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A Microscopic Study of Sodium Cluster Deposition on an Insulating Surface

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Abstract: We present microscopic calculations of the low energy deposition of small sodium clusters on NaCl surface. The substrate surface is taken as inert acting on the cluster through its interface potential. The time evolution of the cluster electronic system is described using the time-dependent density approximation. The dependence of the attachment process on the initial cluster orientation relative to the insulating surface is studied for the case of a Na_6 cluster.

Keywords: Cluster dynamics, deposited clusters.

1 Introduction

Clusters on surfaces constitute a broad subfield of cluster physics. Placing a cluster of a surface significantly modifies its electronic structure and core geometry in comparison with equivalent free cluster due to the impact of the interface energy, the electronic band structure of the substrate and the surface corrugation. Thus there exists a world of publications on that topic. A fair overview is provided by the proceedings of the series of ISSPIC conferences, see e.g. [1-4]. From the many possible combinations of materials, we consider here in particular the metal cluster on insulator surface. Even in that range, there is a wide choice of possibilities and existing studies, most of them dealing with the pronounced electronic-optical properties in the plasmon regime, e.g. [5-9]. We aim here at a model study of principle effects and concentrate on clusters from the simple metal Na and the well insulating surface NaCl. This combination employs fairly simple materials throughout. Thus there exist fully detailed microscopic calculations of the NaCl surface and Na_n clusters on it [10, 11]. The detailed *ab-initio* calculations of [11] have shown that the NaCl substrate remains rather inert and interacts with the cluster as an effective surface interaction potential. This result has been exploited to develop a simple effective interface potential for Na_n clusters on NaCl [12, 13]. It was found that the strong interface attraction in such system leads to the existence of stable planar isomers, where the electronic shell effects manifest themselves in a way different from the case of fully three-dimensional clusters, although competing stable three-dimensional isomers also exist. The spatial modulation of this attraction due to the crystalline structure of the substrate, the periodic corrugation [11, 13], significantly influences the equilibrium position of the deposited cluster with respect to a Cl^- (more attractive) and a Na^+ (less attractive) site. The same effective interface potential has also been used to study dynamical properties as optical response [14] and second harmonic generation [15] for that combination of materials. These studies as well as the majority of all the theoretical publications in the field deal with structure or dynamics of clusters that are already attached to a surface. Less is available on the process of cluster deposition and almost all theoretical studies on that topic deal with molecular dynamics simulation using effective atom-atom potentials, for a few recent examples see [16-19]. The goal of the present work is to study the dynamics of cluster deposition with a fully detailed description of electronic and ionic dynamics. We concentrate on low-energy collisions of a small neutral sodium cluster with a NaCl surface. Test case is Na_6, that tends to have a stable ground-state with axial symmetry [12]. A proper theoretical description of the system requires to account for the coupled dynamics of both electronic and ionic degrees of freedom; we thus treat the real-time motion of the electronic system using the Time-Dependent Local Density Approximation (TDLDA) method in full coordinate-space grid, while the ionic motion of the cluster core is described using the standard methods of molecular dynamics (MD). We present there the microscopic study of deposition of the sodium cluster on the insulating substrate for different initial kinetic energies of the projectile and its different orientations with respect to the surface interface.

Atomic system of units ($\hbar = e = m_e = 1$) is used throughout the paper.

2 Theoretical background

We simplify the treatment of the cluster by confining the degrees of freedom to delocalized valence electrons and positive ions, assuming that the NaCl substrate remains essentially inert [11] and can be taken into account through an external interface potential [12, 13].

The valence electrons of the Na atoms in the cluster are described using density-functional theory methods [20]. The single-electron wavefunctions $\psi_\alpha(\mathbf{r}, t)$ follow the well-known time-dependent Kohn-Sham [21] equations with the Kohn-Sham potential taking into account the interaction with the surface. The interaction of the residual core Na ions with the valence electrons is described by local pseudopotential [24] in the smooth form of error-functions [13]. The interaction amongst ions is modeled as a simple Coulomb interaction of point charges.

Taking into account that the substrate is only very little affected by the attached cluster [11], it is possible to describe the interaction of the cluster with the surface using the effective interface potential [13, 14], which can be derived from *ab-initio* data [11]. The interface potential incorporates both the Coulomb forces and the polarization of the surface by the deposited cluster (for the sake of simplicity hereafter we choose the surface parallel to the XY plane), where the polarization effects are described by a polarization potential of Lennard-Jones type [13, 14]. The potential has been chosen periodic in the XY-plane to account for the surface corrugation when moving from a Cl^- to a Na^- cite [13, 14]. The ionic motion was described by the standard molecular dynamics (MD) equations.

3 Results and discussion

For the present study we have chosen the small neutral sodium cluster Na_6 which in both free and deposited cases has only one ground state isomer. The equations describing the evolution of electronic and ionic subsystems were solved self-consistently on the three-dimensional coordinate-space grid. It was found [12, 14] that ionic substrate corrugation is important for definition of the ground state configuration of the deposited cluster. In Fig.1 we represent the ground state electron density distribution and ionic configuration of free Na_6 cluster (a) and of Na_6 deposited on the NaCl substrate (b) in the (XY) and (XZ) planes, respectively. One can see that in both cases the system has a nearly plane geometry with one "extra" atom above the five-atomic pentagonal "ring". The ground state of the system Na_6@NaCl corresponds to the cluster deposited above a Cl^- site (see Fig.1(b)) with the extra atom "face up", in good agreement with model calculations

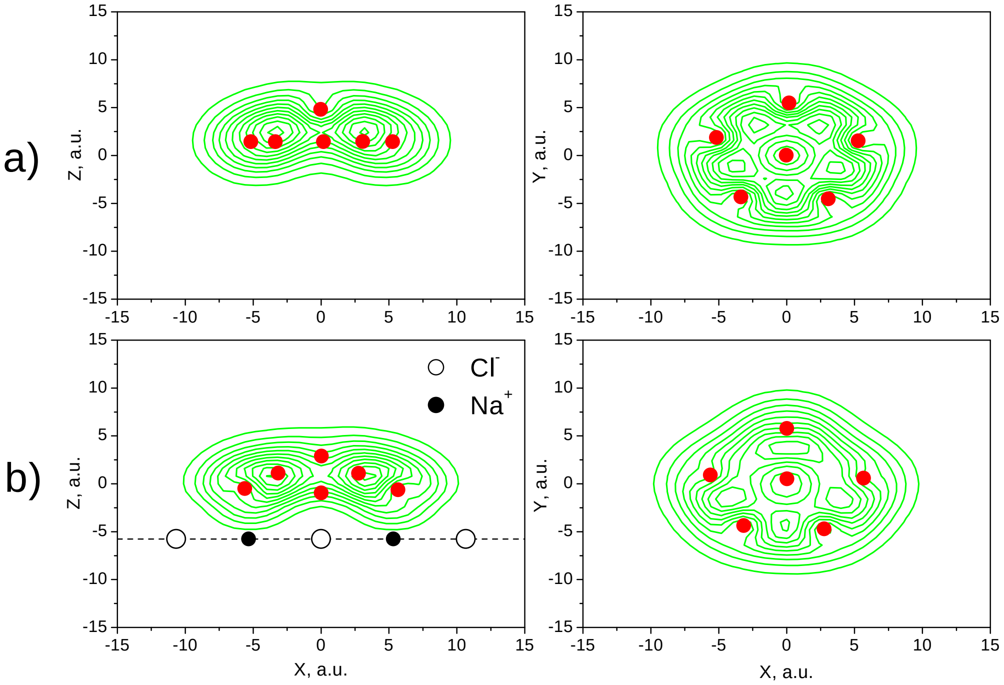

Figure 1: Ground state configuration of (a) free Na_6 cluster and (b) Na_6 deposited on a Na-Cl substrate.

[13]. For sake of simplicity here and throughout the paper we designate the latter configuration of the cluster above the surface as "Up" configuration, in contrast to the "Down" geometry with the sixth atom "face down".

Our study is devoted to the (possibly non-adiabatic) deposition dynamics of the cluster in real time. In Fig.2 we represent the dependence of the effective force (reduced to the cluster mass) acting on the cluster center of mass (CM) as a function of the distance between the cluster and the surface interface for two particular cases with a Na^+ and a Cl^- ion in the center, calculated for the "Up" geometry of the projectile. The sign of the force is defined as positive for the case of the force repulsive from the substrate (along the positive Z-axis within the chosen reference frame). One can see that the force is sensitive to the type of the substrate ion in the center, and that the Cl^- ion results in the more attracting site. It is a bit puzzling to see that the force exhibits an oscillating spatial dependence with a sequence of zeroes which means that there are possibly several (stable and unstable) equilibrium points underway, and the one closest to the surface corresponds to the minimal energy of the cluster. Looking at these plots one can expect that cluster deposition can be accompanied by oscillations in the effective "potential well". Here we note that our model (with substrate described as an effective potential) does not take into account a possible energy transfer from cluster to surface ionic excitations (phonons) that could

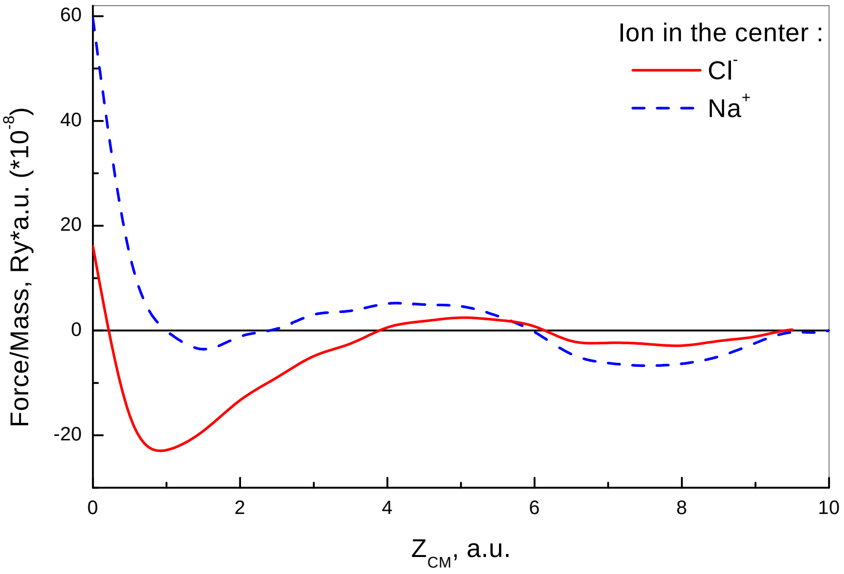

Figure 2: Effective force as a function of the distance between cluster and surface for two cases with a Na^+ and a Cl^- ion in the center.

lead to a damping of the cluster oscillations.

We have simulated the real-time cluster deposition process by calculating the system evolution described by the self-consistent equations, where free ground state Na_6 was initially (i.e. at time $t = 0$) positioned in Z-direction above the surface interface at the distance where the effective force (Fig.2) is negligible (i.e. $Z_{cm}(0) > 10\,a_0$) with the non-zero Z-projection of CM momentum towards the surface. The corresponding initial kinetic energy is $E_{kin} = \sum_i E_{kin}^{(i)}$, where $E_{kin}^{(i)} = P_Z^2/2M_{ion}$ is the kinetic energy of a single cluster ion, where M_{ion} is ionic mass, i.e. we start with equal initial conditions for all the cluster ions $P_{i(Y)} = P_{i(X)} = 0$, $P_{i(Z)} = P_Z$ for all i.

In Fig.3 we represent the time evolution of the cluster CM during the Na_6 deposition for the case of deposition centered on a Cl^- substrate ion both for "Up" and "Down" initial orientations of the projectile and for three different initial kinetic energies (a) 1.72 eV, (b) 6.9 eV and (c) 13.04 eV. First of all, one can see that there is a deposition energy threshold (i.e. the maximal initial kinetic energy of the cluster that can be attached to the surface) and that it depends on the initial cluster orientation. In the first case (a) the relatively low initial kinetic energy leads to the cluster attachment for both initial orientations, i.e. this energy is below the deposition threshold. As expected, the center of mass motion has oscillating character. In the second case (b) the attachment takes place only for the "Up" orientation, while the "Down"-oriented cluster

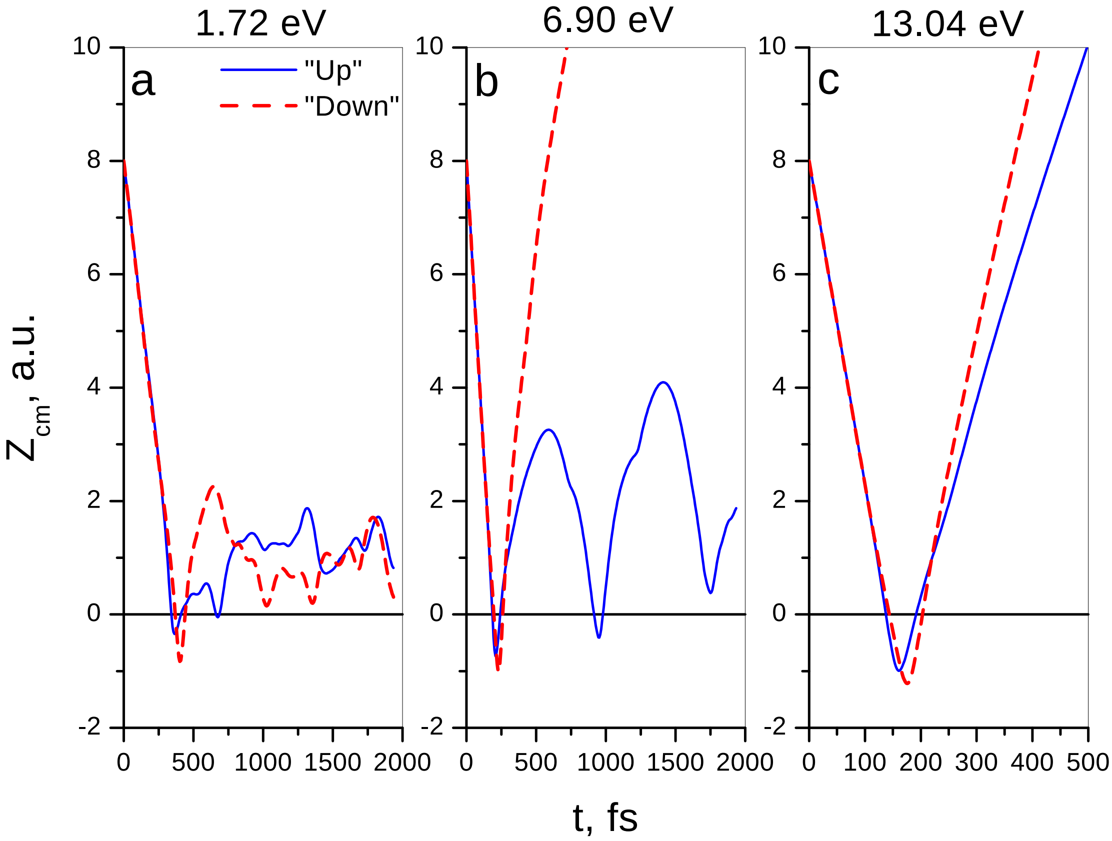

Figure 3: Time evolution of center of mass of the cluster during the deposition process for the initial kinetic energies a) 1.72 eV, b) 6.90 eV and c) 13.04 eV.

is inelastically reflected from the surface. That means that the "Up" initial configuration results in the larger kinetic energy loss of the projectile (i.e. the larger part of the initial energy is transferred to excitations of cluster internal degrees of freedom). The same tendency we see on the last plot (c) that corresponds to the initial kinetic energy above the deposition threshold for both orientations, where the asymptotic CM velocity (and, naturally, the kinetic energy) of the outgoing "Up" cluster is significantly lower than that of the "Down" one. In Fig.4 we represent the "snupshots" of electron density distribution and ionic configuration (in the (XY) and (XZ) planes) of Na_6 cluster with "Up" orientation in different time during its deposition on the Na-Cl surface for initial kinetic energy of 6.9 eV, i.e. close to the deposition threshold. One can see that the collision leads to the significant cluster deformation and, as a result, to excitation of internal degrees of freedom, especially the internal ionic motions, that can be characterised by internal ionic kinetic energy or "ionic temperature". The more detailed study of the energy transfer to the cluster internal degrees of freedom will be done in the separate publication.

The observed difference between "Up" and "Down" Na_6 orientations may have a simple explanation. In Fig.5 we represent the "snapshots" of the Na_6 cluster ions during the deposition process for an initial kinetic energy of 1.72 eV (i.e. below the deposition threshold). In the "Down" case the "extra" (out of plane) atom plays the role of a damper, when the cluster-surface collision mainly results in the excitation of the degree of freedom corresponding to this sixth atom, while for the residual five-atomic "ring" the deposition occurs more softly, than for the "Up" geometry, for which all the internal ionic motions are excited simultaneously. As a result, the attached cluster that initially had the "Down" orientation finally comes to the configuration with the "extra" atom "face up" (as in Fig.1b), but heated to a lower ionic temperature.

4 Conclusions

A theoretical study of deposition of low-energy small neutral sodium clusters on insulating surface was performed. Our work was based on the self-consistent calculations of real-time dynamics of electronic and ionic subsystems of the projectile. The interaction of the cluster with the substrate was described using the effective interface potential incorporating both Coulomb forces and the polarization of the surface by the deposited cluster with account of the surface crystalline corrugation. The low-energy cluster in its deposition process undergoes center of mass oscillations in the vicinity of the equilibrium position. It was demonstrated that there is an energy threshold for initial kinetic energy of a cluster that can be attached to the surface. It was found that the attachment process is sensitive to the initial cluster orientation with respect to the surface as well as whether the deposition occurs over a Cl^- or Na^+ site of the substrate lattice. In particular, the deposition energy threshold for "Up" orientation of a Na_6 cluster (with sixth atom situated above

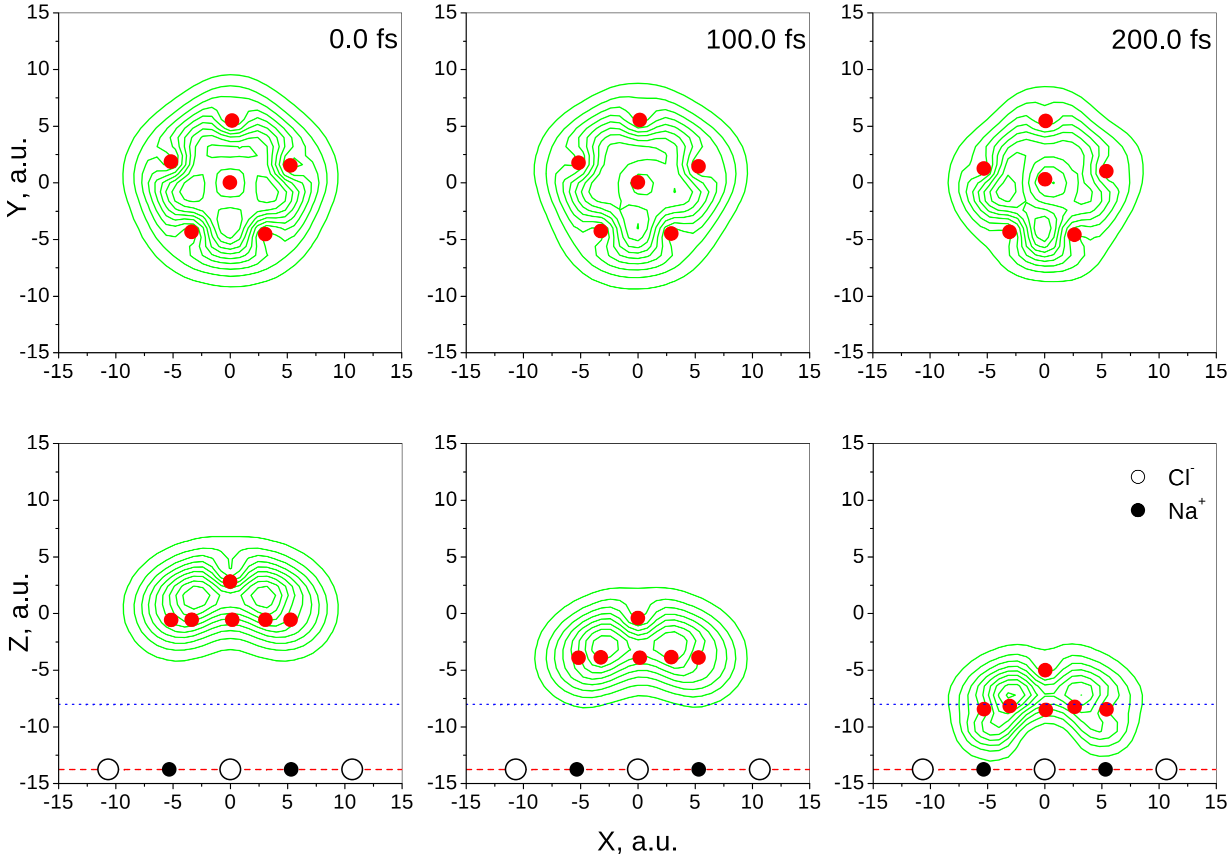

Figure 4: Electron charge density and ionic positions for the Na_6 cluster with "Up" orientation in different time of deposition for an initial kinetic energy kinetic energy 6.9 eV.

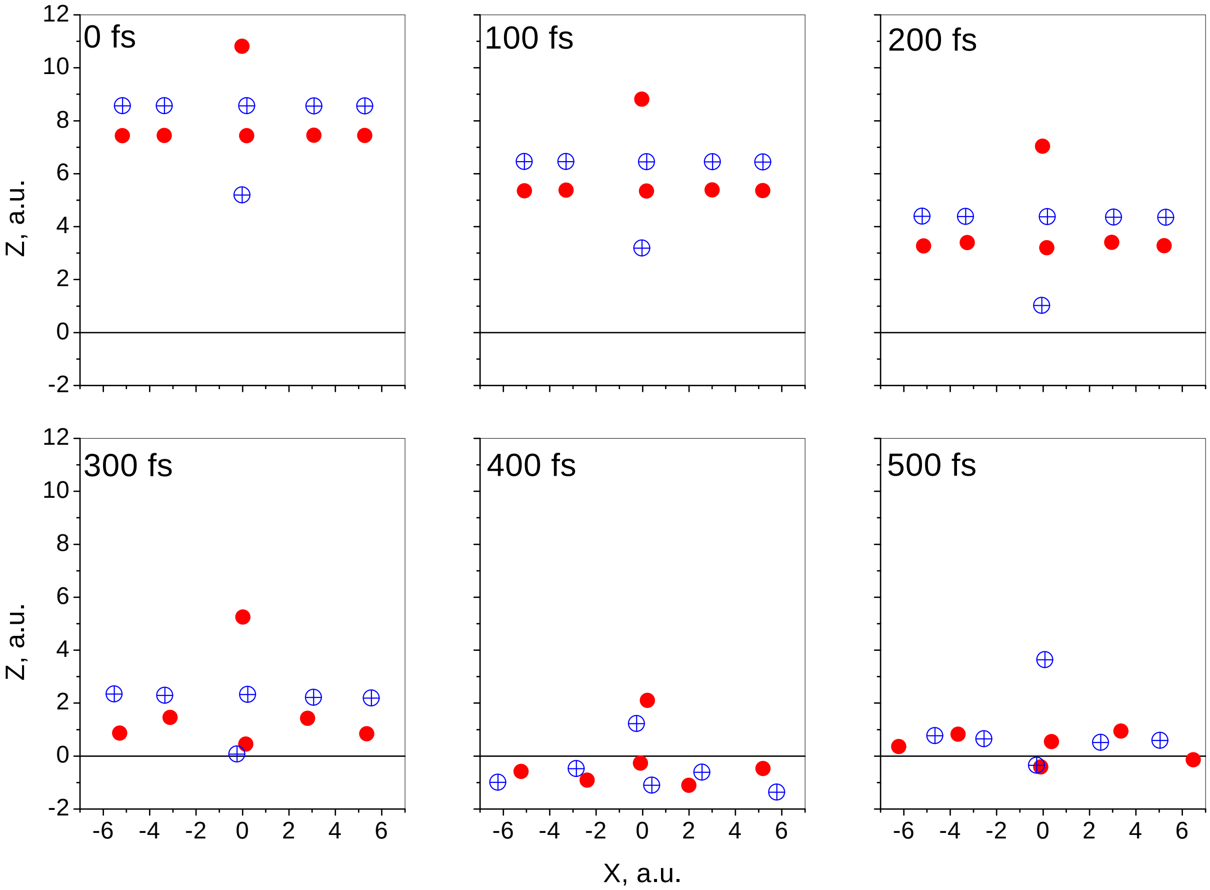

Figure 5: Time evolution of the Na_6 cluster ions during the deposition process for an initial kinetic energy 1.72 eV. Solid circles designate the ions of cluster with "Up" orientation, and the crossed hollow circles - to the "Down" geometry, respectively.

the pentagonal five-atomic ring) is higher than that for the opposite "Down" configuration due to the fact that the "extra" atom in the latter case contributes to the damping of the process.

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