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The rule of synchrotron radiation in the prebiotic evolution

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Abstract: Synchrotron radiation-based spectroscopic techniques are discussed. Their relevance to obtain information regarding the prebiotic evolution problem is pointed out. We present photoelectron–photoion coincidence (PEPICO) spectra of adenine and glycine obtained using 12 and 21 eV photons. The fragmentation pattern belonging to these molecules was found to present striking differences, which are discussed. Adenine partial ion yield in the energy region 12–21 eV is also presented. The neutral fragments were found to have very simple assignment. The importance of hydrogen cyanide (HCN) as a building block of these molecules is confirmed. A special instrumentation allowing precise comparisons between photon-induced desorption and energetic ion bombardment desorption is described. As an example, we show, for the first time, the frozen CO_2 ice mass spectra bombarded by photons and energetic ions, under the same experimental conditions. The comparison shows that prebiotic evolution may only be properly understood if more than one particle, as energy source, is considered.

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Introduction

Photo-ion spectroscopy (PIS) and photoelectron spectroscopy (PES) are related by the photoelectric effect described by Albert Einstein in the beginning of the last century. These techniques find many applications, among them, there is one, perhaps most people do not think about: simulation of realistic prebiotic scenarios in a laboratory. Why those testing are of interest in the first place? Most readers will agree that molecular origin of life is one of the most intriguing and interesting problems to be researched. Despite this easy-to-agree interest, one may never find out exactly how life emerged on Earth. The best we can hope for is to propose feasible pathways for its emergence. One of the key premises, behind this field of research, is that life, even in its simplest form, is too complex and it is not reasonable to assume that it could be formed simply by a random mixture of atoms and molecules. Some prebiotic evolution, at a molecular level, is bound to have taken place prior to life emergence. Further to this, prebiotic evolution is considered necessary for the creation of the basic constituents of living organisms such as amino acids, DNA basis and bio-molecules that are more complex. As many of these essential bio-molecules reach a certain degree of complexity, they can exist in two mirror image forms. Often, we call them left and right symmetry. For example: all 20 amino acids can be classified into one of these two forms except glycine, which is too simple. Chirality is the name of this property of molecules that have a non-superposable mirror image. Life on Earth is made of left-handed amino acids. This is a fact called homochirality. Before going into detail and hypothesis on how this conspicuous characteristic of life originated, let us focus on how bio-molecules could be created in the first place. Indeed, simple biomolecular building block can be rather easily be produced abiotically by adding a source of energy and simple molecules such as CO, H_2O and NH_3. These are the so-called Miller-type experiments after the pioneering work of Miller (Miller 1953). In his experiment, biomolecular building blocks were created abiotically using electric discharges in a gas mixture simulating the primeval atmosphere of Earth. In fact, in the first half of the 20th century Urey, from United States, knew that the giant planets, Jupiter and Saturn, atmosphere was dominated by H_2, CH_4 and NH_3. He argued that these gases were captured from Solar nebula and were maintained in these planets, which were too large to loose hydrogen to space. He also speculated that Earth, including other smaller planets, had this atmosphere in the beginning before they had time to evolve (Urey 1952). Miller used an electric discharge (simulating lightning) and an atmosphere made of H_2O, CH_4, NH_3 and H_2, producing amino acids and other more complex organic compounds. Among these organic compounds, the absolute majority had relevance for the molecular origin of life. This is of importance since a random combination of these compounds could generate other organic molecules not important for the origin of life on Earth. In 1969, a carbonaceous meteorite fell in Murchison, Australia. The meteorite turned out to have high concentrations of the same kind of amino acids you get in prebiotic experiments like Miller's. This discovery made it plausible that similar processes of those in Miller's experiment could have happened on primitive Earth or on an asteroid. The agreement supported greatly the assumptions of Miller and Urey for decades. Experiments were also performed using ultraviolet light in this type of atmosphere (Sagan & Khare 1971). Ultraviolet light as well as electron and energetic ion beams have advantage compare to the discharge, as replacement to the energy source, because they can be found in space abundantly. The advantage of considering prebiotic evolution in space comes from obvious reasons such as: in space we have access to longer prebiotic evolution time (the universe have >10 G year compare to 4.4 G years of the Solar System). On top of that, the composition of the prebiotic atmosphere, assumed by Miller, did not explain the presence of volcanic gases on prebiotic earth. An alternative composition was proposed by Rubey (Rubey 1955). This theory was further developed by Holland (Holland 1962). Accordingly, during recent year, geochemical opinion is that the prebiotic atmosphere was weakly reducing and not strongly reducing as in Miller–Urey-type experiments. The more realistic mixture would be CO_2, N_2 and water combined with smaller amounts of CO and H_2 (Walker *et al.* 1983; Holland 1984; Kasting *et al.* 1993). Choosing ultraviolet light as the energy source together with the more realistic mixture of prebiotic atmosphere leads to the situation where bioorganic compounds are difficult to be synthesized (Schlesinger & Miller 1983). Therefore, according to this discussion, ultraviolet light as an option for the energy source does imply that the prebiotic molecules would be formed preferably in space where the conditions regarding gas mixture are much less strict and the exposure time is not restricted to Earth lifetime. In space, energy sources such as energetic ions and electrons do present an overall higher cross-section with the prebiotic molecules. This fact alone would make these sources more relevant to the prebiotic chemistry. However, Miller-type experiments, using as energy sources: ions, electron or discharge, present a serious problem: the amino acids and other more complex biomolecules are always produced as a racemic mixture in those experiments. This is in complete disagreement with the conditions required for the emergence of life: namely, the homochirality of its building blocks. In Miller-type experiments, molecular excitation and dissociation are two key processes: the simple molecules are converted into ions and free radicals, via photoelectric effect for example. Subsequently, they form molecules that are more complex. In this process, however, left- and right-handed molecules are produced in equal amounts. The specific homochirality of terrestrial biomolecules may be accidental, but possible mechanisms for its origin are a vital and growing cross-disciplinary research field (Cline 1997; Brack 1998). Several possible mechanisms have been proposed, e.g. charge-parity (CP) violation in nuclear decay and catalysis on asymmetric mineral surfaces. Most proposed mechanisms have severe problems; CP violation is estimated to be much too weak and mineral surfaces of the two symmetries exist in equal amounts (Brack 1998). Photons, however, like those bio-molecules we discussed, do also present chiral (helicity) properties. If their spin and momentum are parallel (anti-parallel), the particle is said to be right-handed (left-handed). This is also known as photons being right- (left-) handed circularly polarized. But do we have circularly polarized radiation in space where possible prebiotic evolution took place? Cosmic circularly polarized radiation has been observed, and various mechanisms for its production are astronomically possible (Cline 1997; Bailey *et al.* 1998; Bailey 2001). The proposed mechanisms all result in equal total amounts of left- and right-handed circularly polarized radiation due to symmetry, but the two handedness are emitted in different directions. Symmetry may thus be broken locally, where locally, however, could mean star-formation regions on the cubic light years scale. Recent results using synchrotron light shows that circularly polarized light is more absorbed by one enantiometer (Meierhenrich & Thiemann 2004). This experiment is relevant since the wavelength with shown absorption asymmetry has exactly the Hydrogen Lyman Alpha energy. It does also suggest another interesting pathway to produce an excess of a particular enantiometer which can be amplified by other methods. Radiation in a Miller-type experiment was shown to produce more complex molecules, but this same radiation is also very effective to destroy enantiometer belonging to a particular symmetry. In this context, many energy sources can act on simple prebiotic molecules producing more complex building block such as amino acids but circularly polarized ultraviolet are candidates to produce the much needed asymmetric photolysis. These sets the grounds for the research lines our group has pursued along the last few years. It has been our aim to critically test many steps comprising this vast puzzle. Our first goal was to abiotically produce bio-molecules important to the origin of life. Perhaps the most important result obtained in this line of research consisted in the simulation of Titan atmosphere. The Miller–Urey-type experiment used Synchrotron-produced X-ray as energy source. The resulting tholin, after 73 hours of irradiation has shown the presence of DNA basis, Adenine among other compounds (Pilling *et al.* 2009). Despite the success, namely: this experiments shows for the first time the presence of life building blocks in an astronomical object different from Earth, some questions still remain unanswered. For example: can we track down the intermediate steps, starting from simple molecules to the final products? How important are each intermediate step to the final product? In order to enter into the physics and chemistry belonging to these intermediate steps, we have developed, during a number of years, appropriate instrumentation and devised methods to tackle these interesting questions. Synchrotron radiation was our main choice of excitation source not only because it does produce chiral photons at easy but also because it is tunable from the ultraviolet to the X-ray region. Furthermore, if needed, it can also deliver wide frequency band. This feature is important to allow mimicking Solar or other stars radiation in space or in Earth. In our case, we produced this last broadband, in the ultraviolet region, using a special gas filter called MIRHACLLE developed in our SR facility (Cavasso Filho *et al.* 2007a). A source also requires experimental stations for the successful experiments. We develop several.

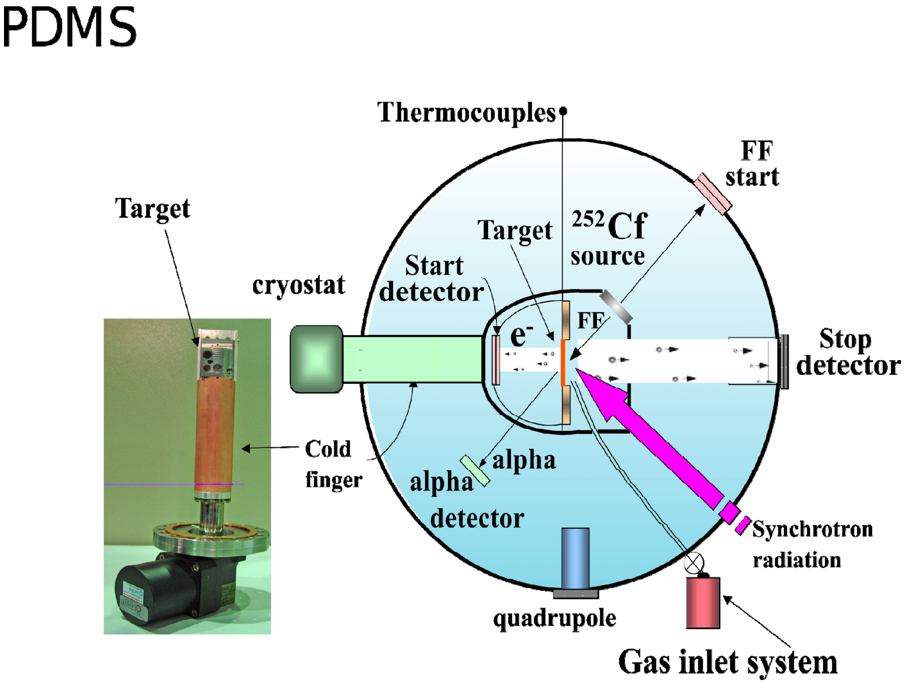

Fig. 1. Experimental chamber for plasma desorption mass spectroscopy (PDMS). It is composed by ^{252}Cf radioactive source and allows the use of SR source as well. The target can be cooled by a cryostat. In the target, space ice analogous may be formed by introducing gases via an inlet gas system. Four detectors are available, three micro-channel plate detectors: one to detect electrons giving the start signal, another gives an alternative start signal and the last one is used to detect ions providing the stop signal. There is an alpha particle detector for sample thickness evaluation.

Here, however, we will briefly discuss two of them: a multicoincidence time of flight spectrometer, which we used to follow photo-fragmentation of amino acids and DNA basis in the gas phase (Burmeister *et al.* 2010). As an example, we will describe two experiments with interesting consequences to the present subject. A second experimental chamber was designed specifically to monitor *in situ* photo catalyses and photolysis. This experimental chamber has, in special, the ability to perform, under the same conditions, mass spectra of space ice analogues bombarded by energetic ions or synchrotron radiation (Farenzena *et al.* 2005, 2006; Martinez *et al.* 2006; 2007a, b; Ponciano *et al.* 2006, 2008; Homem *et al.* 2007). In these experiments we also used another important property of SR: its timing. SR laboratories around the world can operate in a special mode called single bunch. In it, researchers have access to pico-second pulses, which are perfect for time of flight mass spectroscopy. We will show one experiment using this capability. In it, we compare, for the first time, under the same conditions, photolysis resulting from energetic ions and Vacuum Ultra-Violet photons (VUV).

Experimental details

One of the main problems we, as physicist, faced, performing Miller–Urey-type experiment, is the outcome dependence of enormous amount of parameters. The scientist knows the initial conditions and other parameters such as temperature, photon flux and length of time for some macro stages. He also knows the resulting compounds created via gas phase chromatography analysis. In this classical approach, cause and effect might turn out to be difficult to properly screen systematically. Another question we asked was: how was the chemical development of the system during the Miller-type experiment? Our solution to these questions materialized in the development of the first synchrotron-based plasma desorption mass spectroscopy (PDMS) instrument, see Fig. 1. This instrument is not well described in the previous literature data and we will devote some attention to pinpoint its most relevant aspects to our present discussion. In this set-up, we employ a radioactive source producing ^{252}Cf fission fragments. Their energy is about 65 MeV (after passing the protection foil of the Cf source). The radioactive source produces fission fragments in two opposite directions. A target receives one of the fragments and a cryostat is used to keep its temperature as low as 20 K (monitored by a thermocouple). Thus, we can simulate, in the SR laboratory, space ice analogues. The fragments aiming towards the target penetrated the ice layer at its front side, from where target ions were backward ejected with respect to the incident projectiles and accelerated towards the stop detector.

If the target is thin enough, the fission fragments trespasses it as well as a thin supporting metal foil. The crossing produces electrons at the back of the foil, which are accelerated towards a micro-channel plate detector placed behind the target. The generated signal is used as 'start' in the time counting process to determine the flight time of ions ejected from the target surface. The radioactive source also produces alpha particles. The energy loss from alpha particles is a statistical process, often resulting in a wide energy loss distribution; however, if the fluctuations of the acquired data are relatively small, then the average energy loss is precise and target thickness can be determined. This allows target thickness determination *in situ*. The second fission fragment (FF), emitted in the opposite direction, is also detected by another micro-channel plate 'start FF'. The originated pulse gives a second 'start' signal that can be used when the target is too thick. It can also be used in coincidence with the electron 'start' allowing possible spurious electron signal to be eliminated. An opening is placed so that the sample can be irradiated with synchrotron radiation or any other photon source. Using a special operation SR can deliver pulses of 60 picoseconds width and 311 nanoseconds period. In this case, mass spectrum of photo-induced desorption can be obtained.

The other two relevant instrumentations, which we will provide results from, are the Toroidal grating monochromator, briefly discussed in the introduction and thoroughly discussed in Cavasso Filho *et al.* (2007a). All the gas phase experiments were performed in the electron ion coincidence spectrometer described in detail in Burmeister *et al.* (2010).

Discussion

The problems we will treat in this section will follow the criteria base on its increasing complexity. In this way, we will discuss initially gas phase molecules which are building blocks of leaving organisms, i.e. amino acids and DNA basis. Isolated molecules are excellent candidates to investigate intrinsic properties and behaviours. This knowledge can be used to help elucidate the extrinsic behaviour present in ice analogues, solid-state matter or bio-molecules in solution. Another advantage of pursuing this research line is the access of experimental data which is in better condition to be compared with theoretical calculations.

In Fig. 2, we present a result compiled from Pilling *et al.* (2007). In it, the ion yield of adenine from 12 to 21 eV is presented. This spectrum was taken at the Toroidal Grating Monochromator (TGM) beamline using the multi-coincidence spectrometer (Cavasso Filho *et al.* 2007b; Burmeister *et al.* 2010). The figure shows the expected ion yield behaviour. In this figure, the energy corresponding to the maximum of each curve shows that the ions having maximum yield at lower (higher) energy have larger (lower) mass. We can also observe an interesting pattern in the missing neutral fragment. They are formed simply by NxHCN ($N = 1, 2, 3, 4$). Excluding a hydrogen, in one case, which, being the most abundant atom in the universe, this fact bears no practical importance. HCN is known to be very poisonous to living organisms today, but, it is also known for being important in the prebiotic chemistry (Zahnle 1986). Here, we see the manifestation of this importance since only HCN is needed as a building block to this important molecule for the prebiotic chemistry. The relevance of HCN also emphasizes, in turn, the validity to perform Miller-type experiments using synchrotron radiation as energy source. Most of the Miller-type experiments, using ultraviolet as energy source, were restricted to fix wavelength, for example, Groth *et al.* used 8.4 and 9.6 eV photons (Groth & Weyssenhoff 1960). They were plagued by their lack of effectiveness in synthesizing organic compounds. There were also reports of experiments using even lower wavelength, 6.7 eV. This restriction in the wavelength prevented the production of amino acids containing nitrogen (Bar-Nun & Chang 1983). Further to this HCN was found to require synchrotron radiation with an energy of 15.58 eV for its production in photochemical processes (Zahnle 1986). Indeed Fig. 2 shows how critical is it to be able to produce HCN in the prebiotic chemistry.

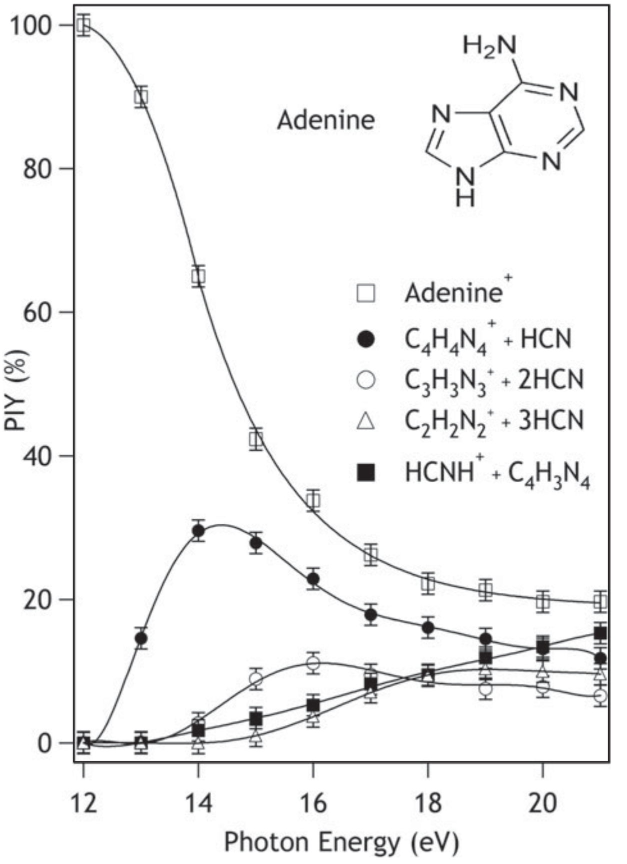

Fig. 2. The partial ion yield of adenine molecule obtained from PEPICO (photo electron- photo ion coincidence) spectra in the energy region 12–21 eV. The points in the spectra are measured with 1 eV energy step. The molecular ion is the most abundant in the complete energy range. The others ion fragments, and neutral fragments are made of multiples of HCN, see text for details.

Both DNA basis and amino acids are building blocks of living organisms. One interesting question we may ask about these two classes of biomolecules is their behaviour with regard to photo-degradations. During the last few years, we performed a number of photo-fragmentation studies in these two classes of important molecules (Lago *et al.* 2004; Coutinho *et al.* 2005; Marinho *et al.* 2006; Pilling *et al.* 2007, 2011). As we described previously, photo-degradations studies may hold the explanation for the homochirality observed in amino acids. In Fig. 3, we show the mass spectra taken at the TGM beamline at two energies 21 and 12 eV (Lago *et al.* 2004). The lower energy is very close to the He-I emission line, while the higher

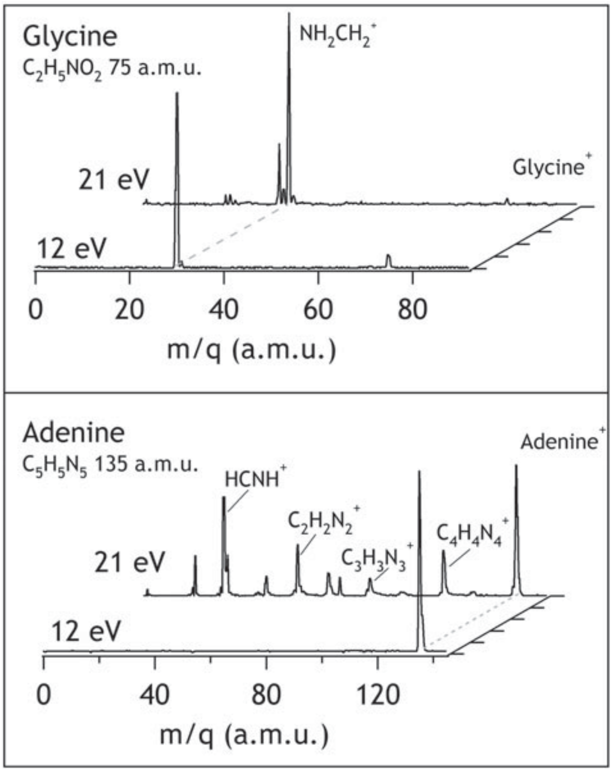

Fig. 3. PEPICO spectra of adenine (bottom panel) and glycine (top panel) molecules. Each molecular spectrum was obtained at 12 and 21 eV photon energy. The spectra were normalized by the area under the curve. It is interesting to observe that for adenine, in 12 or 21 eV, the most abundant ion is the intact molecule. In contrast, in the glycine spectra the ion $NH_2CH_2^+$ dominates the spectra in both energies, this fragment releases the neutral COOH radical.

is some how close to Hydrogen Lyman alpha emission-line. Both are the most abundant elements in the Universe making these photon energies relevant to the prebiotic photochemistry. Adenine shows a very distinct mass spectrum at 12 eV compared to glycine. Adenine shows no sign of photo-fragmentation at this energy, while amino acids, such as glycine, loose the COOH group already at 12 eV. At 21 eV, further fragmentation takes place for glycine. The DNA basis, at this energy, shows sign of fragmentation. However, even at this energy, substantial amounts of intact ionized adenine remains. The stability of adenine comes in part from its ring-type molecular structure. It bears nitrogen atoms which are more electronegative than carbon. These two atoms, in the molecule, are well distributed. Thus, configuration is unfavourable to the creation of an electric repulsion between neighbour atoms leading to a possible bond break. Glycine is constituted by two electronegative ends, one having O and OH and the other NH_2. Consequently, the electron deprived central carbons become positive. Upon ionization, another negative charge is removed leaving the two carbons even more positive. In this situation, the two carbon atoms face Coulomb repulsion. If the Coulomb repulsion is strong enough, the chemical bond between the carbons will break explaining qualitatively the experimental observations. It is known that the DNA basis holds the genetic code information. It seems that nature kept, in this key position, molecules that are comparatively much more resistant to radiation damage.

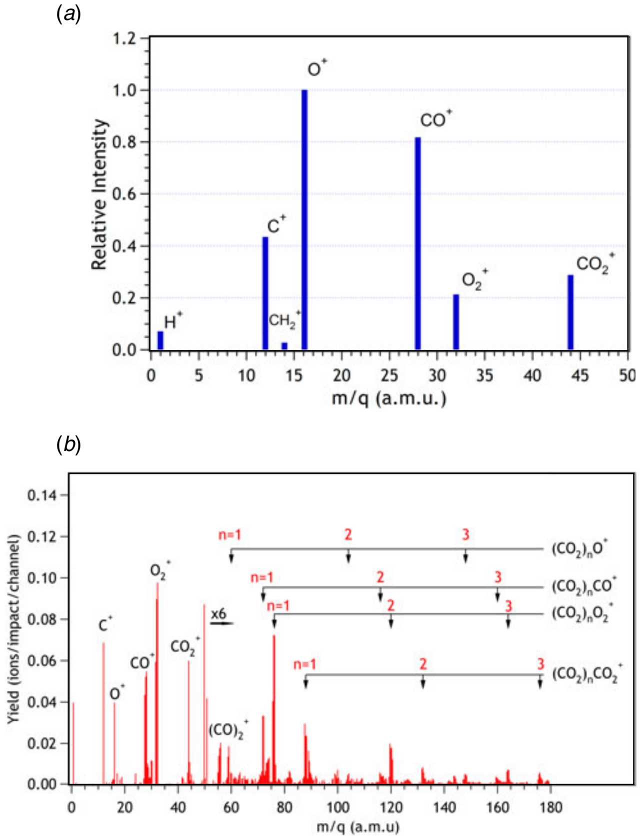

Fig. 4. (a) Time of flight mass spectrum showing the secondary ions emission from condensed CO_2 bombarded by 40 eV photons from SR in the single bunch mode. (b) Time of flight mass spectrum showing the secondary ions emission from condensed CO_2 heavily bombarded by MeV fission fragments. The spectrum intensities for mass above 50 a. m.u. are multiplied by 6 to show the molecular cluster formation.

Another question we investigated with our PDMS special experimental station was the prebiotic chemistry resulting from two different energy sources namely: energetic ion bombardment and 40 eV photons. We remind the reader that He II line has around 40 eV energy. As we discussed in the introduction, Miller-type experiments employing fix energy ultraviolet sources show pure bio-molecules productions. Here, we put forward the concept that more than one source of energy may need to be considered for a proper simulation of the abiotic production of amino acids other biomolecules. Indeed, abiotic biomolecular chemistry is made of many steps. It is possible that for a particular step a certain energy source is required while other steps require another source. In order to test this hypothesis, we compared the results of ions production originating from two different energy sources. This testing requires equal conditions for the sample, thus avoiding false results.

Our developed PDMS station is suitable for this test since both ion-impact and photon-impact ionic desorption can be performed using the same sample. One of the key points for this to be possible is related to the nature of the radioactive source. This source impinges MeV fragments in the sample at a relatively small rate (about 1 kHz). Simple calculations show that in practice an ion never hits the same spot in the sample. The surface remains practically unaltered by the PDMS probing. Therefore, it is possible to make a mass spectrum with only the radioactive source on and followed this measurement by another using SR pulsed source. The new measurements using the SR source will not be affected by the previous measurements. Let us now discuss, briefly, the synchrotron-based measurements. In order to measure the ejected ions time-of-flight, there is a need for a start signal marking the instant of the ion creation. Usually, the synchrotron delivers radiation pulses with duration of less than 100 picoseconds at a period of about 2 nanoseconds. This period is far too small and a special SR ring-filling pattern is required. Achieving longer periods requires a special filling pattern where only one electron bunch is kept in the ring. In the Brazilian synchrotron, this single bunch mode results in a period of 311 nanoseconds between pulses. Therefore, during single bunch operation mode we were able to use the pulsed radiation as start signal and measure the time-of-flight of the desorbed ions. The resulting spectrum is shown in Fig. 4(a) (Homem, M.G.P. *et al.* to be published 2012). In it, we use frozen CO_2 as test molecules. As a comparison, the same sample spectrum bombarded with energetic ions is shown in Fig. 4(b). A detailed description of the spectrum, shown in Fig. 4(b), can be found in Ponciano *et al.* (2006). Here, we will only keep our attention in the ions with smaller mass compared to CO_2. The photon spectrum in Fig. 4(a) has its highest ion production given by O^+ and the smallest O_2^+. In this spectrum, we see a small amount of contamination coming from H^+ and CH^+. In the energetic ion-impact spectrum, the opposite yield is observed; O^+ is the smallest peak and O_2^+ the largest. Small contaminations such as H^+, etc., are also present. As a conclusion, from the clear observed contrast, we may argue that, depending on the ion fragment needed in a specific step in the abiotic production, one source of energy may be needed to provide that species while, in another step, another energy source may be required to provide the needed ionic species. Therefore, only after studying carefully the intermediate reactions, we will be able to evaluate the importance of each energy source.

Concluding remarks

The PEPICO spectra of Adenine and Glycine obtained using 12 and 21 eV photons were presented. Adenine was found to be considerably more stable towards photo-fragmentation in the VUV range, compared to glycine. This may point out to a more general behaviour where amino acids, in general, seems to be more damaged by VUV radiation than DNA basis. Adenine partial ion yield was studied in the energy region 12–21 eV. The neutral fragments related to all ionic fragments detected could be described as X(HCN) for $X=1$, 2, 3 or 3(HCN)CN. The ionic fragments are also very simply related to HCN. This reveals the importance of HCN as building block to the DNA basis. The experimental set-up called PDMS is described. Emphasis is given to its first implementation in a synchrotron environment. Specifically, the PDMS chamber allows precise comparisons between photon-induced and energetic ion-induced desorption. The mass spectra of photon- and ion-induced desorption of frozen CO_2 are compared. The most (less) intense ionic fragment in the photon-induced mass spectrum is O^+ (O_2^+). The opposite was observed in the energetic ion bombardment spectrum. In this case, only ions with mass smaller than the parent ion CO_2 were considered. This supports the general idea that prebiotic evolution may only be properly understood if several excitation sources are taken into account. We hope to have shown the importance of synchrotron radiation source to the molecular origin of life.

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