J. Nucl. Phys. Mat. Sci. Rad. A. Vol. 6, No.1, Aug. 2018, pp.103–108

CHITKARA

Journal of Nuclear Physics, Material Sciences, Radiation and Applications
Journal homepage: https://jnp.chitkara.edu.in/

Laser Radiation Effects on Adenine

L.X. Hallado, J.C. Poveda, E. Prieto, A. Guerrero, I. Álvarez, and C. Cisneros*

Institute of Physical Sciences, National Autonomous University of Mexico (UNAM). 1001 University avenue. 62210 Cuernavaca Morelos, Mexico

*Email: carmen@fis.unam.mx

ARTICLE INFORMATION

Received: June 16, 2018
Revised: June 27, 2018
Accepted: July 19, 2018

Published online: August 6, 2018

Keywords:
photodissociation of adenine, gas phase adenine, multiphoton ionization spectroscopy

DOI: 10.15415/jnp.2018.61018

ABSTRACT

Laser interaction whit the gas phase nucleobase adenine is studied. A linear TOF mass spectrometer is utilized for measurements that require high mass resolution, high sensitivity, and sufficient ion yields of low mass fragment cations. The ion mass spectra are discussed at different laser energy intensities and two temperatures. In contrast to previous studies a number light ion is present in the mass spectra. The ion formation curves for 23 different ions are measured for the laser energy range from about 10^9 to 10^{10} W cm^{-2} and masses between 1 and 43 besides mass 57 which was present in the mass spectra and will be discuss. Data were taken heating the sample at 235 C°. The number of 355nm absorbed photons was calculated accordingly to Keldysh theory and similar results were found using adenine -Ar mixture. Our results are compared with those reported formed by protons, electrons or multiple charged ions interactions. Different ions were found indicating the possible effect of multiphoton absorption.

1. Introduction

One of the interest on the study of biological molecules, clusters and their radicals, nitrogenous bases, glycopeptides and polysaccharides, could be focused on the effects exerted by radiation in the macromolecules as, DNA and RNA. Radiations can cause damage to biological material or the generation of genetic mutations mediated by free radicals, increasing the risk of cancer. This is one of the reasons of the present research, analyze the effect of the radiation on each of the DNA constitutes, thereby elucidating the mechanism of damage caused by radiation and preventing the multiplication of genetic damage. Aided in specific radiological therapies [1]. Ultraviolet (UV) radiation is part of the spectrum of electromagnetic radiation emitted by the sun and includes the wavelength range from 100 to 400 nm: UVC (100–280 nm), UVB (280–315 nm), and UVA (315–400 nm). The oxygen and ozone in the atmosphere completely absorb the UVC radiation (< 280 nm) and absorb the majority (approximately 90%) of UVB. Thus, the solar UV radiation of relevance to human health and ecosystems consists of UVA and UVB wavelengths [2].

The study of biomolecules is essential to understand the development of life and why DNA replication processes show low fluorescence yields and very short excited life states. These structures have a high resistance ratio, but it is possible that they decompose and that they are very sensitive to thermal changes and that a low vapor pressure is present. [3] The evolution of the spectroscopic techniques, the optimization and the generation of technological devices together with the refinement of the laser sources, allows the study of the simple molecules and has increased the photochemical, photophysical studies and the effects of the UV light in biomolecules of simple structure. These characteristics were used to propose models of the kinetically unstable molecules, when analyzing the results of the mechanisms for the liberation of excess energy. Within these studies is the multiphoton ionization spectroscopy, this technique comprises a wide range of highly sensitive experiments, which study the interaction processes in the basal state of individual atoms or molecules with two or more photons; that it is not possible to study by means of conventional spectroscopy. When in a multiphoton interaction, the system absorbs two or more photons, the processes of absorption and emission are closely related, the simplest example of this type of experiment is when only absorption is involved [4, 5].

Adenine is one of the four nitrogen bases that belong to DNA. It is one of the building blocks of DNA the last years special interest has been concentrated on the study of the effects under UV radiation in nucleic acids also it has been considered the role that this molecule could have played in the origin and development of life on our planet [6-8]. Different aspects of astrochemical, medical or biological

ISSN No.: 2321-8649(Print) ISSN No.: 2321-9289(Online); Registration No. : CHAENG/2018/51628

have being addressed. The objective of the present study are the effects of radiation on the adenine molecules, present on the processes of dissociation and ionization. Recently, it was shown that radiation can produce secondary ions/fragments with kinetic energies from thermal up to several hundred eV in a biological medium, and in the subsequent scattering events these energetic ions/fragments can also cause severe damage to DNA [9-10].

The Monte Carlo simulations for radiation damage studies on DNA and RNA [11], account for ionization. However, the probability of simultaneous ionization and dissociation and high energy deposition (known as dissociative ionization) has not been considered in these simulations, mainly due to lack of data until very recently. Most of the available experimental data by the interaction with electrons, protons laser in the range [12-14], synchrotron light of energy from 6-22 eV [15] or multiple charged ions [16-18]. In the present study, the photodissociation and photoionization of adenine in the multiple photon absorption regime were investigated at the wavelengths of 355 nm and intensities of radiation in the range 10^9 to 10^{10} W·cm^{-2}. Radiation interacts with a molecular beam of Ar-adenine mixture, produced by the adiabatic expansion of vapors into a high vacuum chamber at 10^{-8} torr. Adenine was heated at 235°C, the resulting ions were analyzed using a home-assembled Jordan R-TOF mass analyzer used in a linear mode. On the basis of the detected ions, the processes were identified as a Dissociation- Ionization. The mass spectra (MPI) were obtained, the resulting ions identified and compared with the previously reported. The identification of the ions in the mass spectra (MPI) is presented. The MPI show that the presence and intensity of the ions depends on the density power as well as the wave length and the fact of the use Ar as carrier gas. The order of the process was determined plotted the logarithm of the ion yield as a function of the logarithm of the laser intensity. Accordingly, with the Keldysh approximation [19] the order of the processes can be related whit number of photons required to form an ion. The MPI show that the presence and intensity of the ions depends on the density power. The results are compared with those reported by other laboratories under different experimental conditions [12-15]. Different ions from those previously identified were observed and its presence is discussed.

2. Experimental

The photofragment spectra for adenine multiphoton absorption were obtained by a high resolution time of flight mass spectrometer, a commercial spectrometer (Jordan) modified in the laboratory [20], coupled to a vacuum chamber 60 cm diameter, housing the interaction zone to produce the fragment ions. The adenine powder sample (Sigma-Aldrich, purity ∼99 %) was introduced, by pulsed valve, seeded with Ar, into the ionization chamber in gas phase. The pulse valve has an extension with a conical tip termination inside the chamber that allows the adiabatic gas expansion closer to the skimmer for the generation of the supersonic molecular beam. A heated molecular beam of adenine /Ar was produced by adiabatic expansion in a high-vacuum chamber at 2×10^{-8} torr. To heat the adenine sample, a controlled coiled resistive heater in the reservoir was used, the temperature was monitored and held at 235-240°C. No indication of thermal decomposition was observed at these temperatures.

The pulsed valve was synchronously coupled with the laser pulses with an opening time of 250 μs in order to ensure that the adenine molecules and laser light coincide at the center of the interaction zone. The operating pressure was: 2×10^{-6} torr. The 355 nm laser radiation was produced from the second harmonic of a Nd:YAG laser (Spectra Physics), operating at 30 Hz repetition rate. The laser pulse width is 5.5 ns and the energies per pulse from 1 to 30 mJ. The laser radiation (with a Gaussian profile and vertically polarized) was focused into the interaction region using a 15 cm focal length lens. The diameter at the focal point was 80.0 μm. Under these experimental conditions, radiation intensities between 10^9 and 10^{10} W·cm^{-2} were achieved. The molecular beam interacted orthogonally with the laser radiation at a point located between two parallel plates continuously polarized at 5.0 KeV and 4.5 KeV, corresponding to the extraction and the acceleration potentials, respectively. The distance between the plates was 0.6 cm. Pinholes of 10 mm diameter at the center of each plate covered with a fine metal mesh were used to extract the positively charged ions from the interaction region. The ions were driven along the field-free region of the RTOF analyzer and they reached a dual Chevron microchannel plate detector after they were refocused. The ions arrived at the detector, according to the ratio charge/masses (e/m). The resolution achieved was of the order of 1000. The current signal was pre-amplified, voltage-converted, digitized and sampled in time using a picosecond time analyzer from EG&G Ortec.

3. Results and discussion

Adenine molecules were multi-photon ionized at the wavelength of 355nm with fluence between 10^8–10^9 W cm^{-2}. There are at least two theories to characterize multiphoton ionization and dissociation processes DeWitt [21] and Keldysh [19]. Accordingly, to Keldysh's theory [19], there is an adiabaticity parameter, γ, which characterize the regime in which n photons couple simultaneously into the molecule to allow excitation to an intermediate electronic

state or directly to an ionic state. The other regime for radiation-molecule coupling involves the production of field ionization via tunneling or barrier suppression. If γ is much greater than unity, the coupling mechanism is in the multiphoton ionization limit MPI, if is less than the unity the coupling mechanism is in the tunneling limit ATI.
γ can be written as:

$$\gamma = [I_p/(1.87 \times 10^{-13} I \lambda^2]^{1/2}$$

Were I_p corresponds to the ionization potential of the molecule; I is the intensity of the laser (W cm^{-2}) and λ is the laser wave length. Accordingly, to our parameters we are on the MPI regime. Although the processes could be a mixture contain contributions from both MPI/ATI and less contribution from ATI, however this issue demands further consideration. Also, from Keldysh theory the relation the logarithm of the ion yield Y plotted as a function of the logarithm of the laser intensity determine the order of the process

$$Y = \sigma_n I^n$$

where Y is the ion yield, σ_n is the nth order cross in units and n is the order of the process. Usually the order is considered the smallest number of photons required to form an ion. The ion yields for the most prominent ions and calculated the number of photons involved, the results are displayed in Table 1.

Table 1. Order of the process.

m/z	*Ion*	*Photon Order*
1	H^+	3,11
12	C^+	2,07
13	CH^+	2,56
15	NH^+	3,02
17	NH_3^+	3,80
18	H_2O^+ or NH_4^+	3,03
24	C_2^+	1,91
25	C_2H^+	1,28
26	CN^+ o $C_2H_2^+$	2,93
27	HCN^+	1,84
28	$HCNH^+$	1,84
29	NH_2CH^+	2,21
30	$N_2H_2^+$	2,00
39	$HCCN^+$	2,07
41	N_2HC^+	0,81
43	NH_3CN^+	0,74
57	$C_2N_2H_5^+$	1.11

Figure 1., shows the case for m/z = 15, HN^+ and m/z = 13, $CH^{+\cdot}$ Overall uncertainty is estimated as 20%

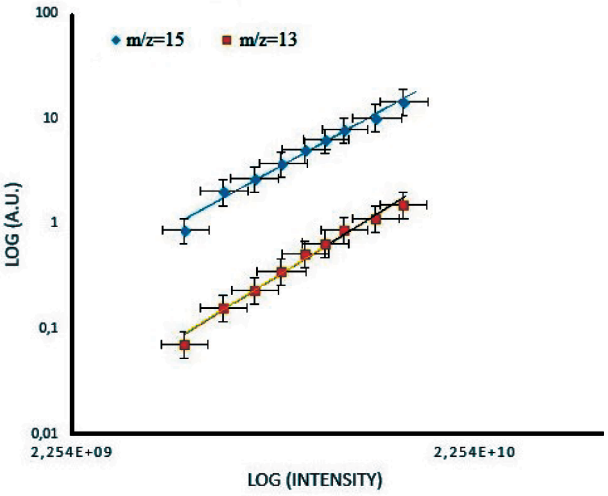

Figure 1. Power dependence of NH^+ and CH^+ from MPI on laser intensity.

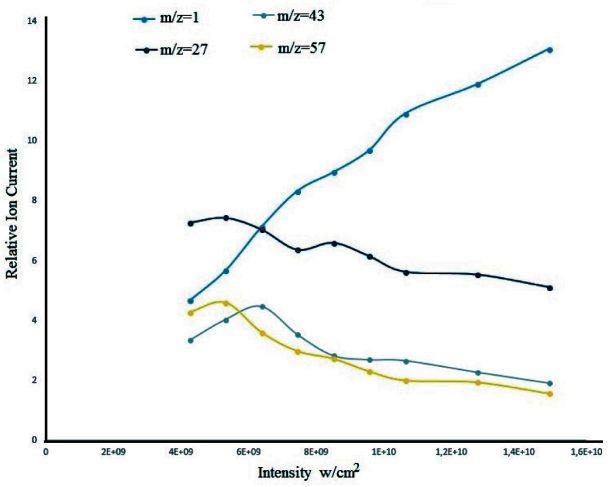

Figure 2. Formation of H^+ and destruction of HCN^+, NH_3CN^+ and $CN_3H_3^+$.

The corresponding energies calculated from the number of photons to our knowledge have not being reported as some of the light ions. Most of the positive ions are the products resulting from the interaction of adenine with electrons, protons or multiple charged ions [12-18]. We also observed the presence of the ion corresponding to m/z = 57, m/z = 28, 14 y 12 the relative intensities are higher, in our measurements than the previously reported. Those facts deserve further investigation. Figure 2 shows the increased and decreased of selected ions. Table 2. presents the relative intensities of the m/z peaks taken from a ratio

of each individual intensity to the 95% of the total light ion current in Ar-adenine spectrum, at 280 Mw.

Table 2. Relative Intensity of the m/z peaks.

mass	relative intensity
1	13,08
12	29,60
13	5,89
14	0,85
15	5,55
17	4,68
18	3,45
24	7,01
25	1,01
26	12,27
27	5,11
28	1,07
29	5,50
30	1,44
43	1,91
57	1,57

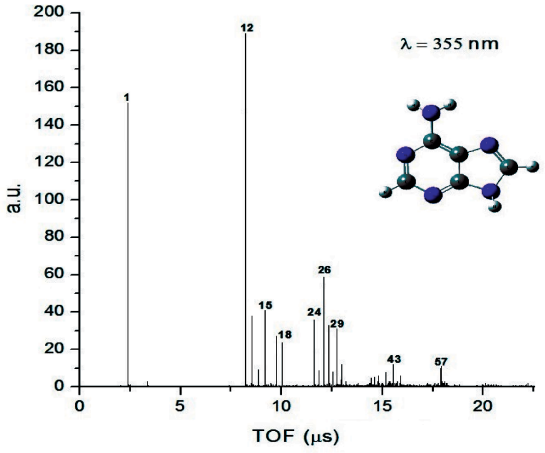

Figure 3. Time of flight spectra.

Figure 3. Shows the time of flight mass spectra at 355 nm of 230°C pure adenine. From the ions observed, at different laser intensities the fragmentation process corresponds to a ladder switching mechanism. The parent ion, was not detected in the present study. We concentrate on the low mass ions, from m/z = 1 up ion m/z = 57. Several dissociation patterns have been proposed for the fragmentation mainly for ions with high values of m/z using electrons, protons or synchrotron radiation. The parent ion m/z = 135, $C_5H_5N_5$ successive loss HNC [12-14, 22] giving ions m/z = 108 to m/z = 27 trough intermediate ions type $C_nH_nN_n^+$ (n = 4,3,2) The ion m/z = 27 n = 1 is present in the mass spectra perhaps the is the possibility of the loss of the isomer HCN. Other fragmentation pathways can explain the presence of the different ions observed in this experiment:

With regard to m/z = 57 in a detailed electron adenine collision, [22] has measured the m/z = 70 ion [15] and proposed a fragmentation pathway: $C_4H_4N_4^+$(m/z = 108) to $C_2H_4N_3^+$(m/z = 70) + C_2N(m/z = 38) by further decomposition we propose $C_2H_4N_3^+$(m/z = 70) to $CH_3N_3^+$(m/z = 57) + CH; m/z = 57 has not being reported. Also, ion m/z = 43 is originated from ion m/z = 70 (J S). Ion m/z = 42 was not observed in the present experiments. Ion m/z = 41 has been reported by (J) as $NHCN^+$ m/z = 40 NCN^+ as it is mention in (J) involves loss from NHCN of two CHN units. Loss of NH_2CN from m/z = 81 constitutes a possible pathway to form the C_2HN^+ (m/z = 39) ion a via which involves the m/z = 66 ion.as is pointed out in [15] m/z = 39 ion, is weak. Ion with m/z = 30 is reported on [13] as part of the peak 31 m/z = $N_2H_3^+$ in the present experiments is fully resolved as $N_2H_2^+$.The same situation is with m/z = 29, 28 and 27 they are part of the peak 28[14], however for the case of photon impact [15]m/z = 28 is reported clearly as $HCNH^+$. Ion m/z = 27 probably comes from the ionization of the corresponding neutral fragment. Lighter ions as m/z = 26, $C_2N_2^+$ or CN^+ has not been previously reported as C_2H^+ and C_2^+, m/z = 25 and m/z = 24 respectively. Regarding to peak m/z = 18 it is not rule out it comes from H_2O, however the low background pressure (10^{-7} mbar) in our experiments heating to 235°C would generally be expected to remove water from the sample prior to measurements, then it can be attribute to NH_4^+. As m/z =17, NH_3^+ or assuming water contamination could be OH^+ and it is possible to assign to m/z = 16, to O^+ or CH_4^+. m/z = 15-12 and the detection of H^+ agree whit the ones reported by [14]. The present experiment shows significant production of both H^+ and C^+. Table 3: is the summary of different TOF data for adenine when electrons, protons or synchrotron radiation is used along with that obtained in the present experiment.

Table 3. Summary of different TOF data.

	Present work	Tabet et al[13]	Rice et al[12]	Jochims et al[15]
m/z	Ion			
1	H^+	1	-	-
12	C^+	12	-	-
13	CH^+	13	-	-
14	N^+, CH_2^+	14	-	14
15	NH^+	15	-	-
16	NH_2^+	16	-	-

17	NH_3^+	17	-	17
18	H_2O^+ o NH_4^+	18	-	18
24	C_2	-	-	-
25	C_2H^+	-	-	-
26	CN^+ o $C_2H_2^+$	-	-	-
27	HCN^+	27	27	27
28	$HCNH^+$	28	28	28
29	NH_2CH^+	29	29	29
30	$N_2H_2^+$	30	-	-
-	$N_2H_3^+$	31	-	-
-	C_3H^+	37	-	-
-	$C_3H_2^+$ C_2N^+	38	38	38
39	$HCCN^+$	39	39	39
40	NCN^+	40	40	40
41	$NHCN^+$	41	41	41
-	NH_2CN^+	42	42	42
43	NH_3CN^+	-	43	43
44	CN_2H_4	-	-	-
45	$CN_2H_5^+$	-	-	-
46	$CN_2H_6^+$	-	-	-
-	$C_3H_2N^+$	52	-	-
-	$C_3H_3N^+$ $C_2HN_2^+$	53	53	53
-	$C_2H_2N_2^+C_3H_4N^+$	54	54	54
57	$CN_3H_3^+$	-	-	-

4. Conclusions

In conclusion, we have presented here results based on the multiphoton ionization and dissociation of gas-phase adenine. This allowed us to analyze the low mass positive ions as well as detect ions not reported before, produced by the interaction of laser radiation. From the comparison with former experiments were a wide variety projectiles were used (from photons to multiple charged Ar) there is still to prove what of the many fragmentation paths contribute to the observed ions and to understand the response to such complicated molecules to radiation. We hope that the type of experiments reported here motivate further theoretical calculations and more refined experiments about the studies of these reactions and their influence on radiation biology.

Acknowledgements

The present work was supported by DGAPA UNAM grants IN102516 and IN104318

References

[1] A. Shimoyama, S. Hagishita, K. Harada, *Geochemical Journal*, 343–348. (1990). https://doi.org/10.2343/geochemj.24.343

[2] S. A. Passaglia *et al*, *Free Radical Biology and Medicine* **107**, 110–124 (2017). https://doi.org/10.1016/j.freeradbiomed.2017.01.029

[3] L. B. Clark, G. G. Peschel, and I. Tinoco, *Journal of Physical Chemistry,* **69**, 3615–3618(1965). https://doi.org/10.1021/j100894a063

[4] N. J. Kim *et al., The Journal of Chemical Physics* **113**, 10051 (2000). https://doi.org/10.1063/1.1322072

[5] J. Stepanek and V. Baumruk, *Journal of Molecular Structure.* **219**, 299–304 (1990). https://doi.org/10.1016/0022-2860(90)80072-R

[6] A. Conconi, & B. Bell, *The long and short of a DNA-damage response,* Molecular biology doi:10.1038/nature22 488(2017).

[7] E. A. Kuzicheva, M. B. Simakov, *Advances in Space Research* **23**, 391, (1999).

[8] G. F. Joyce, *Nature* **418**, 214–221(2002). https://doi.org/10.1038/418214a

[9] J. de Vries, R. Hoekstra, R. Morgenstern, T. Schlatholter, *Physical Review Letters* **91**, 053401(2003). https://doi.org/10.1103/PhysRevLett.91.053401

[10] T. Schlatholter *et al., Physical Review Letters* **94**.233001 (2005).

[11] H. I. Nikjoo, D. E. Charlton, D. T. Goodhead, *Advances in Space Research* **14**, 161–180 (1994). https://doi.org/10.1016/0273-1177(94)90466-9

[12] J. M. Riceand, G. O. Dudek, *Journal of the American Chemical Society,* **89**, 2719–2725 (1967). https://doi.org/10.1021/ja00987a039

[13] J. Tabet *et al., Physical Review A* **82**, 022703 (2010). https://doi.org/10.1103/PhysRevA.82.022703

[14] J. Tabet *et al., International Journal of Mass Spectrometry.* **292**, 53 (2010). https://doi.org/10.1016/j.ijms.2010.03.002

[15] H. W. Jochims, M. Schwell, H. Baumgärtel, S. Leach, *Chemical Physics,* **314**, 263–282 (2005). https://doi.org/10.1016/j.chemphys.2005.03.008

[16] V. V. Afrosimov *et al., Technical Physics* **57**, 594–602 (2012). https://doi.org/10.1134/S1063784212050027

[17] S. Martin *et al., Physical Review A,* 77.062513 (2008). https://doi.org/10.1103/PhysRevA.77.062513

[18] T. Cunha *et al., The Journal of Chemical Physics* **148**, 134301 (2018). https://doi.org/10.1063/1.5021888

[19] L. V. Keldysh, *Soviet Physics JETP* **20 (5)**, 1307–1314 (1965).

[20] J. C. Poveda, I. Álvarez, A. Guerrero-Tapia, C. Cisneros, *Revista Mexicana de Física* **62**, 206–212 (2016).

[21] M. J. DeWitt, and R. J. Levis, *The Journal of Chemical Physics* **110**, 11368 (1999). https://doi.org/10.1063/1.479077

[22] S. K. Sethi *et al., American Chemical* **104**, 3349–3353, (1982). https://doi.org/10.1021/ja00376a017