State-of-the-art laboratory experiments combined with quantum chemistry to study reactive ion-molecule collisions under interstellar conditions

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'Physique et chimie du milieu interstellaire' 2022, *Paris, 24-28 October 2022*

Motivation

- **Molecular ions are important ingredients of interstellar molecular clouds**, despite their low fractional abundances relative to H_2 [1-3]

- **Ion-molecule reactions often do not possess activation-energy barriers** (unlike most neutral-neutral reactions) [3]

- **Ion-molecule reactions synthesize complex ions** that often undergo dissociative recombination reactions to form somewhat smaller neutral species. [3]

- One of the **most important classes of ion-molecule reactions are carbon insertion** [3]

[1] Roueff E. 2015. EPJ Web of Conf. 84:06004
[2] Herbst, E. 2021. Astron. Space Sci. 8:776942
[3] Herbst E. 2005. J. Phys.: Conf. Ser. 4:17–25

EPJ Web of Conferences **84**, 06004 (2015)
https://doi.org/10.1051/epjconf/20158406004

(New) molecular ions in the interstellar medium

Evelyne Roueff[a]

Molecular ions in interstellar reaction networks

To cite this article: Eric Herbst 2005 *J. Phys.: Conf. Ser.* **4** 17

REVIEW article

Front. Astron. Space Sci., 08 December 2021
Sec. Astrochemistry
https://doi.org/10.3389/fspas.2021.776942

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Unusual Chemical Processes in Interstellar Chemistry: Past and Present

Eric Herbst[1,2]*

Experimental method for ion-molecule reactions

Uniform supersonic flow reactors can provide **reaction rates under well-controlled thermalized conditions.**

The ***CRESU*** (Cinétique de Réaction en Ecoulement Supersonique Uniforme) reactor is combined with a mass-selective ion source (***SIS***) [Joalland *et al* 2019], which allows one to measure **absolute** <u>reaction rate coefficients</u> **and** <u>product branching ratios</u> at low temperatures.

Our instrument is capable to produce stable ionic species at thermal energies (down to about 10 K)
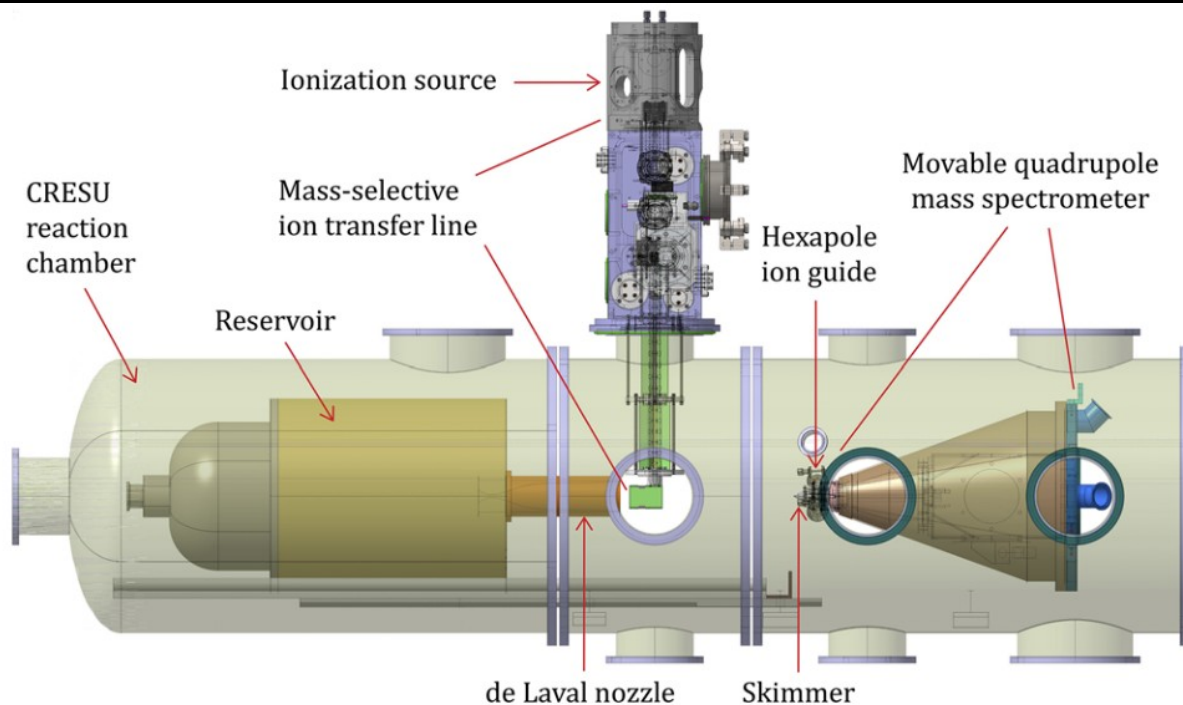

FIG. 1. The CRESU reaction chamber incorporating the new mass-selective ion transfer line. A movable quadrupole mass spectrometer updated with a skimmer/hexapole ion guide combination is used for monitoring ions in the de Laval expansion. High-capacity Roots pumps maintain the desired pressure (0.1–2.0 mbar) in the reaction chamber.

The N_2^+ – C_3H_4 reaction

Propyne or methyl acetylene (CH₃CCH) has been first uncovered in the Voyager IR spectrum of **Titan** in the 80's [1].

Another C_3H_4 isomer, **propadiene or allene (CH₂CCH₂)**, was observed in Titan's atmosphere by TEXES observations on the *NASA Infrared Telescope Facility* [2].

Propyne and allene is *the first hydrocarbon isomer pair detected on Titan* with a **CH₃CCH/CH₂CCH₂ abundance ratio of 8.2** [3]

The dense **atmosphere of Titan** dominated by **N_2** and CH₄. N_2^+ is generated by photo-ionization.

Propyne (CH₃CCH) was widely detected in different ISM regions [4-6].

The non-polar allene is obviously **not detected**, but the **CH₂CCH radical was recently reported** by Agúndez *et al.* (2021) [7]

[1] Maguire, W. C., Hanel, R. A., Jennings et al., Nature 292, 683 (1981).
[2] McEwan, M. J. & Anicich, V. G., Mass Spectrometry Reviews 26, 281–319 (2007).
[3] Vuitton, V., Yelle, R. V, Klippenstein, S. J., *et al.*, Icarus 324, 120–197 (2019).
[4] Buhl, D. *et al.* in Molecules in the Galactic Environment (New York: Wiley), 187 (1973)
[5] Turner, B. E.,Herbst, E and Terzieva, R., Astrophys. J. Suppl. Ser. 126, 427–460 (2000).
[6] Pardo, J. R., and Cernicharo, J., Astrophys. J. 654, 978–987 (2007).
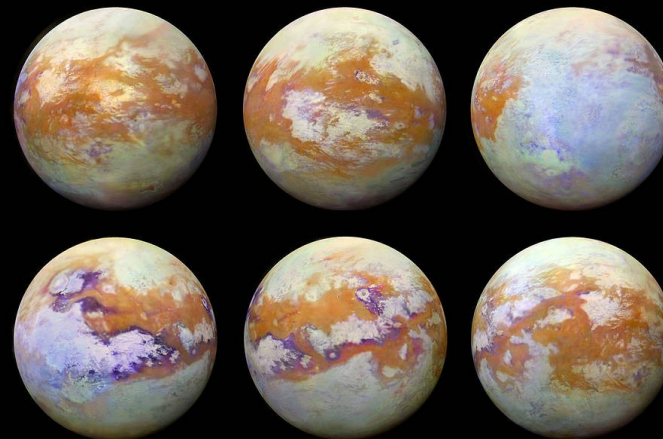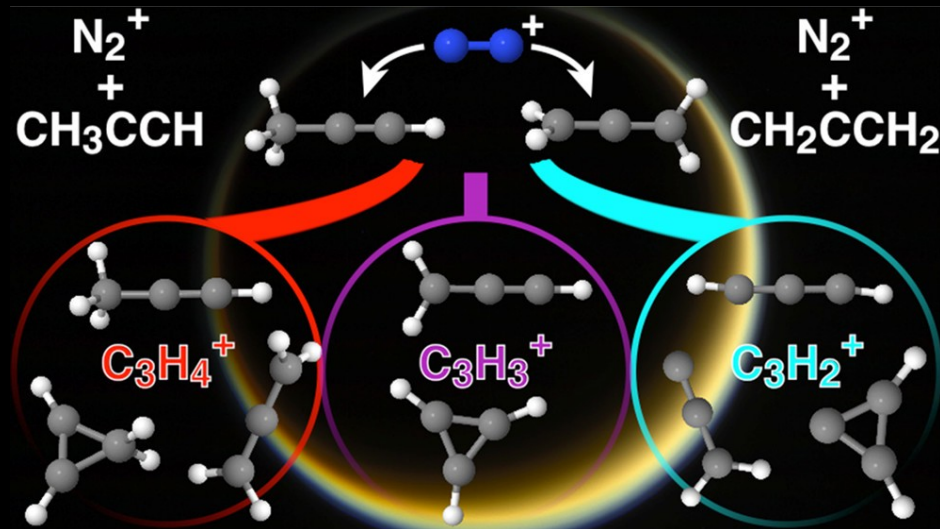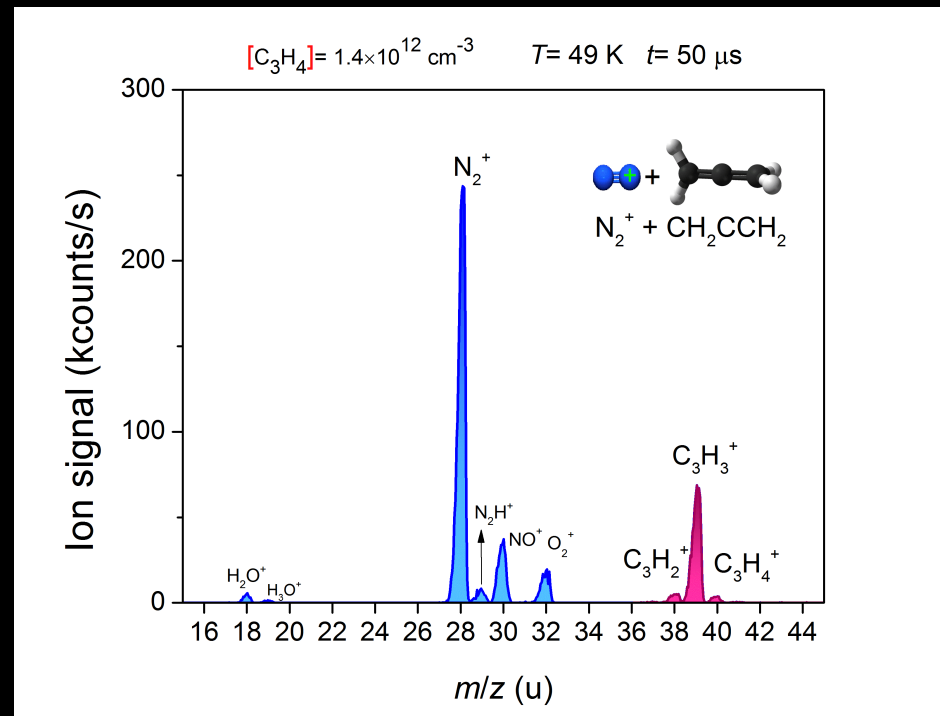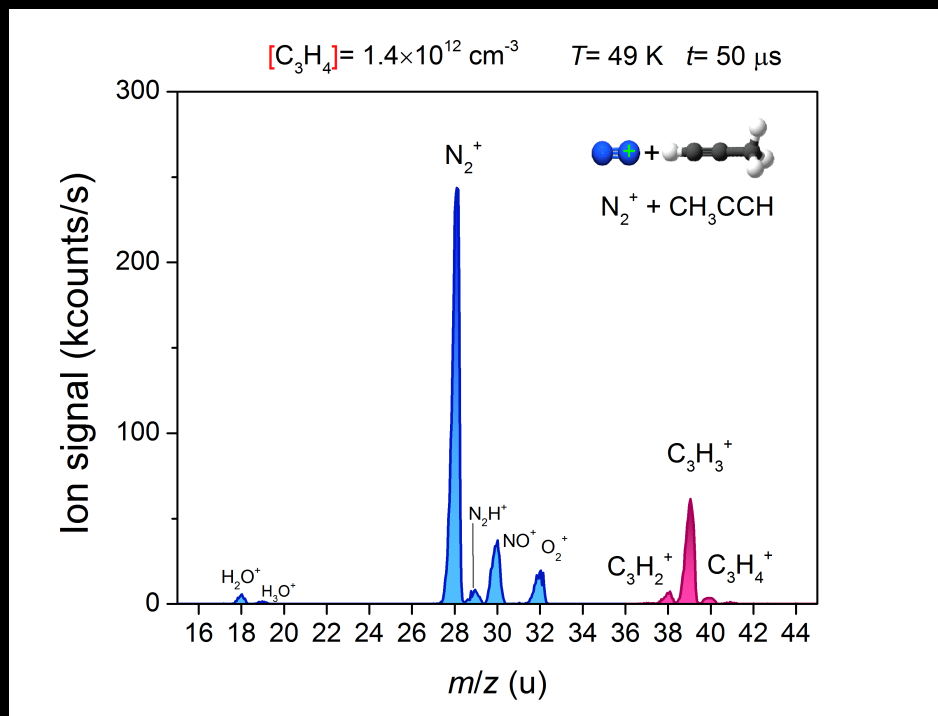[7] Agúndez, M., Cabezas, C., Tercero, B., *et al.*, A&A, 647, L10 (2021).

Image credits: NASA/JPL
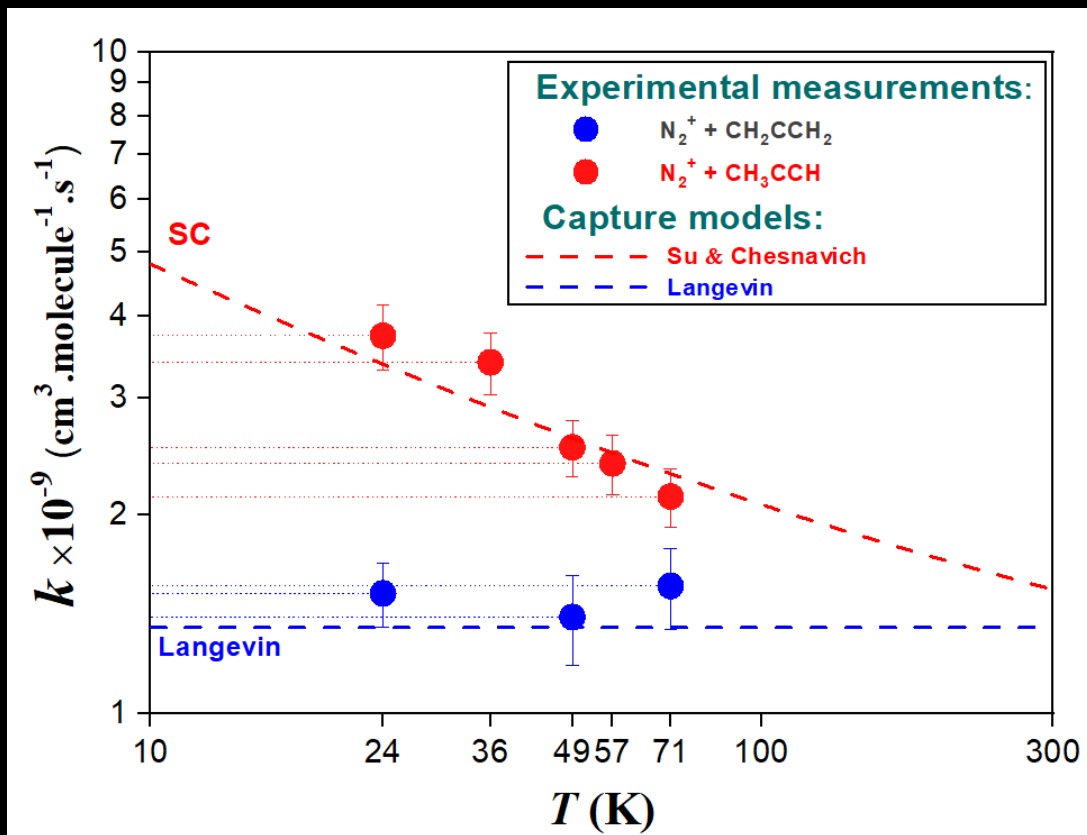
N$_2^+$ – C$_3$H$_4$: mass spectra

Mass spectra recorded at 49 K for **propyne** (left) and **allene** (right).

- For both reactions, the **main ion product** detected is **C$_3$H$_3^+$**, **followed by** C$_3$H$_2^+$ and C$_3$H$_4^+$.
- **N$_2$H$^+$, NO$^+$, O$_2^+$, H$_2$O$^+$ and H$_3$O$^+$ cations** are the products of the **reaction of N$_2^+$ with impurities**

N₂⁺ – C₃H₄ : reaction rates

For **allene** reaction the **reaction rate shows a quasi-independence with temperature**, which is in good agreement with the **Langevin** value:

$k_L = 2\pi e\sqrt{\alpha/\mu} = 1.38 \times 10^{-9}$ cm³ mol.⁻¹ s⁻¹

For the **reaction with propyne** the Langevin model is not suitable. For this polar reactant the model of **Su and Chesnavich** [1] gives a rate coefficient:
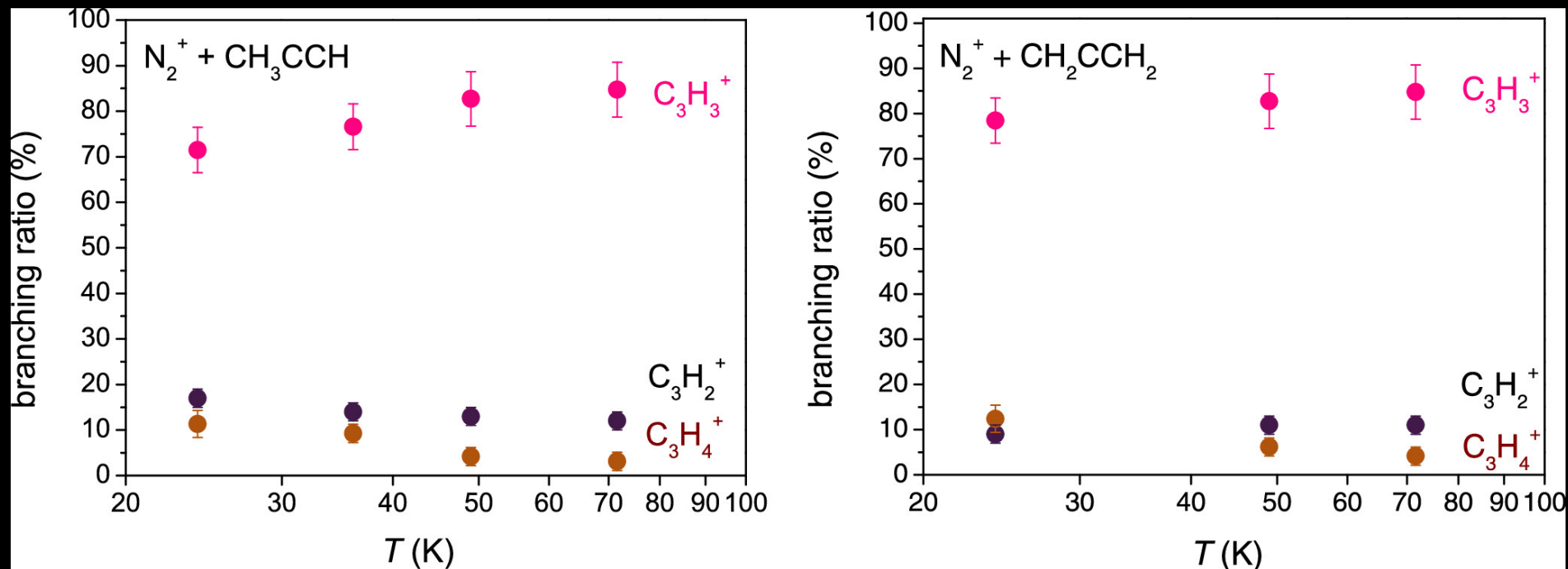
$k_{SC} = K_{cap} \times k_L$ with $K_{cap} = 0.4767x + 0.62$
where $x = \mu D/\sqrt{2\alpha T k_B}$.

[1] Su, T. & Chesnavich, W. J., J. Chem. Phys. 76, 5183 (1982).

Measured reaction rates as a function of temperature for the reaction of **N₂⁺ with CH₃CCH** (red filled circles) and **CH₂CCH₂** (blue filled circles) along with the reaction rates calculated with capture models

N₂⁺ – C₃H₄ : branching ratios

The **temperature dependence of the branching ratios** between the primary products of **N₂⁺/CH₃CCH** (left) and **N₂⁺/CH₂CCH₂** (right) reactions.

- For both reactions **the branching ratio of the dominant exit channel (C₃H₃⁺) increases** with temperature.
- The **C₃H₂⁺ slightly decreases (*propyne*) or remains quasi-constant (*allene*).**
- The route of ***pure charge transfer* (C₃H₄⁺) significantly decreases**.

The unimolecular decomposition of CH₂CCH₂⁺

max. available energy for the decomposition of C₃H₄⁺ after charge transfer with N₂⁺
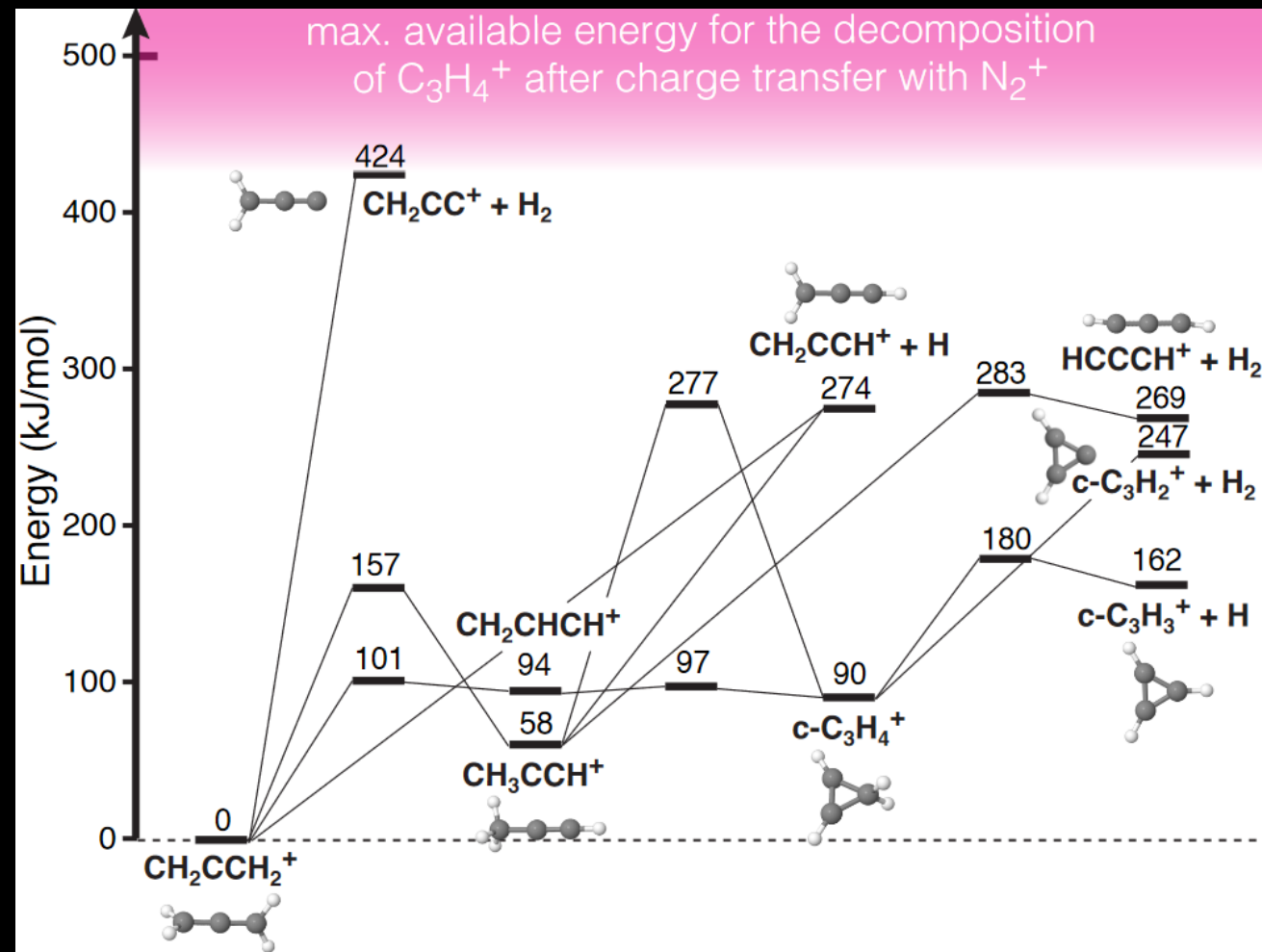
- Once supposing that the **reactions proceed** with an initial **formation of C₃H₄⁺** parent ion first, a **unimolecular decomposition** scheme can be proposed then.

- Based on the study of **Mebel and Bandrauk [1]** for the photo-dissociation of **CH₂CCH₂⁺** *(CCSD(T)/cc-pVTZ // B3LYP/ 6-311G** theory)*, we provide a new, **quantitative explanation for the branching ratios** for **propyne and allene reaction with N₂⁺**.

- **What about the temperature dependence of the reaction rates then?**

[1] Mebel, A. M. & Bandrauk, A. D. *J. Chem. Phys.* **129**, 224311 (2008).

Interstellar noble gas chemistry

Before 2013, noble gas molecules have not been detected in space.

The first detection of **argonium cation (ArH⁺) was published by Barlow et al (2013)** [1]. It is also actively studied recently [2]

Later **another important detection** was reported: **HeH⁺ in nearby interstellar space** [3]. Our **understanding of the chemical networks** that control the formation of this molecular ion, **including the rates of radiative association** and dissociative recombination are still very limited [3]

[1] Barlow MJ, et al. 2013. Science. 342(6164):1343
[2] Jacob AM, et al. 2020. A&A. 643:A91
[3] Güsten R, et al. 2019. Nature. 568(7752):357–59

Sándor Demes, PCMI, Paris, 24 Oct 2022

Detection of a Noble Gas Molecular Ion, ³⁶ArH⁺, in the Crab Nebula

M. J. BARLOW, B. M. SWINYARD, P. J. OWEN, J. CERNICHARO, H. L. GOMEZ, R. J. IVISON, O. KRAUSE, T. L. LIM, M. MATSUURA, [...] E. T. POLEHAMPTON   +3 authors

Authors Info & Affiliations

Extending the view of ArH⁺ chemistry in diffuse clouds⋆

Arshia M. Jacob[1],⋆⋆, Karl M. Menten[1], Friedrich Wyrowski[1], Benjamin Winkel[1], and David A. Neufeld[2]

Astrophysical detection of the helium hydride ion HeH⁺

Rolf Güsten ✉, Helmut Wiesemeyer, David Neufeld, Karl M. Menten, Urs U. Graf, Karl Jacobs, Bernd Klein, Oliver Ricken, Christophe Risacher & Jürgen Stutzki

The Ar⁺ – CH₄ / C₂H₄ reactions

The **reactivity of Ar⁺ ions with hydrocarbons** has been the subject of numerous investigations including saturated (CH_4, C_2H_6,…) and unsaturated species (C_2H_2, C_2H_4, c-C_6H_6,…) [1], with some potential interest for astrophysical environments.
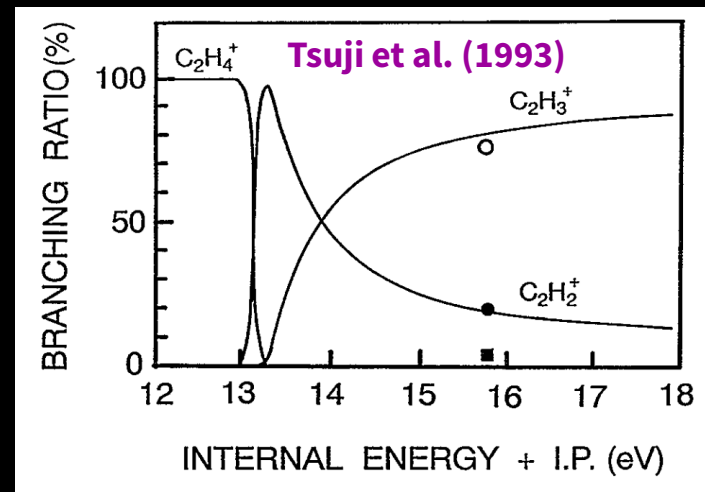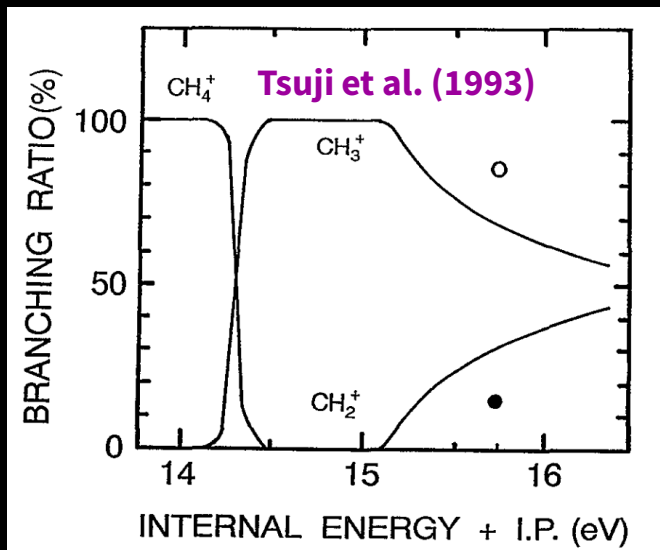
Most of the studies have been performed **at room temperature and show multiple fragmentation pathways**. E.g., the rate coefficient and the branching ratios of the Ar⁺ + C_2H_4 / CH_4 reactions were measured at room temperature by Tsuji et al. (1993) [2]

The temperature dependence of some of these reactions has been explored, but mainly above room temperature.

[1] V. G. Anicich, JPL-Publication-03-19 1194 (2003)
[2] Tsuji M et al. 1993. The Journal of Chemical Physics. 98(3):2011–22
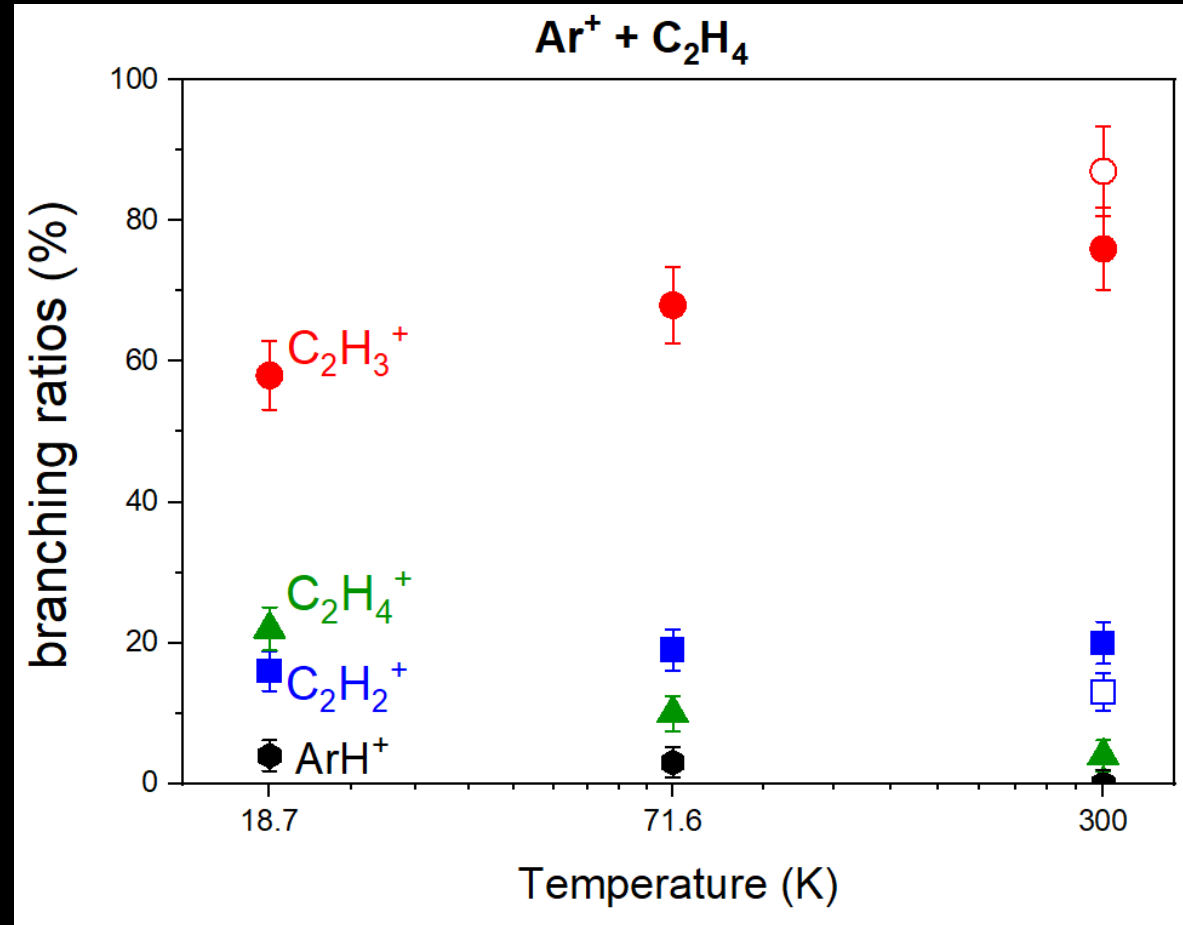
Ar⁺ – C₂H₄ : measured branching ratios

Temperature dependence of the branching ratios for the
primary products of the **Ar⁺ – C₂H₄ reaction**

|	T (K)	Primary products of the Ar⁺ + C₂H₄ reaction			
		$C_2H_4^+$ (*m/z*= 28 u)	$C_2H_3^+$ (*m/z*= 27 u)	$C_2H_2^+$ (*m/z*= 26 u)	ArH^+ (*m/z*= 41 u)
CRESU-SIS	18.7	0.22 ± 0.03	0.58 ± 0.05	0.16 ± 0.02	**0.04 ± 0.02**
	71.6	0.10 ± 0.02	0.68 ± 0.05	0.19 ± 0.03	**0.03 ± 0.02**
Previous measurements					
Tsuji *et al.* (1993)	298	0.04	0.76	0.20	-
Franklin *et al.* (1961)	298	-	0.87	0.13	-

Ar⁺ – C₂H₄ : measured branching ratios

Temperature dependence of the branching ratios for the primary products of the **Ar⁺ – C₂H₄ reaction**

- **The branching ratio of the dominant exit channel ($C_2H_3^+$) increases** with temperature, while the **$C_2H_2^+$ channel slightly decreases**

- The strength of the *charge transfer channel ($C_2H_4^+$)* **significantly decreases**.
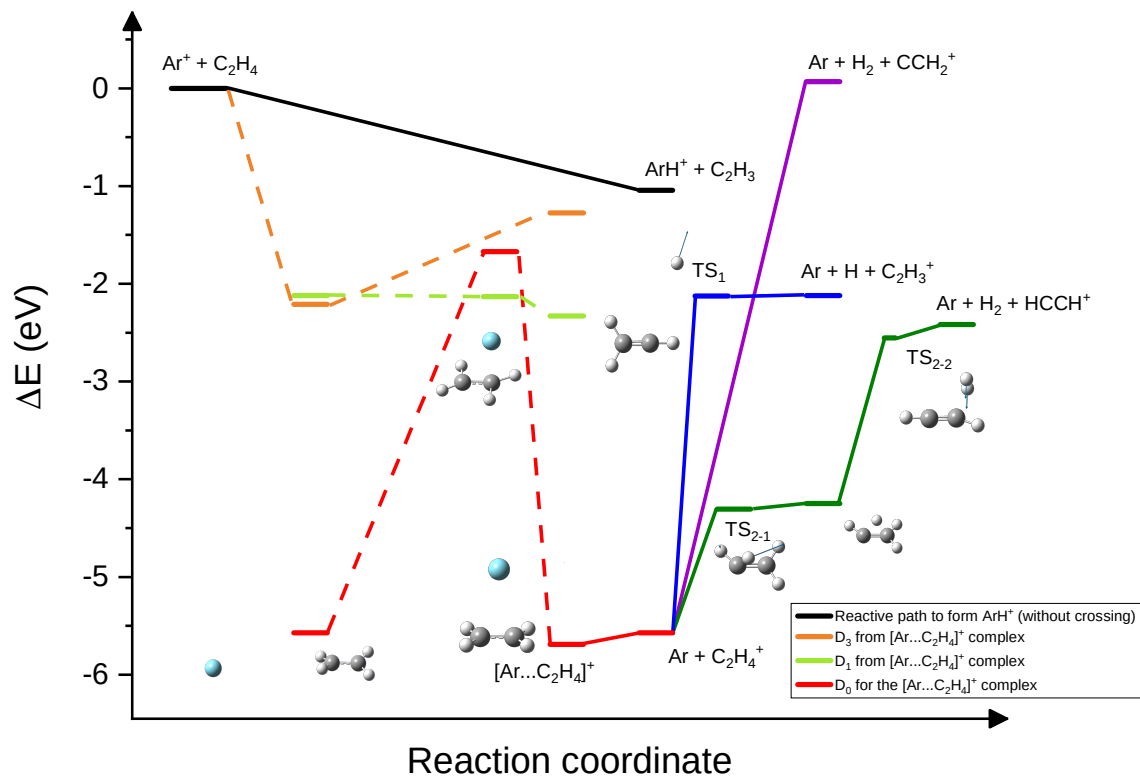
- **ArH⁺ is formed** only at lower temperatures
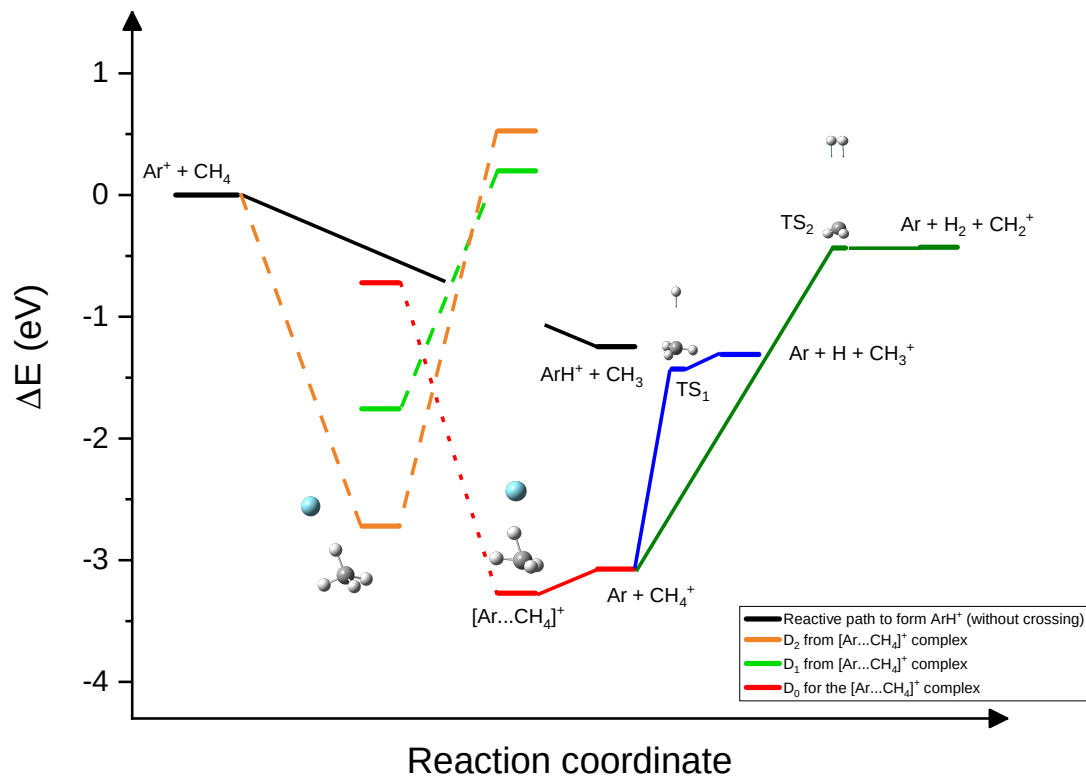
Energy diagram for the **Ar⁺ – CH₄ reaction**, calculated at the M06-2X / 6-31G(2df,p) level of theory

- The most exothermic channel is the **charge-exchange process,** but it is not likely to proceed, since the large excess energy cannot be distributed by its vibrational modes, which will always favor a dissociation.

- The **two** only **possible reaction** channels lead to **CH₃⁺** (the dominant) and **CH₂⁺ production**

- **ArH⁺ cannot be formed** due to a large barrier

Ar⁺ – C₂H₄ : energy landscape

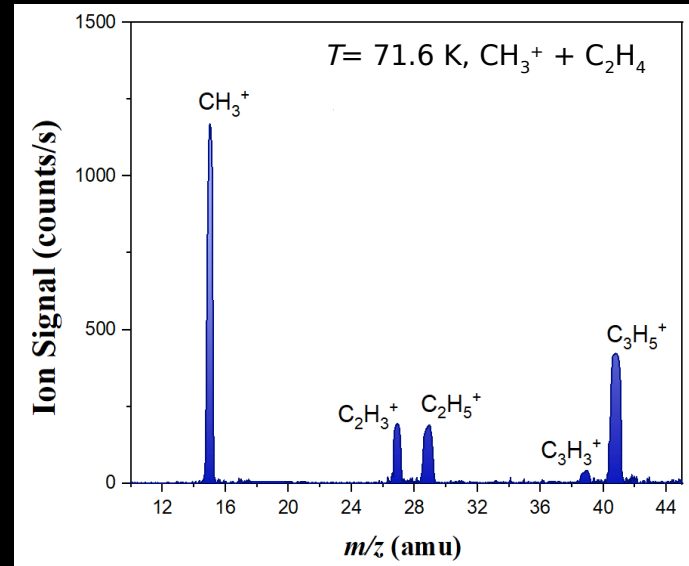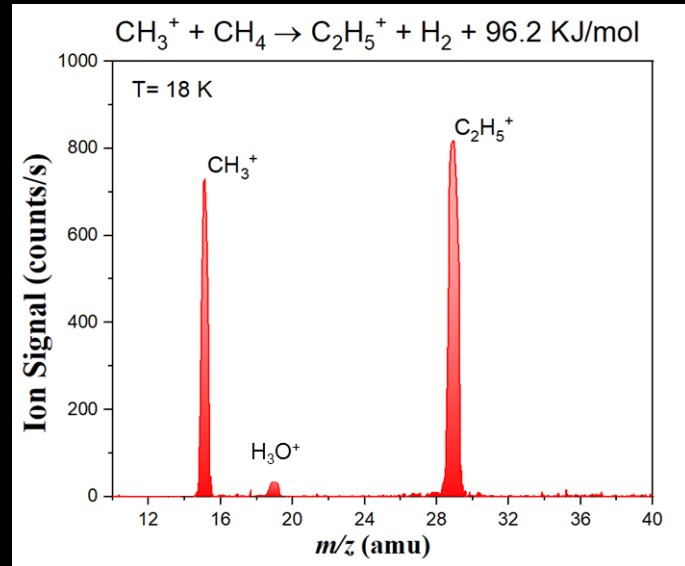**Energy diagram** for the **Ar⁺ – C₂H₄ reaction**, calculated at the M06-2X / 6-31G(2df,p) level of theory

- The most exothermic channel is again the pure charge-exchange process. **C₂H₄⁺ is formed, but is not a strong channel.**

- The **most dominant** product formation **channel is C₂H₃⁺**

- **C₂H₂⁺ is also efficiently formed**

- **ArH⁺ can be formed effectively**, but in tiny amount only.

Ar$^+$ – CH$_4$/C$_2$H$_4$: calculated branching ratios
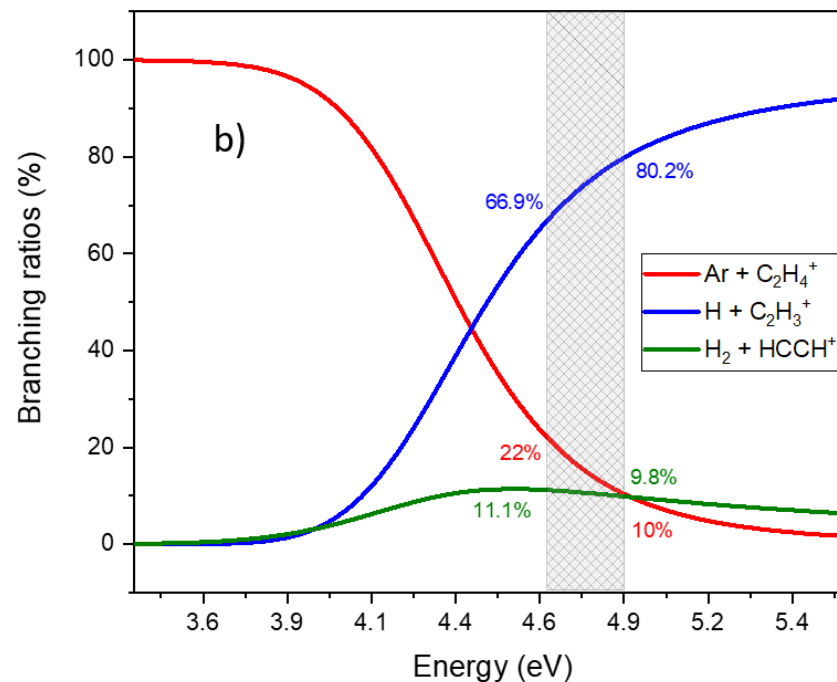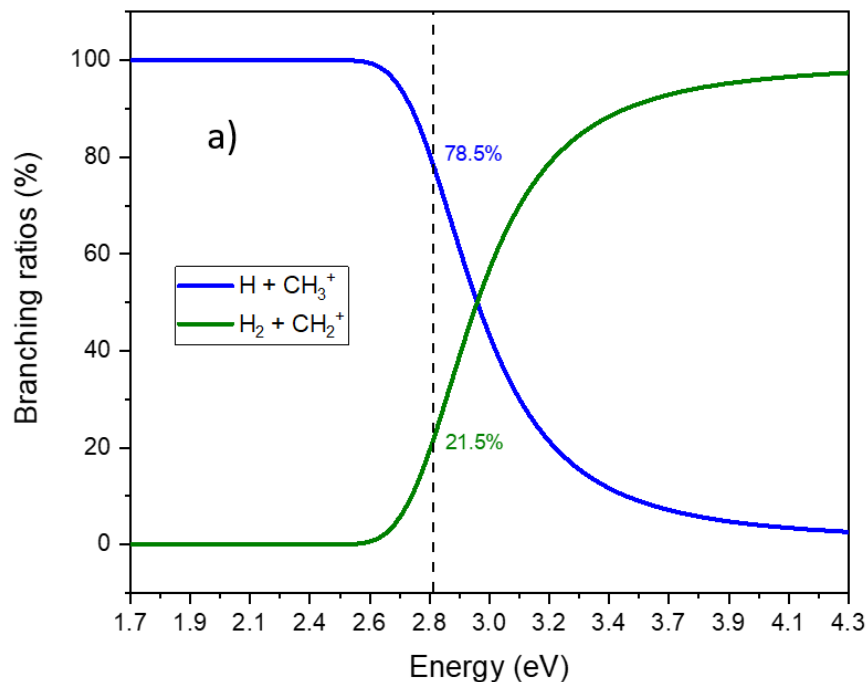
Calculated branching ratios (*RRKM*) **as a function of the internal energy** for the **Ar$^+$ + CH$_4$ (a)** and **Ar$^+$ + C$_2$H$_4$ (b) reactions**. In case of (b) a direct dissociation pathway of the [Ar…C$_2$H$_4$]$^+$ complex is considered instead of the dissociation following the minimum energy path.

Perspectives: the growth of molecular complexity

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 + 96.2 \, KJ/mol$$

T= 18 K

T= 71.6 K, $CH_3^+ + C_2H_4$

CRESU experiments for $CH_3^+ + CH_4 / C_2H_4$

- **$CH_3^+ + C_2H_4$** highlights the **evolution of branching ratios at low temperatures** from 51 to 69%.

- All heavy atoms are conserved in the dominant product, leading to the **formation $C_3H_5^+$ reaction promoting rapid growth.**

What is the role of ions in the growth schemes of molecular complexity?

The synthesis of large interstellar molecules

Eric Herbst

Take home message

- **State-of-the-art laboratory experiments combined with quantum chemistry** are powerful and perspective tools to study ion-molecule reactions at thermal energies to explore interstellar chemistry

- **Temperature-dependent reaction rates and branching ratios** could be measured and calculated, which is a double validation of the results.

- **Different structural isomers and isotopologues can be studied separately** with this combined laboratory method

- **Our future work will focus on the reactivity of key molecular species** to extend and enhance the interstellar chemical networks, which involve ionic species

Acknowledgments
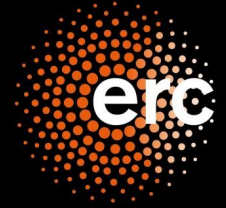
COLLEXISM

COLLisional EXcitation of InterStellar Molecules: towards reactive systems

- Ludovic **Biennier**
- François **Lique**
- Sophie **Carles**
- Rafael Alejandro **Jara-Toro**

- Ahmad **Mortada**
- Baptiste **Joalland**
- Abdessamad **Benidar**