Molecular fragmentation of acetylene by VUV double photoionization

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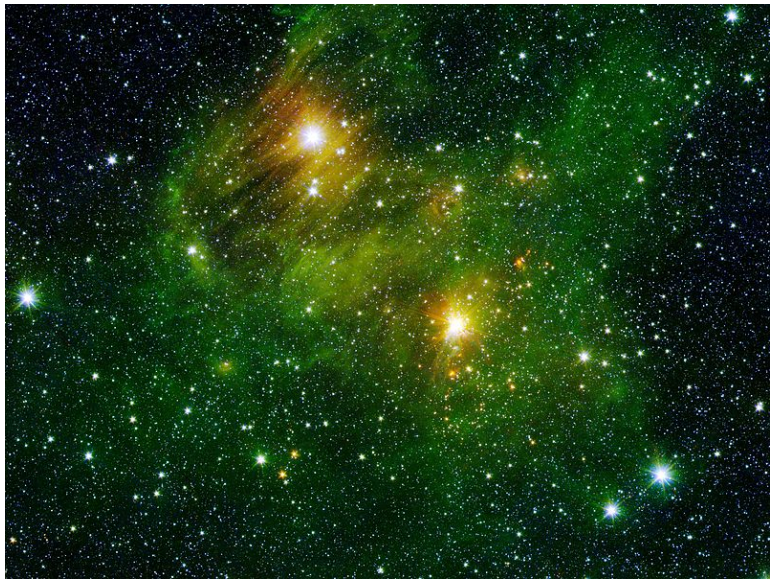
A very important characteristic for the chemistry of molecules in the interstellar medium and planetary ionospheres is that they interact with the electromagnetic waves: γ and X rays, UV light.

For example, the interaction with the ultraviolet light is responsible of the limited growth of the organic molecules.



The UV photochemistry studies can be performed by using an intense and tunable light source as the synchrotron radiation

By using the UV light, molecules can be ionized producing mono and di-cations

It has to be noted that molecular CO_2^{2+} and N_2^{2+} dications have been predicted to exist with significant densities in Mars, Venus and Titan ionospheres.

O. Witasse, et al. Geophys. Res. Lett., 2002, **29**, 104.

O. Witasse, et al. Geophys. Res. Lett., 2003, **30**, 12.

J. Lilensten, et al. Geophys. Res. Lett., 2005, **32**, 03203.

G. Gronoff, et al. Astron. Astrophys., 2007, **465**, 641–645.

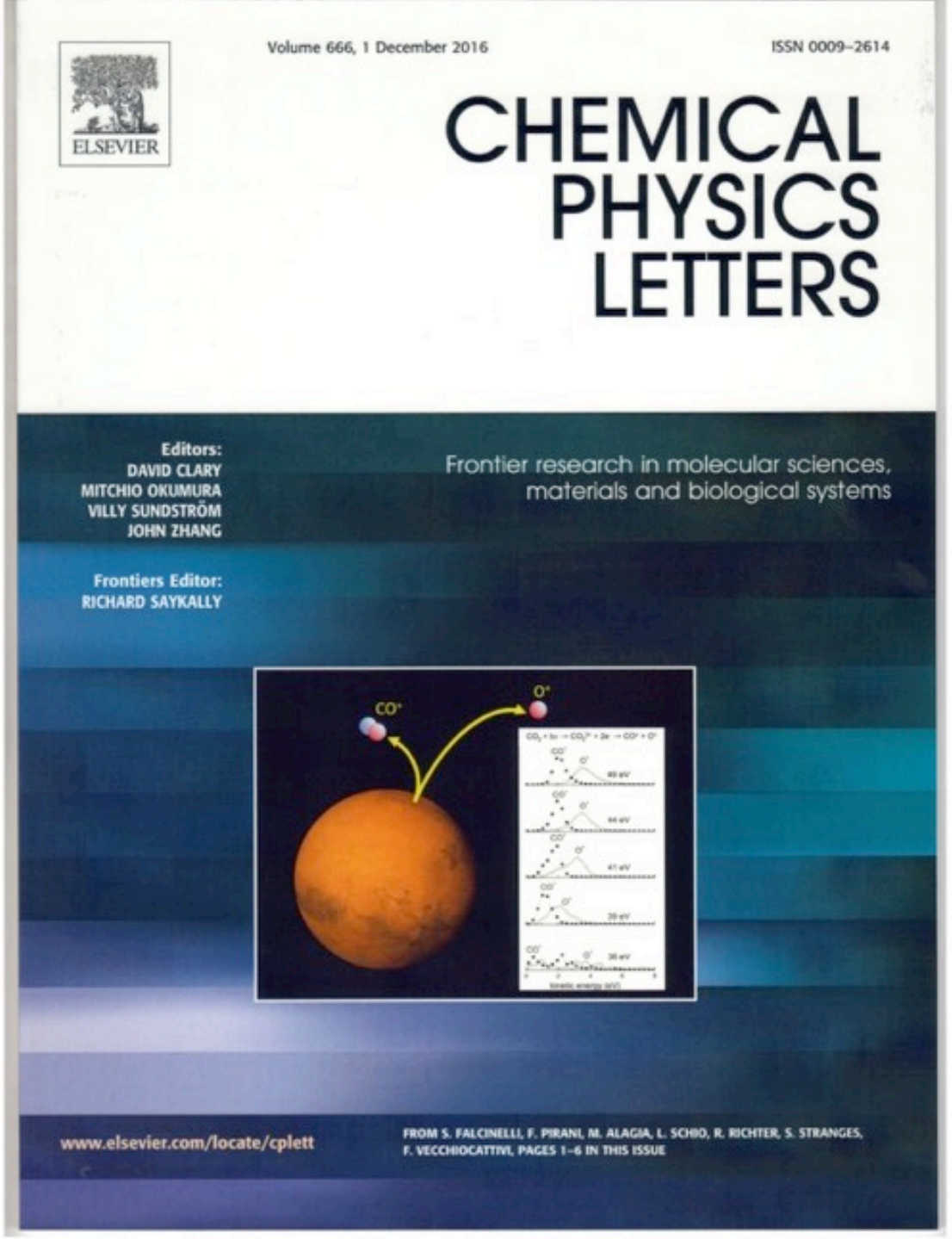
In the case of CO_2, by using 34-50 eV photon energy, the molecular fragmentation can be observed:

$$CO_2 + hv \rightarrow CO^+ + O^+ + 2e^-$$

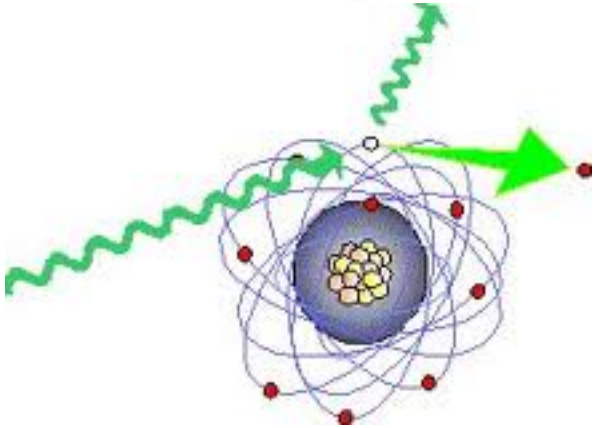
With a total kinetic energy of product ions ranging between 2 and 6 eV

This high kinetic energy relesead into CO^+ and O^+ ions can explain the lack in the O^+ concentration observed in the upper atmosphere of Mars by Viking 1 and Mariner 6

S. Falcinelli, F. Pirani, M. Alagia, *et al.*, *Chem. Phys. Lett.*, **666**, 1-6 (2016).

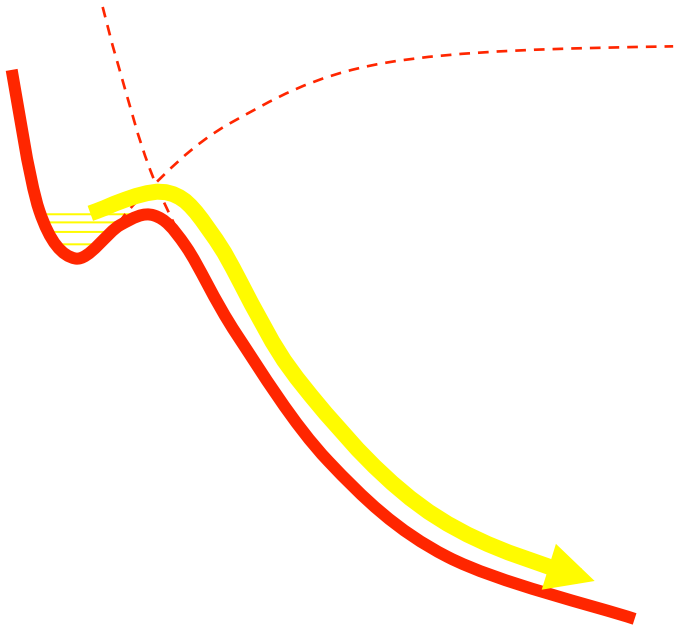


In general, when a molecule is ionized, can change deeply its chemical behavior because:



1 – the removed electron may change sensibly the electronic configuration of the neutral species modifying its chemical reactivity;

2 – the ion-molecule interaction is much more intense than the neutral-neutral one, making more probable the collision;



3 – the double ionization producing a molecular dication can induce Coulombic explosion and fragment ions formation with high kinetic energy content.

The importance of C_2H_2…

Acetylene molecules have been detected in interstellar medium.
Astronomers have observed it in the infrared, in both molecular clouds and in the envelopes of evolved stars. It is an important link in the chemistry of heavier carbon chain molecules and related species in these regions.

Acetylene is also found as a minor component in the atmospheres of gas giants like the planet Jupiter, in the atmosphere of Saturn's satellite Titan, and in comets.

Photochemical experiments have demonstrated that acetylene is a likely precursor of C_2, a widely observed component of comets.
It may therefore be itself a ubiquitous constituent of comets.

It has been proposed that polymerization of acetylene in cometary impact on planetary atmospheres may be responsible for the formation of polycyclic aromatic hydrocarbons (PAHs) which may in turn be responsible for the colors of the atmospheres of Jupiter and Titan.

T.Y. Brooke, A.T. Tokunaga, H.A. Weaver, J. Crovisier, D. Bockelee-Morvan, D. Crisp,
Nature 1996, *383*, 606.
J. Cernicharo *et al.*, Astrophys. J. 2001, *546*, L123.
P.M. Woods *et al.*, Astrophys. J. 2002, *574*, L167.
R. Kaiser, Chem Rev. 2002, *102(5)*, 1309-1358.
P.O. Momoh, S.A. Abrash, R. Mabrouki, M.S. El-Shall, J. Am. Chem Soc. 2006, *128*, 12408-12409.

The double photoionization of C_2H_2 molecules has been studied in the 31.9-50 eV photon energy range, by the use of synchrotron radiation…

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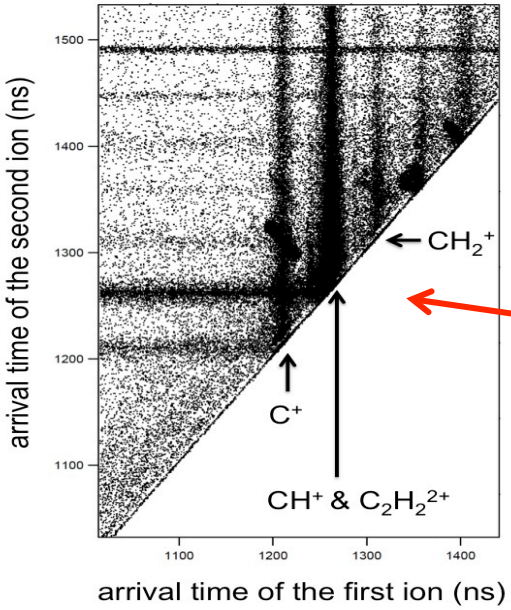
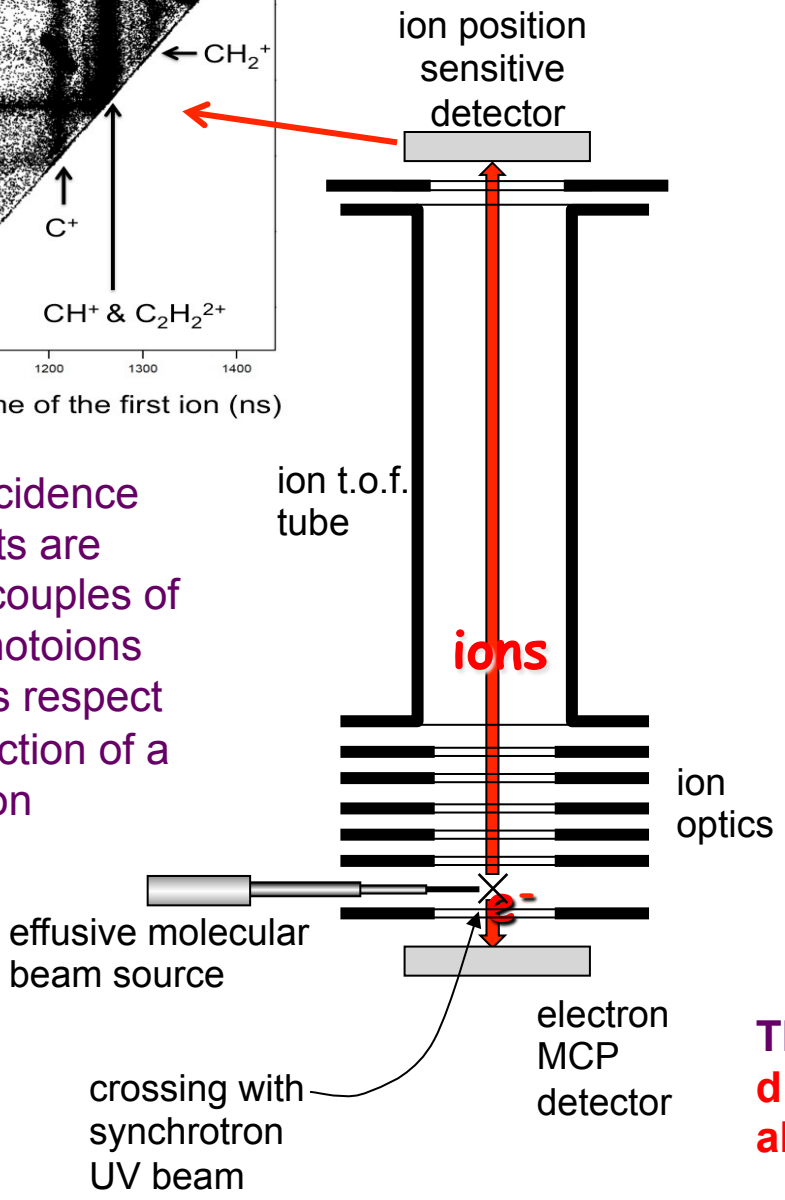
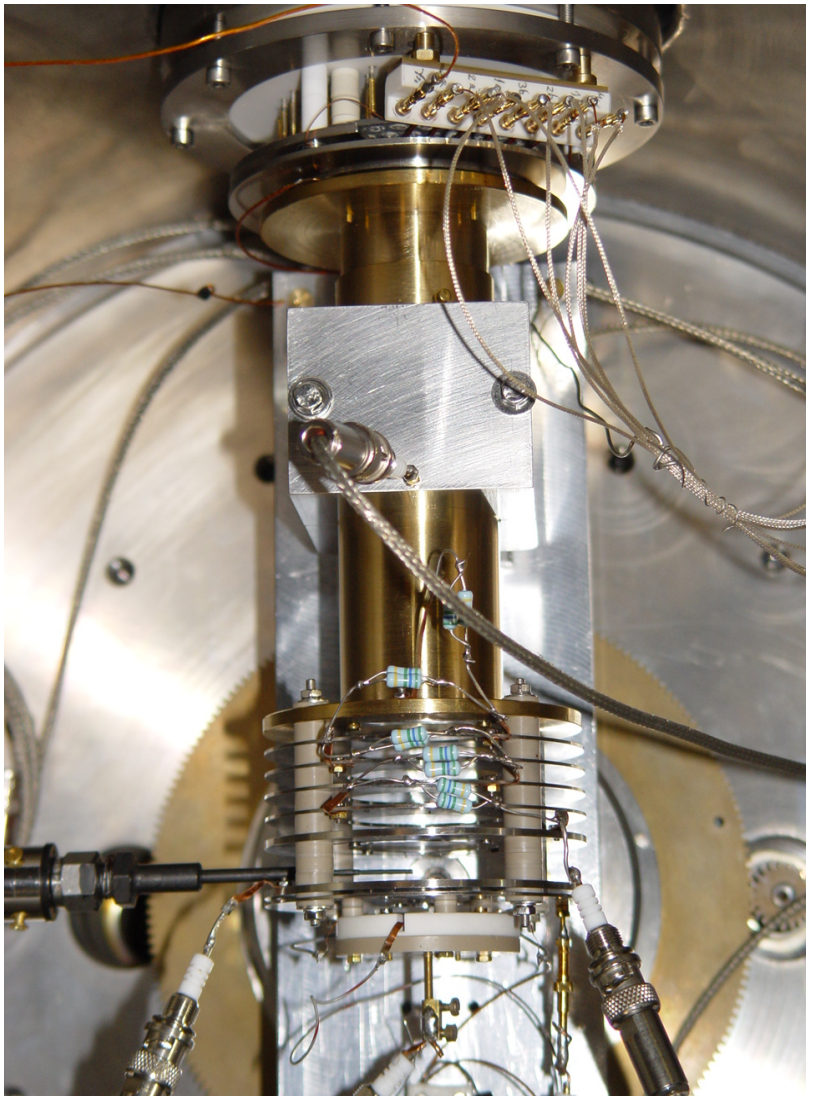
and detecting electron-ion and electron-ion-ion coincidences…



In the coincidence plot the dots are related to couples of t_1 and t_2 photoions delay times respect to the detection of a photoeletron





The light beam is linearly polarized and the direction of the polarization vector is aligned parallel to the molecular beam axis.

Photoionization in the 35-65 eV photon energy range produces ethyne dication with subsequent two-body dissociation reactions:

$C_2H_2 + h\nu \rightarrow (C_2H_2^{+2})^* \rightarrow H^+ + C_2H^+$ $h\nu \geq 33.8$ eV (slow component)

108 ns

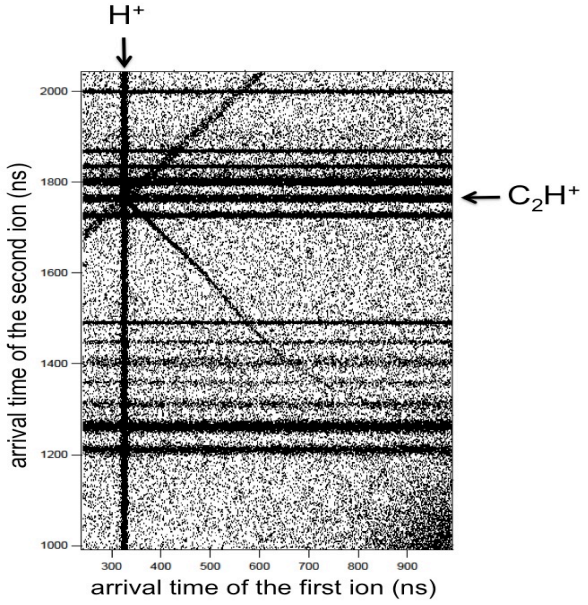
$C_2H_2^{+2} \rightarrow H^+ + C_2H^+$ $h\nu \geq 34.0$ eV (fast component)

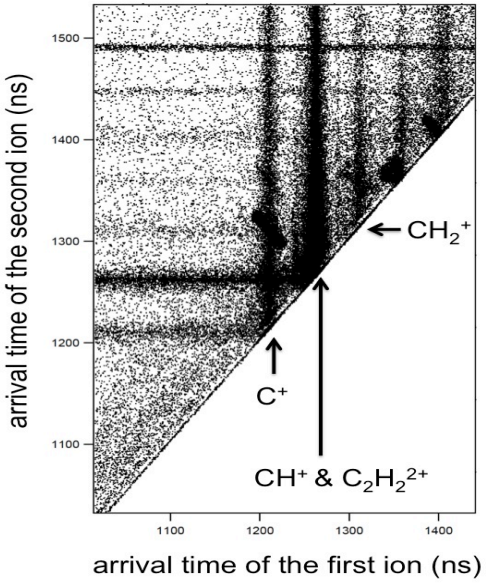
$\rightarrow CH^+ + CH^+$ $h\nu \geq 34.0$ eV

$\rightarrow C^+ + CH_2^+$ $h\nu \geq 34.0$ eV

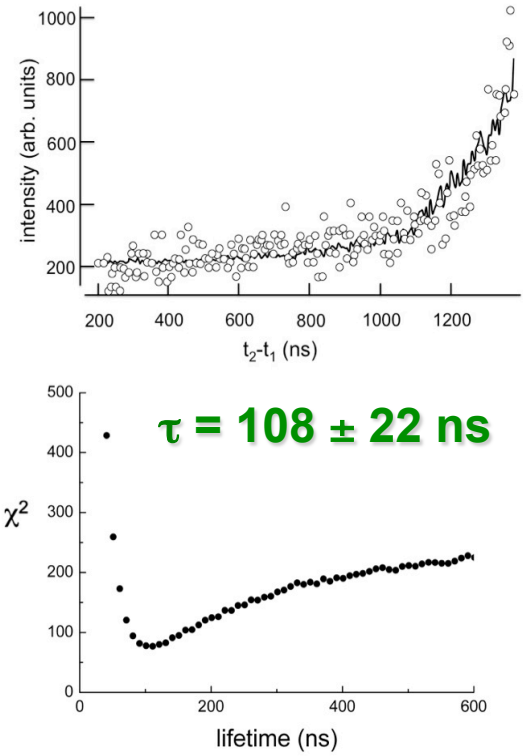
Thissen, R.; Delwiche, J.; Robbe, J.M.; Duflot, D.; Flament, J.P.; Eland, J.H.D. *J. Chem. Phys.* **1993**, *99*, 6590.

Alagia, M.; Callegari, C.; Candori, P.; Falcinelli, S.; Pirani, F.; Richter, R.; Stranges, S., Vecchiocattivi, F. *J. Chem. Phys.* **2012**, *136*, 204302.

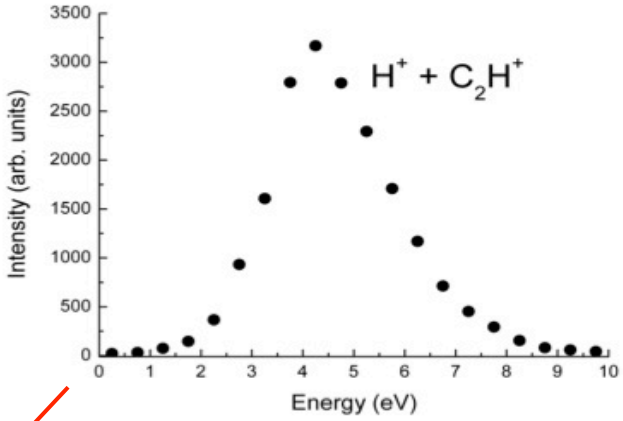


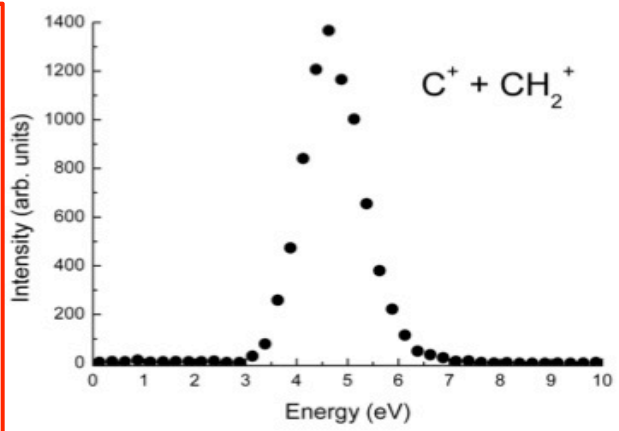


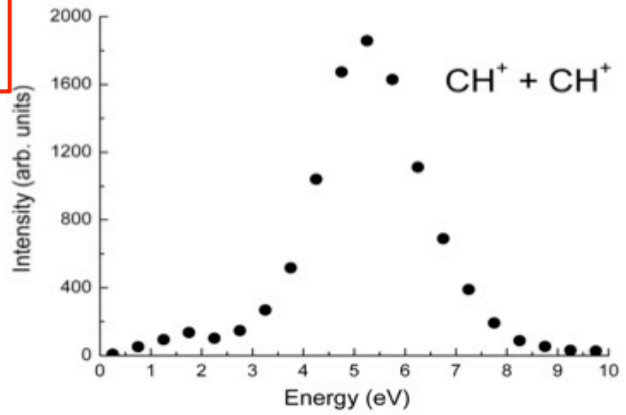
In the case of acetylene, the dissociation leading to $C_2H^+ + H^+$ products occurs through a metastable dication with a lifetime of 108±22 ns, and a KER of about 4.3 eV.



Because of the high KER for fragmentation products, C^+, CH^+ and CH_2^+ ions could participate in atmospheric escape of Titan

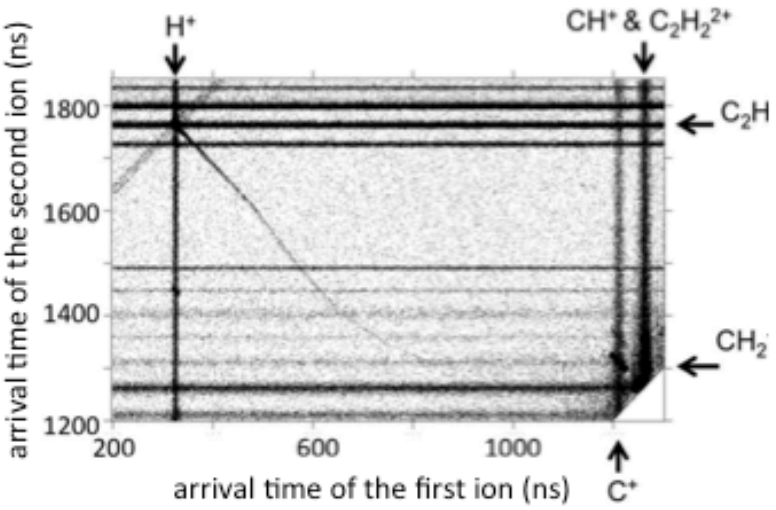


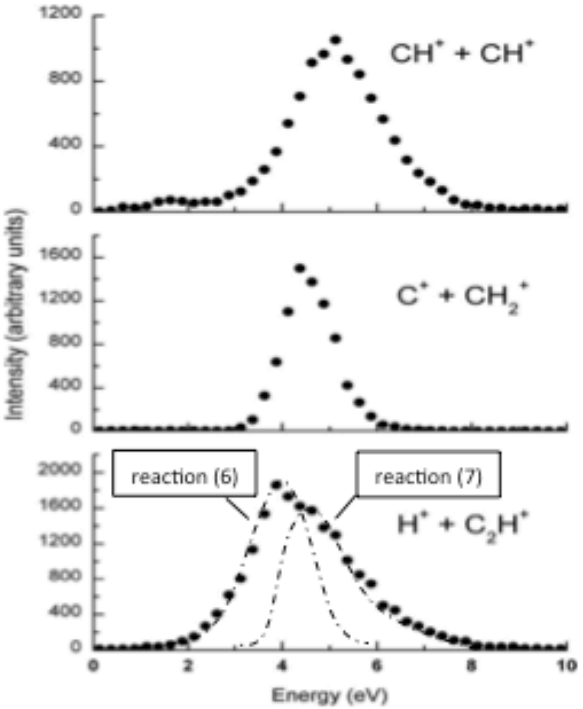


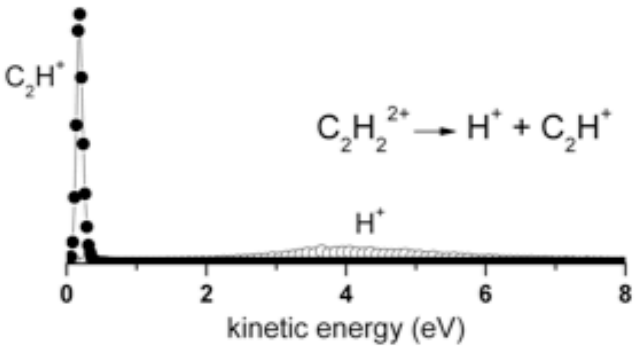


The reaction leading to $CH_2^+ + C^+$ occurs in a time shorter than the characteristic time of our apparatus (~ 50 ns) with a KER of ~4.5 eV. The symmetric dissociation, leading to $CH^+ + CH^+$, exhibits a KER distribution with a maximum at ~5.2 eV.

This can better be seen looking at the kinetic energy distributions of each fragment ions at 39 eV







$C_2H_2^{2+} \rightarrow CH^+ + CH^+$

$C_2H_2^{2+} \rightarrow C^+ + CH_2^+$

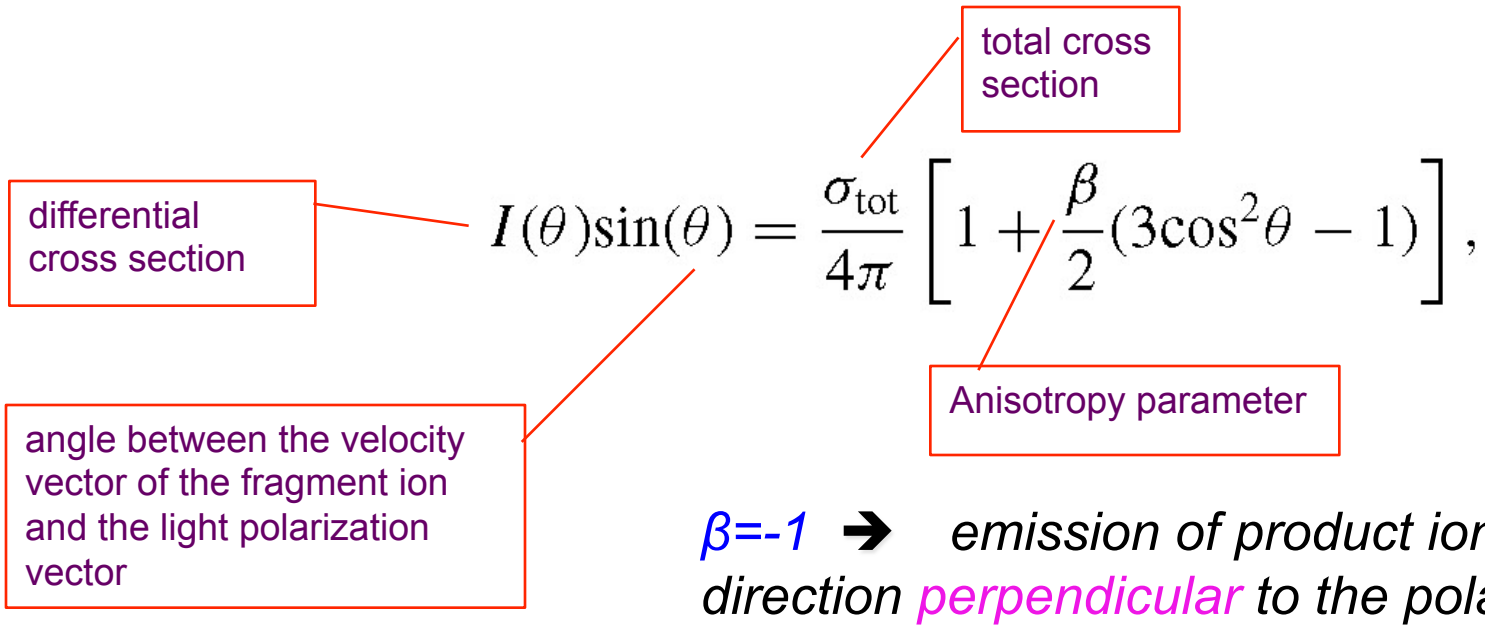
$C_2H_2^{2+} \rightarrow H^+ + C_2H^+$

Looking at the typical escape energy for various ions we can argue that the measured kinetic energy content, in the range 2.0÷5.5 eV for C^+, CH^+, and CH_2^+ ion products are compatible with their possible escape from the upper atmosphere of Mars and Titan

Ion	Measured KER distribution range (eV)	Typical escape energy (eV) for various ions in the atmosphere (at the exobase) of some planets of the Solar System			
		Earth	Venus	Mars	Titan
H^+	2.5÷6.0[a]	0.60	0.51	0.11	0.02
C^+	1.7÷3.5[b]	7.2	6.2	1.35	0.28
CH^+	1.5÷4.0[c]	7.8	6.7	1.5	0.30
CH_2^+	1.5÷2.8[b]	8.4	7.2	1.6	0.32
N^+	2.0÷5.5[d]	8.4	7.2	1.6	0.32
O^+	0.8÷5.2[e] 2.0÷3.7[f]	9.6	8.2	1.8	0.37
C_2H^+	0.1÷0.3[a]	15.0	12.8	2.9	0.58
CO^+	0.5÷2.5[f]	16.8	14.3	3.2	0.65
N_2^+	0.5÷2.8[e]	16.8	14.3	3.2	0.65
NO^+	1.0÷2.8[d]	18.0	15.3	3.4	0.70

Angular Distributions

The ion imaging detector provides the angular distribution of product ions with respect the light polarization vector direction. Such angular distributions can provide valuable information about the dissociation dynamics and are usually represented as follow (R.N. Zare, Mol. Photochem., **1972**, 4, 1)**:**

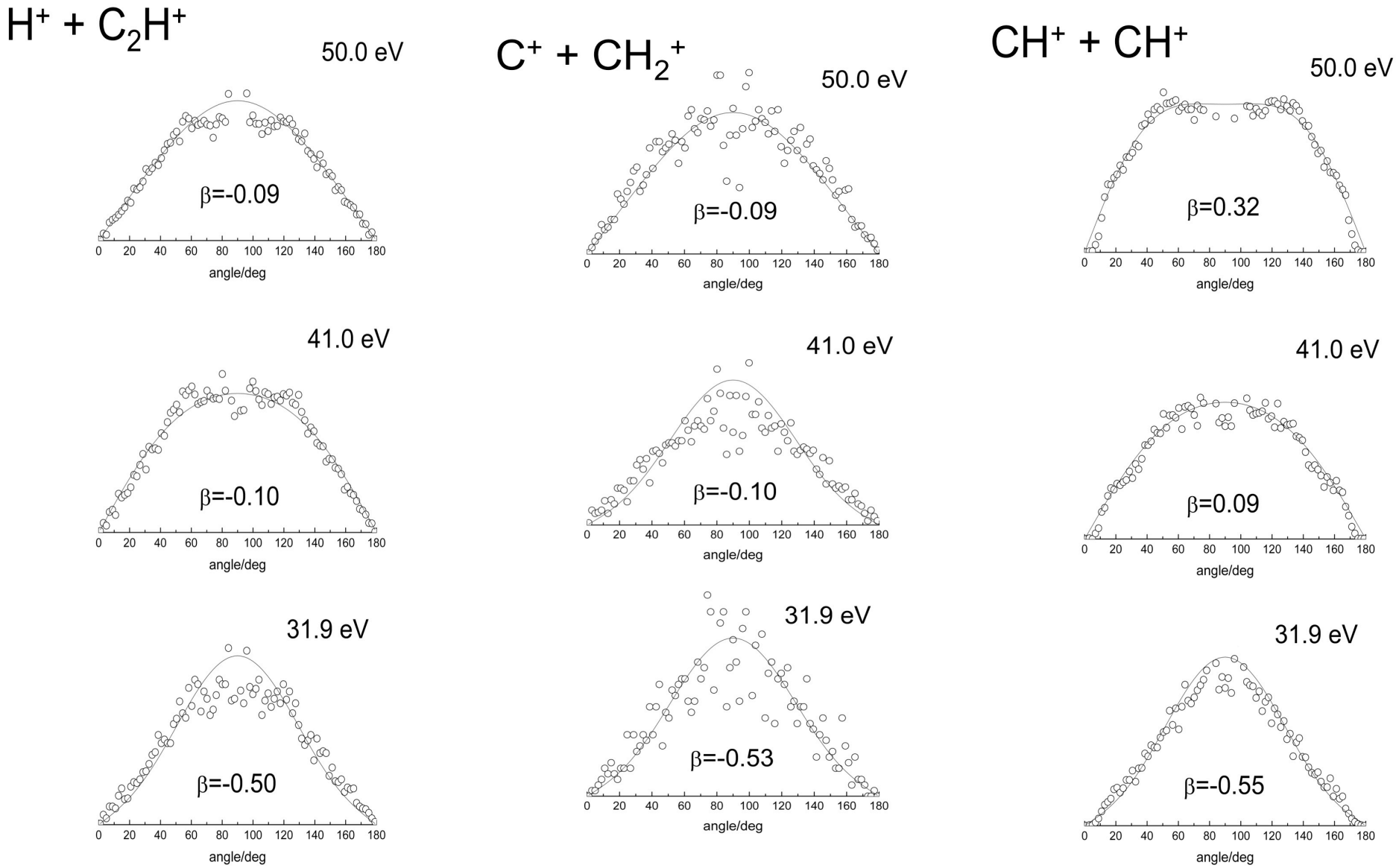


β=-1 ➔ *emission of product ions along a direction perpendicular to the polarization vector*

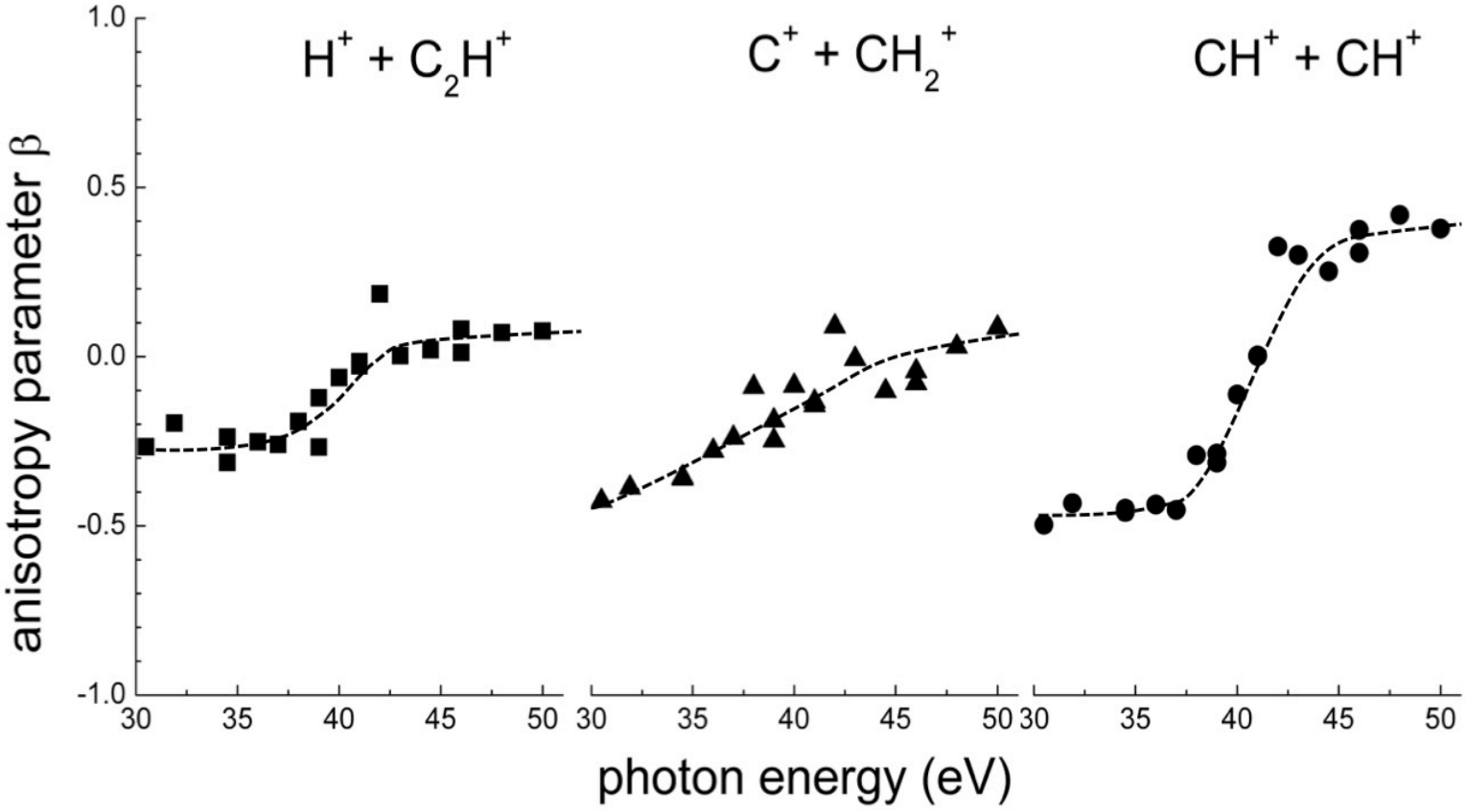
β=0 ➔ *isotropic distribution of fragment ions*

β=2 ➔ *emission of product ions along a direction parallel to the polarization vector*

The angular distributions of final ions for the recorded two body fragmentation channels



The photon energy dependence of the β parameter for the three investigated dissociation channels



CONCLUSIONS

- The UV photochemistry studies useful to understand the atmospheric chemistry of the Earth and of other planets can be perfomed by using an intense and tunable light source as the synchrotron radiation

- The double photoionization of C_2H_2 has been studied in the 31.9-50 eV energy range

- The fragmentation of $C_2H_2^{2+}$ dications takes place producing fragments ions with a kinetic energy release (KER) ranging between 1.5 and 4.2 eV

- The measured cross sections for the different fragmentation channels togheter with the KER can be useful to understand the chemistry of the Mars and Venus atmospheres

- The production of CH_2^+, CH^+, and C^+ with a high kinetic energy content are compatible with their possible escape from the upper atmosphere of Mars and Titan

- The measured angular distribution of product ions can provide valuable information about the dissociation dynamics

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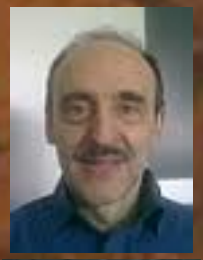

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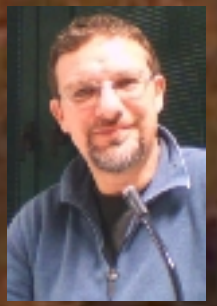

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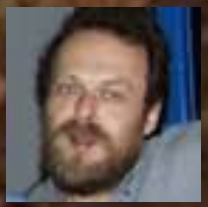

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