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Effect of Laser Radiation on Biomolecules

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ABSTRACT

Time of flight laser photoionization has been used to study the response of some molecules of biological interest under laser radiation. One of the questions of great interest today is the effect of radiation on DNA and RNA molecules. Damage to these molecules can be caused directly by radiation or indirectly by secondary electrons created by radiation. As response of the radiation field fragmentation process can occur producing different ions with kinetic energies of a few electron volts. In this paper we present the results of the interaction of 355nm laser with the nitrogen bases adenine(A) and uracil(U) using time-of-flight spectrometry and the comparison of experimental results on the effects of laser radiation in (A) and (U) belonging to two different ring groups, purines and pyrimidines respectively, which are linked to form the AU pair of the RNA.

1. Introduction

One of the questions of great interest today is the effect of radiation on DNA and RNA molecules. Damage to these molecules can be caused directly by radiation or indirectly by secondary electrons created by radiation. The study of the ionic fragments produced in their components: uracil (U), adenine (A), cytosine (C), guanine (G) or thymine (T) by photon interaction is very important, since these play a fundamental role in coding, decoding, regulation and gene expression. It is believed that some of them played an important role in the origin of life. Space observations indicate that they could be found outside the Earth and has been detected in meteorite debris.

Investigating the interaction of light with biologically relevant molecules has gained interest for a wide variety of research fields including photochemical reactions such as light harvesting as well as radiation damage in proteins, RNA and DNA related to cutting-edge cancer treatment techniques. Understanding the nature of molecular dynamics in detail, such as visualization of molecular bond breaking, charge-transfer processes, proton migration, Interatomic Coulombic Decay (ICD), photoprotection, ring opening, and isomerization phenomena induced by the interaction of photons with matter has become viable with the advent of the laser [1]. Moreover, photodissociation is an important method used to thoroughly investigate the fundamental issues of chemical reactivity. It involves the formation of fragments form molecular ground and many different excited states.

The photodissociation of small molecules occurs upon irradiation by the interaction with ultraviolet or visible light. The fragments observed in the mass spectra allow us to discern the structure of these ions and how they are produced. The effect of UV radiation on nucleic acids is of great importance due to the ability of solar radiation to reach the Earth's surface directly, especially radiation in the range of 315-400nm. Incoming radiation can cause damage to nucleic acids, lipids and proteins, although the specific mechanisms of damage are still unclear [1, 2] and one of the main concerns of astrophysics is to identify the effect of radiation in space missions [3]. The mechanisms of damage to DNA and RNA molecules due to the interaction with electromagnetic radiation are complicated to study, due to the complexity of these molecules, so it is necessary to know the behavior of their fundamental units to demonstrate the reactions that such biomolecular suprastructures have [4].

The nitrogen bases have been related to the origin of our planet's life, recent studies report the possible discovery in the outer space of its structural bases (purines and pyrimidines) [5] in addition some nucleobases have been found in meteorites [6]; which suggests that they could arrive from outer space. Therefore, it is important to study how they interact with radiation. Also, geological records suggest that primitive life was based on DNA and protein enzymes

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and it is believed that it began with simpler structures, based on RNA [7] of which adenine and uracil are part.

Fragmentation dynamics of small biomolecules have drawn much attention from growing scientific communities during the last decades. This is mainly due to the fact that the dissociation of small molecules, as the building blocks of DNA and RNA , might play key roles in the understanding of the radiation induced damage of living tissues at the primary steps and at the molecular levels. In the laboratories, different species of particles such as electrons, photons and ions have been employed to excite the biomolecules and to induce their dissociation. Numerous works about this topic can be found in the literatures covering a large energy range. Different ions formation from Adenine (A) and Uracil (U) have been previously reported using electrons, synchrotron radiation or laser at different wavelengths and techniques [8-11].

2. Experimental

The photo fragment spectra were obtained from a high-resolution time of flight mass spectrometer, reflectron (R-TOF). It is a commercial spectrometer (Jordan TOF Products Inc) modified in the laboratory coupled to a vacuum chamber with a 60 cm diameter, housing the interaction zone where are generated the fragmented ions to be analyzed according to their mass to charge ratio (m/z). We use a pulsed valve and a skimmer to generate a supersonic molecular beam that allowed the adiabatic gas to expand closer to the interaction zone. The results show the multiphoton dissociation of the sample using laser radiation of 355nm corresponding to the third harmonic of an ND-YAG laser with a pulse duration of 6 nm and radiation intensities in the range of 10^9–10^{10} W/cm^2. The cation fragments were accelerated with a potential difference of 1000 V and sent to the flight to spectrometer operating as reflector mode, and detected by an microchannel plate (MCP) and registered by a picoameter by ORTEC (9308).

The positive ions were accelerated with a potential difference of 1000 V and sent to the flight operating in reflector mode and detected by an MCP and registered by 9308 of ORTEC. Both molecular beams were produced from Sigma Aldrich samples with 99% purity and introduced into a reservoir with an inert gas (Ar), and heated to ≅220°C-230°C. The sample was acquired from SIGMA ALDRICH with 99% purity and heated to 230°C where it is reported that thermal dissociation does not occur and the parent ion has its highest intensity in relation to heating temperature dependence (9) (40), so the sample is taken to the gas phase and is introduced into the mass spectrometer by means of a pulsed valve. The spectrometer pressure is of the order of 10^{-8} torr before introducing the sample and it rises to 10^{-6} torr when the sample is introduced. Then the sample goes through a skimmer, where an adiabatic expansion occurs, reducing the degrees of freedom of the molecule to a minimum.

3. Results and discussion

Fig.1 illustrates the geometries of uracil and adenine showing their pyrimidine and purine character.

Adenine C_5H_5NUracil $C_4H_4N_2O_2$.

Figure 1: Schematic structures of the of uracil and adenine.

An intense fragmentation of both molecules was observed, the number of products be significant. In the present study the most intense signals correspond to fragments of low molecular weight. Figure 2 shows the time of flight mass spectra at 355nm laser wave length and of 230°C temperature for adenine and uracil. From the ions observed, at different laser intensities it is possible that the fragmentation processes correspond to a multiphoton ladder switching mechanism, the formation of the positive parent ion was not observed. Among the identified ions, 19 coincidences were found between both molecules, including the prebiotic precursors fragments such as HCN^+ in both cases and NH_3CN^+ for the case of adenine, also these two molecules intervened in the generation of U and A.

The laser intensity was $\sim 1\times10^{10}$ W/cm^2, with λ = 355nm and IP is less than 10 eV being the ionization potentials for each molecule which corresponds to a Keldysh parameter of $\gamma = [I_{p\,/}\ (1.87\times10^{-13}\ I\ \lambda^2\ ]^{1/2}$ much greater than unity indicating that the experiment was performed deep into multiphoton ionization (MPI) regime. [13, 14]

From the spectra taken at different laser intensities the growth of different ions was calculates and shown in Fig. 3 for some of the produced ions.

Also, from the different spectra as the one on Fig. 2, the relative yield FR_i for fragmentation of the adenine and uracil molecules have been calculated for each fragment where FR_i is defined as:

$$FR_i = Int_i / I_{tot}$$

Where Int_i is the sum of one peak integral and I_{tot} is the sum of all the peak integral, the results are shown in Table 1 for comparison.

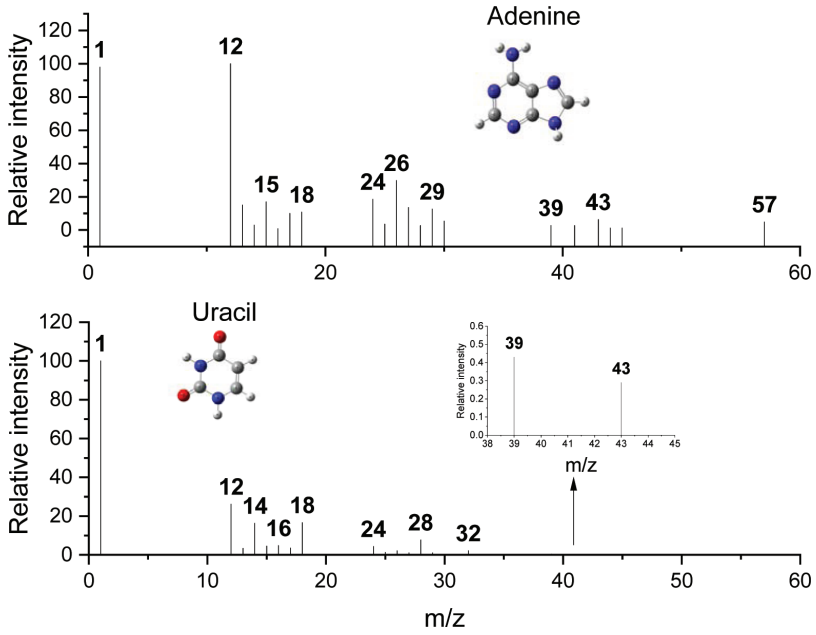

Figure 2: Comparison of MPI mass spectra of uracil and adenine at 355nm 500mW/pulse. The strongest peaks observed in photoionization are labeled accordingly to the m/z ratio.

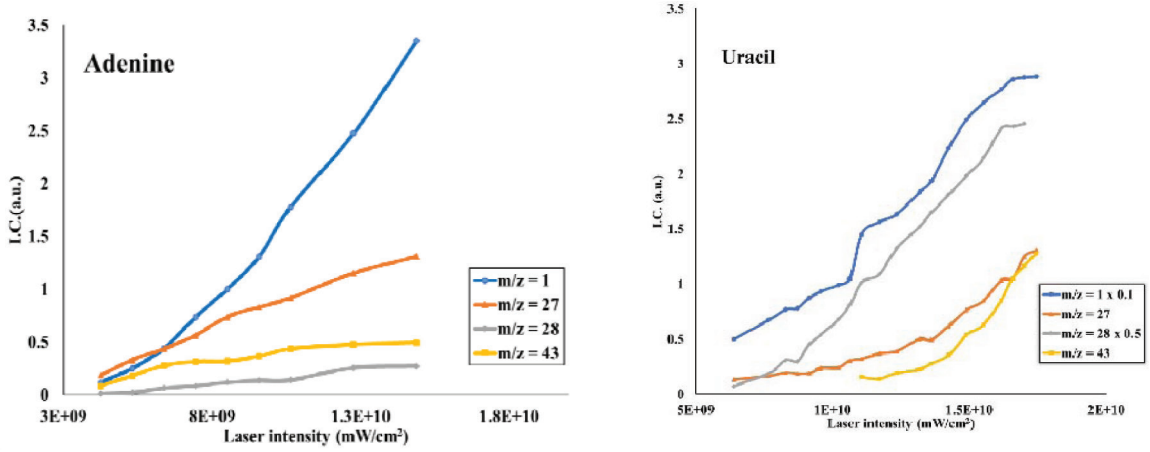

Figure 3: Formation of H^+ of HCN^+, NH_3CN^+ and $CN_3H_3^+$.

Table 1: Results for the main peaks, relative yield at laser intensity of $1.49E^{+10}(W/cm^2)$

m/z	Uracil	m/z	Adenine
1	30.0	1	13.1
2	0.1	2	0.1
12	13.2	12	29.6
13	2.0	13	5.9
14	16.6	14	0.8
15	2.6	15	5.5
16	4.7	17	4.7
17	2.3	18	3.4
18	9.6	24	7.0
24	3.8	25	1.0
25	1.3	26	12.3
26	2.1	27	5.1
27	0.9	28	1.1
28	4.8	29	5.5
29	2.0	30	1.4
32	2.1	43	1.9
39	0.6	57	1.6
43	0.6		

As an illustration, in Fig. 4, the formation and destruction for ions m/z = 1 and m/z = 43 are plotted showing the differences depending on the particular molecule.

According to Fig 4 for energies of the order of 10^9 W/cm^2 it was observed that the production of H^+ from uracil and NH_3CN^+ from adenine follow a tendency, while for powers of the order of 10^{10} W/cm^2 this tendency is reversed; where the mass ion 43 from uracil has the structure $HNCO^+$ or $C_2H_3O^+$.

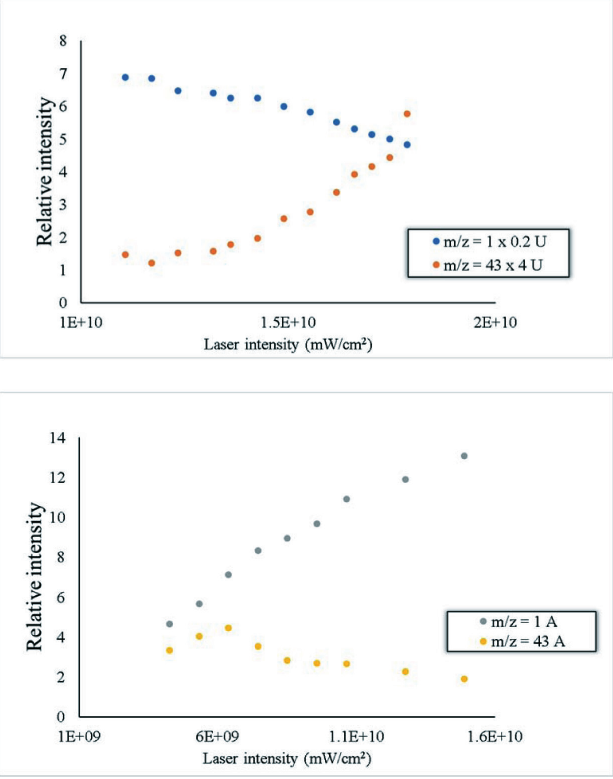

Figure 4: Formation and destruction of m/z=1 and m/z=43 normalized for better clarity.

From the measured spectra the energy absorbed to form some ions was calculated from the relation Y = σ n. Y is the ion yield, σ is the cross section, I is the laser intensity, and n is the order of process. We estimate the number photons absorbed using the mention equation the results are shown on Table 2.

Then the striking differences observed on the number of photons (energy) needed to produce each ion, depending whether they are originated from (A) or (U), [15] can be an indication of the structural differences between those molecules. Ions with the same m/z ratio require different energies, depending if they are result from adenine or uracil (purine orpyrimidine) dissociation.

Table 2: Photon order for the most abundant detected ions.

m/z	Uracil		Adenine	
	Photonorder	Ion	Photonorder	Ion
1	1.91	H^+	3.11	H^+
12	1.70	C^+	2.07	C^+
13	2.23	CH^+	2.56	CH^+
15	2.28	NH^+	3.02	NH^+
17	2.46	OH^+	3.8	NH_3^+
18	1.80	H_2O^+	3.03	H_2O^+ NH_4^+
24	2.24	C_2^+	1.91	C_2^+
25	2.31	C_2H^+	1.28	C_2H^+
26	2.45	$C_2H_2^+$or CN^+	2.93	$C_2H_2^+$ or CN^+
27	2.43	$C_2H_3^+$or HCN^+	1.84	HCN^+
28	3.31	$HCNH^+$	1.84	$HCNH^+$
29	3.33	$HNCH_2^+$	2.21	$HNCH_2^+$
39	3.33	HC_2N^+	2.07	HC_2N^+
43	5.27	$HNCO^+$ or $C_2H_3O^+$	0.74	NH_3CN^+

Conclusions

In conclusion, we have presented here the comparison of results based on the multiphoton ionization and dissociation of gas-phase adenine and uracil. It is possible to argue that dissociation is followed by ionization a D-I processes. Future studies employing different laser wavelengths will be useful for discerning the differences found here and hope this type of experiments motivate further theoretical calculations and more refined experiments about the studies on radiation phenomena. To our knowledge, there is not reported similar information were adenine and uracil multiphoton ionization are compared, in fact the data reported here are the beginning of a series of experimental studies undertaken in our Laboratory to study of the ionic fragments produced from laser interaction of uracil (U), adenine (A) [16], cytosine (C), guanine (G) or thymine (T).

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