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Polynitrogen/Nanoaluminum Surface Interactions (PREPRINT) (Challenge Project C2V)

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ABSTRACT

First-principles density functional theory (DFT) calculations using the generalized gradient approximation (GGA) have been conducted to study the adsorption of a series of high-nitrogen compounds of increasing sizes and complexity on the Al(111) surface. The calculations employ periodic slab models with 4 Al layers, ranging in size from (3x3) to (7x7) surface unit cells, and containing up to 196 Al atoms. Complementary quantum chemical calculations, utilizing DFT and second-order perturbation theory methods, of the ground state potential energy surfaces of the corresponding polynitrogen/high nitrogen species in the absence of the aluminum surface also have been performed. For the set of chemical species N_x ($x=1,5$), NH_x ($x=1-3$), N_2H_x ($x=1-4$) and N_3H , N_3H_3 and N_4H_4 the adsorption configurations at different surface sites and the corresponding binding energies have been determined. This analysis has been further extended to high-nitrogen compounds N_5H and N_6H_2 . For these two systems it was found that the initial bonding to the surface takes place through a molecular mechanism (nondissociatively) with involvement of single or multiple N atoms of the molecule. However, dissociation on the surface can take place with small activation energies. This set of calculations has been further extended to include 1,3,5-triazene and 1,2,3-triazine ($C_3H_3N_3$) as well as larger substituted triazene systems such as C_9N_{30} and $C_{15}N_{18}$. For these large systems it was found that bonding takes place through multiple N centers with formation of highly strained and deformed adsorption configurations. In a number of instances the adsorption takes place dissociatively with N_2 elimination.

I. Introduction

Investigation of the interaction of energetic high-nitrogen compounds with ultrafine or nanophase particles of aluminum is a topic of current interest with potential DoD applications in rocket and missile propulsion. One of the topics of prime importance is to determine if the thermal instability inherent in many high nitrogen compounds might be reduced by adsorption or chemisorption onto the surface of aluminum, while simultaneously forming a protective coating on the metal surface which minimizes the formation of an inert oxide surface layer.

II. Computational Method

The calculations performed in this study were done using the Vienna *ab initio* simulation package (VASP).¹⁻³ This program evaluates the total energy of periodically repeating geometries based on density-functional theory and the pseudopotential approximation. In this case the electron-ion interaction is described by fully non-local optimized ultrasoft pseudopotentials similar to those introduced by Vanderbilt.^{4,5} Periodic boundary conditions are used, with the one-electron pseudo-orbitals expanded over a plane-wave basis set with a cutoff energy of 435 eV. Calculations were performed using the generalized gradient approximation (GGA) density functional theory with PW91 exchange-correlation functional.⁶ The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme.⁷ The minimum energy path between different minima was determined using the climbing image nudged elastic band method developed by Jónsson and co-workers.^{8,9}

The GAMESS¹⁰ quantum chemistry code was used to predict the structures and properties of isolated polynitrogen and high-nitrogen compounds. The theoretical methods employed included second order perturbation theory¹¹ (MP2, also known as MBPT(2)) and density functional theory (DFT) using the hybrid B3LYP¹² functional. The 6-311G(2df,p) basis set¹³ was used throughout.

III. Results and Discussion

In order to provide a comprehensive analysis of the interaction of polynitrogen systems with aluminum surface in our studies we focused on four different categories of high nitrogen and polynitrogen systems of increasing complexity. The first set is composed by individual atomic and molecular all nitrogen systems from the series N_x ($x=1,5$). The second set is formed by small hydrogenated nitrogen systems including NH_x ($x=1,3$), N_2H_x ($x=1-4$), N_3H_x ($x=1,3$), N_4H_4 , N_5H and N_6H_2 . The third set includes systems of increased complexity such as (1,3,5) and (1,2,3) triazene ($C_3N_3H_3$) as well as mono-substituted derivatives of triazenes such as $C_7N_8H_2$ and

C₅N₁₂H₂. Finally, the fourth set is represented by large high-nitrogen compounds of trisubstituted triazene molecules such as C₉N₃₀ and C₁₅N₁₈.

Given the large variety of molecular sizes involved, the adsorption studies of the above compounds were done using slab models varying from (3x3) for the case of small molecular systems to (7x7) surface units for the largest systems. In all cases the slab models contained four layers of atoms. The optimizations have been performed for both the adsorbate and the Al atoms in the top two layers while the bottom two layers were frozen at the bulk optimized conditions. Adsorption at different surface sites and for different molecular orientations have been determined and the corresponding adsorption energies have been calculated using the expression $E_{\text{ads}} = E_{\text{molec}} + E_{\text{slab}} - E_{(\text{molec}+\text{slab})}$, where E_{molec} is the energy of the isolated molecular species at its equilibrium geometry, E_{slab} is the total energy of the isolated aluminum slab, and $E_{(\text{molec}+\text{slab})}$ is the total energy of the adsorbate/slab system. A positive E_{ads} corresponds to a stable adsorbate/slab system. In the present study, only neutral species have been considered.

N_x (x=1,5) Adsorption on Al(111). The binding of individual N_x(x=1,5) has been determined using the (3x3) supercell model and representative adsorption configurations are represented in Figure 1. The most stable species was found to be the N atom which binds to the surface in a three fold configuration with an energy of 150.2 kcal/mol at a face-centered cubic (fcc) surface site and of 142.2 kcal/mol at a hexagonal closest packed (hcp) site. By increasing the atomic coverage, the binding energy further increases to 161.5 kcal/mol at full coverage when all fcc and hcp sites are occupied. In this case, the resulting atomic configuration resembles the aluminum nitride (AlN) phase. In the case of the N₂ molecule, the adsorption on the surface is not stable relative to isolated N₂ in the gas phase. The N₃ species can adsorb by simultaneous binding to three Al surface atoms and maintaining a triangular gas phase geometry ($E_{\text{ads}}=62$ kcal/mol) (see Fig. 1c) or in an open chain geometry which involves bonding to four Al surface atoms ($E_{\text{ads}}=75.7$ kcal/mol) (see Fig. 1d). In the latter case we note that the fourth Al atom involved in bonding is significantly pulled up from the surface. In the case of the N₄ molecule, several geometries have been considered, including tetrahedral, rectangular, and linear geometries. The tetrahedral geometry was found to be either weakly physisorbed on the surface or unstable with respect to dissociation into two N₂ molecules. For the other two isomers of N₄, stable adsorption sites were found as indicated in Figs. 1e and 1f, where three or all four of the N atoms are involved in direct bonding to the surface Al atoms. Finally, for the N₅ species our calculations indicate that the most stable configuration corresponds to a vertical geometry where bonding can take place either on-top site (see Fig. 1h) or in a bridge-like configuration (see Fig. 1g). In the latter case, the binding energy is 90 kcal/mol relative to the isolated N₅ species and slab.

The energies of different adsorbed N_x(x=1,5) species are presented in a common diagram in Fig. 1i), in which the energy zero is taken to be the sum of the isolated Al slab and that of three isolated N₂ molecules in the gas phase. From this diagram it can be easily seen that the adsorbed N atom is the most stable species, followed by the N₃ and N₄ molecular species. This diagram also indicates that for the adsorbed N_x (x > 1) species, further dissociation leading to formation of adsorbed N atoms is energetically favorable.

N_xH_y Adsorption on Al(111). The adsorption properties of the series of compounds NH_x(x=1-3), N₂H_x(x=1-4), N₃H_x(x=1,3), N₄H₄, N₅H and N₆H₂ have been predicted using the (3x3) slab model described above. Representative adsorption configurations of these systems are presented in Figure 2. Among the most strongly bound species in this series are NH ($E_{\text{ads}}=130$ kcal/mol), NH₂ ($E_{\text{ads}}=72.9$ kcal/mol), NNH₂ ($E_{\text{ads}}=76.3$ kcal/mol), and N₃H₃ ($E_{\text{ads}}=75.9$ kcal/mol). The larger systems in this series have significantly smaller binding energies, with values of 14.1 kcal/mol for N₂H₄, 8.7 kcal/mol for N₅H, and 9.9 kcal/mol for N₆H₂.

Minimum Energy Path for N₅H and N₆H₂ Dissociation. Starting from the most stable adsorption configurations of N₅H and N₆H₂, the minimum energy pathways for molecular dissociation of these species have been characterized. Two representative pathways are shown in Figs. 2 q) and 2 r), respectively. In the pathway shown in panel q), one of the N-N bonds of the N₅H ring breaks with a small activation energy of about 4.8 kcal/mol. Following this step, a second N-N bond of the remaining ring dissociates without any additional barrier, leading to formation of two N₂ molecules and the NH radical adsorbed at a three-fold hollow site. This reaction is highly exothermic, by -92.5 kcal/mol. Similar behavior is observed in the case of N₆H₂ dissociation (see Fig. 2r). In this case, the NH₂ group dissociates from the N₅ ring with a small activation energy of 1.8 kcal/mol. In the final configuration, both the NH₂ group and the N₅ ring are adsorbed on the surface. The overall dissociation reaction is also exothermic, by -63.7 kcal/mol. These results suggest that dissociation of N₅H and N₆H₂ on the Al surface is very efficient.

Adsorption of Triazene and Mono-substituted Triazene. Representative adsorption configurations of (1,3,5) and (1,2,3) triazene molecule are shown in Figs. 3a)-d), which have been calculated using a (6x6) surface slab model. For (1,3,5) triazene, both adsorption through a single nitrogen atom (Fig. 3a) or through multiple bonds involving both N and C atoms (Fig. 3b) can take place, leading to total binding energies of 11.2 and 16.9 kcal/mol,

respectively. In the case of (1,2,3) triazene, two or three of the N atoms of the molecule can be involved in bonding to surface, which increases the binding energies to 37.2 kcal/mol for the η_4 configuration depicted in Fig. 3c) and 31.4 kcal/mol for the η_3 structure in Fig. 3d).

The adsorption configurations of mono-substituted triazenes $C_7N_8H_2$ (see panels (e)-(g) in Figure 3) and $C_5N_{12}H_2$ (panels (h)-(j) in Figure 3) have also been analyzed. In these instances, the adsorption takes place with significant deformations of the molecular structure and with involvement of different sites of the molecule. In the case of $C_7N_8H_2$, adsorption takes place molecularly and the overall binding energy is relatively small with a maximum value of 6.80 kcal/mol for the structure in Fig. 3g). A significant portion of the stabilization gained from formation of Al-N or Al-C bonds is lost in the deformation of the gas phase structure of the $C_7N_8H_2$ molecule. In the case of the $C_5N_{12}H_2$ system, similar interactions with the surface are observed, with formation of multiple bonds (for example eight bonds are present in the structure shown in Figure 3i) and significant structural deformation of $C_5N_{12}H_2$. In addition, dissociative adsorption via N_2 elimination can take place, as shown in Figure 3, panel (j). Note that the strong molecular interactions between the adsorbate and the metallic surface leads to significant upward shifts of some of the Al surface atoms.

Adsorption of Trisubstituted Triazenes. Calculations in this case have been done using the largest supercell models employed in this study, containing (7x7) surface units and 4 layers of aluminum atoms. The overall trends observed for mono-substituted triazene are also seen in the case of trisubstituted triazenes C_9N_{30} and $C_{15}N_{18}$ (see Figs. 3 k-o). Specifically, the adsorption to the surface can take place through formation of multiple bonds, primarily between Al and N. As a result, significant deformations and structural changes take place, both within the adsorbate molecule and the uppermost layer of Al atoms, several of which are displaced upwards. Binding energies as high as 69.4 kcal/mol are calculated for $C_{15}N_{18}$ (see Fig. 3m). Note that in the case of the $C_{15}N_{18}$ molecule, which contains six N_3 groups, elimination of several N_2 molecules can take place (panel o) in Figure 3.)

IV. Conclusions

A systematic study of a series of polynitrogen and high nitrogen species ranging from small N_x ($x=1,5$) and N_2H_x ($x=1-4$) to complex C_9N_{30} and $C_{15}N_{18}$ systems interacting with the aluminum (111) surface have been investigated using plane-wave DFT calculations in conjunction to slab models as large as four layers of (7x7) surface units. Our calculations indicate that, with the exception of N_2 , the majority of polynitrogen and high nitrogen compounds will bind to the surface through formation of Al-N bonds, while formation of Al-C bonds is observed in only few instances. For the ensemble of molecular systems considered, a significant range of variation in binding energies has been determined depending on the number of surface bonds involved, surface site and molecular orientation. Additionally, in the great majority of cases investigated, adsorption was found to take place with important molecular deformations and often with significant displacement of aluminum atoms from the surface. For the systems containing N_3 groups ($C_5N_{12}H_2$ and C_9N_{30}), adsorption leads to elimination of multiple N_2 molecules. For smaller systems such as N_5H and N_6H_2 , small activation energies were found for dissociation pathways leading to formation of NH and NH_2 species adsorbed on the surface.

Future work will extend this set of investigations to include the thermal effects upon surface adsorption and adsorption on nanoclusters of different sizes.

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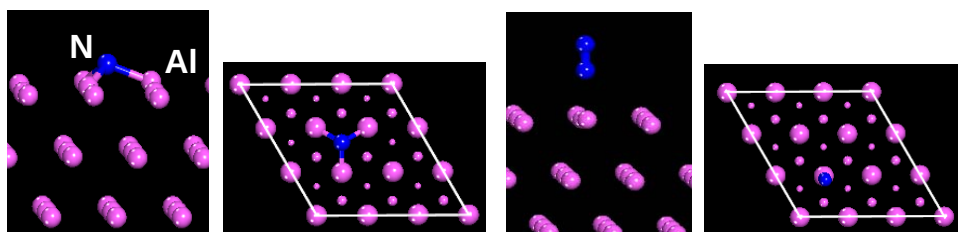
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Figure Captions

Figure 1. Side and top views of the most stable adsorption configurations of (a) N, (b) N₂, (c), (d) N₃, (e), (f) N₄ and (g), (h) N₅ on the Al(111) surface. Panel i) indicates the corresponding potential energy diagram for the relative stability of the N_x(x=1,5) species on the Al(111) surface. The sum of energies of the isolated slab and three N₂ molecules in the gas phase was taken as the zero of energy. The labels (a) and (ph) denote adsorbed and physisorbed species, respectively, while (ch), (tr) and (rect) denote chain, triangular, and rectangular configurations, respectively.

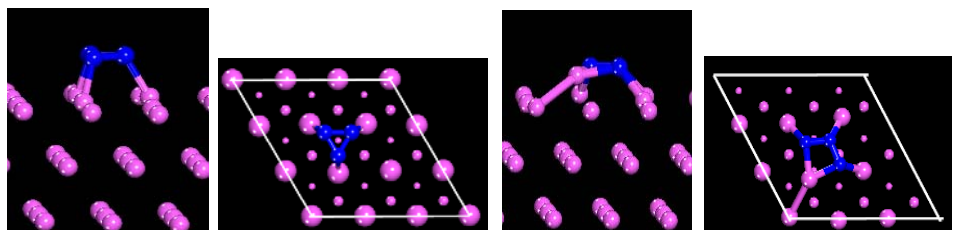
Figure 2. Side view of representative adsorption configurations of (a) NH, (b) NH₂, (c) NH₃, (d) N₂H, (e) N₂H₂, (f) NNH₂, (g) N₂H₃, (h) N₂H₄, (i),(j) N₃H, (k) N₃H₃, (l) N₄H₄, (m),(n) N₅H, (o),(p) N₆H₂. The panels q) and r) show the potential energy surface for dissociation of the N₅H and N₆H₂ species on the Al(111) surface.

Figure 3. Side views of the most stable adsorption configurations for (a), (b) (1,3,5) triazene, (c), (d) (1,2,3) triazene, (e)-(j) mono-substituted triazene, and trisubstituted triazene molecules (k-m) C₁₅N₁₈ and (n),(o) C₉N₃₀ adsorbed on the Al(111) surface.



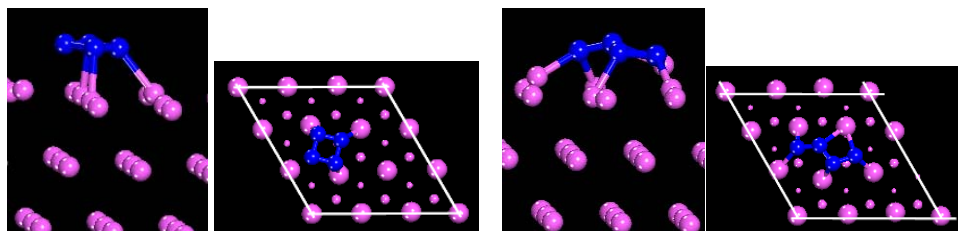
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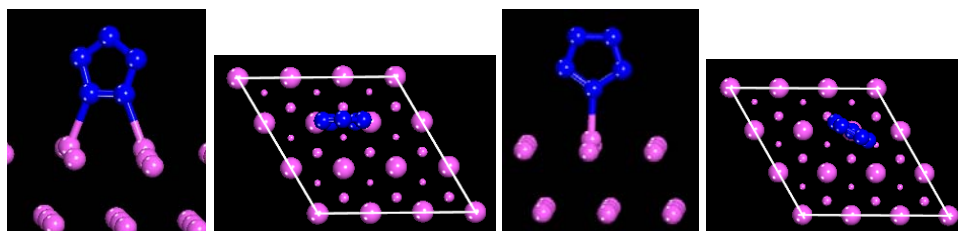
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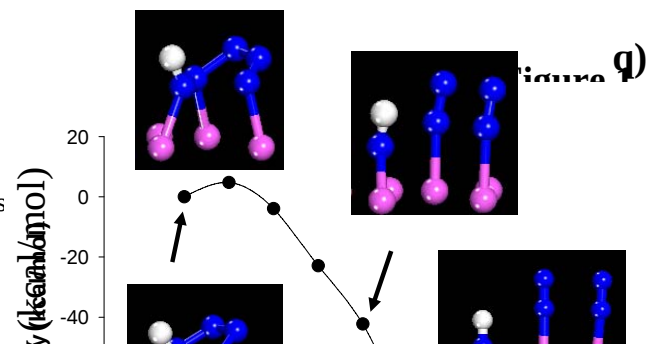
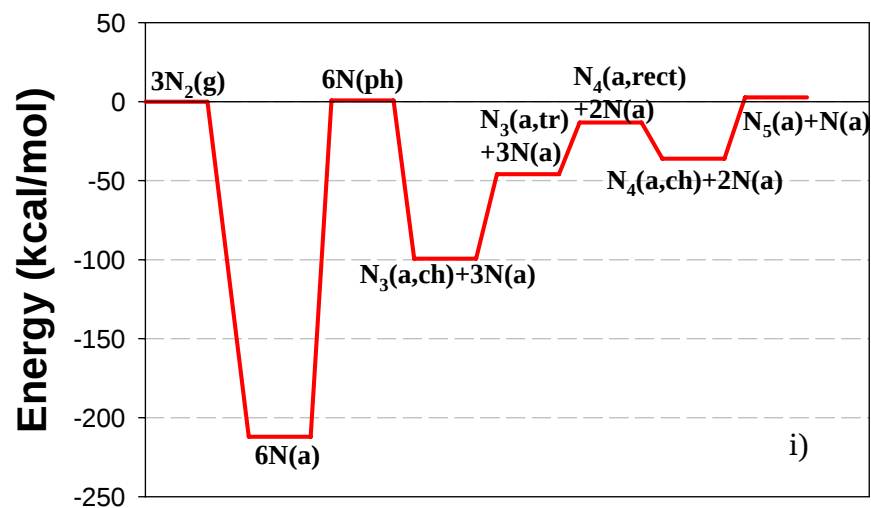
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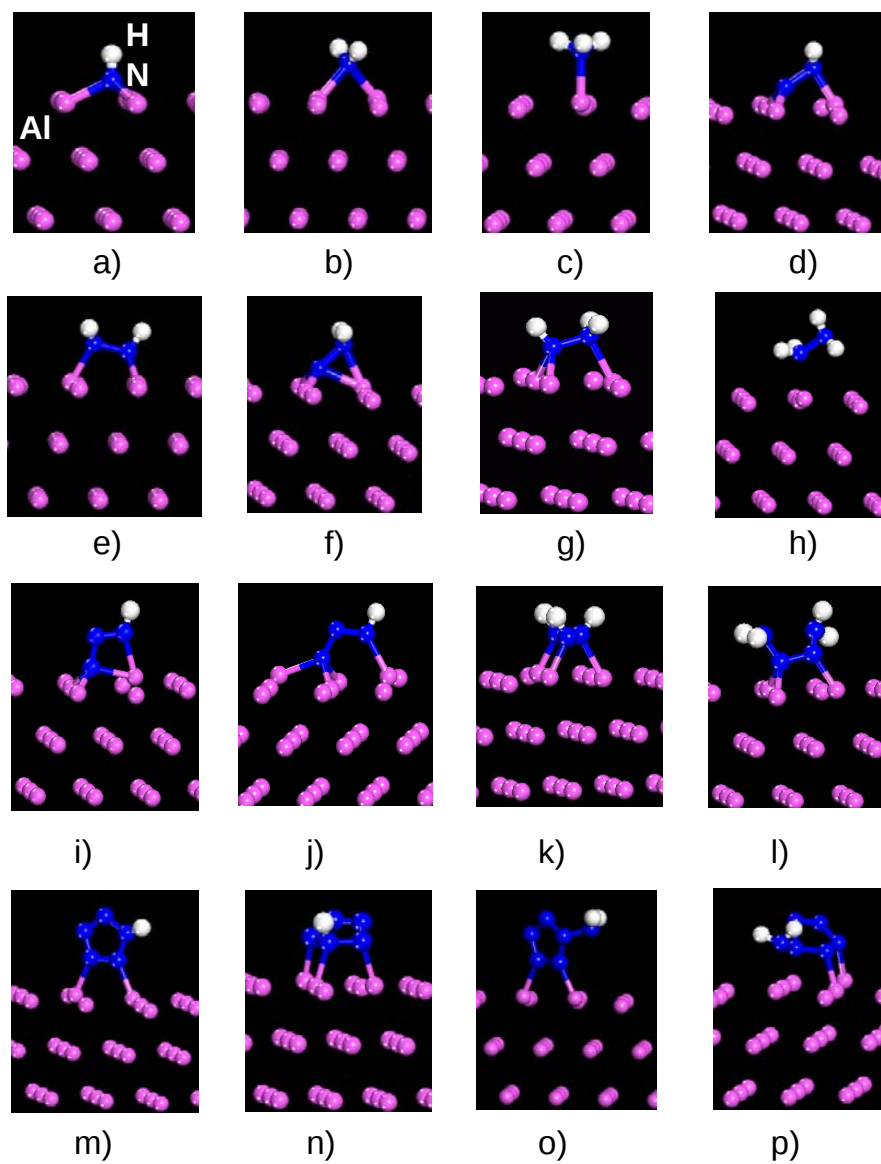


Figure 2

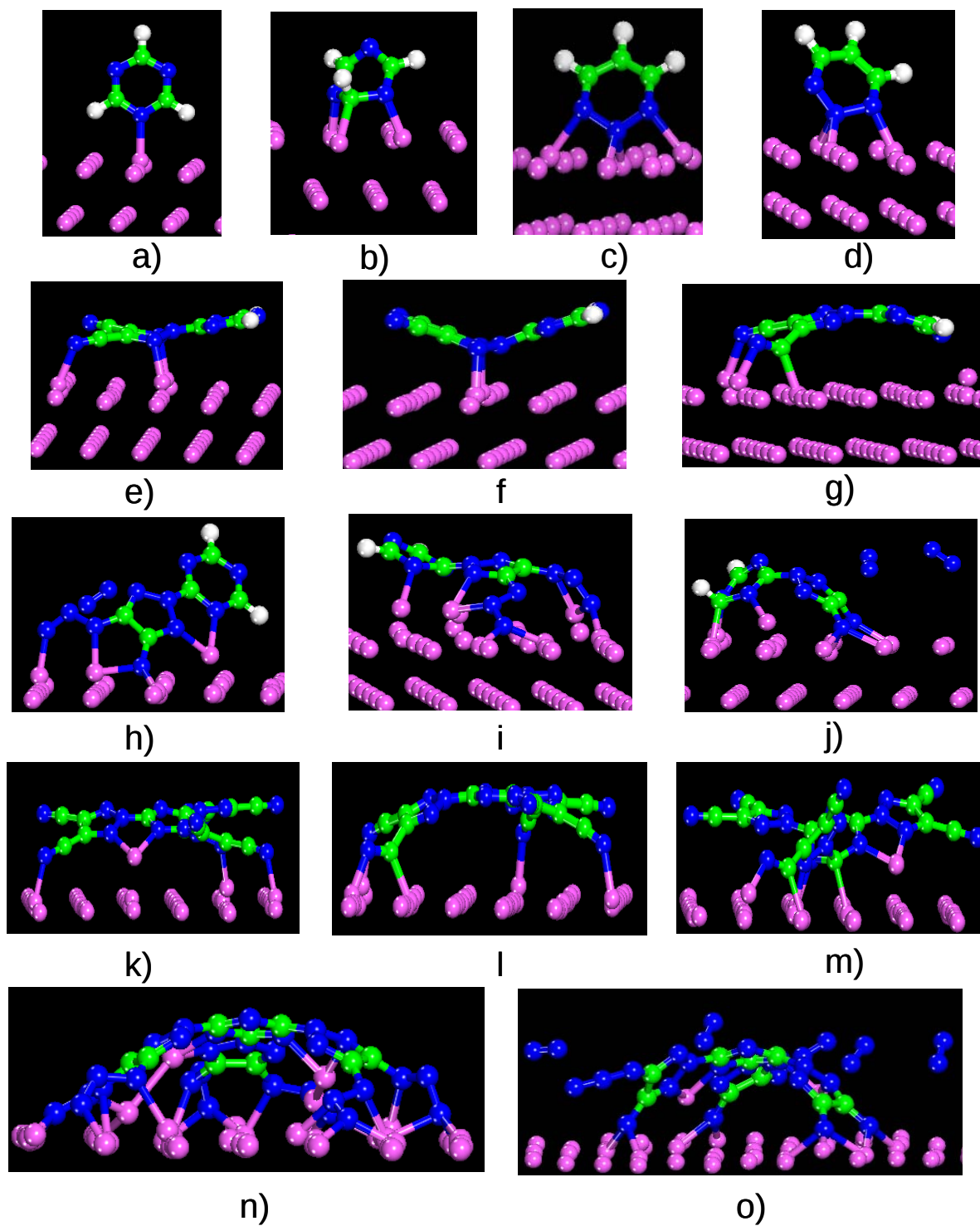


Figure 3