



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Multiphoton ionization and dissociation of naphthalene at 266, 355, and 532 nm

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ARTICLE INFO

Article history:

Received 6 April 2010

Received in revised form 26 July 2010

Accepted 31 July 2010

Available online 7 August 2010

Keywords:

Naphthalene

PAHs

Photoionization

Photodissociation

Time-of-flight mass spectrometry

ABSTRACT

A comparison of laser-induced multiphoton ionization/dissociation and dissociation/ionization pathways of naphthalene, $C_{10}H_8$, is presented at 266, 355, 532 nm, using time-of-flight mass spectrometry, ToF-MS. From the spectra several processes were identified: molecular ionization, simple dissociation, hydrogen transposition, hydrogen loss, and total deprotonation. The dependence on the wavelength and the radiation intensity is clear. At 266 nm energies per pulse, <1.0 mJ (9.23×10^2 MW cm^{-2}), $C_{10}H_8^+$ dominates the spectra and new ions were observed as the laser intensity was increased. At 355 nm, hydrogen loss was the principal dissociative route, with the formation of low mass ions: CH_n^+ , $0 < n < 6$, in particular CH_6 was identified by isotopic analysis. At 532 nm, the $C_nH_m^+$ ions, $2 < n < 5$, were the most abundant species. The calculated numbers of absorbed photons along with previous calculations were used to propose different fragmentation channels.

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1. Introduction

There is strong spectroscopic evidence to suggest that polycyclic aromatic hydrocarbons, PAHs, their ionized forms, or/and clusters are responsible for the diffuse interstellar bands, DIBs [1–4], observed from a wide variety of space regions, molecular clouds, and astronomical objects. It is now clear that cationic forms of PAHs dominate these emissions. In regions where the photon energy reaches the VUV spectral region, it is possible for the photodestruction of PAHs to occur; in addition, radiative processes are present as a consequence of the inter- and intra-molecular relaxation of ionized or electronic excited species. PAHs cations have been confined with radiofrequency fields using ion traps; these results [5–8] support the DIBs astrophysical hypothesis. On the other hand, it has been pointed out the importance of the PAHs [9–11], for instance as carcinogenic substances, in the environment as a result of combustion processes, or as a model to understand some aspects of the photon–molecule interaction.

Naphthalene is a PAH, that can be proposed as a model molecule to perform experimental studies and an analysis of its photon–molecule interaction behavior, to acquire a better understanding of photon–PAHs interactions and to provide some information about the ion fragmentation.

DeWitt and Levis [12] had reported the photoionization, PI, and photodissociation, PD, of PAHs, with 780 nm ultrashort laser pulses

(170 fs) and intensities of up to 3.8×10^7 MW cm^{-2} . Jochims et al. [13–16] had measured the photodestruction efficiency as a function of photon energy 7–24 eV using synchrotron radiation. They observed the predominance of parent ions in the ToF spectra at low energies per pulse, similar results were obtained in our experiments at 266 nm.

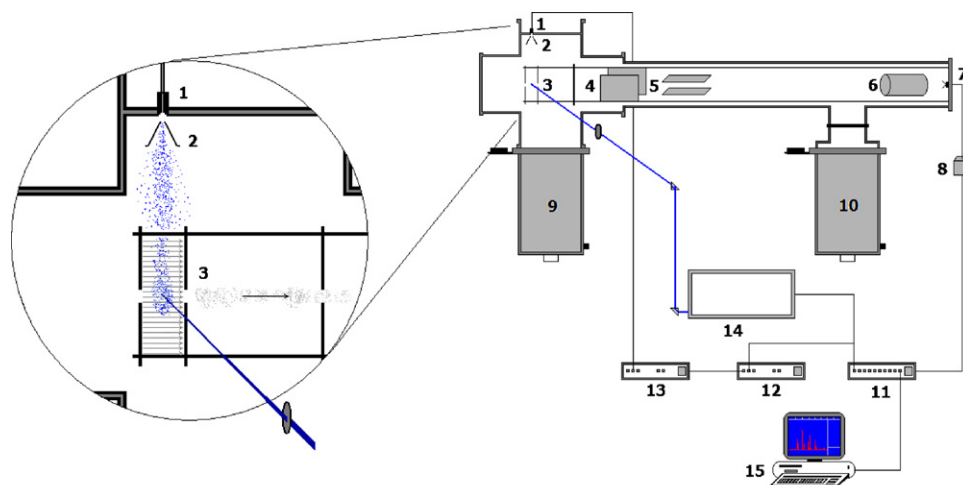
In the present paper we report the multiphoton ionization, MPI, and multiphoton dissociation, MPD of naphthalene resulting from the interaction with 266, 355 and 532 nm laser radiation in the nanosecond regime. The different products are a result of the characteristics of the laser radiation (wavelength, intensity, and width of laser pulse). The different photoions resulting as a function of the photon energy and radiation intensities were identified using a ToF analyzer, and the possibility of resonant or non-resonant photon absorption from the neutral molecule is discussed. At intensities from 10^3 to 10^5 MW cm^{-2} , ionization is possible by multiphoton absorption, as it was seen at 266 nm and also dissociative states can be reached, resulting in an extensive fragmentation as was observed at 355 and 532 nm in the experiments reported in the present paper.

2. Experiment

Naphthalene sample was purchased from Sigma–Aldrich (spectroscopic grade, purity >99.9%). The sample was located in a controlled thermal chamber; the vapor pressure of the sample was increased by raising the temperature to 373 K. The sample was introduced into the ionization chamber using a pulsed valve, synchronously coupled to the laser pulse. Argon was used as carrier gas. A cooled molecular jet was generated by adiabatic expansion

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1. Pulsed valve, 2. Skimmer, 3. Extraction and acceleration plates, 4.-5. Electrostatic lenses, 6. Einzel lens, 7. Detector, 8. Signal amplifier, 9.-10. Vacuum system, 11.–13. Pulsed valve control, delay system and data acquisition system, 14. Nd:YAG laser, 15. Personal computer.

Fig. 1. Experimental setup in the PI and PD experiments.

of naphthalene vapors in a high vacuum chamber at 2.7×10^{-6} Pa, reaching a final pressure of 2.7×10^{-4} Pa when the sample is introduced.

The fourth, 266 nm, third, 355 nm, and second, 532 nm, harmonics from an Nd:YAG laser, with 4.5, 6.5, and 8.5 ns pulse widths, respectively, and a repetition rate of 10 Hz, were used. The energy per pulse used was varied from tenths up to 10 mJ at 266 nm, from tenths up to 50 mJ at 355 nm, and from 40 to 100 mJ at 532 nm, with equivalent intensities to up to 9.24×10^3 , 3.78×10^4 , and 6.40×10^4 MW cm $^{-2}$, respectively. For each wavelength, 50 different energies per pulse were measured. 5000 laser shots per energy per pulse were added to obtain the ion spectra in a ToF window from 0 to 20 μ s. The radiation was focused into the interaction region using a lens with a focal length of 25 cm. Area in the focal point was measured using a polish copper film, several laser shots were sent, marking different spots, their diameters were measured and from average the area was calculated, with this focal area, and pulse widths and energies per pulse, intensities used here were derived.

The ions resulting from MPI and MPD were extracted by an electrode-mesh polarized to +5.0 kV and subsequently accelerated by a repulsive voltage of +3.5 kV toward a grounded grid electrode at the entrance of the 1 m long field free flight tube, and were separated according to their mass-to-charge ratio. The positive ions were recorded according with the arrival time using a channel electron multiplier detector, and the signal was amplified by a fast preamplifier and subsequently digitized using a multi-channel analyzer with 5 ns width per channel, to reconstruct the ToF mass spectra. Detailed experimental setup is shown (Fig. 1).

The detected ions were identified according to their mass-to-charge ratios. The effect of energy per pulse on the resulting photoions, photoion currents at different wavelengths was analyzed. From the relation between the ion currents and the laser intensities, the number of absorbed photons was calculated and the possible dissociation channels were proposed.

3. Results and discussion

The first three electronic transitions to S_1 , S_2 , and S_3 states were observed in the near-UV region [17]. The first is an $S_1 \leftarrow S_0$ transition with B_{2u} symmetry, 3.94 eV of energy and oscillator strength

0.002 [17], hence it is a very weak transition. The $S_2 \leftarrow S_0$ transition has been reported as a transition with symmetry ${}^1A_g \rightarrow 2{}^1B_{1u}$, energy of 4.34 eV and moderate intensity, with oscillator strength of 0.18 [18]. The strongest $S_3 \leftarrow S_0$ transition to a B_{3u} state has energy of 5.62 eV and oscillator strength of 1.3 [17]. Those transitions are shown (Fig. 2) and from them it is possible to identify the electronic transitions when photons of different energies are absorbed.

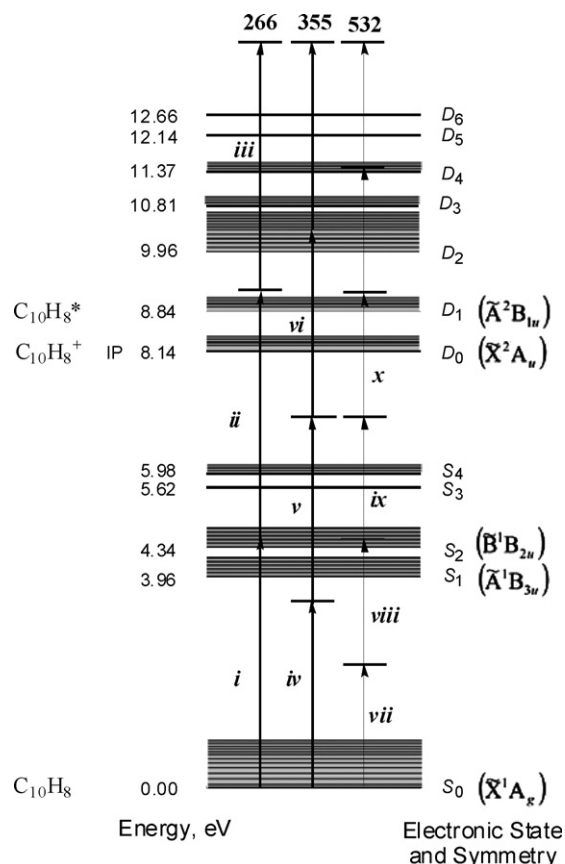


Fig. 2. Electronic states and energies, and photon absorption.

A comparison of the wavelength effect on the dissociation pattern is shown (Fig. 3), the parent ion is only observed at 266 nm. Accordingly with Lubman and Kronick [19] the parent ions appeared, for several PAHs studied, included naphthalene at relatively low laser power, of the order of 1 mJ at 266 nm, and the fragmentation pattern is very sensitive to the laser power as it was observed in the present experiments. The fact that the parent ions are not observed at 355 and 532 nm has been pointed out by Lubman et al. [20]. The process which takes place at 266 nm is an ionization–dissociation process whereas at 355 and 523 nm they are dissociation–ionization processes. The lower energies needed to produce different ions are in some cases lower than the nominal appearance energies due to the extensive fragmentation of the molecule to form smaller ions and neutral products. At 266 nm the ionization occurs by a resonant [1+1] two-photon absorption processes, increasing the two-photon absorption cross-section; while at 355 and 532 nm resonant photon absorption was not feasible, decreasing significantly the probability of such processes. Comparative ToF spectra for different energies per pulse at 266 nm are shown in Fig. 3, as can be seen as the energy per pulse increases, new ions appear. At this wavelength similar results have been reported by Lubman et al. [20], which discuss the changes in fragmentation patterns as a function of wavelength and energy per pulse, being significant the saturation processes as a consequence of the increments in the energy per pulse. Our experimental setup differs from previous experiment [20], pulsed molecular beams and fluxes of the order of 10^7 – 10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ in the interaction region were used here. The saturation thresholds occur at energies per pulse close to 9.3 mJ ($8.59 \times 10^3 \text{ MW cm}^{-2}$), 27.5 mJ ($2.08 \times 10^4 \text{ MW cm}^{-2}$), and more than 100 mJ ($6.39 \times 10^4 \text{ MW cm}^{-2}$) per pulse for 266, 355 and 532 nm respectively. Perhaps at 532 nm the saturation threshold is not possible to reach in the present experiments, because, considering the energy photons, higher energies per pulse than 100 mJ are required to reach densities up to the saturation limit.

In order to estimate the number of photons absorbed which lead to a particular ion, the logarithm of the measured photoion current was plotted as a function of the logarithm of the laser intensity accordingly to the following relation [12]:

$$C = f(\sigma_n) \cdot I^n \quad (1)$$

where C is the photoion current, $f(\sigma_n)$ is a function of the n th-order cross-section of the processes, MPI or MPD, in units commensurate with the units used for the intensity, and n is the order of the process. From the present experimental results it is not possible to calculate σ_n itself. The order n , is equivalent to the number of photons required to ionize or dissociate the molecule through an intermediate excited electronic state; n photons supply the energy required to induce a particular process. n values were calculated below the energies per pulse where the saturation threshold occurs.

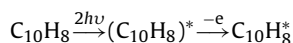
From photoion current the numbers of absorbed photons were calculated for the groups of ions, C_nH_m^+ (m from 2 up to 10), as well as for different particular ions. At 266 nm, were observed the formation of ions by the absorption from two to four photons; at 355 nm, were observed ions formed by the absorption of two, three and four photons; and at 532, the formation of the detected ions require more than four-photon absorption. Under the present experimental conditions: high energies per pulse and low cross-sections, some of the ion currents do

not follow the potential law earlier discussed, and the number of absorbed photons were not calculated. The results as a function of the laser wavelength are discussed and interpreted as follows.

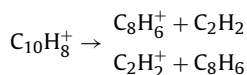
3.1. Photoionization at 266 nm

At 266 nm, the process that takes place is a multiphoton absorption follow by molecular ionization and dissociation. A first photon with an energy of 4.66 eV can be resonantly absorbed [21] to a vibrational level of the second excited state, S_2 (step *i*, Fig. 2); at the intensities used here, the absorption of a second photon is also probable (step *ii*, Fig. 2), so that the molecule reaches a superexcited state which decays, leaving an ionized molecule and one free electron.

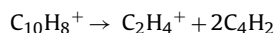
This process can be described as follows:



Two-photon absorption, at energies per pulse lower than 1 mJ, gives rise to the formation of heavy ions: $\text{C}_{10}\text{H}_8^+$, C_9H_n^+ and C_8H_n^+ , and low mass ions C_2H_n^+ , particularly C_8H_6^+ and C_2H_2^+ , as the result of direct dissociations from molecular parent ion:

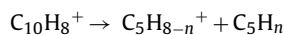
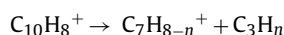
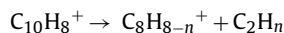


Also the ion C_2H_4^+ was observed but its formation is only possible by a double hydrogen transposition:

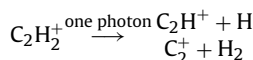
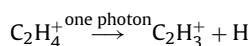


If the $\text{C}_{10}\text{H}_8^+$ ion absorbs one additional photon it can reach other excited dissociative states forming lighter ions (step *iii*, Fig. 2). Three photons supply enough energy to reach a dissociative state which results in the formation of C_7H_n^+ , C_6H_n^+ , C_5H_n^+ , and C_2H_n^+ , either by a direct dissociative mechanism from parent ion or by one photon absorption from the already resulting ions by the two-photon processes, a step by step dissociative mechanism.

The direct dissociation from superexcited molecular parent ion is interpreted as:



And the step by step dissociative mechanism, which involves one or two C–H bond break, corresponding to neutral hydrogen loss mechanism, represented as:



Other ions observed by the absorption of three photons are: C_4H^+ , C_5H_2^+ , C_5H_3^+ , C_6H_2^+ , C_6H_4^+ , C_6H_5^+ , and C_6H_6^+ . Being important the formation of C_6H_4^+ , and C_6H_6^+ , represented as:

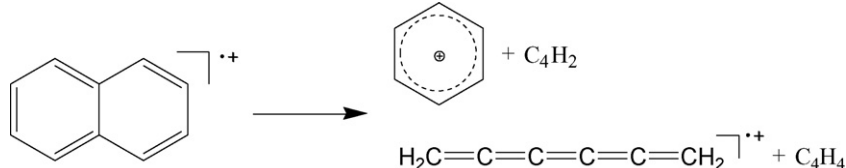


Table 1

Relative naphthalene fragmentation, per cent, at 266 nm.

Energy (mJ/pulse)	Ion group									
	CH _n ⁺	C ₂ H _n ⁺	C ₃ H _n ⁺	C ₄ H _n ⁺	C ₅ H _n ⁺	C ₆ H _n ⁺	C ₇ H _n ⁺	C ₈ H _n ⁺	C ₉ H _n ⁺	C ₁₀ H _n ⁺
1.1	0.09	1.00	3.01	6.45	4.99	11.75	4.02	12.91	2.27	53.35
4.7	0.15	4.03	14.85	20.07	13.44	16.89	4.93	10.13	1.97	13.54
11.3	0.39	8.21	24.59	19.92	12.03	11.42	4.11	7.10	2.13	10.08
14.7	0.63	11.00	28.91	18.98	10.61	9.09	3.58	6.43	2.02	8.75
19.0	0.91	14.76	34.01	17.87	8.50	6.69	2.77	5.52	1.79	7.17

Four photons open new dissociative channels that lead mainly lighter ions: C₃H_n⁺ and C₄H_n⁺. Particularly were observed the ions C₃⁺, C₃H⁺, C₃H₂⁺, C₃H₃⁺, C₄H₂⁺, C₄H₃⁺, C₄H₄⁺. Also were observed low currents of ions with five and six carbon atoms such as: C₅H⁺, C₅H₆⁺, and C₆H⁺.

Table 1 shows the changes in the ion yields as the energy per pulse was increased at 266 nm. At low energies, the parent ion dominates the ToF spectra, and it is possible to observe how its current diminishes as a consequence of the formation of new ions at higher energies (Fig. 3).

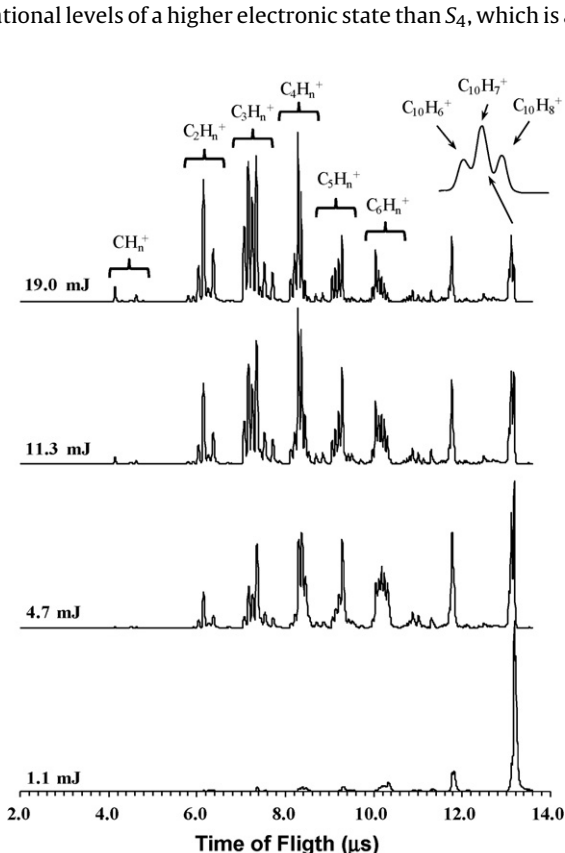
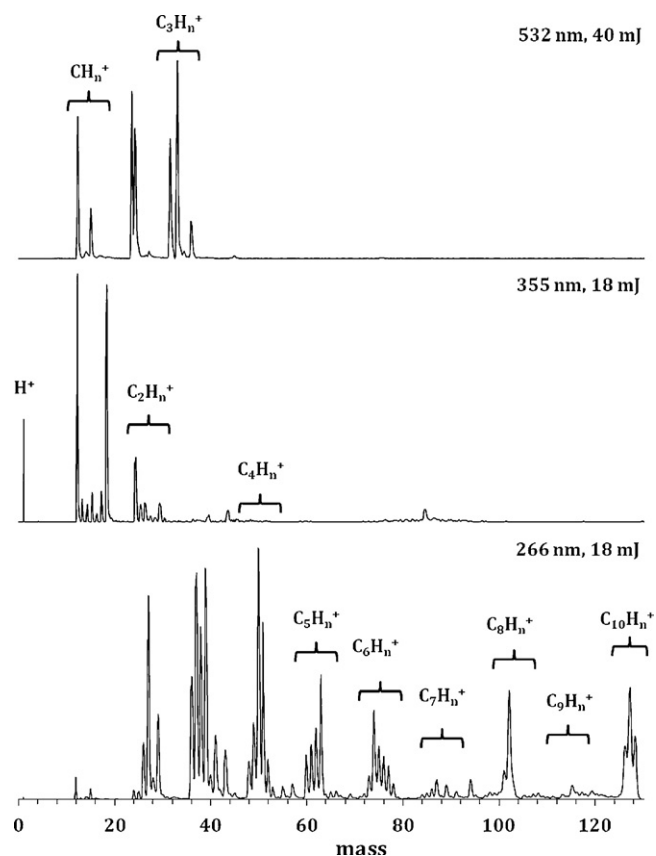
3.2. Photodissociation at 355 nm

At 355 nm the photon energy is 3.49 eV; one photon is not enough for the molecule to reach the first excited state, S₁ (step iv, Fig. 2), but with one additional photon (step v, Fig. 2), higher excited electronic states, S_n, n > 4 can be attained, all which are dissociative. Direct ionization by three-photon absorption (steps iv, v and vi, Fig. 2) was not observed at this wavelength, the molecular parent ion was not detected; the ions were formed by a dissociation–ionization process. According to Eq. (1), three energy regimes were identified: two-, three- and four-photon absorption.

With the absorption of two photons, the molecule reaches high vibrational levels of a higher electronic state than S₄, which is a pre-

dissociative state, giving rise to the observed C₂H_n⁺ (n = 0–6), C₃H_n⁺ and C₄H_n⁺ ions. The absorption of three photons lets to molecule reach a excited state related with the formation of H⁺ and CH_n⁺ (n = 0–6) ions. Unfortunately to our knowledge there is not information about the electronic structure above the S₄ electronic state, it is not possible to identify the process as resonant or not. The absorption of four or more photons was only observed in the formation of H₂⁺ ion.

The highly protonated carbon ions formation: CH_n⁺, 4 < n < 6, can be related with the formation of H⁺, since all their currents decrease as a function of the laser energy per pulse following the same trend. With regard the formation of CH₆⁺ Asvany et al. [22] proposed that the formation of CH₅⁺ is through CH₆⁺, an intermediary complex, coming from the H₂ addition to CH₄⁺. CH₆⁺ has a short life time, of 4.5 ns, explained as the result of its rapid dissociation as CH₅⁺ + H, but its structure and stability was under discussion. In the present experiments the lifetime of CH₆⁺ was derived from ToF measurements being longer than 5.21 μs. In order to explain the stability of CH₆⁺ we made the use of the density functional theory, DFT, and Möller–Plesett perturbation theory, MP_n, and three different stable geometries were found. In late 1990, *ab initio* calculations on the stability of the multiple charged ions: CH₆²⁺, CH₆³⁺, and CH₆⁴⁺, were

**Fig. 3.** PI-ToF spectra of naphthalene at 266 nm and different energies per pulse.**Fig. 4.** PI-PD-ToF spectra of naphthalene.

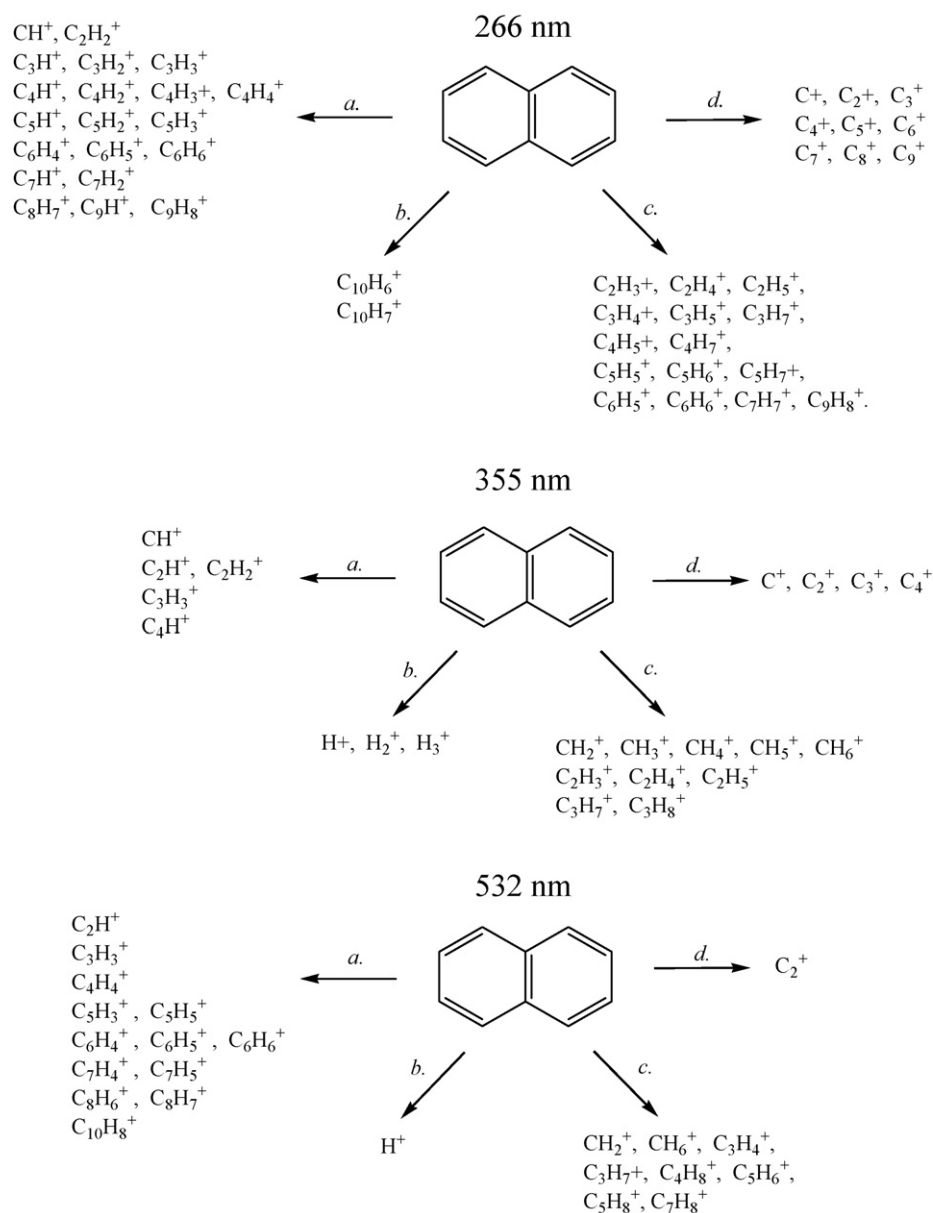


Fig. 5. Dissociation pathways of naphthalene.

reported [23,24] applying the methods mention above we perform the same calculation finding a very good agreement.

3.3. Photodissociation at 532 nm

At 532 nm, two-photon absorption allows the molecule to reach the second excited state, S_2 (steps *vii* and *viii*, Fig. 2); the absorption of additional photons lets the formation of H^+ , CH_n^+ , C_2H_n^+ , C_3H_n^+ , and C_5H_n^+ ions. The very low H^+ ion current detected, here, suggests that this dissociative channel is not energetically favorable, and H^+ formation come from the C–H dissociation from the neutral molecule which is agreement with the reported values [25,26]. The number of photons required to the naphthalene molecular dissociation at this wavelength is four (step *x*, Fig. 2), but no parent ion was observed, at this wavelength the observed ions follow a dissociation–ionization regime.

From the behavior of the relative ion currents as a function of the energy per pulse it was observed that the ion groups:

C_3H_n^+ and C_4H_n^+ , were the most abundant. The first group, C_3H_n^+ , shows high ion currents at energies per pulse lower than 50 mJ ($3.20 \times 10^4 \text{ MW cm}^{-2}$), decreasing as the energy per pulse increases. While the formation of C_4H_n^+ ions was most favorable at energies per pulse higher than 50 mJ. This fact can be an indication that the absorption of higher number of photons depends on the energy per pulse, as well the possibility of that a resonant photon absorption processes take place, which mediate the formation of a particular ion. At this wavelength the detected ions come from a dissociation–ionization process requiring a lower number of photons, below than the required to the ionization.

Comparative ToF-MS of PI and PD of naphthalene are 266, 355, and 532 nm are presented in Fig. 4.

3.4. Identified dissociation pathways

Fig. 5 shows a scheme of different mechanisms (a–e) proposed for the formation of the detected ion products.

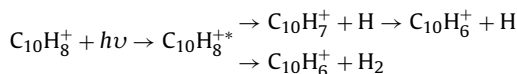
3.4.1. Simple dissociation, a

This ion group constitutes the most abundant type of ions observed in the MPI and MPD of naphthalene, but they are not responsible for high ion currents.

3.4.2. Hydrogen loss, b

The opening of one of the dissociative channels from the neutral or ionized molecular parent ion results in the formation of atomic hydrogen or H^+ and other ionized molecular systems such as H_2^+ and H_3^+ . An alternative mechanism for forming H_2^+ can be the recombination of neutral hydrogen produced by the dissociation of the C–H bond and one proton.

With 266 nm laser radiation, H^+ , H_2^+ and H_3^+ were not detected, however $C_{10}H_7^+$ and $C_{10}H_6^+$ deprotonated molecular ions were observed as the laser pulse intensity was increased; as shown in Fig. 6. Those ions could be formed by neutral hydrogen loss from the molecular ion; Van-Oanh et al. [10] had proposed the sequential deprotonation of fluorene leading to $C_{10}H_6^+$ this supposition can be extended for naphthalene. However there is another deprotonation way to produce $C_{10}H_6^+$, by losing H_2 , a concerted dissociative process, Jolibois et al. [27]:



In the present experiment, both cases were observed (Fig. 6), the total parent ion monotonically decreases as the energy per pulse increases, up to 11 mJ were there is a change on the tendency to decrease more abruptly, whereas $C_{10}H_7^+$ current increases monotonically and around the 7 mJ per pulse ($6.47 \times 10^3 \text{ MW cm}^{-2}$) the ion current becomes flat. In the case $C_{10}H_6^+$ ion current it increases almost linearly as the energy per pulse increases up to around 7 mJ were a second region for the increase was observed. The two different regions, shown for the decrease of $C_{10}H_8^+$ and the formation of $C_{10}H_6^+$ can be attributed to the sequential and concerted hydrogen lost mechanisms respectively.

At 355 nm considerable ion currents of H^+ , H_2^+ were detected, with three and more than four-photon absorption, respectively, they supply enough energy for the C–H bond to break, as have been observed in previous experiments [28–30]. The present results may be attributed to that at 355 nm the molecular dissociation occurs through a predissociative state with further C–H bond breaking.

At 532 nm, very low ion currents of H^+ were detected; and it is not an important dissociative channel.

3.4.3. Hydrogen transposition and formation of highly protonated ions, c

In general, a low atomic H/C ratio characterizes the PAHs; an increase in the fused ring number lowers the H/C ratio, being 0.8 the value for naphthalene. Ions with high H/C values cannot be produced by direct dissociation, but by hydrogen transposition.

At 266 nm, only $C_2H_3^+$, $C_2H_4^+$, and $C_3H_5^+$ were detected, and they do not constitute important dissociative channels.

At 355 nm, there is a considerable hydrogen transposition resulting in the production of CH_n^+ , $1 < n < 6$, ion species, with a predominance of odd number of hydrogen atoms. This phenomenon has not been observed in previous photodissociation experiments with methane and other small hydrocarbons. In the ToF mass spectra, the ion with m/z 18 could be assigned to CH_6^+ , C_2^{2+} and H_2O^+ ions. Isotopic analysis of the relative abundances of ions $M+1$ and $M+2$ let to distinguish between them. In the ToF spectra the ion m/z 18.5 that could correspond to the isotope $M+1$ for the C_2^{2+} ions was not detected, which in turn lead to eliminate this ion. The relative abundances from ToF spectra for $M+1$ and $M+2$ ions was calculated and compared with natural isotopic abundances for each

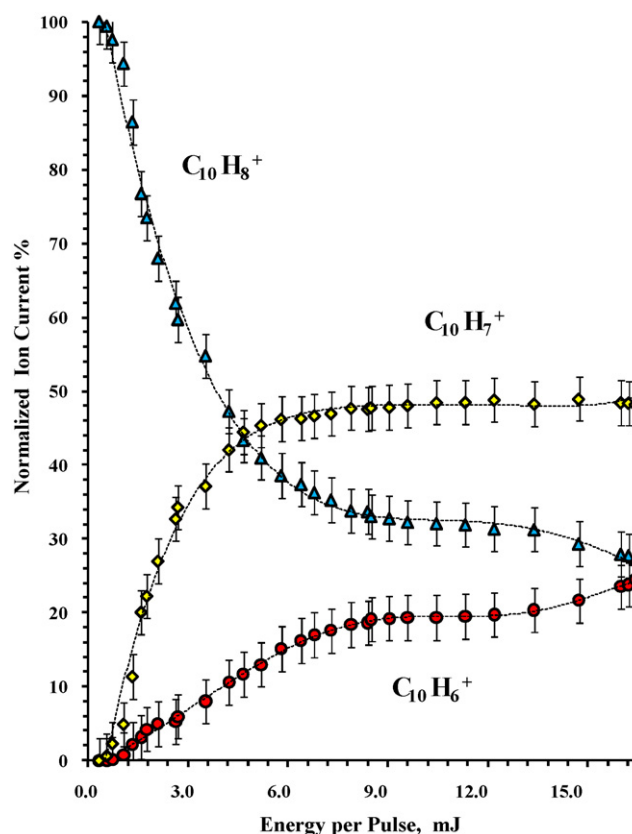


Fig. 6. Deprotonation of molecular ion as a function of energy per pulse.

value for CH_6^+ and H_2O^+ ions, lead us to conclude that the ion with m/z 18 is CH_6^+ . As it has been pointed out there are previous experimental and theoretical reports on the structural stability [31] and spectroscopy [32,33] of the CH_n^+ , $n=1-5$, ions, and their properties have been well established. To our knowledge, there are no previous reports on the characteristics of the CH_6^+ ion. It [22,34] has been proposed that CH_6^+ appears previous to the formation of CH_5^+ through, the H_2 addition to CH_4^+ . The short life of CH_6^+ , is explained as the result of its fast dissociation leading $CH_5^+ + H$. In our experiments CH_6^+ was detected and its lifetime was derived from ToF, been longer than 5.21 μs , even though its structure is still under discussion.

At 532 nm, CH_2^+ , $C_3H_4^+$, $C_3H_7^+$, $C_4H_8^+$, $C_5H_6^+$, $C_5H_8^+$, and $C_7H_8^+$ were detected, and the existence of hydrogen transposition is clear; the ratio H/C is higher than one in all cases.

3.4.4. Total deprotonation and formation of carbon clusters, d

The formation and detection of carbon clusters from polycyclic aromatic hydrocarbons such as from naphthalene confirm their structural stability. The cluster formation may not occur from a single dissociative process where the hydrogen atoms are simultaneous eliminated. According with previous [10] the results, a most adequate mechanism is the step by step hydrogen loss. In our experiments, at 266 nm, carbon clusters with two to eight carbon atoms were detected. At this wavelength, the ions are the result of molecular MPI following dissociation. Different results were obtained at 355 nm: where C^+ was the main product, and clusters with two, three, and four carbon atoms were also observed, but at very low ion currents. At 532 nm only C_2^+ was detected, and it is the principal product of molecular dissociation of naphthalene at this wavelength and it can be formed from a predissociative state reached by four-photon absorption.

4. Conclusions

The multiphoton ionization and multiphoton dissociation of naphthalene has been studied using a ToF technique combined with a laser and molecular jet, in order to investigate the effects of the wavelength and intensity on the different mechanisms that lead to the wide variety of ion products. The absorption up to four photons is possible at the intensities used here. Five different pathways were identified: simple dissociation, hydrogen loss, total deprotonation, hydrogen transposition and formation of double-charged ions. There are marked differences in the results obtained at 266, 355, and 532 nm.

At 266 nm, the resonant absorption of two photons provides the energy to reach an ionized state of the molecule. The formation of the molecular parent ion is very sensitive to the radiation intensity; small increments allow the parent ion to absorb additional photons, which can open new dissociative channels to form deprotonated parent ions, $C_{10}H_7^+$ and $C_{10}H_6^+$, or ions with a lower number of carbon atoms. In this case, molecular ionization–dissociation is a ladder-switching mechanism. At 355 nm, the shape of ToF spectra changes dramatically as a consequence of two-, three- and four-photon absorption: with two photons, the molecule reaches a higher vibrational predissociative state of S_4 , leading to the formation of ions by a simple dissociative process; the absorption of a third photon acts in favor of the formation of high ion currents of H^+ and CH_n^+ . Also at 355 nm, the formation of higher protonated carbon ions was detected, especially CH_6^+ , which have not been widely investigated. The atomic composition of the 18 m/z ion was unambiguously assigned by isotopic analysis and a distinction of CH_6^+ from C_2^{2+} and H_2O^+ ions is definitive. In the present study its mean life was measured being of the order of 5.21 μs . At 532 nm, processes of the order of more of four were detected, with the formation of ions with one to four carbon atoms in their structure, as the result of dissociative processes from high vibrational predissociative electronic states: S_2 by two-photon absorption, follow by ionization by two-photon additional absorption. At this wavelength parent molecular ion and high protonated structures were not observed. Some of our results are in good agreement with previous data reported.

Acknowledgements

The authors wish to express their thanks for the financial support of DGAPA grants IN-109407, IN-108009, CONACYT 24929 and 82521, as well as for the technical support of A. Gonzalez.

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