Carbon/hydrogen clusters \([C_nH_x]^+\) formation from laser irradiation of coronene

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Abstract. This article presents the photo induced dehydrogenation of a cooled molecular jet of coronene, exposed to 266 nm laser radiation. Using unfocused laser radiation of 1064 nm, synchronously coupled with the ionization laser pulses, a system recently developed. Molecular beams were produced by laser desorption of coronene. Analysis of the photoproducts made by time-of flight mass spectrometer showed that a wide variety of ionic species were formed; more than 300 different species were observed. The results showed carbon clusters \(C_n^+\) with \(n\) up to 24 as well as carbon/hydrogen clusters \(C_nH_x^+\) with masses higher than 300 m/z. The effect on the laser irradiance on the formation of different ions, in the rage from \(10^9\) W/cm\(^2\) to \(10^{10}\) W/cm\(^2\), is discussed as it is reflected on the evolution from the big ions to the smaller ones.

1. Introduction
The polycyclic aromatic hydrocarbons, PAH, constitute a family of compounds with a molecular structure base of carbon and hydrogen, characterized by \(sp^2\) hybridization of a carbon atom, and delocalization of electrons \(\pi\) type. The broad spectrum of applications and their spectroscopic characteristics makes them very attractive for study. PAH are the main compounds present in crude oils and their heavy fractions. In nanotechnology, they are suggested as electric conductors by the production of molecular wires, [1] and in the case of astrophysics, they are considered to be carriers of the ubiquitous aromatic infrared bands observed at different wave lengths from interstellar molecular clouds. They may play a major role in the physics and chemistry of photo dissociation regions of the interstellar media, which has motivated a major area of studies of their properties [2-5]. In general PAH are also considered to be an important component of the extraterrestrial carbon materials. It has been proposed that many diffuse interstellar bands can be identified as result of \(\pi-\pi^*\) transitions of dehydrogenated coronene \((C_{24}H_{x}^+)\) in the IV-VIS region or vibrational emissions in the infrared. This explains why dehydrogenated coronene is studied in order to model the evolution of PAH in photodissociation regions.

Different measurements of dehydrogenation of coronene and carbon clusters formation have been reported using, for instance Xe lamp, [6] electrons [7], or eximer laser pulses [8]. Dehydrogenated
cations of coronene are supposed to be responsible of many diffuse interstellar bands [9], excellent new models of PAH chemical evolution [8] relay on the available molecular data such as the hydrogenation state of coronene ion.

In an attempt to contribute to the characterization of the response of coronene molecules to multiphoton interactions, an experimental system based on desorption preparation of a particular PAH coupled with a R-TOF (Reflectron Time of Flight) mass spectrometer has been developed and the resulting ions have been characterized. When these molecules were exposed to a laser light of 266 nm, a considerable number of ion products were observed. These ion products included type $C_n^+$ carbon clusters with $n$ from 1 up to 24 and carbon/hydrogen clusters $C_nH_x^+$ with masses higher than 300 m/z.

2. Experimental

A system for desorption and ionization of solid samples using laser radiation of 1064 nm, and 266 nm respectively was constructed. Desorption processes took place in a chamber at $10^{-3}$ torr seeded with helium gas although, other inert gases can be used if desired. Low energy laser pulses of 1024 nm (Nd:YAG fundamental) were used to desorb the sample of coronene. Vapors of coronene were adiabatically expanded through a cone with pin hole of 0.2 mm into a high vacuum chamber at 10^-8 torr. As a consequence of the expansion, molecules were rotationally and vibrationally cooled. The molecular jet was collimated using a skimmer of 0.2 mm previous to access the ionization region. The ionization processes were produced by multiple photon absorption using laser radiations of 266 nm, synchronously coupled with the desorption step. Delay times for desorption and ionization laser pulses were experimentally optimized to obtain the maximal total ion current, in the present case were between 20-30 microseconds. Ions resulting from ionization processes were extracted and accelerated using two continuously polarized plates at 4500 and 3500 volts respectively, with an electrolytic cooper mesh to allow the positive and negative ions to travel in opposite directions. The positive ions formed by the laser interaction, were analyzed using an R-ToF mass spectrometer analyzer; reaching resolutions up to 7000. Figure 1 shows the experimental apparatus. As shown, ions were detected using a microchannel plate detector; current signal was preamplified and digitized using a picoammeter.

![Experimental apparatus](image)

3. Results and Discussion

The first step is to identify well known masses, in present experiment $H^+$ and $C^+$, and a reasonable combination of both. The correct position of each maximum on the time of flight spectrum is set by adjusting a Gaussian to each one. By using the positions of maxima obtained, a second degree curve is generated, plotting the masses (maximums) versus time of flight. Then it is obtained the equation that determines the relationship between the flight time of an ion and it’s mass. Twenty mass spectra for
different intensities of radiation were measured. Figure 2 shows one of the time of flight spectrum for a laser intensity of $2.70 \times 10^{10}$ W/cm².

![Figure 2 R-ToF mass spectra.](image)

Figure 3a and Figure 3b focus on light masses, while Figure 3c focuses on masses around 300 amu displaying the products with masses close to that of coronene molecular ion.

![Figure 3a Ion signal versus amu for ion products from 1 to 42 amu](image)

The loss of H₂ was observed at all the range of ions detected. Champeaux, et al. [11] suggested that, as a result on the ionization/fragmentation of isolated coronene by a 100-keV proton, loss of even
numbers of hydrogen atoms are evidence of dehydrogenation processes. In our case, the loss of even numbers of hydrogen atoms is observed. The H\(_2\) elimination path could be a result of hydrogen transfer from one carbon to another in two possible ways to form a -CH\(_2\) structure [12]. After this transfer a neutral H\(_2\) is formed. Other evidences of this process [11] are the detection of CH\(_2^+\) and H\(_2^+\), because the multiple pathways possible for the reaction. In the present experiment only the peak corresponding to the H\(^+\) ion was detected.

![Figure 3b](image)

**Figure 3b** Ion signal versus amu for ion products from 48 to 95 amu

![Figure 3c](image)

**Figure 3c** Ion signal versus amu for ion products from 288 to 336 amu

Results of this experiment showed that at higher laser intensities light ions predominate, while at relatively lower laser intensities greater masses are more frequent. With this, it can be inferred that light or heavy ions formations depend on the laser intensity as it was expected. This is relevant for experiments dealing with multiphoton absorption since it will facilitate the possibility to concentrate the study of certain families of ions by, knowing the laser radiance at which its appearance is more favored.

From the experimental results the relative calculated currents for groups of different range of masses are presented in Figure 4. This figure shows the relationship between the ion currents and the laser radiance for different mass ranges.
From our results it is possible calculate the number of photons absorbed, leading the formation of each of the ions. The number of photons needed to ionize the coronene was calculated and subsequently the same analysis was carried out for each particular ion. For the case of coronene ion the number of absorbed photons was 1.7 consistent with ionization energy for this molecule. Knowing the number of absorbed photons needed to produce each particular ion it is possible to propose dehydrogenation paths much more complicated than one early proposed [10] for the case were electrons are used.

![Figure 4](image)

**Figure 4.** Relative ion currents as a function of the laser radiance

### 4. CONCLUSIONS

Fully dehydrogenated carbon ions, C<sub>n</sub><sup>+</sup>, with n from 0 to 24 were produced. Carbon/hydrogen clusters C<sub>n</sub>H<sub>x</sub><sup>+</sup> were detected, some of them for the first time. The presence of masses higher than 300 suggest that coronene clusters are form during the desorption process. All the ions observed are stable. The main coronene dissociation process is hydrogen lost. The loss of acetylene was observed however it is not predominant channel as in the case of other PHA. The dehydrogenation process, via H<sub>2</sub> loss, was observed. Finally the results leave several open questions on the explanation of the resulting cations formation. In particular, processes involving multiphoton ionization provide an excellent insight into ionization and dissociation dynamics. Understanding such mechanisms will be an advance in the study of PAHs important in many fields ranking from health to astrophysics.

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