Growth (and destruction) of COMs with ion-molecule reactions

Daniela Ascenzi

Department of Physics

University of Trento, Italy

Outline

- Introduction: ions in space - chemical reactions with ions

Selected examples from our lab:

- Reactivity of CH_3^+ with but-2-yne (C_4H_6)
- Selective generation of CH_3CN^+ / CH_2CNH^+ radical cations and reactivity with C_2H_4
- Destruction of COMs by collisions with He^+

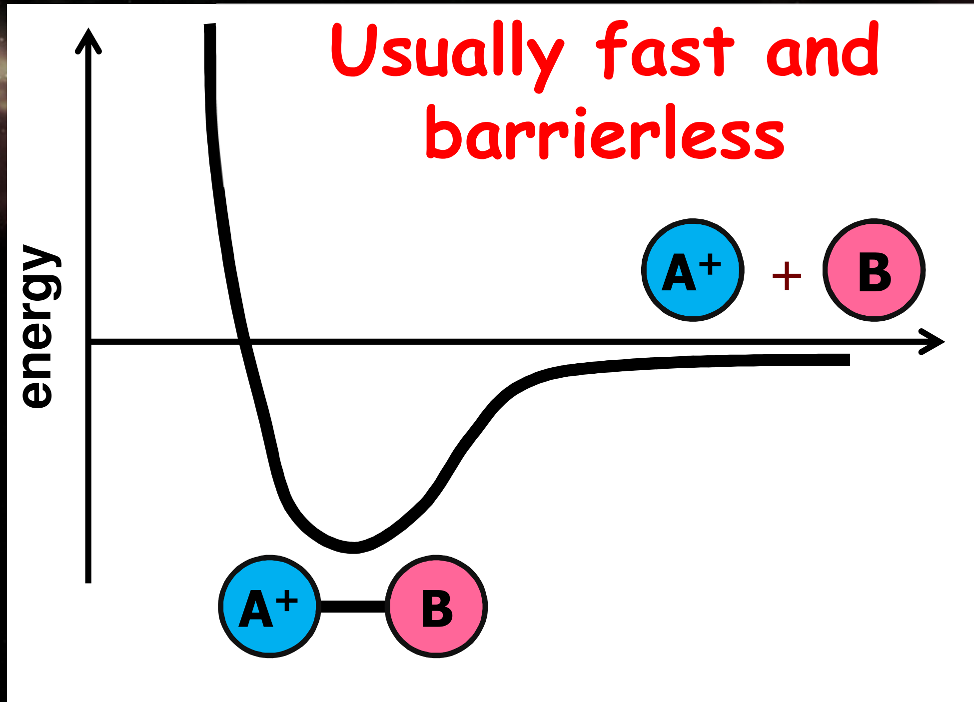
Ion chemistry in space

Chemistry of the Early Universe

Diffuse and dark coulds

Protostars

Planetary atmospheres and ionospheres



CHEMICAL REVIEWS
Review
pubs.acs.org/CR

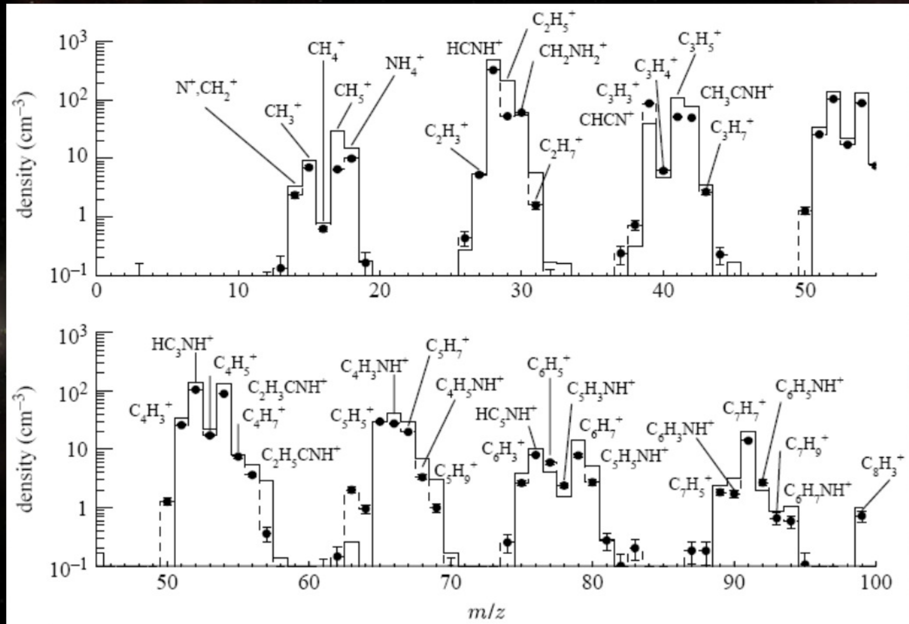
Experimental Investigations into Astrophysically Relevant Ionic Reactions

W Geppert, M Larsson 113, 8872-8905 (2013)

Chemistry of Titan's atmosphere (I)

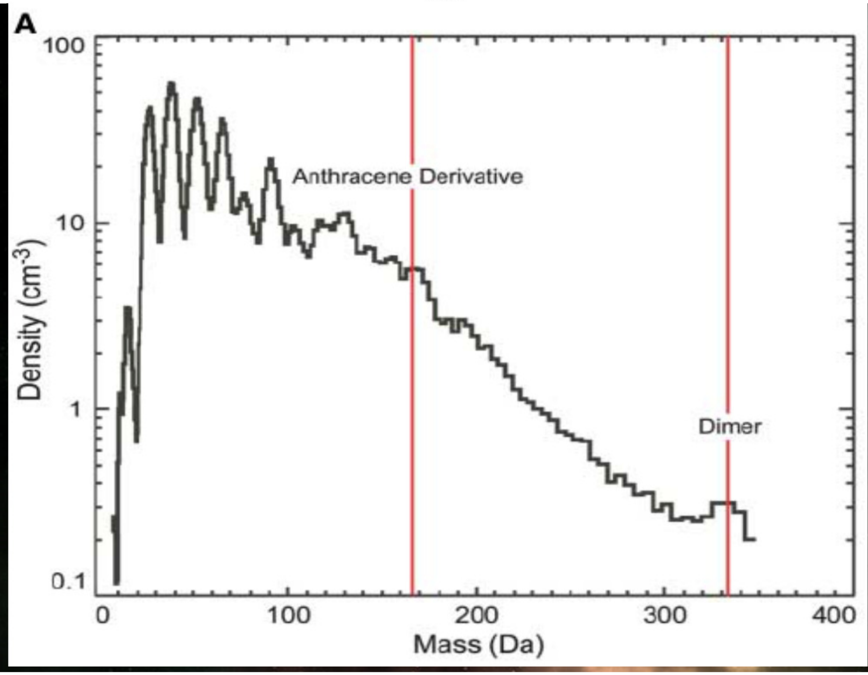
Complex $C_nH_m^+$ and $C_nN_kH_m^+$ ions (up to 100 m/z) by INMS

V. Vuitton et al. (2014), Chemistry of Titan's atmosphere, in "Titan: Interior, Surface, Atmosphere, and Space Environment", Cambridge Univ. Press

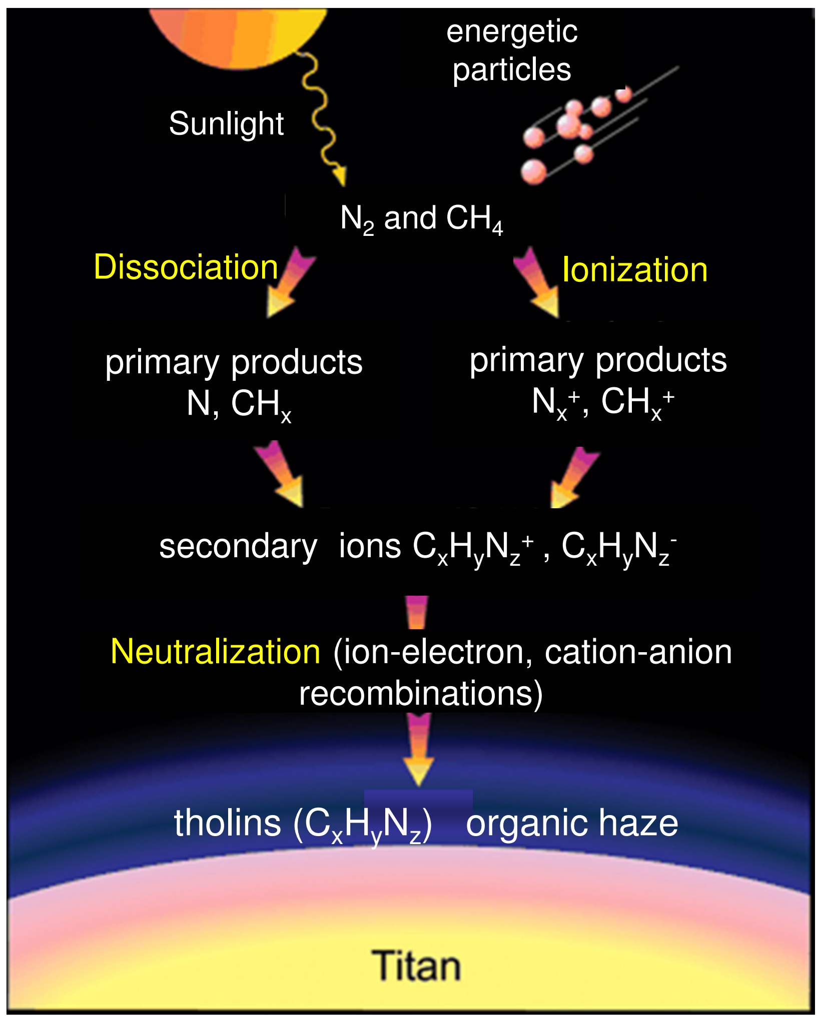


Heavy positive ions (up to 350 m/z) at ~1000km

F.J. Crary et al. *Planet. Space Sci.* **57** 1847 (2009)
J.E. Wahlund et al. *Planet. Space Sci.* **57** 1857 (2009)



Chemistry of Titan's atmosphere (II)



- Molecular growth/aereosol formation starts in the ionosphere
- ion chemistry plays a relevant role (also to explain density of neutrals)
- heavy cations and anions drift towards the lower levels of the atmosphere
- ion recombination → organic compounds → aereosol

S. Atreya &al. *Science* **316** 843 (2007) ; Lavvas &al. PNAS 110, 2729 (2013); E.C. Sittler &al. *Plan. Space Sci.* **57** 1547 (2009); ibid **57** 1857 (2009)

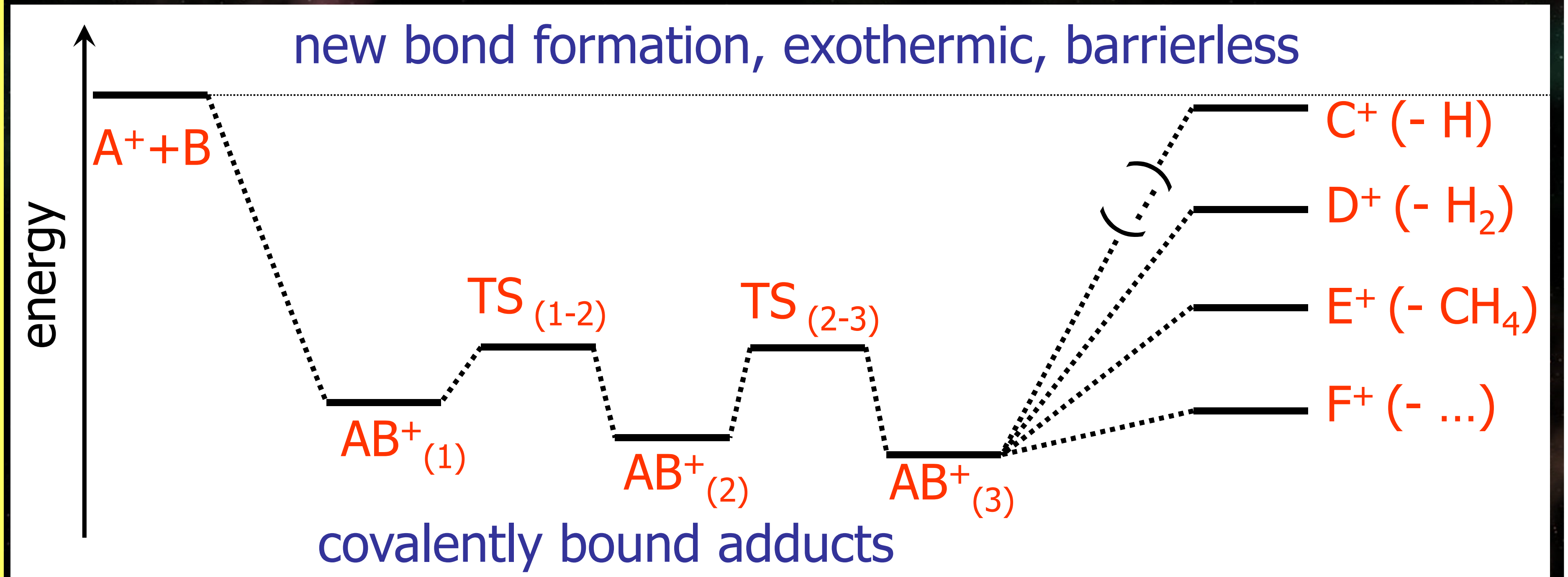
Ion-molecule reactions

Charge Transfer $A^+ + BC \rightarrow A + BC^+$

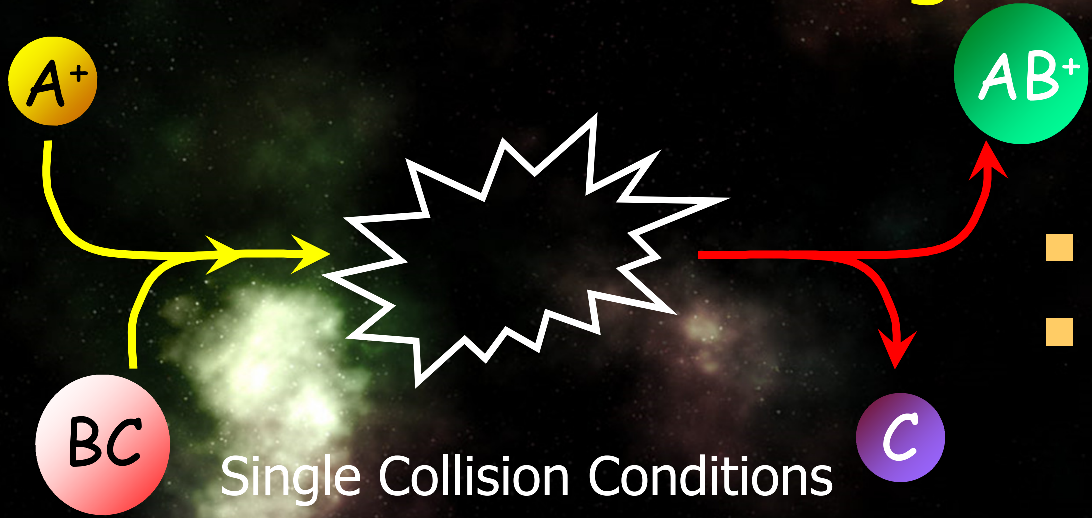
Proton transfer $B + HA^+ \rightarrow HB^+ + A$

Bond Forming (C-C, C-N) $A^+ + BC \rightarrow AB^+ + C$

Growth of complex molecules



Reactive scattering experiment



- Collision Energy E_{CM}
- Internal Energy (quantum state)

Each scattering experiment is characterized by:

Branching ratio $A^+ + BC \longrightarrow \begin{matrix} AB^+ + C \\ AC^+ + B \end{matrix}$ $\dfrac{[AB^+]}{[AB^+]+[AC]^+}$

Reactive cross section

$\sigma_P\,(E_{CM})$

$k = \langle \sigma_P \cdot v_{rel} \rangle$

Rate constant $k\,(T)$

Guided ion beam mass spectrometry

Ionization → **mass selection** → **reaction** → **mass selection**

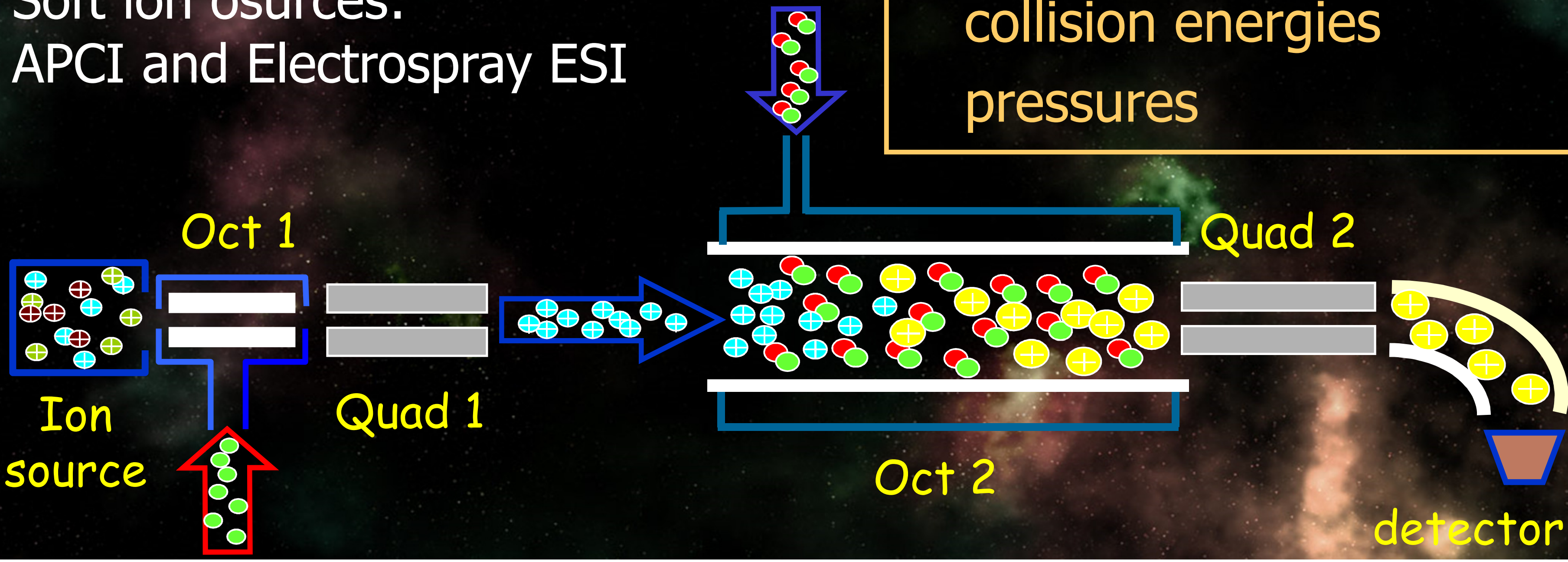
cooling

mixture of ions → **A⁺** → **C⁺, D⁺, etc.**

B

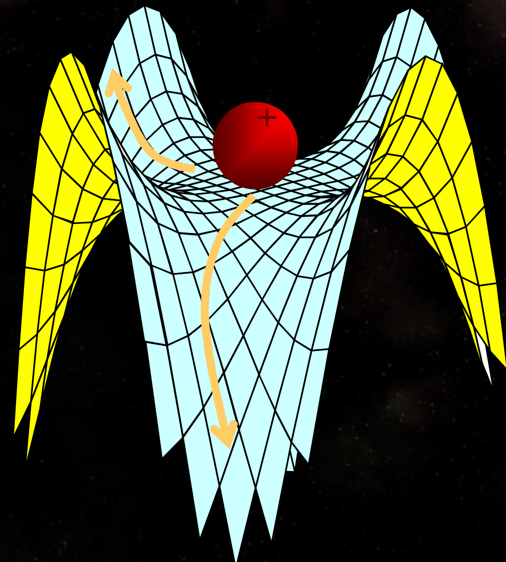
Ion sources:
Electon impact/CI
Soft ion osurces:
APCI and Electrospray ESI

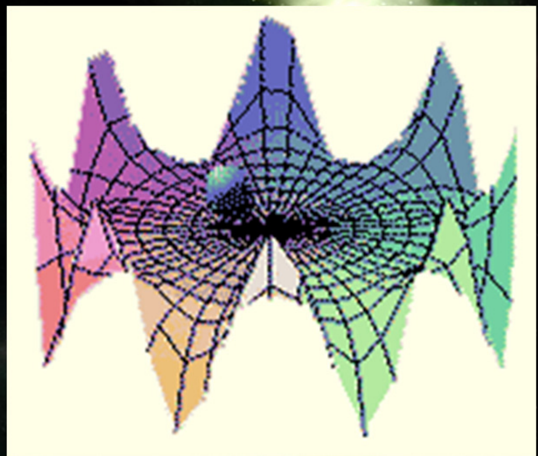
Measurements at variable:
collision energies
pressures



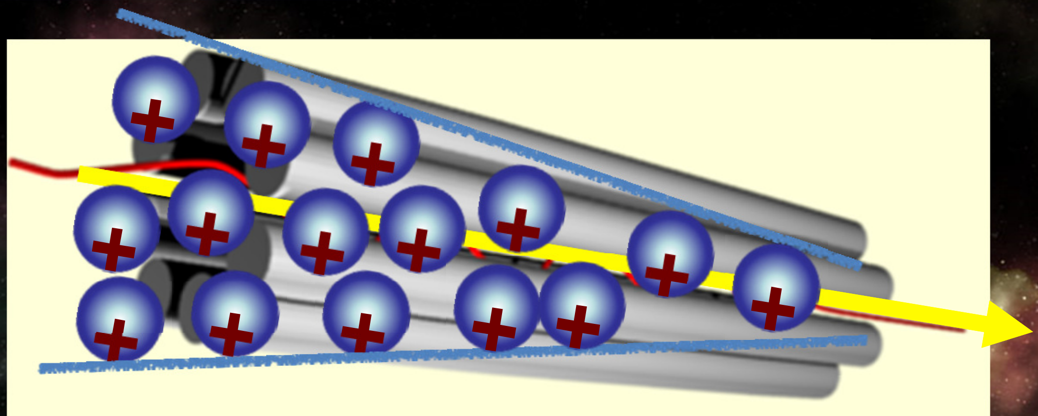
Octupolar ion guide: a 2D trap for ions

Trapping of ions is not possible with electrostatic fields (saddle point only)



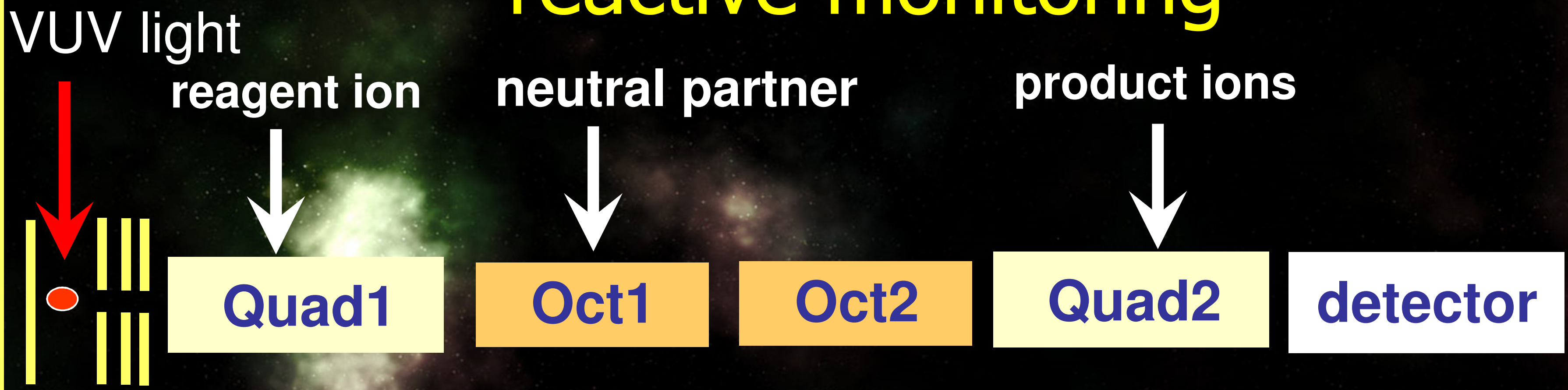


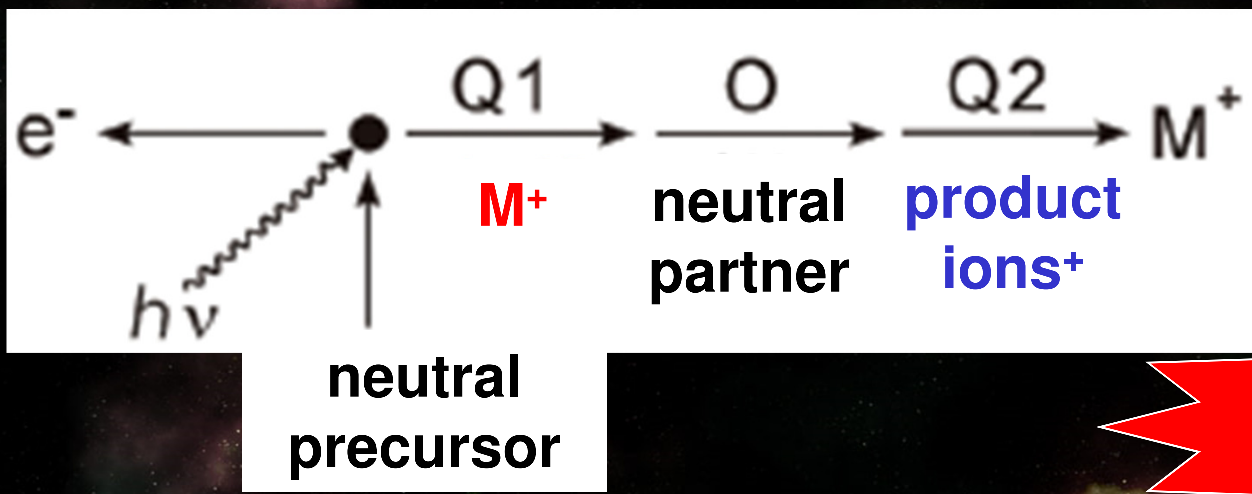
Trapping is possible in a fast oscillatory electric field
(MHz range for trapping molecules)



low energy (meV- eV) ion beam

Ion generation via photoionization + reactive monitoring

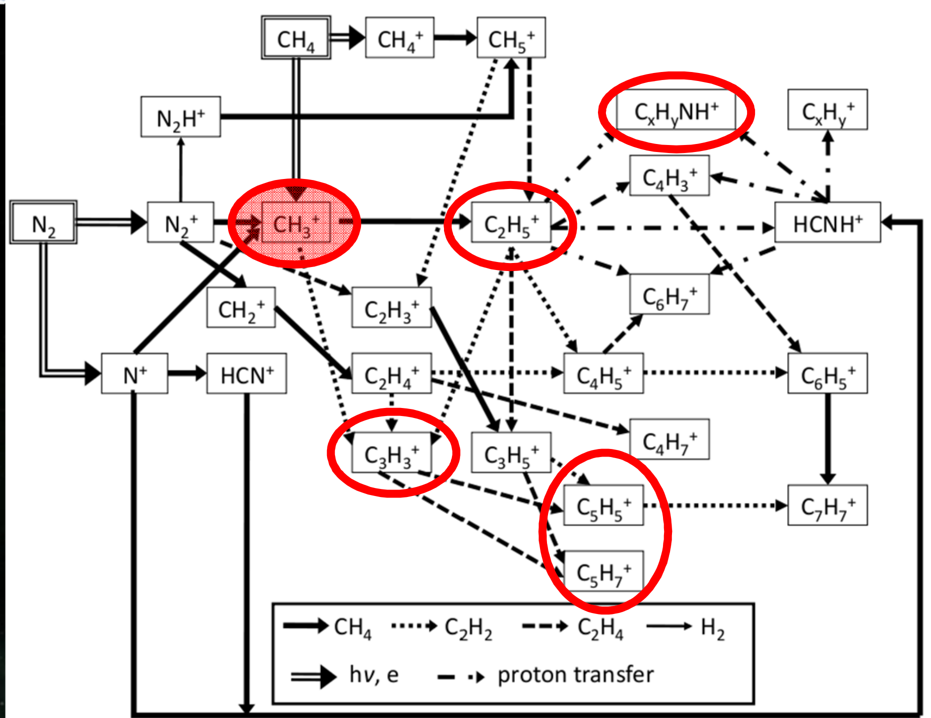




Chr. Alcaraz & his team

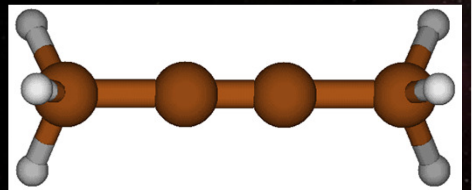
The CERISES set-up @SOLEIL synchrotron
DESIRS beamline (5-40 eV)

Reactivity of CH_3^+ with C_4H_6



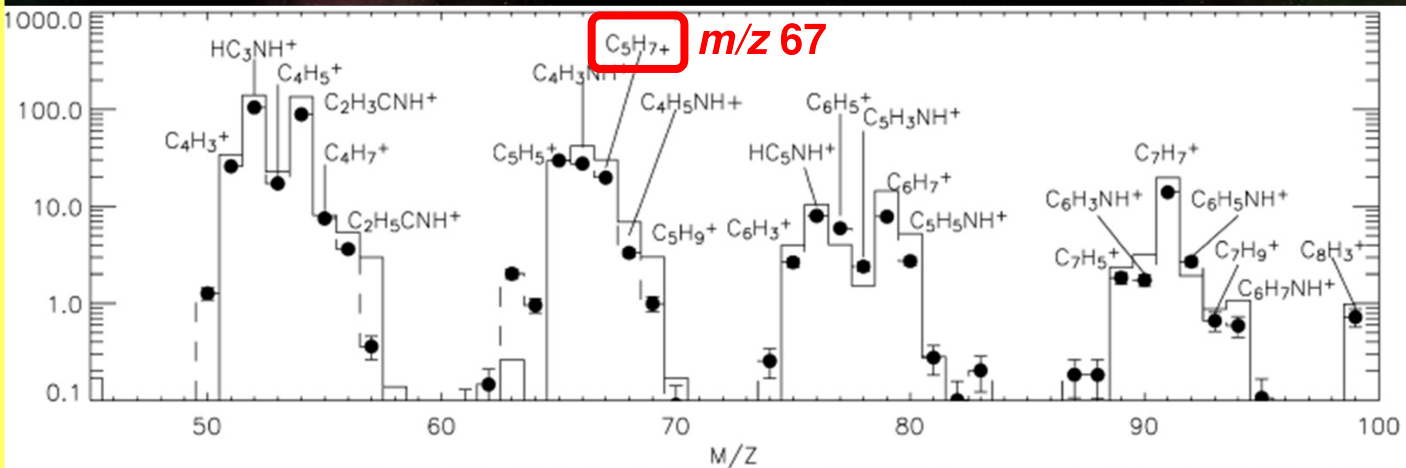
V. Vuitton et al. (2014) «Chemistry of Titan's atmosphere»

CH_3^+ (30-50 cm^{-3} @1100km): key role in the formation of complex HC on Titan

Reactivity with 

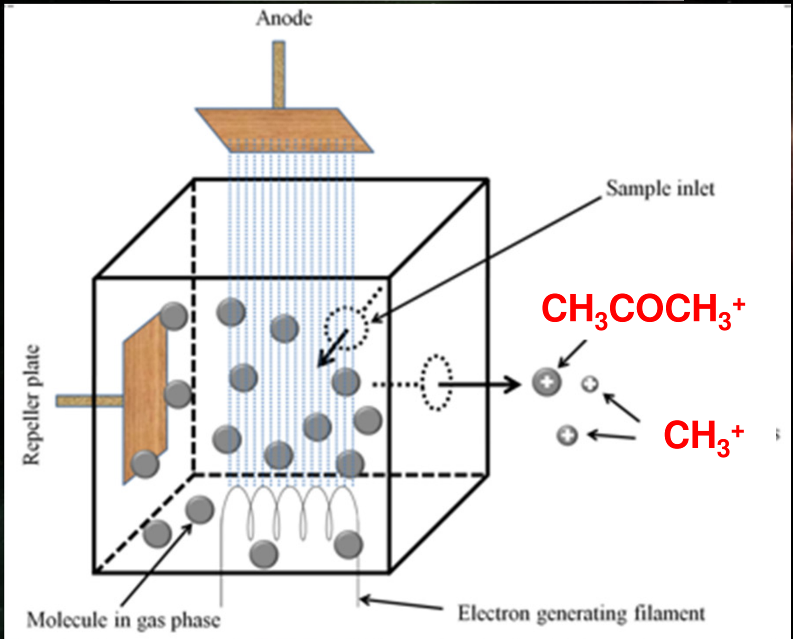
C. Puzzarini &co. *Planetary Space Sci. (2013)* **87**, 96-105

$$CH_3^+ + CH_3CCCH_3$$
$$\downarrow$$
$$c\text{-}(CH_3)_2C_3H^+ + H_2$$



Role of CH_3^+ internal energy on reactivity

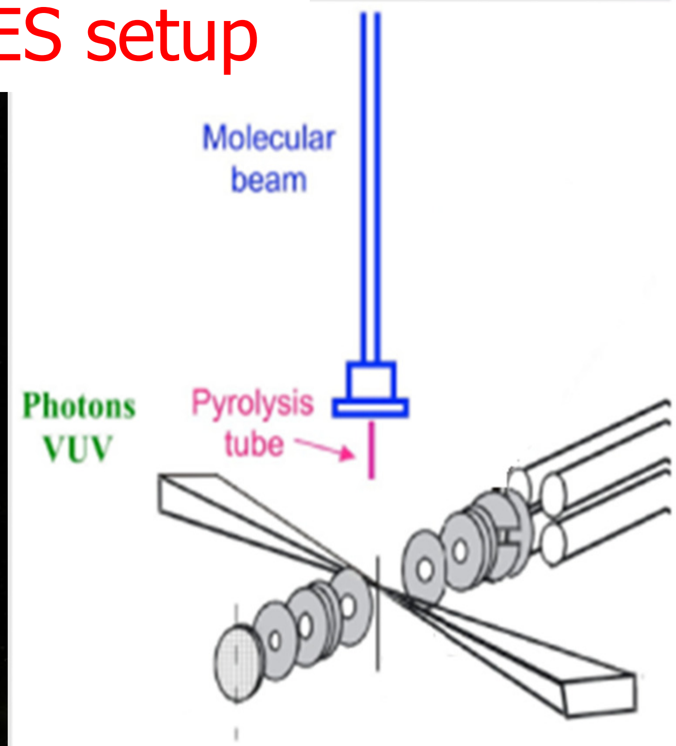
TRENTO setup



Dissociative ionization of acetone in an electron ionization source

«uncontrolled» internal excitation

CERISES setup



VUV photoionization of CH_3 radicals from a molecular beam flash-pyrolysis source

«controlled» internal excitation

Experimental results -1

$CH_3^+ + C_4H_6 \rightarrow C_4H_5^+ + CH_4$ H^- abstraction

$\rightarrow C_4H_6^+ + CH_3$ CT

$\rightarrow C_3H_5^+ + C_2H_4$

$\rightarrow C_2H_3^+ + CH_4 + C_2H_2$

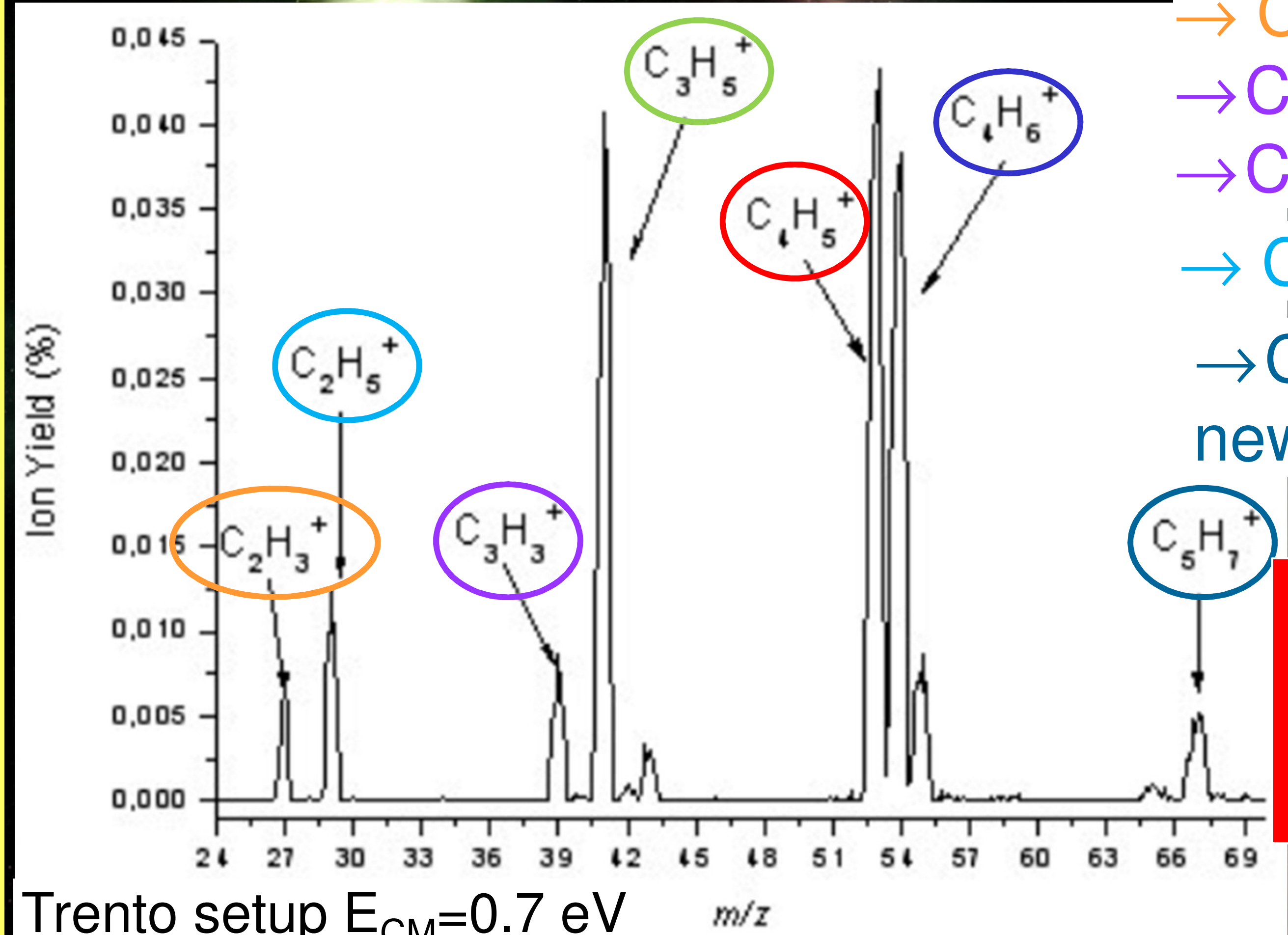
$\rightarrow C_3H_3^+ + 2CH_3$

$\rightarrow C_3H_3^+ + C_2H_4 + H_2$

$\rightarrow C_2H_5^+ + C_3H_4$

$\rightarrow C_5H_7^+ + H_2$

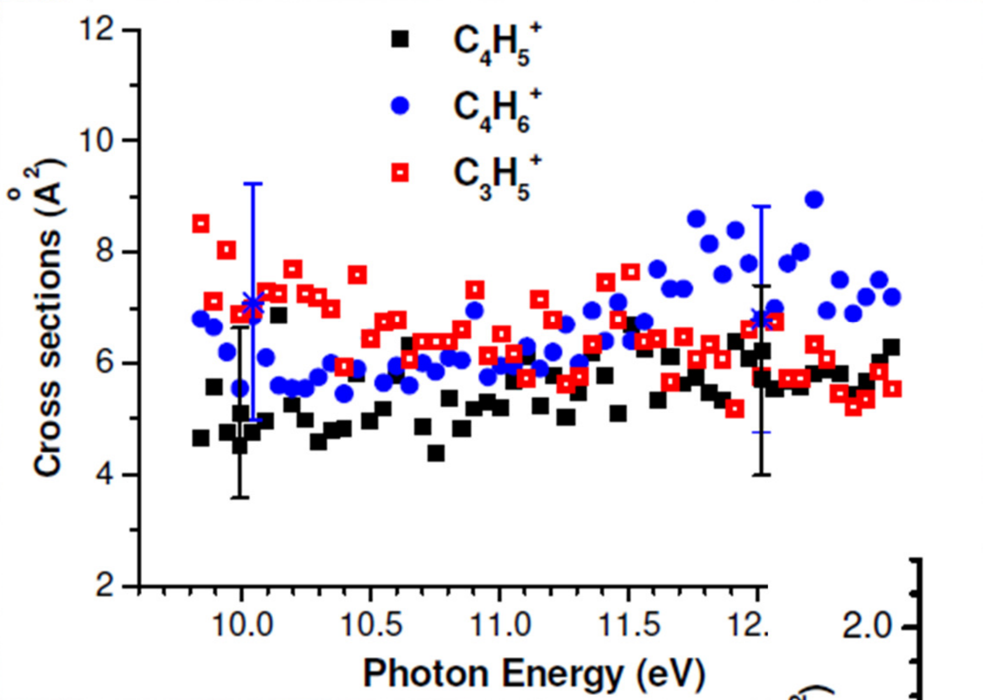
new C-C bonds



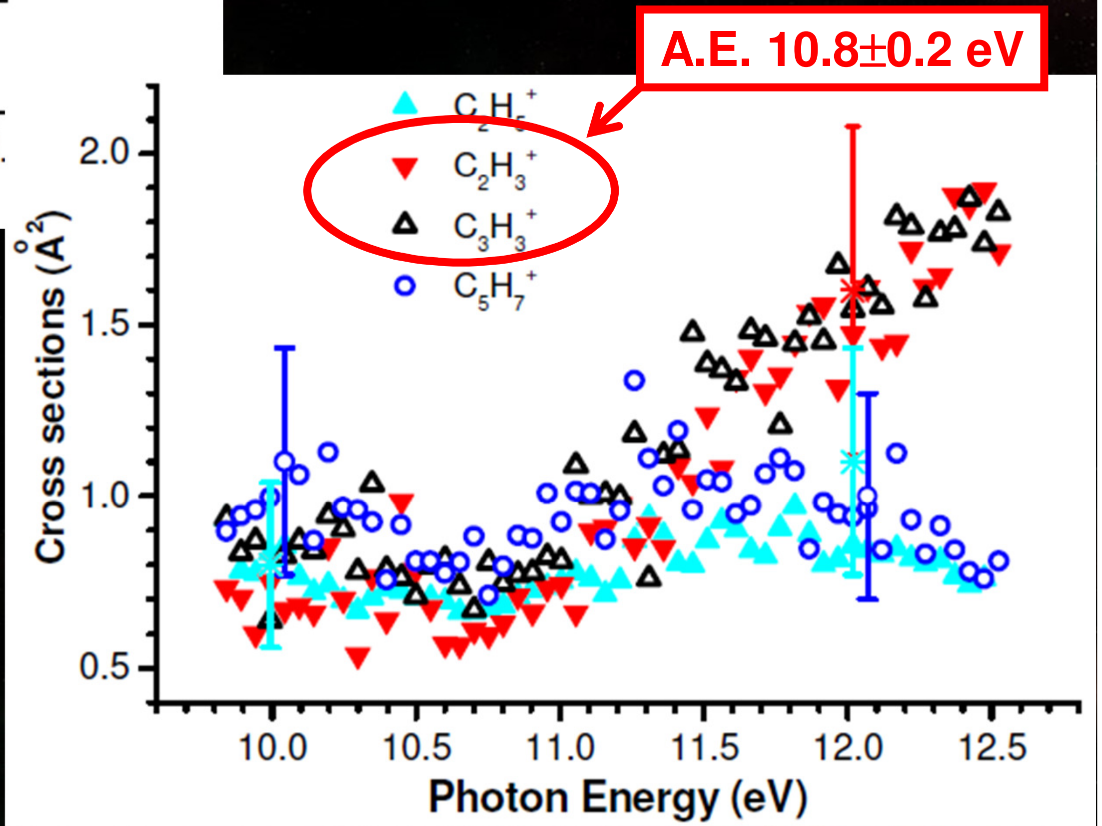
Trento setup E_{CM}=0.7 eV

Complex mediated molecular growth

Experimental results -2

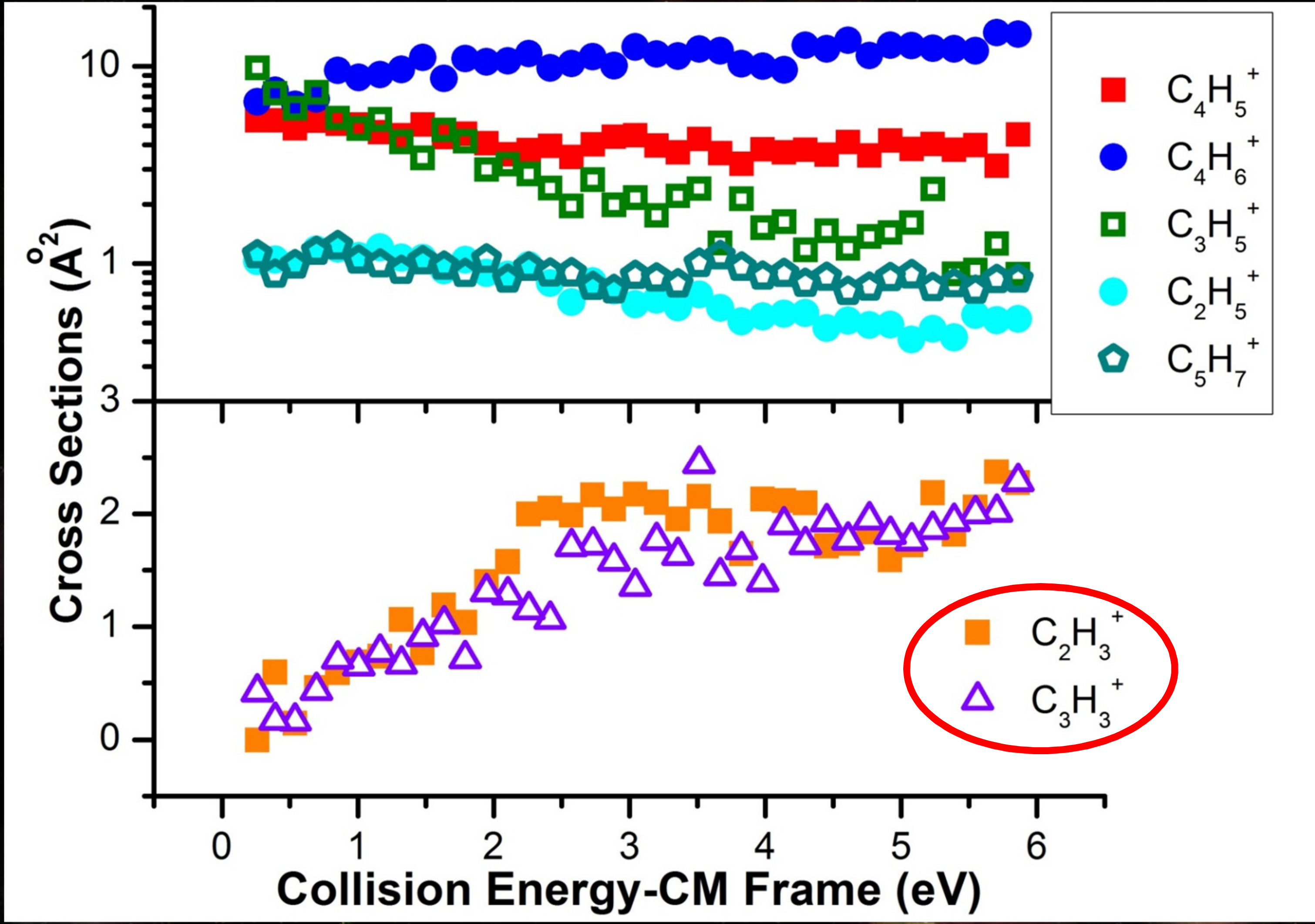


Cross sections at increasing photon energies (at fixed E_{CM}=0.3 eV)



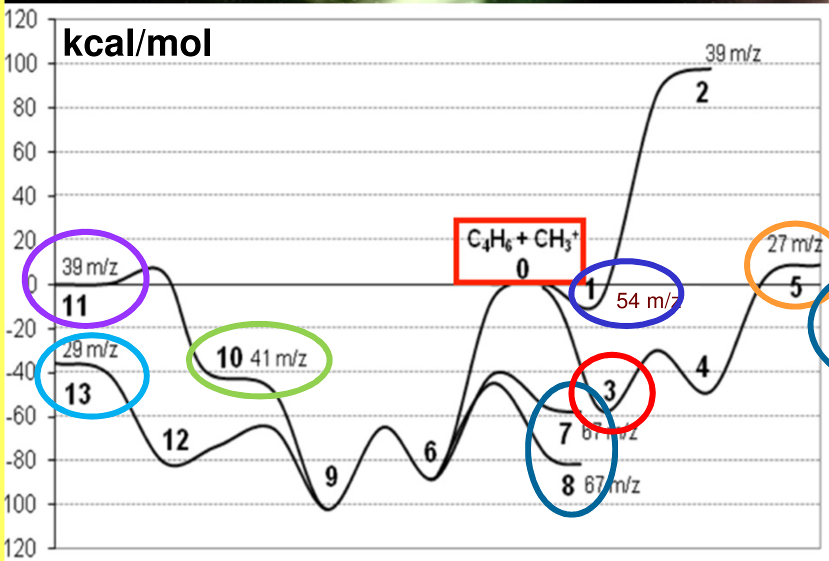
1. Internal excitation of CH_3^+ changes with photon energy
2. Reactivity depends on the CH_3^+ excitation

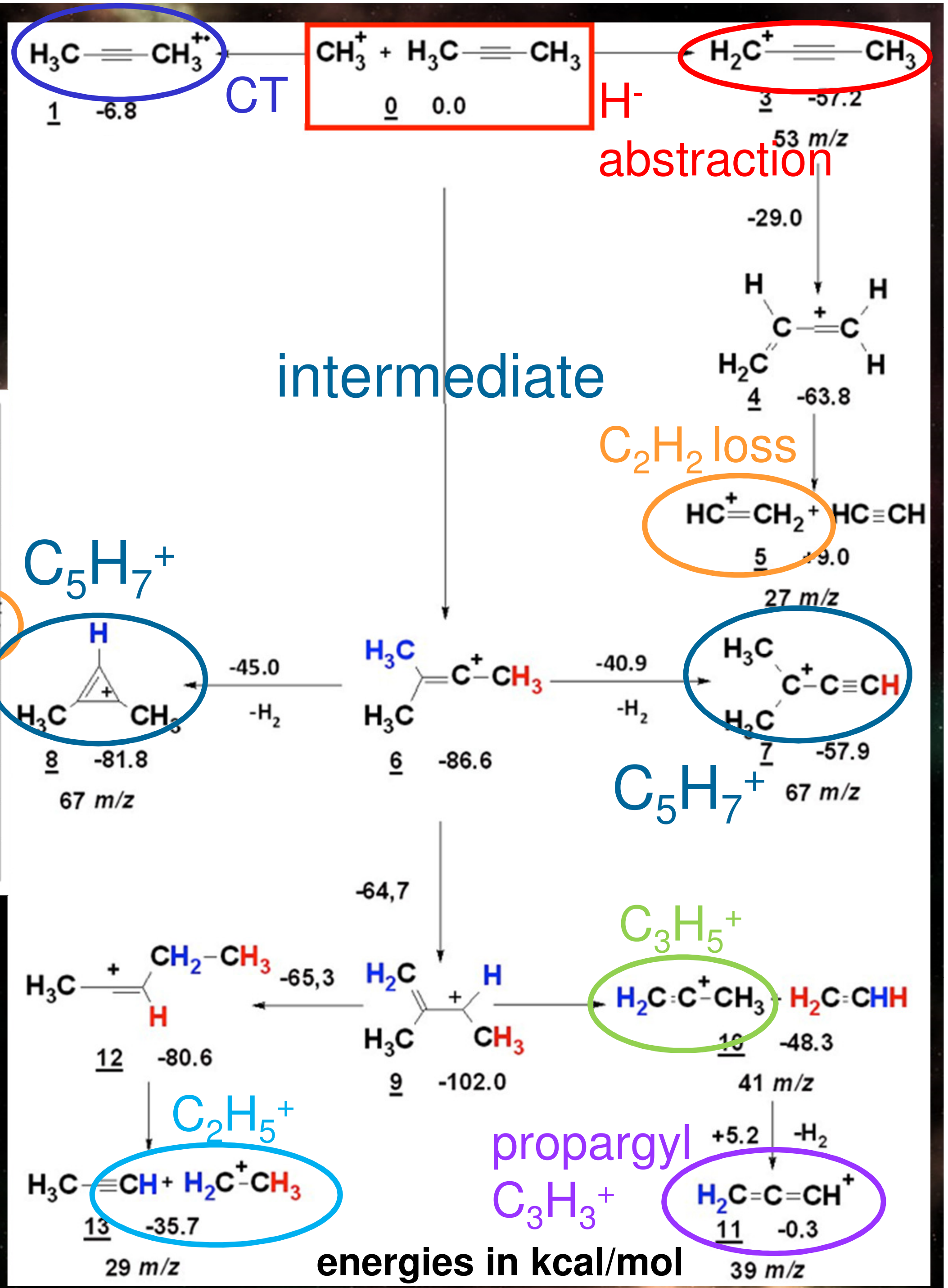
Experimental results -3



Cross sections as a function of E_{CM} (at fixed photon energies =10 eV)

Reaction mechanisms





DFT: M06-2X/cc-pVTZ

G. Tonachini, A. Maranzana
University of Turin

Isomer-selective generation of $CH_3CN^{+\bullet}$ / $CH_2CNH^{+\bullet}$ radical cations

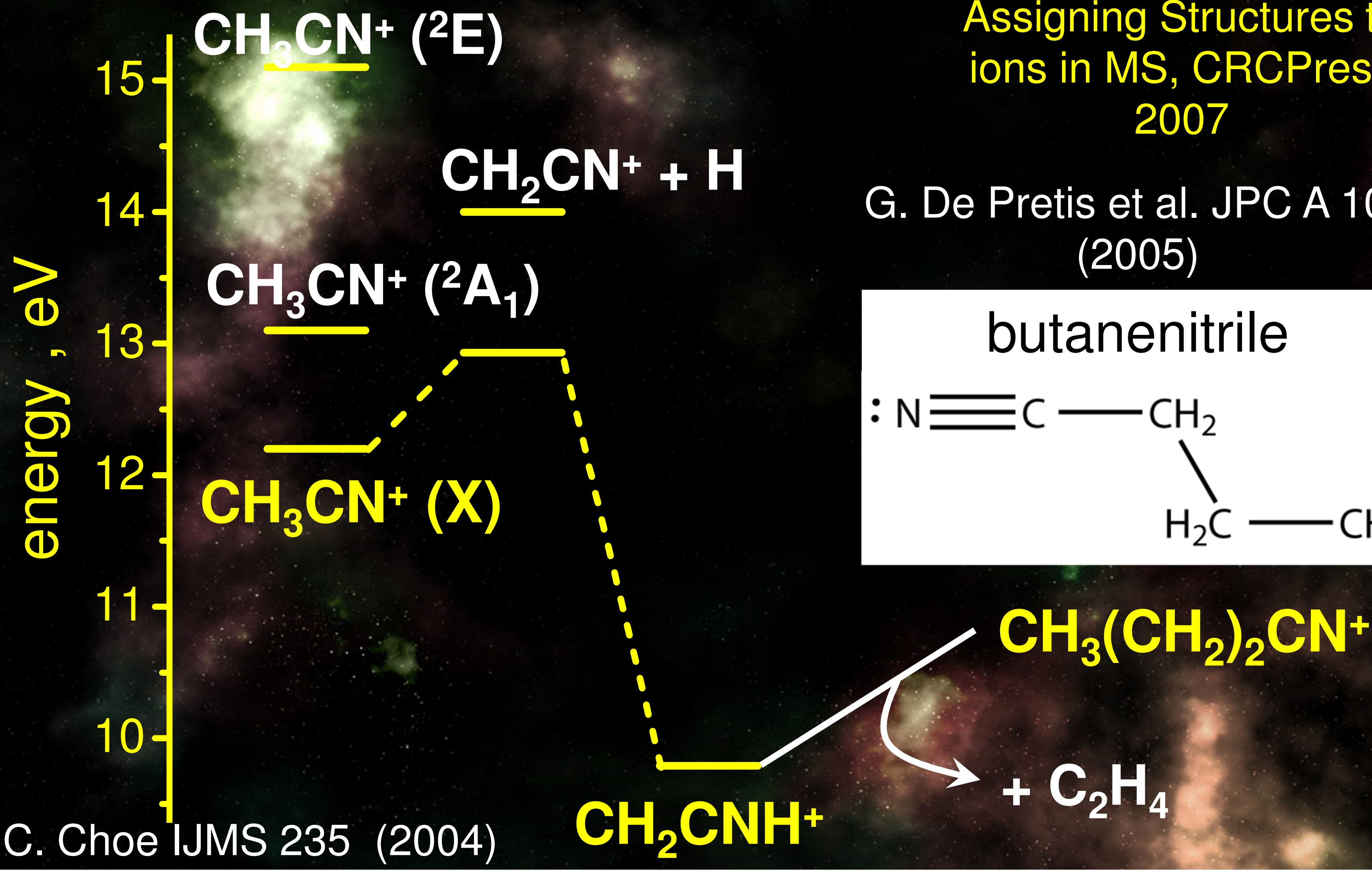
- $[C_2H_3N]^{+\bullet}$ + C_2H_4

The CH_3CN^+/CH_2CNH^+ isomerization

Upon ionization acetonitrile can isomerize into the keteneimine cation

J.L.Holmes et al. Assigning Structures to ions in MS, CRCPress 2007

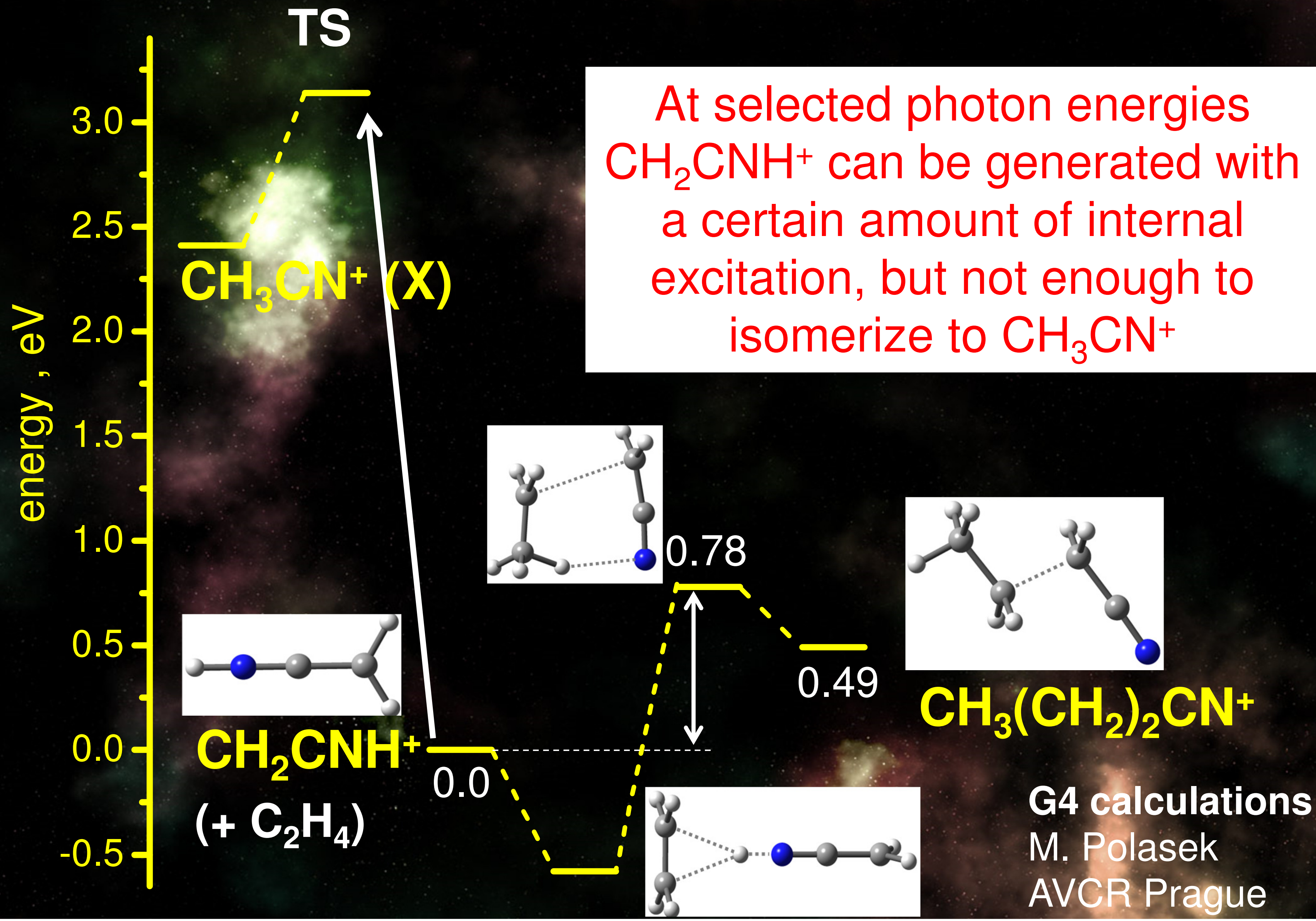
G. De Pretis et al. JPC A 109 (2005)



J. C. Choe IJMS 235 (2004)

Internal energy of CH_2CNH^+

At selected photon energies CH_2CNH^+ can be generated with a certain amount of internal excitation, but not enough to isomerize to CH_3CN^+



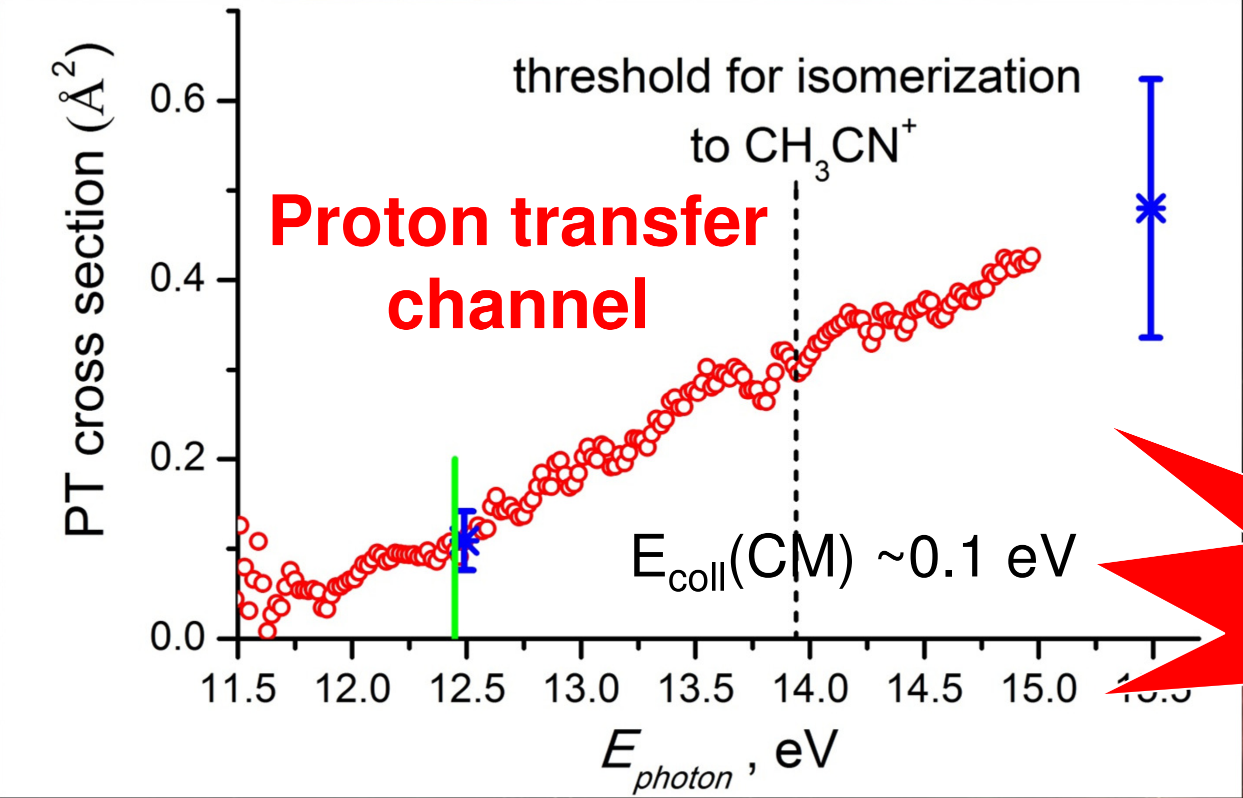
Reactivity of CH_2CNH^+ with C_2H_4

Proton transfer

$CH_2CNH^+ + C_2H_4 \rightarrow CH_2CN + C_2H_5^+$ $\Delta H = +0.83$ eV

Charge transfer

$CH_2CNH^+ + C_2H_4 \rightarrow CH_2CNH + C_2H_4^+$ $\Delta H = +1.79$ eV



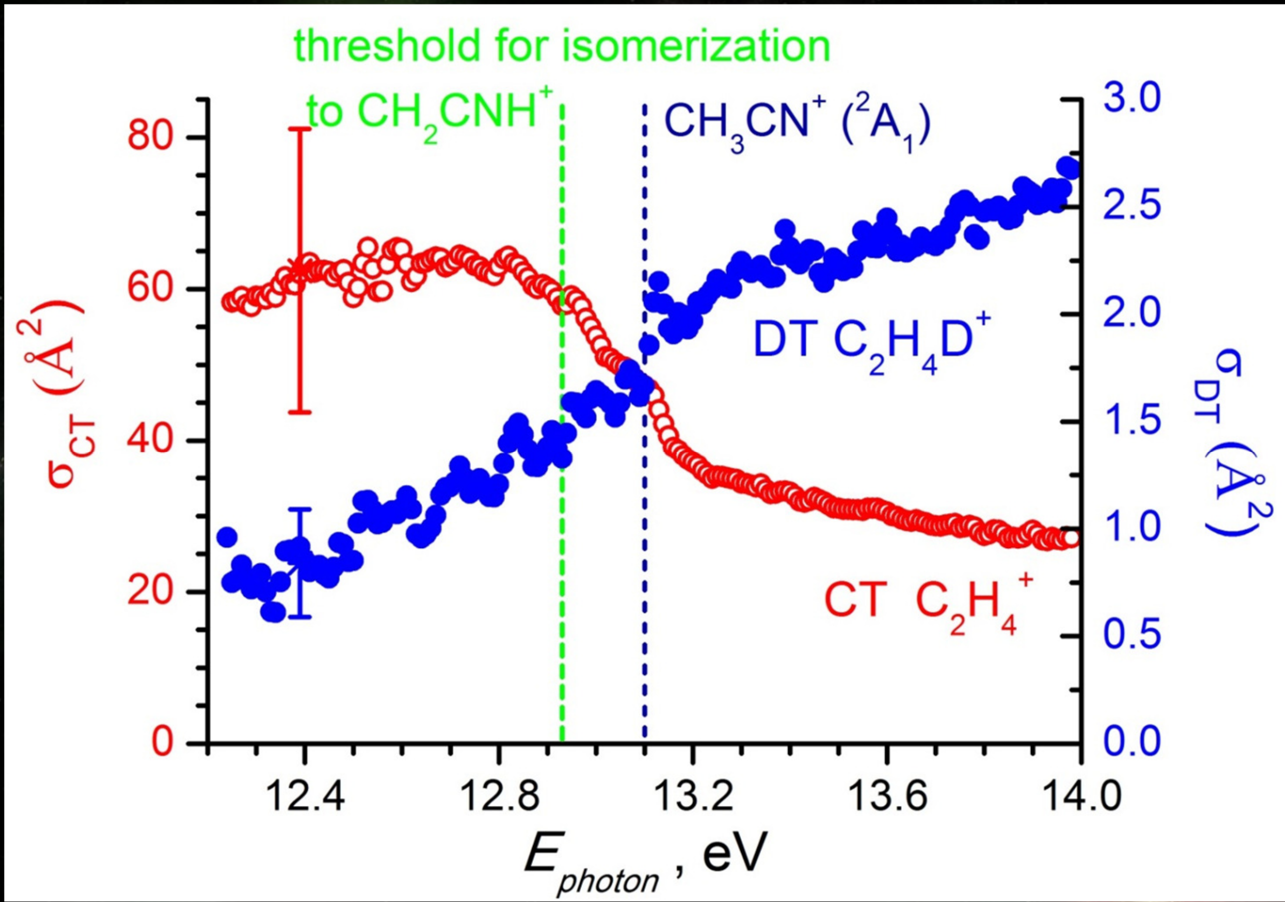
Effect of internal excitation

CT is never observed

Reactivity of CD_3CN^+ with C_2H_4

DT $CD_3CN^+ + C_2H_4 \rightarrow CD_2CN + C_2H_4D^+$ $\Delta H = -1.5$ eV

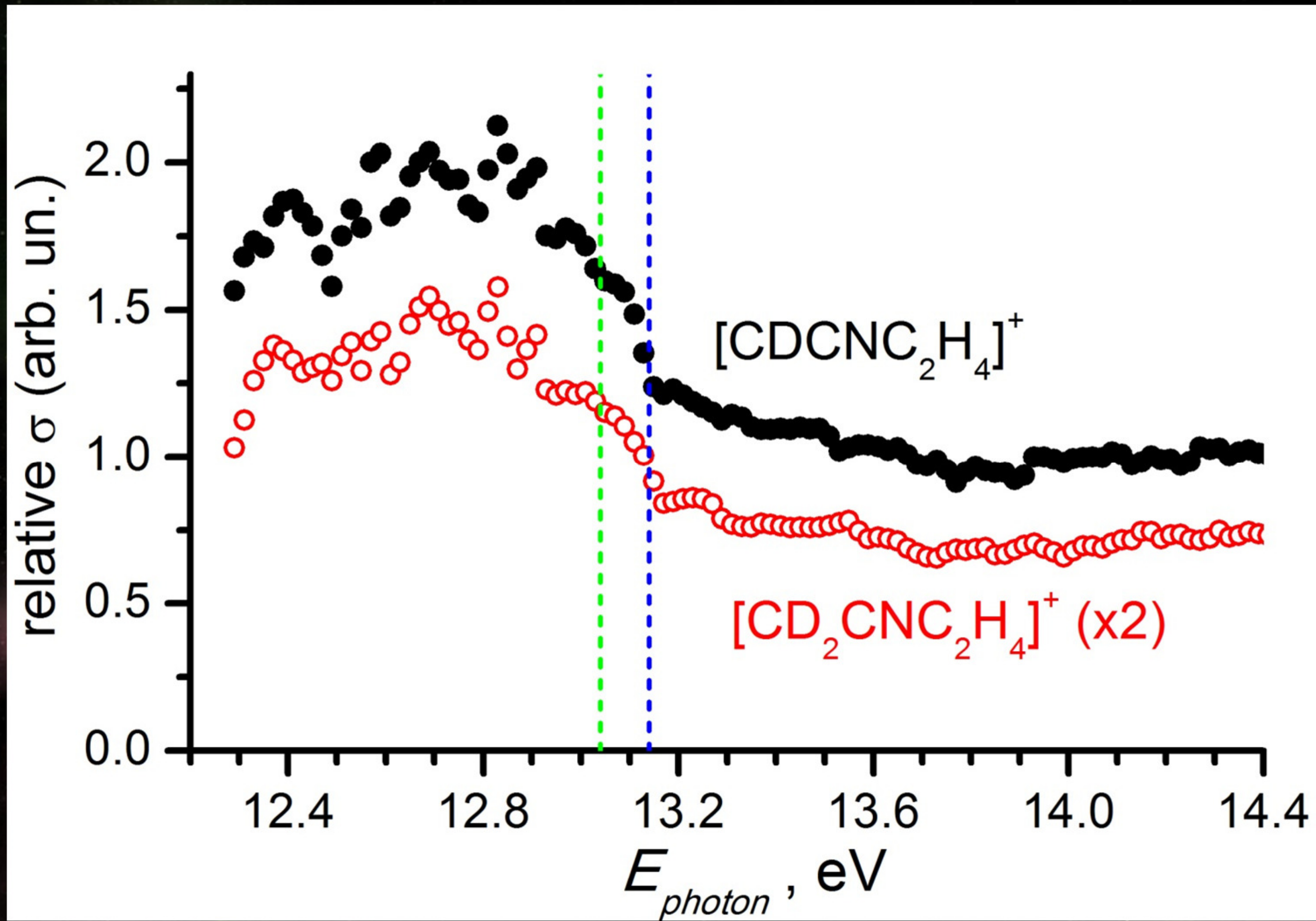
CT $CD_3CN^+ + C_2H_4 \rightarrow CD_3CN + C_2H_4^+$ $\Delta H = -1.7$ eV



- Reactivity dominated by CT
- DT more likely at the opening of electronic excitation and isomerization

CT decrease at opening of isomerization/el.excitation: at hν<12.8 eV the ion beam is essentialy CH_3CN^+

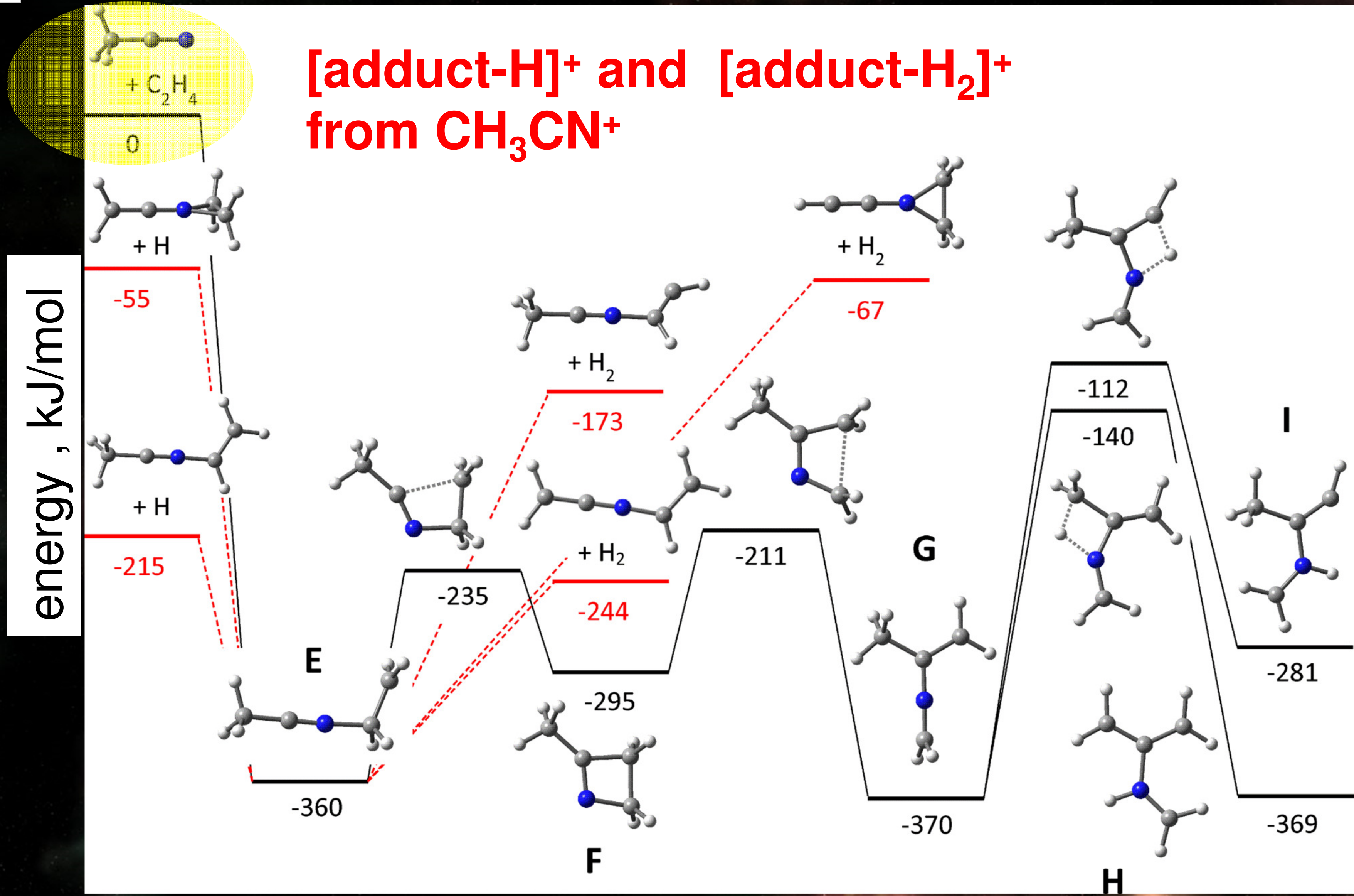
$CD_3CN^+ + C_2H_4$: new C-C bond formation



Products formally corresponding to loss of D and D_2 from an adduct are observed from the CH_3CN^+ isomer but NOT from CH_2CNH^+

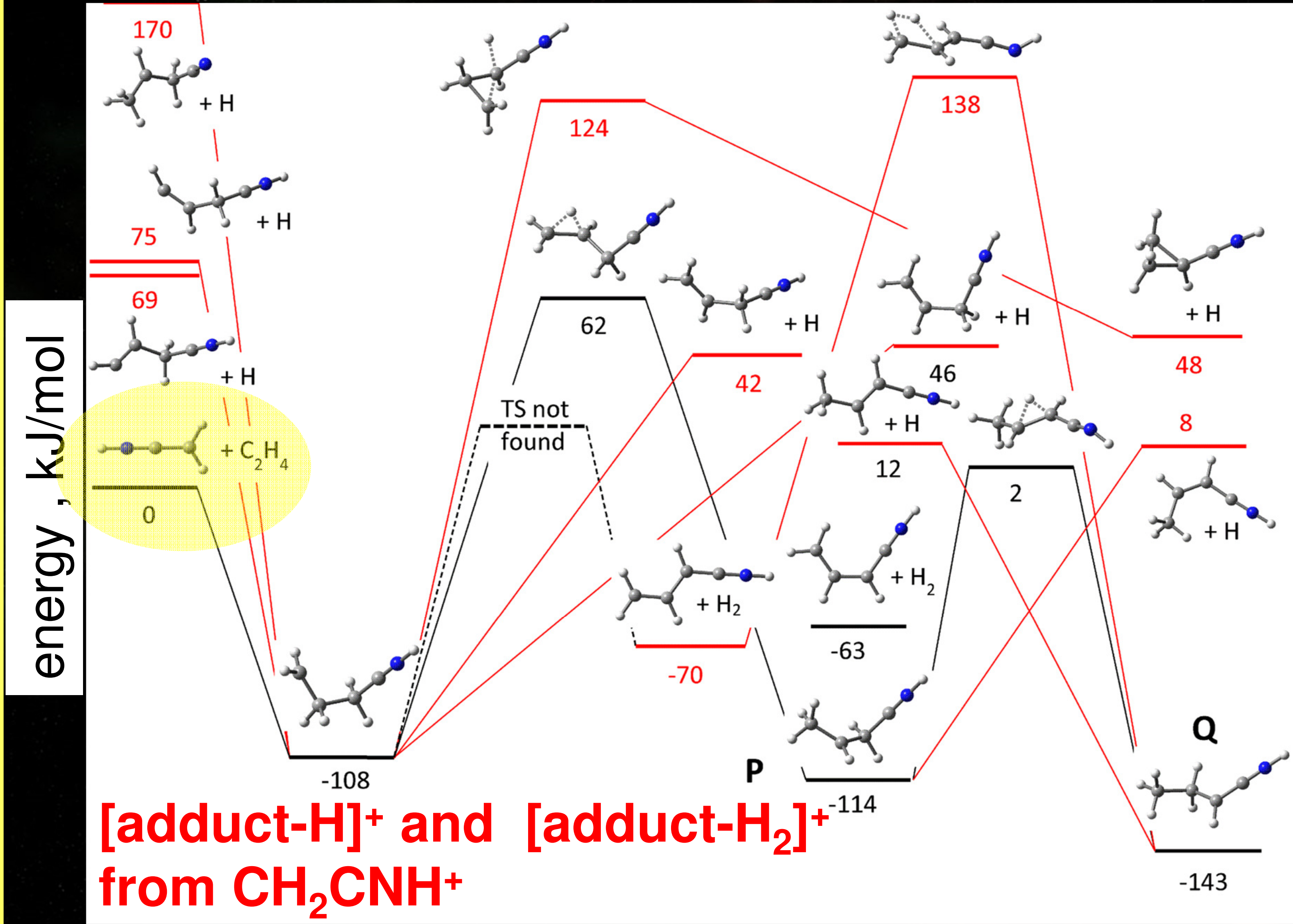
$CH_3CN^+ + C_2H_4$: C-C bond formation

[adduct-H]⁺ and [adduct-H₂]⁺ from CH_3CN^+



M. Polasek et al. JPCA (2016) in press, Casavecchia and Laganà Festschrift DOI 10.1021/acs.jpca.5b12757

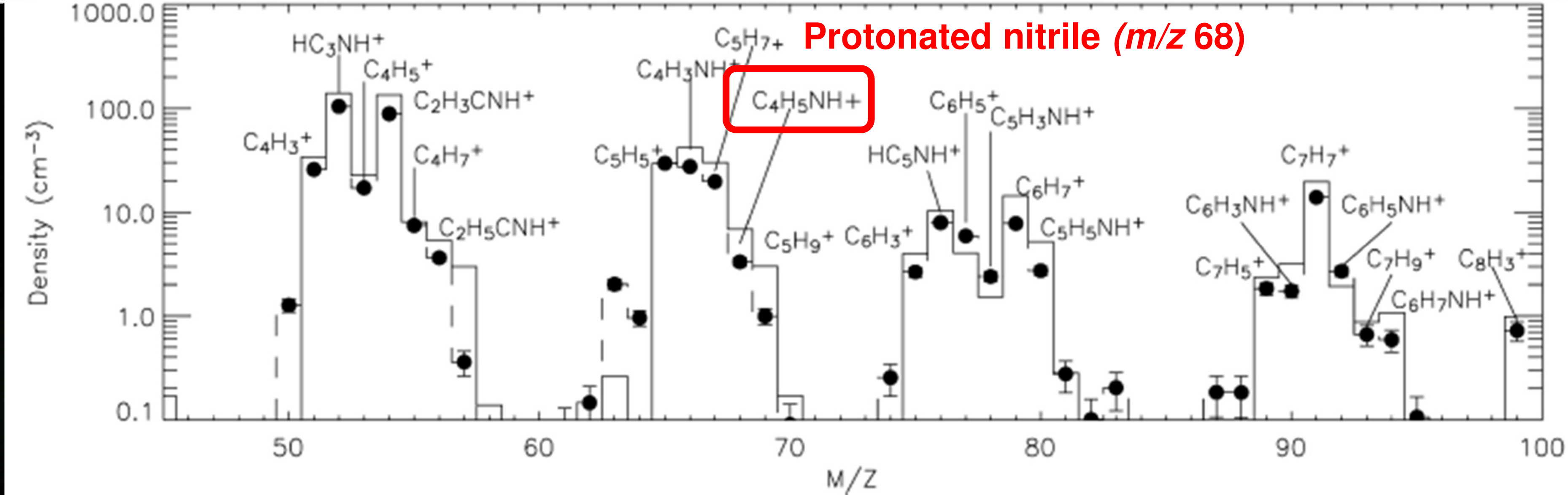
$CH_2CNH^+ + C_2H_4$: no C-C bond formation



[adduct-H]$^+$ and [adduct-H_2]$^+$ from CH_2CNH^+

M. Polasek et al. JPCA (2016) in press, Casavecchia and Laganà Festschrift DOI 10.1021/acs.jpca.5b12757

Implication for Titan chemistry



V. Vuitton et al. Icarus 2007 **191**, 722–742.

Proposed formation mechanism:

1) $C_3H_5^+ + HCN \rightarrow C_4H_5NH^+ + h\nu$ radiative association

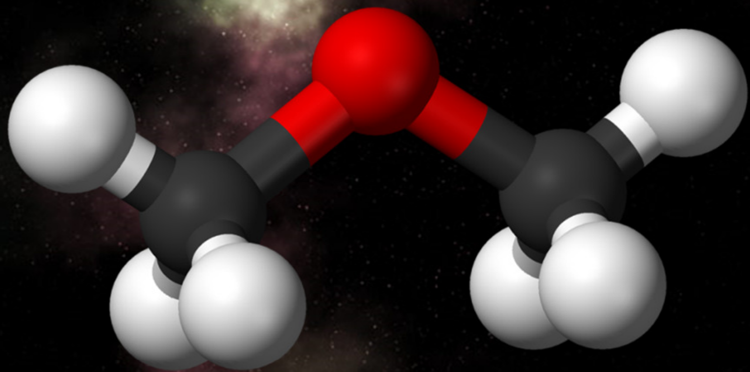
2) $C_2H_5^+ + C_4H_5N \rightarrow C_4H_5NH^+ + C_2H_4$

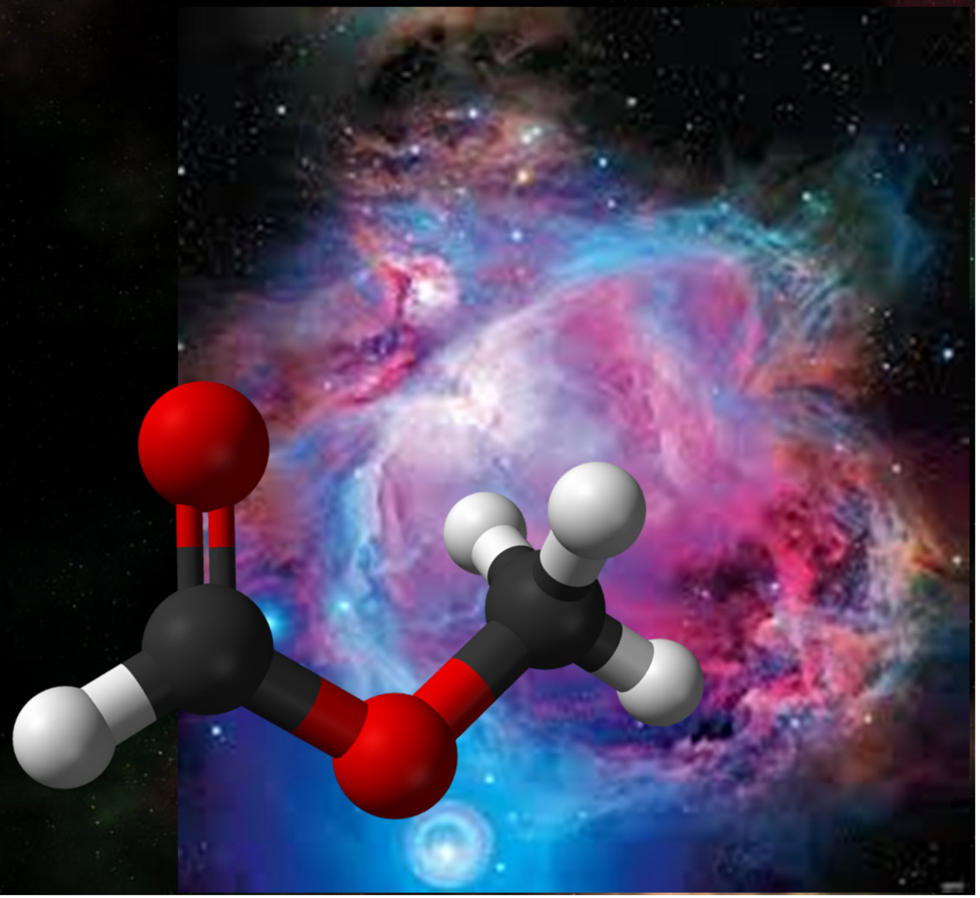
$HCNH^+ + C_4H_5N \rightarrow C_4H_5NH^+ + HCN$ proton transfer

Our additional suggestion:

$CH_3CN^+ + C_2H_4 \rightarrow C_4H_6N^+ + H$

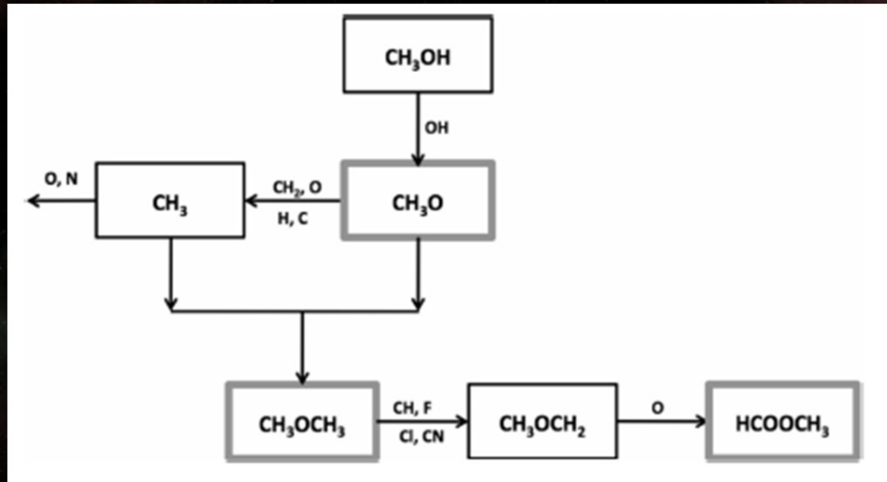
Dissociative charge transfer of CH_3OCH_3 (DME) and $HCOOCH_3$ (MF) in collisions with He^+ ions





Formation Mechanisms

Combined grain and gas-phase chemistry

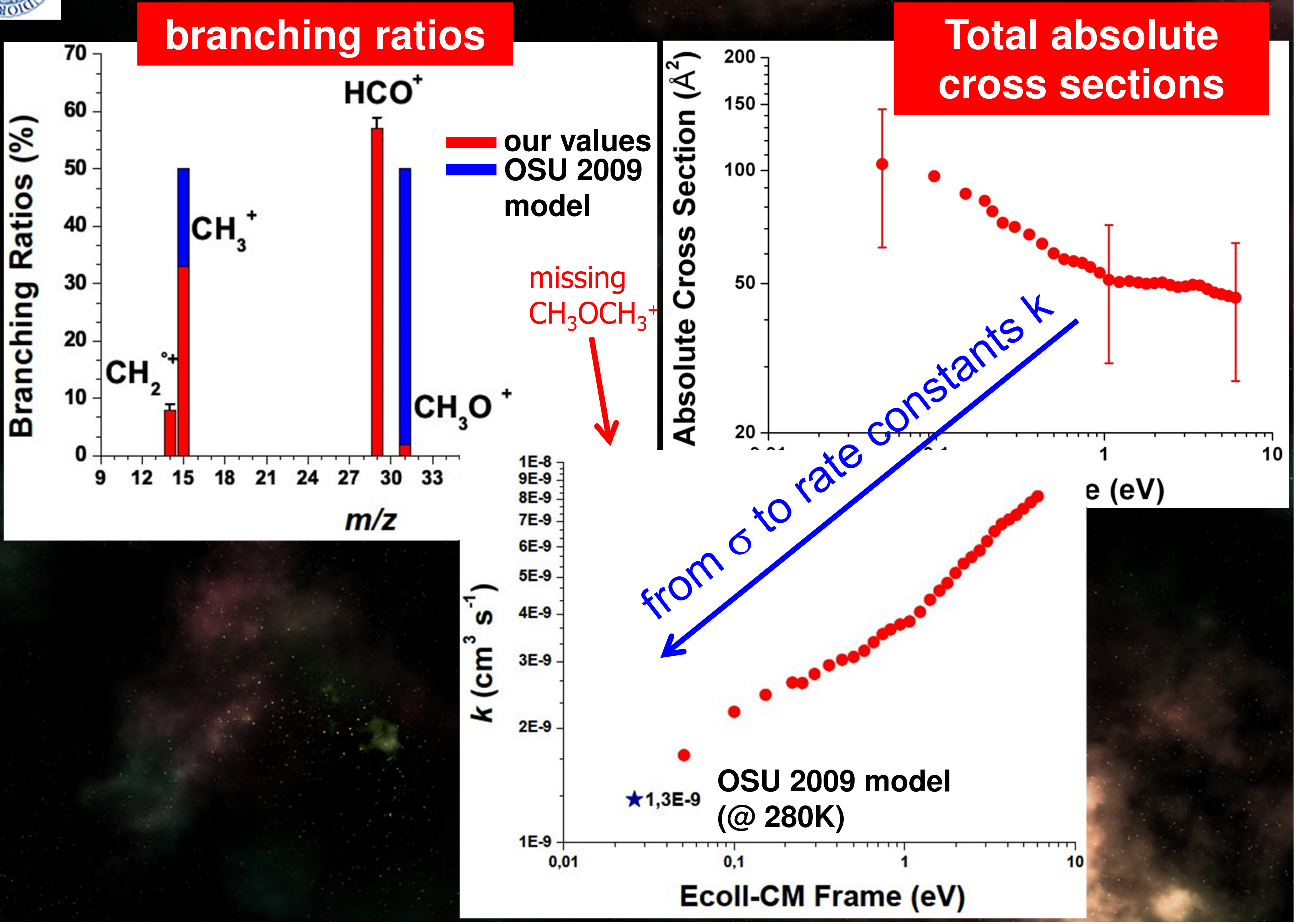


N.Balucani et al., *M.N.R.A.S*, 2015, **449**, L16-L20.

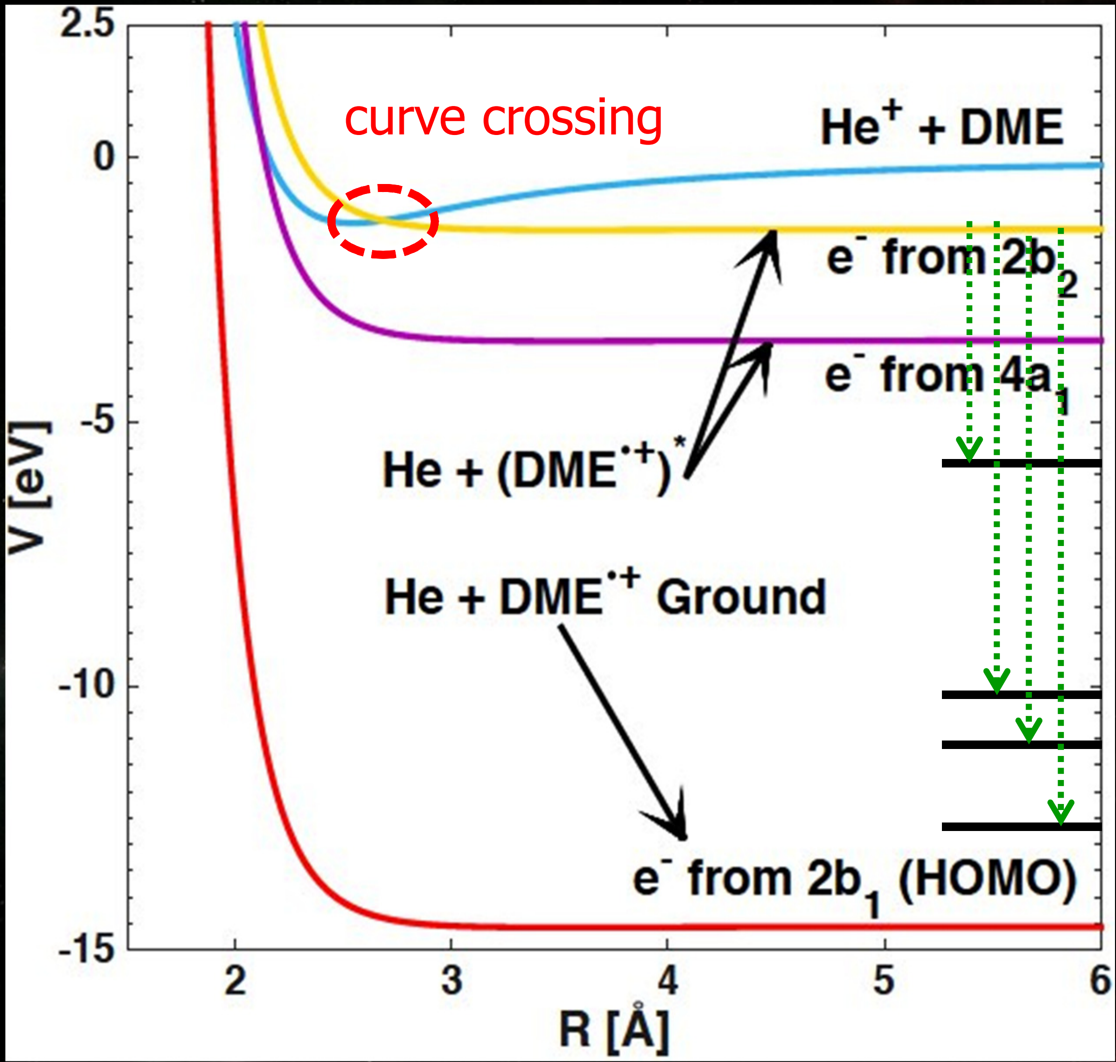
Destruction Mechanisms

- photons
- cosmic rays
- ion-molecule reactions
  - fragmentations by energetic ions (H^+, He^+ C^+)
  - protonation (by H_3^+, HCO^+, H_3O^+)

He^+ plus DME


branching ratios
Branching Ratios (%)
HCO+
CH3+
CH2°+
CH3O+
m/z
our values
OSU 2009 model
missing CH3OCH3+
Total absolute cross sections
Absolute Cross Section (Å2)
from σ to rate constants k
k (cm3 s-1)
OSU 2009 model (@ 280K)
1,3E-9
Ecoll-CM Frame (eV)

He^+ plus DME: PES modelling



inner valence orbitals of DME

CH_2^+ + H + CH_3O + He

CH_3O^+ + CH_3 + He

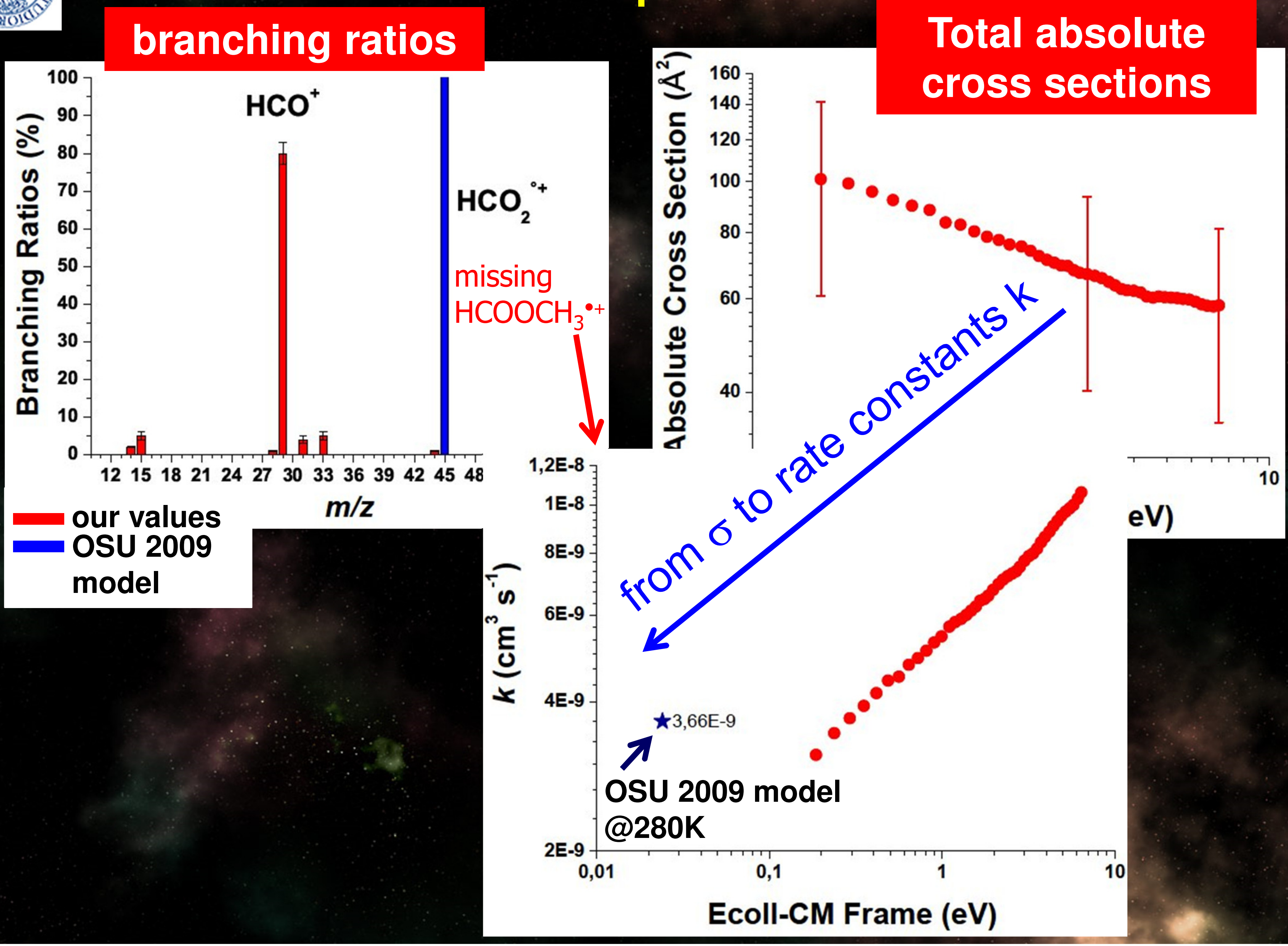
CH_3^+ + CH_3O + He

HCO^+ + H_2 + CH_3 + He

In collaboration with Fernando Pirani (Univ. Perugia)

Y.R. Miao et al., *JESRP*, 2014, **193**, 1-5

He^+ plus MF


branching ratios
Branching Ratios (%)
100
90
80
70
60
50
40
30
20
10
0
HCO+
HCO2°+
missing
HCOOCH3•+
12 15 18 21 24 27 30 33 36 39 42 45 48
m/z
our values
OSU 2009 model
Total absolute cross sections
Absolute Cross Section (Å2)
160
140
120
100
80
60
40
10
eV)
from σ to rate constants k
k (cm3 s-1)
1,2E-8
1E-8
8E-9
6E-9
4E-9
2E-9
3,66E-9
OSU 2009 model
@280K
0,01
0,1
1
10
Ecoll-CM Frame (eV)

Conclusions

- Reaction of CH_3^+ with CH_3CCCH_3 leads to new C-C bond product $C_5H_7^+$ in two different isomeric forms

- Photoionization of adequate precursors (CH_3CN and butanenitrile) is a good way to obtain pure CH_3CN^+/CH_2CNH^+ isomers

- Absolute cross sections and BR for destruction of DME and MF by collisions with He^+

Credits

University of Trento

- Paolo Tosi
- Andrea Cernuto (PhD student)
- Linda Giacomozzi (ex grad.stud.)

In collaboration with:

University Paris-Sud-CNRS & SOLEIL Synchrotron

- Christian Alcaraz
- C. RomanzinAllen Lopes, B. Cunha de Miranda

University of Turin

- Andrea Maranzana
- Glauco Tonachini

University of Perugia

- Fernando Pirani
- Nadia Balucani

IPAG Grenoble

- Cecilia Ceccarelli

Acad. Science Czech Rep., Prague

- Jan Zabka
- Miroslav Polasek

Thanks to Our Astro-Chemical History cost for support via STSM