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1 **Methane production by CO₂hydrogenation reaction with**
2 **and without solid phase catalysis**

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4 *Stefano Falcinelli^{a,*}, Andrea Capriccioli^b, Fernando Pirani^c, Franco Vecchiocattivi^a, Stefano*
5 *Stranges^d, Carles Martí^c, Andrea Nicoziani^c, Emanuele Topini^a, and Antonio Laganà^e*

6
7 *^aDepartment of Civil and Environmental Engineering, University of Perugia,*
8 *Via G. Duranti 93, 06125 Perugia, Italy.*

9 *^bENEAC.R. Frascati, Via E. Fermi 45, 00044 Frascati, Italy.*

10 *^cDepartment of Chemistry, Biology and Biotechnologies, University of Perugia,*
11 *Via Elce di Sotto 8, 06123 Perugia, Italy.*

12 *^dDepartment of Chemistry and Drug Technology, University of Rome “La Sapienza”, 00185*
13 *Rome, Italy.*

14 *^eMaster-up srl, Via Elce di Sotto 8, 06123 Perugia, Italy*

15
16 * Corresponding author: Tel. +39 0755853856, - 5527; Fax: +39 0755853864; E-mail:
17 stefano.falcinelli@unipg.it (S. Falcinelli).

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25 **Abstract**

26 Leveraging on the experience gained by designing and assembling a prototype experimental
27 apparatus reusing CO₂ to produce methane in a reaction with H₂, we are developing an
28 alternative innovative cost effective and contaminant resistant synthetic strategy based on the
29 replacement of the solid phase catalysis with a homogeneous gas phase process going through
30 the forming CO₂²⁺ molecular dications.

31 **Keywords:** methanation reactor; CO₂ waste; free methane; catalyst; plasma, dications.

32

33 **Introduction**

34 As reported during the 2nd SMARTCATs general meeting of the COST Action CM1404 we
35 are carrying out a research aiming at re-using CO₂ and implementing a *validated laboratory*
36 *technology* based on an experimental prototype apparatus (called ProGeo) producing carbon
37 neutral methane through the chemical conversion of CO₂ waste flue gases using renewable
38 energies.

39 The research is being carried out in collaboration by researchers of the laboratories of the
40 University of Perugia and of ENEA (the Italian National Agency for New Technologies,
41 Energy and Sustainable Economic Development of Frascati) with the support of a cluster of
42 Small and Medium-sized Enterprises (SME)s coordinated by the Master-up srl company. In
43 particular, the project leverages a) on the expertise of the Departments of Chemistry, Biology
44 and Biotechnology and of Civil and Environmental Engineering of the University of Perugia
45 on the experimental and theoretical treatment of elementary reactive and non reactive
46 molecular processes [1-8] and b) on the engineering capabilities of designing, building and
47 experimenting innovative apparatuses of ENEA [9] researchers with the support of the above
48 mentioned SMEs specialized in the field of molecular science software modeling. Such

49 collaboration has been incubated by the networking activities of some COST actions [10,11]
50 and of some virtual communities of the European Grid Infrastructure EGI.eu [12, 13].

51 The first purpose of this paper is to illustrate how the developed distributed computing
52 machinery (i.e. the collaborative (workflowed) sharing of high level accurate and approximate
53 ab initio and empirical calculations of the electronic structure of the involved molecular
54 systems, the fitting and, as an alternative, force field formulations of the related potential
55 energy surfaces together with accurate quantum, quantum-classical, quasi-classical
56 dynamical calculations of the detailed properties of the system plus their integration with
57 statistical averaging of the detailed properties over the unobserved parameters as well as their
58 combination in multi-scale treatments) has provided a solid ground for a converging
59 comparison of experimental and computational investigations of the methane formation from
60 CO₂ using solid state catalyzed processes.

61 The second purpose of the paper is to illustrate how the progress made in the above
62 mentioned research line has prompted a new one based on the use of the Synchrotron and the
63 Free Electron Laser light sources to investigate the possibility of developing routes alternative
64 to solid state catalyzed techniques. In particular, details are given on how CO₂ hydrogenation
65 can occur via plasma generation by either electrical discharges or by vacuum ultraviolet
66 (VUV) excitations of a CO₂ + H₂ gas mixture.

67 Accordingly, the paper is articulated as follows:

68 in section 2 structure and performances of the methanation reactor are illustrated;

69 in section 3 the computer simulation of the involved processes is analysed;

70 in section 4 the research lines driving the evolution of the apparatus towards a pure gas phase
71 one are discussed.

72

73

74 2. The present methanation reactor

75 Experimental measurements of methane yields of *ProGeo* have been carried out using CO₂
76 bottles (some measurements have been performed also using CO₂ produced (in the ratio of 1.9
77 kg per litre) from grapes fermentation of Marsala, a famous wine of the region where
78 Garibaldi got ashore when starting the unification of Italy, kindly provided by IRVO (Istituto
79 Regionale Vini e Oli)). The measurements show a complete compatibility with the catalyser
80 used for the methanation process in *ProGeo*. The used catalyser is KATALCO_{JM} 11-4MR a
81 commercial product of the Johnson Matthey company (made of silicate hydrous aluminum,
82 silicon oxide, nickel, nickel oxide, magnesium oxide, graphite porous small cylinders of
83 average diameter 3.1 mm and height 3.6 mm containing metallic nickel) whose 2500X
84 micrography is shown in Fig. 1.

85 The ProGeo reactor is designed for an exit CH₄ maximum flux of 1 Nm³/h. As shown in
86 Figure 2, it is articulated in twin columns (twin flow channels) externally cooled thanks to
87 shared laminar elements in order to dissipate the heat produced by the exothermicity of the
88 reaction ($\Delta H_{298K} = -164.9 \text{ kJ mol}^{-1}$). Design parameters of the reactor are:

89 GHSV (Gas Hourly Space Velocity) (ml h⁻¹ gr⁻¹) and SV (Space Velocity) (h⁻¹).

90 Another useful parameter is the ratio between the total flux of gas and the exposed surface of
91 the catalyser indicated as GHCS (Gas Hourly Catalyst Surface) (cm h⁻¹).

92 The value of the reactor parameters of the present version of the ProGeo apparatus are: GHSV
93 = 3200 ml h⁻¹gr⁻¹ and SV = 2100 h⁻¹ leading to a GHCS parameter of 155 cm h⁻¹.

94 The resulting features of the present ProGeo apparatus shown in Fig. 2 are:

- 95 - External diameter of the single channel 60 mm;
- 96 - Catalysed total length 660 mm;
- 97 - Maximum inlet flux (H₂+CO₂) 6 Nm³/h;

- 98 - Reference Molar ratio (CO_2/H_2) 1/5;
99 - Maximum outlet flux (CH_4) 1 Nm^3/h .

100 Experimental measurements have been carried out by varying:

- 101 - the CO_2/H_2 molar ratio from a minimum of 1/4 to a maximum of 1/5.5;
102 - the reactor temperature from a minimum of 220 °C to a maximum of 450 °C;
103 - the H_2 flux from a minimum of 0.8 Nm^3/h to a un maximum of 2.5 Nm^3/h ;
104 - the pressure from a minimum of 1 bar to a maximum of 2 bar.

105 A key element for a quantitative measurement of the reaction yield is the regular monitoring
106 of the temperature both along the central axis of each channel (maximum temperature) and
107 along the peripheral axis (minimum temperature). In Figure 3 the location and labels of the
108 channel thermocouples (6 axial and 3 peripheral) are shown as dots together with the cross
109 section of the twin columns.

110 The methanation reactions occur mainly on the top segment of the reactor close to the inlet
111 (90% in the first 200 mm). Accordingly, most of the produced heat is detected by the central
112 thermocouples (T5, T6 and T14, T15). The average of the measured percentage of produced
113 methane is plotted as a function of the molar ratio and temperature in Fig. 4. As is apparent
114 from the Figure, the threshold temperature is 240°C and the range of temperature of optimal
115 yield is 300 - 350°C. The molar ratio has a significant impact on the percentage of produced
116 methane with the optimum value of the CO_2 / H_2 ratio being 1/5.

117

118 **3. Computational simulation of methane production from the CO_2+H_2 reaction with** 119 **solid phase catalysis**

120 In our laboratory the initial rationalization of the processes involved in producing methane via
121 the Sabatier reaction (i.e. by making H_2+CO_2 react on a catalytic surface [14]) has been

122 performed by following the flowchart of ZACROS [15], a Kinetic Monte Carlo (KMC)
123 [16,17] software package written in Fortran 2003. ZACROS leverages on the Graph-
124 Theoretical KMC methodology coupled with both cluster expansion Hamiltonians for the ad-
125 layer energetics and the Brønsted-Evans-Polanyi relations for the activation energies of
126 elementary events [16]. ZACROS enables researchers in the areas of Computational Catalysis
127 and Surface Science to perform dynamic modelling of adsorption, desorption, surface
128 diffusion, and reaction processes on heterogeneous catalysts. Although in our traditional
129 GEMS (Grid Empowered Molecular Simulator) [18] approach based on distributed
130 computing platforms the rates (r) of elementary processes are computed by running molecular
131 dynamics calculations based on Potential Energy Surfaces (PES)s originating from *ab initio*
132 treatments, in the version of ZACROS implemented by us, for all the elementary steps
133 potentially participating in the mechanism, the values of r to be used are taken from the
134 literature and are usually given the following Transition State (TS) theory formulation [19,20]

$$135 \quad r = A \cdot \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

136 in which A is a pre-exponential factor (quantifying the propensity of the system to cross from
137 TS to products) while the exponential term brings in the information on the PES of the related
138 elementary process (either forward “f” or backward “b”) as the energy difference E_a between
139 the stationary point of the potential Minimum Energy Path (MEP) at the transition state and
140 that associated with the reactant asymptote with k_B being the usual Boltzmann constant and T
141 the temperature. The lowest approximation level formulates the pre-exponential factor as
142 $k_B T/h$ where h is the Plank constant.

143 In the adsorption of gaseous species, however, the most frequently used expression for the
144 rate of reaction is the well known Hertz-Knudsen equation:

145
$$r_i^{\text{ad}} = S_{0,i} \cdot A_{\text{site}} \frac{p_i}{\sqrt{2\pi m_i k_B T}} \quad (2)$$

146 where $S_{0,i}$ is the sticking coefficient (for which we take the value 1 in this work), A_{site} is the
 147 area of the adsorption site, p_i is the partial pressure of species i and m_i its mass.

148 A more accurate formulation of the rate coefficients makes use of the partition function for
 149 both, the intermediate state (incorporating so far the information about the remaining degrees
 150 of freedom) and the reactants:

151
$$A = \left(\frac{k_B T}{h} \right) \left(\frac{Q^\ddagger}{Q_r} \right) \quad (3)$$

152 where Q^\ddagger is the transition state partition function and Q_r the partition function of reactant
 153 species.

154 Each partition function is calculated considering that rotations and translations are frustrated
 155 (hindered), due to the fact that they are adsorbed, and therefore can be assimilated to
 156 vibrational degrees of freedom. In that case, the vibrational partition function takes the form:

157
$$Q_{\text{vib},X} = \prod_k \frac{\exp\left(\frac{-h\nu_k}{2k_B T}\right)}{1 - \exp\left(\frac{-h\nu_k}{k_B T}\right)} \quad (4)$$

158 where $Q_{\text{vib},X}$ is the total vibrational partition function of the species X , and ν_k is the frequency
 159 of the vibrational mode k .

160 In this way ZACROS can also simulate desorption/reaction spectra at a given temperature
 161 providing so far a rationale for designing kinetic mechanisms and understanding experimental
 162 data.

163 The elementary processes considered for the simulations are given in refs. [21,22] together
164 with the numerical value of the related parameters. Hexagonal periodic default lattice will be
165 the one of our choice for the Ziff, Gulari and Barshad (ZGB) reference model [23] as well as
166 for the Sabatier Process.

167 An important outcome of our calculations is illustrated in Fig. 5 (see also ref. [19]) in which,
168 in contrast with the suggestion of ref. [21] of a dominance of the CO* decomposition, it is
169 apparent from the analysis of the ZACROS calculations that the dominant process leading to
170 the production of CH₄ is the hydrogenation of CO. This has suggested us to investigate
171 possible alternative gas phase processes producing CO. For this reason, we decided to
172 investigate the possibility of inducing CO₂ dissociation and producing CO+O and CO⁺+O⁺
173 neutral and ionic chemical pairs reacting with hydrogen, respectively, via a plasma generation
174 either by electrical discharges or by vacuum ultraviolet (VUV) photons on a CO₂+H₂ gas
175 mixture as will be discussed in the next section.

176

177 **4. Methane production from the CO₂+H₂ reaction without solid phase catalysis**

178 The investigations carried out on our ProGeo 20kW apparatus [22] based on the well
179 known Sabatier reaction:



181 at moderately high pressure (2-3 atm) and high temperature (200-300°C) with the use of a
182 solid phase catalyst (nickel, ruthenium, or alumina) has prompted us to further progress (as
183 will be illustrated in detail in this section) to use either low cost or renewable energy to reuse
184 waste CO₂ to produce methane in a circular economy scheme [22]. To this end we have
185 undertaken the investigation of a new methanation pathway aimed at avoiding the use of the
186 solid phase catalysis, by exploring mechanisms involving a plasma generation by electrical
187 discharges or by vacuum ultraviolet (VUV) photons on a CO₂+H₂ gas mixture. This effort is

188 based on the since long established expertise of our laboratories in promoting and modeling
 189 molecular processes (atomic hydrogen and excited metastable species generation by electrical
 190 discharge [24-26] to study gas phase processes induced under controlled conditions) and in
 191 fully characterizing the microscopic dynamics of elementary reactions by experimentally
 192 determining related main kinetic parameters such as rate constants, cross sections,
 193 intermolecular potentials, structure, and energy of the transition state, reaction pathways,
 194 etc. Furthermore, we can perform high resolution experiments in single collision conditions
 195 using crossed molecular beam apparatuses and studying plasma induced gas phase reactions
 196 both by microwave and RF (Radio Frequency) discharges [24-26] and by synchrotron
 197 radiation [27-29]. In particular the mentioned experiments are performed on the crossed
 198 molecular beams apparatus of the Perugia University [30,31] to measure PIES (Penning
 199 Ionization Electron Spectroscopy) data, and on the ARPES (Angle Resolved PhotoEmission
 200 Spectroscopy) end station at the GasPhase Beamline of the Elettra Synchrotron Radiation
 201 Facility (Trieste) [32,33] (more details are given later in the specific subsection).

202 The need of avoiding the use of the solid phase catalyst to perform reaction (5) and
 203 investigating possible alternative microscopic reaction mechanisms occurring in the
 204 homogeneous gas phase, is motivated by concurrency of reaction (5) and the following two
 205 main reactions:



208 as well as by the wish of avoiding unwanted reactions, like the (8), (9), (10), and (11) listed
 209 below,





214 responsible for a rapid loss of catalytic activity. Further reservations on the use of a Ni based
215 solid phase catalyst are related to the environmental and safety issues associated with the
216 possible formation of Ni(CO)₄ that is a highly toxic gaseous species produced when Ni is
217 exposed to a gas mixture containing high pressure CO as typical of experimental conditions
218 commonly used to maximize the yield of CH₄ in the methanation reaction.

219 For this purpose we have undertaken the study of the Sabatier reaction (5) in a homogeneous
220 gas phase environment by generating and characterizing controlled plasmas via electrical
221 discharges and VUV photons on a pure CO₂ and CO₂+H₂ gaseous mixture a technology in
222 which our research group is leader since early 1990 [24,34,35]. In our experimental
223 apparatuses (described in the next section) the energy pumped in the produced plasma can be
224 controlled using both electrons and photons. In the first case we use an inhouse electrical
225 microwave or RF discharge. In the second case we use a tunable synchrotron radiation. At the
226 same time we can control and characterize the chemistry of the generated plasmas by studying
227 the microscopic dynamics of the elementary chemical reactions because in molecular beam
228 techniques [38-40] they occur in single collision regime (see again below in the specific
229 subsection).

230

231 *4.1. Experimental methods*

232 As already mentioned, a first attempt to produce plasmas containing carbon dioxide, has been
233 made in our laboratory using a microwave discharge beam source operating in pure CO₂ and
234 in an approximately 50-50% CO₂-H₂ mixture at a global pressure of about 1600 Pa. The
235 microwave discharge is produced in a cylindrical quartz tube (10 cm in length and 2 cm in
236 diameter) in a brass resonance cavity (water cooled) working at 2450 MHz [24,34,35]. The
237 applied microwave power was varied in the range 70-200 W with a reflected power lower

238 than 5%. A preliminary characterization of the produced plasma has been performed using the
239 crossed molecular beam apparatus shown in Figure 6. Such an apparatus, usually devoted to
240 the study of the microscopic dynamics of autoionization reactions induced by excited
241 metastable species (also called Penning Ionization or Chemi-ionization reactions), for the
242 experiment considered here was used by keeping the secondary beam switched off. In this
243 way it was possible to detect only the main chemical species flowing out of the plasma
244 microwave discharge source as an effusive molecular beam. Such an analysis was performed
245 using the mass spectrometry characterization of the beam by means of a quadrupole mass
246 filter located below the crossing beams region. Measured data is consistent with that
247 previously recorded by Dobrea *et al.* [39,40] who found a large dissociation rate of carbon
248 dioxide, according to reactions (12) and (13) below, in the case of the plasma discharge in
249 pure CO₂ with respect to the one measured in CO₂+H₂ gas mixture.



252 The CO₂ dissociation percentage, χ (determined by keeping the inlet gas pressure at a constant
253 value of 1600 Pa) was obtained by recording the CO₂⁺ intensities I_i and I_f (measured with the
254 microwave discharge off and on, respectively) using the following relationship:

$$255 \quad \chi = \frac{I_i - I_f}{I_i} \cdot 100 \quad (14)$$

256 The values of χ amounted to about 27% in the case of the plasma discharge in pure CO₂, and
257 lowered to about 19% in the case of CO₂+H₂ gas mixture at an applied microwave power of
258 100 W. The measured values increased up to 52% (for plasma in pure CO₂) and 36% (in
259 plasma in CO₂+H₂ mixture) when the microwave power was doubled to about 200 W.
260 Measured data is reported in Table 1 and compared with that of refs. [39,40].

261 Then the same apparatus of Figure 6 was used to measure plasma-assisted CO₂ conversion
262 into hydrocarbons as an alternative way of producing synthetic fuel (this technique has been

263 recently applied by Welzel *et al.* [41] who determined the experimental conditions suited to
264 give a 20% yield for CH₄ formation. We better characterized the chemistry of the produced
265 plasmas by investigating the detail of the chemical reactions induced by the ionic species that
266 can be formed in such gaseous environments using VUV photons as a source of energy to
267 induce excitation and ionization processes responsible for the plasma generation. The
268 experiment was performed at the ELETTRA Synchrotron Light Laboratory (Trieste, Italy),
269 using the ARPES end station at the Gas Phase having a very high photon intensity and a
270 tunable wavelength. Details of the beam-line and of the end station have been already
271 reported elsewhere [42,43] and the characteristics of the apparatus used for the experiment are
272 discussed in detail in refs. [44,45]. Specific features of the experiment reported here are: i) the
273 use of a synchrotron radiation tunable energy source, working in the energy range of 35-50
274 eV with a resolution of about 1.5 meV; ii) the detection of all produced charged particles
275 (electrons and ions) in the generated plasma, recording them in a time resolved measurements
276 in which we are able to extract the spatial momentum components of final ions by using the
277 electron-ion-ion coincidence technique coupled with an ion position sensitive detector (see
278 below).

279 Figure 7 shows: i) on the left hand side panel, a scheme of the main part of the experimental
280 apparatus based on the electron-ion-ion coincidence technique, and, as an example, the
281 coincidence plot recorded in the double photoionization experiment of carbon dioxide at a
282 photon energy of 44 eV (in such a panel are also shown the recorded mass spectra of the
283 product ions at the same photon energy); ii) on the right hand side panel, a picture of such a
284 device. As can be seen from the Figure, the monochromatic synchrotron light beam crosses at
285 right angles an effusive molecular beam of CO₂ neutral precursors, and the product ions are
286 then detected in coincidence with photoelectrons. The coincidence electron-ion-ion extraction
287 and detection system consists in a time of flight (TOF) mass spectrometer equipped with an

288 ion position sensitive detector (stack of three micro-channel-plates with a multi-anode array
289 arranged in 32 rows and 32 columns). As mentioned above, such a detector has been
290 especially designed in order to properly measure the spatial momentum components of the
291 ionic products [46].

292 Carbon dioxide was supplied from a commercial cylinder at room temperature (99.99%
293 nominal purity) to a needle effusive beam source. An adjustable leak valve along the input gas
294 pipe line was used in order to control the gas flow, which was monitored by checking the
295 pressure in the main vacuum chamber.

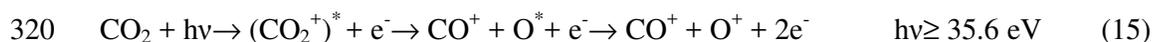
296

297 *4.2. The chemical role of CO₂ in the generated plasma*

298 When using excitation energies higher than 35 eV, it is possible to induce ionization
299 phenomena in gaseous mixtures containing carbon dioxide with the production of CO⁺, O⁺
300 and CO₂²⁺ ions (as a matter of fact plasmas constitute over 99% of the known matter of the
301 Universe). Indeed, the formation of doubly charged positive ions in gas phase using VUV
302 photons or energetic electrons as ionizing source is routine in a number of laboratory
303 experiments able to reproduce the physical conditions of the upper atmosphere of some
304 planets of the Solar System (such as Mars, Venus, and Titan) [27-29, 49-52]. Once these ionic
305 species are produced in metastable states, after their typical lifetime they can, dissociate into
306 ionic fragments having a high kinetic energy content due to the strong Coulomb repulsion
307 characterizing the low stability of their electronic structure. This so called “Coulomb
308 explosion” of molecular dications provides their fragments with a large amount of translation
309 energy (several eV) that enhances the chemical reactivity of the plasma with the following
310 consequences on the properties of a gas mixtures: i) the chemical behavior is radically
311 changed because the removed electrons may change sensibly the electronic configuration of
312 the neutral species and modify its chemical reactivity; ii) the interaction is much more intense

313 than the neutral-neutral one, making more likely collision events and increasing the chemical
 314 reactivity in plasma environments; iii), the formation of fragment ions with large kinetic
 315 energy increase chemical reactivity.

316 In particular our experiments with a plasma containing CO₂ confirmed the carbon dioxide
 317 dissociation paths singled out by previous studies [53-56] and quantified the following ones
 318 allowed to indicates that the following main processes are possible with their respective
 319 threshold energies:



323 together with relative threshold energies. In particular, reaction (15) is an indirect process
 324 occurring below the double photoionization threshold of 37.34 eV, via the formation an
 325 excited state of the (CO₂⁺)^{*} monocation, followed by the production of an intermediate
 326 autoionizing oxygen atom O^{*}. Reaction (16) produces a stable CO₂²⁺ dication. Reaction (17)
 327 mainly occurs via the formation of a long lived dication with lifetime $\tau \geq 3.1 \mu\text{s}$,
 328 corresponding to the production of CO₂²⁺ ions in the ground X³Σ_g⁺ electronic state with an
 329 internal energy below the threshold towards the Coulomb explosion [53-56].

330 Figure 8 shows the relative cross sections measured in the investigated photon energy
 331 range for reactions (15), (16), and (17) recorded using the electron-ion-ion coincidence
 332 technique discussed in the previous section. The analysis of data, collected at each
 333 investigated photon energy, is based on the density distribution evaluation of coincidences in
 334 the measured coincidence spectra, such as the one reported in the left panel of Fig. 7. On such
 335 an analysis, the total counts (recorded at each investigated photon energy) corresponding to
 336 the ion pair peak coming out from the same reaction gives the relative cross section for the
 337 three investigated reaction channels of Fig. 8. At the same time, the KER (Kinetic Energy

338 Released) of product ions can be evaluated by analyzing the dimension and the shape of the
339 recorded peaks using the method suggested by Lundqvist *et al.* [57]. This procedure, applied
340 to the CO^+/O^+ coincidences signal related to reactions (15), (16) and (17), has allowed us to
341 evaluate the KER distributions of all product ions for different values of the investigated
342 photon energy (36.0, 39.0, 41.0, 44.0 and 49.0 eV). The results shown in Fig. 9 tell us that the
343 KER value for the O^+ ions ranges between 1.0 and 5.0 eV, while the CO^+ KER can reach 3.0
344 eV or more and, changes the maximum value depending on the investigated photon energies.
345 These results demonstrate that the chemical reactivity of plasmas containing CO_2 is strongly
346 increased by the presence of CO^+ and O^+ ions having a very high kinetic energy. In particular,
347 the fast CO^+ ions, are expected to react with molecular and atomic hydrogen (both produced
348 in a plasma generated by a microwave discharge in a gaseous CO_2+H_2 mixture [24-26,
349 39,40]) playing a pivotal role in the plasma-assisted CO_2 conversion on CH_4 fuel. In this
350 respect, it has to be noted that Knott *et al.* measured reactive cross section for the $\text{CO}^+ + \text{H}_2 \rightarrow$
351 $\text{HCO}^+ + \text{H}$ reaction, obtaining a related rate constant value ranging between 1.6×10^{-9} and
352 $3.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in the collision energy range of 0.01 – 3.0 eV, indicating a pronounced
353 decline at elevated collision energies, higher than 7.0 eV [58]. An analogous situation has
354 been recorded by Farrar and coworkers in their study of $\text{H}_2^+ + \text{CO}$ proton transfer reaction
355 producing HCO^+ in the 0.74 - 9.25 eV collision energy range [59]: at higher energies, the
356 cross section drops rapidly whereas, at low energies, the HCO^+ products are highly excited,
357 with 90% of the available energy in internal excitation.

358 A first consideration can be made regarding the production of a low energy $\text{CO}_2\text{-H}_2$
359 plasma. In such a case, it has to be noted that, by using CO^+ ions coming from the Coulomb
360 explosion of CO_2^{2+} molecular dication, a projectile reactive species is available with a
361 translational energy content of about 2.0-2.5 eV (see Fig.9). This means that in our plasma the
362 $\text{CO}^+ + \text{H}_2$ reaction, also favored by a stronger long range trapping attraction, can occur with a

363 rate constant value higher than those of neutral-neutral reactions (having in most cases typical
364 rate constant values of about 10^{-10} - 10^{-12} $\text{cm}^3 \text{s}^{-1}$ [60]). In the case of the production of high
365 energy CO_2 - H_2 plasmas, further considerations can be made, in order to take into account that
366 the CO^+ + H_2 measured cross section shows a strong decrease when the collision energy
367 becomes higher than 7 eV [58]. In this case, Knott *et al.* explain their results by invoking a
368 dissociation process of the HCO^+ product with a threshold beyond 7.0 eV. In fact, since CO^+
369 ($^2\Sigma$ symmetry) has a predissociating state close to 8.0 eV (vertical) [61] and the vertical
370 transition to the first excited state of H_2 ($^3\Sigma_u^+$) represents a step of about 9.0 eV, the CO^+ + H_2
371 collision should result in an excitation of CO^+ rather than of H_2 . We fully agree with such
372 authors and it is important to note that the possible predissociation of CO^+ appears to be
373 energetically accessible at lower energies (about 5 eV) as demonstrated by more recent
374 calculations by Okada and Iwata [62]. Furthermore, Nobes and Radom in 1981 [63] first
375 calculated the energy profile for the fast isomerization reaction between HCO^+ and COH^+
376 demonstrating a higher stability for HCO^+ and a triangular structure of the $[\text{HCO}]^+$
377 intermediate complex. This corroborates the absence of H_2^+ + CO and $\text{CO}+\text{H}^+$ + H possible
378 competitive products in the CO^+ + H_2 reaction for which Knott *et al.* [58] have recorded only
379 HCO^+ ions with any evidence of both H_2^+ and H^+ products. In their analysis such authors,
380 following ref. [61], did not consider the possibility of the HCO^+ with the rupture of the C---O
381 bond, because their relatively low investigated collision energy range. Moreover, such a
382 dissociation process is energetically allowed and can occur in high energy CO_2 - H_2 plasmas,
383 where the formed HCO^+ ions are compatible with electron attachment dissociation processes
384 towards the production of $\text{CH}+\text{O}$ neutral reactive species, as demonstrated since 1972 by
385 McGregor and Berry [64].

386 Finally, the efficient conversion of CO^+ and CO_2^+ ions into HCO^+ by collisions with
387 H_2 and H reactive partners (all these species can be formed in a CO_2 - H_2 plasma), with the

388 $\text{HOC}^+ \leftrightarrow \text{COH}^+$ isomerization, has been experimentally observed by Gerlich and coworkers
389 [65, 66] and by Tosi *et al.* [67], corroborating the observation that in plasma environments
390 HCO^+ results a very stable species as it is confirmed by astronomical observations indicating
391 HCO^+ as one of the most important ions in dense molecular clouds [68,69].

392 In conclusion, it appears that the production of a $\text{CO}_2\text{-H}_2$ plasma by a microwave discharge
393 allowed us to generate: i) a large dissociation of carbon dioxide, according to reactions (12)
394 and (13) (see data of Table 1); and ii) CO_2^+ , CO_2^{2+} , CO^+ and O^+ ionic species (see reactions
395 (15)-(17) and Figures 8 and 9) able to react with atomic and molecular hydrogen in order to
396 produce HCO^+ ions. All such experimental evidences are compatible with the possible
397 formation of CH and CH^+ species, being the first hydrogenation step on the carbon atom, for
398 a plasma-assisted CO_2 conversion into hydrocarbons as an alternative transformation route in
399 synthetic fuel processing.

400 Further experimental work is in progress in our laboratory in order to investigate such
401 possibility, and to optimize the experimental conditions in an attempt to perform the CO_2
402 hydrogenation reaction (5) via an alternative microscopic mechanism with respect to the use
403 of the solid catalyst.

404

405 **5. Conclusions**

406 The reported concerted efforts of University, ENEA and SMEs researchers in
407 investigating engineering and distributed computing have shown in this paper to what extent
408 the advances in basic research on plasmas are amenable to the assembling of an experimental
409 prototype applying the Sabatier reaction to a homogenous gas phase catalytic environment
410 and to the activation of a circular process turning waste CO_2 flue gases into methane. The
411 measurements performed have not only shown the viability of the proposed solution but have
412 also allowed the extension of computer simulations to a family of innovative mechanisms.

413 Furthermore, as a result of the investigation, useful indications have been obtained on how to
414 proceed to develop alternative solutions to the present Ni catalysed Progeo apparatus by
415 resorting to a gas-phase-only process for the reduction of CO₂ to CH₄. In this work new results
416 obtained by electrical discharges into CO₂-H₂ gas mixtures by using molecular beam
417 technique at different pressure regimes has been presented. Such results together with VUV
418 CO₂ photoionization data collected by synchrotron radiation are then of great help in
419 identifying the microscopic mechanisms to be exploited. Finally, the production of a CO₂-H₂
420 plasma by a microwave discharge allowed us to generate a large dissociation of carbon
421 dioxide, and to produce CO₂⁺, CO₂²⁺, CO⁺ and O⁺ ionic species able to react with atomic and
422 molecular hydrogen in order to produce HCO⁺ ions. All such experimental evidences are
423 compatible with the possible formation of CH and CH⁺ species, representing the first
424 hydrogenation step on the carbon atom, for a plasma-assisted CO₂ conversion into
425 hydrocarbons. This is an alternative transformation route in synthetic fuel processing that we
426 shall investigate further to the end of grounding Progeo on more robust methanation
427 processes.

428

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434

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641

642 **Table 1** – The percentage of CO₂ dissociation in microwave discharge plasma source
 643 produced in pure CO₂ and in a 1:1 CO₂/H₂ gaseous mixture for different values of applied
 644 microwave power. The percentage values are calculated using the simple equation (2), and are
 645 collected working at a constant pressure of 1600 Pa into the plasma source (see text). The data
 646 are compared with those previously collected by Dobrea *et al.* in an analogous experiment
 647 performed at a constant pressure of about 600 Pa [41,42].

648

Microwave discharge power (W)	% of CO ₂ dissociation in pure CO ₂ plasma		% of CO ₂ dissociation in a 1:1 CO ₂ /H ₂ plasma mixture	
	This work	ref. [14]	This work	refs. [39,40]
70	19±4	---	11±4	---
100	27±3	23	19±3	14
150	40±3	---	28±3	---
200	51±2	48	36±2	33

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653 **Figure captions**

654

655 **Fig. 1.** 2500X micrography of the commercial catalyser KATALCO_{JM} 11-4MR (by courtesy
656 of University of Rome Tor Vergata, Rome, Italy).

657

658 **Fig. 2.** A picture of the twin columns of the ProGeo reactor.

659

660 **Fig. 3.** Cross section of the reactor twin columns and locations of the related thermocouples
661 (red dots). On the right hand side the labels of the thermocouples.

662

663 **Fig. 4.** Average measured percentage of the methane produced in our experiments plotted as a
664 function of the molar ratio and of the temperature with a pressure of 2 bar.

665

666 **Fig. 5.** Relative contributions of the different elementary channels to the production of
667 methane evaluated from the minimum energy path of the PES (triangle) and from the
668 ZACROS simulation (diamonds, squares, reverse triangles for the different temperatures
669 connected by solid lines). The green triangle is the value suggested in ref.[24].

670

671 **Fig. 6.** The crossed molecular beam apparatus (mainly used in Penning ionization studies and
672 adapted for plasmas generation containing carbon dioxide) in which the secondary beam was
673 maintained off in order to detect the main chemical species coming out as an effusive
674 molecular beam from the plasma microwave discharge source (see text).

675

676 **Fig. 7.**The electron-ion extraction and detection system used for the electron-ion-ion
677 coincidence measurements to characterize the charged species produced in the CO₂ plasma by
678 tunable synchrotron radiation. Left panel: a scheme of the set-up with a typical coincidence
679 spectrum recorded by the double photoionization of CO₂ at a photon energy of 44 eV (see
680 text). Right panel: a picture of such a device.

681

682 **Fig. 8.**Measured cross sections for the three main processes observed in the CO₂ plasma
683 generation by using synchrotron radiation in the energy range of 34-50 eV and the electron-
684 ion-ion coincidence technique (see text).

685

686 **Fig.9.**Kinetic energy distributions for CO⁺ and O⁺ fragment ions originating by Coulomb
687 explosion of CO₂²⁺ dication produced in the CO₂ plasma by tunable synchrotron radiation.

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690 FIG. 1

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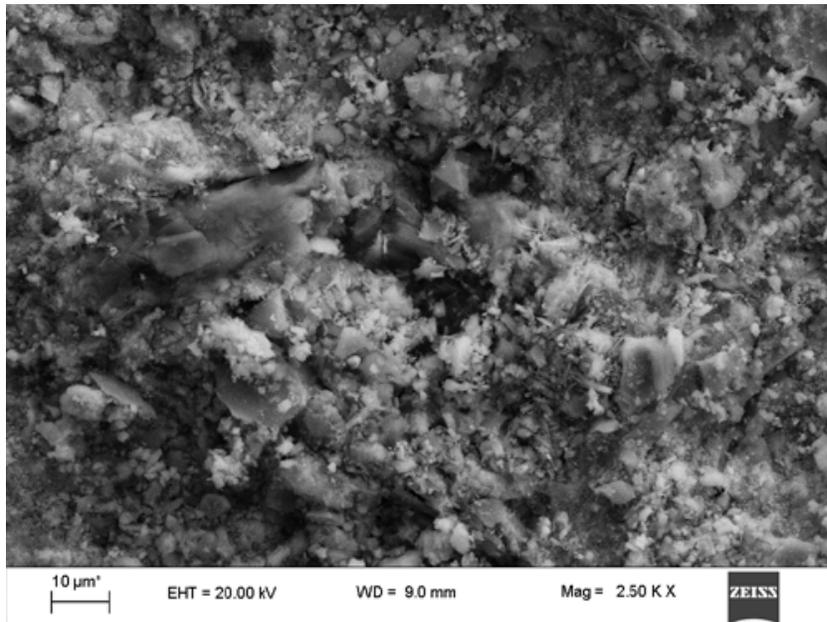
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707 FIG. 2

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731 FIG. 3

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Methanation Reactor: inner thermocouples in channels A and B

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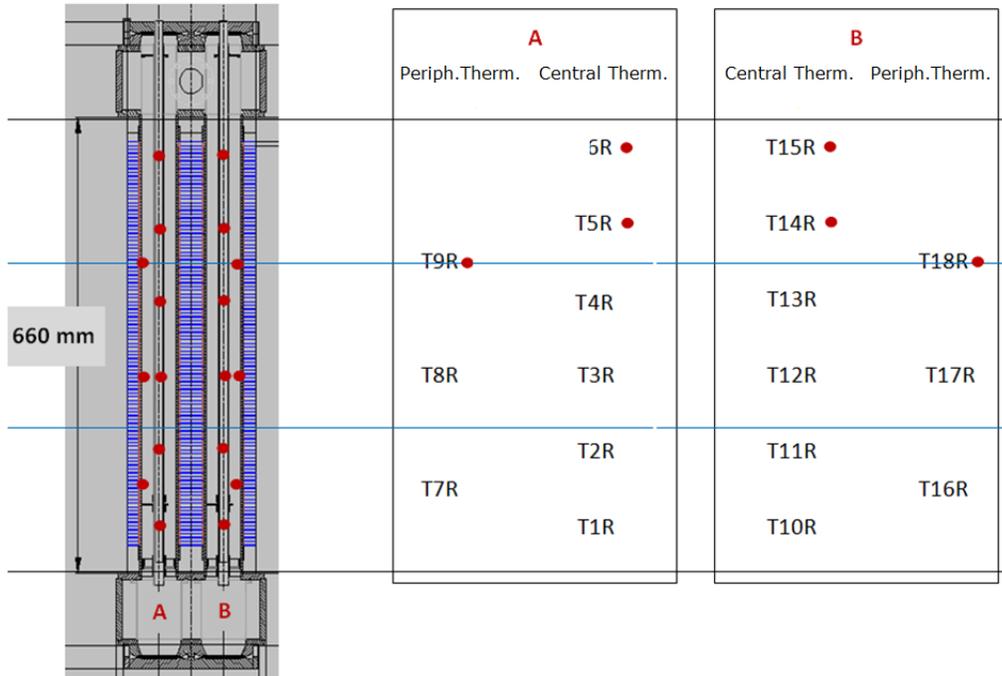
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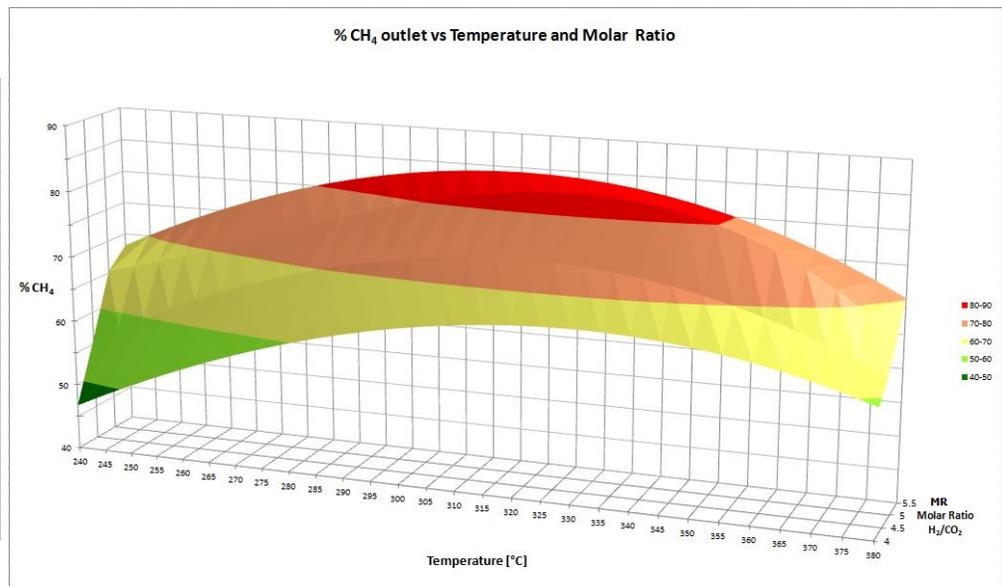
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743



744 FIG. 4

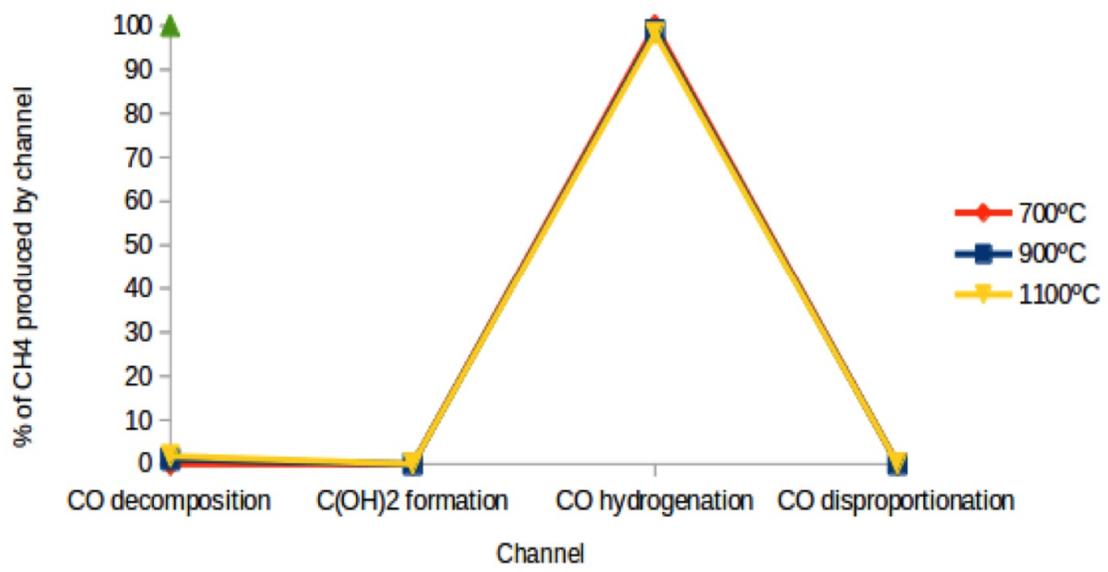
T [°C]	MR 4	4.5	5	5.5
240	47	56	65	68
245	49	58	66	70
250	51	60	68	72
255	52	62	69	74
260	54	63	70	75
265	56	65	71	77
270	57	67	73	78
275	58	68	74	79
280	60	69	75	81
285	61	70	77	82
290	62	71	78	82
295	63	72	79	83
300	64	73	80	84
305	64	73	81	84
310	65	74	82	84
315	65	74	82	84
320	66	74	83	84
325	66	74	83	84
330	66	74	83	84
335	66	73	83	83
340	66	73	82	82
345	65	72	81	82
350	65	71	80	80
355	64	70	79	79
360	64	69	77	78
365	63	67	75	76
370	62	66	72	74
375	60	64	69	72
380	59	62	66	70



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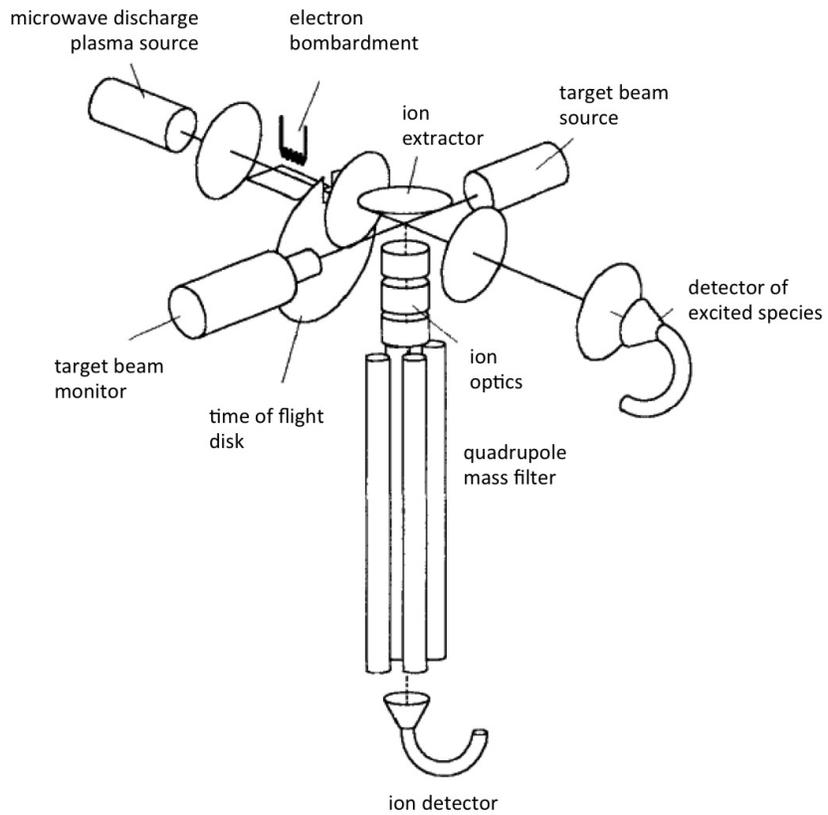
747 FIG. 5



748

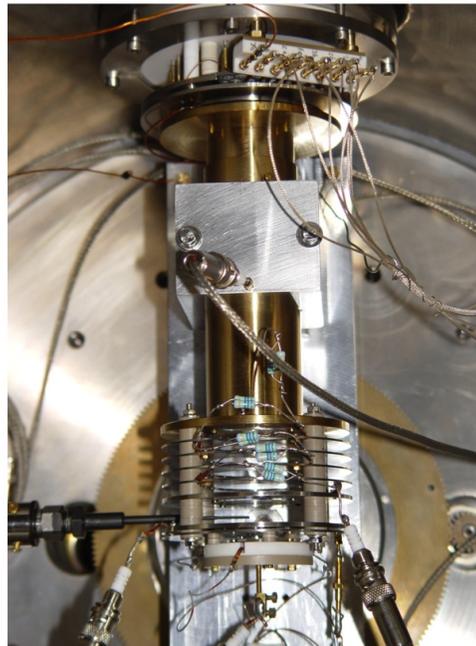
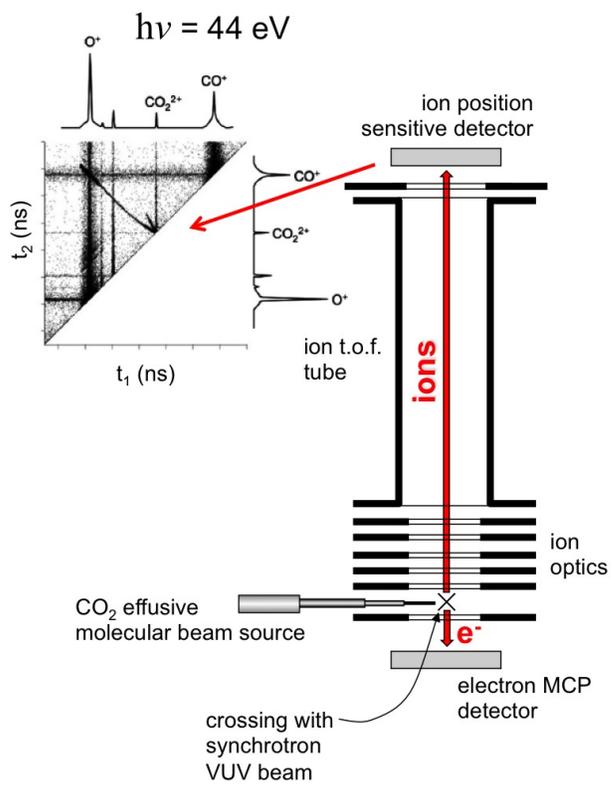
749

750 FIG. 6



751

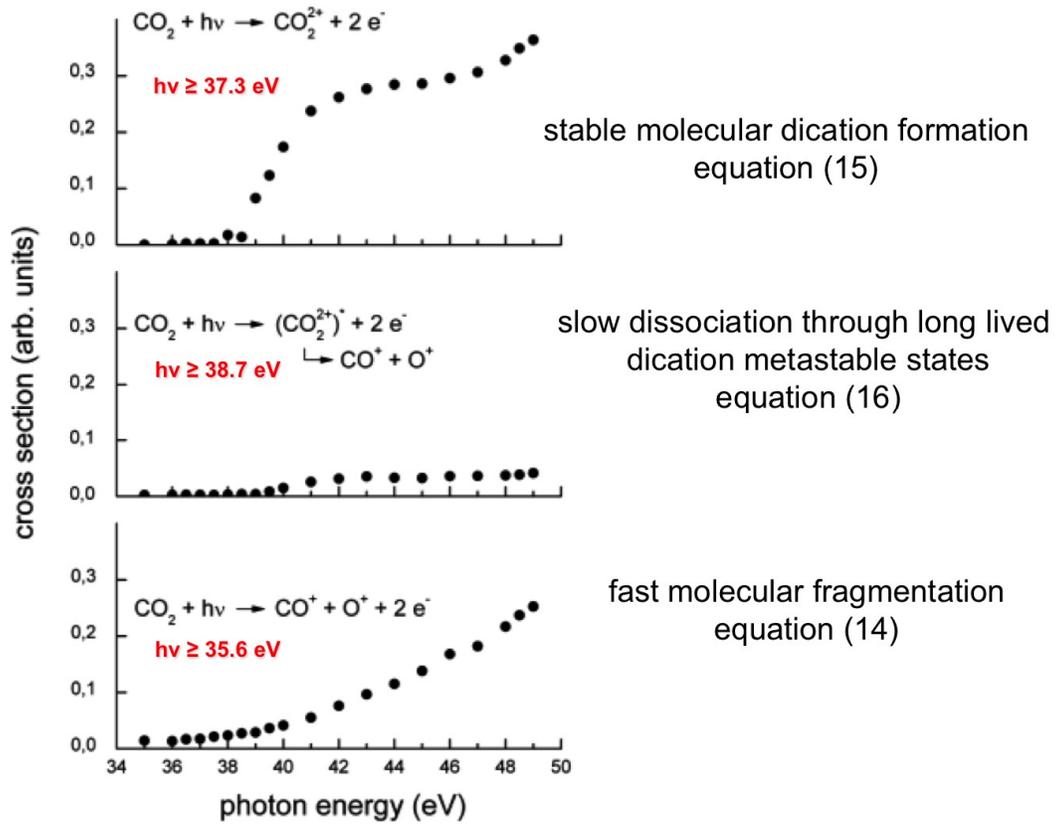
752 FIG. 7



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754

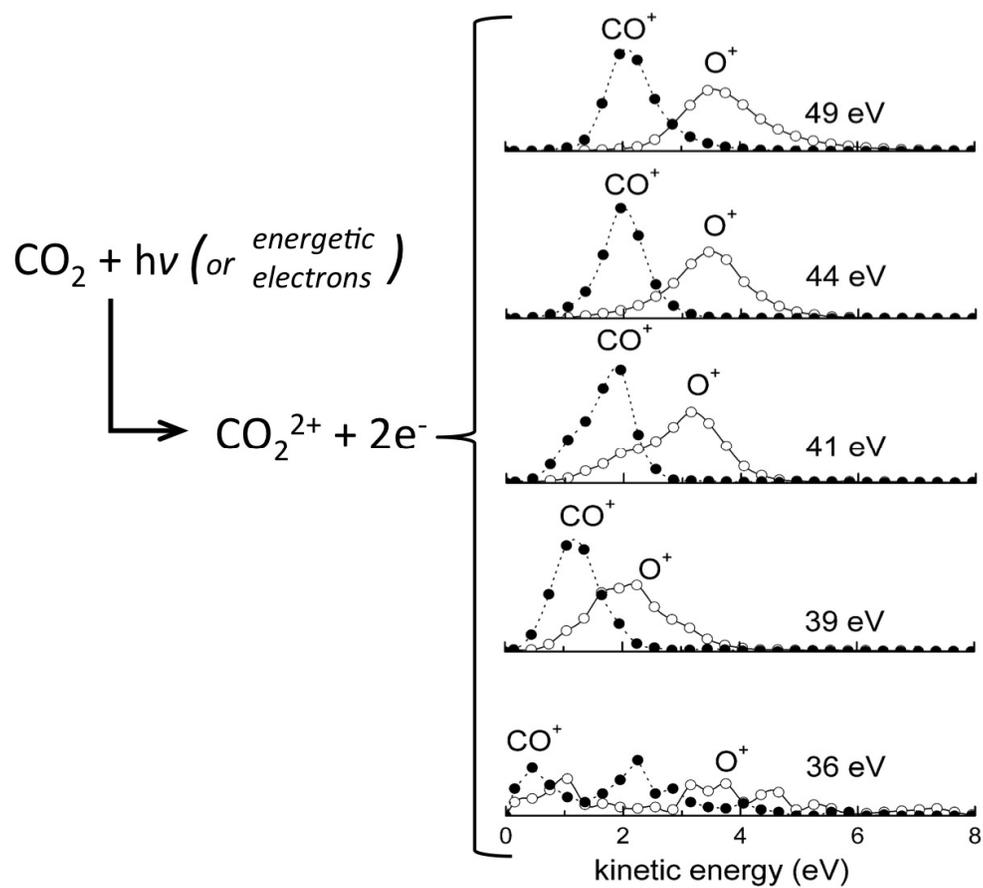
755 FIG. 8



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