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ABSTRACT
We present results from experiments and molecular dynamics (MD) simulations obtained with C$_{60}$ and Au$_{400}$ impacting on free-standing graphene, graphene oxide (GO), and graphene-supported molecular layers. The experiments were run on custom-built ToF reflectron mass spectrometers with C$_{60}$ and Au-LMIS sources with acceleration potentials generating 50 keV C$_{2+}$ and 440–540 keV Au$_{4+}$. Bombardment-detection was in the same mode as MD simulation, i.e., a sequence of individual projectile impacts with separate collection/identification of the ejecta from each impact in either the forward (transmission) or backward (reflection) direction. For C$_{60}$ impacts on single layer graphene, the secondary ion (SI) yields for C$_2$ and C$_4$ emitted in transmission are ~0.1 (10%). Similar yields were observed for analyte-specific ions from submonolayer deposits of phenylalanine. MD simulations show that graphene acts as a trampoline, i.e., they can be ejected without destruction. Another topic investigated dealt with the chemical composition of free-standing GO. The elemental composition was found to be approximately COH$_2$. We have also studied the impact of Au$_{400}$ clusters on graphene. Again SI yields were high (e.g., 1.25 C$^-$/impact). 90–100 Au atoms evaporate off the exiting projectile which experiences an energy loss of ~72 keV. The latter is a summation of energy spent on rupturing the graphene, ejecting carbon atoms and clusters and a dipole projectile/hole interaction. The charge distribution of the exiting projectiles is ~50% neutrals and ~25% either negatively or positively charged. We infer that free-standing graphene enables detection of attomole to zeptomole deposits of analyte via cluster-SI mass spectrometry.

I. INTRODUCTION
A number of studies have dealt with the interaction of energetic ions (mostly atomic ions) with graphene deposited on substrates (e.g., Refs. 1–3). However, the collision of hypervelocity particles with free-standing graphene has so far received limited attention. Yet, the interaction exhibits many unusual aspects not present in bulk materials. The 2D target material occupies a niche between a gas and a solid, and the collision process occurs under extreme dynamic conditions.
We refer here to experiments and molecular dynamics (MD) simulations detailing graphene’s response to impacts of single atomic ions, clusters, or nanoparticles with velocities of 1–30 km s\(^{-1}\). It has been reported that impacts with nanometer diameter particles initiate peculiar track mechanisms that can lead to the formation of nanopores.\(^2\) The result is a molecular sieving membrane combining unmatched mechanical strength with a low transport resistance and a high flux rate.\(^2\) Bombardment with larger (≥ micrometer diameter) projectiles has shown that multilayer graphene has spectacular mechanical strength in the ballistic regime due to a highly efficient mode of energy absorption.\(^1\) The straining and rupturing of graphene under bombardment are accompanied by ultrafast processes with characteristics modulated by those of the projectiles. For instance, a single highly charged ion passing through free-standing graphene causes within femtoseconds emission of a burst of electrons corresponding to an astounding current density in an excess of 10\(^{12}\) A cm\(^{-2}\).\(^3\) This observation opens prospects for graphene-based ultrafast high current-electronic applications.

Another intriguing finding is a sizable energy loss experienced by medium and large cluster projectile passing through free-standing graphene.\(^4\) Further, bombardment combined with mass spectrometric identification of the ejecta showed a dramatic increase in the ionization probability of organic molecules deposited on graphene.\(^5\) Akin to this observation are reports of enhanced ionization in secondary ion mass spectrometry (SIMS) experiments where samples were covered with graphene.\(^6\)

This paper is not a comprehensive review but an introduction to a key aspect of hypervelocity projectile-graphene interactions, namely, the characteristics of the ejecta which in turn should provide insight into the mechanisms of energy dissipation. The focus is on the ejecta from free-standing graphene, graphene oxide (GO), and graphene-supported molecular layers under impact of a 2D (C\(_{60}\)) or 3D (Au\(_{40}\)) massive cluster projectiles at impact velocities of 1–30 km s\(^{-1}\). The directly relevant literature is sparse and consists mainly of MD simulations with attention on defect creation in the graphene rather than on the ejection of matter.\(^1\) We focus here on observations from experiments and MD simulations run under equivalent conditions on like-targets.

A schematic of the experimental setup is provided in Fig. 1. A detailed description is provided in Refs. 4, 14, and 15. Briefly, the emitted secondary ions and ionized fragments of projectiles are detected as time-of-flight mass spectra.\(^16\) The applied experimental setup allows the separate recording of the emitted ions from each collision. The event-by-event bombardment-detection mode allows for the selection of specific impacts, i.e., those involving free-standing graphene at the exclusion of signals from the target holder and support. The instrument has two ion sources and a single mass spectrometer, allowing a direct comparison of mass spectra measured in either transmission (graphene) or reflection (bulk target) experiments.

The graphene targets referred to herein consist of graphene or graphene oxide layers placed on a lacey carbon structures itself placed on a 300 mesh Cu grid.\(^17\)

As noted, we combine experimental observations with molecular dynamics (MD) computer simulations of cluster bombardment. In this approach, the movement of particles is determined by integrating Hamilton’s equations of motion. A detailed description of the MD method can be found elsewhere.\(^1\) The forces among atoms in the modeled system are described by the AIREBO\(^19\) (C–C interactions in earlier simulations\(^5\)) or by ReaxFF-lg force fields.\(^22\) Both these potentials allow for the creation and breaking of covalent bonds; however, the ReaxFF-lg force field is more advanced. It gives predictions that are more accurate and is able to describe interactions between C, H, N, O atoms. The forces between Au atoms are described by the embedded atom model (EAM) potential,\(^21\) while a purely repulsive Ziegler-Biersack-Littmark (ZBL) potential is used to model Au–C interactions.\(^22\) Electronic energy losses are ignored due to a low velocity of moving projectile atoms. The shape and size of the samples are chosen based on visual observations of energy transfer pathways stimulated by impacts of C\(_{60}\) and Au\(_{40}\) projectiles. As a result, cylindrical samples with a diameter of 40 nm are used. Rigid and stochastic regions are applied to simulate the thermal bath that keeps the sample at required temperature, to prevent reflection of pressure waves generated by cluster projectile impacts from the boundaries of the system, and to maintain the shape of the sample.\(^18,23\) Samples with a thickness between 1 (1L) and 16 (16L) graphene layers with a highly oriented pyrolytic graphite structure, a monolayer of phenylalanine (Phe) deposited on a 2L graphene substrate, and a bulk system of Phe molecules are probed. The kinetic energy and the impact angle of the projectile are changed to investigate the effect of these parameters on the particle ejection process. Particles emitted both in the direction of the primary beam (transmission direction) and in the opposite direction (sputtering direction) are collected. The simulations are run at a target temperature of 0 K in an NVE ensemble and extend up to 20 ps for a clean graphene, up to 40 ps for a monolayer of Phe molecules, and up to 80 ps for a bulk Phe system. These values are long enough to achieve saturation in the ejection yield versus time dependence. Between 8 and 32 randomly selected impact points located near the center of the sample are chosen to achieve statistically reliable data.

Returning to the topic of this perspective, the challenge here is to gain insight into the mechanism(s) of ejection and ionization.
Clearly, the sputtering mechanism valid for bulk targets is not applicable. It may be recalled that in a bulk target, sputtering results from the dissipation of the projectile kinetic energy via linear collision cascades (atomic projectiles) or high density collision cascades, or spike, in the case of cluster impacts. It should be mentioned that a spike is also reported for impacts of the atomic projectiles at specific conditions. Such conditions occur during bombardment of weakly bound solids (frozen gases) or when heavy projectiles (Xe) are use. There are several differences between ejection stimulated by a linear collision cascade and spike. The presence of the dense collision cascade leads to a more efficient sputtering and emission of less energetic atoms. Cluster projectile impacts are particularly prone to form high-density cascades due to shallow deposition of the primary kinetic energy. Impacts of such clusters generate correlated momenta toward the surface around the impact point leading to a formation of almost hemispherical craters. In the case of the bulk molecular target, the projectile impact at the surface initially creates an energized volume primarily composed of molecular fragments. Expansion of this volume stimulates sputtering of energetic molecules at off-normal angles by means of fluid type motions. The development of the both linear collision cascade and spike requires a 3D medium, which is at least a few tens of nanometers thick. There has to be a certain number of atomic collisions to randomize a linear collision cascade or form a high-density core in spike. For 2D targets, the amount of material is not sufficient and sputtering-ionization does not originate from fully developed collision cascades. We examine four cases below to probe processes taking place in 2D targets C60 impacts on graphene, graphene oxide, molecular layers deposited on graphene, and Au400 impacts on graphene. We summarize here the relevant literature describing experiments and MD simulations as well as recent new observations dealing with the characterization of ejecta as well as the evolution of graphene.

II. C60 IMPACTS ON FREE STANDING GRAPHENE

Let us consider the interaction of 50 keV C60 at normal incidence with graphene step by step. As shown in Fig. 2 (Multimedia view), even for a monolayer graphene, there is complete atomization of C60 projectile. The C atoms of projectile and most of knocked-on atoms of graphene travel in the transmission direction.

In the 1L graphene case, the colliding/atomizing C60 projectile (diameter 0.7 nm) spends approximately 10 fs to pass the graphene plane. The presence of a conglomerate of C atoms at a distance of ∼1.5 nm from the graphene at 30 fs indicates that most of projectile atoms retain high velocity as a consequence of a low collisional energy loss. The latter increases with the thickness of graphene as illustrated with the case of 2L and 4L graphene [Figs. 2(b) and 2(c) (Multimedia view)]. In the 4L graphene case, the 30 fs snapshot shows that the atoms of the projectile barely exit the graphene, which indicates that they efficiently transferred the kinetic energy to the knocked-on atoms of graphene. This aspect will be discussed in more details later.

A second phase of the interaction lasting picoseconds is characterized by an abundant ejection of C atoms and clusters from the rim area around the primary graphene rupture (Fig. 3).
The radial movement of C atoms around the rupture initiated by the first fast phase is transformed into collective movements, which develop a wavelike vertical oscillations and radial planar compressions. Similar phenomenon also has been observed on a graphite surface bombarded by \text{C}_{60}.^{29,30} The vibrationally exited rim is the source of the C ejection (see the movies in the supplementary material of Refs. 4 and 9). One should note that although the energy accumulated around the hole is small (a few percent of the total energy), it is sufficient for the ejection of carbon atoms and clusters due to the confined energy dissipation in the 2D material. This process clearly differs from the sputtering induced by impacts on a bulk material.\footnote{Ref. 4}

As visible in Fig. 3, the ejection efficiency depends on the substrate thickness. To probe this phenomena more accurately, the yield of carbon atoms ejected in the transmission and reflection/sputtering directions are plotted as a function of the substrate thickness and primary kinetic energy. The results are shown in Fig. 4(a). For particles ejected in the transmission direction, the yield vs thickness dependence has a maximum, which shifts to thicker systems with the increase in the projectile kinetic energy. For substrate atoms ejected in the sputtering direction, the yield initially increases but ultimately saturates. Variation of the substrate thickness has a different impact on ejection of projectile atoms. The yield decreases monotonically with the sample thickness for carbon atoms ejected in the transmission direction. The yield of backscattered projectile atoms is very low and does not exhibit a consistent dependence on the substrate thickness. The last two observations indicate that projectile atoms are being trapped inside the graphene substrate due to a strong covalent interaction with the surrounding medium. The occurrence of this process is also seen in Fig. 3. The magnitude of this process increases with the sample thickness. Projectiles that are more energetic are able to perforate thicker systems, which explain broadening of the yield versus thickness dependence with the increase in the primary kinetic energy.

Almost all projectile atoms penetrate through a thin substrate, as shown in the inset of Fig. 4(a). However, even in this case, the projectile-graphene interaction is significant, especially for low-energy projectiles. For instance, for 5 keV \text{C}_{60}, almost 40\% of the primary kinetic energy is lost during penetration of the one layer (1L) sample, as shown in the inset of Fig. 4(b). Almost 70\% of impact energy is lost in the 2L system. These numbers drop to 15\% and 20\% for analogous systems bombarded by 40 keV projectiles. Substrate atoms emitted in the transmission direction carry most of the deposited energy away. The energy carried away by sputtered atoms is small and does not exceed 0.5\% of the initial kinetic energy. For a

![Fig. 4](https://example.com/fig4.png)

**Fig. 4.** Dependence of (a) the ejection yield and (b) the fraction of primary kinetic energy carried away by particles emitted in the transmission (top) and sputtering (bottom) directions on the thickness of the sample bombarded by 5, 10, 20, and 40 keV \text{C}_{60} projectiles at normal incidence. Main graphs represent the atoms ejected from the sample, while the insets depict projectile atoms. Reprinted with permission from M. Golunski and Z. Postawa, J. Vac. Sci. Technol. B \textbf{36}, 03F112 (2018).
given primary kinetic energy, the amount of energy deposited in the solid increases with the sample thickness.

The kinetic energy distributions of C ions (Ref. 1, Fig. 5) ejected in the transmission direction obtained experimentally and of C atoms computed by MD simulations are similar, showing that most atoms/ions have kinetic energies in the eV range. However, some C atoms/ions have much higher kinetic energy. The latter corresponds to atoms originating from the projectile or/and substrate atoms ejected via direct elastic atom-atom collisions. The MD simulations show that some of projectile atoms residing at the front of the impinging cluster gain additional kinetic energy during projectile deceleration and deformation. These atoms gain additional kinetic energy from atoms located at the back of the projectile, when these particles collide. Thus, theoretically, after collision, the kinetic energy of few atoms can be higher than the kinetic energy of projectile atoms (50 keV/60 atoms = 833 eV, Fig. 4).

The evolution of the graphene in the first phase (t < 10 fs) is characterized by the generation of a round shaped rupture (diameter ~ 1 nm) and a fast planar wave of collective radial movements of the graphene atoms [Fig. 2 (Multimedia view) and Fig. 3, top view]. The atoms around the rupture (hole) are displaced radially breaking of the atom-atom bonds. This process initiates the formation of a vibrationally exited rim around the rupture.11,12

The flux of emitted particles is composed of single atoms and clusters. The experimental yields of the emitted cluster ions (ions/projectile impact) and the yields of the neutral clusters obtained by MD simulations are shown in Fig. 5 for 50 keV C602+ impacts at 4L graphene.4,5,9

In both cases, ejection of single C atoms is the dominant ejection channel. However, the most interesting observation is an abundant ejection of negative ions. The calculated ionization probabilities are shown in Fig. 6. It is evident that the ionization process is much more efficient than observed in analogous experiments performed on clean metals, semiconductors and organic samples.24,32,33

The abundant ion emission prompts the issues of ionization mechanism(s). The ionization mechanisms in the case of sputtering of bulk matter have been a subject of extensive investigations over decades.32,33 In the case of sputtering of the surface of conductive matter (metal or metal-like materials), the main ionization mechanism is that of electron tunneling from a bulk surface to the sputtered species. The relevance of this mode for ion emission from graphene was evaluated in Refs. 4 and 5. Briefly, the following mechanism was proposed: the knocked-on carbon atoms, along with those from the shattered projectile and the ejected clusters from the rim of the hole, undergo of electron exchange processes before they escape beyond the critical distance for electron tunneling (~1 nm). The electron tunneling from the vibrationally and electronically exited rim, and, i.e., the ionization probability, Pn, can be explained with the thermalized excitation model.17 The adiabatic limit of this model can be expressed as

\[ P_n(T_c) = \left( \frac{Z^n}{Z^0} \right) \exp \left[ \frac{\varphi - EA - \delta_e}{kT_c} \right], \]  

(1)

where \( T_c \) is the average electron temperature of the rim around the graphene hole at the time of the tunneling process, \( \delta_e \) is the image charge correction factor (set to zero in Refs. 4 and 5), and \( Z^n \) and \( Z^0 \) are the partition functions of emitted C ions and neutrals at \( T_c \). The work function of the rim is unknown. For estimation, we may take the value of the work function of the free standing pristine graphene, \( \varphi = 4.5 \) eV. The values obtained for the adiabatic electron affinities of carbon clusters from Ref. 34 are shown in Table I. An approximation of the experimental ionization probabilities by the thermalized excitation model gives an average electron temperature of 3700 K at the rim at the time of the tunneling process. One should note that the tunneling mechanism is applied here for the negative ionization of ejecta, which involves an electron transfer from graphene to ejecta. It means that the electron must be provided...
by the conductive band of graphene. For the case of emission of positive ions, generally, the electron tunneling is not the only mechanism of ionization. The molecular/cluster ejecta, being vibrationally exited, undergo thermionic emission of electrons.

All experimental and computational data discussed so far have been obtained at a normal incidence angle. The effect of the impact angle on the ejection yield from the 2L and 8L systems bombarded by 10 and 40 keV C\textsubscript{60} projectiles is shown in Fig. 7. The results obtained by MD simulations demonstrate that the impact angle has a similar influence on the yield of substrate atoms emitted in the transmission and sputtering directions for both these systems. As in the case of substrate thickness, dependence of the yield of emitted substrate atoms has a maximum. The position of this maximum shifts to a larger impact angle and becomes more pronounced for projectiles that are more energetic. The shape of the plot obtained for sputtered atoms is particularly interesting as it is different from the yields reported for bulk solids bombarded by medium cluster projectiles, like C\textsubscript{60}, where the signal decreases with the impact angle. Such different behavior can be attributed to the limited thickness of the bombarded free-standing graphene.

The impact angle also has a significant influence on a number of ejected projectile atoms. Again, the functional form of this influence

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**TABLE I.** Yields and experimental ionization probabilities of carbon clusters as a function of cluster size. The data were obtained for 50 keV C\textsubscript{60}\textsuperscript{2+} impacts on 4L graphene.

<table>
<thead>
<tr>
<th>Carbon cluster</th>
<th>EA (eV)</th>
<th>Yield of ion, $Y_{C_{n}^-}$</th>
<th>Yield of neutral, $Y_{C_{n}^0}$</th>
<th>Experimental ionization probability, $\frac{Y_{C_{n}^-}}{Y_{C_{n}^0}} = P_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{1}</td>
<td>1.26</td>
<td>0.21</td>
<td>228</td>
<td>0.0015</td>
</tr>
<tr>
<td>C\textsubscript{2}</td>
<td>2.82</td>
<td>0.13</td>
<td>58.5</td>
<td>0.004</td>
</tr>
<tr>
<td>C\textsubscript{3}</td>
<td>1.53</td>
<td>0.06</td>
<td>14.8</td>
<td>0.007</td>
</tr>
<tr>
<td>C\textsubscript{4}</td>
<td>3.52</td>
<td>0.10</td>
<td>3.23</td>
<td>0.052</td>
</tr>
<tr>
<td>C\textsubscript{5}</td>
<td>2.49</td>
<td>0.062</td>
<td>0.77</td>
<td>0.136</td>
</tr>
<tr>
<td>C\textsubscript{6}</td>
<td>4.16</td>
<td>0.063</td>
<td>0.23</td>
<td>0.452</td>
</tr>
</tbody>
</table>

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**FIG. 7.** Dependence of the yields of carbon atoms ejected in the transmission (top) and sputtering (bottom) directions from the (a) two and (b) eight layer systems bombarded by 10 and 40 keV C\textsubscript{60} projectiles on the impact angle. Main graphs represent the atoms originating from the sample, while the insets depict projectile’s atoms. Reprinted with permission from M. Golunski and Z. Postawa, J. Vac. Sci. Technol. B 36, 03F112 (2018).
is different from the one observed for substrate atoms. The number of projectile atoms penetrating through the sample decreases monotonically with the impact angle, whereas the yield of backreflected atoms increases for more oblique impacts. For the 2L system, these yields are almost complementary, which indicates that projectile atoms can be either transmitted or backreflected. In other words, projectile atoms are not trapped inside such a thin system. The situation is different for the 8L system, especially when it is bombarded by low-energy projectiles. In this case, many projectile atoms are trapped inside the sample. Based on all observations, it can be concluded that the yield of graphene atoms is determined by two factors. The first factor is the amount of material available for ejection. This quantity will increase with the sample thickness and with the impact angle as the projectile will travel a longer path inside the substrate. The second factor is the amount of energy stored near the surface from where the ejection occurs. For ejection in the transmission direction, the upper surface is important. The energy stored near this surface will decrease with the sample thickness and the impact angle as projectile atoms have to sacrifice more energy to penetrate through the layer. For conditions where the substrate is perforated, there is an increase in the material available for ejection, and the yield increases with the substrate thickness or impact angle. However ultimately, less energy becomes available near the upper surface and the yield drops. For ejection in the sputtering direction, a bottom surface is important. Both the amount of material available for emission and the energy deposited near this surface increase with the sample thickness, until the layer becomes thicker than a thickness of a volume from where particles are ejected. Subsequently, the yield saturates because emission does not benefit from further increase in the sample thickness. The increase in the impact angle has also a positive effect on the amount of energy stored near the bottom surface as the energy deposition profile is shifted downward and the projectile can interact with a larger volume of material. However, the increase in the impact angle also reduces the projectile momentum component perpendicular to the surface. It becomes easier to backreflect the projectile atoms, and more energy is carried away by these particles. As a result, less energy is deposited near the bottom surface and the yield decreases for too oblique impacts. The yield of the projectile atoms ejected in the transmission direction is determined only by the capability of projectile atoms to perforate the sample. This capability decreases with the increase in both the layer thickness and the impact angle. The yield of the projectile atoms ejected in the sputtering direction will be determined by the capability of the sample to backreflect the projectile atoms. As already discussed, this capability increases with the impact angle. The increase in the primary kinetic energy leads to the deposition of a larger amount of this energy in the sample and to a larger projectile range. Both these factors lead to a stronger ejection of substrate atoms. A larger penetration range increases the substrate thickness, which can be perforated by the projectile. This factor leads to a shift of the emission maximum toward thicker samples for a constant impact angle or toward larger impact angles for a constant thickness when the projectile kinetic energy is increased. The increase in the primary kinetic energy also results in a broader distribution for projectile atoms.

It is known that for standard sputtering geometry, the substrate plays a major role in the ejection of intact molecules from ultrathin organic layers deposited on solid substrates. Direct collisions between projectile atoms and adsorbed molecules lead to molecular fragmentation. Collisions of adsorbed molecules with ejecting substrate atoms or a concerted action of the unfolding of the crater rim in the substrate are the main processes leading to molecular emission from systems bombarded by atomic and cluster projectiles, respectively. The application of graphene combined with a transmission geometry exhibit a significant contribution from both these processes. For instance, as shown in Fig. 4(a), ejection of substrate atoms in the transmission direction is much stronger than that in the sputtering direction. As visible in Fig. 2, the impact of C60 results in a visible collective motion of graphene sheets near the rim area. The effective processes of ejection and ionization of ejecta convey the idea of using of graphene as the support for the small amounts of molecules or nano-objects, which can be ejected/analyzed via cluster projectile impacts. This concept is addressed below.

III. EJECTION AND IONIZATION OF MOLECULES VIA 50 keV C602+ IMPACTS ON THIN MOLECULAR LAYERS DEPOSITED ON FREE STANDING GRAPHENE

To date, there are experimental data and MD simulations for three targets: single layers of molecules of phenylalanine (Phe), single layers of deuterated phenylalanine (D8Phe), and C60 molecules deposited on 2L graphene. The experiments show emission of molecular ions with yields comparable to the yield of ions emitted from the bulk targets (multilayers of molecules). For instance, the yield of negative ions of deprotonated phenylalanine, (D8Phe-H)−, emitted in the transmission direction is 0.10 ion per projectile impact for the target of 2 layer graphene coated by molecular layer of D8Phe (Fig. 8). This yield is comparable to a yield of 0.13 for a bulk target (Fig. 9) measured for secondary ions emitted in the reflection/sputtering direction.

These results raise the question of the mechanism(s) of organic molecule ejection and ionization from the graphene substrate. As noted earlier, the mechanism of molecule sputtering valid for bulk targets of organic molecules (weakly bonded molecular solids) is not applicable for the target of the molecular layer on graphene.

Indeed, the experimental data show notable differences between ion emission from single molecular layer+2L graphene and bulk D8Phe. The first difference is the high yield of C1− for graphene (0.15 ions/impact), which is attributed in part to fragmentation and atomization of the projectile after impact followed by the ionization of the projectile’s atoms. The yield of C1− measured for the bulk target is much lower (0.04 ions/impact) due to less recoiled projectile atoms. In the case of graphene, the shape of C1− peak has an extended tail toward the low mass range. In the experimental range of sensitivity, these ions of high kinetic energies extend up to 1/60 (833 eV) of the projectile energy. A further difference is the shape of the peak of (D8Phe-H)−, which depends on the mechanism/s of molecule ejection. In the case of emission from graphene, the shape of (D8Phe-H)− peak has an extended tail toward the high mass range (Fig. 6). This extended tail is due to fragmentation of molecular cluster ions. The vibrationally excited parent molecular cluster ion of phenylalanine (e.g., Phe dimer) undergoes an unimolecular fragmentation into a daughter Phe ion and a neutral molecule. Indeed, the total yield of Phe molecules computed for this case (165 molecules as separate entities, plus 190 molecules...
as molecular clusters) is significantly larger than the yield of Phe molecules from 1 layer of Phe deposited on graphene (9 molecules per impact). The MD simulations [Figs. 10 and 11 (Multimedia view)] show that the collision process for the latter case evolves in 2 steps. In a first phase ($t < 50$ fs), there is projectile atomization via atom-atom collisions. Interaction of these energetic atoms with the organic overlayer leads to molecular fragmentation and emission of fragments. A second phase ($\sim 3$ ps) is characterized by a post-collision collective process of molecular interaction with the vibrating rim. A notable emission of electrons was also observed ($\sim 3$ electrons/impact).

The critical process, which regulates the abundance of the ejecta, is the separation of the molecular layer from graphene. As a result, the molecules are bound only by weak intermolecular interactions and are easy to eject. The molecular layer evolves as a collective radial movement of Phe molecules, and simultaneously the graphene oscillates downward/upward. The pushed down graphene membrane is bent and stretched around the hole, thus accumulating potential energy. The result of the bending and stretching is an elastic movement of the membrane upward (Fig. 8, screenshot for time 3.1 ps). The accumulated potential energy is transformed into the kinetic energy of a correlated movement upward for membrane atoms. The membrane atoms interact with the atoms of Phe molecules and gently transfer the correlated momenta to them. Thus, the molecules eject without destruction. In other words, the membrane acts as a trampoline for the molecules. The ejection of molecules is clearly observable from the side view [Fig. 11 (Multimedia view)]. The screenshot for the times 0.6 and 3.1 ps [Figs. 10 and 11 (Multimedia view)] shows the strong bending of the graphene membrane followed by the abundant trampoline ejection of molecules. Graphene not only provides the effective trampoline ejection but also enhances the probability of negative ionization for ejected molecules. We postulate that the high rate of negative ionization is due to electron tunneling from graphene to phenylalanine. The mechanism of ionization is the same as for the emission of C clusters from graphene [Eq. (1) and discussion above]. The yield of intact neutral molecules of Phe computed by MD is 9 molecules/impact for the molecular layer of D8Phe deposited on graphene. Taking in account that the measured yield of (D8Phe-H)^− which is 0.1, the ionization probability (PI) is estimated as $\sim 0.02$. The ionization probability of Phe molecules sputtered from a bulk Phe target is $\sim 30 \times$ smaller.
This difference is due to the distinct mechanism of ionization for emission from a bulk molecular matter. The difference was discussed in Ref. 7. The relevant mechanism is the ionization via proton exchange between Phe molecules and negative ions of small fragments. This is a two-step process, when (a) small molecular fragments (e.g., CN), which have a high electron affinity, capture electrons via interactions in the sputtered volume of exited fragments; and (b) those negative fragments experience proton exchange with neutral Phe molecules or molecular clusters. The ionization probability depends mostly on the cross section of fragment/fragment and fragment/molecule interaction in the sputtered medium. The ionization probability is sufficient for the case of bulk molecular matter but 30× smaller than that for electron tunneling from graphene to molecule.

One should note that for the case of “Phe on graphene,” the pre-existing Phe molecules obtain additional kinetic energies via a trampoline effect. The kinetic energies may result in enhanced ionization probability due to the molecule’s fast escape from the tunneling distance.42

Thus, the physical properties of the substrate are key for maximizing ejection-ionization of monolayer deposits of weakly bonded moieties. The prime condition, however, is that of the energy density that must be delivered in a subpicosecond interval into the 2D solid in a way to generate collective motion of the substrate atoms. Future studies (experiments and simulations) focusing on projectile energy loss should provide insight into the energetics required for trampolining-ionization.

IV. TEST OF ELEMENTAL AND CHEMICAL COMPOSITION OF FREE STANDING GRAPHENE OXIDE (GO)

We turn now to C60 impacts on free standing graphene oxide, GO. GO has promising applications in many fields, including nanoelectronics, nanocomposites, as well as in biotechnology and environmental science.45–46 A first issue is the chemical composition of GO. The degree of oxidation (relative elemental concentration of C, O, and H) affects the relative presence of functional groups (epoxy, hydroxyl, and carboxyl). The stoichiometry of GO is a subject of recent investigations.45–47 For instance, elemental combustion analysis of oxidized flakes (thickness ~1.8 nm) shows a variation of composition from C13O10H8.84 for regular GO to C13O12H2.16 for a so-called graphene acid (GA) state.43 XPS analysis performed on the same GO and GA shows lower O contents due to the possible contribution of adsorbed water in the case of combustion analysis. XPS also showed different C to O ratios for GO samples from different commercial sources.46 The accurate elemental composition of GO flakes remains a challenge.46 The assay of free standing GO is fraught with further complications. For instance, elemental analysis via XPS is likely impaired due to contributions from the sample support (lacey carbon nets or quantifoil grids).

We show here that the elemental analysis of free standing GO can be performed with the technique of single cluster impacts of keV C602+, which stimulate the emission/detection of secondary ions from GO in the transmission direction (Fig. 1 and discussion above). The measurements were performed on free standing 2-layer GO film made from a graphene film by a proprietary oxidization process.47 Figure 12 shows the mass spectrum of negative secondary ions emitted from this sample via single impacts of 50 keV C602+. The mass spectrum contains peaks of H+, C+, and O2− [Fig. 12(a)].

The relative abundances of these ions (peak areas) do not correspond to the relative atom concentrations due to the different ionization probabilities of H, C, and O. Atomic ions of H+, C+, and O2− have long tails on the low mass side. The tails are due...
to high energy knocked-on ions which are ionized by direct atom-atom collisions in the 2D material. The peak of C\textsuperscript{-} consists also of ions originating from projectile atomization via collisions with C and O atoms of graphene. The low energy ions emitted from the rim around the rupture are, as noted earlier, likely due to electron tunneling from the hot rim. Thus, the complex picture of the ejection/ionization complicates (even makes impossible) an estimation of the relative concentrations of H, C, and O from abundances of the atomic ions. By contrast, the relative concentrations of H, C, and O can be estimated from the emission of molecular clusters.

The spectrum in the high mass range [Figs. 12(b)–12(d)] consists of molecular cluster ions of the type (a) [C\textsubscript{2n} (H\textsubscript{2}O)\textsubscript{2n+1} (CO\textsubscript{3}H)]\textsuperscript{−} (n = 3, . . . , 8) and (b) [C\textsubscript{2n} (H\textsubscript{2}O)\textsubscript{2n} (C\textsubscript{2}O\textsubscript{3}H\textsubscript{5})]\textsuperscript{−} (n = 1, 2, . . . , 8). These ions have as main constituents clusters such as C\textsubscript{2n} (H\textsubscript{2}O)\textsubscript{2n+1} and C\textsubscript{2n} (H\textsubscript{2}O)\textsubscript{2n}, which are bonded to the moieties CO\textsubscript{3}H (mass 61 amu) and C\textsubscript{2}O\textsubscript{3}H\textsubscript{5} (mass 77 amu). These molecules have high electron affinities of 3.68 eV and 4.08 eV, respectively; thus, the molecular clusters (a) and (b) are efficiently ionized. The core composition of the molecular clusters implies that the relative concentration of H, C, and O is approximately C\textsubscript{1}O\textsubscript{1}H\textsubscript{2} for the free standing 2-layer GO film (PELCO\textsuperscript{®} film from Ted Pella, Inc.). Surprisingly, the main constituent of the cluster is a carbohydrate [Fig. 12(d)]. The presence of carbohydrates indicates that the functional groups for GO are epoxy and hydroxyl and unlikely carboxyl. The absence of carboxylic groups supports data from GO flakes analyzed by Magic Angle Spinning NMR Spectroscopy.

The GO film is hydrophilic and will absorb water when exposed to air prior to insertion into the vacuum chamber of the mass spectrometer. Indeed, some H\textsubscript{2}O in (a) and (b) may be water molecules recombined to that molecular cluster ions. To explore the hydration of GO, we tested oxidized carbon nanotubes with the method of single impact SIMS using keV C\textsubscript{60}\textsuperscript{2+}. The sample was a sponge-like 3D nanostructure made from onionlike carbon nanotubes with a porosity of ~97%. This spongelike hydrophilic nanostructure was completely filled with deuterated water prior to insertion into
FIG. 13. Mass spectrum of negative ions emitted from hydrophilic spongelike 3D nanostructure made from onionlike carbon nanotubes with a porosity of \( \sim 97\% \). The sponge was filled with deuterated water prior to insertion into vacuum.

Vacuum for the mass spectrometry experiment. The sample was in high vacuum for \( \sim 10 \) min prior to the MS experiment. The mass spectrum of negative ions emitted via \( \sim 50 \) keV \( \text{C}_{60}^{2+} \) impacts (Fig. 13) does not contain water molecules. The only evidence of the presence of water before evaporation is the peak of \( \text{D}^- \) and probably peak of \( \text{C}_2\text{D}^- \), which indicate a substitution of hydrogen by deuterium. Thus, under vacuum the water was removed from the carbon nanostructure.

The oxidation process oxidized only the surface of the nanotubes, without oxidation of the inner shells of the onionlike nanotubes. As a result, the mass spectrum of the 3D nanotube structure has dominant peaks of \( \text{C}_n \) and \( \text{C}_n\text{H}_m \) clusters ions. The 2D GO case is different. The concentrations of O and H are high for free standing 2L GO, which as noted earlier as \( \text{C}_1\text{O}_1\text{H}_2 \). The method demonstrated on 2D GO can be applied for any functionalized graphene films.

V. \( \text{Au}_{400}^{4+} \) CLUSTERS IMPACTS ON FREE-STANDING GRAPHENE

We contrast now the 2D projectile impacts with 3D ones, specifically \( \text{Au}_{400}^{4+} \) (of 440–540 keV or 33–36 km/s) again at the level of individual events. The \( \text{Au} \) atoms undergo atom-atom collisions, which are different from those occurring with \( \text{C}_{60} \). First, \( \text{Au}_{400} \) projectile is a 3D object composed from atoms filling up the entire volume. \( \text{C}_{60} \) projectile has a shell 2D structure, in which carbon atoms are located at the surface of the projectile. It will be much easier disrupt such structure. Second, \( \text{Au} \) atoms are much heavier than \( \text{C} \) atoms. The mass difference will result in a less efficient energy transfer in \( \text{Au}--\text{C} \) collisions as compared to \( \text{C}--\text{C} \) interactions present during \( \text{C}_{60} \) impact. It will be also more difficult to change movement trajectories of the heavy \( \text{Au} \) atoms. \( \text{Au}_{400} \) will mostly deform when meeting a network of \( \text{C} \) atoms in graphene rather than disintegrate as the latter requires efficient trajectory deflection of individual gold atoms. Finally, the 500 keV \( \text{Au}_{400} \) projectile will have a much larger momentum as compared to 50 keV \( \text{C}_{60} \) due to larger mass of \( \text{Au} \) atoms and a larger number of atoms composing \( \text{Au}_{400} \) cluster. Most of carbon atoms scatter off the surface of \( \text{Au}_{400} \), a few may experience collisions in the vicinity of \( \text{Au}_{400} \).

Thus, at any moment, each \( \text{C} \) atom residing in the interaction area experiences a gentle correlated action of many \( \text{Au} \) atoms. A pressure exerted by a single object rather than by individual collisions punctures the graphene layer. Consequently, the projectile pushes through graphene as a deformed but single entity. Figure 14

FIG. 14. Snapshot (MD simulations) of the 1 layer graphene taken at (a) 0.1 ps and (b) 0.2 ps after 500 keV \( \text{Au}_{400}^{4+} \) impact at a monolayer of graphene at normal incidence.
shows the MD simulations of 500 keV Au$_{400}^{4+}$ impacting on 1 layer graphene at first 0.1 ps and 0.2 ps. During the passage through graphene (~0.1 ps), the projectile makes a round shaped rupture of ~2 nm in diameter. C atoms, which are knocked on from the ruptured area, are spread into the space around the transmitted projectile. The zone raptured by the impinging projectile is much less that the punched area observed experimentally. This discrepancy will be discussed below.

In punching a hole, the projectile experiences a strong asymmetric atomic disorder in its top hemisphere. Thus, a part of the kinetic energy of the projectile is transferred into the excitation of its electronic system. The exited Au$_{400}$ is for a short time (0.2 ps) present in the vicinity of the hole in the graphene, with a rim area which is also electronically exited. We posit that this excitation in part is spent on electromagnetic interaction between Au$_{400}$ and the graphene hole (discussed below). The remainder of excitation is by electron-phonon coupling, transformed into the vibrational excitation of the isolated Au cluster (time >0.2 ps after impact). The vibrationally excited clusters undergo fragmentation, as observed experimentally. The massive emission of atomic and C cluster ions (negative and positive) from the rim of the raptured graphene is also documented.

Figure 15(a) shows the mass spectrum of negative ions detected in the transmission direction. The mass spectrum was obtained with ~$10^6$ impacts of 540 keV Au$_{400}^{4+}$ on 1-layer graphene. The target bias was set to −15 kV. The main features of the mass spectrum are the C$_n^-$ ions (n = 1–10) followed by C$_n$H$_m^-$ ions. These ions have high SI yields (e.g., 1.25 ions per impact for C$_2^-$). In the higher mass range, there are peaks due to the Au$_{400}$ projectiles and projectile fragments of Au$_{1-3}^-$ ions. These peaks are broad and centered at lower m/z, indicating that these ions have shorter flight times and have initial kinetic energy distributions that come from the hypervelocity Au$_{400}$ projectiles.

When the target bias was set to +10 kV, the positive ion mass spectrum consisted of C$_n^+$ (n = 1–7) and C$_n$H$_m^+$ ions in the low mass range, and Au$_{1-3}^+$ and Au$_{400}^+$ projectile peaks in the high mass range [Fig. 15(b)]. Fragmentation via evaporation of atomic or cluster ions is possible if the parent cluster has a high charge state. The detection of both Au$_{1-3}^-$ and Au$_{1-3}^+$ verifies that the projectile can indeed be charged negatively or positively after passing the graphene.

As the projectile approaches the graphene at a distance shorter than that of electron tunneling, it is neutralized by electron exchange with the target. At the moment of passage, the projectile and the rim around the hole are electronically excited. Upon exiting, the projectile undergoes electron exchange with the rim. The non-adiabatic interaction allows the projectile to carry a random charge (discussion below). The charge state of Au$_{400}$ regulates the number of Au ions that evaporate. Approximately 50% of atomic Au is charged positively or negatively. Most evaporated Au is singly or doubly charged with a small number carrying multiple charges. Another 50% of the transmitted projectiles or fragments are neutral.

FIG. 15. Negative (a) and positive (b) ion spectra of 540 keV and 440 keV Au$_{400}^{4+}$ projectile impacts (−15 kV and +10 kV target bias) on graphene in the transmission direction.

FIG. 16. Normalized (area under distribution is unity) distributions of the number of Au$_i^+$ ions evaporated from a single Au$_{400}$. Number of evaporated ions correlate with the charge state (negative-neutral-positive) of Au$_{400}$ passing graphene.
An analysis of the rates of evaporation\(^5\) shows that \(A_{400}\) carries an internal energy of \(\sim 450\)–500 eV which is dissipated in a multifragmentation process resulting on average in the evaporation of \(\sim 90\)–100 atoms, regardless the charge state of \(A_{400}\). The internal energy is similar for projectiles with different charge states (positive, negative, or neutral). Figures 16 and 17 illustrate the experimental data on the evaporation process. Mostly, the fragmentation via evaporation takes place after randomization of the excitation energy (>0.2 ps), when the classic statistical approach of internal energy fluctuations among the clusters degrees of freedom applies.\(^6\)\(^7\) The fragmentation was measured in the experimental time range from \(t_0 = 0.2\) ps to \(t = 0.1\) \(\mu\)s.

Another important characteristic is the size of the graphene rupture. MD simulations [Fig. 12(b)] show that the diameter of the rupture is comparable with the diameter of the projectile (~2 nm). However, the experimental data show larger ruptures.\(^8\)

Impacts of a sequence of single projectiles on single layer graphene are shown in the transmission electron micrograph in Figs. 18(a) and 18(b). Round holes surrounded by an amorphized graphene are evident. They are distinct in size and shape from the significantly larger holes attributed to defects in the graphene film [Fig. 18(b)]. The holes caused by 480 keV \(A_{400}\)\(^{+}\) impacts on graphene have a size distribution with a mean diameter of \(\sim 2\) nm. Interestingly, the mean diameter of the holes is independent of the number of layers of graphene in the sample (1, 2, or 4 layer graphene).\(^9\)

The density of round shaped holes corresponds to the dose of projectiles. The scanning electron microscopy (SEM) micrograph [Fig. 18(c)] shows a large area of the ruptured graphene. The scale of this SEM image is too coarse to show the correct image of the holes; however, the density of the randomly distributed holes (~120/\(\mu\)m\(^2\)) can be counted. Note, that both micrographs [transmission electron microscopy (TEM) micrograph and SEM] show also the rare mechanical ruptures, which are approximately two times larger than the round shaped holes [Figs. 18(b) and 18(c)]. These ruptures are not round shaped. Graphene is contaminated by CuCl nanoparticles, which are visible in micrograph as black small spots of a size of \(\sim 2\) nm [Figs. 18(a) and 18(b)]. The presence of these particles is due to the process for producing the graphene. The density of CuCl particles is very low. One can speculate that direct impacts on the CuCl nanoparticles are responsible for the generation of large holes. However, their low density and the low probability of direct impacts suggest that the generation of large holes from impacts on the CuCl nanoparticles is negligible.

It must be noted that 50 keV \(C_{60}\)\(^{2+}\) impacts produced no visible holes suggesting a self-healing process.\(^10\)

To explain the effect of large holes, we postulate that a neutral or charged cluster undergoes a dipole interaction with the rim of the rupture. The \(A_{400}\) projectiles, after passing through graphene, are partially neutral (~50%) and partially negatively (~25%) and positively (25%) charged. Charged \(A_{400}\)\(^{\pm}\) are not only singly charged; the charge distribution [Fig. 16] shows that high charge states (8+ and 5−) were detected. The charge is distributed evenly over the \(A_{400}\) surface after passing the critical distance for electron tunneling (1 nm, \(t > 0.1\) ps). The time evolution of \(A_{400}\) was discussed in detail in Ref. 6. Let us consider first the multicharged \(A_{400}\), which passed the graphene and is aligned with the rupture at distance \(>1\) nm (critical distance of electron tunneling).\(^11\) Charged \(A_{400}\) induces the opposite charge at the surface area around the rupture. The electric field lines between the projectile and the rim of the rupture result in a dipole. The electric field of the dipole is strong due to the short distance and high charge. One can estimate the field of the dipole at the surface of the projectile as follows:

\[
E_x = \frac{1}{4\varepsilon_0 \pi} \frac{Q}{r_0^2} + \frac{x}{2\varepsilon_0} \int_{r_0}^{r_{eff}} \frac{\beta(y)y}{\left(x^2 + y^2\right)^{3\slash 2}} dy, \quad \text{(2)}
\]

where \(Q\) is the charge of the nanoparticle, \(r_0\) is the radius of the nanoparticle and the initial puncture in the graphene, \(\beta(y)\) is the radial density of the charge around the primary hole, and \(x\) is distance between the surface of nanoparticle and the hole plane. The boundary condition for the charge around the hole is \(\int_{r_0}^{r_{eff}} \beta(y) dy = Q\), where \(r_{eff}\) is the effective radius of the charge area around hole. Assuming that \(r_{eff} \approx r_0\), the solution of Eq. (2) for the field strength at the surface of the projectile is

\[
E_x = \frac{Q}{4\varepsilon_0 \pi r_0^2} \left(\frac{x}{x^2 + r_0^2} + \frac{1}{r_0^2}\right). \quad \text{(3)}
\]
FIG. 18. Transmission electron microscopy image [(a) and (b)] of single layer graphene after irradiating with 480 keV Au$^{400+}$ projectiles in a 3 mm diameter area (scale bar 20 nm). The small black particles correspond to copper chloride nanoparticles produced from the manufacturing process as indicated by the manufacturer. Scanning electron microscopy image (c) shows the graphene attached to the lacey carbon frame. The density of the randomly distributed holes is $\sim 120/\mu m^2$.

Due to the strong bonding of the poles of the dipole (field of $\sim 1$ V/Å), the movement of the multicharged projectile (one side of dipole) will bend and stretch the graphene around the hole. The projectile will experience an energy loss, when a part of projectile kinetic energy is transferred to the rim via the electrostatic interaction of the dipole poles. The graphene membrane accumulates the strain energy very effectively due to its high Young modulus ($\sim 1$ TPa). The average energy loss of the projectile of $\sim 72$ keV is higher than the energy, which the projectile spends on rupturing the graphene and on the carbon ejecta ($\sim 53$ keV) via atom-atom collisions only. We infer that part of the additional energy loss is due to the dipole projectile/rim interaction, and this energy is accumulated into the stretching of the graphene. The stripping of carbon atomic and cluster ions due to the strong field of the dipole can be considered as a mechanism of the enlargement of the hole size. Thus, the charged nanoparticle-graphene dipole interaction may explain the experimental observations of (a) high kinetic energy loss of the projectiles; (b) charge distribution of projectiles; (c) abundant emission of C$_n^{+}$; and (d) large size of holes made by projectile impact, which are $9 \pm 2$ nm.

The most intriguing part of $A_{400}$ graphene interaction occurs within $t < 0.1$ ps. The Au$_{400}^{4+}$ projectile approaching the graphene surface ($t = 0$) is neutralized by electron tunneling with graphene; thus, the actual impact makes a neutral system of Au$_{400}$ connected to graphene. Indeed, the electronic processes are fast; thus, the system has a joint Fermi level and a small potential gradient due to the different work functions of Au$_{400}$ and graphene (6 eV and 4.5 eV, respectively). After impact, a unique self-organized system is obtained (Fig. 14). MD simulation show that Au$_{400}$ being deformed via interaction is aligned axially within the hole in graphene made by the Au$_{400}$. The deformation is observed in the top semi-sphere of $A_{400}$ only, indicating that electrical contact (joint Fermi level) is lost, when the second half of $A_{400}$ passes the hole. The diameter of the hole (Fig. 14) is slightly larger than the diameter of Au$_{400}$. The difference in the work functions is limited, and the induced charge on Au$_{400}$ cannot be above $+1$. However, the projectile located in the hole is electronically exited due to deformation via impact.

A correct model of time evolution of the electronically exited nanoparticle located in the graphene hole is a subject for future work, but some important features of the behavior of this system can be already discussed. The case of metallic nanovolume electronically excited via keV cluster impact was theoretically examined in Ref. 51. It was noted that fluctuations of the local electron density should be taken in account to describe the transfer of a kinetic energy of projectile into the electronic subsystem. In this case, fast electron density fluctuations, which are generated and then quenched multiple times, characterized the deformed Au$_{400}$, where the displaced atoms are reorganized during the time of passage of $\sim 0.1$ ps (Fig. 14). The fluctuations of the local electron density of Au$_{400}$ within the hole stimulate the production of local random dipoles between Au$_{400}$ and the rim of the hole. The random dipoles are generated by electron density fluctuations and are quenched by electron exchange with graphene during the time of passage. The force of this electrostatic interaction should be always attractive between the $A_{400}$ and the hole, regardless of the dipoles polarities. Moreover, even if the average charge of the projectile is zero, an attractive
force will be generated. As a result, the hole works as a trap for the electronically excited metal cluster. The strength of this force can be described formally by Eq. (2) where instead of the charge of Au400, the fluctuations of local electron density are applied. The non-adiabatic electron exchange between Au400 and graphene may describe the exotic charge distribution of the projectile after interaction (∼50% of neutrals, ∼25% of negatively, and ∼25% positively charged Au400). Again, a more detailed model of the electronically excited nanoparticle located in the graphene hole remains to be developed.

VI. CONCLUDING REMARKS

MD simulations of fullerene impacting free standing graphene at ∼0.8 keV/atom agree well with the experimental observations. This is not the case for impacts with gold nanoparticles at ∼1.2 keV/atom. This interaction has drastic consequences for the emerging projectile in terms of energy loss and evaporation of atoms. Remarkable effects caused by a single layer of graphene!

Setting aside the fate of the projectile, the collision regimes considered here involve distinct ejection-ionization mechanisms. The abundant ionization of atoms, molecular fragments, and entities can be explained with ultrafast cooperative motion and electronic projectile-target interactions. They evolve as the target thickness increases into ultimately the well described process occurring in projectile-bulk matter impact.

We infer from the observations reported here that free-standing graphene is an interesting candidate as a substrate for a chemical analysis of atto/zeptomole samples via cluster-SIMS in the transmission mode. First, the extremely small thickness of the support results in small amounts of emitted substrate material. As a result, there is a minimal interference between the substrate and the analyzed signal. A large portion of the primary kinetic energy can be transmitted to the organic overlay in the direction toward the detector by gentle, collective movement of the graphene layer. Such concerted action of substrate atoms increases a chance that intact molecules can be recorded. These observations confirm the feasibility of detecting of attomole to zeptomole amounts of analyte. Deposition of such small amounts of material opens the potential capability to perform quantitative analysis by SIMS in the way proposed in the so-called storing matter technique.26 In this approach, SIMS analysis is performed on deposit which is sufficiently dilute not to give rise to matrix effects.

The present report focuses on negative ion emission from graphene impacted with 2D and 3D projectiles of comparable velocities. Other target and bombardment conditions remain to be explored for a broader understanding of the effects of projectile characteristics, impact angle/target thickness on the nature, and abundance of the ejecta. A more nuanced insight into fascinating motional and electronic processes will require experiment paralleling MD simulations. In particular, an exploration of lower momentum of impacts should be useful to assess prospects for surface analysis. Here, the observations of ionized ejecta should be complemented with detection of neutrals via postionization. The postionization technique62 can potentially explore the very effective “trampolining” of large intact molecules from the graphene, in the case when the energy of projectile is not enough for graphene rupturing.

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