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<b>1. REPORT DATE (DD-MM-YYYY)</b> 08-05-2007		<b>2. REPORT TYPE</b> Technical Paper		<b>3. DATES COVERED (From - To)</b>	
<b>4. TITLE AND SUBTITLE</b>  Polynitrogen/Nanoaluminum Surface Interactions (Challenge Project C2V) (Preprint)				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Jerry Boatz (AFRL/PRSP); Dan Sorescu (DOE)				<b>5d. PROJECT NUMBER</b> 50260541	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b>  Air Force Research Laboratory (AFMC) AFRL/PRSP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  AFRL-PR-ED-TP-2007-273	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>  Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-70448				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S NUMBER(S)</b> AFRL-PR-ED-TP-2007-273	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b>  Approved for public release; distribution unlimited (PA# 07202A)					
<b>13. SUPPLEMENTARY NOTES</b> For presentation at DoD Users' Group Conference proceedings, held in Pittsburgh, PA, 18-22 June 2007.					
<b>14. ABSTRACT</b> 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 <sub>x</sub> (x=1,5), NH <sub>x</sub> (x=1-3), N <sub>2</sub> H <sub>x</sub> (x=1-4) and N <sub>3</sub> H, N <sub>3</sub> H <sub>3</sub> and N <sub>4</sub> H <sub>4</sub> 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 <sub>5</sub> H and N <sub>6</sub> H <sub>2</sub> . 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 <sub>3</sub> H <sub>3</sub> N <sub>3</sub> ) as well as larger substituted triazene systems such as C <sub>9</sub> N <sub>30</sub> and C <sub>15</sub> N <sub>18</sub> . 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 <sub>2</sub> elimination.					
<b>15. SUBJECT TERMS</b>					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
<b>a. REPORT</b>	<b>b. ABSTRACT</b>	<b>c. THIS PAGE</b>			Wayne Kalliomaa
Unclassified	Unclassified	Unclassified	SAR	8	<b>19b. TELEPHONE NUMBER (include area code)</b> N/A

# 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).<sup>1-3</sup> 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.<sup>4,5</sup> 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.<sup>6</sup> The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme.<sup>7</sup> The minimum energy path between different minima was determined using the climbing image nudged elastic band method developed by Jónsson and co-workers.<sup>8,9</sup>

The GAMESS<sup>10</sup> 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 theory<sup>11</sup> (MP2, also known as MBPT(2)) and density functional theory (DFT) using the hybrid B3LYP<sup>12</sup> functional. The 6-311G(2df,p) basis set<sup>13</sup> 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

C<sub>5</sub>N<sub>12</sub>H<sub>2</sub>. Finally, the fourth set is represented by large high-nitrogen compounds of trisubstituted triazene molecules such as C<sub>9</sub>N<sub>30</sub> and C<sub>15</sub>N<sub>18</sub>.

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  $E_{\text{ads}} = E_{\text{molec}} + E_{\text{slab}} - E_{\text{(molec+slab)}}$ , where  $E_{\text{molec}}$  is the energy of the isolated molecular species at its equilibrium geometry,  $E_{\text{slab}}$  is the total energy of the isolated aluminum slab, and  $E_{\text{(molec+slab)}}$  is the total energy of the adsorbate/slab system. A positive  $E_{\text{ads}}$  corresponds to a stable adsorbate/slab system. In the present study, only neutral species have been considered.

**N<sub>x</sub> (x=1,5) Adsorption on Al(111).** The binding of individual N<sub>x</sub>(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 N<sub>2</sub> molecule, the adsorption on the surface is not stable relative to isolated N<sub>2</sub> in the gas phase. The N<sub>3</sub> 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 N<sub>4</sub> 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 N<sub>2</sub> molecules. For the other two isomers of N<sub>4</sub>, 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 N<sub>5</sub> 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 N<sub>5</sub> species and slab.

The energies of different adsorbed N<sub>x</sub>(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 N<sub>2</sub> 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 N<sub>3</sub> and N<sub>4</sub> molecular species. This diagram also indicates that for the adsorbed N<sub>x</sub> (x > 1) species, further dissociation leading to formation of adsorbed N atoms is energetically favorable.

**N<sub>x</sub>H<sub>y</sub> Adsorption on Al(111).** The adsorption properties of the series of compounds NH<sub>x</sub>(x=1-3), N<sub>2</sub>H<sub>x</sub>(x=1-4), N<sub>3</sub>H<sub>x</sub>(x=1,3), N<sub>4</sub>H<sub>4</sub>, N<sub>5</sub>H and N<sub>6</sub>H<sub>2</sub> 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), NH<sub>2</sub> ( $E_{\text{ads}}=72.9$  kcal/mol), NNH<sub>2</sub> ( $E_{\text{ads}}=76.3$  kcal/mol), and N<sub>3</sub>H<sub>3</sub> ( $E_{\text{ads}}=75.9$  kcal/mol). The larger systems in this series have significantly smaller binding energies, with values of 14.1 kcal/mol for N<sub>2</sub>H<sub>4</sub>, 8.7 kcal/mol for N<sub>5</sub>H, and 9.9 kcal/mol for N<sub>6</sub>H<sub>2</sub>.

**Minimum Energy Path for N<sub>5</sub>H and N<sub>6</sub>H<sub>2</sub> Dissociation.** Starting from the most stable adsorption configurations of N<sub>5</sub>H and N<sub>6</sub>H<sub>2</sub>, 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 N<sub>5</sub>H 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 N<sub>2</sub> 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 N<sub>6</sub>H<sub>2</sub> dissociation (see Fig. 2r). In this case, the NH<sub>2</sub> group dissociates from the N<sub>5</sub> ring with a small activation energy of 1.8 kcal/mol. In the final configuration, both the NH<sub>2</sub> group and the N<sub>5</sub> ring are adsorbed on the surface. The overall dissociation reaction is also exothermic, by -63.7 kcal/mol. These results suggest that dissociation of N<sub>5</sub>H and N<sub>6</sub>H<sub>2</sub> 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  $\eta_4$  configuration depicted in Fig. 3c) and 31.4 kcal/mol for the  $\eta_3$  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 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.

#### Acknowledgements

The authors gratefully acknowledge grants of computer time at the Army Research Laboratory, Aeronautical System Center, and the Naval Oceanographic Office Major Shared Resource Centers, sponsored by the Department of Defense High Performance Computing Modernization Program.

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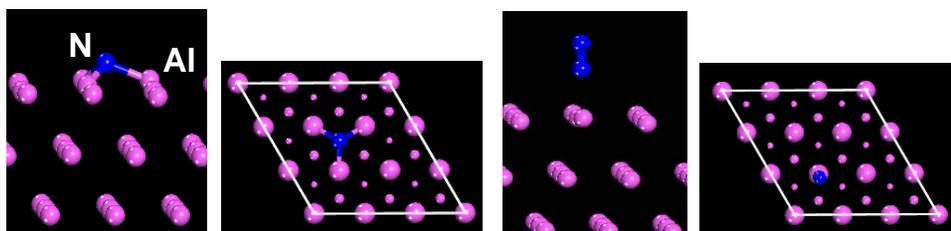
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### Figure Captions

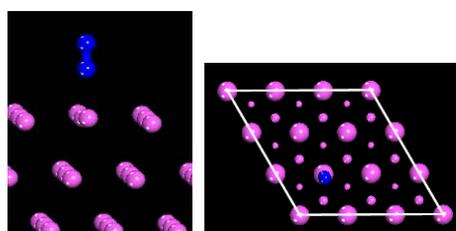
**Figure 1.** Side and top views of the most stable adsorption configurations of (a) N, (b) N<sub>2</sub>, (c), (d) N<sub>3</sub>, (e), (f) N<sub>4</sub> and (g), (h) N<sub>5</sub> on the Al(111) surface. Panel i) indicates the corresponding potential energy diagram for the relative stability of the N<sub>x</sub>(x=1,5) species on the Al(111) surface. The sum of energies of the isolated slab and three N<sub>2</sub> 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) NH<sub>2</sub>, (c) NH<sub>3</sub>, (d) N<sub>2</sub>H, (e)N<sub>2</sub>H<sub>2</sub>, (f) N<sub>2</sub>H<sub>3</sub>, (g) N<sub>2</sub>H<sub>3</sub>, (h) N<sub>2</sub>H<sub>4</sub>, (i),(j) N<sub>3</sub>H, (k) N<sub>3</sub>H<sub>3</sub>, (l)N<sub>4</sub>H<sub>4</sub>, (m),(n) N<sub>5</sub>H, (o),(p) N<sub>6</sub>H<sub>2</sub>. The panels q) and r) show the potential energy surface for dissociation of the N<sub>5</sub>H and N<sub>6</sub>H<sub>2</sub> species on the Al(111) surface.

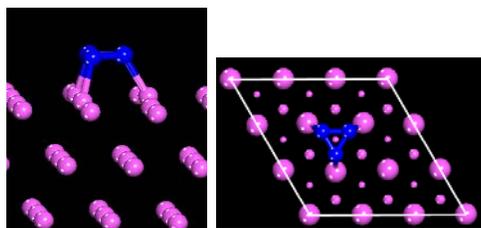
**Figure 3.** Side views of the most stable adsorption configurations for (a), (b) (1,3,5) triazene, (c), (d) (1,2,3) triazene, (e)-(j) mono-substituted triazene, and trisubstituted triazene molecules (k-m) C<sub>15</sub>N<sub>18</sub> and (n),(o) C<sub>9</sub>N<sub>30</sub> adsorbed on the Al(111) surface.



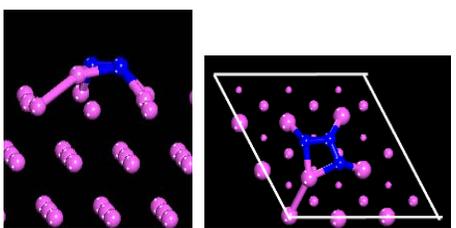
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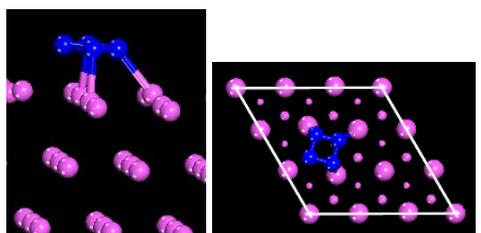
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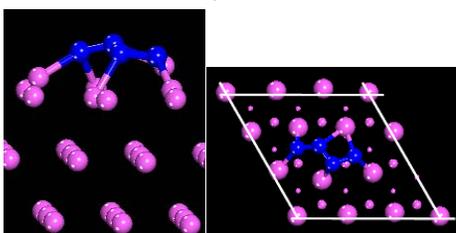
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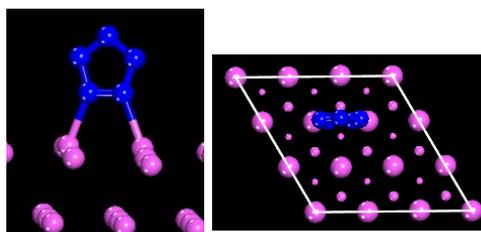
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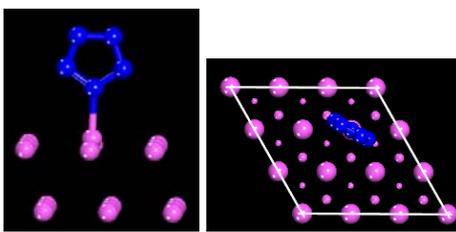
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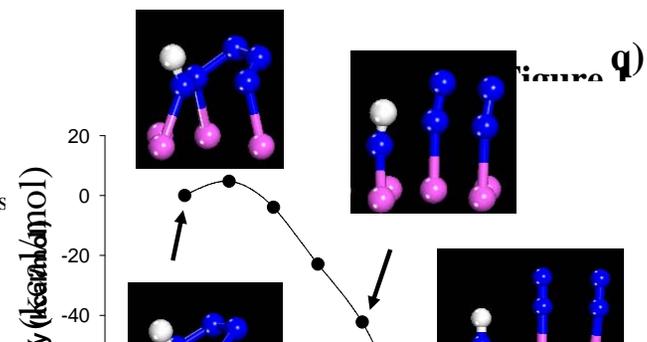
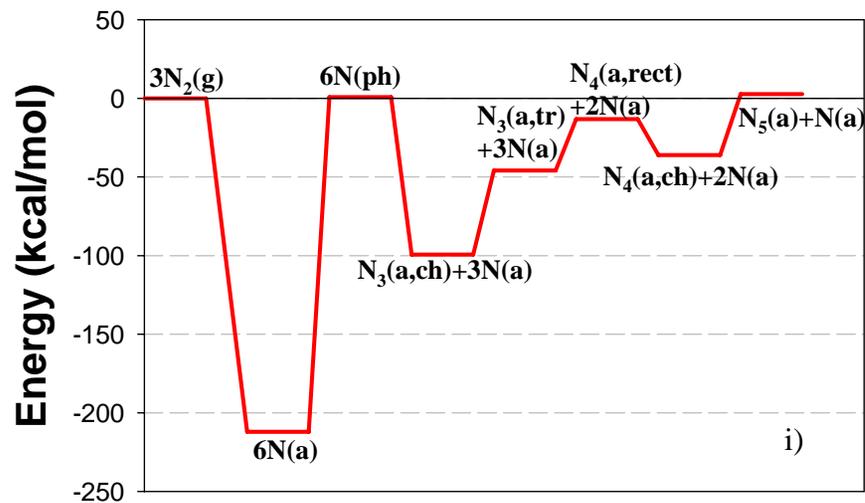
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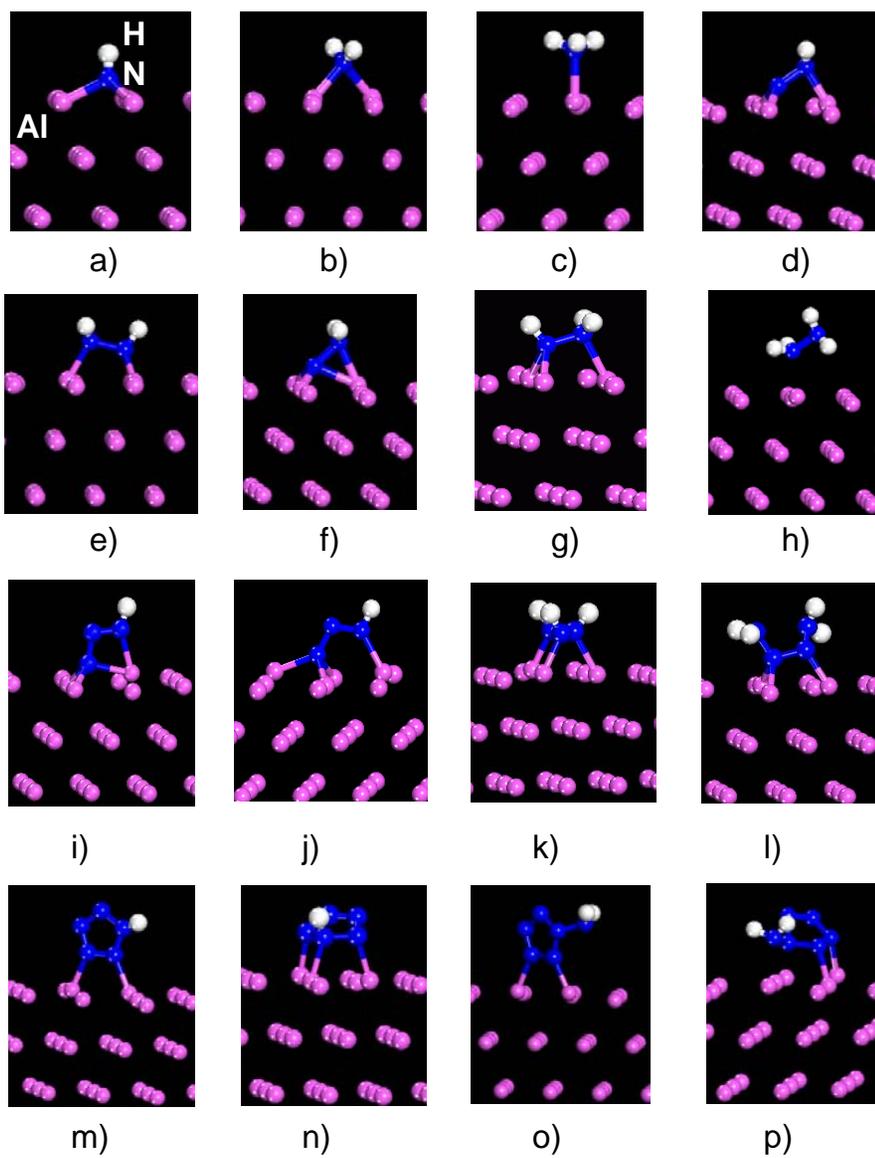


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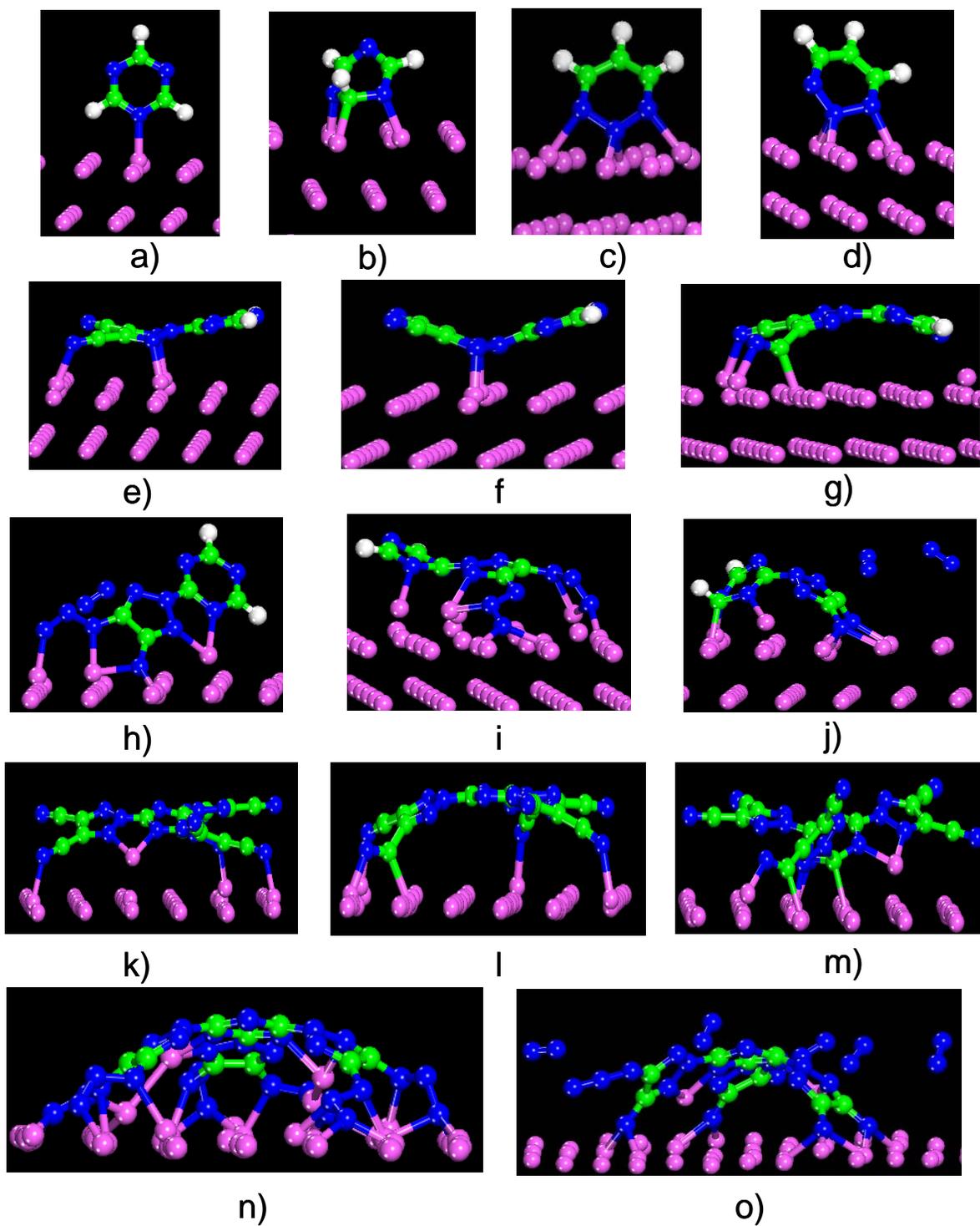


h)





**Figure 2**



**Figure 3**