Astronomy
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Astrophysics

Photoinduced products from cold coronene clusters

A route to hydrocarbonated nanograins?

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ABSTRACT

Free cold pure coronene clusters have been formed in a gas aggregation source and irradiated with excimer laser pulses. Analysis of the photoproducts thanks to a reflectron time-of-flight mass spectrometer showed that new ionic compounds are formed. These species may include Polycyclic Aromatic Hydrocarbons (PAHs) larger than coronene, PAH-coronene clusters, as well as coronene clusters branched with unsaturated aliphatic chains. The relevance of these results in the context of interstellar medium chemistry, and in particular the carriers of the so-called aromatic infrared emission bands (AIBs), is discussed.

Key words. astrochemistry – molecular processes – methods: laboratory – ISM: molecules – ISM: dust, extinction – infrared: ISM

1. Introduction

Polycyclic aromatic hydrocarbons (PAH's) have been proposed as a chemical family that is ubiquitous in interstellar space and is responsible for the set of mid-infrared emission bands now commonly observed at 3.3, 6.2, 7.7, 8.6, 11.3 microns from a wide variety of regions of the interstellar medium exposed to starlight (Tielens et al. 200). These regions include the diffuse interstellar medium (ISM) (Mattila et al. 1996; Chan et al. 2001; Li & Draine 2001), as well as external galaxies (Reach et al. 2000; Peeters et al. 2004). The intensity radiated through these bands, initially called UIB's (unidentified infrared bands), is very large, representing typically up to 20% of the total power radiated by interstellar dust (Li 2004). The good spectral coincidence between these bands and the C–C and C–H infrared active modes of *aromatic* hydrocarbons (hence their name AIBs = aromatic infrared bands) was recognized very early (Duley & Williams 1981). The total abundance of these "astro-PAHs" is estimated to be large enough to account for a large portion (up to 20%) of the cosmic carbon available in the galaxy (Boulanger et al. 2000; Li & Draine 2001). Two main formation mechanisms need to be invoked to explain this large abundance: (i) circumstellar chemistry taking place in the outflows of carbon-rich stars (Latter 1991); and (ii) shattering of carbonaceous dust grains

provoked by grain-grain collisions in shock-heated regions (Jones et al. 1996).

As already proposed from the beginning by Léger & Puget (1984), quickly followed by Allamandola et al. (1985), the physical processes involved in the infrared band formation mechanism rely on the internal conversion process within isolated polyatomic molecules. It allows conversion of electronic excitation, induced by starlight absorption, into vibrational excitation. The resulting hot molecules then cool down by radiating their internal energy through infrared active modes. The effectiveness of such a transient heating mechanism (Sellgren 1984) has been demonstrated by Boulanger et al. (1996, 1998), who showed that the IR flux collected in these bands is proportional to the local interstellar radiation field (ISRF). The consequence is that the AIBs carriers must be free-flying species.

Considerable progress in the understanding of these infrared features has been achieved during the last twenty years thanks to many experimental and theoretical efforts. In particular it was shown that the spectral properties of the PAH monocations provide much better agreement with interstellar spectra than do those of neutral PAHs (Allamandola et al. 1999; Langhoff 1996). Other solid phase alternative laboratory analogues have been proposed for the carriers of the AIBs, such as hydrogenated amorphous carbon (HAC) (Duley & Williams 1981), or coal grains (Papoular et al. 1996). Although some of these models are able to spectrally account

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for the observations from some particular regions (Guillois et al. 1996), many strong arguments favor the PAH model (Allamandola & Hudgins 2003), mainly the scaling of IR bands with ISRF (Boulanger et al. 1998; Uchida et al. 2000) and the local variability in the spectra (Werner et al. 2004). It is worth noting that the average size of the astro-PAHs estimated from ISO observational data is on the order of a few hundred Carbon atoms (Boulanger et al. 1998), i.e. the same size as the clusters studied in the present work.

However, despite these facts, none of the attempts to match the interstellar spectra from laboratory data, using the properties of either a single PAH (Cook Saykally 1998) or of a distribution of PAHs of different sizes (Allamandola et al. 1999; Draine & Li 2001; Verstraete et al. 2001; Pech et al. 2002), has yet been able to provide fully satisfactory agreement. Then it is quite widely accepted nowadays that some kind of hydrocarbonated "nanograins" should exist, with sizes intermediate between the PAHs, which are easily accessible to laboratory studies, and the "standard" interstellar grains (*ca* 50 nm, Li 2004).

The present paper reports the first results of a new experimental work that has been recently initiated at Orsay, aiming at the investigation of the nature and/or structure of the species which can be synthesized in the laboratory under conditions which realistically mimic the interstellar ones, i.e. cold gas phase UV-irradiated species. It has already been suggested that, in cold environments, the sticking of PAH molecules onto grains and their photo-evaporation from grain surfaces could be important mechanisms controlling their abundance (Boulanger et al. 1990; Bernard et al. 1993). But it is also plausible that free-flying PAH clusters are also present under such conditions. In this context it is interesting to note that, in a recent observational study, Rapacioli et al. (2005a) suggested that the AIBs carriers could involve PAH clusters, which could contain a few hundred carbon atoms.

The very stable coronene molecule, $C_{24}H_{12}$, the first compact *peri*-condensed PAH above pyrene $C_{16}H_{10}$, has long been considered as a good laboratory prototype of interstellar PAHs. Indeed we succeeded in generating gas-phase pure cold coronene clusters containing up to 13 coronene molecules, i.e. 312 carbon atoms. When these clusters were exposed to laser light at $h\nu = 4$ eV, we observed a rich photo-induced chemistry leading to the formation of new covalently bound species, whose size is larger than the initial coronene units, thus contributing to the PAH growth.

2. Experimental

The coronene clusters are produced in a gas aggregation source. Coronene powder (Sigma-Aldrich C8, 480-1) is thermally evaporated from a fused silica crucible (85–240 Celsius) into a liquid nitrogen cooled He-atmosphere at 4 mbar. The coronene vapor condenses to clusters and is thermalized by the helium gas within the aggregation chamber to 77K ((a) in Fig. 1). The first coronene monomer signal is detectable at 85 Celsius oven temperature. After aggregation, the cold clusters are transferred into vacuum by differential pumping and are analyzed by a reflectron time-of-flight (RETOF) mass spectrometer (Bergmann et al. 1989a,b, 1990).
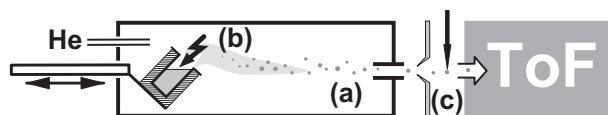
Fig. 1. The schematic experimental set-up: see text for description. The aggregation chamber **a)** is liquid nitrogen (77 K) cooled. For ionisation serves either a discharge in the evaporation and clustering region of the coronene **b)** or a laser beam focused in vacuum after differential pumping.

There are two different modes for ionizing the clusters. On the one hand, there is an optional discharge close to the crucible that ionizes the coronene during or just after the clustering process ((b) in Fig. 1). In this case the ionization does not heat the clusters, since they are thermalized during and after the ionization. The clusters, embedded in the heat bath of helium, are forming a canonical ensemble. In this mode the source produces cold coronene cluster ions at 77 K.

As an alternative mode of ionization, a focused excimer laser pulse (XeCl 150 mJ) can be used to irradiate the neutral clusters in vacuum after their separation from the helium buffer gas by differential pumping ((c) in Fig. 1). Note that the discharge is switched off when the clusters are ionized by the laser. The laser wavelength of 308 nm is very close to the strong $S_0 \longrightarrow S_\beta$ transition of neutral coronene (Nijegorodov et al. 2001). Upon absorbing several photons, the coronene is electronically excited and ionized. By contrast to the ionization in the aggregation chamber, the high vacuum precludes any further interaction, collision, or chemical reaction between different clusters or background gases during or after the laser excitation. The clusters are thus completely decoupled from environment, similarly to interstellar medium conditions, and only unimolecular or intracluster reactions and/or energy relaxation can take place. The amount of energy that is relaxed into vibrational degrees of freedom heats the cluster, which in turn evaporates subunits before, during, and after entering the RETOF mass spectrometer. All species detected after laser excitation are products of a complex transformation and evaporation process. While the discharge produces *cold* cluster ions, the laser ionization is coupled to a strong heating of the clusters.

Independent of the mode of ionization, the clusters are analyzed by the reflectron time-of-flight mass spectrometer (Bergmann et al. 1989a,b, 1990) that detects the positively charged ions. A broadening of the peaks therefore indicates decays of the species.

3. Cold coronene cluster distribution

First we focus on the size of the particles synthesized in the gas aggregation source. In order to obtain a mass spectrum that reflects the relative intensities of neutral species, we used the discharge mode that has the advantage of neither heating the species nor generating their fragmentation, as shown by Schmidt et al. (2003).

A low resolution mass spectrum is shown in Fig. 2. It exhibits a series of equally spaced peaks that are readily assigned to cationic coronene clusters $(C_{24}H_{12})_n^+$, with n varying from
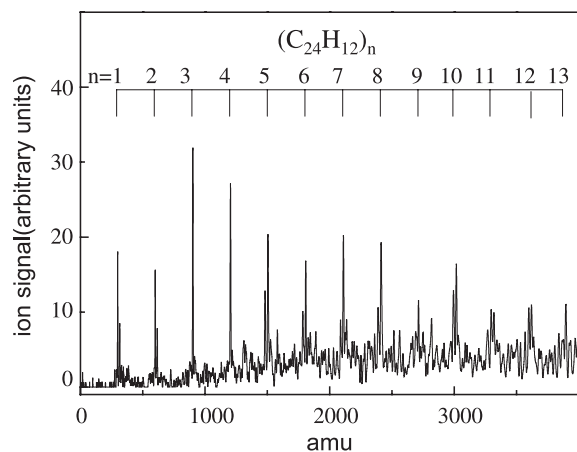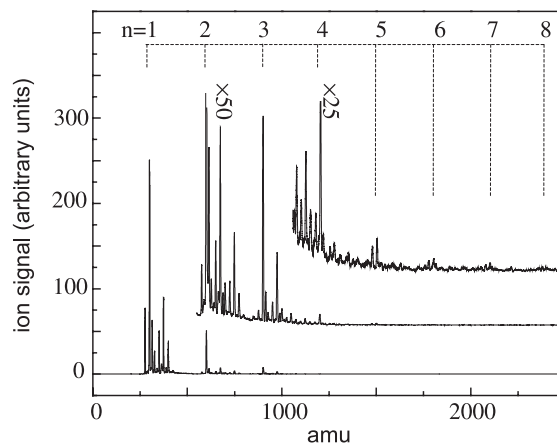
Fig. 2. Mass spectrum showing the distribution of the free cold pure coronene clusters formed in the gas aggregation source depicted in Fig. 1. The intensity of the detected ions signal is plotted versus the mass of the ions (in atomic mass units). Both scales are linear.
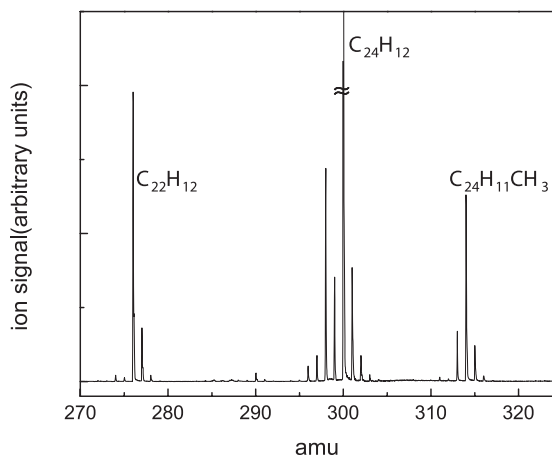

Fig. 3. Mass spectrum showing the products of the laser irradiated coronene clusters. Note the successive magnifying factors in the vertical scale. The initial cluster distribution of Fig. 2 has been drastically modified by the laser, being shifted toward smaller masses as a result of evaporation of coronene monomer units. Moreover the onset of many additional peaks indicate the photoinduced formation/enhancement of new species.

1 to 13. Previous studies have reported observations of small PAH clusters up to the size of anthracene (Piuzzi et al. 2002; Mitsui et al. 2004, and references therein). Duncan et al. (1999) have reported about the formation in a laser ablation puled nozzle source of coronene clusters made of a few coronene units. With such a source they were able to measure the electron affinity of $(C_{24}H_{12})_n$ for $n = 1$ to 3 (Duncan et al. 1999). But to our knowledge this is the first report of such purely aromatic cluster formation for large PAHs and large cluster sizes (i.e. large n values). Indeed in our experimental set-up, the high number of collisions between the coronene vapor and the helium buffer gas in the nucleation chamber provides the proper conditions for such cluster formation and ensures a good thermalization of the species at a temperature of 77 K. In contrast to the case of metal-PAH "sandwiches" (Buchanan et al. 1998; Boissel et al. 1995), these coronene clusters are expected to be bound mostly by a van der Waals type of interaction, similar to the case of PAH molecules deposited on graphite surfaces (Zacharia et al. 2004) and to form stacked structures. Such structures have recently been theoretically explored by Rapacioli et al. (2005b), who obtained a binding energy of about 1.0 eV for coronene dimer, in good agreement with the experimental value of 52 meV per C-atom derived from desorption measurements by Zacharia et al. (2004).

4. Photoinduced products

We focus now on the results obtained under excimer laser irradiation at $h\nu = 4$ eV. The discharge in the cluster source is switched off, so that only cold neutral coronene clusters enter the first acceleration zone of the RETOF. Thanks to the presence of strong absorption bands in both neutral coronene (Nijegorodov et al. 2001) and its cation (Shida 1988) in this energy range, multiple sequential absorption of several photons is expected to occur within the cluster during the laser pulse (typical duration 10 ns). Only two photons are needed to overpass the IP of the coronene monomer, i.e. (7.21 +/− 0.02) eV (Schroder et al. 2001). Moreover the presence of nearby

adjacent coronene units is expected to lower the IP of the clusters by virtue of excitonic resonance. Although such multiple photon absorption is not expected to occur in the interstellar medium, we must consider at the present stage that the laser is just a way to deposit energy in the clusters. This point will be further discussed in Sect. 5.

Figure 3 shows a typical example of the extended mass spectra obtained under these conditions. Striking differences arise upon comparison with the spectrum of Fig. 2:

- the coronene clusters $(C_{24}H_{12})_n$ size distribution is strongly shifted to lower masses, and no signal emerges from the noise above the $n = 8$ cluster mass;
- almost no products are seen within the mass window 0–300 amu, except for a mass peak at 276 amu (and a few de-hydrogenated compounds);
- new photoinduced chemical products build up within the mass range from 300 to 1250 amu. Careful examination of this spectrum also reveals that products are seen up to 100 amu greater than the mass of pure coronene within the mass window 300–600 amu, then up to 200 amu greater than the mass of pure coronene dimer within the mass window 600–900 amu, and up to 300 amu greater than the mass of pure coronene trimer within the mass window 900–1200 amu;
- finally the overall sensitivity of the experiment is such that barely any products can be observed above 1500 amu.

The first point is not surprising, since the deposit of internal energy into the clusters resulting from laser absorption is expected to produce evaporation of monomer units (Bréchignac et al. 1989), and their binding energy is not large (although not exactly known for cations) and clearly smaller than the photon energy. Hence after photon absorption, the coronene clusters shrink in size by evaporation before entering the RETOF. The efficiency of this process actually depends on both the degree of coupling between intramolecular and
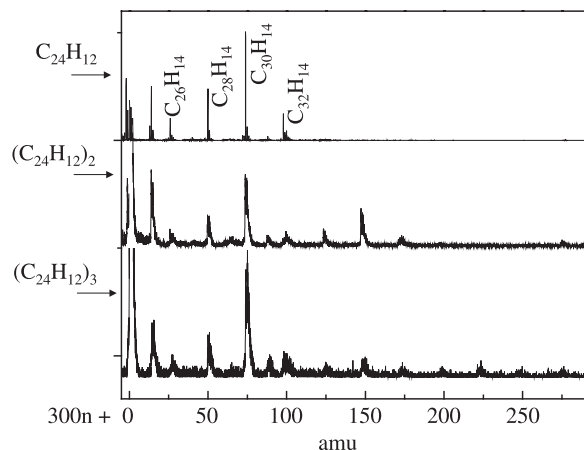
Fig. 4. Extended portion of the mass spectrum around 300 amu showing the products with masses close to that of the coronene molecule.

Fig. 5. Mass spectrum showing the same data as in Fig. 3 but displayed in 3 successive panels of 300 amu width. The *new* products seen, whose masses are listed in Table 1, extend over 100 amu up from the coronene monomer mass 300 in the top panel, then over 200 amu up from the coronene dimer mass 600 in the middle panel, and over 300 amu up from the coronene trimer mass 900 in the bottom panel.

intermolecular modes and the relevant densities of vibrational states.

The second observation confirms the well known great stability of the coronene molecule. A detailed view of the 270–325 amu window is displayed in Fig. 4, which shows that each peak in Fig. 3 is in fact a "bunch" of peaks around each mass 276, 300, and 314 amu.

The most intense peak at 300 amu is due to coronene. Its isotopic distribution due to ^{13}C natural abundance is clearly visible at 301, 302, 303 amu. The second most intense peak at 276 amu, is also accompanied by its isotopic distribution. It could be assigned to the benzo(ghi)perylene, which is known to be a common impurity in coronene samples, but alternative PAH isomers can be invoked, like anthanthrene (which is dibenzo[cd,jk]pyrene or dibenzo[def,mno]chrysene), or 13 other isomers involving at least one 5-membered ring. The peak at 314 amu can be securely assigned to methyl-coronene, and its isotopic distribution is seen. The intensities of these peaks relative to the coronene monomer are 20 and 14% respectively, which is rather large in comparison to the maximum 3% impurity of our sample. Then, these species should be formed by the photoexcitation.

The pattern formed by mass peaks at 299, 298, 297, 296 amu can be recognized as a photo-dehydrogenation distribution. As already demonstrated by Ekern et al. (1997), the loss of H atoms by pairs seems to be preferred. This observation has been explained by Joblin et al. (2005), who showed that the activation energy is much weaker in the case of an odd number of H atoms than in the case of an even number of H atoms. But the present pattern differs from the one classically observed in experiments under continuous irradiation, where photoproducts have time to reabsorb photons and further dissociate. In our experiment the species were irradiated during the few nanoseconds laser pulse, and only restricted dehydrogenation occurs. The peak at 313 amu corresponds to a single H-atom loss from the methyl-coronene, and the peak at 312 amu (loss of 2 H-atoms) is much smaller. It seems to show that presumably the H-atom that is ejected is adjacent to the methyl substituent, and the second loss is the ejection of the methyl radical, giving a signal at 298 amu, which superimposes on the doubly

dehydrogenated coronene signal. As a final remark, it can be noted that the peak assigned to benzo(ghi)perylene at 276 amu exhibits very little dehydrogenation, and its methyl-substituted derivative is also present at 290 amu.

The third point is the most interesting one, since it demonstrates that *new* products with a number of carbon atoms much larger than 24, as in the coronene molecule, can be observed under laser irradiation. It is, of course, of primary importance to securely identify, whenever possible, the exact atom content of these new products and, ideally, their structures. Actually the detailed mass analysis of each peak of Fig. 3 reveals the same kind of bunch pattern as the one depicted in Fig. 4. Thanks to the detailed structure of all bunches an unambiguous chemical analysis has been achieved.

In Fig. 5 the mass spectra are displayed in a special way through three panels on top of each other, which differ in mass scale by 300 amu, i.e. the mass of a coronene monomer. This makes it very clear that the new products involve at least one subcluster unit which is larger in size than coronene. Moreover, the larger the "basis" cluster, the more additional carbon atoms can be involved in these products. Table 1 gives the masses of the main peaks observed from $n = 1$ to $n = 4$, related to an even number of carbon atoms. There must be some important information about the responsible mechanism contained in the multiple occurrence of the same succession of mass intervals: 26, 24, 24, 24 (when scaling up), which was used to define series. Each series is "built" upon a pure coronene cluster mass. The fourth member of each series (appearing in bold characters) shows relative maximum intensity, and it serves as the starting point of the next series (when present). The second (resp. third) series #nb (resp. #nc) only appears for $n \geq 2$ (resp. $n \geq 3$).

A similar table can be built for the odd-C-numbered compounds. It is remarkable that in this other set of series the peaks (significantly less intense) are found at masses exactly shifted by $\Delta m = 14$ relative to the values in Table 1. They are then

Table 1. List of the masses of the photoinduced products. Series similar to #1a and #2a are also seen in methyl substituted species, shifted by $\Delta m = 14$. Mass values in bold faces correspond to the relative highest intensities, those in italics to the neat coronene clusters.

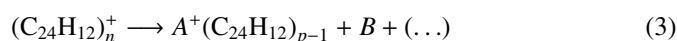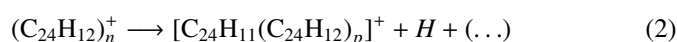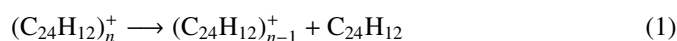| Ser #1a	Ser #2a	Ser #2b	Ser #3a	Ser #3b	Ser #3c
300	*600*		*900*		
326	626		926		
350	650		950		
374	**674**	**674**	**974**	**974**	
398	698	700	998	1000	
		724		1024	
		748		**1048**	**1048**
		772		1072	1074
					1098
					1122
					1146
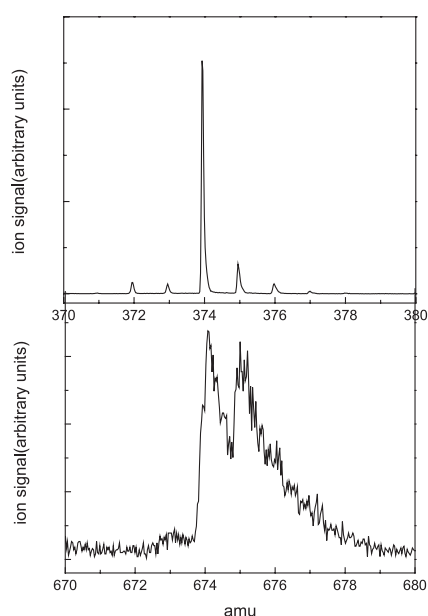
Fig. 6. Comparison of the TOF signal profiles around peaks at 374 and 674 amu. The broadening of the ion signals around 674 amu is due to the evaporation of a coronene monomer from the stacked $C_{24}H_{12}$-$C_{30}H_{14}$ cluster within the acceleration zone of the RETOF.

easily assigned to the methyl substituted derivatives of the main series products.

To go further in the assignments, the observed pattern suggests one question. Is it possible to assign the signals of the series #2a and #3a to a cluster assembly consisting of the products of the series #1a bound to one or two extra coronene molecules? Careful analysis of the TOF signals profiles does bring some light. As an example, Fig. 6 shows such profiles associated to $C_{30}H_{14}$ (374 amu) and $C_{54}H_{26}$ (674 amu). The broadening of the signals in the $C_{54}H_{26}$ bunch, as compared to the $C_{30}H_{14}$ one, can be easily interpreted as due to the slow evaporation of a coronene unit within the acceleration zone of the RETOF. We thus interpret the structure of $C_{54}H_{26}$ as a stacked coronene-$C_{30}H_{14}$ cluster. A similar reason applies to

all members of the series #2a (resp. #3a), which by detachment of one coronene molecule themselves give rise to their corresponding members of series #1a (resp. #2a). From similar arguments, we assign the members of the series #3b as clusters formed by the binding of a coronene molecule on the members of the series #2b. It is also conceivable that members of series #3a evaporate two coronene molecules to create members of series #1a, but the probability that this occurs during the time spent in the acceleration zone is probably very small. The next question to address concerns the exact chemical structures of the main series members.

In summary, three kinds of processes can be involved in the laser coronene cluster interaction, which can be written as follows:

$$(C_{24}H_{12})_n^+ \longrightarrow (C_{24}H_{12})_{n-1}^+ + C_{24}H_{12} \tag{1}$$

$$(C_{24}H_{12})_n^+ \longrightarrow [C_{24}H_{11}(C_{24}H_{12})_p]^+ + H + (\dots) \tag{2}$$

$$(C_{24}H_{12})_n^+ \longrightarrow A^+(C_{24}H_{12})_{p-1} + B + (\dots) \tag{3}$$

with the number of carbon atoms in A (resp. B) larger (resp. smaller) than 24. Additionally, pre-formed or just created species of the kind $A^+(C_{24}H_{12})_{p-1}$ can evaporate coronene monomer units, as shown in Fig. 6, according to:

$$A^+(C_{24}H_{12})_{p-1} \longrightarrow A^+(C_{24}H_{12})_{p-2} + C_{24}H_{12}. \tag{4}$$
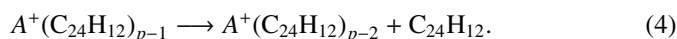
The value of p in channels (2) and (3) is most probably equal to $n-1$, although simultaneous ejection of one or more coronene units in the process cannot be ruled out. It is assumed that the larger units retain the positive charge. Channels (1) to (3) are obviously in competition within the dynamical timescale (a few microseconds) of the experiment, since all products are observed in the same mass spectrum. It is interesting to note that, while channels (1) and (2) correspond to cluster erosion or dehydrogenation, channel (3) leads to a growth in size of the aromatic units. Finally several similar processes of this sort can occur sequentially to form the final distribution of products. The only process that definitely relies on intracluster reactions is channel (3). Whether or not there is a chemical relation between processes (2) and (3) is certainly difficult to prove. But it can be said speculatively that, apart from the presence of the charge, the vacancy in the local electron density created by the loss of one (or more) hydrogen atom(s) can play the role of a trigger for a subsequent intracluster reaction.

We have no experimental information on the chemical nature of neutral fragments B. In contrast, experiment gives the chemical composition of all possible products A, which offer a wide variety of compounds, as seen from Table 1.

The reported observation of methyl-substituted compounds demonstrates that the branching of aliphatic radicals takes place in the experiment. Can the members of Series 1a be assigned to longer aliphatic chains? The mass change between 300 and 326 involves 2 C and 2 H atoms. Then it could correspond to the substitution of one H by a vinyl radical $-CH=CH_2$. The next three additional mass changes of 24 involve 2 more C atoms each. They could correspond to substitution of one H by the cumulenic radicals $-CH=C=C=CH_2$, $-CH=C=C=C=C=CH_2$, and $-CH=C=C=C=C=C=C=CH_2$.

The mechanism by which these products could be formed from coronene clusters is unclear (ring-opening of peripheral cycles of a coronene neighbor is a possibility), and should be investigated theoretically. But the existence of such substituted cumulene-containing aromatic molecules is quite plausible both from the chemical point of view (Norman et al. 1999), and particularly from the astrophysical one, since they are suggested by the analysis of infrared spectra (Duley 2000) and free cumulene chains have been widely detected in molecular clouds (Cernicharo et al. 1991; Langer et al. 1997). Moreover it has been recently established that chains like C_2H or C_4H are also abundant in photodissociation regions, despite the strong UV field. Their spatial distribution correlates well with that of the small cyclic molecule, cyclopropenylidene (c-C_3H_2), which can be traced by radiotelescopes, as well as with that of the AIBs emission (Teyssier et al. 2004; Pety et al. 2005).

On the other hand, the chemical formulas of the newly formed photoinduced products can find a correspondence with known PAH structures. It is remarkable that apart from the methylated compounds all species contain an even number of C atoms. It seems to point towards stable *peri*-condensed 6-ring PAH structures. For instance the peak at mass 326, $C_{26}H_{14}$, could be any of the 16 possible isomers: 4 are isomers of dibenzo-perylene, 2 are isomers of naphtho-perylene, and 7 involve at least one 5-membered ring. Similarly mass 350, $C_{28}H_{14}$ could be benzo[a]coronene or 9 other isomers. Mass 374, $C_{30}H_{14}$, has less candidates: 2 dibenzo-coronene, 1 naphtho-coronene or 3 other isomers with 1 or 2 5-ring(s). Interestingly, the higher member of series #1a, mass 398, $C_{32}H_{14}$, has a single *peri*-condensed isomer, which is ovalene. This peculiarity could explain why the series does not grow further to larger sizes. It can be noted that the last three products can be explained by PAH structures preserving the integrity of the coronene subunit. It is not the case for the first peak at mass 326 for which a vinyl side-group structure must be preferred. It is interesting to note that we only observe species which are even-C and even-H numbered and that the C/H ratio suggest *peri*-condensed structures. Similar results were noticed by Keller et al. (2000) in mass spectrometric analysis of benzene-oxygen flames, who found that the abundances did not depend on the number of possible isomers. The apparent lack of *cata*-condensed species is not clear. Is the chemistry biased by the precursor structure? Or do the mechanisms favour *peri*-condensed structures? This remains an open question.

Finally the eventuality that covalently bound 3D structures could be involved to account for the observed photoproducts can be put forward. A first possibility along this line is the formation of "bridges" between planar aromatic subunits, the planar units being connected through chains, for instance. Such structures are indeed found in theoretical modelling of soot formation in flames (Violi 2004; Unterreiner et al. 2004), and also observed in cosmic samples like carbonaceous meteorites (Henning & Salama 1998; Llorca 2004). Although the present experimental data do not contain evidence for such structures, its possibility is quite interesting in the astrophysical context, as it will be discussed later in Sect. 5. But another possibility is the formation of non-planar aromatic compounds

similar to helicenes. This family of compounds, which are benzologues of phenanthrene with a chiral helical structure, was discovered by Newman in 1955 (Martin 1974). They are made of aromatic benzoid rings organized in a kind of twisted ribbon (Ferrarini et al. 1999), in which the 3D extension induces spatial constraints. Such species could play a role as intermediates in the photoinduced reactions observed in this work. As an example we noted that benzo(ghi)perylene could be formed by the adequate breaking of a corono-hexahelicene.

One can also note that, if a $-CH=C=C=CH_2$ radical is branched to the coronene, it can presumably isomerize easily into benzo-coronene and vice versa by chain folding or ring opening, as soon as the energy is high enough to provide some mobility of the hydrogen atoms. This mobility may be enhanced by the presence of some "extra" H-atoms which would remain "trapped", loosely bound in "chemisorption" sites between the aromatic planes. An observation in favor of this suggestion is the small degree of dehydrogenation found considering the order of magnitude of the average internal energy necessary to induce such chemical reactions. The enhancement of reactivity by hydrogen atoms in PAH growth chemistry in flames has been discussed by Keller et al. (2000).

Up to now we have only discussed possible assignments of the members of the series #1a. The structures for the members of series #2a and #3a can be straightforwardly obtained by stacking on them one or two coronene units, independent of the kind of structures considered (chain side-groups or PAHs as proposed above).

Series #2b, #3b and #3c raise another question. First the series of mass intervals being exactly the same, one is tempted to think that the same kind of structures are involved a second time. Whether these "adducts" are bound to the same coronene unit or not is extremely difficult to guess. But the fact that not all the possible combinations of Δm values (expected in the case of independent processes) appear in series #2b seems to show that the growth associated to series #2b is built on the same coronene unit as the series #2a.

As a final remark to this section on the photoinduced gas phase cluster reactivity, it can be noted that this experiment is quite different from the laser ablation of pyrolyzed coronene samples reported by Joblin et al. (1997), because it gave completely different products. The same remark holds for the results on laser ablation of hydrogenated amorphous carbon samples reported by Scott et al. (1997).

5. Discussion/astrophysical implications

The most important finding of this experiment is to demonstrate that UV irradiation of free cold coronene clusters is able to induce an original chemistry leading to the growth of the aromatic network. It also suggests that chain side-groups can be formed simultaneously. Such side-groups could be further released upon irradiation. Presumably, smaller aromatic units (the fragment called B in channel (3)) are also released during this kind of photo-processing. Do these results shed new light on our present understanding of the role of very small grains and astro-PAHs in the ISM?

The first question is whether PAH clusters form in the ISM? As shown by Boulanger et al. (1990) and Bernard et al. (1993), they will form preferentially in cold dense regions. At the edges of such clouds, if UV starlight is intense as in the bright IR boundary of the Horsehead nebula exposed to σOri far-UV flux, their photo-induced chemistry can take place, as suggested by Teyssier et al. (2004). Rapacioli et al. (2005a) have also recently proposed, on the basis of spatial variations of the AIBs spectra in NGC7023 and ρ Oph-SR3 photodissociation regions (PDRs), that the very small grains would be PAH clusters subject to photo-erosion.

The second question is whether the photochemistry induced in the present experiment is representative of the one expected in such regions? Since the radiative fluxes are obviously very different in the laser beam and in space, the pertinent quantity is the average internal energy that can be stored in the PAH clusters. Its value under these experimental conditions can be estimated in two independent ways. The threshold for observation of the first de-hydrogenation of coronene cation within a 100 microsec time window has been found to be 12.05 eV by Jochims et al. (1999) in photoion yield measurements using synchrotron radiation. From the observed degree of de-hydrogenation in the experiment (time window of the RETOF is a few microseconds), we can then estimate an internal energy larger by a few eV. On the other hand, recent calculations based on statistical theories of the rate constant for evaporation of coronene monomer units from $(C_{24}H_{12})_n$ coronene clusters (see Eq. (1)), when putting energy into the intermolecular modes (Rapacioli 2005c), lead to estimation of this intermolecular energy to about 1.2 eV for $n = 4$ in our experimental conditions. Considering thermal equilibrium between intra- and inter-molecular heat baths and counting the number of degrees of freedom in each case, it is found that both values are consistent and the energy to inject in the aromatic system is not too far from the 13.6 eV cut-off of ISRF. Detailed theoretical modelling of these processes is presently under way, in order to put precise constraints on the interpretation of experimental data. Alternative ways to inject more energy into the system can also be invoked, as in all situations of interstellar chemistry (cosmic rays, shocks).

That both questions can find a positive answer suggests that PDRs resulting from illumination of dense molecular clouds by hot bright stars are probably the adequate astronomical environments for the activity of photoinduced intracluster processes similar to those observed in the laboratory.

It has been recognized recently that the carbonaceous dust formation rate resulting from circumstellar chemistry is too small to account for the observed abundance of astro-PAHs (Li 2004). Grain erosion processes resulting from shocks have been proposed as an alternative PAH formation process to explain this discrepancy (Jones et al. 1996). We propose that photoinduced intracluster reactivity can also contribute to this formation rate, since it is also a route to PAH growth, at least when the clusters involve PAHs of the size of the coronene molecules studied here. This route could lead to the formation of the hydrocarbonated nanograins, having the proper chemical composition, sizes, and structures to account for the AIBs observations.

Is the size of coronene clusters (or larger ones after some photoinduced growth), i.e. ~0.7–1 nm, pertinent to astronomical observations? Indeed, in the carbonaceous dust analogue proposed very early by Duley & Williams (1981) – the hydrogenated amorphous carbon- protographitic islands with dimension ~1–5 nm were actually observed embedded in thin films of HAC by scanning tunnelling microscope (Scott & Duley 1996). Following the suggestion by Beegle et al. (1997), Duley and coworkers (Duley & Seahra 1998; Duley & Lazarev 2004) have shown that stacks of PAH molecules and/or cations, whose typical size correspond to coronene or ovalene, can account for the 2175 Å extinction feature through the excitation of the $\pi \longrightarrow \pi^*$ plasmon resonance. This "stacked" structure is indeed very interesting, since it is also very similar in size to the so-called "basic structural units" (BSUs) which are the main constituents of coal (Papoular et al. 1996). In partially graphitized coals like semi-anthracite that have been proposed to account for mid-infrared emission features (Guillois et al. 1996), these BSUs are interconnected by aliphatic side-groups or by hetero-atoms. These various approaches of interstellar dust particles are really complementary, as shown by Duley (2000).

First Duley (2000) put forward a link between infrared and UV properties by considering aromatic islands bridged by $(C = C)_n$ structures. It is highly plausible that photoproducts made of *peri*-condensed PAH stacks with aliphatic side-groups, as suggested by this experiment, can combine with themselves to make the very small carbonaceous grains, and vice versa. This would be in agreement with the spatial separation of PAHs from small grains observed by Rapacioli et al. (2005a) in NGC 7023 and ρ Oph-SR3. Secondly he emphasizes the role of H atom reactions in PDRs where the UV field is intense enough to destroy H_2. We have seen above that the combination of PAH dehydrogenation and H-atom trapping in chemisorption sites within the cluster seem to provide a key to understanding the intracluster reaction mechanism of PAH growth. This can be related to the findings of Habart et al. (2004) concerning the rate for H_2 formation in PDRs. It is influenced by a non "standard" mechanism involving H atoms chemisorbed on very small grain surfaces. The "loose" (or porous) structure of PAH clusters clearly provides a very large and favorable surface for chemisorption within the wide inter-layer (0.34 nm spacing) volume.

In light of this discussion, there are several aspects of the experimental findings reported here which find an echo when confronted with the current knowledge of carbonaceous interstellar dust particles, in particular those responsible for the AIBs emission. We tentatively propose then that these free, cold, coronene clusters that we have synthesized and their UV-light photoproducts must play a major role in the search for the "correct" laboratory analogues of hydrocarbonated interstellar nanograins.

6. Conclusion

The present paper reports new results of an experimental work in which the nature of hydrocarbonated compounds are

investigated when synthesized under conditions which realistically mimic the interstellar ones.

The generation of gas-phase pure and cold coronene clusters containing up to 13 coronene molecules, i.e. 312 carbon atoms, has been achieved in a gas agregation source. Under irradiation of these clusters with laser light at $h\nu = 4$ eV, new covalently bound species are created. Their chemical composition, when analyzed by a reflectron time-of-flight mass spectrometer, reveals the presence of species whose size is larger than the initial coronene units, which implies the possibility of intracluster reactions that contribute to the PAH growth, while the stacking of aromatic planar units is partially preserved. Additionally, aliphatic side-groups could be formed. As a consequence, if the same reactions do occur in space, cumulenic radicals may either be released in the gas or serve as bridges between clusters in forming larger grains.

This growth mechanism could be different from the well known HACA (hydrogen abstraction carbon addition) mechanism proposed for combustion chemistry (Frenklach & Wang 1994). This last mechanism has, in fact, been questioned by Keller et al. (2000), who emphasize the dominant role of the PAH structure and unimolecular rearrangement for the growth of PAHs larger than coronene in flames.

Such photoinduced chemistry taking place at the boundary of molecular clouds may provide a route to the hydrocarbonated nanograins responsible for the mid-infrared emission bands. This suggestion is supported by the good spatial correlation between high resolution millimetric observations of chains and infrared observations of astro-PAHs (Pety et al. 2005). It is also in line with previous discussions of hydrogenated amorphous carbon as a laboratory analogue of carbonaceous interstellar dust. Further characterization of these new compounds, including primarily their spectral properties is highly desirable in order to confirm and exploit these first findings.

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