Ion-Induced Reactivity in Pyrene Clusters

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Abstract. We report experimental indications of chemical reactions inside clusters of pyrene ($C_{16}H_{10}$) molecules following collisions with 11.25 keV He$^+$- and 12.0 keV Ar$^{2+}$ ions. It appears that bond-forming reactions are more likely with the heavier projectile. We have also performed classical molecular dynamics simulations of these processes where we treat the interaction between the projectiles and all atoms in the cluster as well as non-dispersive and dispersive forces between all atoms in the cluster before, during and after the collision. The time step is typically $10^{-17}$ s and the total simulation time 1 picosecond. The simulations were performed for a fixed cluster size with 36 pyrene molecules, although there is a broad range of cluster sizes in the experiment. Still, there is good qualitative agreement between the experimental and the simulated mass spectra exhibiting reaction products with masses between those of the $C_{16}H_{10}$-monomer and dimer in both cases. Additional studies of the influence of the projectile charge and mass is planned as well as simulations on longer time scales and as functions of cluster size.

1. Introduction

Polycyclic Aromatic Hydrocarbon molecules, or PAHs for short, attract considerable interest in several fields of research. PAHs, which typically consists of three or more aromatic rings of carbon atoms, are common combustion products and are believed to play key roles in soot formation processes although the exact mechanisms for this is not yet clear [1, 2]. As PAHs are formed in combustion processes they are also of great interest for environmental and health research. Some PAHs are toxic [3] and some may even be cancerogenic [4, 5]. It has been suggested that PAHs are involved in the formation of fullerenes in sooting flames [1] and that large dehydrogenated PAH molecules lead to the formation of $C_{60}$ and $C_{70}$-fullerenes in space [6]. It is generally believed that PAHs or closely related molecules are responsible for the characteristic infrared emission features of a very large number of astrophysical objects including the interstellar medium [7, 8] and it is generally believed that they play important roles in astrochemical reactions. The IR-emission from astrophysical PAHs are most likely caused by comparatively large PAHs containing at least 50-100 carbon atoms which are heated mainly in UV-absorption processes, but it is also possible that they are heated in collisions with electrons, ions or other particles. Interestingly, ion collisions may lead to other fragmentation processes than photo-absorption and as discussed below these fragments are more reactive and effective in molecular growth processes. The latter of course requires that a fragment collides with other molecules or atoms before it is destroyed.
This may happen when the PAH is part of a cluster. Here, we will study cases where molecular growth processes seem to occur inside clusters of only pyrene molecules.

Recently, growth pathways for fullerenes have been discovered in collisions between keV ions and clusters of fullerene molecules [9, 10, 11]. In short range collisions between 400 keV \( \text{Xe}^{20+} \) ions and mixed clusters of \( \text{C}_{60} \) and \( \text{C}_{70} \) (containing 4 % \( \text{C}_{70} \)) the ions induced significant damage to molecules along the projectiles path, creating a hot gas/plasma of C atoms and small carbon molecules [9]. Fullerene molecules containing up to 180 carbon atoms were then formed through either the coalescence of the small fragments with neighbouring fullerene molecules in the cluster, or through self-assembly of the fragments. These growth processes were only detected when the initial clusters were very large, containing several tens of molecules, showing that the cluster environment is crucial for these mechanisms to take place. In later experiments with collisions between 22.5 keV \( \text{He}^{2+} \) ions and clusters of \( \text{C}_{60} \) molecules, the dumbbell shaped \( \text{C}_{119}^+ \) and \( \text{C}_{118}^+ \) molecules were detected [10]. These molecules are formed when the projectile ion transfers sufficient energy to one (or two) C atom(s) in a molecule to knock out the atom(s) on the femtosecond timescale. The so formed \( \text{C}_{59} \) (\( \text{C}_{58} \)) radical forms covalent bonds with a neighbouring intact \( \text{C}_{60} \) molecule on the picosecond timescale with a reaction barrier close to 0 eV [10, 12]. This is much lower than the \( \sim \) 60 eV kinetic energy required to induce covalent bond formation between two intact \( \text{C}_{60} \) molecules [13, 14, 15]. Dumbbell fullerene formation was also observed in collisions between 22.5 keV \( \text{He}^{2+} \) and mixed clusters of \( \text{C}_{60} \) and the polycyclic aromatic hydrocarbon (PAH) coronene (\( \text{C}_{24}\text{H}_{12} \)) [16]. However, equivalent covalent bond formation reactions involving (intact or fragmented) coronene molecules were not detected in that experiment [16].

Here we present early results showing the possible growth of PAH molecules induced by collisions with keV ions. We have studied collisions between 11.25 keV \( \text{He}^+ \) or 12 keV \( \text{Ar}^{2+} \) projectile ions and loosely bound clusters of pyrene (\( \text{C}_{16}\text{H}_{10} \)) and found that the latter collisions lead to the formation of molecules larger than pyrene. The experimental results are compared to those from simulated collisions and there is a good agreement in the distribution of molecular masses formed by the collisions and subsequent bond-forming reactions.

2. Experimental Details

The experiments are performed at the ARIBE beamline at GANIL in Caen, France. Clusters of pyrene are formed in a liquid nitrogen cooled gas aggregation source [17]. Ions are produced in an Electron Cyclotron Resonance (ECR) ion source, accelerated to 11.25 keV for \( \text{He}^+ \) and 12 keV for \( \text{Ar}^{2+} \) and pulsed into 500 ns bunches. The ions collide with the neutral clusters in the interaction region of a linear time-of-flight (TOF) mass spectrometer. Following \( \sim \) 100 ns delay, a voltage is applied to the extraction electrodes and the cationic products from individual collision events are detected in coincidence by a microchannel plate (MCP) detector. A schematic of the experimental setup is shown in Fig. 1. The clusters in our target follow a log-normal intensity distribution as a function of their size [18].

3. Simulation Details

We model the collisions between projectile ions/atoms and pyrene clusters containing 36 molecules (Fig. 2) using classical Molecular Dynamics (MD) simulations. The present MD-simulations are performed for neutral systems as it has been shown that the location of the charge does not influence the bond formation or fragmentation processes to any large extent for systems with many delocalized electrons [12, 19]. The molecules and their mutual interactions are modelled using the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [20] as implemented in the LAMMPS molecular dynamics suite [21] using a microcanonical (constant energy and volume) ensemble. Interactions with the projectile are modelled using the Ziegler-Biersack-Lattmark (ZBL) potential [22] in order to simulate nuclear
scattering of colliding atoms and does not include electronic stopping. The exclusion of electronic stopping is compensated for by assuming a temperature of 2000 Kelvin for the individual molecules at the beginning of the simulations. This corresponds to an internal energy of 480 eV distributed evenly over the whole $[\text{C}_{16}\text{H}_{10}]_{36}$ cluster. This is a reasonable approximation in view of estimates of energy transfers to the electronic degrees of freedom in the individual molecules (see e.g. ref. [19]). Further, it has been shown that PAH clusters rapidly redistribute internal energy and charge evenly across the cluster [23]. Time steps of $5 \times 10^{-17}$ s and $1 \times 10^{-17}$ s are used for simulation with 12 keV Ar and 11.25 keV He projectiles, respectively. In a simulation, the cluster and projectile are randomly positioned and oriented. Then the projectile is given a velocity corresponding to the desired kinetic energy. The collision and subsequent bond-forming reactions are then followed for a few picoseconds. For the results presented here, $10^4$ trajectories have been simulated for each projectile species and energy.

4. Results and Discussion
We show mass spectra from experiments and simulations in Fig. 3. All four panels of Fig. 3 show a mass range which includes the pyrene monomer (mass 202 amu) and the dimer (mass 404 amu). With 12 keV Ar$^{2+}$ projectiles we see that a series of peaks corresponding to masses between that of the monomer and dimer are visible in the experimental mass spectrum. Each subsequent peak in this range is due to an additional C atom, and a distribution of the number of H atoms, above the mass of the intact pyrene molecule. These additional features are largely absent from the mass spectrum with the 11.25 keV He$^+$ projectile. Here, only a few weak peaks are visible in the mass range between the pyrene monomer and dimer. Also visible in this case is a tail to the right of the monomer caused by the delayed fragmentation of clusters during the extraction of the charged products in time-of-flight mass spectrometer. This feature is present in the case with Ar$^{2+}$ projectiles as well, but is masked by the additional peaks in this mass spectrum.
Figure 3. Mass spectra from experiments (left panels) and MD simulations (right panels) for 11.25 keV He\(^{+}\) (bottom row) and 12 keV Ar\(^{2+}\) (top row) projectiles colliding with clusters of pyrene molecules.

The right panels of Fig. 3 show calculated mass spectra from MD simulations. The simulations show results very similar to the experimental ones with respect to the distribution of fusion products in the mass range between the monomer and the dimer. Molecules with these masses are created when the projectile atom promptly knocks one or several atoms out of molecules along the trajectory - this is the so called knockout mechanism which has been shown to be dominant at lower energy collisions with H and He atoms and to lead to highly reactive fragments [19, 24, 25]. These fragments may then easily form covalent bonds with neighboring molecules, either with intact pyrene molecules or other pyrene fragments. We see from the simulations that the primary source of masses between the intact monomer and dimer is from bond coalescence between two rather than several molecules/fragments, typically between an intact pyrene and a single fragment. The region of the mass spectrum around the dimer mass contains contributions from both H knockout, giving reactive radicals which form covalent bonds with neighboring molecules, and intact dimers bound by the dispersion forces. The Ar projectiles are capable of causing more severe damage to the pyrene molecules than the lighter He projectiles, with projectiles colliding with edge-on molecules creating more small fragments than trajectories where the molecules are closer to face-on where the projectile may pass through the molecular rings without transferring significant amounts of energy. The result of this is the lower intensity of fusion products and fragmented molecules in the case of He projectiles. This is expected based on previous studies with fullerenes [26].

The mechanisms driving the growth of pyrene molecules observed here appear to be similar to those seen in the growth of fullerenes. As is the case with fullerenes, atom-knockout in the collisions is key to forming radical fragments which in a second step form bonds with neighboring molecules within picoseconds. For these processes to occur, the cluster environment is crucial as it both supplies the radical with a reactant and also allows the energy transfered in the collision to be redistributed among many degrees of freedom, increasing the probability of the new molecular species surviving the experimental microsecond timescales and longer.

5. Conclusions
We have seen indications of covalent bond forming molecular growth processes inside medium sized clusters of the PAH molecule pyrene due to keV collisions with Ar\(^{2+}\) and He\(^{+}\). The igniting process seems to be knockout of individual atoms from one or several molecules in
the clusters which is followed by bond forming reactions with another molecule or fragment from the cluster. The effect is much stronger with the Ar projectile which may be explained by the larger probability for multiple atom knockout in this case. The qualitative agreement between the experimental and simulation results are remarkable and reproduces the difference between reactions following He$^+$ and Ar$^{2+}$ collisions. These results suggest efficient pathways to molecular growth in space due to interactions between ions from supernova shock waves and stellar winds with PAH molecules in clusters and grains [27]. It is of considerable interest to extend the study to other projectile masses and charge states and to study the influence of the cluster size both in the experiment and in the simulations. It is expected that there is a smallest possible, critical, cluster size for which the molecular growth processes become important.

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