Molecular dications
in planetary ionospheres

Astronomical Complex Organic Molecules in different environments

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Stefano Falcinelli, Marzio Rosi, Franco Vecchiocattivi
Department of Civil and Environmental Engineering, University of Perugia- Italy

**Nadia Balucani, Fernando Pirani**
Department of Chemistry, Biology and Biotechnologies– University of Perugia - Italy

DICA
DIPARTIMENTO DI INGEGNERIA
CIVILE E AMBIENTALE

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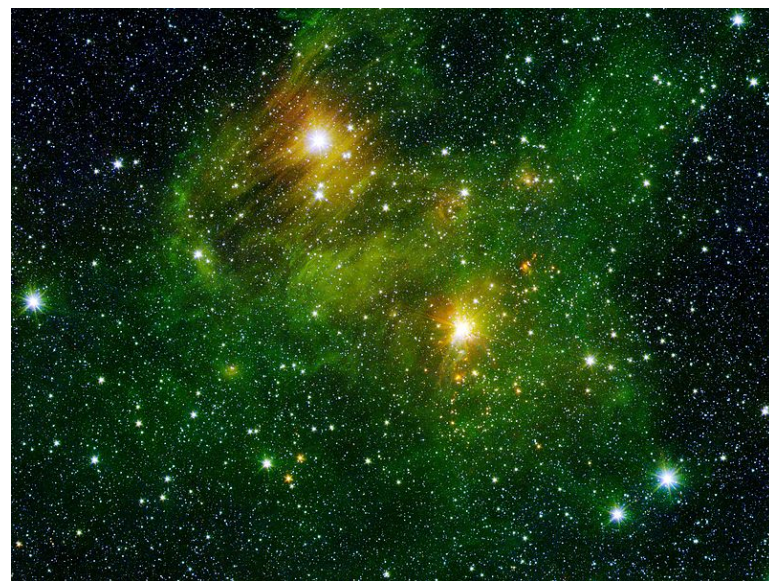
The UV photochemistry studies can be performed by using an intense and tunable light source as the synchrotron radiation

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:

$$CO_2 + h\nu \rightarrow CO^+ + O^+ + 2e^-$$

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

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.
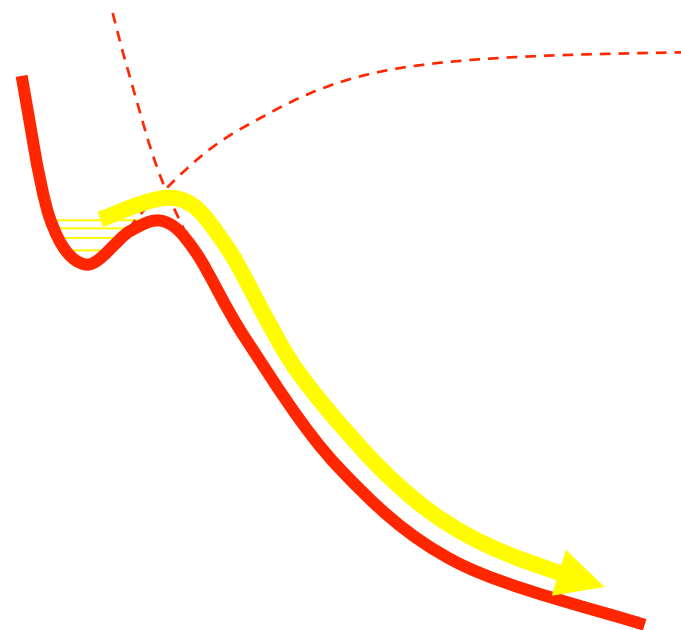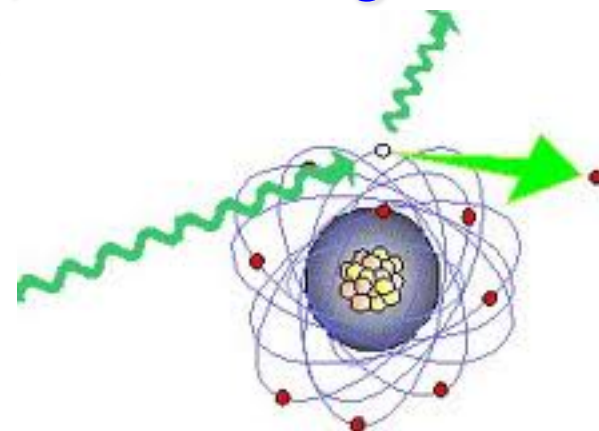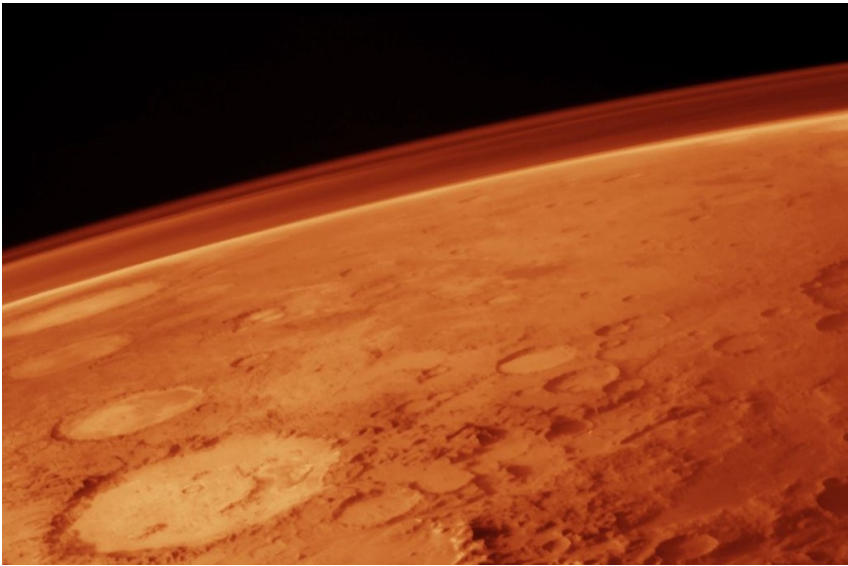
CO_2 is involved in several atmospheric phenomena of the Earth and of other planets like Mars and Venus
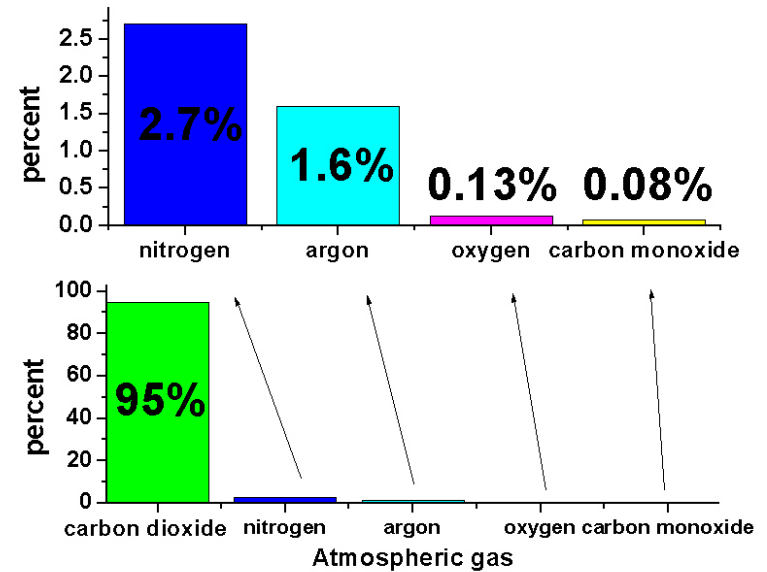
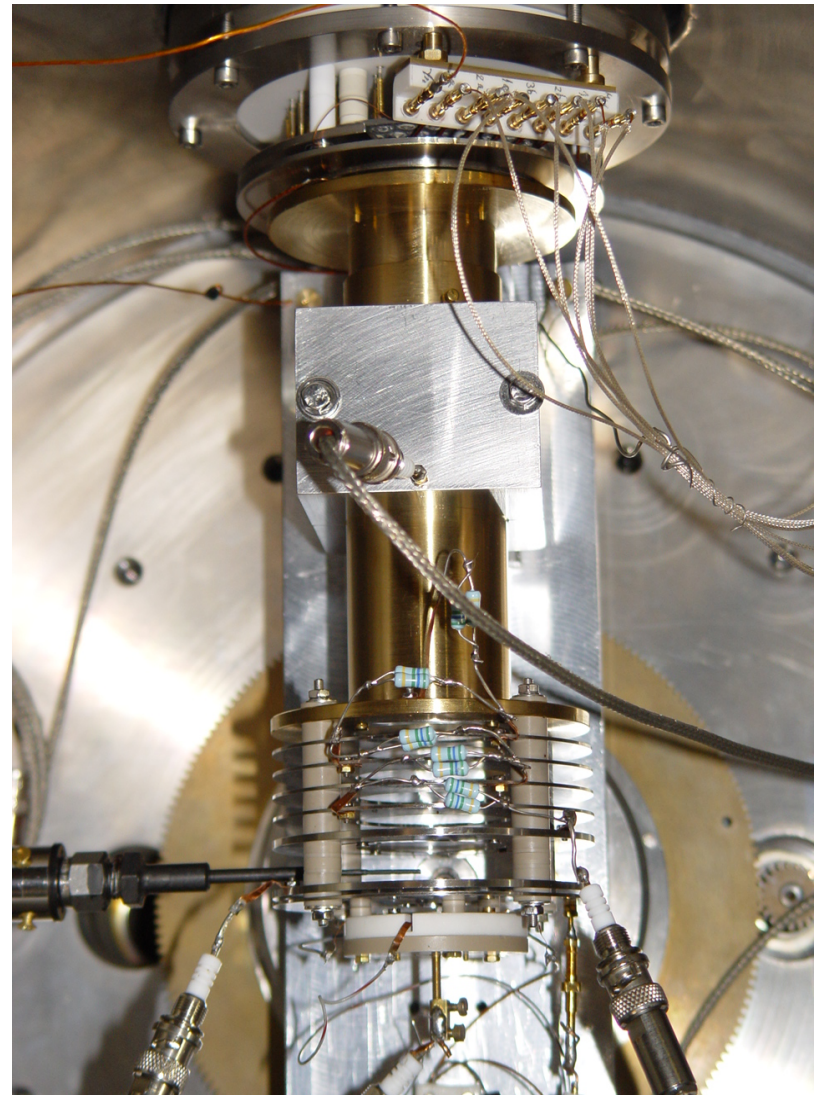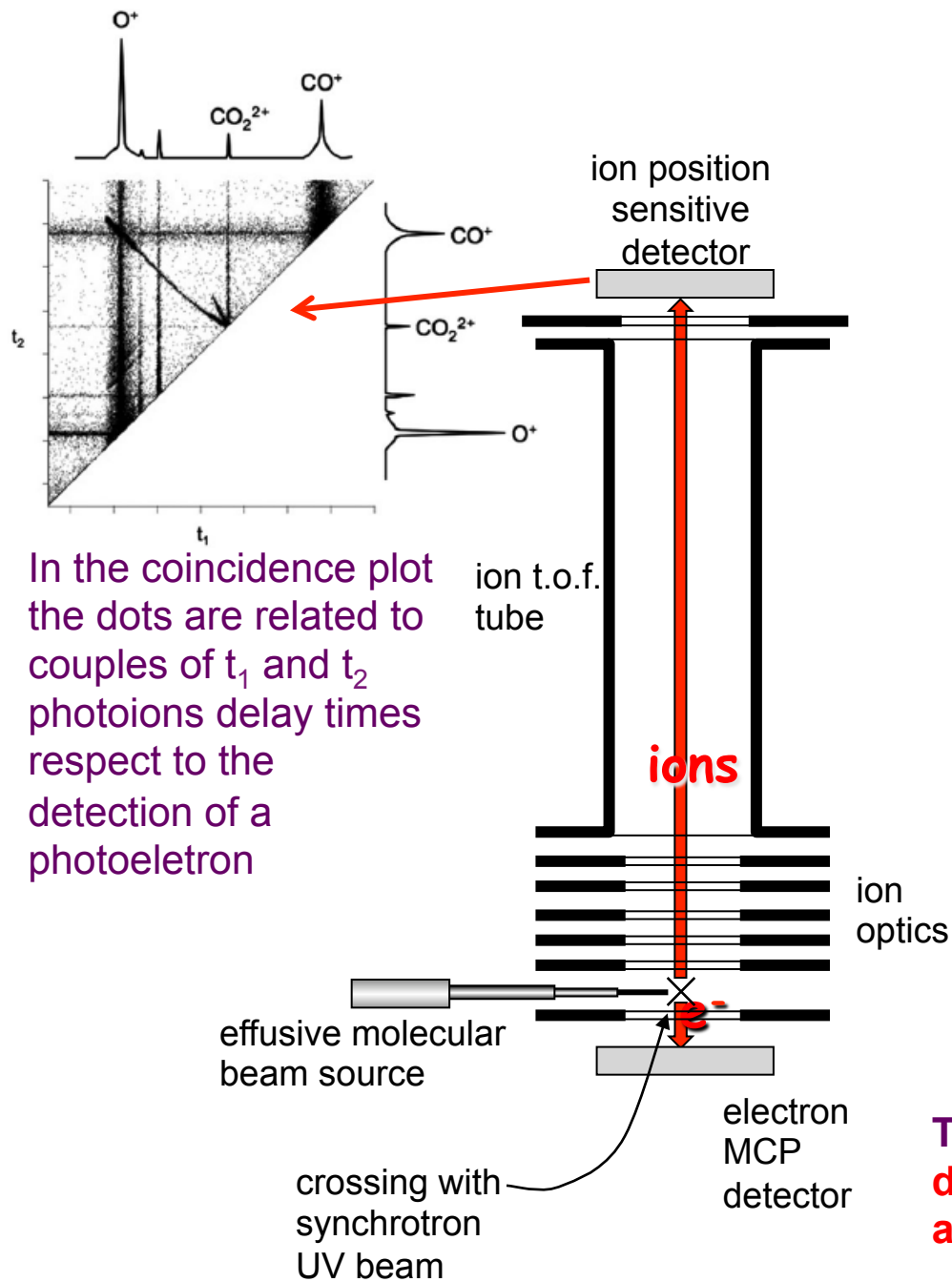C_2H_2 has been detected in interstellar medium.

Acetylene is 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.

N_2O has been recently suggested to be present in the upper atmosphere of Titan in a detectable amount by Dobrijevic et al. [*Icarus* **228**, 324-346 (2014)]

The double photoionization of N_2O, CO_2, and C_2H_2 molecules has been studied in the 34-50 eV photon energy range, by the use of synchrotron radiation…
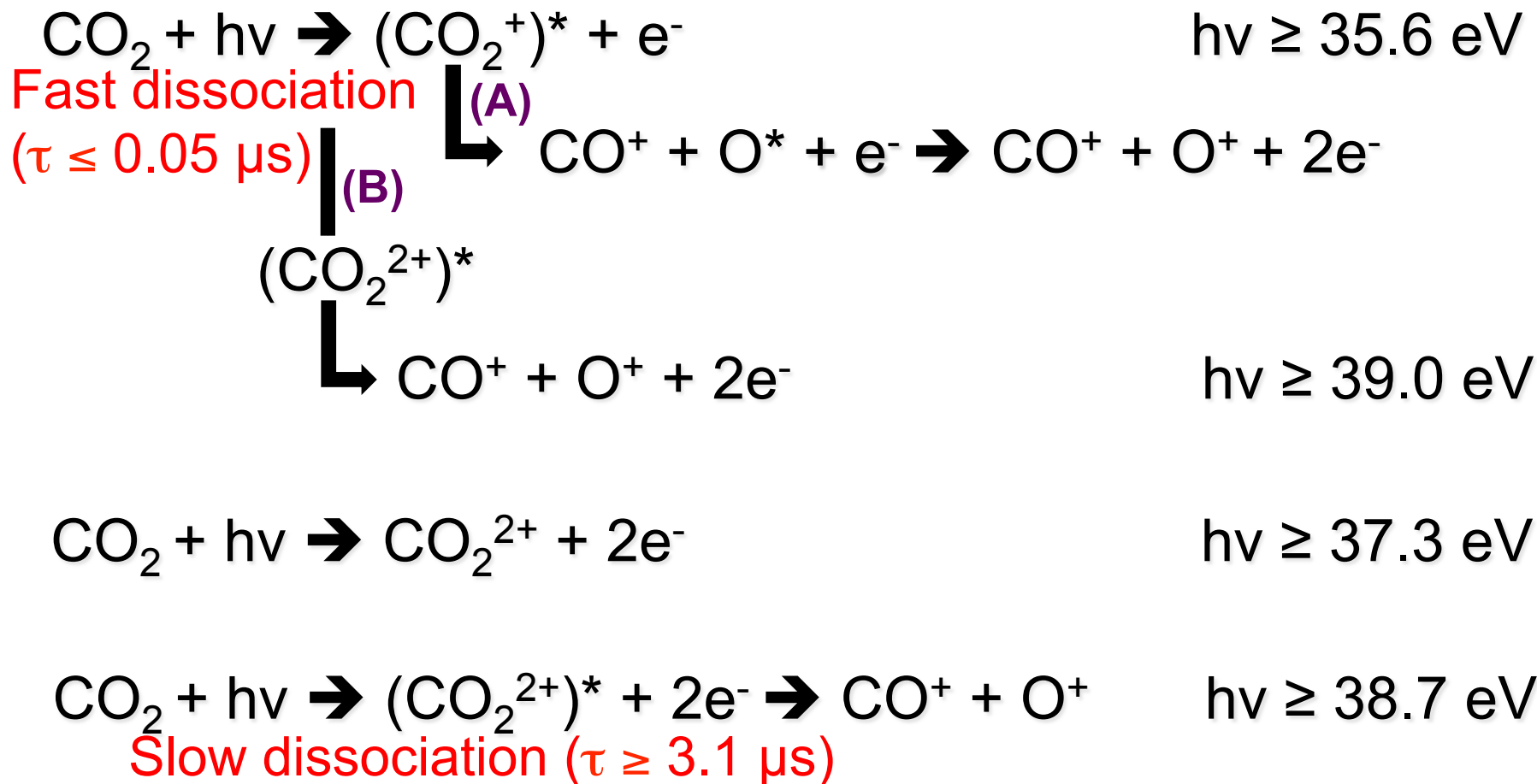

elettra

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

O$^+$ CO$_2^{2+}$ CO$^+$

t_2

t_1

CO$^+$

CO$_2^{2+}$

O$^+$

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

ion position sensitive detector

ion t.o.f. tube

ions

ion optics

effusive molecular beam source

e$^-$

crossing with synchrotron UV beam

electron MCP detector

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

Interacting with 34-50 eV photons, the CO_2 molecule gives four different processes:
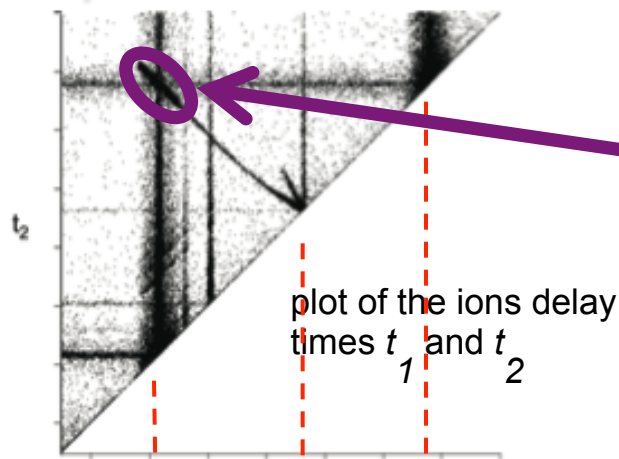
$$CO_2 + h\nu \rightarrow (CO_2^+)^* + e^- \qquad\qquad h\nu \geq 35.6 \text{ eV}$$

Fast dissociation
($\tau \leq 0.05$ µs)

(A)

$$\rightarrow CO^+ + O^* + e^- \rightarrow CO^+ + O^+ + 2e^-$$

(B)

$$(CO_2^{2+})^*$$

$$\rightarrow CO^+ + O^+ + 2e^- \qquad\qquad h\nu \geq 39.0 \text{ eV}$$

$$CO_2 + h\nu \rightarrow CO_2^{2+} + 2e^- \qquad\qquad h\nu \geq 37.3 \text{ eV}$$

$$CO_2 + h\nu \rightarrow (CO_2^{2+})^* + 2e^- \rightarrow CO^+ + O^+ \qquad h\nu \geq 38.7 \text{ eV}$$

Slow dissociation ($\tau \geq 3.1$ µs)

Franceschi, P.; Thissen, R.; Zabka, J.; Roithová, J.; Herman, Z.; Dutuit, O. *Int. J. Mass Spectrom.* **2003**, *228*, 507.

Slattery, A. E.; Field, T. A.; Ahmad, M.; Hall, R. I.; Lambourne, J.; Penent, F.; Lablanquie, P.; Eland, J. H. D. *J. Chem. Phys.* **2005**, *122*, 084317.
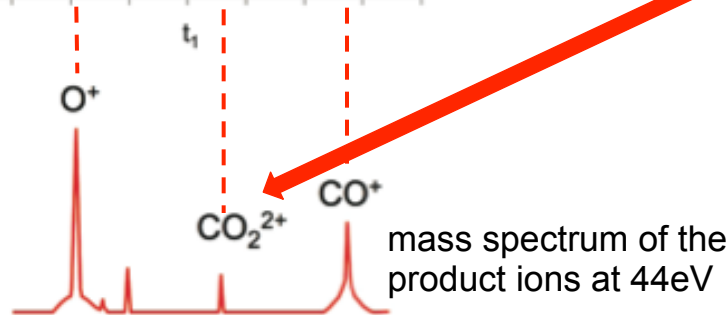
Alagia, M.; Candori, P.; Falcinelli, S.; Lavollée, M.; Pirani, F.; Richter, R.; Stranges, S.; Vecchiocattivi, F. *J. Phys. Chem. A* **2009**, *113*, 14755.

Spectra of coincidences for the double photoionization of CO_2 at a photon energy of 44 eV

plot of the ions delay times t_1 and t_2

mass spectrum of the product ions at 44eV

the different areas for the analysis of the lifetime of metastable $(CO_2 2+)^*$ dication are indicated

At each wavelenght the total counts in the peak for each ion pair gives the intensity and the cross section, and the peak dimensions and shapes give the Kinetic Energy Released (KER) for product ions
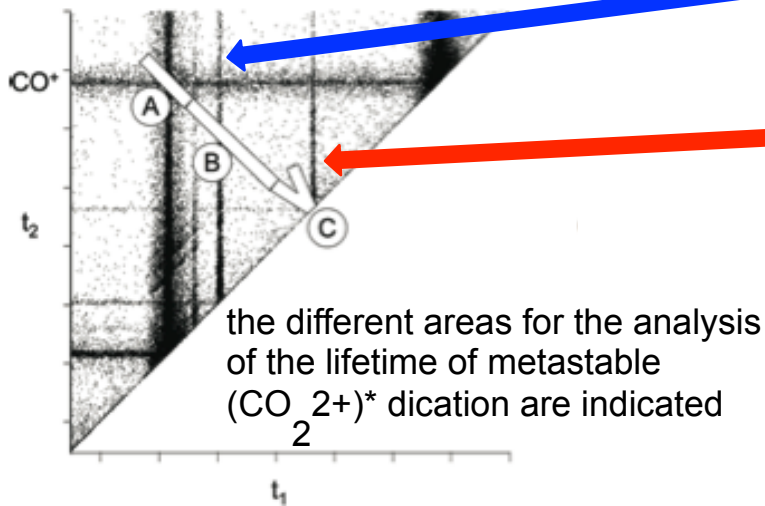
The intensity of the CO_2^{2+} peak in the mass spectrum, as a function of the photon energy, normalized for the photon flux, gives the relative cross section for the molecular dication formation

Counting the true coincidences in area "A" provides the cross section for the "direct fast dissociation", while counting the true coincidences in the areas "B" and "C" provides the cross section for the formation of the metastable $(CO_2 2+)^*$ (slow dissociation).
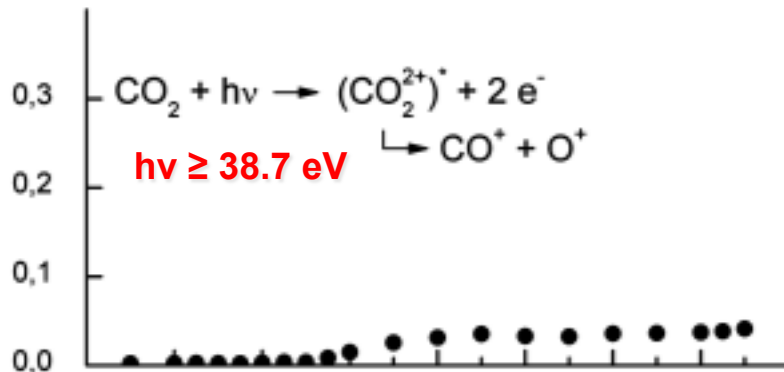
The relative cross sections as a function of the photon energy are so obtained and the density distribution of the coincidences along the areas "A", "B" and "C" is related to the lifetime of the molecular dication
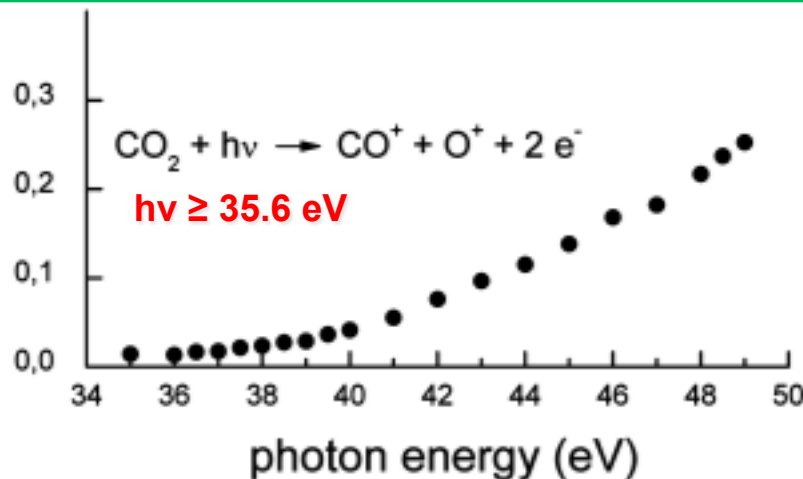
$CO_2 + h\nu \rightarrow CO_2^{2+} + 2e^-$

$h\nu \geq 37.3$ eV
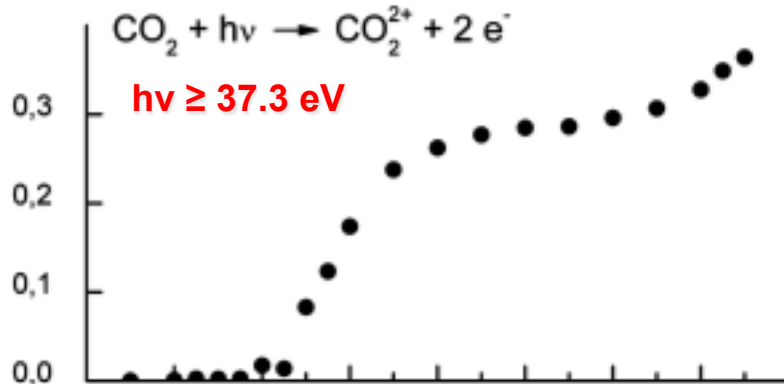
Stable molecular dication formation

$CO_2 + h\nu \rightarrow (CO_2^{2+})^* + 2e^-$
$\hookrightarrow CO^+ + O^+$

$h\nu \geq 38.7$ eV

Slow dissociation through long lived dication metastable states

Via formation of a metastable $(CO_2^{2+})^*$ dication having a lifetime of 3.1±0.9 µs

$CO_2 + h\nu \rightarrow CO^+ + O^+ + 2e^-$

$h\nu \geq 35.6$ eV

Fast molecular fragmentation

Via formation of $(CO_2^{2+})^*$ dication having a short lifetime ($\tau \leq 0.05$ µs)

Which become dominant for $h\nu \geq 41.0$ eV

cross section (arb. units)

photon energy (eV)

Atmospheric escape of O⁺ by dissociative double photoionization of CO₂ molecules

**One consequence of the exotic behavior of doubly charged molecular ions in planetary atmospheres is the possibility of creation of dissociative products with a kinetic energy of several eV.**

In the case of CO_2, the production of CO^+ and O^+ fragments with a high kinetic energy content (2.0 and 3.8 eV respectively) could explain the lack in the O^+ expected concentration of the Mars Atmosphere.

This energy is large enough in the case of Mars and Titan to allow these fragments to reach sufficient velocity to escape into space. Therefore this process can in principle contribute to the continuous erosion of these atmospheres.
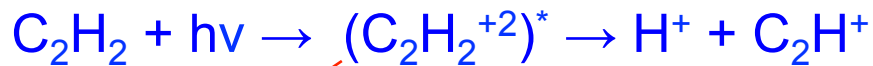
Typical escape energy (eV) for the C^+, N^+ and O^+ ions in the atmosphere of Venus, Earth, Mars and Titan, at the exobase

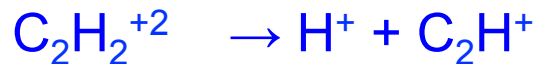| Ion/planet	Venus	Earth	Mars	Titan
C^+	6.4	7.4	1.5	0.28
N^+	7.5	8.6	1.8	0.32
O^+	8.6	9.8	2.0	0.37
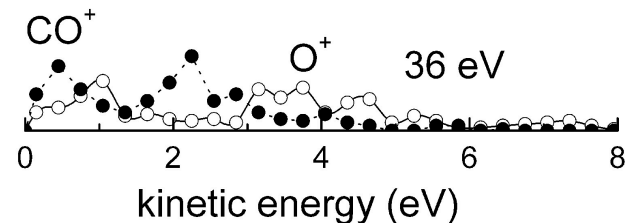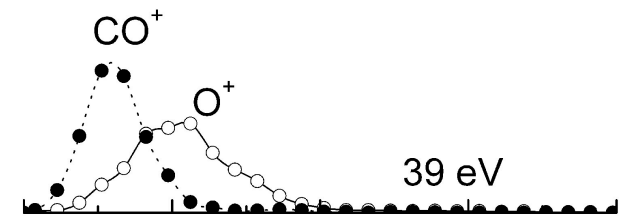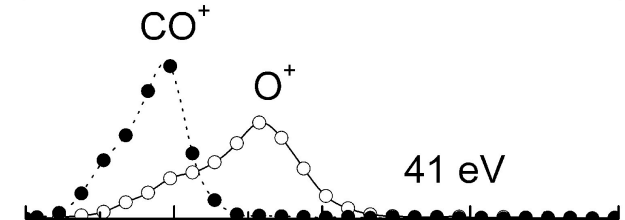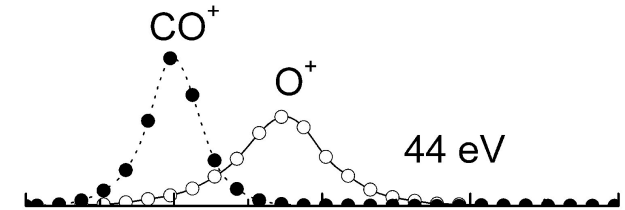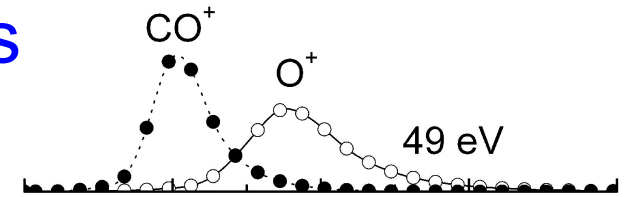
The kinetic energy distributions of product CO^+ and O^+ ions as obtained from the analysis of ion images as a function of the photon energy.

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

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

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

$$\rightarrow CH^+ + CH^+ \qquad h\nu \geq 34.0 \text{ eV}$$
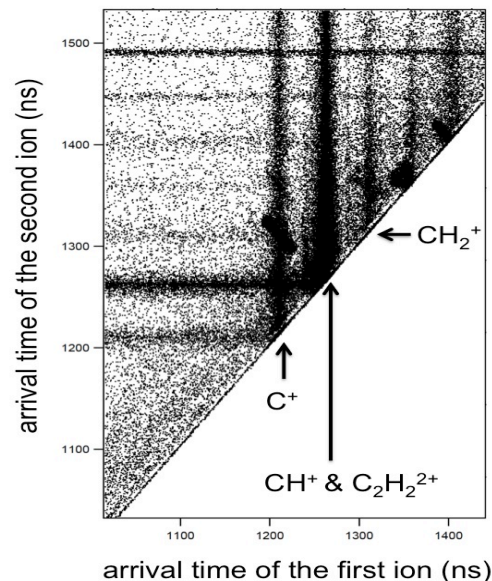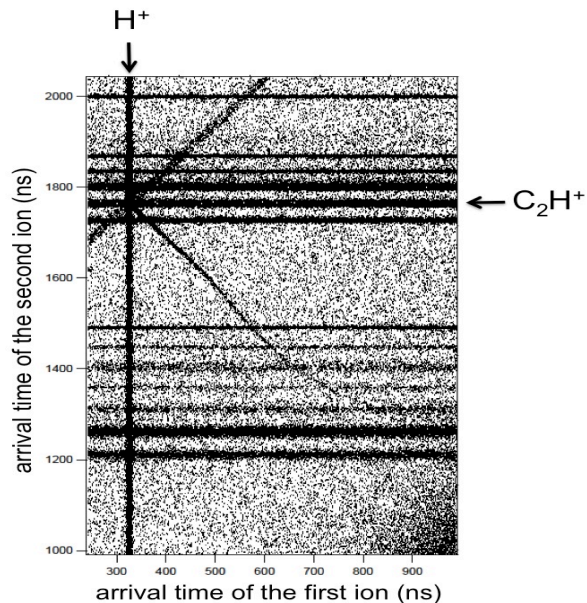
$$\rightarrow C^+ + CH_2^+ \qquad h\nu \geq 34.0 \text{ eV}$$

108 ns

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.
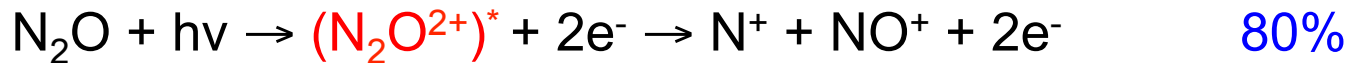

$\tau = 108 \pm 22$ ns
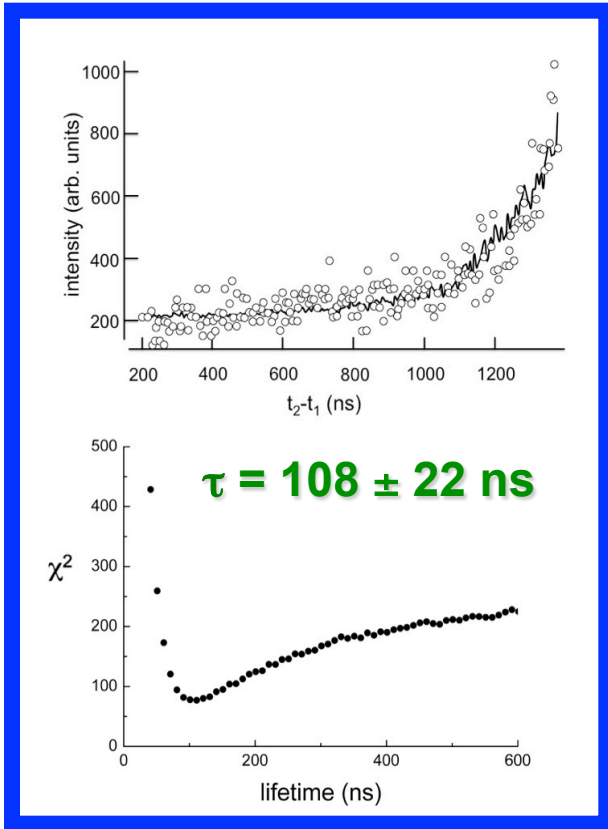
Because of the high KER for fragmentation products, C^+, CH^+ and CH_2^+ ions could participate in atmospheric escape of Titan

$H^+ + C_2H^+$

$C^+ + CH_2^+$

$CH^+ + CH^+$

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.
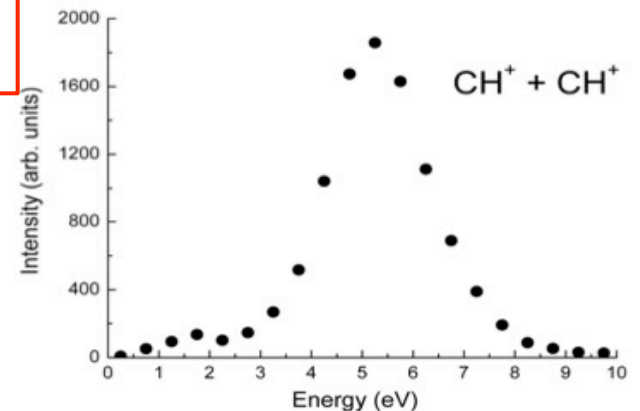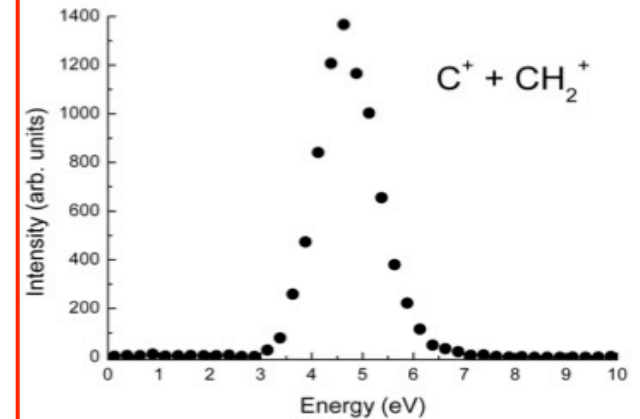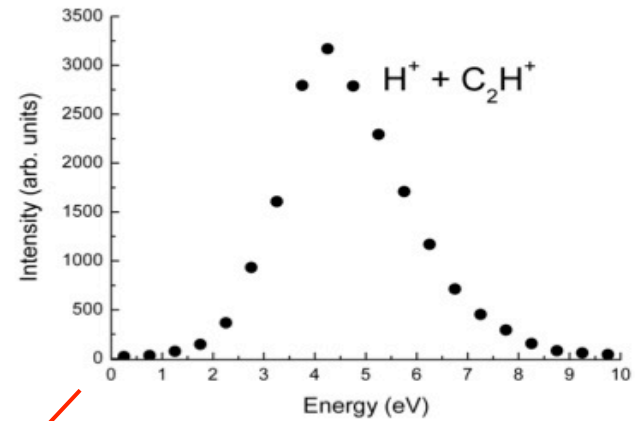
The double photoionization of N_2O in the 28-40 eV photon energy range

In the whole investigated energy range, we observed two dissociation channels with a threshold energy of 32.2 eV:

$$N_2O + h\nu \rightarrow (N_2O^{2+})^* + 2e^- \rightarrow N_2^+ + O^+ + 2e^- \qquad 20\%$$

$$N_2O + h\nu \rightarrow (N_2O^{2+})^* + 2e^- \rightarrow N^+ + NO^+ + 2e^- \qquad 80\%$$
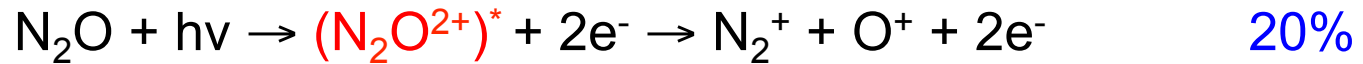
intermediate "short lived" molecular dication
with a lifetime shorter than 10^{-6} sec
(typical average ion time-of-flight in our detection device)

The analysis of our results, with the same procedure applied to CO_2 and C_2H_2 molecules, can provide the total kinetic energy of ionic fragments as a function of the investigated photon energy:
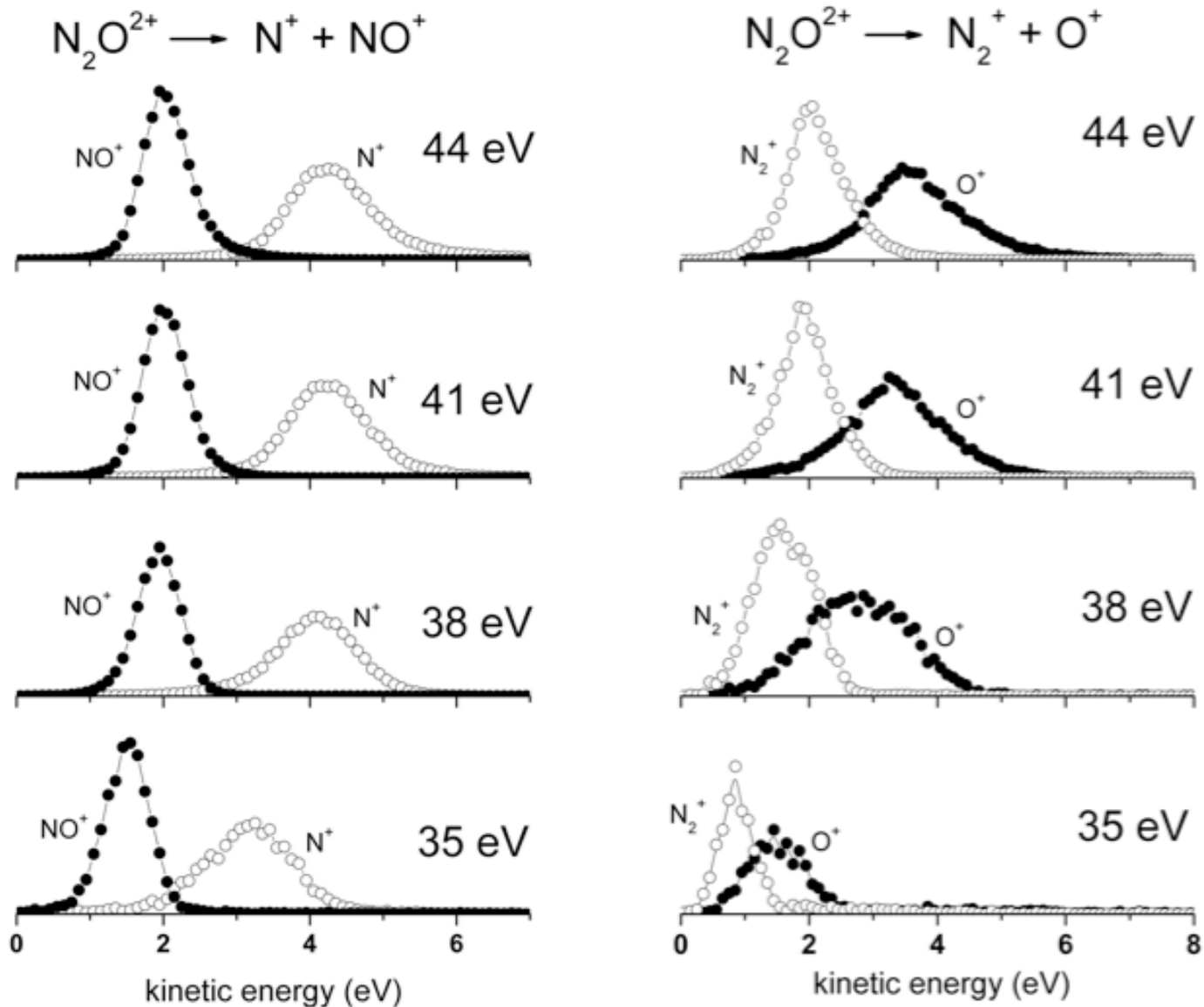
Looking at the typical escape energy for various ions we can argue that the measured kinetic energy content, in the range 2.0÷5.5 eV for N^+ and 0.8÷5.2 eV for O^+ ion products are compatible with their possible escape from the upper atmosphere of Mars and Titan

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

N_2O has been recently suggested to be present in the upper atmosphere of Titan in a detectable amount by Dobrijevic et al. [Icarus **228**, 324-346 (2014)] who considered for the first time the coupling between nitrogen and oxygen chemistry in that environment

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)**:**

total cross section

differential cross section

$$I(\theta)\sin(\theta) = \frac{\sigma_{\text{tot}}}{4\pi}\left[1 + \frac{\beta}{2}(3\cos^2\theta - 1)\right],$$

Anisotropy parameter

angle between the velocity vector of the fragment ion and the light polarization vector

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*

Angular Distributions: N$_2$O

hv = 39 eV

N$^+$

O$^+$

N$_2$O beam

hv

NO$^+$

N$_2$$^+$

N$^+$ + NO$^+$

36 ev

β = 1.5

θ (deg)

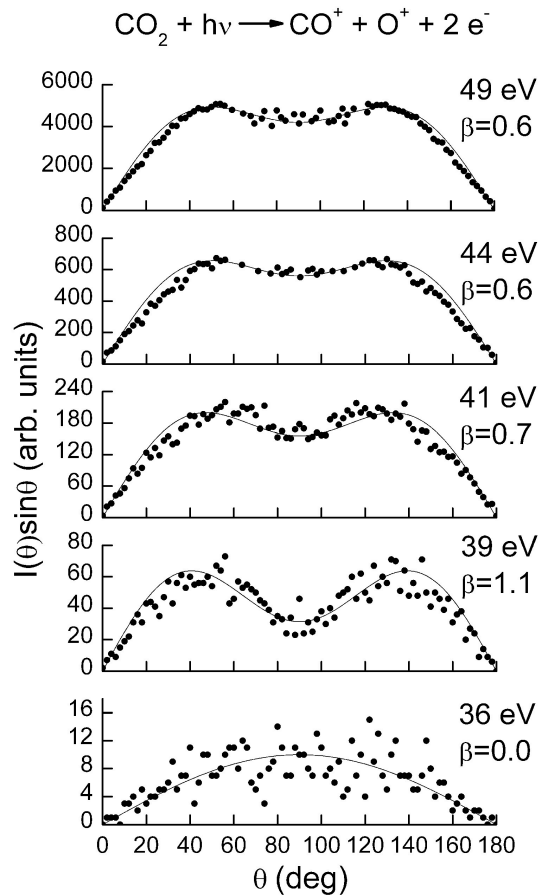O$^+$ + N$_2$$^+$

36 ev

β = 1.5

θ (deg)
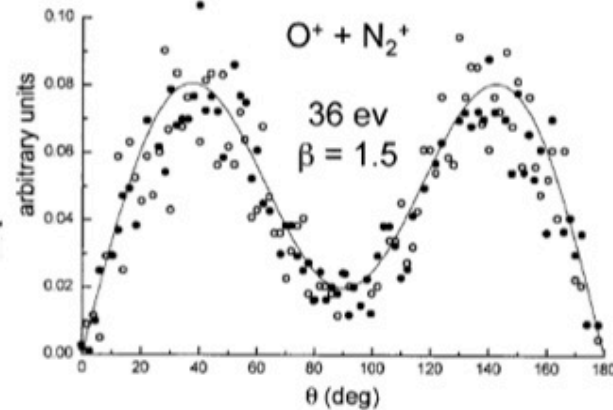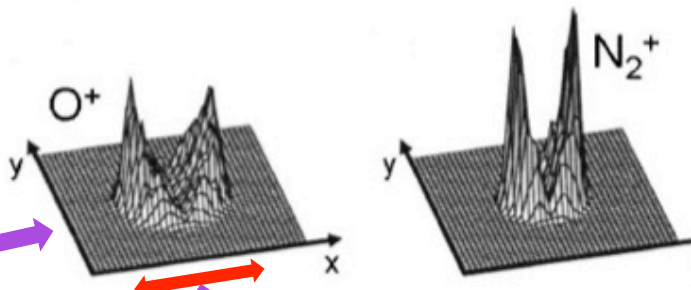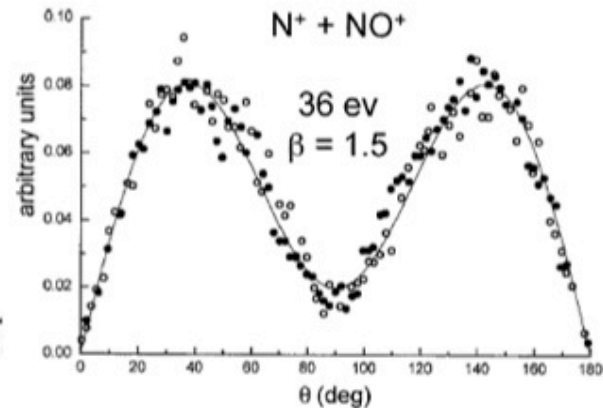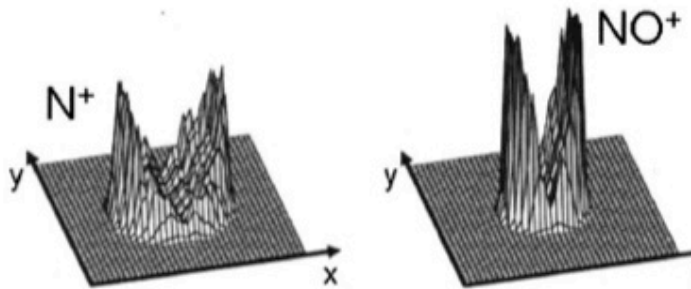
The intensity maps, recorded at a photon energy of 39 eV, for N$^+$ ions correlated with NO$^+$, and for O$^+$ ions correlated with N$_2$$^+$ (the light polarization vector is parallel to the x axis)

The angular intensity distributions of products of the two dissociative channels leading to N$^+$+NO$^+$ and O$^+$+N$_2$$^+$ on the plane perpendicular to the light beam direction, as measured at a photon energy of 36 eV. In both plots, the intensities of the two ionic products are reported as open circles for the atomic ions (N$^+$ or O$^+$) and as full circles for the diatomic ions (NO$^+$ or N$_2$$^+$). The curve is a fitting obtained by setting β =1.5.

Angular Distributions: CO$_2$ and C$_2$H$_2$

When the photon energy increases, the distribution of products became anisotropic, with the two ions preferentially emitted along the direction of the light polarization vector. This implies that the molecule photoionizes when oriented parallel to that direction, and also that the CO$_2^{2+}$ dication just formed dissociates in a time shorter than its typical rotational period.

proton transfer rearrangement reaction via vinylidene dication H$_2$CC^{2+} formation

CO$_2$ + hν $\longrightarrow$ CO$^+$ + O$^+$ + 2 e$^-$

C$_2$H$_2^{2+}$ $\longrightarrow$ C$_2$H$^+$ + H$^+$

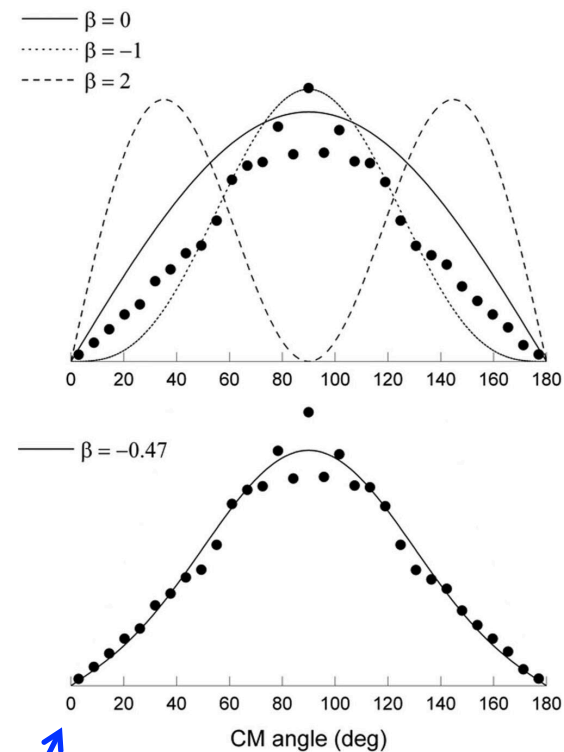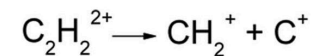C$_2$H$_2^{2+}$ $\longrightarrow$ CH$_2^+$ + C$^+$

At low energy the reaction occurs by the indirect mechanism involving the formation of CO$^+$+O* autoionizing atom with an isotropic final ions distribution
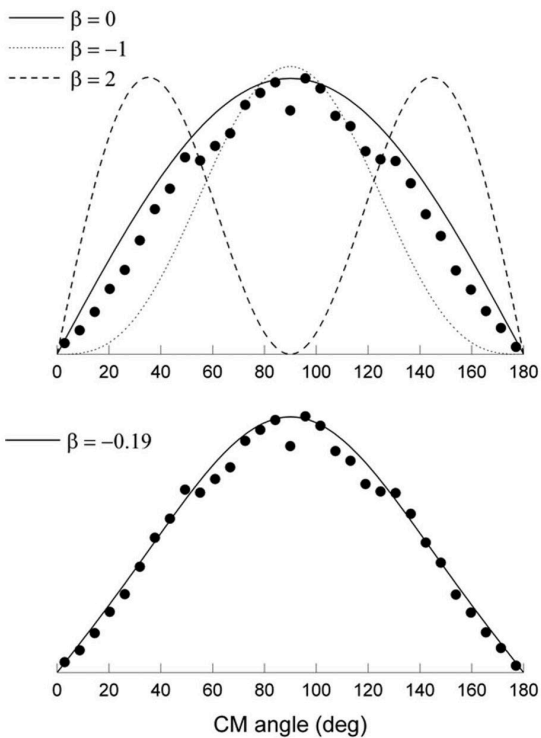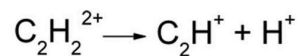
Almost isotropic distribution probably due to the lightness of H$^+$ ion

The reaction occurs in a time shorter than the typical rotational period of the acetylene molecules (of the order of 10^{-12} s)

Fragment ions produced prevalently in a perpendicular direction respect to the polarization light vector direction

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 CO_2, N_2O, and C_2H_2 has been studied in the 34-50 eV energy range

- The fragmentation of CO_2^{2+}, N_2O^{2+}, and $C_2H_2^{2+}$ dications takes place producing fragments ions with a kinetic energy release (KER) ranging between 2 and 6 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 CO^+, O^+, NO^+, N_2^+, 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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James M. Farrar
Department of Chemistry, University of Rochester, NY - USA

Kostantinos S. Kalogerakis
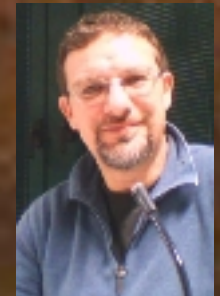**Aeronomy Program, SRI International, Menlo Park, CA 94025, USA**

Stefano Stranges
Department of Chemistry– University of Rome "La Sapienza"

Michele Alagia
ISMN-CNR (Sect. Rome1) Rome – IOM-CNR Lab. TASC - Trieste - Italy

Robert Richter
Sincrotrone Trieste – Area Science Park – Basovizza, Trieste - Italy