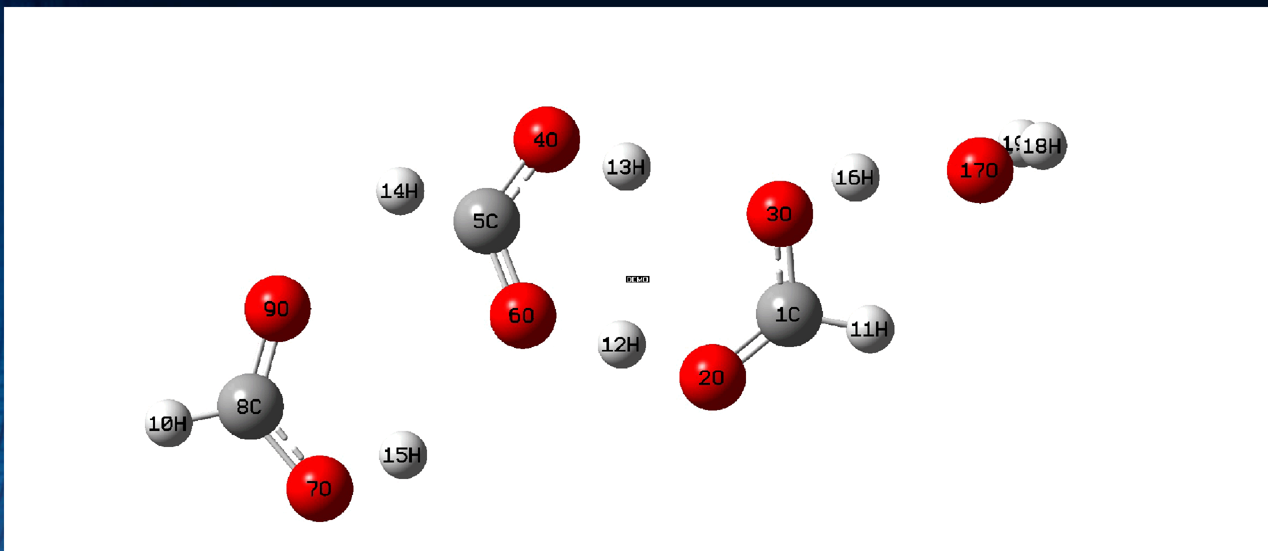


Optmized geometries at MP2/6-311G**

a) Neutral dimer
b) $(HCOOH)nH^{+}$
c) $(HCOOH)nH_3O^{+}$

D.P.P. Andrade et al. Journal of Electron Spectroscopy and Related Phenomena 155 (2007) 124–128
D.P.P. Andrade et al. J. Phys. Chem. C 2008, *112*, 11954–11961

Formic Acid Clusters



Cluster stability is related to hydrogen migration between formic acid unities

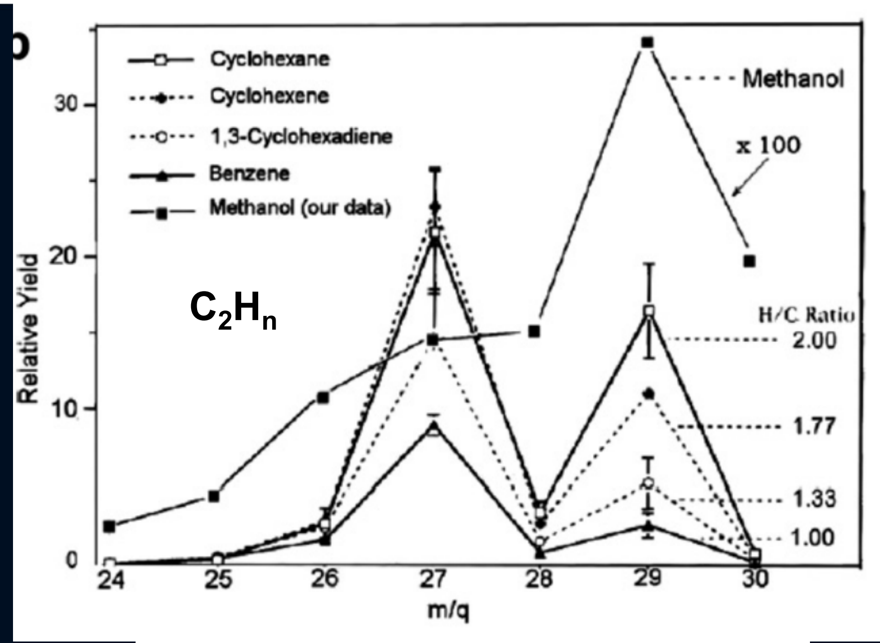
The right assignment of $(HCOOH)_nH_3O^+$ clusters is $(HCOOH)_n(H^+)H_2O$

Born-Oppenheimer molecular dynamics at PBE1PBE/6-311G. Trajectory of 652 fs at 56K.**

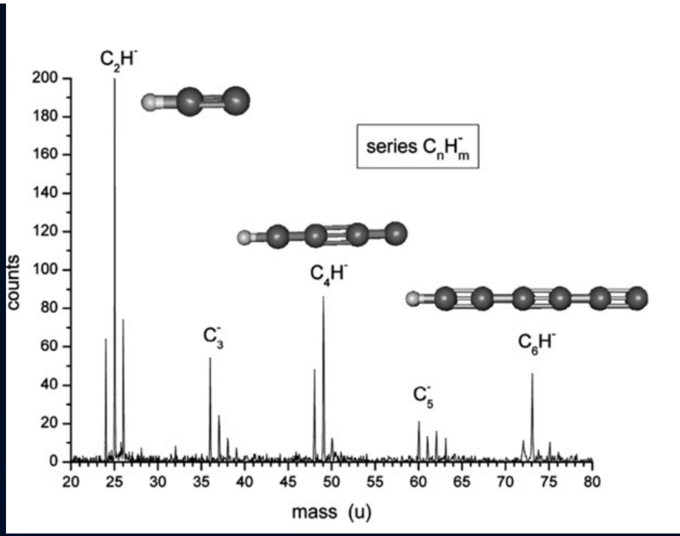
Baptista et al. J. Phys. Chem. A 2008, 112, 13382–13392

Hydrocarbon clusters

- **Can be observed after irradiation of solid hydrocabons, methanol, cholesterol and other targets by heavy ions and fission fragments**
- **It is observed regular patterns despite of the original target**
- **Cluster reactivity depends upon its structure**



PDMS desorption yields from different targets



F. Fantuzzi et al Chemical Physics 410 (2013) 109–117

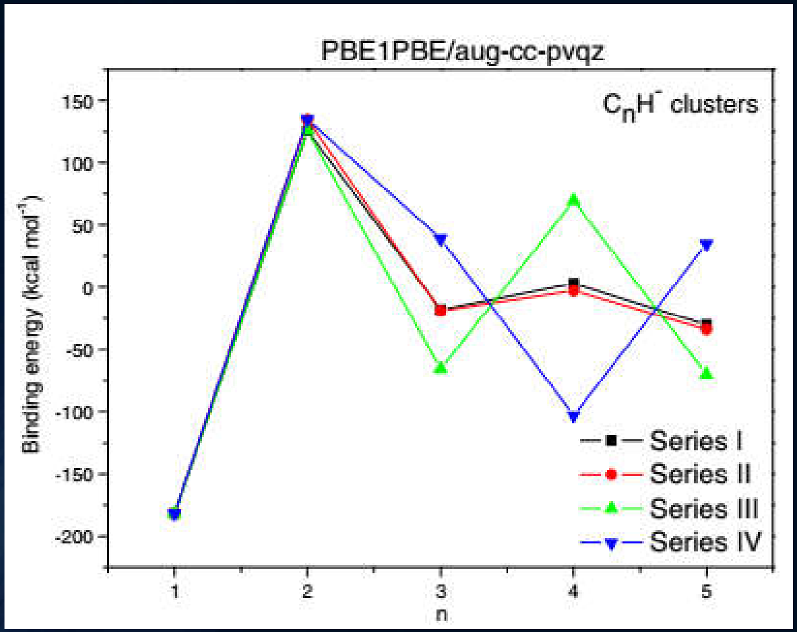
Hydrocarbon clusters

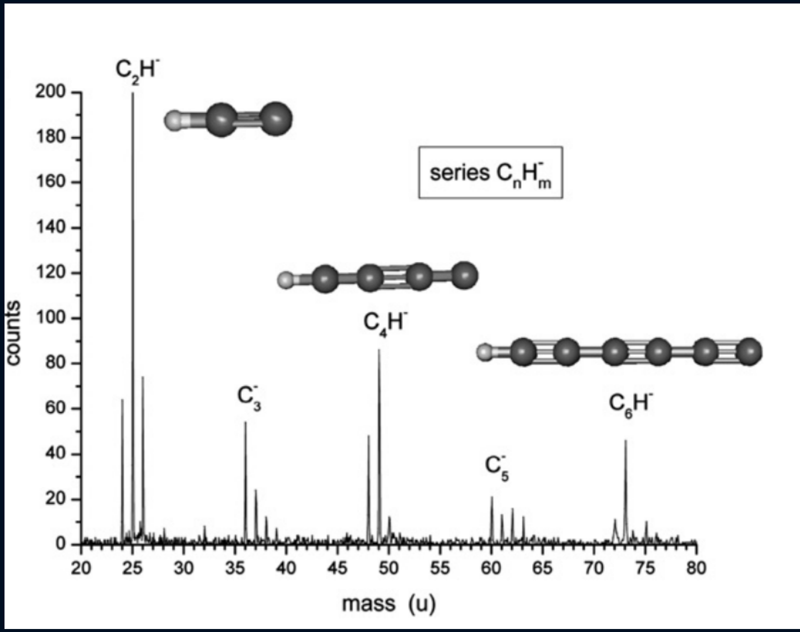
- Were proposed the possible geometries for each cluster
- The relative stability of structures were evaluated

- Negative clusters
  - Geometry optimization at B3LYP and PBE1PBE level
  - Single point calculations at CCSD level
  - Basis: 6-311++G**, 6-31++G**, aug-cc-pvTZ, aug-cc-pvQZ

- Positive clusters
  - Geometry optimization at B3LYP level
  - Single point calculations at CCSD and CRCC(2,3) levels

Hydrocarbon clusters-Results

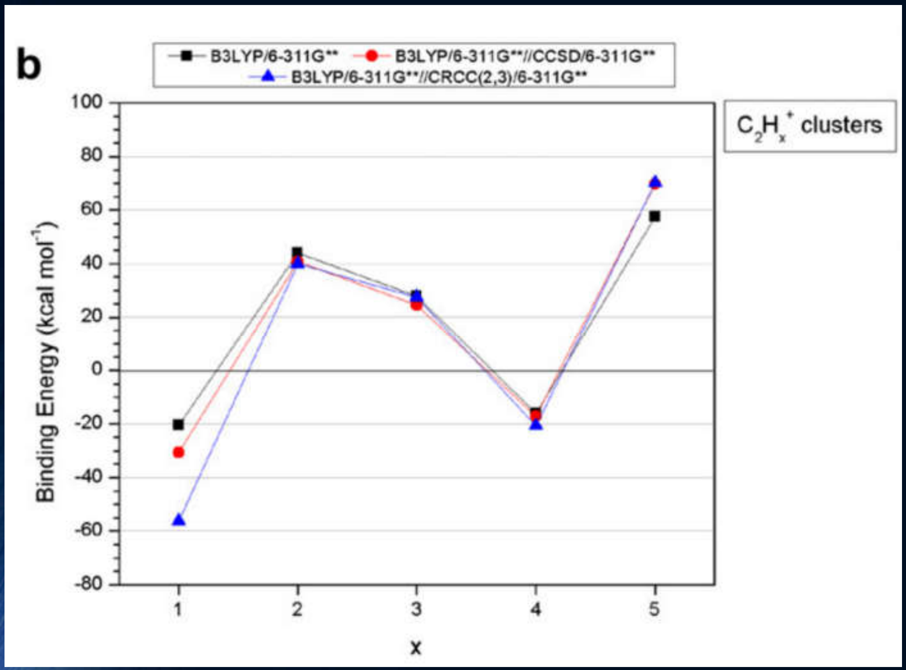


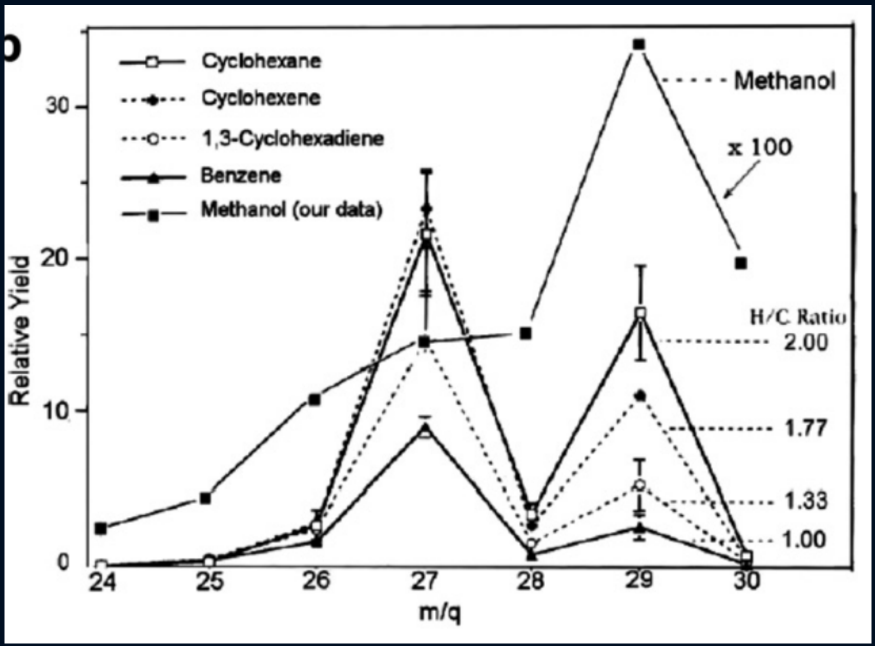


$$2C_nH^- \rightarrow C_{n-1}H^- + C_{n+1}H^-.$$

F. Fantuzzi et al. / Chemical Physics 410 (2013) 109–117

Hydrocarbon clusters-Results



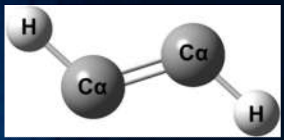


$$2C_nH_x^+ \rightarrow C_nH_{x+1}^+ + C_nH_{x-1}^+,$$

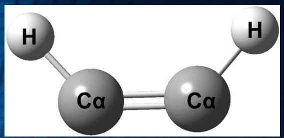
$$\Delta E_b = E(C_nH_{x+1}^+) + E(C_nH_{x-1}^+) - 2E(C_nH_x^+)$$

F. Fantuzzi et al. / Chemical Physics 410 (2013) 109–117

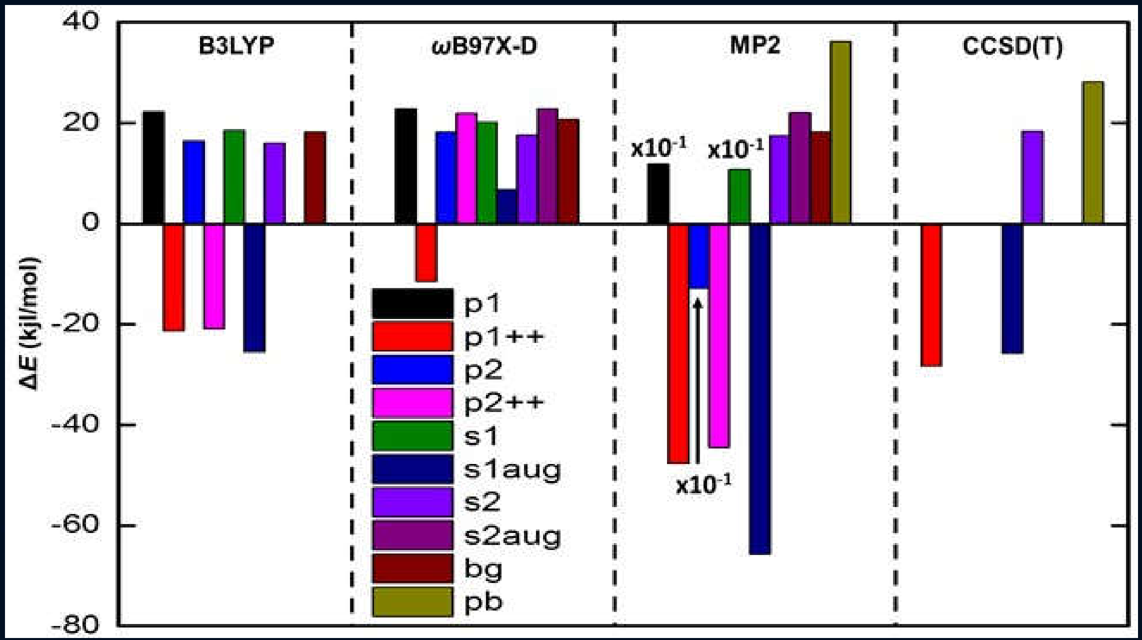
Hydrocarbon clusters-Results



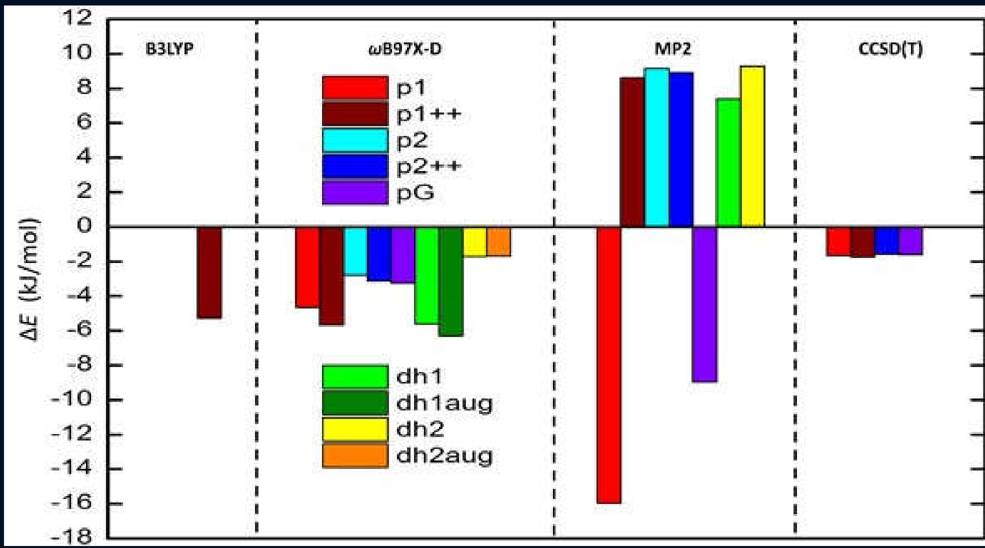
a) *trans*-HCCH

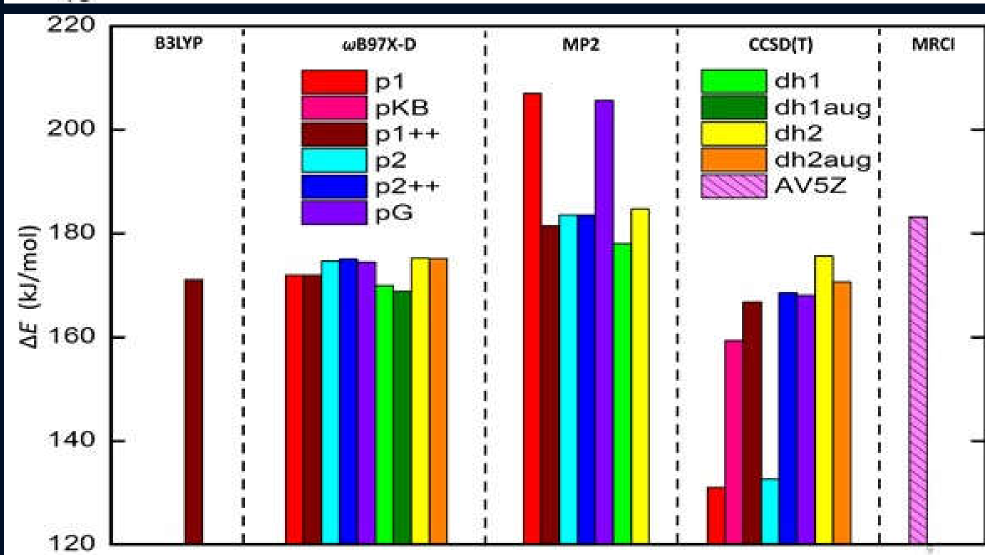


b) *cis*-HCCH



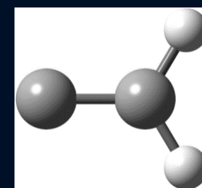
$$\Delta E = E_{\text{cis}} - E_{\text{trans}}$$





E = E[vinyl$^+$ (nonplanar)]-E[vinyl$^+$ (planar)]

Vinylidene



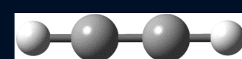
Dihedral angle

Planar 180°

Nonplanar [155°- 162°]

E = E[vinyl$^+$ (planar)]-E[ace$^+$]

Acetylene



Pople basis: 6-31G(d, p) [**p1**]; 6-31G(0.25 0.15) [**pKB**]; 6-31++G(d,p) [**p1++**]; 6-311(d, p) [**p2**]; 6-311++(d, p) [**p2++**]; and 6-311++G(d, p) with diffuse functions exponent: α_H = 0.05602, α_C 0.07434 [**pG**].
Dunning/Huzinaga basis: cc-pvdz [**dh1**]; aug-cc-pvdz [**dh1aug**]; cc-pvtz [**dh2**]; aug-cc-pvtz [**dh2aug**].

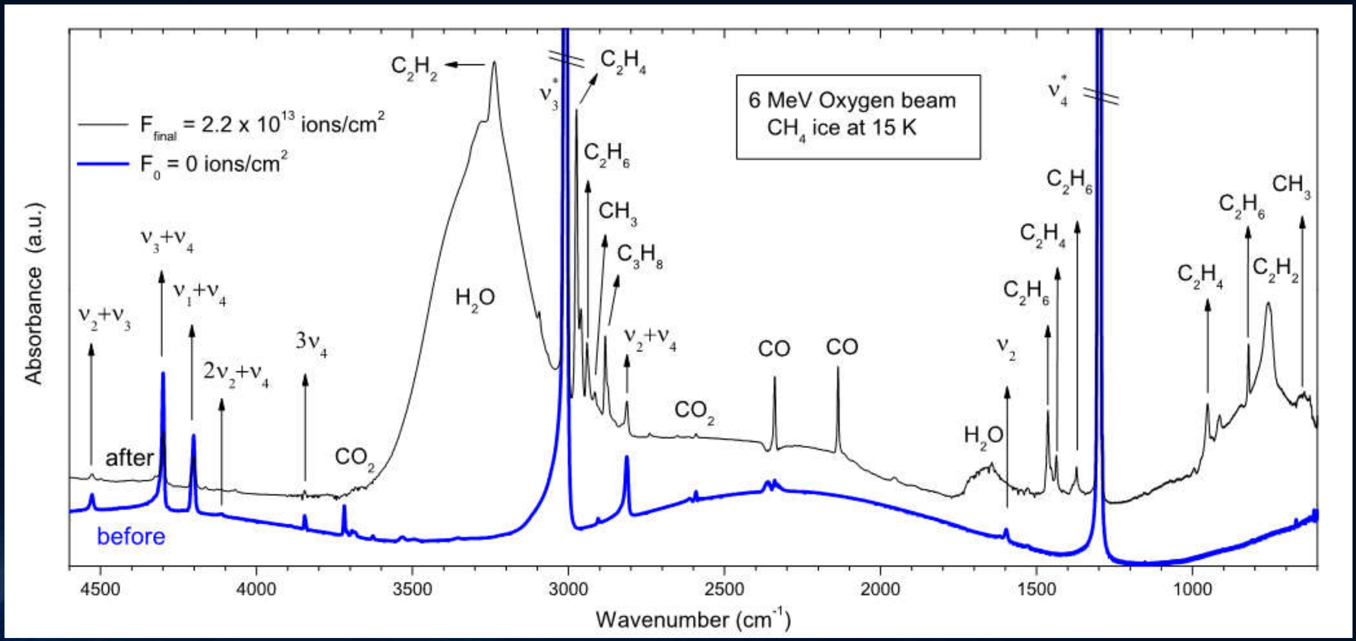
Methane in the interstellar medium

2.4% of CH_4 in the atmosphere

- It is found in several icy bodies of Solar System:
  - Icy clouds of Jovian planets
  - Saturn's moon Titan
  - Surface of Pluto
- The exposion to radiation induces erosion of solids and synthesis of new molecules
- The incidence of cosmic rays in solids leads to the desorption of several species and formation o molecular clouds

Effect of radiolysis and heavy ion impact on solid methane

- FT-IR measurements characterized C_2H_2, C_2H_4, C_2H_4 , C_3H_8 and CH_3 radical



A. L. F. de Barros A&A 531, A160 (2011)

Objectives:

- Describe the reactivity of methane ions (gas phase)
- Study the dissociation recombination of ethane
- Calculate thermodynamics and kinetics parameters that roles the decomposition of these ions

$$CH_4^+ \rightarrow CH_2^+ + H_2$$

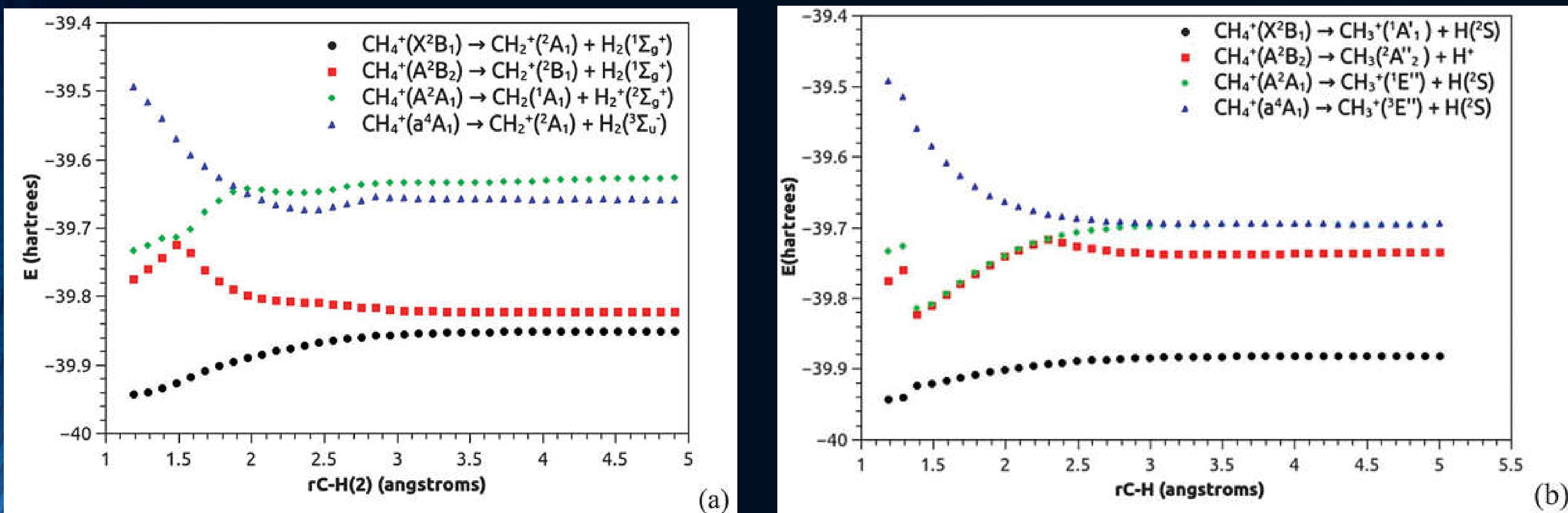
$$CH_4^+ \leftrightarrow CH_3^+ + H$$

$$CH_4^- \rightarrow Products$$

$$C_2H_6 \leftrightarrow CH_3 + CH_3$$

- Relates the ions reactivity to the FT-IR measurements performed after heavy ion impact

Reactions of CH_4^+



MRCISD(7,8)/6-311G(d,p)//NEVPT2(7,8)/6-311G(2df,2pd)

Baptista and da Silveira *Phys. C hem. Chem. Phys.* 16 (2014) 21867-21875

Arrhenius equation were calculated in the range of 273-500K

- Electronic structure data: MRCISD(7,8)/6-311G(d,p)//NEVPT2(7,8)/6-311G(2df,2pd)
- Rate coefficients: RRKM theory

$$CH_4^+ \rightarrow CH_2^+ + H_2 \qquad k_{diss}^{\infty} = 9.18 \times 10^{1\ 4}\mathrm{exp}(\ \frac{55.77}{RT})$$

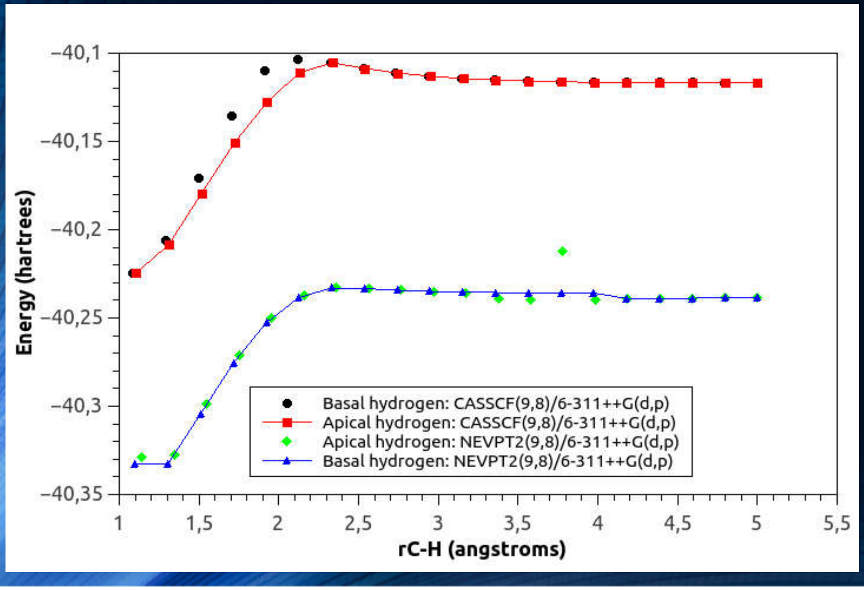
$$CH_4^+ \rightarrow CH_3^+ + H \qquad k_{diss}^{\infty} = 1.42 \times 10^{1\ 4}\mathrm{exp}(\ \frac{37.12}{RT})$$

$$CH_3^+ + H \quad \rightarrow CH_4^+ \qquad k_{rec}^{\infty} = 1.05 \times 10^{-08}\ \mathrm{exp}(\ \frac{0.23}{RT})$$

Reactions of CH_4^-

Reaction	ΔE		ΔE_0	
	CASSCF(9,8)	NEVPT2(9,8)	CASSCF(9,8)	NEVPT2(9,8)
$CH_4^- \rightarrow CH_3 + H^-$	67.6	69.8	58.0	55.6
$CH_4^- \rightarrow CH_3^- + H$	103.1	84.7	93.6	69.2
$CH_4^- \rightarrow CH_2 + H_2^-$	134.2	101.4	122.2	85.0
$CH_4^- \rightarrow CH_2^- + H_2$	89.2	71.5	76.4	53.0

All values are in kcal mol^{-1}. All results were obtained with 6-311++G(d,p) basis set.

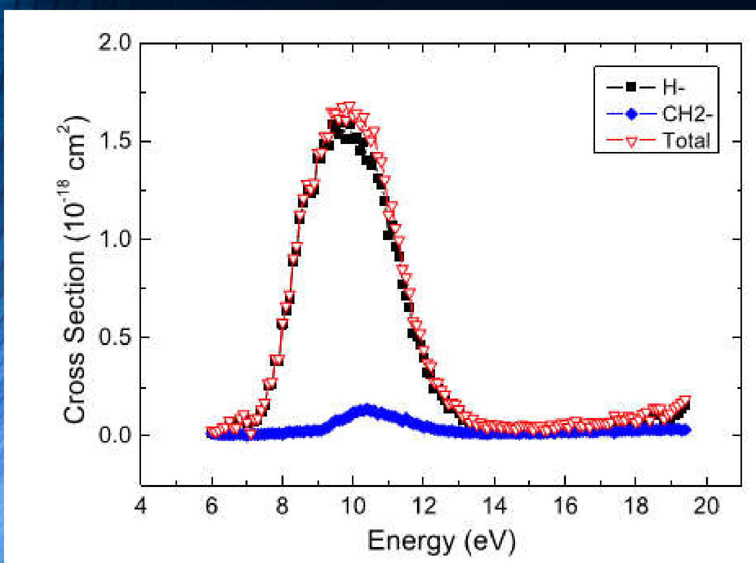


Rate coefficients for CH_4^- decomposition

- Electronic structure data: NEVPT2(9,8)/6-311++G(d,p)
- Rate coefficients: canonical TST

$CH_4^- \rightarrow CH_3 + H^-$ k = 3.7 × 10^{-21} s^{-1} for apical stretching (T = 298)

$CH_4^- \rightarrow CH_2^- + H_2$ k = 1.0 × 10^{-42} s^{-1} (T = 298)



Recommended cross sections for the formation of H and CH_2 and total dissociative electron attachment cross section from methane.

Song et al. J. Phys. Chem. Ref. Data, Vol. 44, No. 2, 2015

Proposition of an initialization mechanism

$$CH_4 \rightarrow CH_4^+ + e^-$$

$$CH_4^+ \rightarrow CH_3^+ + H$$

$$CH_4 + e^- \rightarrow CH_4^-$$

$$CH_4^- \rightarrow CH_3 + H^-$$

Majors chain carriers

Conclusions and Perspectives

- Experimental studies associated with theoretical studies provides an insightful way to assign the chemical structure of species observed in the interstellar medium
  - Geometry and electronic structure will role the reactivity of molecules
- The electronic charge influences the geometry of carbon clusters
- The kinetic and thermodynamic parameters calculated for these species may be used to justify or predict the existence of some species in the interstellar medium
  - Formation of CH_3 and CH_3^+ should be related to formation of new specis after irradiation of methane ices.

Acknowledgments

- CAPES, CNPq and FAPERJ
- Profª. Diana Andrade from UNIVAP for lending me some images
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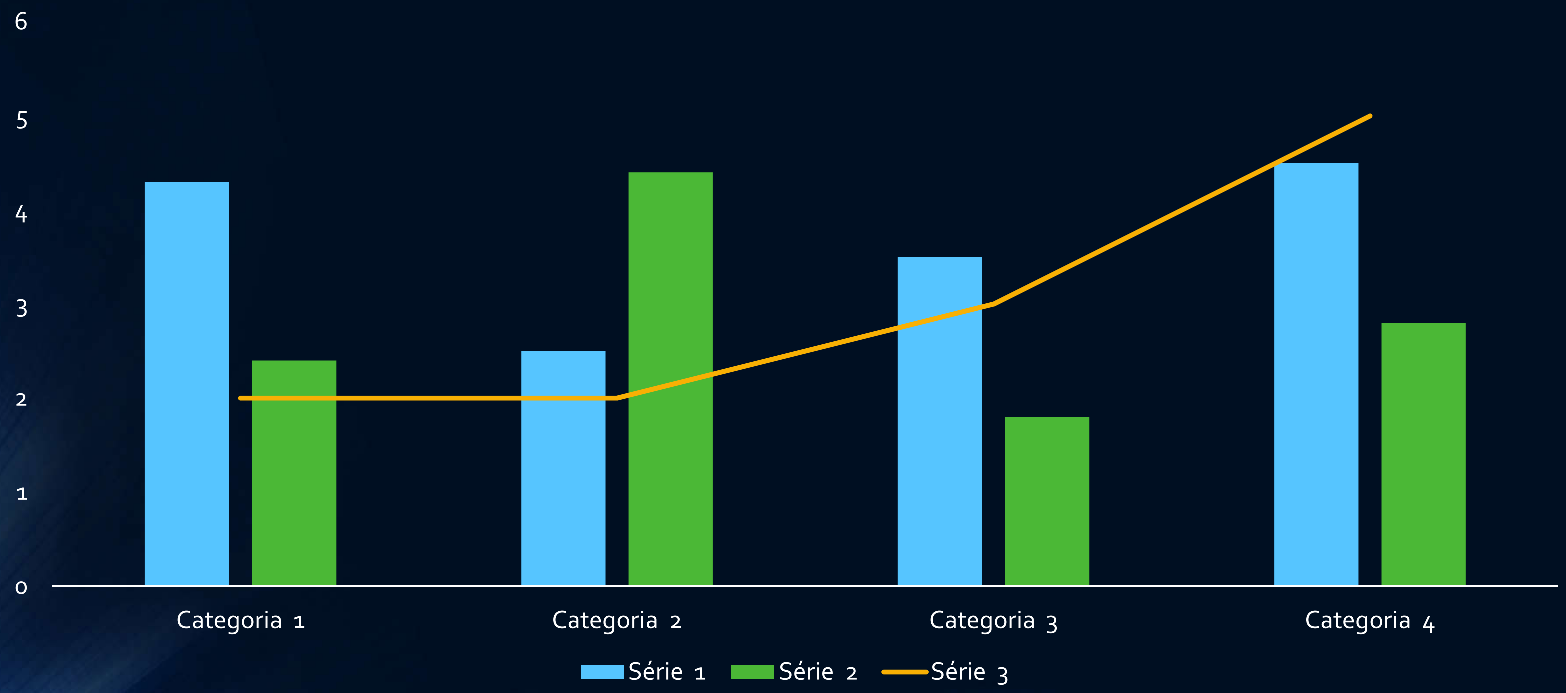
- Profª. Mária Luiza Rocco – DFQ/UFRJ
- MSc Felipe Fantuzzi – IQ/UFRJ

Título e layout do conteúdo com gráfico



Layout de duas partes de conteúdo com tabela

- Primeiro marcador aqui
- Segundo marcador aqui
- Terceiro marcador aqui

	Grupo 1	Grupo 2
Classe 1	82	95
Classe 2	76	88
Classe 3	84	90

Título e layout do conteúdo com SmartArt

- Descrição da tarefa
- Descrição da tarefa

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