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RESEARCH ARTICLE

C-O Bond Dissociation and Induced Chemical Ionization Using High Energy $(CO_2)_n^+$ Gas Cluster Ion Beam

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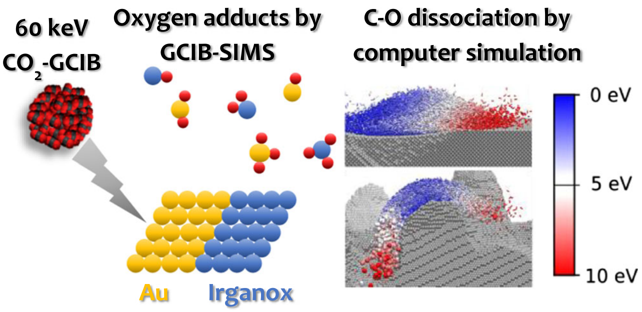

Abstract. A gas cluster ion beam (GCIB) source, consisting of CO_2 clusters and operating with kinetic energies of up to 60 keV, has been developed for the high resolution and high sensitivity imaging of intact biomolecules. The CO_2 molecule is an excellent molecule to employ in a GCIB source due to its relative stability and improved focusing capabilities, especially when compared to the conventionally employed Ar cluster source. Here we report on experiments aimed to examine the behavior of CO_2 clusters as they impact a surface under a variety of conditions. Clusters of $(CO_2)_n^+$ ($n = 2000$~10,000) with varying sizes and kinetic energies were employed to interrogate both an organic and inorganic surface. The results show that C-O bond dissociation did not occur when the energy per molecule is less than 5 eV/n, but that oxygen adducts were seen in increasing intensity as the energy is above 5 eV/n, particularly, drastic enhancement up to 100 times of oxygen adducts was observed on Au surface. For Irganox 1010, an organic surface, oxygen containing adducts were observed with moderate signal enhancement. Molecular dynamics computer simulations were employed to test the hypothesis that the C-O bond is broken at high values of eV/n. These calculations show that C-O bond dissociation occurs at eV/n values less than the C-O bond energy (8.3 eV) by interaction with surface topological features. In general, the experiments suggest that the projectiles containing oxygen can enhance the ionization efficiency of surface molecules via chemically induced processes, and that CO_2 can be an effective cluster ion source for SIMS experiments.

Keywords: Gas cluster ion beam, C-O bond dissociation, Carbon dioxide cluster, Irganox 1010, Au film, Molecular dynamics computer simulations

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Introduction

Gas cluster ion beam (GCIB) sources have gained popularity in conjunction with secondary ion mass spectrometry (SIMS) experiments. These beams provide an effective means of eroding an organic material without damage accumulation, resulting in improved molecular depth profiling behavior. Moreover, when employed as a SIMS source, the GCIB yields mass spectra that exhibit improved detection of larger intact molecular ions and reduced formation of molecular fragment ions relative to atomic ion and C_{60} clusters conventionally employed [1–4]. The most commonly employed GCIB consists of clusters composed of Ar, generally in the size range of $n = 100$ to 10,000 atoms. At a typical acceleration energy of 20 keV, each Ar atom carries between 2 and 200 eV/n. This eV/n value spans the range of energies associated with chemical bonds and is the primary reason that less fragmentation is observed during desorption, particularly for the larger clusters.

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An advantage of the GCIB design is that the composition of the cluster can be varied at will. For example, it has been possible to tune the chemistry of the GCIB to enhance ionization probability, and hence, expand the range of applications amenable to study. We have employed the concept of a mixed cluster whereby a hydrogen-containing small molecule is doped into the Ar cluster to create an environment suitable for protonation of desorbed molecules [5]. This approach has been particularly successful when using HCl as a dopant, especially when H_2O is present either in the vacuum or on the sample surface. The water presumably enhances the formation of H_3O^+ and the formation of $[M + H]^+$, where M is the molecule of interest. In a related effort, large water clusters have been generated directly, and have demonstrated ion yield enhancements of greater than a factor of 10 [6–8]. Moreover, the HCl-doped Ar cluster beam can overcome salt suppression by promoting the protonated molecule ion, mitigating the pronounced matrix effect in biological samples [7].

In an effort to search for the ideal gas candidate for the cluster, we explored the possibility of employing clusters of CO_2 as the GCIB. In earlier work, we demonstrated that this cluster is more stable than Ar clusters and hence is produced using lower pressures in the expansion region of the GCIB source [9]. Moreover, this stability results in better focusing properties than Ar clusters. For example, using a 20-keV beam, Ar clusters could be focused to a 20-μm spot, while a similar CO_2 beam could be focused to a 7-μm spot. This result is obviously critical for molecule-specific imaging experiments where it has been a goal to reach submicron spatial resolution, a value important for imaging of biological cells. And finally, both molecular dynamics computer simulations and experiments suggested that the behavior of CO_2 was very close to that of Ar when energy per molecule < 5 eV/n, where the CO_2 molecule acts as a pseudo-atom of mass 44 amu [9]. To improve the spatial resolution of GCIB sources for bioimaging applications, an ion gun has been constructed with an acceleration voltage of 60 keV, allowing submicron spot sizes to be achieved. However, this expanded energy range opens the possibility that CO_2 molecules will be dissociated during ion impact. Akizuki et al. have reported that SiO_2 film forms on silicon surface upon the CO_2 cluster beam irradiation with minimum energy per molecule of 40 eV/n, resulting from the high density energy deposition within localized surface area [10]. Here we show from experiment and computer simulations that for energy per molecule above 5 eV/n dissociation is observed as evidenced by ejected molecular ions that have incorporated oxygen atoms. We present a systematic study over the kinetic energy range of 20 to 60 keV, and for cluster sizes of 2000 to 10,000 CO_2 molecules to examine the magnitude of the effect. As a consequence of this new chemistry, the intensity of molecular ions containing oxygen can be enhanced by more than a factor of 10 with organic molecules and more drastically on metal surfaces. In general, we show that this ion source offers new opportunities for GCIB SIMS.

Experimental

Sample Preparation

The Irganox 1010 thin film was purchased from the National Physical Laboratory (NPL, Huntington, UK). The film was deposited onto finely polished silicon wafers (1.0 × 1.0 × 0.5 mm^3). The thickness of the film was monitored during the deposition process at NPL by a quartz crystal microbalance calibrated by spectroscopic ellipsometry. Specifically, the sample measured in this work had a thickness of 49.5 nm.

A gold film was purchased from Electron Microscopy Sciences (Hatfield, USA) with a thickness of 18 μm. The film was pre-sputtered using a 20-keV Ar_{1000}^+ cluster beam with a current of 100 pA for 30 min to remove the organic contaminants on the surface.

SIMS Characterization

The initial motivation for this work stems from an observation of intense gold oxide ions from a Au surface under bombardment by $(CO_2)_n^+$. Due to the limited supply of oxygen in the vacuum chamber where the sample is analyzed, it was speculated that O is produced by dissociation of CO_2 molecules. This study is aimed toward elucidating the conditions where C-O bonds break and if the oxidization occurs on organic surfaces as well.

The gas cluster ion beam utilized here (GCIB SM from Ionoptika, UK) is shown schematically in Figure 1. The system is designed to operate at kinetic energies of up to ~ 60 keV,

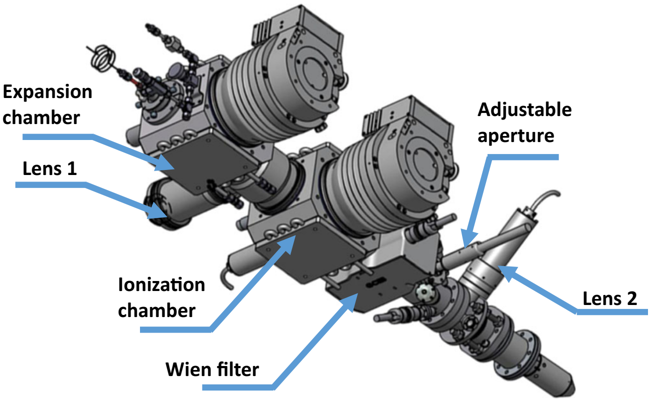

Figure 1. Schematic of GCIM SM. The GCIB SM is a gas cluster ion beam source developed by Ionoptika (Chandler's Ford, UK), for molecular imaging SIMS. It operates at a maximum acceleration potential of 70 kV, using a two lens system to form a spot size of 1 μm. Running CO_2 gas, the system is capable of operating with cluster sizes of < 30,000. Cluster generation occurs as high pressure input gas passes through a de Laval nozzle, condensing into clusters at the exit due to rapid expansion and cooling of the gas. The neutral gas beam is then ionized by electron bombardment, before being focused through the column. A Wien filter allows for mass filtering, and a narrower cluster size distribution. Time of flight measurements enable precise tuning of the clusters size

with a cluster size of up to 30,000 molecules. The GCIB SM was installed on a buncher-TOF SIMS instrument, J105 3D Chemical Imager (Ionoptika, UK) [11] and is incident upon the sample with an angle of 45°.

The spectra from fresh Irganox and Au surfaces were acquired using $(CO_2)_n^+$ with varying cluster sizes and energies. The kinetic energy of the clusters has a range of 2.5~30 eV/n, determined by the availability of the cluster from the GCIB SM. Specifically, $(CO_2)_n^+$ clusters consisting of 2000, 4000, 6000, 8000, and 10,000 molecules with an energy range of 20~60 keV were used. The cluster size was selected using a Wien filter. A spread of ~ ± 5 µs (FWHM) ToF was measured, which, for instance, corresponds to a spread ± 370 CO_2 molecules for 50 keV $(CO_2)_{2000}^+$ and ± 830 for 50 keV $(CO_2)_{10000}^+$ cluster projectiles.

On the Irganox film, the spectra were acquired over area of $50 \times 50\ \mu m^2$ using 10 pA of each cluster ion beam with 32 × 32 pixels and 100 shots per pixel. The ion dose for each spectrum is 2.5×10^{13} ions·cm^{-2}. Five parallel measurements on a fresh Irganox 1010 film surface were conducted. On the gold surface, 10 parallel measurements were conducted on the same spot, but only the last five spectra were used for data processing to avoid surface contamination by organic adventitious sources of organic molecules.

Control experiments were performed using 50 keV $(Ar)_n^+$ with a cluster size of 2000, 4000, 6000, 8000, and 10,000 with the same condition as corresponding $(CO_2)_n^+$ clusters on both the Irganox 1010 and the Au film.

Data Processing

The software Ionoptika Image Analyser (Version: 1.0.8.14) was used to read the intensity of selected ions, $[M + 2O]^-$ at *m/z* 1207.77 (Δ*m/z* 0.6) for Irganox 1010 and *m/z* 228.96 (Δ*m/z* 0.2) for Au. The average intensity and the standard deviation of selected ions were plotted against energy per molecule of the cluster ions beams.

Computer Simulation

A detailed description of the molecular dynamics computer simulations used to model cluster bombardment can be found elsewhere [12]. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. The forces among the particles are described by a blend of pairwise additive and many-body potential energy functions. The interaction among cluster projectile molecules consisting of C and O atoms is described by the ReaxFF-lg [13] potential splined with a ZBL potential [14] to properly describe high-energy collisions. For interaction among gold atoms, the EAM potential [15] is used while the interaction between gold atoms and cluster projectile atoms is described by a ZBL potential. The calculations are performed with a LAMMPS code [16] that was modified for a more efficient modeling of sputtering phenomena.

The experiments were performed on an organic substrate (Irganox) and a metal (gold) with the measured quantities being attachment of O atoms to the ejected molecule or atom. The more straightforward of the samples to model is Au because the only source of O in the ejected species is the incident cluster beam. Thus, the dissociation of the CO_2 molecules that occurs early in the collision cascade can be used as a signal that Au-O adducts can be formed. Two types of Au samples were studied, a flat Au(100) surface and an Au sample with already developed morphology which was created in a previous study [17]. In the case of flat Au(100), a hemisphere with a diameter of ~ 40 nm, consisting of ~ 1 million atoms, was cut out of perfect gold crystal. For the roughened surface, a cylinder with a diameter of ~ 60 nm and height of 25 nm, consisting of ~ 2.4 million atoms, was chosen. In both cases, rigid and stochastic regions with a thickness of 0.7 and 2.0 nm, respectively, were used around the sample. These boundary conditions simulate the thermal bath that keeps the sample at the required temperature and helps inhibit the pressure wave reflection from the system boundaries [18]. These samples were bombarded by 50 keV $(CO)_n$ cluster projectiles consisting of 4000, 6000, 8000, and 10,000 molecules at 45° impact angle to reproduce experimental conditions. For the roughened surface, two types of impacts were chosen, one that aimed at a hill or protrusion into the vacuum and one that aimed at a depression or hole position. The simulations are calculated for a 0-K target temperature. Each impact event is evaluated to 8 ps, which is sufficiently long to determine the number of CO_2 molecules that dissociate.

Results and Discussions

Investigation of Oxygen Adducts from Organic and Inorganic Surfaces Under Bombardment of $(CO_2)_n^+$ Beams

During bombardment by the $(CO_2)_n^+$ cluster ion beam, oxygen adducts $[M + nO]^-$ were observed to be emitted from the surface of Irganox 1010 and Au, as shown in Figure S1. Several oxide ions are seen from Irganox 1010, described as $[M_{Irganox}\text{-}H + nO]^-$ $n = 1$~4. Correspondingly, *m/z* values at *m/z* = 1191.77, 1207.77, 1223.76, and 1239.76 are observed. The intensity of the oxygen adducts decreases slightly with the addition of O atoms. On the Au surface, $[M_{Au} + nO]^-$ $n = 1$~3 are the most intense ions, with *m/z* values of 212.96, 228.96, and 244.95. Meanwhile, oxygen adducts of gold clusters are observed with composition of $[2M_{Au} + nO]^-$ and $[3M_{Au} + nO]^-$ $n = 1$~3, with intensities that are lower when compared to $[M_{Au} + nO]^-$. Only the bi-oxygen adducts, $[M_{Irganox}\text{-}H + 2O]^-$ and $[M_{Au} + 2O]^-$ are discussed as they are representative of the other oxide products.

The Study on the Formation of Oxygen Adducts at Varying Kinetic Energy of $(CO_2)_n^+$ Beams

To understand the formation of oxygen adducts, a systematic study was performed using $(CO_2)_n^+$ beams with varying cluster size and energy. The ion intensities of $[M_{Irganox}\text{-}H + 2O]^-$ and $[M_{Au} + 2O]^-$ are plotted versus the kinetic energy per molecule, eV/n, in Figure 2a, c, respectively. It is clear that oxygen adducts occur beyond a threshold value ~5 eV/n. Above the threshold, the intensity of the oxygen adducts increases along with the increase of the energy per molecule. In general, for a given energy per molecule value, the beam with the higher kinetic energy yields higher oxygen adduct intensities than the beam with lower kinetic energy at the same energy per molecule. For example, at energy per molecule of 10 eV/n, the intensity of $[M_{Irganox}\text{-}H + 2O]^-$ from Irganox 1010 is 30% higher using 60 keV $(CO_2)_{6000}{}^+$ than using 40 keV $(CO_2)_{4000}{}^+$, and 63% higher compared with 20 keV $(CO_2)_{2000}{}^+$ as shown in Figure 2. A similar trend of $[M_{Au} + 2O]^-$ from the Au surface is observed in term of the intensity changes of oxygen adducts with varying eV/n of the analyzing beams, except that there is more dramatic enhancement of oxygen adducts at higher kinetic energy and eV/n. These results certainly suggest that oxygen originates from the $(CO_2)_n{}^+$ cluster itself. Above 3 eV/n according to our observations, the C-O bonds dissociate during impact on the sample surface. The energy carried by each CO_2 molecule allows the free O atoms to interact with the sample surface instead of escaping, yielding the various oxygen adducts. The ratio of C-O bond dissociation increases along with the increasing kinetic energy and energy per molecule of the beams, resulting in the higher intensity of oxygen adducts. The very low intensity of oxygen adducts on the Au surface using 20 keV $(CO_2)_n{}^+$ beams could result from the lower sputter rate of metal atoms. At higher kinetic energy, 30, 40, and 50 keV, the sputtering yield increases and more free O atoms promote the formation of Au oxide. This concerted action leads to the enhancement of the Au oxygen adducts at higher kinetic energy.

To rule out the possibility of other sources of free O atoms, the control measurements were carried out using $(Ar)_n{}^+$ beams at the same cluster size. Here, only the measurements using 50 keV $(Ar)_n{}^+$ beams are plotted as in Figure 2b, d to simplify the presentation. It is clear that only 16~30% of oxygen adducts, $[M_{Irganox}\text{-}H + 2O]^-$, are observed on the Irganox 1010 surface using 50 keV $Ar_n{}^+$ compared with corresponding $(CO_2)_n{}^+$ beams when energy per molecule is over 8 eV/n as shown in Figure 2b. The source of the O atoms for these oxide products could be fragmented from the Irganox 1010 molecule during bombardment. While on the Au surface, the oxygen adducts, $[M_{Au} + 2O]^-$, are barely detectable using 50 keV $Ar_n{}^+$ beams as shown in Figure 2d. The oxygen adducts of Au are drastically increased by up to 850-fold using 50 keV $(CO_2)_n{}^+$ beams. It is evident that $(CO_2)_n{}^+$ beams with

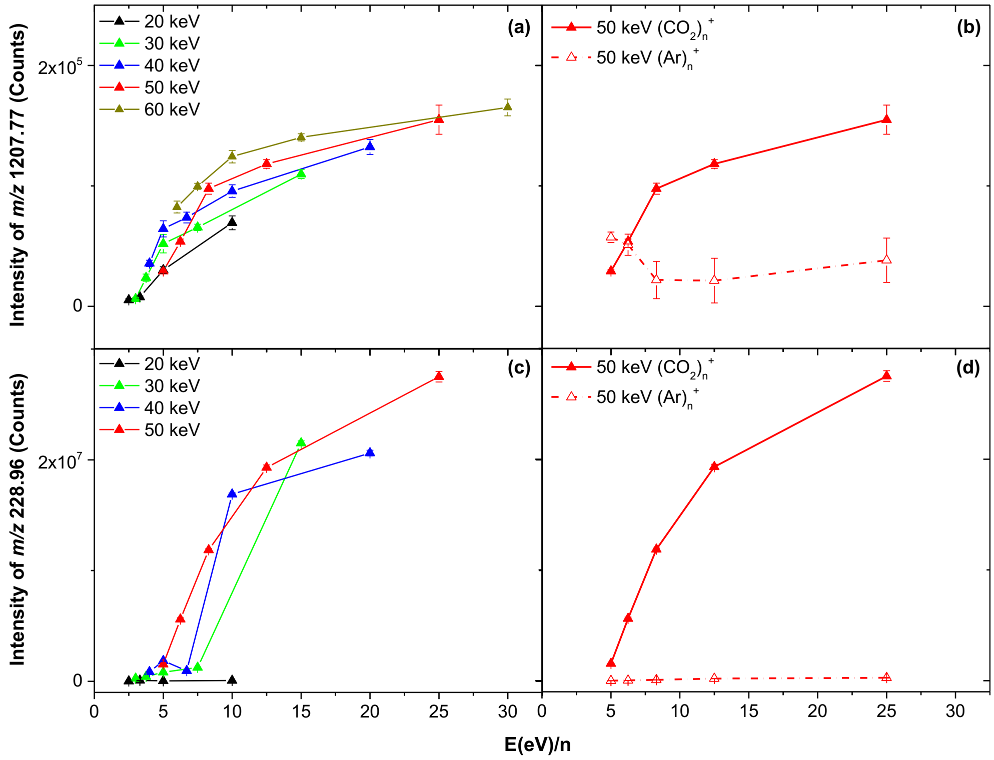

Figure 2. Ion intensities as a function of kinetic energy per molecule, eV/n for different total energies of CO_2 or Ar cluster. (**a**) Signal of *m/z* 1207.77, assigned as $[M_{Irganox}\text{-}H + 2O]^-$ from Irganox 1010 using 20–60 keV $(CO_2)_n{}^+$ cluster at energy per molecule of 2.5~30 eV/n. (**b**) Comparison of signal of *m/z* 1207.77 from Irganox 1010 using 50 keV $(CO_2)_n{}^+$ and $Ar_n{}^+$ at energy per molecule of 5–25 eV/n. (**c**) Signal of *m/z* 228.96, assigned as $[M_{Au} + 2O]^-$ from Au film using 20–50 keV $(CO_2)_n{}^+$ cluster at energy per molecule of 2.5~25 eV/n. (**d**) Comparison of signal of *m/z* 228.96 from Au film using 50 keV $(CO_2)_n{}^+$ and $Ar_n{}^+$ at energy per molecule of 5–25 eV/n

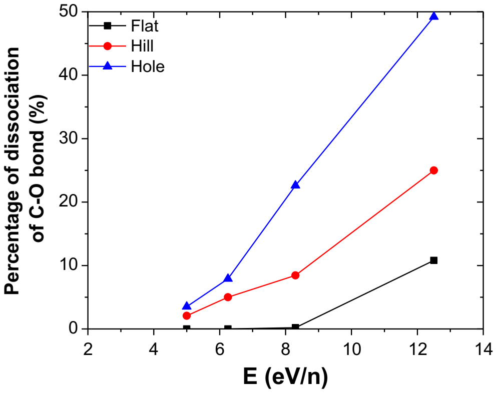

Figure 3. Percentage of dissociated CO_2 molecules for 50 keV $(CO_2)_n^+$ impact on different configurations of Au surface

higher energy per molecule favor the oxygen adducts, leading to the enhanced chemical ionization by providing an oxygen atom source through the dissociation of C-O bonds in the cluster beam itself.

Computer Simulation of C-O Bonds Dissociation at Energy per Molecule below 5 eV/N

The percentages of CO_2 molecules that dissociate in the simulations as a function of energy per molecule are shown in Figure 3 for impacts on the flat Au surface, the hill position, and the hole position. Examining first the flat surface results (black line and points), there is no dissociation below eV/n ~ 8 eV, consistent with the CO bond energy in CO_2 of ~ 8.3 eV. The results for the roughened surface (red and blue lines and points) indicate that the CO_2 molecule dissociates at incident energies as low as 5 eV/n. The side views of the 50 keV $(CO_2)_{10000}^+$ cluster-surface impact event at the flat and roughened surface are shown in Figuer 4 for three times at the beginning of the impact event for the flat surface and a hill configuration. For these impact events, the initial kinetic energy per molecule is 5 eV/n. Small balls depict intact molecules, while large balls represent molecules that have undergone dissociation. The impact at the bottom of the valley is not shown but leads to the same conclusions. The color of the species is based on the current center of mass kinetic energy where white is the original value of 5 eV, blue molecules have less energy, and red molecules have more kinetic energy.

The initial sequence of events is similar for the flat and roughened surfaces. The cluster projectile flattens during the impact, which leads to a buildup of pressure inside the projectile. The pressure is subsequently relieved by material ejection in a lateral direction. As indicated by the red color, many molecules during the decompression phase are accelerated to a kinetic energy higher than the initial value. The fate of accelerated molecules is, however, different on the flat and roughened surfaces. On the flat surface, most of these molecules slide along the surface and are reflected into the vacuum intact. For the roughened surface, however, some of accelerated (red) molecules collide with the nearby irregular surface. Now the kinetic energy per molecule can be as high as 10 eV, sufficient to cause dissociation on the second collision. We would expect the same process to occur on a roughened organic substrate such as Irganox.

The effect of the buildup in pressure and subsequent increase in the kinetic energy of a molecule during the impact event should be greater the higher the total incident energy for a given initial energy per molecule value. This effect is seen in the experimental data shown in Figure 2c. There are no $[M_{Au}+2O]^-$ ions observed for a total energy of 20 keV up to energy per molecule of 10 eV/n. On the other hand, for a total energy of 50 keV, the $[M_{Au}+2O]^-$ ions are observed at less than energy per molecule of 5 eV/n.

Conclusion and Outlook

A systematic study was performed to investigate the dissociation of C-O bonds in a CO_2 GCIB upon impact with a sample surface, consisting of an Irganox 1010 thin film and a Au film. The clusters with varying eV/n at different kinetic energy were employed to interrogate the sample surface. The dissociation of C-O bonds and the observation of oxygen adducts occurs above ~ 5 eV/n for both samples. The moderate increase ~ 2 times of oxidation was observed on organic Irganox 1010 film along with the energy per molecule and kinetic energy of the

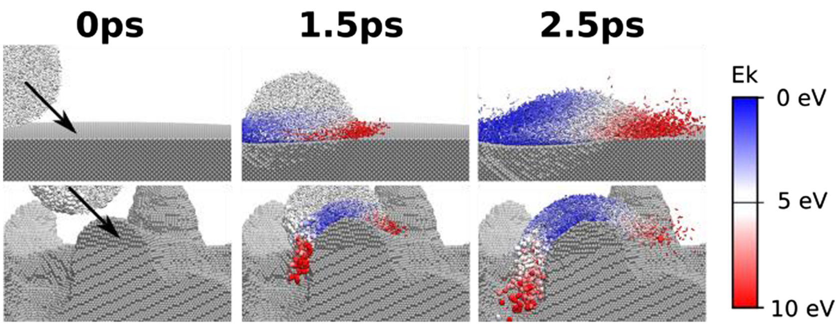

Figure 4. Time lapse images of distribution of energy per molecule in 50 keV $(CO_2)_{10,000}$ cluster during the impact on the flat (top panels) and roughened (bottom panels) Au(100) surface. The small balls represent intact CO_2 molecules. The larger balls represent dissociated molecules. The color scale is the center of mass kinetic energy of each particle. The initial kinetic energy is energy per molecule of 5 eV/n, denoted by the white color

beam, and the enhancement tends to reach a plateau when energy per molecule reaches 25 eV/n. The same trend was observed on Au films but with more drastic enhancement up to 14-fold compared the beams at 5 and 20 eV/n with kinetic energy of 60 keV; moreover, the trend points to further increases if the beam energy could be increased beyond 60 keV.

The unexpectedly observed dissociation of $(CO_2)_n^+$ below 8 eV/n is shown via computer simulation to arise from surface topography. The results demonstrate that on a rough surface, CO_2 molecules may be compressed during interaction with surface features, yielding higher kinetic energies during the decompression phase. Our findings provide new insight into the cluster-sample interaction, revealing a new chemical ionization pathway that could lead to enhanced sensitivity. Moreover, operating in a high kinetic energy regime opens the possibility of finding additional gas candidates that may more effectively exploit the chemical ionization mechanism.

Acknowledgments

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