

Chemical reactions in collisions of C_{60}^+ ions with solid surfaces

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Collisions of C_{60}^+ ions with pyrolytic graphite (HOPG), diamond (111), Ni(100) and epitaxially grown crystalline fullerite surfaces have been studied under UHV conditions. Experimental data and MD simulations give evidence for an adsorption reaction of C_{60}^+ ions on HOPG and diamond (111) for impact energies E_{in} higher 300 eV. In contrast hereto, a complete dissociation of the C_{60}^+ on the Ni(100) surface was found for E_{in} between 90 and 700 eV leading to the formation of a $c(2 \times 2)C-p4g$ superstructure. In collisions with fullerite films large ions C_{100}^+ to C_{130}^+ arising from a pick-up fusion reaction have been detected.

1. INTRODUCTION

Chemical reactions represent a common form of ion-surface [1] and atom/molecule-surface interactions [2]. Molecular beam techniques have revealed that the kinetic energy of the incident molecule influences its reactivity on surfaces due to collision induced activation [3].

Concerning collisions of polyatomic organic ions with solid surfaces, Cooks and co-workers first demonstrated reactions with surface adsorbed molecules [1]. Pickup of H, CH_3 , C_1 , C_2 and C_3 has been reported for several precursor ions and a variety of surfaces. These reactions have been assigned to the interaction of the incident ions with adsorbates present on the surface under the given vacuum conditions [1]. More recently, self-assembled alkanethiol monolayers on gold have been used as scattering surfaces [4].

Williams and co-workers showed the attachment of C_1H_n - C_6H_n to naphthalene and phenanthrene ions [5]. These reactions are thought to proceed by an Eley-Rideal mechanism, as it is supported by MD calculations.

Experiments on collisions of C_{60}^+ ions with solid surfaces gave insight into the dynamical properties of this interaction [6]. While the ions lose up to 95% of their kinetic impact energy E_{in} , they come off the surface virtually without disintegration at E_{in} up to 130 eV [7]. Metastable fragmentation of scattered C_{60}^+ has been observed for higher

E_{in} . This process is caused by transfer of a substantial fraction of E_{in} into thermal energy of the receding C_{60}^+ [7]. Reactive collisions of C_{60}^+ ions with solid surfaces should contribute to the basic understanding of fullerene chemistry. We therefore summarize in this paper experimental results on a chemisorption reaction on HOPG and diamond (111) surfaces, on a complete dissociation on Ni(100) and on a fusion reaction on the surface of a fullerite film.

2. EXPERIMENTAL

Details of the experimental system have been described elsewhere [6]. In brief, the UHV apparatus consists of three chambers, a main chamber with a base pressure of 2×10^{-10} mbar, a fullerene ion source chamber, and a chamber with a reflectron type time-of-flight mass spectrometer. C_{60}^+ ions are produced by 308 nm excimer laser desorption from a rotating stainless steel plate covered with a thin fullerite film. They are accelerated and mass separated from a 10%-fraction of C_{70}^+ . The ion beam is shaped by ion optics and directed onto the target in the main chamber. The primary beam can be monitored by a secondary electron multiplier mounted opposite to the source chamber exit aperture. The laser fluence was kept at about 9 mJ/cm² in order to minimize fragmentation and to provide an intense primary beam.

A scanning ion gun is available for surface preparation. A four grid LEED optics is mounted for

surface structure analysis and can also be used to record Auger spectra of the target surfaces.

The preparation of the scattering samples is described in previous papers [7,8,9]. The HOPG samples were cleaned in ambient conditions by "stripping off" the first few surface layers and baking out for several hours at 720 K in UHV. The natural diamond was etch cleaned and baked at 1100 K in UHV. The polished Ni(100) surface was sputtered with 1 keV argon ions at grazing incidence and annealed by subsequent heating to 800K. The (111)-oriented fullerite film was epitaxial grown on mica by gas phase deposition. The film thickness is 40 nm.

3. RESULTS AND DISCUSSION

3.1 HOPG and diamond (111)

Figure 1 shows the total ion yield of the back-scattered C_{60}^+ ions and its fragments for HOPG and diamond (111) as a function of the impact energy E_{in} . A pronounced maximum of the scattering yield at around 270 eV is found for both surfaces. This is in good agreement with data reported by Yeretzian et al. for the graphite surface [10]. The increase of the ion yield with increasing E_{in} in the energy range between 100 and 270 eV is most probably due to collision induced emission of a slow electron (so called delayed or thermionic ionization) [11].

STM investigations of the scattering HOPG surfaces after bombardment with C_{60}^+ of 450 and 700 eV revealed defect structures which may be assigned to collision induced surface corrugations or/and deposited molecules [6]. Recent molecular dynamic simulations of C_{60}^+ collisions with H-terminated diamond (111) based on a semiempirical density functional approach revealed the importance of the orientation of the molecules when touching the surface [12]. Strongly reactive collisions are found in those cases, in which the molecule first reaches the surface with a hexagon. The sticking probability increases with increasing E_{in} . For $E_{in} > 300$ eV all molecules are deposited onto the surface independently on the initial orientation concerning the surface. The deposition process leads to amorphous carbon structures.

3.2 Ni (100)

In contrast to graphite and diamond, nickel is known to be very reactive against organic molecu-

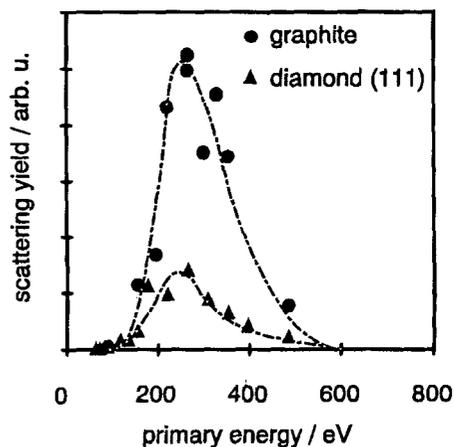


Figure 1. Total ion yield of the C_{60}^+ ions and its fragments after collision with diamond (111) and oriented graphite as a function of the impact energy E_{in} .

les. In particular, the carbidic phase of Ni(100) is found to be the reactive phase of nickel catalysts.

In fact, we have not observed any C_{60}^+ ions or fragments scattered from the clean Ni(100) surface in the range of E_{in} between 90 and 700 eV. In order to get evidence for a deposition of the projectiles, the carbon concentration on the surface for different exposure doses and impact energies E_{in} was traced by means of AES. In figure 2, the measured ratios of the nickel $M_1M_{45}M_{45}$ to the carbon KVV peak-to-peak intensities are shown for different exposure doses and impact energies E_{in} , the exposure dose defined as the product of the primary C_{60}^+ beam intensity and the number of pulses. An increase of the carbon concentration until saturation is common for all curves in the investigated energy range. This gives evidence for a deposition of the fullerenes on the surface.

Furthermore, there are differences in the slopes of the curves for different impact energies. From this slopes a sticking coefficient (in arbitrary units because of the exposure dose in arbitrary units) can be derived, assuming that the adsorption probability is proportional to the number of free adsorption sites and that no desorption of already adsorbed atoms or molecules takes place. The sticking coefficients derived from the experimental data in this manner are plotted in figure 3 as a function of E_{in} . The curve shows a minimum at around 300 eV.

Low energy electron diffraction was used to clarify the question whether the C_{60} exists on the sur-

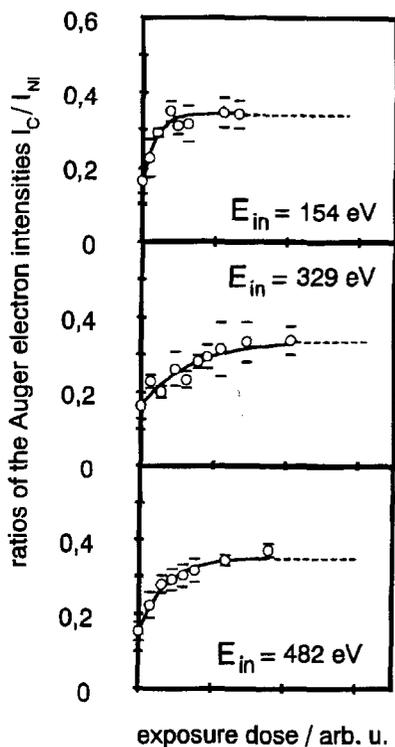


Figure 2. Measured carbon Auger electron intensities normalized to the substrate intensities as a function of the exposure dose for different C_{60}^+ impact energies.

face as intact molecules or in a disintegrated form. Extraspots appear with increasing exposure dose. According to Onuferko et al. [13], the observed LEED pattern can be attributed to a $c(2 \times 2)C-Ni(100)$ superstructure with $p4g$ -symmetry. Thus the C_{60}^+ ions become completely disintegrated in collisions with a $Ni(100)$ surface for E_{in} between 90 and 700 eV.

Photoemission spectroscopy of Ni deposited on a C_{60} -multilayer has shown the strong interaction between the free electrons of the nickel crystallites and the π -system of the C_{60} leading to a partial electron transfer to the carbon atoms [14]. Consequently, the intramolecular bonds in the C_{60} are weakened. Thus we assign the observed disintegration of C_{60}^+ ions in collision with a $Ni(100)$ surface to a chemical reaction following the chemisorption.

The decreasing sticking coefficient with increasing E_{in} in the range between 90 and 300 eV indicates that the adsorption reaction is exothermic. With increasing E_{in} , more and more energy has to be dissipated into the surface heating it up. Thus, an exothermic chemisorption of C_{60} on the $Ni(100)$ sur-

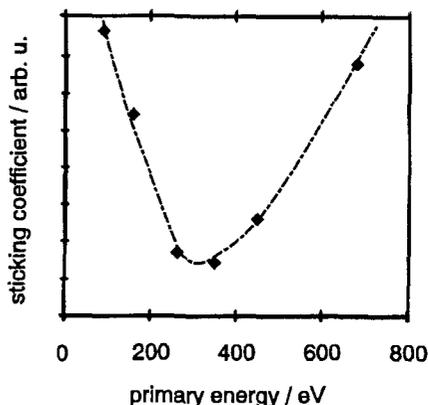


Figure 3. Sticking coefficients of C_{60}^+ at a clean nickel (100) surface for different impact energies E_{in} .

face would be suppressed. The increasing sticking coefficient for E_{in} higher 300 eV can be explained by direct collision induced disintegration of the molecule.

3.3 Fullerite

A typical mass spectrum of ions after C_{60}^+ ion impact on an epitaxial fullerite film on mica is shown in figure 4. The impact energy was 275 eV and the impact angle 25° to the surface normal. The detected ions left the surface with 2000 m/s at an emerging angle of 15° . For comparison, a mass spectrum for collisions with a HOPG surface is also shown. The collision parameters are the same as in the fullerite case. Reflected C_{60}^+ ions occur in both spectra, however, the very weak fragmentation in the case of the fullerite target already indicates the more elastic character of the collision as compared to the graphite and diamond target.

Furthermore, the fullerite film yields higher fullerenes as well. Since the C_{70}^+ ion signal was observed exclusively for C_{70} containing films (about 10% C_{70}) we have reason to attribute these ions to a sputtering process. This is corroborated by the velocity distributions shown in figure 5. The curve for the C_{70}^+ ions shown in the lower part of this figure follows very closely the low velocity part of the bimodal C_{60}^+ velocity distribution. The high velocity component represents ions directly scattered from the surface.

The ions in the mass range C_{100}^+ to C_{130}^+ originate from a fusion process of the impinging C_{60}^+ with C_{60}/C_{70} on the surface. The fact, that these ions survive several μs before entering the TOF gi-

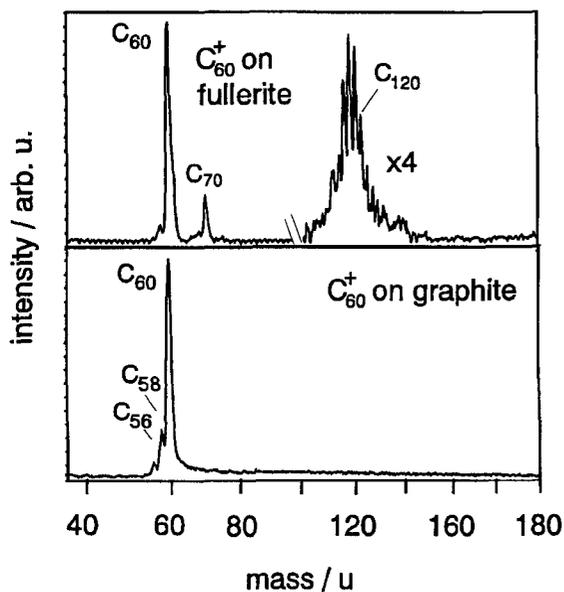


Figure 4. Typical mass spectra of ions produced by C_{60}^+ ion impact on an epitaxial fullerite film (upper panel) and on oriented pyrolytic graphite (lower panel). Collision parameters see text.

ves evidence for genuine large fullerenes. The velocity distribution peaks at about 2500 m/s. This is substantially faster than for the desorption products. Thus we conclude, that the formation of large fullerenes by surface collisions of C_{60}^+ with fullerite films proceeds by a direct pick-up reaction via an Eley-Rideal mechanism.

CONCLUSIONS

The ability of C_{60}^+ to survive collisions with graphite and diamond for impact energies up to 450 eV is surely one of its most remarkable properties [7, 10]. In this paper, we demonstrate that C_{60}^+ ions colliding with solid surfaces can undergo a variety of chemical reactions, such as chemisorption, surface induced dissociation, and pick-up of other molecules from the surface. The demonstrated sputtering of intact fullerene molecules by C_{60}^+ impact is interesting in the light of an application in static SIMS.

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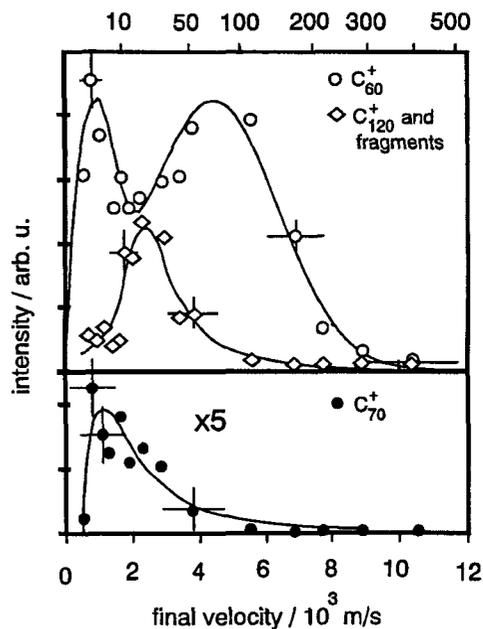


Figure 5. Velocity distributions of the ions detected after C_{60}^+ impact on an epitaxial fullerite film on mica: C_{60}^+ ions, desorbed C_{70}^+ ions and fusion products.

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