Methane production from H_2+CO_2 reaction without solid phase catalysis

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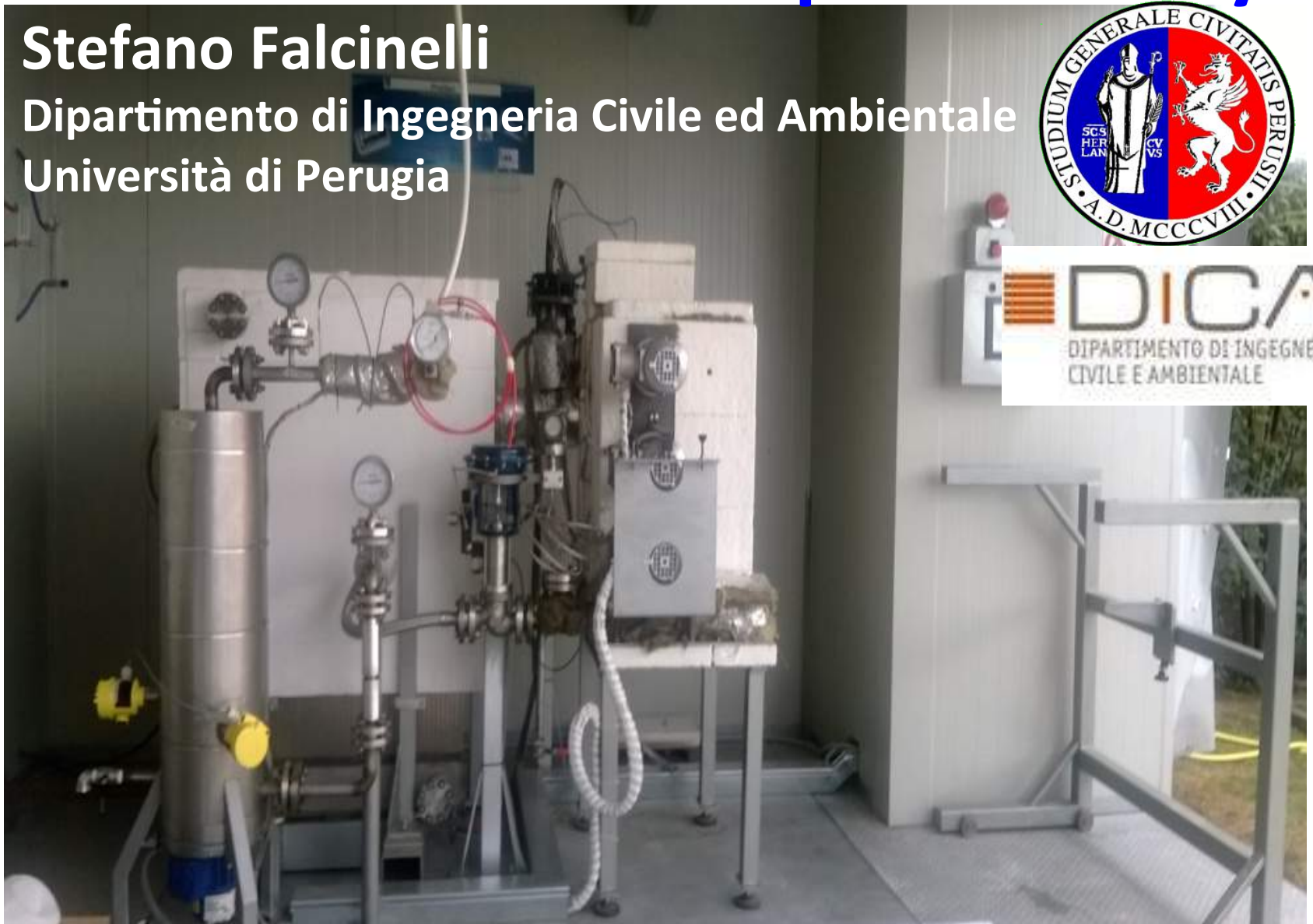
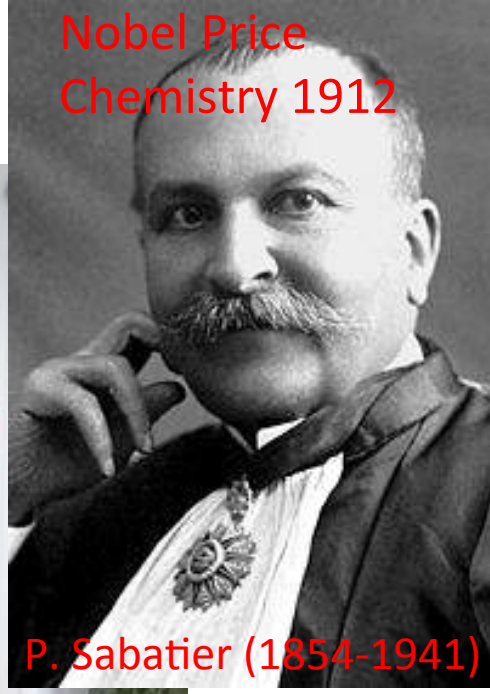


THE METHANATION REACTOR



The Paul Sabatier reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

high temperature: 200-300°C

high pressure: 2-3 atm

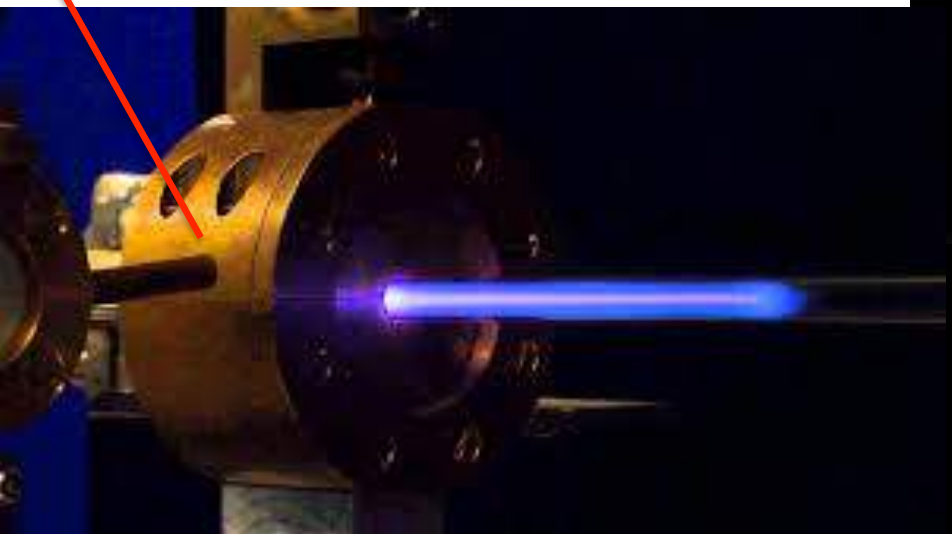
Using a solid phase catalyst:
Nickel, ruthenium, or alumina

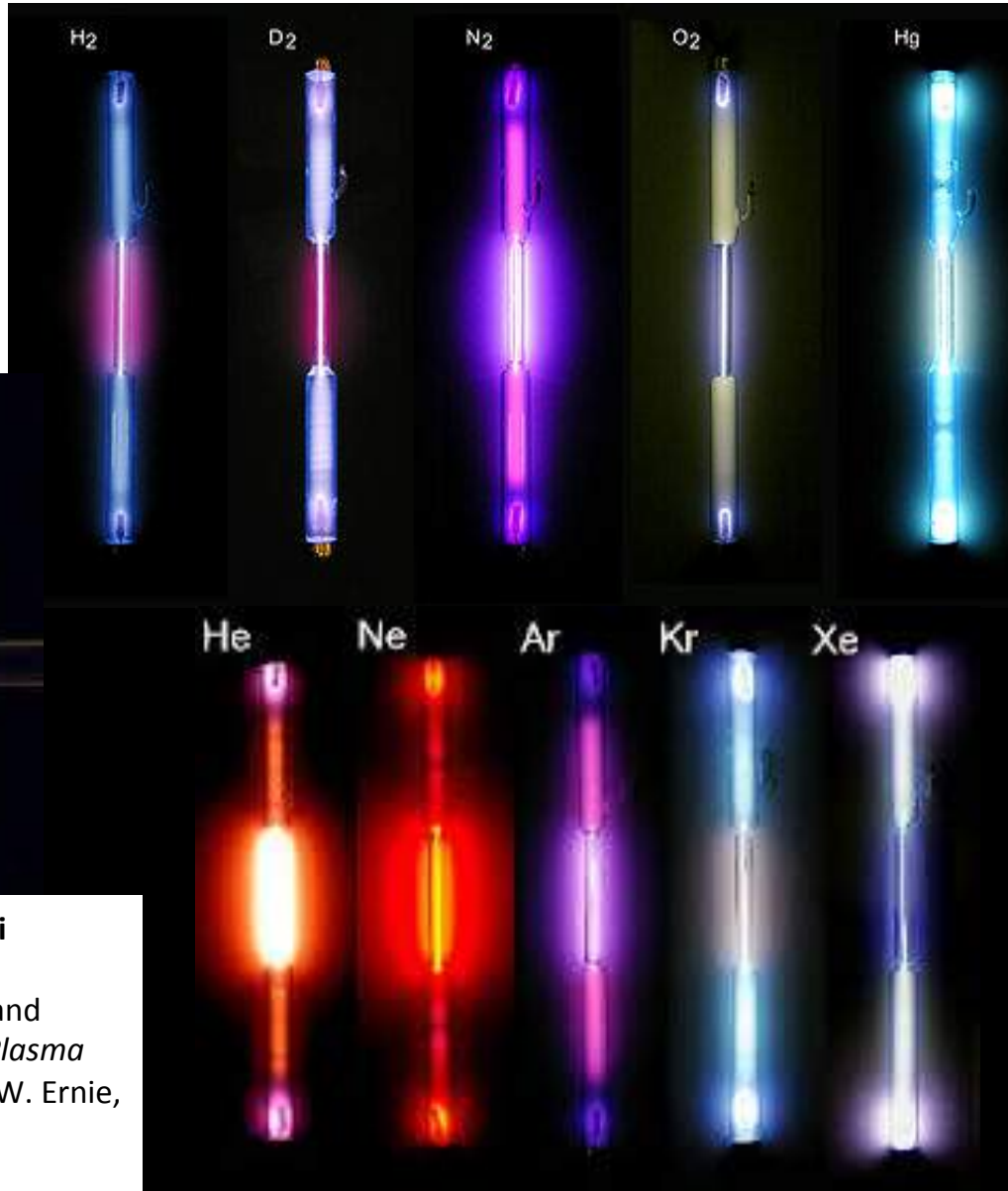
May we avoid the use of the solid phase catalyst, trying to perform the reaction in the homogeneous gas phase?

generation of a controlled plasma through electrical discharges or UV photons on a $CO_2 + H_2$ gas mixture

by using tunable electron or photon energy (by self made electrical microwave or RF discharges or by synchrotron radiation), and studying the elementary chemical reactions in a single collision condition (by crossed molecular beams technique)

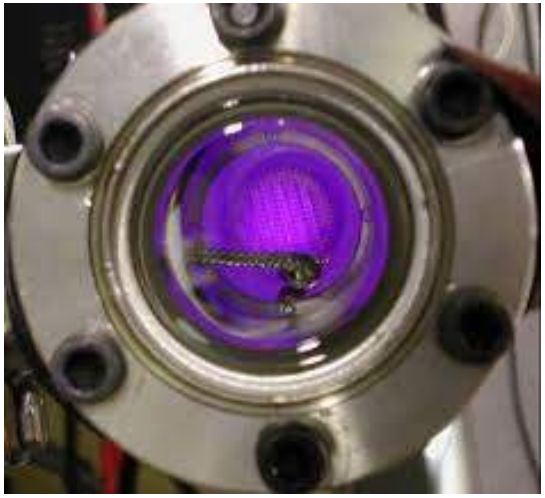
Microwave discharge plasma source



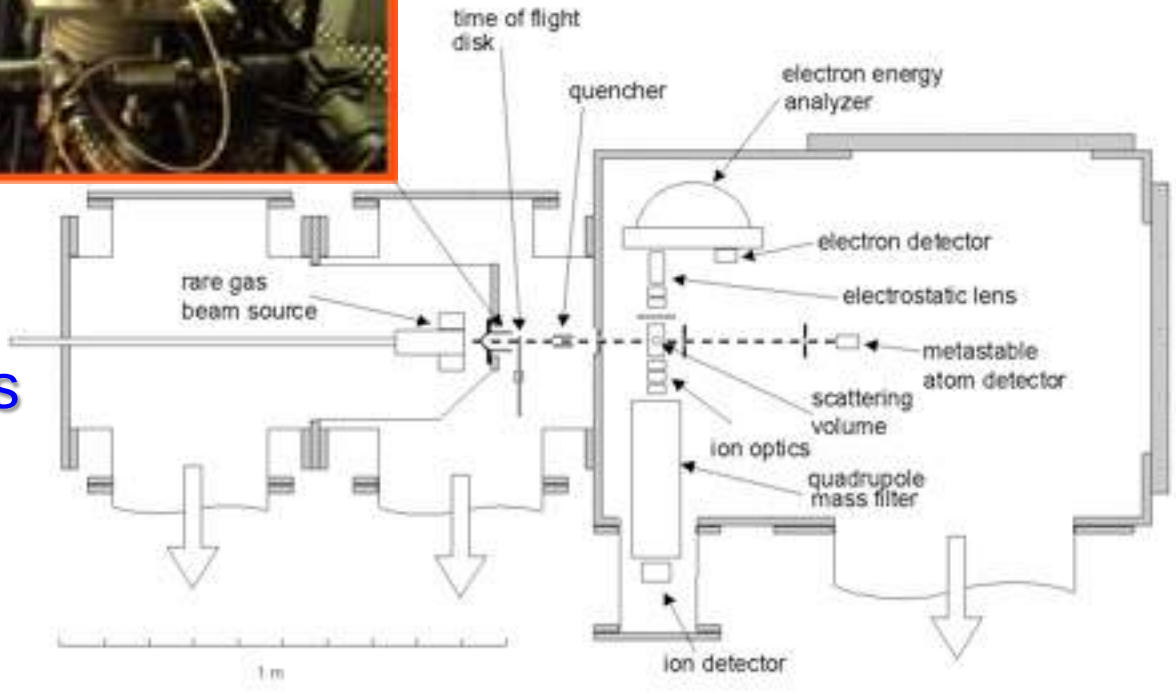


S. Falcinelli, F. Pirani, B. Brunetti, G. Liuti, and F. Vecchiocattivi
Atomic and molecular beams from electrical discharges: their characterization and applications useful for plasma diagnostic and chemical modeling. In *"ISPC 12 – International Symposium on Plasma Chemistry Proceedings"*, **Vol. 1** (1995), Ed. by J.V. Heberlein, D.W. Ernie, J.T. Roberts (Minneapolis, Minnesota, USA), pp. 343-348.

The controlled plasma can be generated by using a microwave discharge beam source on a H_2-CO_2 gas mixture



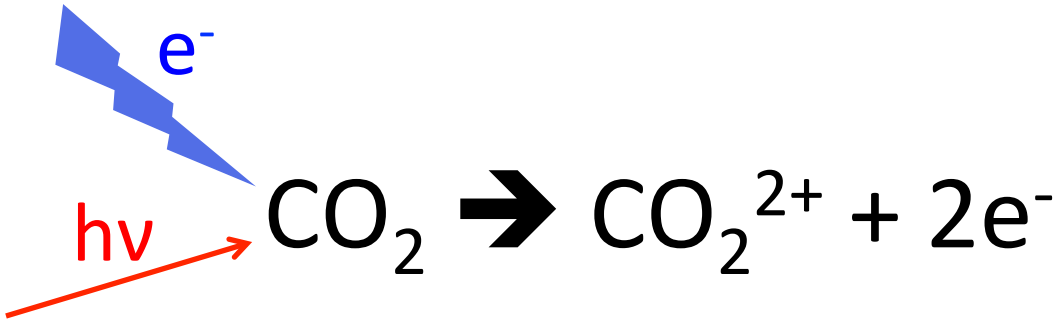
The Penning ionization crossed molecular beams apparatus operating in our unipg lab



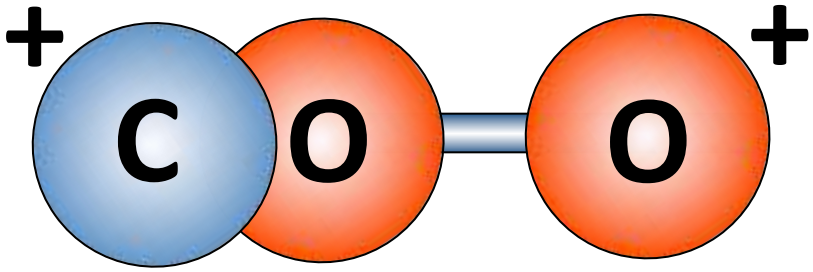
it is a very common phenomenon in nature

The PLASMA is an ionized gas consisting of electrons and ions; It is the fourth state of matter and constitutes over 99% of the known matter of the Universe

If the used energy in a CO_2+H_2 plasma is higher than 38 eV, it is possible to have double ionization with production of CO_2^{2+} dication:

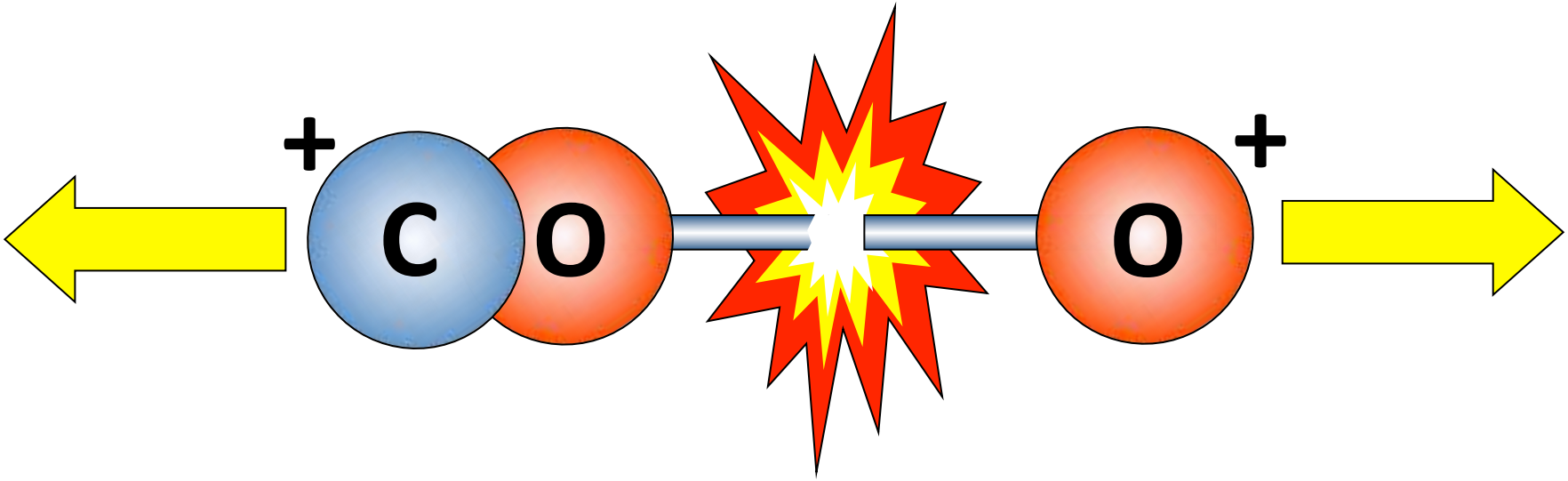


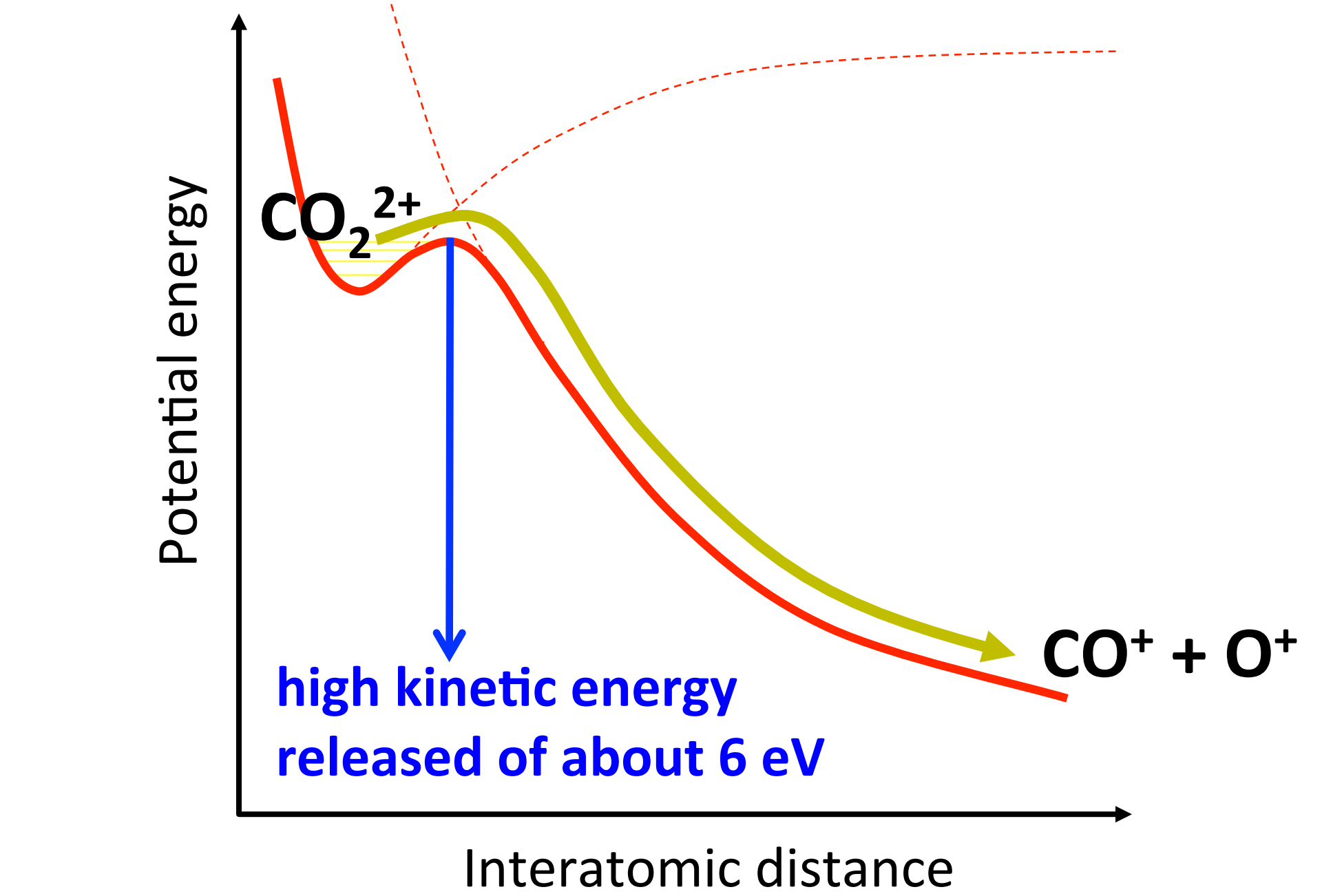
CO_2^{2+} is a metastable species: it dissociates in two ionic fragments having high kinetic energy content:



Repulsion and Coulomb explosion:

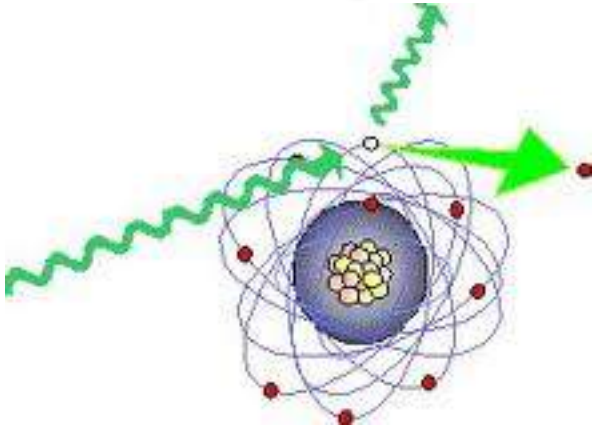
$$V_{rep}(R) = \frac{14{,}4}{R(\text{Å})}\,\text{eV}$$





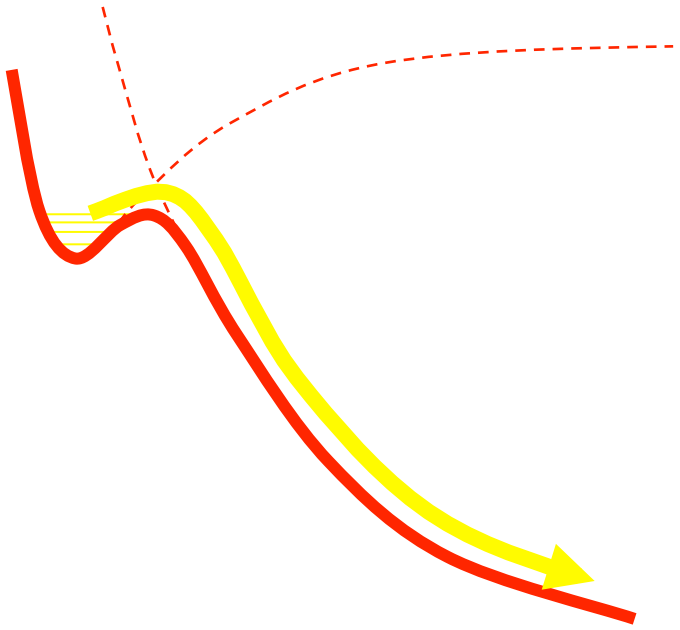
The chemical reactivity can be increased because…

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



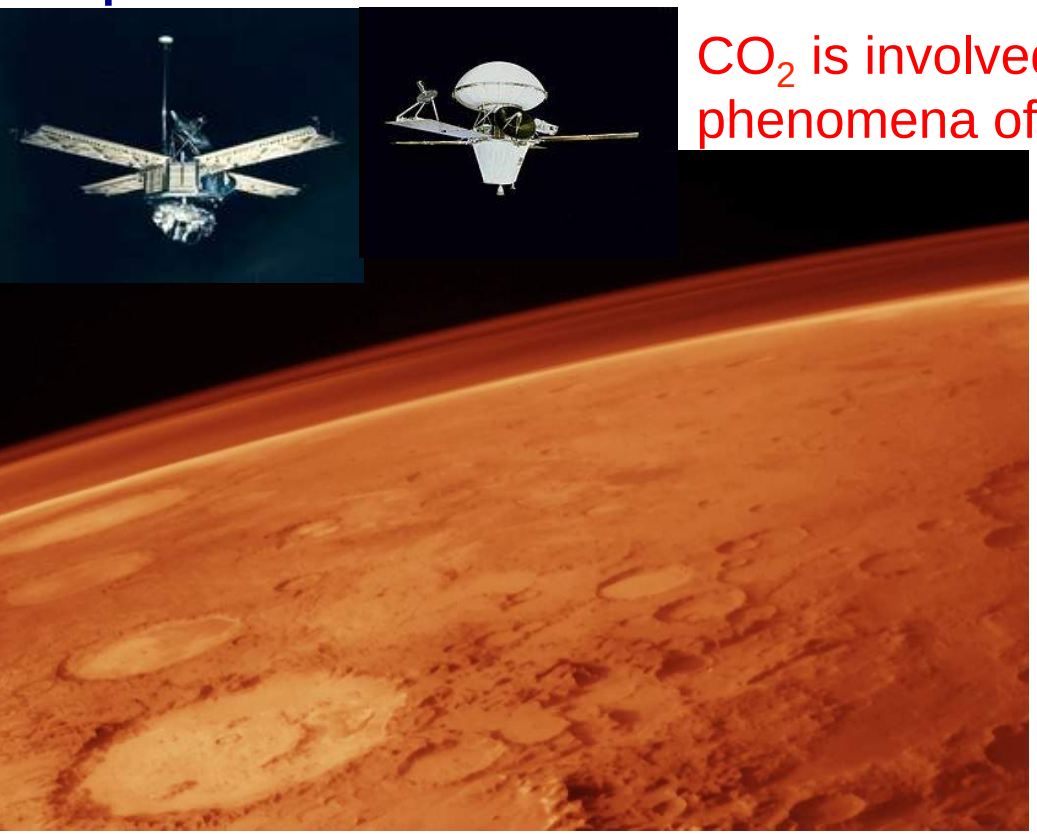
1 – the removed electron may change sensibly the electronic configuration of the neutral species modifying its chemical reactivity;

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

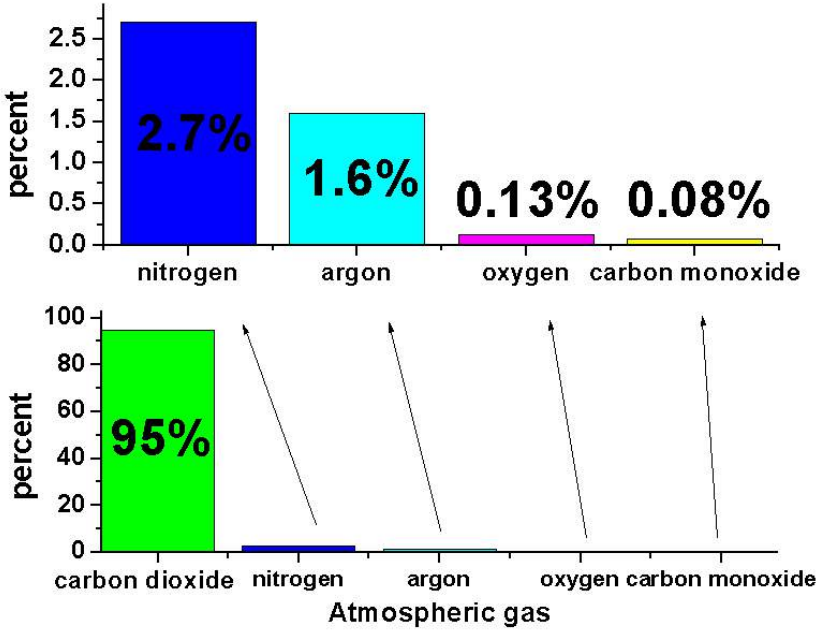


3 – the double ionization producing a molecular dication can induce Coulombic explosion and fragment ions formation with high kinetic energy content.

This process, widely studied by our research group, can explain the lack in the O^+ expected concentration of the Mars Atmosphere, as measured by MARINER 6 spacecraft and VIKING 1 lander



CO_2 is involved in several atmospheric phenomena of the Earth and of other planets like Mars and Venus



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Falcinelli, S.; Pirani, F.; Alagia, M.; Schio, L.; Richter, R.; Stranges, S.; Vecchiocattivi, F. *Chemical Physics Letters* **2016**, in press. DOI: 10.1016/j.cplett.2016.09.003

The production of CO_2^{2+} dications by double photoionization of CO_2 has been studied in the 34-50 eV photon energy range, by the use of synchrotron radiation....

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

Atmospheric escape of O^+ by dissociative double photoionization of CO_2 molecules

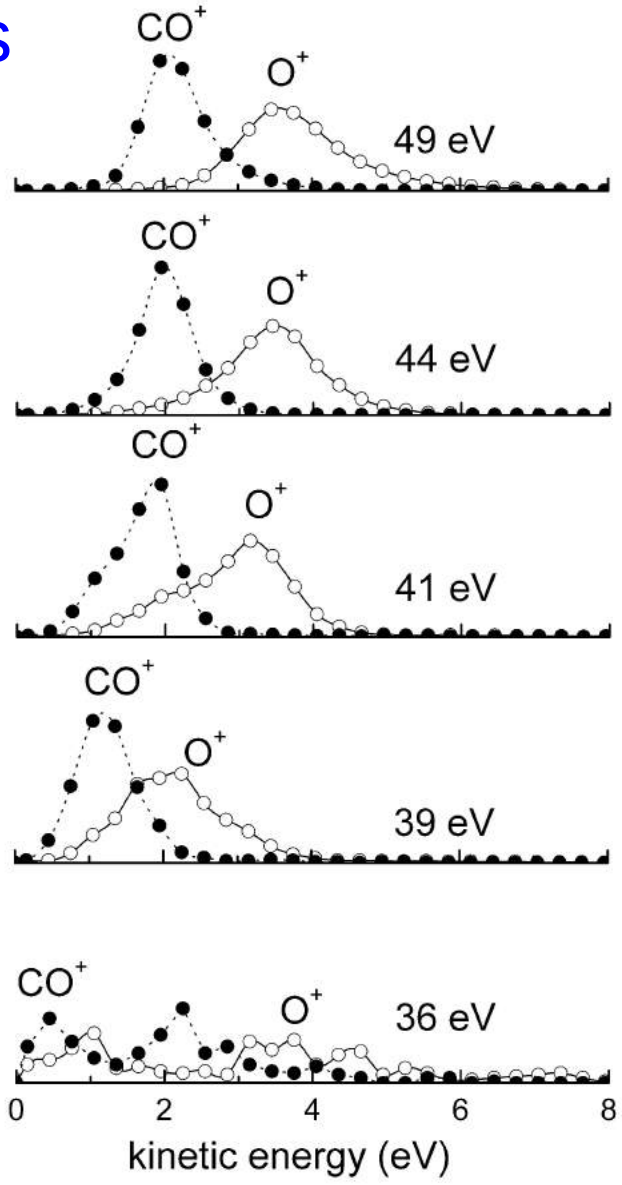
One consequence of the exotic behavior of doubly charged molecular ions in planetary atmospheres is the possibility of creation of dissociative products with a kinetic energy of several eV.

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.

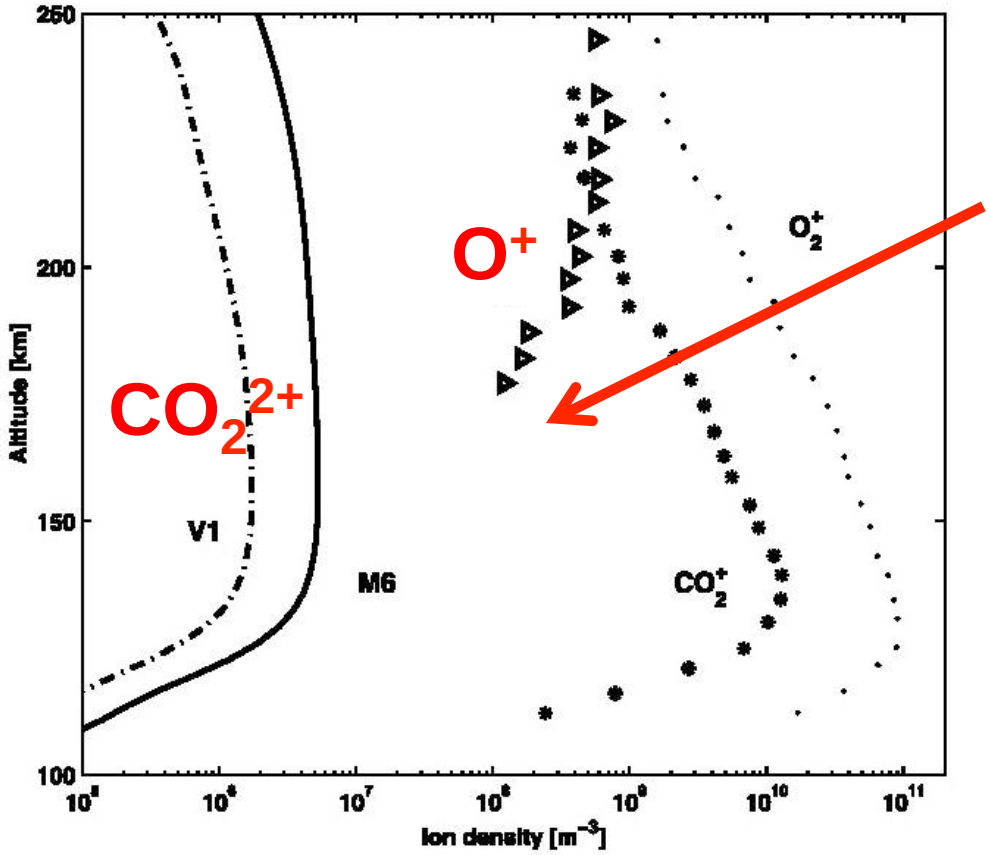
Typical escape energy (eV) for the C^+, N^+ and O^+ ions in the atmosphere of Venus, Earth, Mars and Titan, at the exobase

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.

Atmospheric escape of O^+ by dissociative double photoionization of CO_2 molecules



CO_2^{2+} ion density profiles for Viking 1 lander (V1) and Mariner 6 spacecraft (M6) geophysical conditions. Ion density profiles measured by Viking 1 lander are also plotted.

Where the O^+ concentration become lower, the concentration of CO_2^{2+} increases.

This could be explained by the CO_2^{2+} fragmentation towards the CO^+ and O^+ ions production with a high kinetic energy content (3.5-3.8 eV for O^+ ions).

This energy is large enough to allow the O^+ escape from the Mars atmosphere.

Witasse, O.; Dutuit, O.; Lilensten, J.; et al. *Geophys. Res. Lett.* **2002**, 29, 1263.

Falcinelli, S.; Pirani, F.; Alagia, M.; Schio, L.; Richter, R.; Stranges, S.; Vecchiocattivi, F. *Chem. Phys. Lett.* **2016**, in press. DOI: 10.1016/j.cplett.2016.09.003

POSSIBILI COLLABORAZIONI

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Acknowledgements



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