

Multiphoton ionization of naphthalene clusters at 266 nm

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In this work we analyze the photoionization of Naphthalene clusters: dimer, trimer and tetramer when radiation of 266 nm from Nd:YAG laser at intensities up to $10^9 \text{ W}\cdot\text{cm}^{-2}$ was used, in the range from 0.5 to 20.0 mJ per pulse. The clusters were formed by thermal desorption of a sample at 373 K and translational and vibrationally cooled in a jet by adiabatic expansion. At these experimental conditions the ionization processes were accomplished in the multiphoton regime by two photon absorption. A complete identification of fragment ions arising from the clusters was carried out, using a linear time of flight mass analyzer, ToF-MA. Evidence of proton and carbon atoms migration between molecular units in the clusters was observed, and the ions $\text{C}_{10}\text{H}_8\text{-H}^+$ and $(\text{C}_{10}\text{H}_8)_2\text{-H}^+$ were detected. The analysis of ion yield of clusters as a function of the energy per pulse showed that the dimer stability is higher than trimer and tetramer structures. The efficiency of clusters formation, and ionization processes were analyzed as a function of different carrier gases, CG: He, Ne, Ar, Kr and Xe. With He and Ne as CG, the ion yield decreases comparatively when Ar, Kr, Xe or not CG were used.

Keywords: Naphthalene; photoionization; molecular clusters; PAHs.

En el presente trabajo analizamos la fotoionización de clústeres de Naftaleno: dímeros, trímeros y tetrámeros, usando radiación de 266 nm obtenida del cuarto armónico de un láser Nd:YAG a intensidades del orden de $10^9 \text{ W}\cdot\text{cm}^{-2}$, en el rango de 0.5 a 20.0 mJ por pulso. Los clústeres se formaron por desorción térmica de la muestra a una temperatura de 373 K y enfriados translacional y vibracionalmente por expansión adiabática en un jet molecular. A estas condiciones experimentales los procesos de ionización se llevaron a cabo en el régimen multifotónico por la absorción de dos fotones. Los iones resultantes de los clústeres fueron caracterizados mediante el uso de un analizador de masas de tiempo de vuelo tipo lineal, ToF-MA. Se observó evidencia de procesos de transferencia de átomos de hidrógeno y carbono entre las unidades moleculares en los clúster y se detectaron los iones $\text{C}_{10}\text{H}_8\text{-H}^+$ and $(\text{C}_{10}\text{H}_8)_2\text{-H}^+$. El análisis de las corrientes iónicas de los diferentes clústeres en función de las energías por pulso láser utilizadas, mostró que el dímero es más estable que las unidades de trímero y tetrámero. Las eficiencias de formación de los clústeres y los procesos de ionización se analizaron en función de los diferentes gases acarreadores, CG, utilizados, He, Ne, Ar, Kr, Xe. Utilizando He y Ne como CG, la eficiencia iónica decrece comparativamente con Ar, Kr, Xe y cuando no se utiliza el gas acarreador.

Descriptores: Naftaleno; fotoionización; clúster moleculares; hidrocarburos aromáticos policíclicos.

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1. Introduction

The polycyclic aromatic hydrocarbons, PAHs, have received special attention due to several interesting chemical and physical properties; and as carcinogenic compounds. They can form clusters by $\pi - \pi$ stacking, a well known electron interaction correlation mechanism [1, 2]. This phenomenon has been observed in homo- or hetero- clusters, produced under specific experimental conditions [3]. Phenomena as charge transfer, excitonic and excimer interactions have been evidenced from spectroscopic measurements [4,5]. The possibility of different geometrical arrangements has been reported in an extensive series of papers where different spectroscopic techniques have been used, *i.e.* high vacuum fluorescence [6,7], time resolved fluorescence at pico and femtosecond resolution [8,9], trapped molecules in inert matrices as neon and argon [10,11,12], and cavity ringdown experiments [13,14]. In astrophysics, several years ago, the PAHs, single neutral and charged molecules and its clusters have been proposed as molecular systems responsible for the infrared emissions from interstellar media; these emissions are known as diffuse interstellar bands, DIBs [15]. This funda-

mental hypothesis has received special attention in the atomic and molecular physics, and a large series of experiments had been carried out to obtain its spectroscopic properties [16,17], to support the observations, and therefore an intense theoretical work [18,19] has been done.

Van der Waals interactions with inert gases such as He, Ne, and Ar had been analyzed and spectroscopic properties measured, and evidence of molecular clustering of PAHs has been obtained [20,21]. Unfortunately, from a group of combined experiments the elucidation of the structure of clusters of PAHs is really difficult as in the case of Naphthalene dimer [22]. Nevertheless, for trimer arrangement, a symmetry C_{3v} is in good agreement with spectroscopic and theoretical data [23,24]. Clusters were also studied using time resolved fluorescence and the evidence of the stability of dimer and dimer core in higher clusters was discussed [25].

Extensive works have been directed to understand the ionization and dissociation dynamics at different intensities, up to $10^7 \text{ W}\cdot\text{cm}^{-2}$: soft ionization and high molecular ions yields were observed. Increasing the intensity up to $10^9 \text{ W}\cdot\text{cm}^{-2}$, the ionization occurs, and a progressive molecular fragmentation is observed [26]. In our previous experi-

ments with single molecules this phenomena was observed at intensities up to $10^{10} \text{ W}\cdot\text{cm}^{-2}$ [27,28].

Theoretical analysis of PAHs neutral clusters and its cations had been carried out using *ab-initio* calculations [19,22]. New theoretical models and interaction potentials have been developed to obtain the best quality of theoretical results [29,30]; the proposed interaction potentials include van der Waals interactions of PAHs with inert gases such as He, Ne and Ar. Interaction energies between Naphthalene and inert gases, CGs, have been calculated, as well as PAHs homoclusters in deferent geometrical arrangements [22,31,32].

In this work, a molecular jet of Naphthalene and their clusters were produced by adiabatic expansion of sample vapors in a high vacuum chamber, 10^{-8} torr. Clusters are the results of the thermal desorption of the sample previous to the adiabatic expansion. Different CGs were used and their effects were analyzed. The cooled molecular jet interacted with laser radiation of 266 nm, 4.66 eV, from the fourth harmonic of an Nd:YAG laser at intensities from 10^8 up to $10^9 \text{ W}\cdot\text{cm}^{-2}$. The ions resulting from radiation-molecules or cluster interactions were analyzed using a ToF mass analyzer. The ions in the ToF patterns resulting from clusters photoionization and dissociation were fully identified. Naphthalene clusters with up to four molecules per cluster were identified, and its ions yields measured as a function of the energy per pulse. The effect of CGs on the clustering formation was analyzed and interpreted on the basis of Naphthalene-CG interaction forces and number of CGs atoms which can interact with cluster unit.

2. Experimental

The experimental setup of photoionization experiments was previously described [26]; only a brief description will be given here. A thermal chamber with Naphthalene was heated up to 398 K to increase vapor pressure of the sample. It was coupled with an access to insert the different CG. Pressure in thermal chamber was maintained at 40 psi by increasing the pressure of CG. Vapors of sample were adiabatically expanded in a high vacuum chamber through a pulse valve, opening synchronously with laser pulses; following the expansion a skimmer was placed to produce a translational cooled molecular jet. Background pressure in the chamber was maintained close to 10^{-8} torr by two turbo molecular pumps and reaching pressures close to 10^{-6} torr when valve was opened.

The molecular jet interacts with photons in a point located between two parallel plates separated by 1 cm, continuously polarized at 5.0 and 3.5 kV, respectively. Ions drive into a 1.0 meter long field free region in a Wiley-McLarent type ToF mass analyzer. Ion dispersion was suppressed using two sets of parallel plates located at the starting point of driven region and polarized at 30 volts. Ions were separated in time in accordance to the mass-charge ratio and detected using a

channeltron detector; signal from the detector was preamplified and digitized using a multichannel analyzer EG&G Ortec. The signal was sampled using 6000 channels with a time width of 5 ns; 5000 shots from laser were acquired and added to finally obtain the ToF spectra.

Laser radiation was obtained from the forth harmonic, 266 nm, of an Nd:YAG laser (Spectra Physics, GCR170) at a repetition rate of 10 Hz. Laser radiation was focused into the interaction regions using a lens of 20 cm focal distance. Thirty ToF spectra were taken at different energies per pulse in the interval from 0.5 to 15 mJ. With the focal area and energies per pulse used here, radiation intensities are in the order of 10^8 - $10^9 \text{ W}\cdot\text{cm}^{-2}$.

3. Results and discussions

3.1. Naphthalene photoionization

In a previous report, we discussed the photoionization and photodissociation of Naphthalene, in the multiple photon absorption regimes at wavelengths of 532, 355 and 266 nm [33]. Laser radiation of 532 and 355 nm at intensities of up to $10^{10} \text{ W}\cdot\text{cm}^{-2}$ produce the molecular dissociation previous to the ionization; at these experimental conditions molecular parent ions were not observed. At 266 nm, the absorption of one photon lets the molecule reach an intermediate state in resonant conditions, followed by the absorption of a second photon which makes feasible the ionization processes. Progressive increments in laser intensity, from 10^8 to $10^9 \text{ W}\cdot\text{cm}^{-2}$, produce dramatic changes in ToF spectra appearance.

Single Naphthalene molecules exhibit an electronic structure which has been characterized [33]. But the formation of homo- or hetero-clusters with single atoms or molecules perturbs its electronic structure. As had been previously reported [34,35], from absorption and emission spectroscopy, Naphthalene neutral molecules and their cations trapped in inert matrices, Ne and Ar, show three different absorption bands, the first: ${}^1B_{3u}(S_1) \leftarrow X^1A_g(S_0)$, very weak, was observed at 309.2 nm in Air and 307.6 nm in Ne; while in He it was observed by Even [36], appearing at 312.3 nm in Ar; the second, band II, attributed to a transition

$${}^1B_{2u}(S_2) \leftarrow X^1A_g(S_0),$$

appears at 272.5 and 268.56 nm in Ar and Ne, respectively; the absorption band III,

$${}^1B_{3u}(S_3) \leftarrow X^1A_g(S_0),$$

characterized by an strong absorption at 216.2 and 211.6 nm in Ar and Ne, respectively. The second band is the responsible for the 266 nm photon absorption, which correspond to a molecular vibration resulting from vibrational couplings [$\nu_4(a_g) + \nu_8(b_{1g})$]; $2\nu_7(b_{1g})$; $2[\nu_8(b_{1g}) + \nu_9(a_g)]$ [36,37].

Effective interactions with inert CGs perturb the molecular electronic structure; this perturbation includes energy levels and vertical ionization energies [37,38]. The interactions

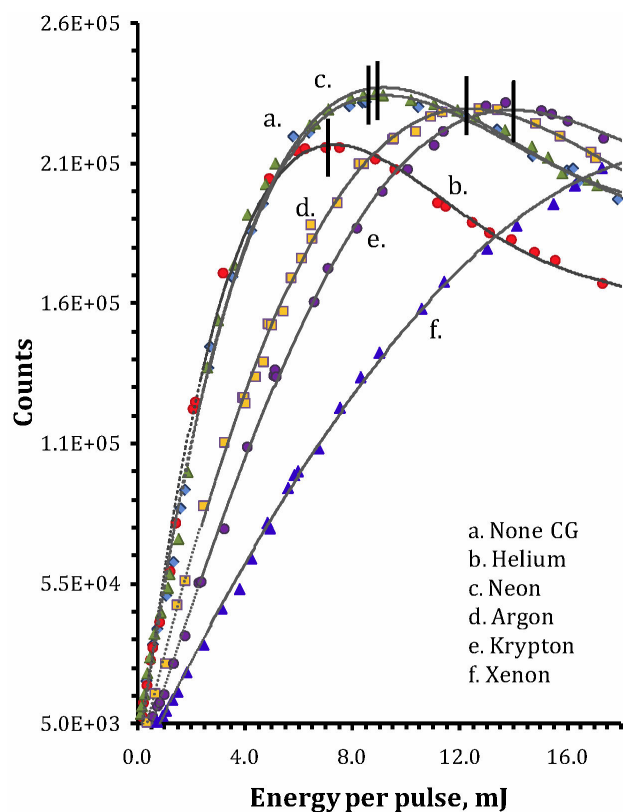


FIGURE 1. Total Ion Currents Single Molecule Naphthalene Photoionization at 266 nm

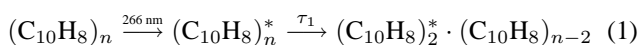
can be considered as the result of dispersive and repulsive forces. When van der Waals clusters with inert gases are formed the gases can form a solvation sphere around the Naphthalene molecules, which produce a shield effect over the energy levels of molecule. When He or Ne interact the dispersive interactions do not contribute significantly because this term is proportional to the atom polarizability, low in He and Ne. When the interaction occurs with heavy atoms, such as Kr and Xe, the interaction is dominated by dispersive contributions; thus, the molecular environment is strongly perturbed and spectral shifts are observed in the electronic spectra, as it was earlier mentioned. When Ar is used as CG, its interaction with Naphthalene molecules is established by a balance between dispersive and repulsive interactions, and this case is the breakpoint between low and high mass CGs, and also shows a similar behavior as when CG was not used. When the total ion currents, resulting from photoionization of a Naphthalene single molecule, are plotted as a function of the energy per pulse, Fig. 1, the decrease as polarizability of CG increases is observed. Also, as the CG increases in size, from Ar to Xe, ion currents decrease, resulting from an effective interaction which can perturb the efficiency of the processes; the gases act as shielding layers which produce a decrement in the absolute cross sections of two photon absorption processes.

3.2. Naphthalene clusters photoionization

Naphthalene clusters excitation is a competitive process between different electronic states, which involve single molecules and clusters. Energy transfer times and charge resonance stabilities determine the most probable channel to energy relaxation, ionization or dissociation of such clusters. In our experimental conditions, at 266 nm laser wavelength, the single molecule and clusters can reach a vibrational level of electronic state [37] by one photon absorption.

For all the clusters studied (n 2-4), the ionization occurs well below the monomer ionization potential of 65664 cm^{-1} (8.14 eV) [39], the absorption of two 266 nm photons supplies an energy higher than the ionization potential. These excesses of energy can be attained for clusters to reach excited vibrational levels either or higher excited electronic states. Figure 2 shows the ToF spectra of Naphthalene clusters as contour plots, where the effect of CGs can be observed, the ToF is displayed in microseconds in the horizontal scale, from 13.0 to $30 \mu\text{s}$, while the vertical scale corresponds to the energies per pulse in mJ. Colored scale represents the absolute measured ion current; it changes from few counts, colored in blue, to ion currents higher than one hundred counts, colored in red. The identification of the ions in the ToF plot was performed for every signal corresponding to a particular mass of ion. Signals from a single naphthalene molecule and their fragments were not displayed in contour plots, being detected at ToFs lower than $13.80 \mu\text{s}$. Signals from dimmers, ion parent and their fragments were detected at ToFs in the interval between 13.80 and $18.53 \mu\text{s}$, the dimmer parent ion being detected at $18.53 \mu\text{s}$. Trimmer and their ions were detected at ToFs in the range of 18.56 to $22.64 \mu\text{s}$. Signals detected at ToFs higher than $22.70 \mu\text{s}$ correspond to tetramers and possibly to pentamers but have not been analyzed because they were detected at very low ion currents. With and without CGs, higher ion currents of the dimmer were observed showing its stable structure. From Fig. 3 we can observe that a relative population of dimmer reaches up to 46 per cent, close to 0.2 mJ per pulse, $5.0 \times 10^9 \text{ W} \cdot \text{cm}^{-2}$, when heavy CGs were used, and 10 to 16 per cent when lighter CGs were employed. It is notorious that heavy CGs act in favor of the formation of dimmers and trimmers, been detected higher relative ion currents at low energies per pulse and diminishing as the energy was increased. The transition from trimmer to dimmer is not favored by energetic considerations. The transition from trimmer to dimmer is possible due to molecular rearrangement. In the tetramer the structure of cluster is more complicated, and a stable structure has not been postulated.

Formation of different clusters can be explained on the basis of the work from [25], a series of structural changes occur in the clusters by photon absorption; it consists in the formation of a stable dimmer type core structure, after a characteristic reordering time, path 1.



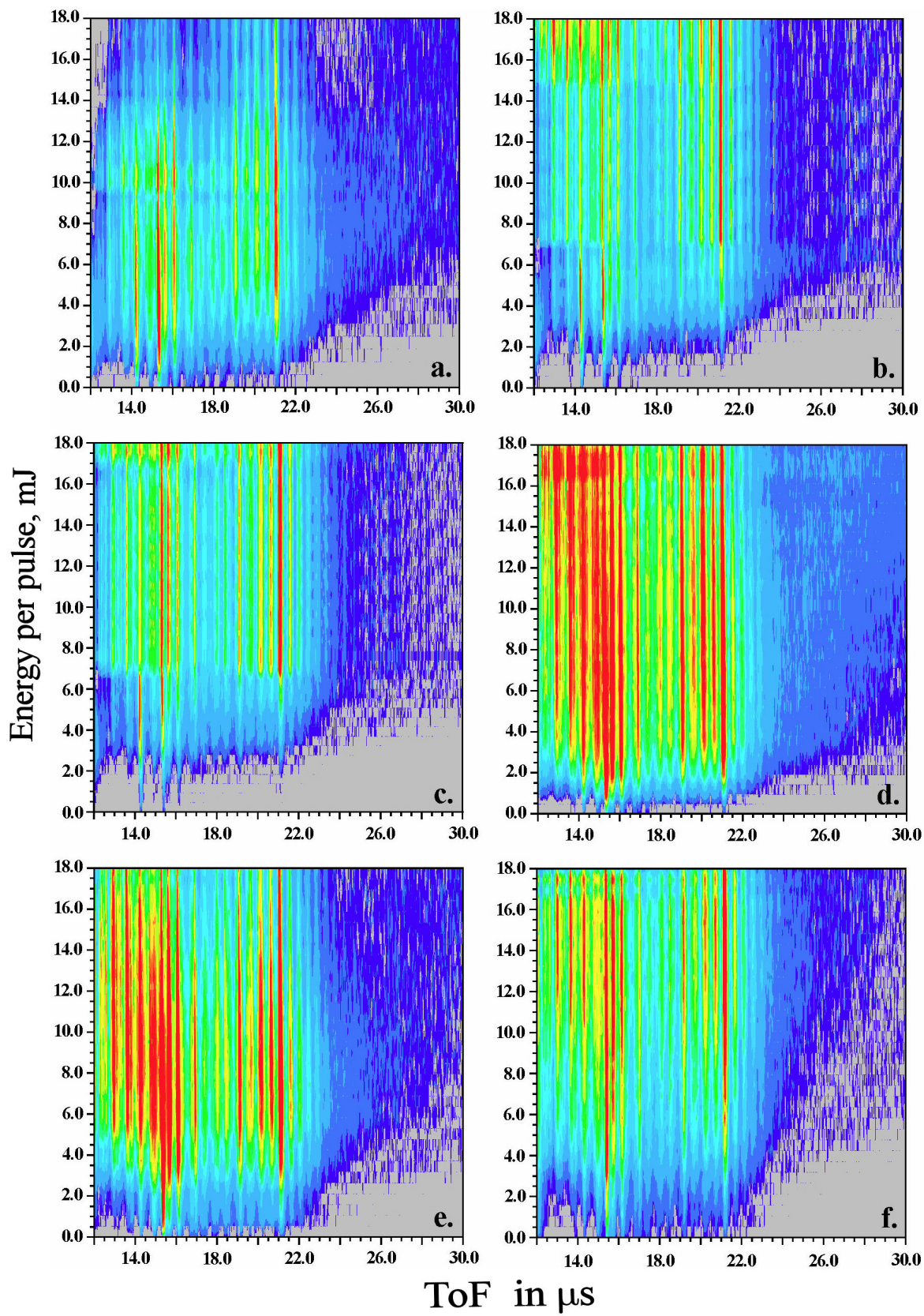


FIGURE 2. Contour Plot Photoionization ToF-Spectra of Naphthalene Clusters at 266 nm. a) Without CG, b) Helium, c) Neon, d) Argon, e) Krypton, f) Xenon.

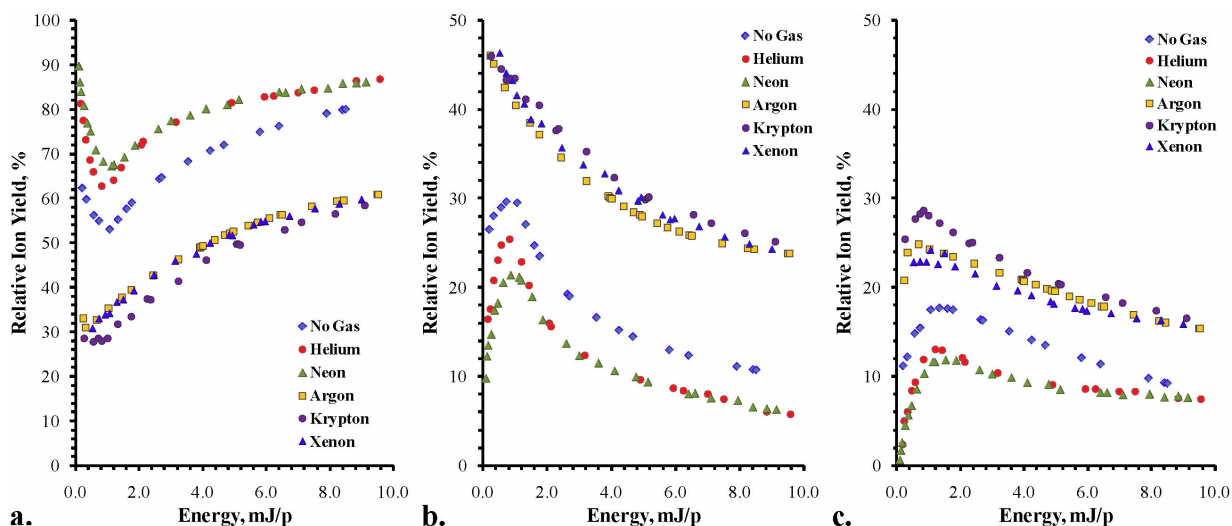
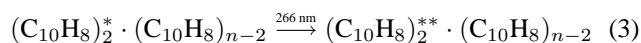
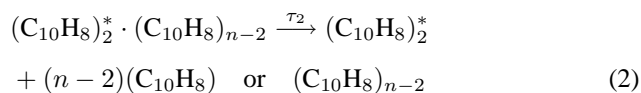
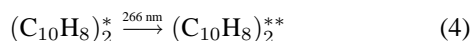


FIGURE 3. Relative Ion Current for Dimmer and Trimmer in ToF spectra.

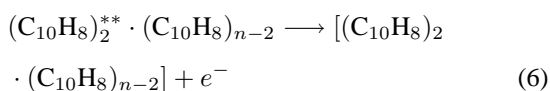
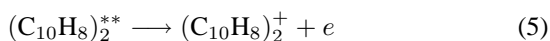
That resulting cluster, in excited state, can either dissociate after a characteristic time, path 2, or absorb one additional photon, path 3.



If path 2 takes place the dimmer can absorb additional photons and reach and superexcited state, path 4.



Follow a sequential mechanism, the super excited clusters $(\text{C}_{10}\text{H}_8)_2^{**}$ or $(\text{C}_{10}\text{H}_8)_2^{**} \cdot (\text{C}_{10}\text{H}_8)_{n-2}$ losses an electron and produces the cluster ions, paths 5 and 6.



If n is 3 a trimer will be formed; for the case of n equal 4 the result is a tetramer. From our results, the observation of relative higher ion currents of dimmer ions and their fragments supports the supposition of a stable dimmer core structure in higher size clusters, since those can in turn be dissociated as the energy per pulse increases.

3.3. Effect of carrier gases

The interaction energies of Naphthalene in clusters have been calculated using different theoretical models [22, 31]. From a theoretical point of view, the interactions of inert gases with a Naphthalene single molecule are dominated by repulsive and dispersive forces, as mentioned in a previous section. Dispersive forces are important when the interaction occurs with

Ar, Kr and Xe, but poorly notorious with He and Ne, because the repulsive forces are predominant and also because of the lower polarizability of these gases [32]. Experimental evidence clearly shows that the size and number of inert gases atoms interacting with the single Naphthalene molecule perturbs both the electronic structure and the electronic transition energies [11]. The increment in size of inert gas produces a red shift in the electronic spectra of several cm^{-1} , as was early mentioned.

In our work the effect of CGs was observed and this shows the evidence of the stability of the dimmer and its nature as core in clusters with higher sizes. The nature of the interactions of CGs with single molecules and clusters of Naphthalene was observed in the ion yields of dimmer and trimer as a function of the energies per pulse, as it is shown in Fig. 3. With He and Ne it was observed that lower relative ion yields, 10 to 16 per cent, for dimmer appear at few mJ per pulse, 0.2 mJ, reaching a maximum as the energy per pulse was close to 1.6 mJ, at higher energies per pulse the ion current decreasing progressively up to close to 6 per cent. When Ar, Kr and Xe were used, the maximum in ion yield was reached at lower values of energies per pulse, 0.2 mJ, indicating that the formation of dimmers is more efficient at these energies, decreasing progressively as the energies per pulse were increased up to 10 mJ per pulse, not detecting a maximum as in the case of He and Ne. If the CGs were not used the total ion currents of dimmer show a similar behavior as He and Ne, the result of the soft interactions with this CGs and the low perturbation of the dimmer electronic structure. The decreasing behavior observed as the energies per pulse were increased was attributed to the absorption of additional photons, which in turn open fast dissociative channels which destroy the dimmer core structure into single molecules to form smaller fragment ions. For the case of the trimmers an enhancement of the ion currents as the size of carrier gases

increase, was also observed; whereas the maximum ion current is closely reached at the same energy per pulse, 1.0 mJ, softly decreasing close to 8 per cent with He, Ne and non CG, and 16 per cent when Ar, Kr and Xe were employed.

3.4. Dissociation pathways

In previous work [27] we report the photoionization of Naphthalene single molecules; there, we presented an analysis of dissociative pathways observed at 266 nm. At this wavelength a resonant absorption occurs and the direct ionization is possible by two photon absorption. Taking in to account the observed ions the dissociative channels were classified as: sequential hydrogen loss, total deprotonation to formation of carbon clusters, fragmentation without hydrogen transposition, and intramolecular hydrogen transposition with the formation of high protonated ions.

Here, the ionization of clusters followed by dissociation involves other dissociative channels, in ToF spectra different fragments have been observed which can result only if hydrogen transposition occurs between molecules. A single molecule coupled to carbon unit which is the result of total hydrogen elimination has also been observed. To analyze the clusters dissociation the electronic interaction in the excitation process, excitonic interactions or charge related with the cluster structure must be taken into account. Different stable arrangements are possible in the dimer case, being the parallel shape $\pi - \pi$ staking the preferential interaction. According with our previous observations in Naphthalene, the hydrogen transposition is more likely to occur in this arrangement, the proximity with the π electrons to another molecule plays in favor of it, and it is clear that the hydrogen transposition is very efficient given a protonated Naphthalene single molecule or protonated ions resulting from dimer or trimer dissociation, as it was observed.

4. Conclusions

In this paper we present the results of multiphoton absorption of Naphthalene clusters at 266 nm in the nanosecond regimen. The results had shown that in our experimental conditions with the thermal desorption, the formation of clusters was possible at least with up to four molecules per unit. Here the effect of CGs used, had been reflected on the relative abundance of clusters. With He and Ne the formation of dimers and trimers decreases comparatively as when CG was not used. But with Ar, Kr and Xe the relative population was increased, being the results characteristic of the interaction between single atoms of CGs and Naphthalene molecules in the cluster. As a consequence of interactions with CGs, the electronic structure of a Naphthalene single molecule and its cluster molecule, changes. With He and Ne a balance between repulsive and dispersive forces is established; the dispersion forces do not contribute significantly because this term is proportional to the atom polarizability, low in He and Ne. When the interaction occurs with heavy atoms, such as Ar, Kr and Xe, it is dominated by dispersive contributions; the molecular environment is strongly perturbed. The analysis of daughter ions, resulting from dissociation of cluster let us identify that hydrogen transposition between molecules in clusters effectively takes place. Total deprotonation resulting in clusters of Naphthalene and carbon ions were also detected.

Acknowledgments

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