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Coronene cluster experiments: Stability and thermodynamics

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Abstract

Neutral coronene clusters are produced in a gas aggregation source at 77 K. They are excited either by a UV-laser in vacuum or thermally by a heat bath of helium. Fragmentations of clusters and molecules are investigated. Two well-separated thermodynamic regimes have been found for the evaporation of coronene from the cluster and the fragmentation of the coronene molecule. The stability of the cluster has been measured and the distribution of inner energies on inner- and intermolecular modes has been deduced.

Keywords: Coronene cluster; Polycyclic aromatic hydrocarbon; Caloric curve

1. Introduction

Coronene $C_{24}H_{12}$ is polycyclic aromatic hydrocarbon molecule (PAH) with a mass of 300 amu. Its highly symmetric structure is shown in the inset of Fig. 1. Due to its stability it is a common product of incomplete combustion of organic material. In the soot formation PAH molecules in the mass range of coronene are of specific interest since they mark the transition between different growing mechanisms [1–3]. Small PAH molecules grow by the HACA (hydrogen abstraction, carbon addition) mechanism [4], while for soot particles products bigger than coronene the coagulation or clustering of preformed PAH molecules dominates.

PAH molecules are also widely present in cosmic space. They have been identified by their IR emission [5]. There are synthesized in the outflows of carbon-rich stars [6]. High velocity collisions of grains, PAH-molecules and clusters can further influence the their size [7]. Recently we proposed an additional growing mechanism that involves PAH-clusters and UV-radiation [8]. The idea is that UV photons could dehydrogenate some molecules in a cold van-der-Waals (vdW) bond PAH-clusters. These molecules could then react in the cluster by their dangling C-bonds. In analogy to the HACA mechanism the reaction is based on the substitution of a C–H bond by a C–C bond. The products are chemically bond PAH-clusters that are similar to soot particles. In order to support this possibility we performed coronene cluster experiments that are reported here.

We will first discuss the thermodynamics of coronene molecules, clusters, and bulk. Based on the caloric curve and the concept of evaporative ensembles we extract typical energies and temperatures for the ejection of coronene from the cluster and for hydrogen from a single molecule. In the experiment coronene clusters are excited either by a laser in vacuum or thermally in a heat bath. The products are analyzed by a mass spectrometer. Results on thermal stability, laser-ionization, and laser-dehydrogenation and fragmentation dynamics are extracted and interpreted within the thermodynamics of the special system.

2. Coronene cluster thermodynamics

2.1. Caloric curves of coronene molecule, cluster and bulk

Fig. 1 shows the caloric curve of the coronene molecule [9]. The classical Dulong–Petit limit is shown in comparison. Due to rigidity of the C–C and C–H bonds coronene has a high Debye temperature. At low temperature many degrees of freedom are "frozen". This reduces the heat capacity and thus the slope of the caloric curve. Similar to graphite, which has a Debye temperature of $\Theta_D \sim 2500$ K for the in-plane and 900 K off-plan modes [10] the coronene molecule needs more than 2000 K before the heat capacity reaches the Dulong–Petit limit.

Following the classical rule of Dulong–Petit the heat capacity of a hot bulk material is k_B per geometric degree of freedom

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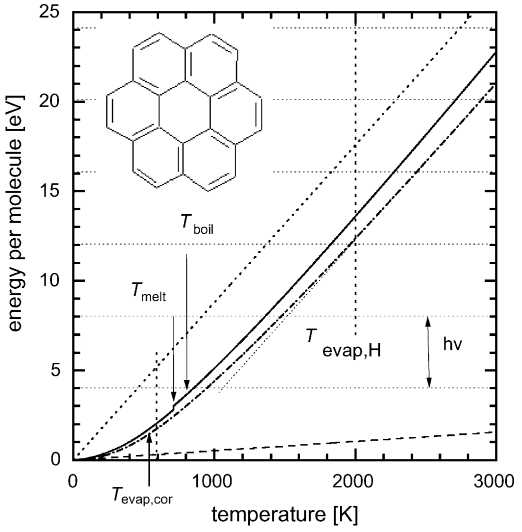

Fig. 1. Dot-dashed line: caloric curve of the coronene molecule; thick dotted line: classical limit for inner modes of the coronene molecule; the thin dotted line is parallel to classical limit. Dashed line: classical limit for inter-coronene modes in bulk; solid line: caloric curve of bulk coronene.

or $3k_B$ per atom. Thus, a coronene bulk with its 36 atoms per coronene molecule has a heat capacity of $3 \times 36k_B$ per molecule. An isolated coronene molecule has $3 \times 36 - 6$ *inner* degrees of freedom and a heat capacity of $(3 \times 36 - 6)\ k_B$. Consequently 94.4% of the energy in *hot* bulk coronene is stored in the coronene molecules and only 5.6% in the intermolecular modes.

The horizontal lines indicate the energy steps due to adsorption of one 4 eV photon, the vertical lines the evaporative ensemble temperatures for the evaporation of coronene and H-units form a cluster or molecule of coronene (Section 2.2). The arrows indicate melting and boiling points of bulk coronene under normal conditions.

The caloric curve of a macroscopic sample of coronene powder, the bulk coronene, has been constructed by using the curve of the coronene molecule and treating the intermolecular modes classically. It is included in Fig. 1. The intermolecular modes are soft. Their Debye temperature is low. Since the contribution of the intermolecular modes to the total heat capacity of bulk coronene is anyway small and the modes are soft compared to the intermolecular ones, their quantum effects are neglected. The coronene bulk melts at 710.5 K with a latent heat of fusion is only 0.20 eV [11]. Furthermore the latent heat of a cluster is expected to be smaller than in the bulk and the melting point to be reduced [12]. The step in the caloric curve due to the melting is therefore small (see Fig. 1). The coronene melting can be almost neglected for many thermodynamical aspects.

In a coronene cluster the heat capacity of the inner modes of coronene can be assumed to be almost perfectly bulk-like. The difference between bulk and cluster are the intermolecular modes. However, apart from phase transitions that difference hardly affects the heat capacities even in atomic clusters [13,14]. Since furthermore the heat capacity of bulk-coronene is clearly dominated by the inner modes the bulk caloric curve provides a very good approximation for a cluster.

2.2. Evaporative ensembles

2.2.1. Evaporative ensemble of the neutral coronene cluster

A cluster in vacuum, which is sufficiently heated to evaporate subunits before the detection after 10 μs, forms an evaporative ensemble [15]. Further energy input by a laser or a collision does not increase the temperature of the clusters at the time of detection. Instead the energy is used for fast evaporations of subunits. The process is in analogy to the phase transition in liquid–gas equilibrium [16]. The temperature of the evaporative ensemble is coupled to the stability of the cluster. The higher the dissociation energies D of the subunits are the higher the evaporative ensemble temperature T_{evap}. The link between the two quantities is given by, $k_B T_{\text{evap}} = D/G$, where G is the Gspann factor and k_B the Boltzmann constant. $G = 23.5$ describes many different systems [15]. Only for some special cases like the C_{60} exceptional Gspann values like $G = 31$ have been found [17]. The value of G is logarithmically time-dependent. It is adjusted to 10 μs, the typical time scale of the mass spectroscopy. If the time window of the experiment differs by one or two orders of magnitude from 10 μs the result can be adjusted by using the thermal rates, which are described by the Arrhenius' law $k(T) \sim \exp(-D/k_B T)$ [18].

There are different references for the value of the dissociation energy D_{cor} of a coronene molecule from a coronene cluster. Theoretical calculations have shown that coronene clusters prefer stacked structures with a binding energy of about 1 eV [19]. Experimentally, the enthalpy of sublimation from bulk coronene of 1.41 eV per molecule is known [20]. The cluster value is presumably smaller since many molecules are weaker bond on the surface of the system. The experimental value of the binding energy of a coronene molecule on a graphite surface of 1.15 eV [21] to 1.25 eV [22] gives another approximate value. The value for D_{Cor} of around 1.2 eV is therefore reasonable for neutral coronene cluster. This corresponds to a value of about $T_{\text{evap,Cor}} = 590$ K and an evaporative ensemble energy $E_{\text{evap,Cor}} = 2.0$ eV. A coronene cluster, which is heated by collisions or a laser up to this values, evaporates molecules within some microseconds until its temperature drops below $T_{\text{evap,cor}}$ or the whole cluster is evaporated. The boiling point T_{boil} of bulk coronene is at 798 K.[1] This is another rough upper limit for the evaporative ensemble temperature [16].

$T_{\text{evap,cor}}$ is smaller but quite close to the melting point T_{melt} of bulk coronene. The ratio of melting and boiling points T_{boil} for bulk coronene is relatively high. There is no big temperature gap between melting and boiling. This is typical for bulk- and cluster-vdW systems [23]. Since T_{melt} and T_{evap} of a cluster are usually reduced compared to the bulk melting and boiling, there are two possibilities. Either the cluster melts under heating just before evaporation, or, even more probable, it sublimates the molecules from the solid phase without melting.

In Fig. 1 a vertical dotted line indicates the evaporative ensemble temperature. Obviously the cluster starts to evaporate at a temperature far below the Θ_D of the coronene molecules. One

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[1] Data sheet of Sigma–Aldrich C8, 480-1.

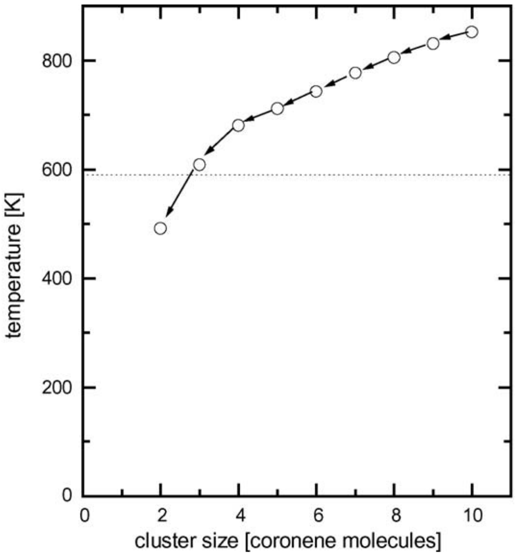

Fig. 2. Calculated temperatures of clusters with decreasing size resulting of a successive evaporation steps. The fragmentation cascade starts with a Cor_{10} cluster and an excitation energy of one photon (4 eV) per molecule. The plot uses the bulk caloric curve shown in Fig. 1 and $D_{cor} = 1.2$ eV. Thermalization of the evaporated molecules in internal and external degrees of freedom is assumed and a kinetic energy release of $(6/2)k_B T$. The cluster temperature only drops slowly. While the starting temperature of 850 K is far below the fragmentation threshold of the coronene molecule (see Section 2.2.3) the trimer still has a temperature above the evaporative ensemble (indicated by the dotted line). By each evaporation between Cor_{10} and Cor_5 the rate, estimated by Arrhenius' law, drops by a factor of about 2. The slight flattening of the curve in the step from $5 \rightarrow 4$ at 713 K is due to the solidification of the particle.

third of the vibrational coronene modes are not yet active. Nevertheless, most of the inner energy in the cluster is stored in the coronene molecules and only 15.2% in the intermolecular modes. For this reasons a coronene cluster forms an unusual evaporative ensemble. In an atomic system the evaporative ensemble is reached when about 10–20% of the dissociation energy is stored per atom in the cluster [24]. Therefore the number of evaporated atoms after excitation is limited, the inner energy and temperature drops with every evaporation remarkably. When on the other hand a coronene cluster becomes hot enough to evaporate within the time window of the experiment, it carries already *more* inner energy than necessary to evaporate the cluster entirely. The coronene molecules buffer most of this energy. Therefore a single evaporation step reduces the cluster's temperature and its evaporation rate much less than in case of an atomic cluster (see Fig. 2). For the same argument coronene clusters evaporate entirely down to the monomer, if they are exited too strongly. As shown in Fig. 2 a Cor_{10} cluster with one 4 eV-photon per molecule evaporates down to the dimer. With 5 eV per molecule it *entirely* evaporates down to the monomer. The same happens to Cor_{80} with 8 eV and Cor_{600} with 12 eV per molecule. The inverted fragmentation chain shows: a Cor_{10} cluster that appears in a mass spectrum can be a fragment of Cor_{50} with 4.2 eV excitation energy per molecule, of Cor_{100} with 5.1 eV or of Cor_{600} with 8 eV per molecule. Clusters that appear in the spectra have therefore very probably absorbed in average less than two photons per molecule.

The concept of evaporative ensemble is based on the rapid drop in rates of successive evaporation steps clusters. Therefore it has certain limits for the cluster size, where the dependences of the precise time window and the original excitation energy becomes more important [25]. Due to the big heat capacity of the molecule a coronene cluster reaches its limits earlier than an atomic system.

2.2.2. *Evaporative ensemble of the charged coronene cluster*

The bonds between neutral coronene molecules are of van der Waals type. As a vdW-cluster the electrical conductivity between neighboring units is very low. Like a rare gas cluster the coronene will therefore localize its charge. But unlike to a rare gases *atom* that entirely changes its character by charging and therefore forms chemically bond cores of two to four atoms inside the vdW-cluster [26], the big coronene molecule can buffer a charge without necessarily forming chemical bonds to its neighbors. It is therefore reasonable to guess the charge as being localized on *one* single coronene molecule. The charge of the molecule could cause strong additional interactions of the neighboring coronene dipoles with the charge and therefore strongly amplify the binding and therefore $T_{evap,cor}$ of a charged cluster. Since no experimental or theoretical data are available predictions of the evaporative ensemble cannot be made. However, the problem only concerns very small clusters, where the evaporating coronene molecules are direct or indirect neighbors of the charged center. With increasing cluster size the effect vanishes due to a bigger distance of the evaporating coronene molecules from the charged center.

2.2.3. *Evaporative ensemble of the single coronene molecule*

At temperatures above $T_{evap,cor}$ only chemically bond units of the clusters like the coronene molecule itself can endure a period of several microseconds. However, after evaporating all vdW-bond subunits the coronene itself can be heated further until it reaches its own evaporative ensemble limit, which is given by the emission of hydrogen or carbon units. The lowest fragmentation channel is here the evaporation of hydrogen atoms [27,28] that are bond with $D_H = 4.5$ eV. The corresponding evaporative ensemble temperature $T_{evap,H}$ is about 2200 K calculated with a Gspann factor G of 23.5 and still 1700 K in case that G is 31 like for of C60 [17]. The stability of different PAH molecules including coronene has already been studied experimentally. An evaporative ensemble energy of 10.6 eV has been found for a time window of 10^{-4} s [29]. Based on the caloric curve (Fig. 1) this corresponds to $T = 1800$ K. The single molecule has to absorb three photons of 4 eV before it starts to evaporate H within 100 μs. For better comparison we transform this values into the 10 μs time range by using the Arrhenius law (Section 2.2.1): $T_{evap,H} = 2000$ K, $E_{evap,H} = 12$ eV. Note, that evaporative cooling at that high temperature already is in concurrence to radioactive cooling by IR emission.

As shown in Fig. 1 there are well-separated temperature regimes for the coronene loss from a coronene cluster and for H loss from a coronene molecule. While a coronene cluster with 2 eV inner energy per molecule already starts to evaporate coronene, it needs 10–14 eV for a H-evaporation. A cluster, which has enough time to thermally distribute its inner energy before fragmentation, will therefore not evaporate hydrogen from a molecule before the last vdW bond unit has left the cluster. However, in case of *non-thermal* activation with a laser or a high-energy collision, the cluster could nevertheless reach a non-equilibrium state, in which single coronene molecules are hot enough to evaporate hydrogen while the intermolecular modes are still too cold to break. It implies a weak coupling of the inner- and intermolecular modes in the coronene cluster. This is not very probable, since the softest modes of the coronene molecule are the off-plane modes [10] like the butterfly mode that should couple well to the intermolecular modes. Let us assume that this non-equilibrium state could be reached in an intensive laser field and some coronene molecules could evaporate H *before* the cluster thermalizes and evaporates. If the dangling C-bonds of the dehydrogenated coronene molecules reacted fast enough intermolecularly, the system could form chemically bond complexes that resist the fragmentation. The simplest forms of those complexes are *n*-coronene molecules that are connected by C–C bonds formed by the dangling bonds after a partial dehydrogenation [30]. Due to the missing H-atoms they have masses slightly smaller than $n \times 300$ amu.

3. Experimental set-up

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 °C) into a liquid nitrogen cooled He-atmosphere at 10–20 mbar. The coronene vapor condenses to clusters and thermalizes in the helium gas with the aggregation chamber at 77 K ((a) in Fig. 3). The first coronene monomer signal is detectable at 85 °C oven temperature. After aggregation the cluster embedded in the helium pass though a thermalization stage (d) with variable temperature (77–500 K). The duration of stay in the thermo stage is 500 μs.

A focused excimer laser pulse (XeCl) irradiates the neutral clusters in vacuum after their separation from the helium buffer gas by differential pumping ((c) in Fig. 3). The laser wavelength of 308 nm (4.02 eV) is close to an UV resonance of coronene [20]. Upon absorbing photons, the coronene is electronically excited. The electronic excitation couples to the vibrations of the coronene molecule and finally to the whole cluster. It ejects subunits in consequence. The high vacuum precludes any further interaction, collision or chemical reaction between different clusters or background gases during or after the laser excitation. Evaporated subunits cannot condense back onto any cluster. The clusters are completely decoupled from environment and are forming here a microcanonical ensemble. All species detected after laser excitation, are products of the complex fragmentation process. Finally a reflectron time of flight mass spectrometer [31] analysis the positively charged cluster ions. A coronene mass spectrum is shown in Fig. 4. The main peak series corresponds to coronene. The diffuse background is due to evaporations within the time of flight in the spectrometer.

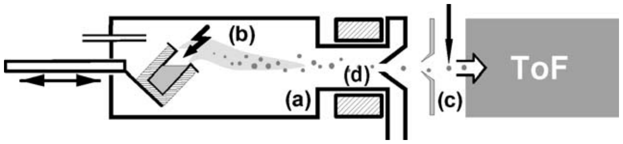

Fig. 3. A schematic experimental set-up: see text for description. The aggregation chamber (a) is liquid nitrogen (77 K) cooled. For ionization serves either a discharge in the evaporation and clustering region of the coronene (b) or a focused laser in vacuum after differential pumping (c). The thermalization chamber (d) serves to regulate the cluster temperature between 77 and 700 K.

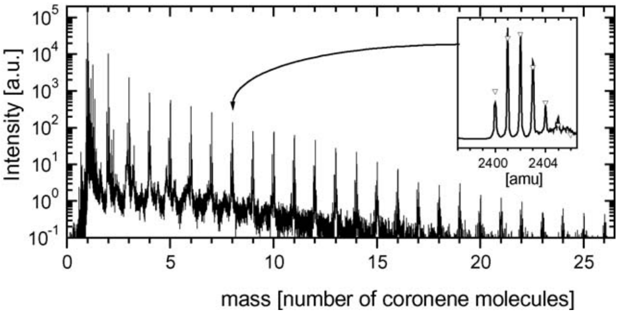

Fig. 4. Mass spectrum of laser ionized coronene clusters Cor_1^+ to Cor_{26}^+. The diffuse background as well as some peaks with reduced resolution corresponds to clusters fragmentations within the spectrometer. The main peaks beside the coronene clusters are due to Benzo[ghi]perylene at 276 amu, which is an impurity in the sample. The inset shows an expansion of the Cor_8 peak, with the isotopic distribution due to ^{13}C (triangles).

4. Results

4.1. Lost hydrogen atoms as thermometer

When the 4 eV excimer laser ionizes the coronene molecules in vacuum there is always a certain percentage of molecules with lost hydrogen atoms. Under normal experimental conditions about 25% of the detected ionized molecules have lost hydrogen, in average 2 atoms. Reducing the laser power reduces the H-loss but also the ionization probability and therefore the ion-intensity. Even at the sensitivity limit of the spectrometer the H-loss cannot be entirely suppressed at this photon energy. Increasing the laser power by additional focusing enhances the H-loss und finally induces even pronounced carbon loss (Fig. 5). Following the caloric curve shown in Fig. 1 and assuming a thermal emission of H-atoms ($E_{\mathrm{evap,H}} = 12$ eV, D_{H} of 4.5 eV and IE 7.21 eV [32]) it turns out that 25% of the ionized coronene molecules have been excited by 24 eV or six photons.

Even under high laser power coronene clusters have been observed. But compared to the monomer, the dehydrogenation of coronene clusters is strongly suppressed (Fig. 6). A lower limit for the suppression ratio is given by $[I(298)/I(300)]/[I(598)/I(600)] \geq 220$, where $I(m)$ is the intensity at given mass m in atomic units. The ratio is limited by ionic background and sample impurities (Section 4.4). This shows that there is a difference in the maximal temperature that is reached in free coronene molecules and in those that are embedded in a cluster. The clusters cool themselves very efficiently

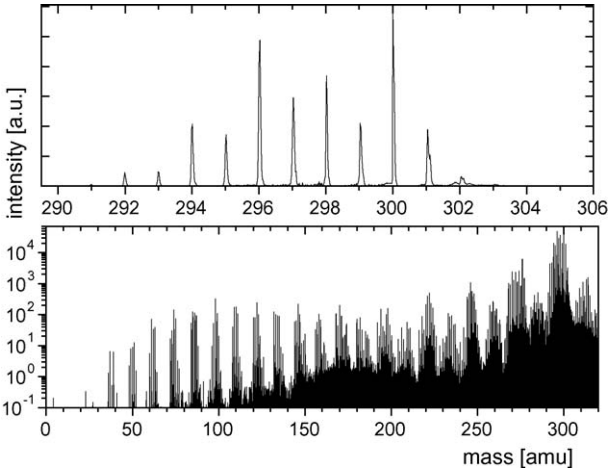

Fig. 5. The coronene molecule (300, 301, 302 amu) after strong laser excitation: a laser power that leads to a mean number of more than three hydrogen atoms (upper figure) excides a small percentage of molecules strong enough to produce charged fragments with many lost carbon atoms (lower figure).

by coronene evaporation even during the laser pulse of 10 ns. The single coronene molecules in the cluster therefore do not reach sufficiently high temperatures to evaporate hydrogen. This implies a relative fast coupling from the coronene vibrations to the intermolecular modes of the cluster: It has to be fast enough to compensate the heating by the multi photon absorption during the laser pulse of 10 ns. Using the Arrhenius law (Section 2.2.1) one finds that the cluster temperature had to be increased by about a factor of 2 from the evaporative ensemble to reach an evaporation rate of about 1 ns. Based on this estimation the coronene evaporation limits the cluster temperature during the laser excitation to about 1200 K even if several photons per coronene molecule are absorbed in average. While the free coronene molecule strongly fragments under this conditions, the dehydrogenation of coronene in a cluster is strongly suppressed. Additional to the evaporative cooling the ionization probabilities enhance the temperature difference between of the clusters ions and the singly charged molecule (see Section 4.2).

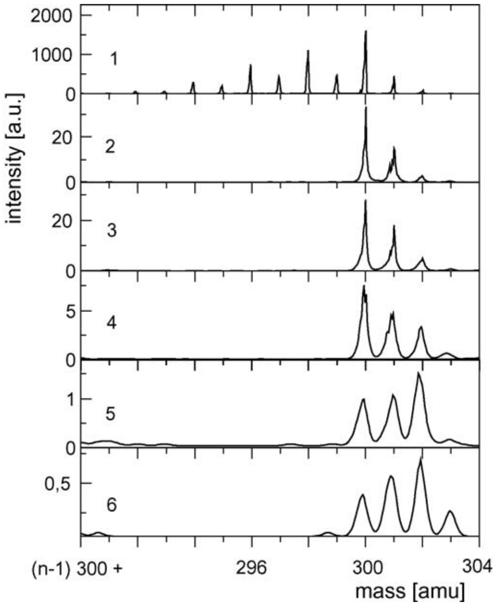

Fig. 6. Mass spectra of the range of $n \times 300 + 10$ to $n \times 300 + 4$ amu with $n = 1$–6. The intensities above $n \times 300$ correspond to the isotopic distribution due to the presence of ^{13}C. The peaks below 300 amu belong to dehydrogenation of the monomer.

4.2. The ionization

The coronene molecule has a first ionization energy IE of 7.21 eV [32]. At least two of the 308 nm-photons are therefore necessary to ionize one of the molecules. Since the electron phonon coupling in the molecule is much faster than the duration of the laser pulse of 10 ns, the second photon has to be adsorbed before the energy of the first photon is transferred into vibrations. This strongly enhances the number of necessary photons. The majority of coronene ions that are shown in Fig. 6 adsorbed more than six photons (Section 4.1). On the other hand all molecules in the cluster pass though the same laser field and it has been figured out in Section 2.2.1 that the neutral coronene molecules do not absorb more than one or two 4 eV-photons per molecule. Otherwise the clusters evaporated entirely down to the monomer before they could be detected. The solution of this apparent contradiction is the small ionization probability. Even if the mean photo absorption probability is one per molecule, there are still 0.5‰ of the coronene molecules that absorb six or more photons.[2] If only those are ionized und thus detected, the average of ionized coronene molecules is much hotter than the invisible neutrals. Assuming an original size of 50 neutral coronene molecules per cluster this correspond to 2.5% ionization probability per cluster. Absorbing in average one photon per molecule Cor$_{50}$ evaporates down to about Cor$_{12}$ before the rate drops below time window of the machine.

No double-charged species have been found. This supports the interpretation of a low ionization probability, but it could also be due to coulomb explosions of multiply charged clusters, since the system is weakly bond.

4.3. Stability of neutral coronene clusters

To test their stability, coronene clusters are produced in the aggregation chamber. After passing through the thermalization chamber they are ionized by the excimer laser and analyzed in the mass spectrometer. When now the thermalization chamber is heated above 470 K the clusters are evaporated during their stay of 500 μs in the thermalization stage. The cluster signal vanishes in the spectra and only the monomer remains. The clusters reappear when the temperature falls again below the critical value. Neutral coronene clusters evaporate coronene within the duration of stay in the chamber at that temperature. Nevertheless, it is only a lower limit for the evaporative ensemble temperature $T_{\mathrm{evap,cor}}$ of coronene clusters. First, the duration of stay in the thermalization chamber is by a factor of 50 longer than the 10 μs,

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[2] This calculation is based binomial distribution and assumes independent absorptions. It is a rough estimate, since the photo absorption cross-section changes by every excitation step.

which correspond to the evaporative ensemble. The influence of the time window to T_{evap} is not strong due to the logarithmically relation (Fig. 2), but it causes nevertheless a reduction of the measured temperature limit by 65 K. Furthermore it cannot be excluded that at 470 K there are still some small clusters, which endure the stay in the heat bath. They might not appear in the spectra, since they are destroyed by the laser excitation after leaving the thermalization chamber. On the other hand bigger clusters have to evaporate not only one but many molecules at 470 K within the thermalization time to appear as monomer in the spectrum. By variation of the source conditions the influence of the original cluster size has been studied and considered in the error bar. Including the correction due to the time window the experimental values for $T_{evap,Cor}$ is 535 ± 50 K. Using a Gspann-factor of 23.5 this corresponds to $D_{Cor} = 1.09 \pm 0.15$ eV, which accords roughly with the expectations in Section 2.2.1.

4.4. *Impurity accumulation by the evaporation process*

Under certain cluster source conditions intensive additional peaks appear beside the coronene clusters in the spectra [8]. The coronene powder, which has been used for the experiments, contains below 3% impurities.[3] The masses of those correspond to the additional peaks that appear in the coronene cluster spectra. However, the observed impurity intensities often exceed the 3% limit. Their yields strongly depend on the cluster source parameters: high oven temperatures, long aggregation tube and high helium pressure are standard parameters to increase cluster size. In the experiments described in this paper they mainly increase the appearance of impurities on the small cluster ions, while it is very difficult to shift the cluster ion intensity to bigger masses. Due to the strong fragmentation (Section 2.2.1) the monomer is always dominating the spectra (Fig. 1).

All detected clusters ions result from a long evaporation cascade (Section 2.2.1). The bigger the original neutral cluster, the higher the probability to build in one or more molecules of impurities. In the fragmentation process after the excitation the cluster preferentially evaporates coronene and enriches the impurities that are *stronger* bond than coronene. Since the binding energies correlate with the mass of the PAH molecules [33], those that are bigger than coronene are accumulated. The longer the fragmentation path is, the more impurities appear in the spectra. This observation is independent of the type of excitation. The fragmentation process can either be induced by the laser or by the heat bath of He-gas in the thermalization chamber at around 500 K (Fig. 3 (d)). The evaporation during the 500 μs in the heat bath leads to the same ensemble of accumulated products as by the laser.

An alternative explication for the intensive additional peaks has been discussed in Section 2.2.3 and [8]. Based on a pronounced non-equilibrium during the laser excitation the coronene molecules in the cluster could evaporate hydrogen and react intermolecularly. However, for the appearance of those peaks the non-equilibrium is obviously not necessary, since the cluster evaporation by the heat bath leads to the same products. That the heat bath induces reactivity just as the laser with the same ensemble of products is not probable. Any coronene–coronene reaction, which could occur at 500 K in a free cluster within 500 μs, should occur just as well in a macroscopic sample. By contrast, it has been found that a macroscopic coronene needs temperatures above 600 °C to pyrolyse on a minute time scale [30]. Coronene is stable enough to endure even hours at 460 K without intermolecular reactions in the oven of the cluster source. Furthermore no pronounced dehydrogenation of coronene molecules in clusters has been found after laser excitation (Section 4.1) and finally, the most probable reaction products, the *n*-coronenes (Section 2.2.3), are missing in the spectra (Fig. 6).

The intensive additional peaks are therefore only due to the enrichment of impurities in the evaporation process and not to intermolecular reactivity in the cluster. If intermolecular reactivity occurred at all under our experimental conditions it is entirely superposed by the accumulated impurities.

5. Conclusion

The fragmentation of coronene clusters and molecules occur in two well-separated energy and temperature regimes. The neutral coronene *clusters* eject coronene molecules on the 500 μs time scale at a temperature of 470 ± 50 K. This corresponds on the 10 μs time scale $T_{evap,Cor} = 535 \pm 50$ K or to an evaporative ensemble energy of 1.8 ± 0.17 eV per coronene molecule and a dissociation energy $D_{Cor} = 1.09 \pm 0.15$ eV. By contrast to atomic systems the total binding energy of the coronene cluster is smaller than its inner energy at the evaporative ensemble. This causes long evaporative chains even after moderate excitations. Although 1/3 of the inner degrees of freedom in the coronene molecule are frozen at $T_{evap,Cor}$, most of the inner energy is stored in the vibrational modes of the coronene molecule and only 16.7 ± 1% in intermolecular modes.

The coronene *molecule* starts to evaporate hydrogen on the 10 μs time scale at temperatures around $T_{evap,H} = 2000$ K or with an inner energy of 12 eV. Compared to the evaporative ensemble of the coronene *cluster* this is a factor of 4 in temperature or a factor of 6 in energy. The corresponding thermodynamic regimes are well separated and cannot mix in equilibrium. The pronounced fragmentation of the detected ionic coronene molecules indicates a low ionization probability. Ionized are only those molecules that adsorbed by chance an exceptional high number of photons.

Even during the 10 ns of multi-photon excitation by the focused excimer laser at 308 nm the temperature equilibration inside the cluster is fast. A cluster dominantly ejects vdW-bond units while isolated molecules in the same laser field are heated sufficiently to dehydrogenate and denature entirely. The reason is the big energy gap between the binding of a coronene molecule to the cluster and the binding of hydrogen to the coronene molecule. By increasing the size of the PAH molecules

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[3] Data sheet of Sigma–Aldrich C8, 480-1. Some of the used samples have an additional pollution with Benzo[ghi]perylene at mass 276 that exceed the 3%. Its appearance in the spectra is additionally enhanced due to a vapour pressure that is higher than coronene [20].

in the cluster this gap could be closed. Most likely dehydrogenation and intermolecular reactions could also be induced in a coronene cluster by a higher laser *power*. Higher photon *energies* could also influence the result, but exceeding the ionization potential the photons will rather ionize the coronene molecules than heat them sufficiently to eject hydrogen atoms. A *resonant* excitation of the C–H bond by monochromatic light [34] could probably also dehydrogenate the coronene molecules in the cluster and induce coronene–coronene reactions. Another possibility to enhance the probability of intermolecular reactions is increasing the cluster size. If the cluster was big enough to cage evaporated and damaged molecules, reactions between them become probable. The reactivity observed by the products of UV-laser ablation experiments from bulk coronene [30] is related to such processes. However, such mechanisms can better be studied by bulk experiments than in a free cluster. No cluster specific effects can be expected. Under our experimental conditions the absorbed photon energy is dominantly used for evaporation of vdW-bond subunits from the coronene clusters. The resulting evaporative cooling effectively protects the single PAH-molecules from dehydrogenation.

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