



## Photostability of amino acids to Lyman $\alpha$ radiation: Glycine

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### ABSTRACT

The amino acids already detected in Solar System bodies and researched in Interstellar Medium are of particular importance for the chemistry related to the origin of life since they are constituents of all living organisms. Several amino acids have been identified in meteorites carbonaceous with significant concentration, while the existence of glycine in regions of star formation has been claimed. To interpret the viability of amino acids in pre-biotic astrochemistry is important to investigate the stability of these compounds in extraterrestrial surroundings. This study investigates, in the laboratory, the stability of glycine to the action of ultraviolet radiation, in spectral region around the wavelength of the Lyman  $\alpha$  line (1216 Å) produced by a hydrogen lamp. <sup>252</sup>Cf-PDMS of positive and negative desorbed ions was performed for glycine, before and during the irradiation, and the dependence of the ion desorption yields on the irradiation time is determined. As a result, the relative photostability curves of the molecular and dimer ions are observed to be a single exponential decay with a time constant 376 min for positive desorbed ions and 675 min for negative ones. The photodissociation cross section found for glycine molecule at room temperature, when positive secondary ions are considered, is 17 Mb; this value drops to 9 Mb when negative secondary ions are analyzed. This new methodology offers a complementary way of understanding the photonic interaction in amino acids, allowing discussion on polymerization and/or radiation induced phase transition effects.

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### 1. Introduction

Pre-biotic molecules arising from space, including aldehydes, ethers, nitriles, quinones, and amino acids, may have played an important role in the origin and evolution of life [1–3]. Among these compounds, the amino acids are involved in a crucial way because they are the basic components of proteins, fundamental constituents of all living organisms.

The vacuum ultraviolet (VUV) photostability of amino acids is of considerable interest in view of the possible delivery of these molecules, and even more complex molecular species, from space to the primitive Earth, and the role that they could have played in the origin and development of life on our planet [4–6]. Amino acids are found in both meteorites and micrometeorites [7,8] and much effort is currently being undertaken to observe them in the interstellar medium (ISM) [9].

Amino acids have been identified in several carbonaceous meteorites in concentrations of up to 3 parts per million versus carbon [10]. Whereas life on Earth is based on L-amino acids (left-handed), those measured in meteorites are 50% in D-form (right-handed) or racemic (mixed handedness). Small excesses of left-handed extraterrestrial amino acids, such as isovaline, have been reported in the Murchison and Murray meteorites [7]. The fact that meteoritic amino acids are deuterium-enriched [11–13] may imply an interstellar heritage [14]. Formation of amino acids in the interstellar medium (ISM) may be possible via specific gas-phase reactions in dark clouds [15]. At present, the detection of glycine (H<sub>2</sub>NCH<sub>2</sub>COOH; the simplest amino acid) in the interstellar gas remains controversial [9,16]; an upper limit of 10<sup>−10</sup> (per H<sub>2</sub>) has recently been estimated in the low-mass protostar IRAS 16293-2422 [17].

To assess the availability of amino acids for pre-biotic chemistry, it is important to investigate the stability of such compounds

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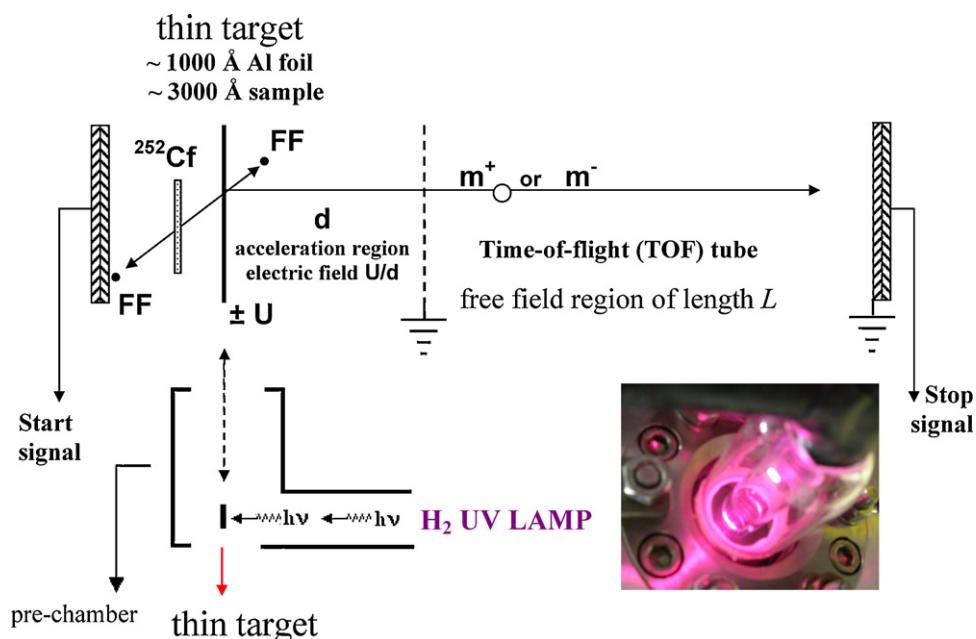


Fig. 1. Sketch of the PDMS spectrometer [21] with the  $\text{H}_2$  UV Lamp.

in extraterrestrial environments. Recent studies focused on the thermal properties of amino acids and their stability upon impact [18,19], other work studies the preservation of amino acids enantiomeric excess with the stability under gamma radiation in comets and meteorites [20]. Another work tested the photostability of four amino acids in Ar,  $\text{N}_2$ , and  $\text{H}_2\text{O}$  ices to explore whether they could withstand radiation in space in order to investigate how the size and structure of amino acids would influence their destruction by UV photons [14].

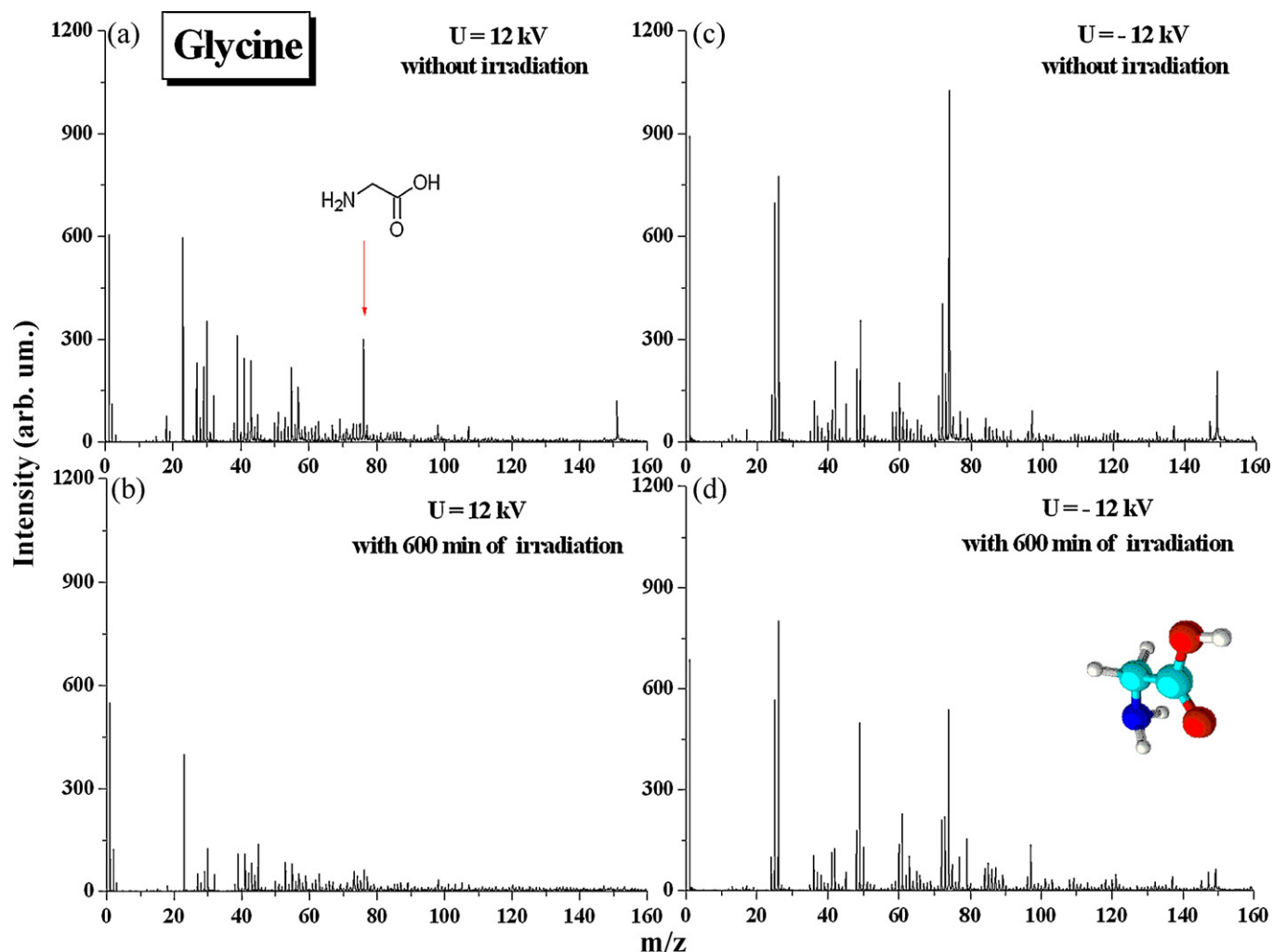
In this paper we report experimental results on photostability of glycine. This molecule is proteinaceous and has been found in meteoritic materials [21]. The sample was exposed to a spectral region around 1216 Å (10.2 eV) UV radiation and its degradation were followed by Plasma Desorption Mass Spectrometry ( $^{252}\text{Cf}$ -PDMS). This is a new methodology for studying photostability, in which the emission of positive and negative ions are analyzed instead of the optical absorption by neutrals, offering possibilities for further understanding of the polymerization induced photolysis of amino acids and/or phase transition induced by UV radiation, as well as the prompt ion emission of the formed chemical species.

## 2. Experimental methods and results

The  $^{252}\text{Cf}$ -PDMS experimental set-up was constructed at the Van de Graaff Laboratory, in the Physical Department of Pontifícia Universidade Católica do Rio de Janeiro – Brazil, and described elsewhere [22,23]. This technique has been largely employed to study several physical chemistry phenomena, some of them of astrophysical interest such as the electronic sputtering of astrophysical ices [24–28]. The experimental set-up, including the  $\text{H}_2$  UV lamp combined with the pre-chamber, is presented in Fig. 1. As the pre-chamber is connected to the main-chamber, the sample is directly transported to it by using a high vacuum manipulator. The  $\text{H}_2$ -UV lamp illuminates perpendicularly a  $\sim 1.5\text{ cm}^2$  sample of glycine in the pre-chamber, under a residual gas pressure of  $6.0 \times 10^{-5}$  Torr provided by a turbomolecular pump. As a precaution, a dry  $\text{N}_2$  gas was used as ballast to attenuate the effects due to chemisorption of pump oil on target. After irradiation, the sample is transported in

vacuum to the  $^{252}\text{Cf}$ -PDMS chamber without being exposed to air. There, the  $^{252}\text{Cf}$  fission fragments (FF) – having energies of about 65 MeV (after passing the protection foil of the Cf source) – traverse the sample and induce ion desorption at the exit surface. The analyzed surface region is a circle of about 6 mm diameter. The ejected secondary ions are accelerated over a 0.7 cm long region and launched towards the stop detector. For further details see Ref. [23].

The base pressure of the time-of-flight (TOF) spectrometer was about  $2.0 \times 10^{-6}$  Torr. The acquisition time was 4000 s for each spectrum. Acceleration potentials were  $U = \pm 12$  kV, for positive and negative desorbed ion analysis, respectively. The sample was commercially obtained from Sigma–Aldrich with purity better than 99.5%. No further purification was used. The targets were prepared by sample dissolution of amino acid in de-ionized water to form 16 mmol concentration; micro-droplets of the solution was deposited on thin Al foils and dried by natural evaporation (to avoid eventual thermal degradation by heating). The spot diameter of the illuminated site was kept greater than the target itself to secure the total irradiation of the target. The  $\text{H}_2$ -UV lamp was separated from the pre-chamber by a magnesium fluoride ( $\text{MgF}_2$ ) window, which is warranted to transmit at least 40% at 1216 Å [29,30]. The photon flux measurements related to the hydrogen lamp were performed using a standard photodiode from International Radiation Detectors (IRD) model AXUV100 with an active area of  $10 \times 10$  mm [31]. The total photon flux was evaluated using the quantum efficiency curve provided by the manufacture without further corrections. The photodiode was mounted in vacuum chamber and between the photodiode and the lamp there was only a window also present in the actual degradation measurements. The total photon flux, measured with the photodiode, is estimated in order of  $1 \times 10^{15}$  photons  $\text{cm}^{-2} \text{s}^{-1}$  in front of the  $\text{MgF}_2$  window; in the target the photon flux of the Lyman  $\alpha$  line reduced to  $4 \times 10^{12}$  photons  $\text{cm}^{-2} \text{s}^{-1}$  considering geometric corrections. Another correction, due to the real UV band exposition, was made: (a) calibrate the  $\text{H}_2$ -UV lamp spectrum obtained by Cottin et al. [32] with the obtained photodiode efficiency curve; (b) determine the area under the curve in this calibrated spectrum; (c) divide the minimum energy of the photon to dissociate glycine by the area obtained in (b) and multiply this result by the photon flux already



**Fig. 2.** Glycine  $^{252}\text{Cf}$ -PDMS spectra, obtained with  $\pm 12$  kV of acceleration potential for: (a) positive desorption ions before irradiation, (b) positive desorption ions after 600 min of UV irradiation, (c) negative desorption ions before irradiation, (d) negative desorption ions after 600 min of UV irradiation.

geometric corrected. After acquiring the positive and negative ion  $^{252}\text{Cf}$ -PDMS spectra of the sample before irradiation, the following procedure was employed for irradiation: in the pre-chamber, the target is irradiated for a given time interval; returned to mass spectrometer chamber without being exposed to air, a subsequent positive and negative ion  $^{252}\text{Cf}$ -PDMS analysis (in random order) was made; again in the pre-chamber, the irradiation proceeds, each time longer.

Mass spectra of glycine, as prepared and after 600 min of irradiation, are presented in Fig. 2. The positive and negative ion spectra are displayed at left (Fig. 2a and b) and right (Fig. 2c and d) sides, respectively.

The two positive ion spectra shown in Fig. 2a and b were selected to illustrate the effect of the UV irradiation on glycine. After 600 min of irradiation, the ion yields for desorbed ions heavier than 80 u have decreased substantially. Among the secondary ions, the protonated fragment  $[\text{M}+\text{H}]^+$  (mass 76 u) and the dimer-protonated fragment  $[\text{2M}+\text{H}]^+$  (mass 151 u) were selected because they are characteristic of the glycine sample and, therefore, their peak area changes indeed quantify the effect of the degradation by the  $\text{H}_2$ -UV irradiation. The peak corresponding to mass 23 u is attributed to sodium ( $\text{Na}^+$ ) contamination, probably originated from the glassware. Fig. 3a display the desorption yield dependence of the  $[\text{M}+\text{H}]^+$  and  $[\text{2M}+\text{H}]^+$  secondary ions as a function of the irradiated time. The main observation is that both yields are proportional to each other and have approximately an exponential decrease on time.

Negative ion spectra are shown in Fig. 2c and d, before and after 600 min of irradiation. Two specific ions of glycine are analyzed in particular, the de-protonated molecular one  $[\text{M}-\text{H}]^-$  (mass 74 u) and the de-protonated dimer one  $[\text{2M}-\text{H}]^-$  (mass 149 u). Fig. 3b display the desorption yield dependence of these two ion species. Again, it is observed that both yields decrease exponentially at the same rate. Inspecting the four spectra in Fig. 2, it is worthwhile to observe that the overall desorption yield of positive ions (including that of the  $\text{Na}^+$ ) is more sensitive to UV radiation than the negative ones.

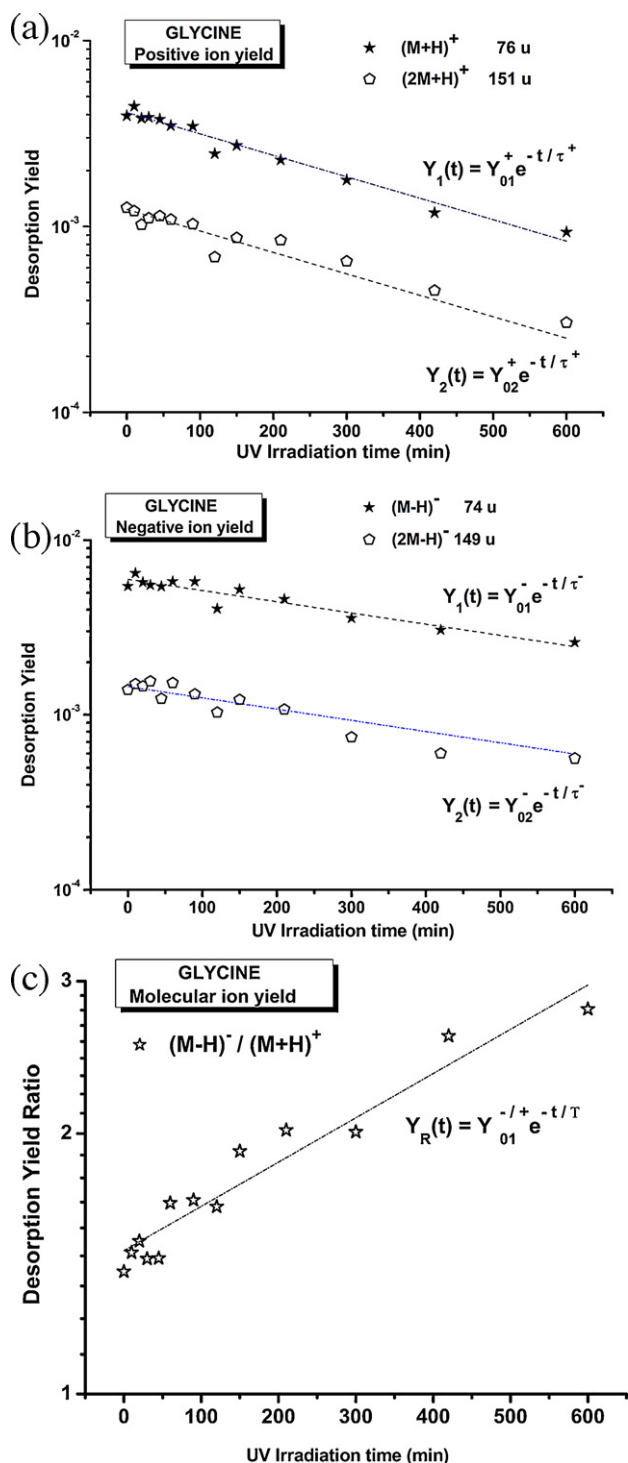
The dashed line, in Fig. 3, is the function  $Y_i = Y_{0i}e^{(-t/\tau)}$  and the obtained parameters from the fitting are:  $\tau^+ = 376$  min,  $\tau^- = 675$  min,  $Y_{01}^+/Y_{02}^+ = 3.34$  and  $Y_{01}^-/Y_{02}^- = 4.81$ .

Brief, the main results are: (i) the degradation of the glycine can be observed via secondary ion emission and occurs exponentially with irradiation time; (ii) the degradation rate seems not to be the same when analyzed by positive or negative secondary ions.

### 3. Discussion

#### 3.1. The methodology based on the electronic sputtering

Whenever a very fast and highly charged ion impinges an insulator, it mainly interacts with the target electrons and triggers several phenomena; in particular, chemical reactions are induced and target material is ejected through a process called electronic



**Fig. 3.** Relative glycine yields depends on irradiation time for: (a) positive desorption ions for 1 –  $[M+H]^+$  and 2 –  $[2M+H]^+$ , (b) negative desorption ions 1 –  $[M-H]^-$  and 2 –  $[2M-H]^-$ , (c) ratio of the molecular negative and positive desorption ion. The dashed line is the function  $Y_i = Y_{0i} e^{-t/\tau}$ ; the obtained parameters from the fitting are:  $\tau^+ = 376$  min,  $\tau^- = 675$  min and  $T = -849$  min,  $Y_{01}^+ / Y_{02}^+ = 3.34$ ,  $Y_{01}^- / Y_{02}^- = 4.81$  and  $Y_{01}^{-/+} = Y_{01}^- / Y_{01}^+ = 1.47$ . Statistical errors are 5–13% for the molecular positive ion and 10–29% for the dimer one; for the negative ions, errors are smaller.

sputtering [33]. Swelling or craters may occur and their sizes (characterized by  $L$ ) lay over the nanometer scale. Since the wavelength of the Lyman  $\alpha$  line is 121.6 nm, the thickness of the layer under photolysis is at least one or two orders of magnitude larger than  $L$ . A typical impact rate in the PDMS technique is  $10^3$  FF  $\text{cm}^{-2} \text{s}^{-1}$  and,

after 25 runs of 4000 s acquisition time,  $10^8$  impacts  $\text{cm}^{-2}$  occurred on sample. Assuming nuclear tracks of 5 nm diameter [34], a surface region with total area smaller than  $10^{10}$   $\text{nm}^2$  has been modified by the FF beam. This area is to be compared to  $3 \times 10^{13}$   $\text{nm}^2$ , which is target area under FF bombardment. The conclusion is that, very likely, each FF explores a virgin site modified homogeneously by the UV radiation. The assumption that the ion desorption yield is proportional to the molecular concentration (areal density) is therefore quite reasonable.

### 3.2. Results obtained with positive ions

Fitting the evolution of the  $[M+H]^+$  and  $[2M+H]^+$  ion yields, presented in Fig. 3a, by the  $Y = Y_0 e^{-t/\tau}$  function, one obtains  $\tau^+ = 376$  min (i.e.,  $\tau_{1/2} = \tau \ln 2 = 1.6 \times 10^4$  s) for both species. This result, associated with the photon flux of  $\phi \sim 4 \times 10^{12}$  photons  $\text{cm}^{-2} \text{s}^{-1}$  on the sample surface, yields to the conclusion that  $\sim 6 \times 10^{16}$  photons  $\text{cm}^{-2}$  are necessary to dissociate 50% of the surface molecules. Assuming the specific mass of  $\rho \sim 1 \text{ g cm}^{-3}$ ,  $4.01 \times 10^{14}$   $\text{cm}^{-2}$  glycine molecules are present on surface, that is,  $\sim 150$  photons traverse each surface molecule for having 50% of chance to dissociate the molecules lying at the region analyzed by the FF (region of  $\sim 5$  nm). Since, in average, each glycine molecule has transversal area of  $2.5 \times 10^{-15}$   $\text{cm}^2$ , the dissociation cross section is found to be 17 Mb. This value overestimates that 12 Mb previously measured by Peeters et al. [35] and that average 0.24 Mb previously measured by Kate et al. [36]. The difference, with the result presented by the first reference [35], could be attributed to the fact that our measurement was realized in room temperature while the other was measured at 12 K. According to the authors Zhu and Kellis, Lanza et al., Ferradaz et al. [37–39], for some molecules there is indeed a dependence on temperature of the dissociation cross section. The increase in absorption cross section as the temperature increases is expected to be due to the contribution at higher vibrational level at room temperature. However, this temperature dependence can be different from molecule to molecule for the same wavelength, requiring further investigation on this subject. In the case of the value presented by Kate et al. [36], the difference could be attributed to the fact that the photon flux in the current experiment, is two orders of magnitude smaller because it was calibrated to represent only the photon flux of Lyman  $\alpha$  radiation.

### 3.3. Results obtained with negative ions

The same reasoning employed to the positive ions can be applied to the analysis of the  $[M-H]^-$  and  $[2M-H]^-$  secondary ions, presented in Fig. 3b. The yield of these species decrease exponentially with the time constant  $\tau^- = 675$  min, almost twice as much as the value obtained for the positive ions, giving an estimated dissociation cross section of about 9 Mb. This result, in contrast with that obtained for positive ions, underestimates the value reported by Peeters et al. [35]. The sample surface degradation seems therefore to affect differently the yield emission of positive and negative ions.

### 3.4. Processes able to change the ion emission yield

Since the positive and negative ion measurements have been performed alternatively during irradiation, the target photodegradation is expected to be even for both cases. Moreover, it should be stressed that the acquisition time was quite long ( $>1$  h) and effects due to surface charging by UV radiation are not likely. Fig. 3c shows the variation of the molecular yield ratio as a function of the irradiation time. It is observed that ratio increases exponentially as a function of the UV irradiation time.

The 1.8 ratio observed in the  $\tau$  measurement of negative and positive desorbed ions is unexpected and leads to conflicting results. The  $\tau$  values were obtained on the basis that: (a) the desorption yield of a given ionic species is proportional to its precursor concentration on the sample surface; (b) the attenuation length,  $\lambda$ , of the UV radiation inside the sample is much larger than the characteristic depth,  $L$ , of the electronic sputtering. These conditions must be discussed.

The measurement of different  $\tau$  values for positive and negative secondary ions must have other origin. Two possibilities should be added: (i) chemical reactions induced by secondary electrons originated from the nuclear track and (ii) surface chemical reactions caused by the UV radiation. The researched process should also have an exponential dependence on irradiation time, characterized by a time constant  $\tau_{S(q)}$  due to surface effects ( $S$ ) which depends on the sign of the desorbed ion charge  $q$ :

$$Y = Y_0 e^{-(t/\tau)} e^{-(t/\tau_{S(q)})} = Y_0 e^{-t((1/\tau)+(1/\tau_{S(q)}))}$$

The hypothesis related to the secondary electrons is ruled out because their effects must be proportional to the acquisition time and not to the irradiation time. If the UV radiation is assumed to be the responsible, the next question is why there is the observed charge  $q$  dependence. The most likely explanation is that UV-induced chemical modification in the surface alter differently the ionization probabilities for cation or anion production/emission.

#### 4. Summary

In this work we analyzed the photostability of the simplest of amino acids, glycine exposed to 1216 Å (10.2 eV) UV radiation and its degradation were followed by Plasma Desorption Mass Spectrometry ( $^{252}\text{Cf}$ -PDMS). This is a new methodology for studying photostability, reason why positive and negative secondary ions were analyzed for testing coherence of results. Our analysis reveals that: (a) the interaction of FF  $^{252}\text{Cf}$  with glycine molecule produces a negative ion desorption yield slightly more intense than the positive one; (b) the relative photostability curve of glycine desorbed molecular ion presents a single exponential decay; (c) the time constants decay are 376 or 675 min for the positive and negative desorbed ions respectively; (d) for glycine, the molecular ion and the dimer have all similar behavior. Therefore, the sample surface degradation affects differently the emission of positive and negative ions, that is, desorption yield of positive ions is about twice (in this case) more sensitive to UV radiation than the negative one. This observation is attributed to polymerization and/or radiation induced phase transition effects on the irradiated sample surface; the photodissociation cross section is 17 Mb for glycine molecule at room temperature when positive secondary ions are considered; this number drops to 9 Mb when negative secondary ions are analyzed. The final conclusion is that the new methodology is able to furnish acceptable values for dissociation cross sections but improvement is necessary to evaluate the polymerization and/or radiation induced phase transition effects on surface.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2011.06.022.

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